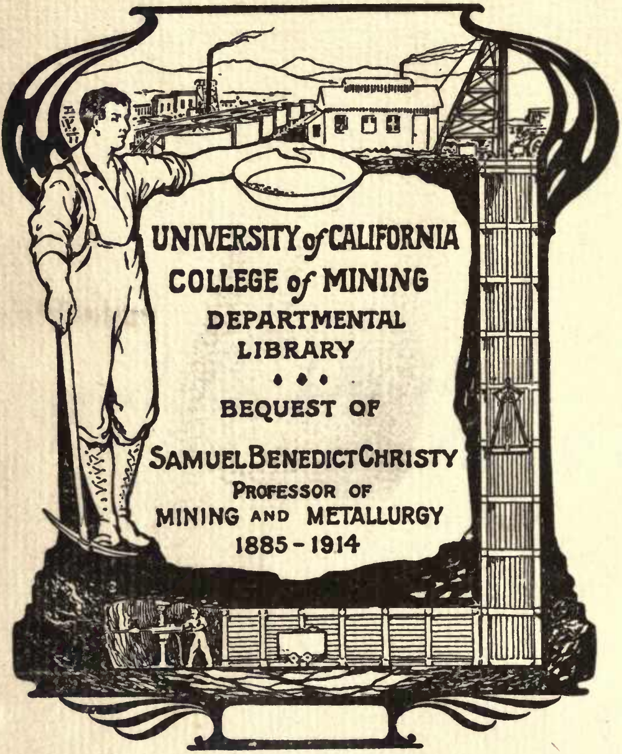

PRACTICAL ASSAYING.

LONDON : PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
AND PARLIAMENT STREET

A MANUAL
OF
PRACTICAL ASSAYING.

BY

JOHN MITCHELL, F.C.S.

EDITED BY

WILLIAM CROOKES, F.R.S.

FIFTH EDITION.

NEW YORK:
JOHN WILEY & SONS, 15 ASTOR PLACE.
1881.

PREFACE

TO

THE FIFTH EDITION.

THE experience of the last eight years has shown that Mr. Mitchell's 'Manual of Practical Assaying' still meets the demands of practical men better than any other work in the language.

A number of improvements and additions have, however, been rendered necessary in consequence of the rapid progress of chemical science. Some of the methods laid down in the earlier editions have been superseded by more accurate, rapid, and convenient processes, and have consequently been omitted.

The Editor's object has been, not to enumerate every known method, but simply to present the reader with such as are found most useful under different circumstances.

The hopes entertained at one time that spectroscopic processes would become available in the assay of the precious metals and their alloys have so far been doomed to disappointment, for reasons which will be found in the body of the work.

The gradual introduction of the new chemical nomenclature and notation into all works of reference has induced the Editor to take the same step in the present volume. The change has been made, however, in a manner which, it is hoped, will not occasion perplexity. The atomic weights of the elementary bodies have been corrected according to the most recent determinations.

London: *July* 1881.

EXTRACTS FROM THE

PREFACE TO THE THIRD EDITION.

IN THIS EDITION are incorporated all the late important discoveries in Assaying made in this country and abroad, and special care is devoted to the very important Volumetric and Colorimetric Assays, as well as to the Blowpipe assays. Most of the chapters are entirely rewritten, whilst the chapter on Crystallography—being a subject only remotely bearing on Assaying—is left out altogether. On the other hand, in some cases, it may seem that by treating of purely analytical details the limits of Assaying have been exceeded. But these departments are so closely related as to make it impossible to fix the line of demarcation between them. Moreover, chemistry is cultivated by almost all to whom this work is of interest or service so that it is hoped these amplifications will add to its value The old equivalents are retained, as they are more generally understood by students of science who do not make chemistry their chief study.

The Editor is under many obligations to his friend Dr. Röhrig, M.E., for assistance in revising the manuscript and incorporating into the work the latest continental improvements, as set forth in Professor Kerl's *Probirkunst.* The author of the best work on volumetric analysis which has yet appeared in English, Mr. Sutton, F.C.S., has kindly placed several cuts, &c., at the Editor's disposal, and some descriptions of German processes have been taken from the last English Edition of Fresenius's *Quantitative Analysi* —a work which should be a standard of reference for all students who desire to carry their chemical researches further than is possible to be treated of in a work professing to deal only with Assaying.

LONDON: *September* 1868.

PREFACE

TO

THE FIRST EDITION.

WHEN the rank our country holds among nations, as regards her Mining interest, is taken into consideration, it must be with all a matter of surprise that no work especially devoted to the elucidation of the processes to be employed in ascertaining the richness in metal of any sample of ore (that is, in other terms, its Assay) has of late years appeared before the British public. Indeed, the only work at present known in England is Berthier's 'Traité des Essais par la Voie Sèche,' which, for the mere purpose of inculcating the principles of Assaying, has many disadvantages—not the least of which is its being written in a foreign tongue; and although a knowledge of French is now so very general, yet many are prevented buying scientific works in that language on account of the difficulties of finding equivalents for the technicalities which must necessarily be employed. It is also a very large work, and one containing much matter which the assayer does not need—matter relating to the composition of wood and coal ashes, furnace products, &c., which are more especially adapted for the metallurgist.

These considerations, coupled with the paucity of any knowledge of Assaying, excepting that confined to a very limited number of persons, induced the author of the following pages to turn a considerable amount of his attention to this subject, more especially as much difficulty was experienced in not having a suitable text-book for the use of his pupils. A portion of the following pages was drawn up as a Manual for such a purpose; but, on consideration, it was thought the extension of such a work was so much needed that it was determined to alter the original plan as far as was consistent with the complete carrying out of the object in view, viz. the production of a Manual embodying information in every branch of assaying, either by the wet or the dry processes.

The following is a sketch of the manner in which this is accomplished; the author having followed the excellent arrangement of Berthier as closely as possible, from whose work also much matter that suited these pages, and which it would have been useless to rewrite, has been inserted. Firstly, the Mechanical and Chemical Operations of Assaying are treated in full, inclusive of a description of the apparatus required, their mode of use, &c. Secondly, Furnaces, Fuel, and Crucibles, together with a description of the best Pyrometers, and their applications. Thirdly, the Fluxes, their properties, preparation, use, &c. Fourthly, an Essay on the use of the Blowpipe, and all its appurtenances; as Fluxes, Supports, &c. Fifthly, the action of the Fluxes on some Mineral Substances. Sixthly, a method of discriminating many Minerals by means of the Blowpipe, aided by a few tests by the humid method. Seventhly, the Humid Analysis of many Mineral Substances, their composition, locality, &c. (All the minerals mentioned in the three last heads comprehend such only as generally come under the notice of the Assayer.) Eighthly, the complete Assay of all the common Metals, in addition to which the Assay of Sulphur, Chromium, Arsenic, Heating power of Fuel, &c., is fully discussed ; and ninthly, and lastly, a copious Table drawn up for the purpose of ascertaining in Assays of Gold and Silver the precise amount, in ounces, pennyweights, and grains, of Noble metal contained in a Ton of Ore from the assay of a given quantity. This Table is the most complete and copious yet published.

Not only has it been endeavoured to collect all that is generally known on the subject of Assaying, but many new facts have been added, and such matter entered into, that the success of an assay is rendered much more certain ; and most assays are conducted more rapidly and with greater exactitude than heretofore.

It has also been endeavoured to introduce a new system, in which is pointed out the rationale of each process, with the chemical action taking place between the fluxes and the ores in course of assay, so that by paying a careful attention to the matters discussed, so much of the chemical nature of all ores that can come under the assayer's hand may be known, that the practice by 'rule of thumb' (a rule on which very little dependence is to be placed, excepting after years of the most laborious practice, and a rule which cannot be imparted, excepting the pupil pursue the same unprofitable course) must, it is hoped, be speedily abandoned when, by knowing the chemical properties of the body operated on, the necessary fluxes and processes might be at once indicated, and with a certainty of perfect success.

Having premised thus much, the author must beg to express his thanks to his friend Mr. F. Field for the kind assistance he afforded him whilst experimenting on the various modes of assay described in the body of the work; and trusting that any little imperfections which may be detected will not be harshly criticised, but that it may be taken into consideration that the author has attempted to improve a branch of mining knowledge to which unfortunately too little attention has been devoted, and to which, if he has added anything useful, he is indebted for the first principles of such knowledge to Berthier's 'Traité des Essais,' for which, to the talented writer of the above work, he is under the most lasting obligation.

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A MANUAL
OF
PRACTICAL ASSAYING.

CHAPTER I.

CHEMICAL NOMENCLATURE—LAWS OF COMBINATION, ETC.

In a treatise intended to be used principally by the practical assayer, it is neither necessary nor practicable to give more than a brief outline of the elements of chemical nomenclature, and of chemical combination. A knowledge of practical chemistry is undoubtedly of great value to the assayer; indeed, no one can attain to any degree of eminence in this branch of industry unless he has had some amount of practice in the laboratory; but it will be beyond the scope of this volume to teach the elements of chemistry. Such instruction in chemistry must be sought for in books which are specially devoted to the science. The student should, above all, endeavour to acquire a practical knowledge of experimental chemistry by going through a course of lessons in a laboratory.

Chemical Nomenclature.—Every material substance with which we are acquainted consists of one or more bodies, termed *elements*, from the fact that with our present means of research we are unable to reduce them to a more simple form. Thus, if a piece of common iron pyrites be exposed to certain chemical operations, it will be found to consist of two substances, both physically and chemically distinct from each other and from the original substance. One body is *sulphur*, an opaque yellow substance, fusing at a very low temperature, igniting readily, and burning with a peculiar suffocating odour. The other constituent is *iron*, a well-known metallic substance, requiring an intense heat for fusion, and not burning at a red heat. If we perform any experiment which, in the present state of knowledge, ingenuity could suggest, we are totally unable to cause either the sulphur or the iron to assume a more simple or elementary state of existence. We can with ease cause either of them to enter into new combinations with other bodies, and these compounds we can decompose—as in the case of the pyrites—and obtain both sulphur and iron again in their separate forms with all their characteristic properties; but nothing more than this can be effected: hence we are led to the belief that both sulphur and iron are *elements*, or bodies containing only one kind of matter.

The following table shows the elements discovered up to the present time. Those substances whose names are printed in italics have hitherto found no practical use; and those marked with an asterisk (*) are often found native, or unassociated with mineralising elements.

Non-metallic Elements or Metalloids.

Names of the Elements	Symbols	Atomic Weights	Names of the Elements	Symbols	Atomic Weights
Oxygen . .	O	16	*Selenium* . .	Se	79·5
Hydrogen .	H	1	*Tellurium*. .	Te	128
Nitrogen . .	N	14	Phosphorus .	P	31
Fluorine . .	Fl	19	Arsenic . .	As	75
Chlorine . .	Cl	35·5	*Carbon . .	C	12
Bromine . .	Br	80	Boron . .	B	11
Iodine . .	I	127	Silicium . .	Si	28·5
*Sulphur . .	S	32	*Zirconium* .	Zr	90

Metallic Elements.

Names of the Elements	Symbols	Atomic Weights	Names of the Elements	Symbols	Atomic Weights
Potassium	K	39·1	Cobalt	Co	58·8
Sodium	Na	23	Nickel	Ni	58·8
Lithium	Li	7	Zinc	Zn	65
Cæsium	Cs	133	Cadmium	Cd	112
Rubidium	Rb	85·4	*Copper	Cu	63·5
Barium	Ba	137	Lead	Pb	207
Strontium	Sr	87·5	*Thallium*	Tl	204
Calcium	Ca	40	Indium	In	74
Magnesium	Mg	24	*Bismuth	Bi	208
Aluminium	Al	27·5	Tin	Sn	118
Glucinum	Be	14	Titanium	Ti	50
Cerium	Ce	92	*Tungsten*	W	184
Lanthanum	La	92	*Molybdenum*	Mo	92
Didymium	Di	96	Vanadium	V	51·2
Yttrium	Y	68	Antimony	Sb	122
Erbium	Er		*Mercury	Hg	200
Terbium	Tr		*Silver	Ag	108
Niobium	Nb	97·6	**Rhodium*	Rh	104
Tantalum	Ta	137·6	*Palladium	Pd	106·5
Thorium	Th	231·5	*Platinum	Pt	197·4
Manganese	Mn	55	*Iridium	Ir	198
Chromium	Cr	52·5	**Ruthenium*	Ru	104
Uranium	U	120	**Osmium*	Os	199
Iron	Fe	56	*Gold	Au	197

The first column contains the name of the element; the second, the symbol, in which all chemical changes and decompositions are most readily understood; and the third, the atomic weight. These atomic weights are not given beyond the first place of decimals, to avoid tedious calculation; for all practical purposes they may be considered accurate. Of the compounds of these elements, only those will be discussed which are likely to fall under the notice of the assayer.

The principal compound bodies with which the assayer will have to deal are *acids*, *oxides*, *salts*, and *binary* substances containing no oxygen.

When a body combines in more than one proportion with oxygen, that compound containing the least oxygen takes the termination *ous*, that containing the most *ic*: thus, sulphurous acid, sulphuric acid; arsenious acid, arsenic acid; ferrous oxide, ferric oxide; mercurous oxide, mercuric oxide; in only one proportion (or when they form only one *basic* oxide) they are distinguished by the termination *ic*, as potassic oxide, aluminic oxide.

Oxides are binary oxygen compounds: they may be divided into three series. The first series comprises those oxides which do not possess the property of combining with acids to form salts—they are termed *indifferent oxides*; the second contains those capable of uniting with acids to form salts, and called *salifiable oxides* or *bases;* the third comprises those oxides which have *acid* characters, and form salts by uniting with bases.

When an elementary body combining with oxygen forms but one oxide, it is simply called the oxide of the element. Thus we say *zinc oxide*, or zincic oxide.

If the body is capable of combining with oxygen in many proportions, the words *proto-*, *sesqui-*, *bin-*, or *per-*, &c., precede the term oxide, to express the progressive amounts of oxygen. Most metals form one salifiable oxide, and many of them have two; these are now generally distinguished by the terminations *ous* and *ic*, in the same manner as are the acids. Thus we have *protoxide* of lead, iron, copper, tin, &c.; *sesquioxide* of aluminium, iron, or chromium, &c.; *binoxide* or *peroxide* of manganese, copper, mercury, &c.; and when we speak of them as salifiable bases, *ferrous* oxide, and *ferric* oxide; *mercurous* and *mercuric* oxide; *potassic* oxide; *aluminic* oxide. Some metals unite with oxygen in still higher proportions; these compounds are almost always acids, such as *chromic acid*, *stannic acid*, *antimonic acid*, &c.

Salts are formed when an acid unites with a base, and usually the properties of the acid and the base are reciprocally neutralised; thus an acid which before combination possesses the power of reddening blue litmus, loses it on combining with the base, and, in like manner, a base which would at first change reddened litmus paper to blue loses this property as the acid saturates it. In this case the acid and base have combined to form a salt.

The names of salts are governed first by the nature of the acid; secondly, by the salifiable nature of the base;

and, thirdly, by the proportions in which the acid and base are combined. Acids terminating in *ic* form salts ending in *ate*. Acids terminating in *ous* form salts terminating in *ite*; and the new names having these terminations are added to the name of the oxide. Thus sulphuric acid and iron protoxide form sulphate of iron protoxide, ferrous sulphate, or, more commonly, protosulphate of iron; arsenious acid and iron protoxide form arsenite of iron protoxide, ferrous arsenite, or protarsenite of iron; nitric acid and iron sesquioxide form nitrate of iron sesquioxide or ferric nitrate.

When the salt exists in the neutral state its name is formed as above, but if the proportion of acid is greater than in neutral salts, it is termed an *acid salt*: thus bisulphate of potassium is sometimes called *acid sulphate of potassium*. If, on the other hand, the base is in excess, the name is preceded by the words sub or basic: thus, subacetate of lead or basic-acetate of lead.

Binary compounds containing no oxygen exist very largely in nature, and it is from them that the greater part of our copper, lead, silver, &c., is obtained.

When a non-metal combines with a metal to form a compound which is neither acid nor basic, its name is derived from the non-metal by the addition of the termination *uret* or *ide*. The latter term is, however, gradually displacing the former, and is now seldom employed except in the case of sulphur compounds, and in these one term is as often used as the other. Thus the compounds of sulphur with iron and chlorine with silver are respectively called *sulphuret* or *sulphide* of iron, and *chloride* of silver.

If a non-metal combines with a metal in more than one proportion, the same rule is followed as with the oxygen compounds: thus we have iron *proto*-sulphide, iron *sesqui*-sulphide, and iron *bi*-sulphide (ordinary iron pyrites or mundic).

Laws of Combination.—On examining the compounds which the same substances afford by their union in different proportions, it has been noticed that the proportions of the elements existing in each compound are definite; a certain weight of one substance will only combine with a certain weight of another substance, and the lowest combining weight of any of the elementary bodies is termed its *atomic weight*, and is represented by the numbers in the third column of the table of elementary substances.

As before stated, all substances combine in fixed or definite proportions; thus, if 223 parts of oxide of lead are analysed, they will be found to consist of 207 parts of lead and 16 of oxygen. Again, the analysis of 18 parts of water or oxide of hydrogen would give 2 parts of hydrogen and 16 of oxygen; now, taking hydrogen as unity, we have 207 as the equivalent of lead, and 16 as that of oxygen. If we follow oxygen further in its combinations, it will be seen that—

16 parts of oxygen combine with 1 part of hydrogen.
" " " " 207 " lead.
" " " " 40 " calcium.
" " " " 118 " tin.
" " " " 63·5 " copper.

The above numbers, therefore, represent the equivalents of the respective elements.

Again, the equivalent of sulphur is 32, and this represents the weight of sulphur which will combine with the above weights of hydrogen, lead, calcium, tin, or copper to form sulphides of the respective bases. 35·5 parts of chlorine, or 79·5 parts of selenium, also combine with the same weights, viz. hydrogen 1, lead 207, &c., to form chlorides and selenides.

Compounds like these are of the simplest class, and consist of single equivalents only; there are, however, many compounds containing more than two equivalents, in which case the following laws are followed.

In one class of compounds the quantity of one of the constituent elements remains constant, while each new compound is formed by the successive addition of another atom of the other constituent element; and it must also be borne in mind that no element will combine with another in less than its atomic weight. Another series will commence with two atoms of an element united with an uneven number of atoms of another element; thus we can have binary compounds in the proportion of 2 to 3, 2 to 5, or 2 to 7.

The atomic weight of a compound body is the sum of the atomic weights of the elements forming it: thus sulphuric anhydride is composed of one atom or 32 parts of sulphur, and 3 atoms, or 48 parts, of oxygen; its atomic weight is therefore 80. The atomic weight of any compound body may be ascertained by adding together the atomic weights of its constituent elements.

Owing to the invariable law of the constancy of chemical compounds, we are enabled to calculate the reaction which occurs between two or more bodies when decomposition takes place: thus 174·2 parts of sulphate of potassium contain 80 parts of sulphuric anhydride and 94·2 parts of potassium oxide; and if it were desired to obtain sulphate of lead by the decomposition of nitrate of lead by adding to it the above quantity of sulphate of potassium, the exact amount of nitrate of lead required would be readily found by adding together the equivalent of the elements forming nitric acid and oxide of lead.

Chemical Symbols: their Employment and Uses.—The symbol of an element standing alone signifies one atom of that element. Thus: S implies not only the element sulphur, but 32 parts of sulphur; a small figure on the right-hand side of the symbol indicates the number of atoms to be represented; thus, S_2 is equal to two atoms, or 64 parts of sulphur.

Two symbols placed thus, FeS, indicate a compound of equal equivalents of iron and sulphur. Separation of elements by the sign + or a comma is employed to show the union of two compound bodies; thus the compound of silver sulphide and lead sulphide may be thus written: $AgS+PbS$, or AgS,PbS. A large figure on the same line as the symbol, and on its left side, multiplies the whole of the symbols to the first comma or + sign: thus, $2AgS,PbS$, or $2AgS+PbS$, represents a compound of two atoms of silver sulphide with one of lead sulphide. If, however, it be thus written, $2(AgS,PbS)$, it means two atoms of the whole of the elements which are inclosed in the brackets.

CHAPTER II.

PREPARATION OF THE SAMPLE—WEIGHING.

THE selection and preparation of the sample is the first and most important operation in assaying. It is of little use for the operator to ascertain with accuracy the percentage of every individual constituent in the mineral operated on, if his sample does not truly represent the average of the ore. It should be borne in mind that samples of mineral are generally selected for their richness, and represent the most favourable portions of the ore; and no pains should be spared to secure a sample for analysis which will truly show the bulk of mineral whose value is required to be known.

The assayer must always bear in mind the *object* which his experiments have in view. If they are to ascertain the actual percentage of one or more constituents existing in a certain stone, his labours are comparatively easy, all that is required being to reduce the *whole* of the specimen to the finest possible state of division, and, having well mixed the powder, to analyse a portion of it.

But if it is desired to find out the composition of a special mineral or crystal, the greatest possible care must be taken to remove the whole of the gangue or other impurities, and to obtain for analysis those portions only which represent with greatest accuracy the pure mineral. To effect this the surrounding rock is first removed as carefully as possible, and then the specimen is crushed into coarse pieces on a sheet of clean paper. By means of a pocket magnifier and a pair of pincers, clean, typical pieces of the mineral are then to be selected for analysis.

If, however, as will most frequently be the case, the object of the assay be to ascertain the average value of a mineral lode or heap or ore, then the assayer must proceed differently. The portion experimented upon must truly represent, in the respective amounts of its valuable material, gangue, quartz, and earthy matters, the whole bulk of that of which it professes to be a sample; and this having been secured, the whole must be carefully powdered and passed through fine sieves, taking care that every portion of the mineral goes through. If this be not attended to, it will frequently happen that the few grains left out are sufficient to vitiate the whole assay; this is especially apt to be the case when examining ores the valuable ingredients of which are of a ductile or malleable nature, such as auriferous quartz. In this case it frequently happens that the great bulk of gold exists in the form of one or two small pieces, and these being flattened and beaten out in the operation of powdering will almost certainly be left upon the sieve. In cases like this it is better to collect and assay such pieces separately, and estimate their proportion to the whole weight of the sample, than to attempt to powder and distribute them uniformly.

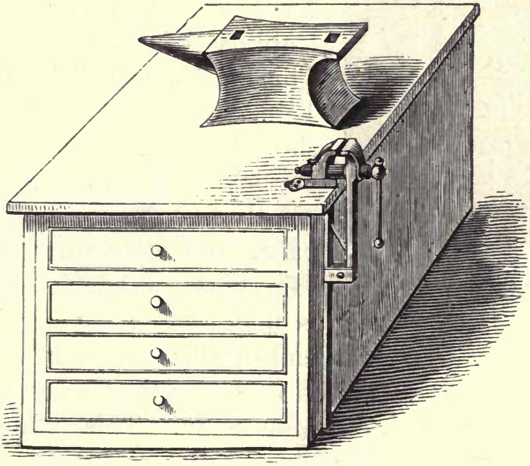
The ore must always be reduced to a powder, more or less fine, according to the nature of the chemical operation or assay to which it is to be subjected. This division is effected by means of the anvil, hammer, pestle and mortar, sieve, method of elutriation, or other means generally in use for the preparation of any fine powder. The actual process to be adopted must vary according to the nature of the different bodies under examination. In some cases simple crushing is sufficient; in others the ore will have to be pounded in a mortar; whilst occasionally it is necessary to reduce it to the very highest degree of fineness by elutriation.

There is another operation, which is as strictly mechanical as are the above, viz. washing, dressing, or vanning a sample of ore, the end and aim of which is to separate, in a suitable vessel, by means of water and difference of specific gravity, the earthy or useless and, in some cases, objectionable portion from the heavier metallic and valuable portion. This operation is almost always employed on the larger scale in dressing ores for the smelter.

The tools and materials employed in preparing the sample are the *anvil* (and stand), *vice*, *hammer*, *files*, *cold chisel*, *shears*, *pestle and mortar*, *steel-crushing mortar*, *sieve*, &c.

THE ANVIL (fig. 1).—The anvil is most useful in size when it weighs about 28 lbs.; but one of 14 lbs. will suffice. The anvil recommended is of the shape usually employed by the blacksmith.

FIG. 1.

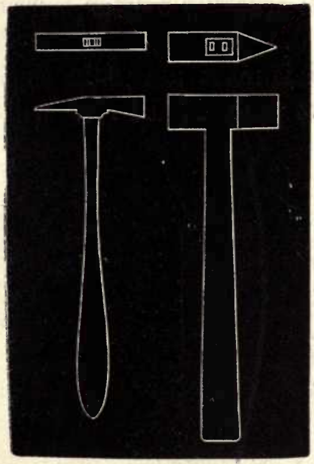


The anvil-stand is constructed of stout wood, about two inches in thickness, and forms a cube of about two feet square. It contains three or four drawers, which serve to hold the hammers, cold chisel, shears, files, &c., which are required in an assay office. In the centre the anvil is fixed, and in one corner a vice may be also secured.

In general the anvil and hammer are employed for the purpose of breaking a small fragment from a mass of ore for examination, or ascertaining whether the button or prill of metal produced in an assay be malleable or otherwise. The anvil is also exceedingly useful as a support for a crucible while breaking it to extract the metallic or other valuable contents.

The hammers (figs. 2 and 3), of which two are requisite, ought to have one end flat and square and the other pick- or wedge-shaped. The horizontal wedge end of fig. 2 is useful for breaking open crucibles and in detaching small fragments from a specimen of ore. The flat end serves for ascertaining the malleability of buttons of metal. This hammer should weigh about 1 lb. The larger hammer, fig. 3, should weigh about 4 lbs., and is employed for breaking coke sufficiently fine for the use of the furnace, and detaching fragments from refractory minerals, in both of which cases either end may be employed, as may seem most serviceable to the operator. The flat end of this hammer is also used for driving a cold chisel in separating masses of gold, silver, copper, lead, &c., for assay. This hammer has a vertical pick or wedge end.

Fig. 2. Fig. 3.



Very hard and stony materials which have to be broken on the anvil (and all such ought to be so treated) scatter many fragments, to the certain loss of a proportion of the substance, and the probable injury of the operator; this can be prevented by wrapping the mineral in a piece of stout brown paper, or if necessary in several folds. The fracture can then be safely attempted.

This latter precaution must be specially taken in fracturing gold quartz, or hard rock containing metallic silver, as the loss of a very minute quantity of metal would involve a considerable error in the result afforded by the assay.

All minerals, unless very friable, must be reduced to a moderate size—say that of a walnut—by means of the anvil and hammer, before pulverisation; otherwise, if the reduction be attempted in a mortar, it is nearly certain to be injured; moreover, the operator will find his labours much abridged by using the anvil for this purpose.

The anvil can also be made very serviceable in repointing worn or burnt-out tongs, &c. It need scarcely be added that it must be placed as far as possible away from bottles or other frangible articles, otherwise accidents may occur by the forcible projection of fragments of crucibles, stones, &c.

The cold chisel (fig. 4) is employed for cutting off metallic masses for assay. It should be five or six inches long, and about half an inch wide, which is the best size for general use. However, for some purposes, as cutting copper and other very tough metals, it is convenient to have a chisel only a quarter of an inch wide, as these metals are so much more difficult to cut, and the small chisel meets with the least resistance.

Fig. 4.

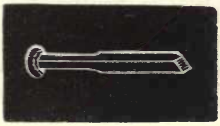
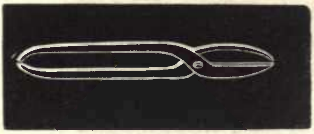


Fig. 5.



Small shears (fig. 5) are also exceedingly useful in cutting off pieces of sheet metal, as lead, for cupellation, scorification, &c.

The Pestle and Mortar.—Mortars are made of various materials, as cast-iron, bronze, porcelain, agate, &c.; the assayer requires one of cast-iron, one of porcelain, and one of agate.

The iron mortar (fig. 6) ought to be of the capacity of from three to four pints; the porcelain (Wedgwood ware) (fig. 7) may contain about two pints. The ease with which a mortar may be used depends much upon its form, and opinion is greatly divided on the subject. Faraday * says that the pestle should be strong, and the size of its upper

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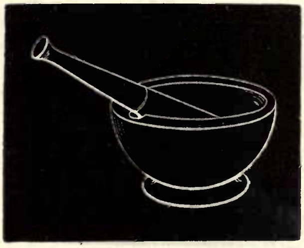
* *Chemical Manipulation*, p. 149.

part sufficient to allow of its being grasped firmly in the hand, and below to permit a considerable grinding surface to come in contact with the mortar. Its diameter in the lower part may be about one third or one fourth of the upper diameter of the mortar. The curve at the bottom should be of shorter radius than the curve of the mortar, that it may not touch the mortar in more than one part; whilst at the same time the interval around may gradually increase, though not too rapidly, towards the upper part of the pestle.

The bottoms of all mortars ought to be of considerable thickness, in order to withstand the smart blows they will occasionally have to receive.

FIG. 6.

FIG. 7.



Berzelius recommended a mass of pumice-stone for cleansing porcelain mortars. It is used with water as a pestle, and in course of time will be worn to the shape of the mortar; its action will then be more speedy.

Iron mortars can be best cleaned by friction with a little fine sharp sand, if washing be not sufficient to remove the adhering substance. Great care must be taken to dry mortars perfectly, especially those of iron, otherwise they will become rusted, and the rust will contaminate the substances pulverised in them.

The iron mortar is principally of use in the reduction of the masses of mineral (broken on the anvil, as before described) to a state of coarse powder, in order to render the substance more readily capable of pulverisation, strictly so called. In the use of the iron mortar, all friction with the pestle ought to be avoided, and the body within it must be struck repeatedly and lightly, in a vertical direction, taking care to strike the large pieces, so that all may be equally reduced. This can be carried on until the whole is about the size of fine sand. It is transferred to the porcelain mortar, where direct blows must be carefully avoided.

The process is now carried on somewhat differently: the pestle is to be pressed with a moderate force, and a circular motion given to it, taking care every now and then to lessen and then to enlarge the circles so as to pass over the whole grinding surface of the mortar, and insure the pulverisation of the mass of mineral submitted to operation. In general, the finer the state of division to which a mineral is reduced, the more accurate and expeditious will be its assay; and in preparing a mineral for assay by the wet method, no labour ought to be spared on this point. Pulverisation is rendered much easier by operating on a small quantity at once, and removing it very often from the sides and bottom of the mortar by means of a spatula. The quantity operated on at one time must be regulated by the hardness and friability of the substance whose pulverisation is to be effected. The harder it is, the less must be taken, and *vice versâ.*

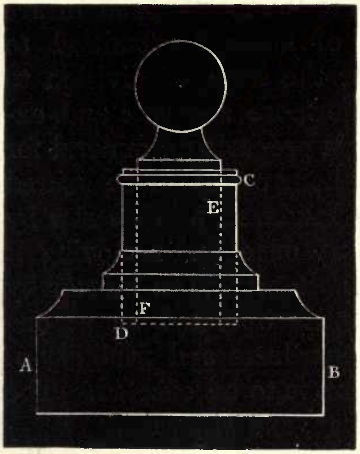
In the use of the iron mortar fragments are occasionally projected. This may be prevented by covering the upper part of the mortar with a cloth. This applies also to the porcelain mortar, for the dust of some minerals has a disagreeable taste and smell. Indeed, in some cases the ambient powder is highly deleterious, as in the pulverisation of arsenical nickel, cobalt, and other ores. Here the simple cloth is not a sufficient protection; it should be slightly damped with water, and tightly tied round the mortar, and firmly held round the pestle, when nothing can escape.

Some minerals can be pulverised with greater ease if they are ignited and suddenly quenched in cold water. Amongst them may be named flint, and many other siliceous matters, as gold quartz. In the pulverisation of charcoal for assays, it will be found useful to heat it, as hot charcoal is more readily pulverised than cold.

In some instances the powder obtained in the iron or porcelain mortar is not fine enough; recourse should then be had to the agate mortar, in which the mineral, in as fine a state of division as the larger mortars will give it, is ground in small portions at a time, until it is reduced to an impalpable powder.

When small specimens or rare minerals are being operated upon, if it is especially desirable to avoid loss, it is advisable to use a steel mortar (fig. 8) for the preparatory reduction of the mineral to coarse powder. *A B* and *C D* represent the two component parts of the mortar; these may be readily taken asunder. The substance to be crushed (having, if practicable, first been broken into small pieces) is placed in the cylindrical chamber *E F*; the steel cylinder, which fits somewhat loosely into the chamber, serves as a pestle. The mortar is placed upon a solid support, and perpendicular blows are repeatedly struck upon the pestle with a hammer, until the object in view is attained. (*Fresenius.*)

FIG. 8.



In the selection of agate mortars, they must be examined to see that they have no palpable flaws in them; very slight cracks, however, that cannot be felt, do not render the mortar useless, although they increase the danger of its destruction by a chance blow.

THE SIEVE.—The operation of sifting is employed when a very fine powder is required, or when a powder of uniform size is needed. Sieves of various materials and different degrees of fineness are necessary. The larger sieve, for preparing coke for the blast furnace, is made of stout iron wire, and must have its meshes from 1 inch to

1½ inch square. The fine coke, which is sifted from that which is the proper size for the blast furnace, may be mixed with that of ordinary size, and employed economically in the muffle furnace. For the preparation of minerals a set of three sieves should be provided, each one finer than the other. The coarsest may contain 40 holes to the linear inch, the finer or medium sieve 60, and the finest from 80 to 100. The coarsest sieve is used for preparing galena for assay; the medium for copper, tin, iron, and other like ores; and the finest for gold and silver ores, or for preparing any substance for the wet assay, as, in the latter case, the finer the state of division the substance attains, the more rapid will be its solution or decomposition by the liquid agents employed.

The sieve fig. 9 is made of wood, over which is strained in the ordinary manner brass wire-gauze of the necessary degree of fineness. When in use, *B*, fig. 10, is fitted into the lower part of *A* (same figure). This contrivance prevents all loss of the fine powder. If the matter to be sifted be offensive or deleterious to the operator, a sieve termed the drum or box-sieve may be employed (see fig. 10), where *C* represents a cover fitting over the sieve. If small, this may be used in the ordinary way; but if large, its method of use is rather peculiar, and requires some practice to fully develop its powers. One side of the under edge must be held by one or both hands according to its size, whilst the other rests on a table or a bench. A semi-circular oscillating motion must now be communicated to it by moving the hands up and down at the same time that they are being alternately brought into approximation with the sides of the operator.

FIG. 9.

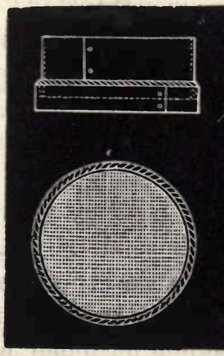
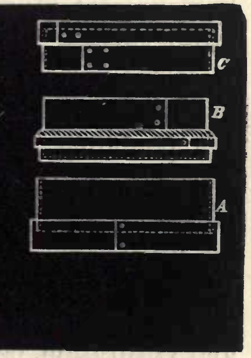


FIG. 10.



In cases of necessity, a sieve may be readily extemporised. Place the powder to be sifted in a piece of fine lawn or muslin, according to the fineness required, tie it up loosely, and shake or tap the powder, with its muslin or other envelope, on a sheet of paper, and the sifting will be rapidly and easily accomplished.

The sieve is also extremely serviceable in the separation of some ores from their gangues or vein-stones, especially if the latter be stony and hard. This point must be particularly noted, as it is the cause of much variance between the results of different assayers; for instance, part of the same sample of ore might be sent to two assayers, and the produce made by one would be 8½ per cent., and that by the other 9 or 9½, or, in some cases, even more. This discrepancy generally arises from the cause above mentioned. In the one case the workman has rejected part of the hard gangue, and so rendered the residue richer; whilst in the other he has pulverised the whole, making the produce less, but giving more accurately the amount of metal in the substance submitted to assay.

A knowledge of this fact is also very useful from another point of view. Suppose it were wished to separate in a speedy manner, as perfectly as possible, any friable mineral, such as galena or copper pyrites, from its matrix by mechanical means, it might be accomplished by the use of the sieve, as follows: Place a small quantity of the mineral in an iron mortar, and strike, repeatedly, slight vertical blows. When it is tolerably reduced, sift it, and it will be found that what passes through is nearly pure mineral, with only a small quantity of matrix; repeat the pounding and sifting operations, until, after a few repetitions, that which remains in the sieve is nearly pure gangue.

Native metals, as gold, silver, and copper, are also partially separated after the manner above described. The fine particles of metal, during the process of pounding and trituration, become flattened, and cannot pass through the sieve, whilst the more brittle portions pass through and are separated.

Elutriation.—This process can only be employed for those bodies which are not acted on by water; and it must be remembered that many substances which are usually considered to be insoluble in water are, when in a very finely divided state, acted upon to a greater or less extent. The operation is thus effected: The substance is reduced to the finest possible state of division by any of the foregoing processes; it is then shaken up with a quantity of water in a glass or other vessel. After a few moments' repose, the supernatant liquid, retaining in suspension the finer particles of the pulverised substance, is poured off, and the grosser parts, which have fallen to the bottom of the vessel, are repulverised, and again treated with water. By repeating these processes a powder of any required degree of fineness may be obtained.

It is seldom, however, that a substance is required for assay by the dry way, in such a minute state of division. In the humid or wet method it is occasionally very useful. If the supernatant water is roughly decanted off, where the powder to be elutriated is light, the least disturbance of the vessel containing it occasions the distribution of the portion which has settled, throughout the liquid, and the consequent mixture of fine and coarse particles. This can be avoided by the employment of the syphon. The operation is then thus conducted: The syphon is filled with water, and the shorter end placed in the liquid whose transversion is to be effected: the forefinger of the right hand, which, during this time, has been applied to the longer end of the instrument, is now removed, when the water will flow out until it is level with the immersed end of the syphon. Fresh water can then be added, the powder stirred up again, and the operation of decantation by the syphon carried on as long as requisite.

Washing, Dressing, or Vanning.—This operation is exceedingly useful for discovering the approximate quantity of pure ore, such as galena, copper pyrites, oxide of tin, native gold or silver, in any sample of earthy matter or ore in which it may be disseminated.

The theory of the operation about to be described is easily understood. Bodies left to the action of gravity in a liquid, in a state of rest, experience a resistance to their descent which is proportionate to their surface, whatever may be their volume and density. Hence it follows, firstly, that of equal volumes the heaviest fall most rapidly; secondly, that of equal densities those having the largest size move with the greatest speed; for in particles of unequal size and like form the weight is proportional to the cube of the dimensions, whilst the surface is only proportional to the square of these dimensions; hence in small particles the surface is greater in relation to the weight than in the large particles. Thirdly, of equal densities and volumes, particles offering the largest surface (those which are scaly and laminated, for example) undergo more resistance in their motion than those which, approaching the spherical form, have less surface. The adhesion of the liquid to the particles of bodies held in suspension is also an obstacle to their subsidence. This force, like the dynamic resistance, is proportional to the surface and independent of the mass or volume; whence it follows that, in a fluid in motion, of bodies having equal volumes, the least dense acquire the greatest rapidity of movement, and are deposited at the greatest distance from the point of departure; whilst with equal densities the smallest grains are carried farthest; and lastly, with equal densities and volumes, the particles exposing most surface traverse the greatest space.

It is, therefore, evident that the most advantageous condition for separating, by washing, two substances of unequal specific gravity or density is that the heavier shall be in larger grains than the lighter; this unfortunately, however, is a condition that can very seldom be fulfilled, as the heaviest substances are those metallic minerals whose frangibility is nearly always greater than the earthy matters accompanying them as gangues. This being the case, it is very important so to arrange that the fragments of the various mixed substances shall be nearly of the same size. This may be effected by very frequently sifting the mineral during the process of pulverisation, reducing it also more by blows than by grinding, so as to get as little fine powder as possible, as that is nearly certain to be washed away during the process.

The operation of washing or vanning may be performed by one of two methods. In the first, a small stream of running water is employed; in the second, water is added to the substance to be washed, and poured off as necessary.

In the first process, a vessel somewhat resembling a banker's gold scoop (but longer in proportion) is employed; the mineral to be washed is placed in the upper part, and a small quantity of water added, with which the mineral is thoroughly and carefully moistened, and mixed with the fingers. The scoop must then be so inclined that a fine stream of water from any convenient source (say a tap) may fall just above the upper part of the mixture of mineral and water; then, firmly holding the larger and upper end of the scoop with the left hand, and sustaining the lower part with the right, it is shaken frequently in the direction of its longitudinal axis. At each shake all the particles in the scoop are so agitated that they become suspended in the water, and the current of liquid running from the tap into the scoop moves them all in its own direction; but they are deposited at different distances from the point at which the water enters, the heaviest being carried through but a very small space. It is now soon seen that the mineral assumes a heterogeneous surface; at the upper part, the heavy portions are seen nearly pure; the light substances, on the other hand, are nearly without mixture at the lower end, and in the intermediate part the heaviest portion of the mixture is nearest the upper end. If the washed matter were now to be divided into horizontal layers, the heaviest matter would be found at the bottom, and the lightest on the surface. Things being in this state, the scoop must be made to oscillate on its axis, so that the latter remain immovable, and in a slightly inclined position. In this manner, the layer of water running over the surface of the mineral agitates that part only, and carries off all light substances there deposited in the previous operation. When necessary, these matters may be removed by the finger, and made to run into a vessel placed below the scoop, in which all the water and matters carried off are received. This operation, however, must not be hurriedly performed, so as to mix the parts already separated : each layer must be removed separately, commencing with the upper one. This being done, the scoop must be alternately kept in motion by shakings, as at first, and then on its axis, and the washing off of the finer particles renewed, and so on until the separation is effected as far as may be judged necessary.

At the commencement of the operation, the water carries out of the scoop the lightest particles, as organic matter, clay, &c.; at a little later period the water carries with it a small but definite quantity of the heavier portion, the proportion of which increases as the operation proceeds, until at last the greatest possible care is required. It is always better to rewash the latter portion which passes off from the scoop; hence the necessity of allowing all the wash-water passing from it to collect in a vessel placed for that purpose.

In the second method of washing, a tin, zinc, or wooden pan is employed. It should be circular, one or two feet in diameter and three or four inches deep; the sides should descend in a conical manner, so that the bottom is not more than four inches in diameter, and the angle between it and the sides as sharp as possible.

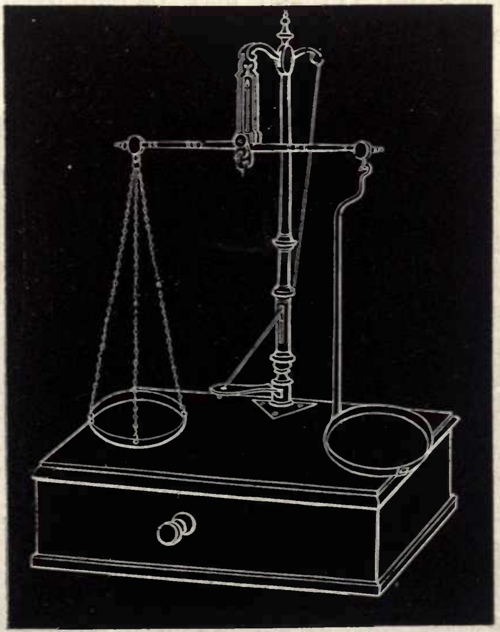
The substance to be examined is placed in the washing-dish, the latter filled with water, and the mineral well mixed with it until perfectly moistened as before. After a moment or so the muddy water is poured off, and the operation repeated until the water passes off clear. When this happens, only so much water must be placed in the pan as will leave a slight layer on the mineral. Now, by holding the pan in one hand, and shaking it with the other, the greater part of the heavy mineral, gold or otherwise, will fall below the sand. If now the pan be inclined towards the hand which is shaking it, the lighter portions, even if tolerably large, will flow off with the water, leaving the heavier matters in the angle, from which, with ordinary care and a little practice, it is difficult to disturb them. If there be a large quantity of earthy matter, this may be (after sufficient shaking) removed by the finger, as in the first-described process. By careful repetitions of these processes, the whole, or nearly the whole, of the sandy and earthy matters may be removed, and the gold or other mineral left nearly pure. This is the plan employed in *prospecting* for gold, diamonds, and other gems, and in some cases for their commercial extraction.

In Cornwall and other mining counties this operation is very cleverly and carefully performed on the miner's common shovel, and the richness of any particular sample of either tin, lead, or copper is thereby determined with a very near approach to accuracy.

THE BALANCE.

Operation of Weighing.—At least three balances will be required in a laboratory where general assays are performed. The first must be capable of carrying three or

Fig. 11.



four pounds in each pan, and must turn with a quarter of a grain. This may be of the form of the bankers' or bullion balance (fig. 11), and may be employed in weighing samples of gold quartz or silver ore containing metallic

FIG. 12.

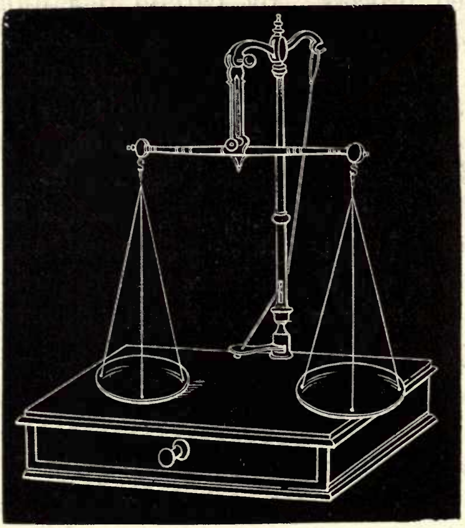
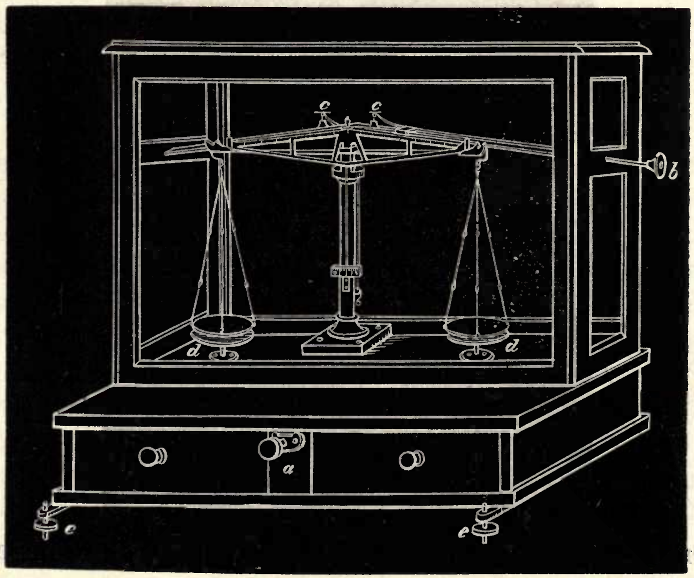


FIG. 13.



grains capable of being separated by the sieve (see p. 18); the second (fig. 12), or rough assay balance, is similar to the apothecary's scales; it should take 1,000 grains in each pan, and turn with one tenth of a grain. This serves for weighing samples of ore and fluxes for assay, and for determining the weight of buttons or prills of lead, tin, iron, copper, &c., obtained in an assay.

The third and most delicate, or true, *assay balance* (fig. 13) should carry about 1,000 grains; must turn distinctly and accurately with the $\frac{1}{1000}$th of a grain. This is employed in the assay of gold and silver bullion, and in the assay of minerals containing gold and silver; also for general analytical purposes. The first two balances may be used, with ordinary care, by any one; but the third balance, in its use and adjustment so as to maintain its extreme accuracy, requires some particular instructions, which necessarily involve the principle of the balance. These have been so admirably given by Faraday, in his 'Chemical Manipulations,' that we can do no better than transcribe them:—

'The theory of this balance is so simple that the tests of its accuracy will be easily understood and as easily practised. It may be considered as a uniform inflexible lever, supported horizontally at the centre of gravity, and supporting weights at equal distances from the centre by points in the same horizontal line with the centre of gravity. If the weights be equal the one will counterpoise the other; if not, the heavier will preponderate. In the balance, as usually constructed, there are certain departures from the theory as above expressed—some from the impossibility of execution, and others in consequence of their practical utility; and a good balance may be said to consist *essentially* of a beam made as light as is consistent with that inflexibility which it ought to possess, divided into two arms of equal weight and length by a line of support or axis, and also terminated at the end of each arm by a line of support or axis, intended to sustain the pans. These three lines of support should be exactly parallel to each other in the same horizontal plane, and correctly perpendicular to the length of the beam; and the plane in which they lie should be raised more or less above the centre of gravity of the beam, so that the latter should be exactly under the middle line of suspension. It will be unnecessary in this place to speak of the coarse faults which occur in the ordinary scales—these will be easily understood; and from what has to be stated of the examination of the most delicate instrument, the impossibility of avoiding them without incurring an expense inconsistent with their ordinary use will be as readily comprehended.'

Two principal things have to be attended to in the selection of a balance—its *accuracy* and its *delicacy*. The accuracy depends upon the following conditions:—

1. *The arms should be equal to each other in length.* The length of each is accurately the distance from the middle to the distant knife-edge, all the edges being considered parallel to each other, and in the same plane. The two arms should accord perfectly in this respect. This equality may be ascertained in two or three ways. Suppose the balance with its pans to vibrate freely, and rest in a horizontal position, and that after changing the pans from one end to the other the balance again takes its horizontal state of rest—in such a case an almost certain proof is obtained of equality in length of the arms. They may, however, be equal, and yet this change of the pans from end to end may occasion a disturbance of equilibrium, because of the unequal distribution of weight on the beam and pans; but to insure an accurate test, restore the pans, and consequently the equilibrium, to the first state: put equal, or at least counterpoising, weights into the pans, loading the balance moderately, and then change the weights from one pan to the other, and again observe whether the equilibrium is maintained; if so, the length of the arms in equal.

Equality of weight is not so necessary a condition, although this should be obtained as accurately as possible. One arm with its pan may be considerably heavier than the other, but from the disposition of the weight in the lighter arm towards the extremity, or in the heavier towards the middle of the beam, the equilibrium may be perfect, and therefore no inaccuracy be caused thereby in the use of the balance. Instruments are usually sent home in equilibrium, and require no further examination as to this particular point than to ascertain that they really are in adjustment, and that after vibrating freely they take a horizontal position.

2. *The beam must be of such a form and strength that it will not bend when loaded with the greatest weight the balance is intended to carry.* All well-made modern balances are sufficiently rigid in this respect, and may be safely trusted to carry their full weight without flexure of the beam. It should also be as light as practicable.

3. *The knife-edges supporting the pans, and the centre one on which the beam vibrates, must be accurately in the same line.*

The *delicacy* of a balance likewise depends upon several conditions.

The centre of gravity *must be very little below the fulcrum.* If it be considerably depressed, then, upon trying the oscillations of the balance by giving it a little motion, they will be found to be quick, and the beam will soon take its ultimate state of rest; and if weights be added to one side, so as to make it vibrate, or to bring it to a certain permanent state of inclination, the quantity required will be found to be comparatively considerable. As the centre of gravity is raised the oscillations are slower, but producible by a much smaller impulse; the beam is a longer time before it attains a state of rest, and it turns with a smaller quantity.

If, however, the centre of gravity coincides with the fulcrum or centre of oscillation, then the balance is said to *set*, that is, the smallest possible weight will turn the beam; the oscillations no longer exist, but one side or the other preponderates with the slightest force, and the valuable indication which is furnished by the extent and velocity of the vibrations is lost.

The case in which the centre of gravity is above the fulcrum rarely if ever occurs. Such a balance, when equally weighted, would *set* on the one side or the other; that side which was in the slightest degree lower tending to descend still further, until obstructed by interposing obstacles.

In balances intended to carry large quantities (as in the balance for weighing gold quartz, &c.) it is necessary to place the centre of gravity lower than in those for minute quantities, that they may vibrate regularly and readily. This is one cause why they are inferior in delicacy, for, as a consequence of the arrangement, they will not turn except with a larger weight.

Balances are also liable to *set* when overloaded. Thus, if a balance be equally weighted in each pan, but overloaded, it will, if placed exactly horizontal, remain so, but the slightest impulse or depression on one side destroys the equilibrium ; the lower side continues to descend with an accelerated force, and ultimately remains down, being to all appearance heavier than the other. Generally speaking, the more delicate a balance the sooner this effect takes place; this is one limit to the weight it can properly carry.

The vibrations of a balance vary with the quantity of matter with which it is loaded: the more the weight in the pans, the slower the vibrations. These should be observed, and the appearances retained in the mind, in consequence of the useful indications they afford in weighing. A certain amplitude and velocity of vibration would indicate to a person used to the instrument nearly the weight required to produce equilibrium ; but the same extent and velocity, with a weight much larger or smaller, would not be occasioned by an equal deficiency or redundancy of weight, as in the former case.

The weight also required to effect a certain inclination of the beam, or to turn it, should be known, both when it is slightly and when it is heavily loaded. Thus, if the instrument turns with $\frac{1}{1000}$th of a grain, with 1,000 grains in each pan, or with $\frac{1}{1000000}$th of the weight it carries, it may be considered perfect.

The friction of the knife-edges must be as slight as possible.

Most of the faults in the working of a balance, if ordinarily well made, depend upon imperfections in the middle knife-edge and the planes upon which it rests.

The edge is made either of agate or steel, preferably the former, and should be formed out of one piece, and finished at once, every part of the edge being ground on the same flat surface at the same time. In this way the existence of the two extreme or bearing parts of the edge in one line is insured; but when the two parts which bear upon the planes are formed separately on the different ends of a piece of agate or steel, or, what is worse, when they are formed on separate pieces, and then fixed one on each side the beam, it is scarcely possible they should be in the same line: and if not, the beam cannot be correct. These knife-edges usually rest on planes, or else in curves. The planes should be perfectly flat and horizontal, and exactly at the same height; the curves should be of equal height, and their axes in the same line. If they are so, and the knife-edge is perfect, then the suspension will be accurately on the line of the edge, and reversing the beam will produce no change. The balance must always be kept perfectly level by means of the three screws on which it stands, and adjusted by the spirit-level or plumb-line with which it is furnished.

The balance should be kept in a well-lighted dry room, quite away from acid or other vapours. The case should be kept closed as much as possible, and a glass vessel full of lumps of good quick-lime should be kept in it. When the lime falls to powder it should be renewed.

In order to test the accuracy and delicacy of a balance, remove the pans and their end supports, and notice how the beam oscillates. When it has been found to oscillate with regularity, and gradually to attain a horizontal position of rest, it should be reversed—that is, taken up and turned half-way round, so as to make that which before pointed to the right now point to the left. The beam should then again be made to oscillate, and if it perform regularly as before, finally resting in a horizontal position, it has stood a severe test, and promises well. Then replace the pans and repeat the tests, noticing the time required for each oscillation. When the pans are hung upon the beam, the balance should of course remain horizontal. They should be tried by changing, then by reversing, the beam, and afterwards by changing the pans again. The pans are best suspended by very thin platinum wire, so as to avoid hygrometrical influence upon them.

Afterwards load the balance with the full weight it is intended to carry—say 1,000 grains in each pan, and notice if the indications are as rapid upon adding or subtracting the smallest weight as they were when the pans were empty.

Tests of this kind are quite sufficient for the purpose of the assayer, who, having ascertained that his balance, whether slightly or fully laden, vibrates freely, turns delicately, has not its indications altered by reversing the beam or changing counterpoising weights, may be perfectly satisfied with it.

The irregularities which may be discovered by these tests are best corrected by a workman; but as in all the best balances now made adjusting screws for these purposes are provided, it has been thought advisable to introduce here such matter as, after careful perusal, will enable every one to adjust and examine his balance properly; so that, in the absence of a skilled workman, it may without much danger be put into working order by the assayer himself, if accidentally damaged by rough treatment.

The Weights.—Various kinds of weights are necessary for the different balances required by the assayer. For the larger balance, Troy-weights from 4 lbs. to $\frac{1}{4}$ grain will be requisite; for the second size, weights from 1,000 grains to $\frac{1}{10}$th part of a grain; and for the assay balance, weights from 1,000 grains to $\frac{1}{1000}$th of a grain.

The best material adapted for weights is unquestionably platinum. This is, however, too expensive for its general adoption, and therefore brass weights are almost invariably employed down to the ten- or twenty-grain weight, the smaller ones only being of platinum. On the Continent weights are generally made of silver, and if of brass are electro-gilt. For the smallest weights of all (those below 0·10 grain) aluminium is often used, its lightness, and consequently greater bulk, enabling these small weights to be made considerably larger than if they were of platinum. The riders are generally of silver-gilt wire. The slight tarnish which gradually forms on brass weights may be disregarded until it becomes thick. Weights ought never to be touched with the fingers, and should, when not in use, be kept tightly fastened in their box, away from all acid fumes. The most convenient series in which to have the weights is 600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1, ·6, ·3, ·2, ·1, &c. This is preferable to the series formerly employed, as it admits of the use of a less number of weights to arrive at any required amount.

According to H. Ste. Claire Deville and Mascart receptacles lined with velvet are not adapted for the preservation of weights, as dust is deposited in the velvet and acts upon the weights when taken out or put in. Small boxes of ivory or smooth wood are preferable.

Peculiar weights are necessary for the assay of gold and silver bullion in England (with the exception of assays for the Bank of England; see Gold assay), gold being reported in carats, grains, and eighths, and silver in ozs. and dwts. The most convenient quantity of either of the precious metals for assay is 12 grains. The quantity taken, however, is of no very great consequence; but whatever its real weight, it is denominated in England the *assay 'pound.'* This assay 'pound' is then subdivided into aliquot parts, but differing according to the metal. The silver assay 'pound' is subdivided, as the real Troy pound, into 12 ounces, each ounce into 20 pennyweights, and these again into halves (the lowest report for silver), so that there are 480 different reports for silver, and therefore each nominal half-pennyweight weighs $\frac{1}{40}$th part of a Troy grain, when the 'pound' is twelve grains.

Assay Weights for Silver.

Silver			Assay grains.
ozs.	dwts.	grs.	
12	0	0	12
11	0	0	11
6	0	0	6
3	0	0	3
2	0	0	2
1	0	0	1
0	10	0	0·500
0	5	0	0·250
0	3	0	0·150
0	2	0	0·100
0	1	0	0·050
0	0	12	0·025

The *gold assay 'pound'* is subdivided into 24 carats, each carat into 4 assay grains, and each grain into eighths, so that there are 768 reports for gold; and the assay 'pound' weighing 12 Troy grains, the lowest report, or $\frac{1}{8}$th assay grain, equals $\frac{1}{64}$th Troy grain; thus—

Assay Weights for Gold.

Gold			Assay grains.
carats.	grs.	eighths.	
24	0	0	12
22	0	0	11
12	0	0	6
6	0	0	3
3	0	0	$1\frac{32}{64}$ths
2	0	0	1
1	0	0	$\frac{32}{64}$ths
0	2	0	$\frac{16}{64}$ths
0	1	0	$\frac{8}{64}$ths
0	0	6	$\frac{6}{64}$ths
0	0	3	$\frac{3}{64}$ths
0	0	2	$\frac{2}{64}$ths
0	0	1	$\frac{1}{64}$th

In cases where the very smallest weights have to be employed, great care must be taken in seizing them with the forceps, as they are apt to spring away and be lost. In the assay balance (fig. 13) the use of weights less than $\frac{1}{10}$th of a grain is avoided by a very ingenious contrivance. Each side of the beam is equally divided into ten parts, and over the beam on each side is placed a sliding rod, as represented in the figure. The object of these rods is to carry, in the direction of the beam, the small bent piece of wire (letter *c*, fig. 13) called a *rider*, which serves in lieu of the smallest weights—the $\frac{1}{100}$th and the $\frac{1}{1000}$th. These riders are thus employed: one weighing $\frac{1}{10}$th of a grain is placed on the cross-piece of the extremity of the sliding rod just mentioned, and the rod thus furnished is brought gradually along the beam from the centre to the end, until the rider can be deposited on the division on the beam marked 10; the balance is then loaded on that side with a weight equal to $\frac{1}{10}$th of a grain. If now the rod be advanced to the centre of the balance, and the rider dropped on the mark 5, the half of $\frac{1}{10}$th of a grain will be pressing on that side of the balance, or, in other words, ·05th of a grain; and when the rider is at the marks 1, 2, 3, 4, respectively, ·01, ·02, ·03, ·04 of a grain will be indicated. With a rider weighing $\frac{1}{100}$th of a grain thousandths of grains may be indicated: thus the last rider placed on the marks 1, 2, 3, 4 would equal ·001, ·002, ·003, ·004 grain, &c.

The Method of Weighing.—The operation of weighing is very simple; but as in the hands of the assayer it becomes one of great frequency, the facilities for its performance require to be mentioned. It should in the first place be ascertained before every operation that the balance is in order, so far as relates to its freedom of vibration, and also that no currents of air are passing through the case, so as to affect its state of motion or rest, a situation being chosen where such influence may be avoided. In most cases there is a small projecting arm on the upper part of the beam, which, being turned either to the right or left hand side of the beam as required, serves to establish perfect equilibrium. Perfect equilibrium is, however, a matter of no consequence if the assayer observes one or two simple rules. He should never on any account *weigh* by the *direct* method, that is, he should never obtain the weight of a substance by putting it at once into one pan and then counterpoising it by adding weights to the other pan. This method is only to be relied on when the balance is of rare perfection, and is used by no one but the assayer himself. The plan of weighing by difference should invariably be adopted. By this means the weight of any body can be readily ascertained, no matter whether the arms of the balance are of unequal length or the pans out of equilibrium.

In the first place, it should be a rule that one pan, preferably the left, be reserved for the substance to be weighed, and the other pan be set apart for the weights.

Supposing the weight of a portion of mineral is required. First place a clean watch-glass, or platinum capsule, in the left pan, and carefully ascertain its weight. Let us suppose it weighs 106·347 grains; now put the mineral in the watch-glass and ascertain the united weight of the two. This we will imagine comes to 763·776. By subtracting the weight of the glass or capsule from this we find the true weight of the mineral, which is $763·776 - 106·347 = 657·429$. The substance to be weighed must *never* be put direct into the pan. By weighing in this manner by difference, the errors arising from inequality in the equilibrium or length of arms are eliminated.

Nothing should ever be weighed until it is perfectly cold. It is also unadvisable to weigh anything immediately after it is taken from a cold place to a warmer one, as the substance in such case will act as a hygroscopic body, and, by condensing moisture, will appear heavier than it really is.

Powders are conveniently weighed by filling a small stoppered tube bottle with them, then weighing the whole, and, after pouring out the requisite amount of its contents, reweighing the bottle and powder. The difference gives the weight of powder used. This is a very convenient plan if several portions of the same substance are required for different analyses. The tube will require reweighing each time after the quantities required for each analysis are shaken out into the receptacles.

A delicate balance is always furnished with means of supporting the pans independent of the beam; and the beam itself is also supported when required by other bearings than its knife-edges, and in such a manner as to admit of the rapid removal of these extra supports when the instrument is to be free for vibration. This is done that the delicate edges of suspension may not be injured by being constantly subjected to the weight of the beam and the pans, and that they may suffer no sudden injury from undue violence or force impressed upon any part of the balance. When, therefore, a large weight of any kind is put into or removed from the pans, it should never be done without previously supporting them by these contrivances; for the weight, if dropped in, descends with a force highly injurious to the supporting edges; also, if a large weight be taken out without first bringing the pans to rest, it produces a similarly bad effect.

The weights should not be put into the pan at random. It is a mistake to suppose that time is saved by such a plan. The highest probable weight should be added first, and then the set should be gone through systematically down to the smallest weight, retaining or removing each weight in order according as it is too little or too much. The exact weight of a body will be found in this manner in far less time than would be required were the weights added by guess.

When a weight is put in which is assumed to be nearly equal to the substance to be weighed, the balance should be brought to a state of rest, and should then be liberated gradually by turning the handle, so as to leave the pans wholly supported by the beam. The whole being on its true centres of suspension, it will be observed whether the weight is sufficient or not; and the rapidity of ascent or descent of the pan containing it will enable a judgment to be formed of the quantity still to be added or removed.

Great care should be observed in recording the weight in the notebook. The weight should first be ascertained from an inspection of the vacancies in the box of weights, and then verified by an examination of the weights themselves. This is conveniently done whilst replacing them in the box, which should be done immediately after each weighing.

In some cases, where great accuracy is not of so much importance as rapidity in getting out approximate results, a plan may be adopted recommended by Mr. F. F. Mayer in the American 'Journal of Science and Art' for 1861.

Mr. Ch. Mène, of Creusot, gave (in the 'Journ. de Pharm. et de Chimie' for October 1858) a mode of weighing which does away to a great extent with the tediousness and difficulties attending the dryness of many precipitates. He washes the precipitate thoroughly by decantation, and then introduces it carefully into a bottle the exact weight of which when filled with distilled water at a certain temperature is known. Since the precipitate is heavier than water, the bottle, when filled again, will weigh more than without the precipitate, and the difference between the two weights furnishes the means of calculating the weight of the precipitate.

In case the precipitate settles but slowly, it may be collected on a filter, and, together with a filter, after washing, be introduced into the bottle, in which case the weight of the filter and its specific gravity, supposing any difference should exist between its own and that of water, is to be taken into account. Precipitates soluble in or affected by water may be weighed in some other liquid.

Mr. Mayer applied this principle on a large scale as far back as 1855.

In that year he was engaged in the manufacture of lead carbonate from refuse lead sulphate, by treating the latter, in a pulpy condition, with sodium carbonate. The lead sulphate used contained very varying proportions of water and soluble impurities, from which latter it had first to be freed by washing. It was then in the state of a thin pulp, and the difficulty was to find the amount of the dry lead sulphate, as it was a matter of importance to use as little sodium carbonate, and to obtain as pure a lead carbonate and sodium sulphate, as possible. This could only be done by weighing it in the bulk or in portions; but as the drying of a tubful of lead sulphate (from 500 to 1,200 lbs.) was impracticable, and sampling not less so, since the upper strata contained a much larger proportion of water than the lead at the bottom, the following method was contrived, which enabled the management of the process to be left in the hands of a workman:—

A strong oaken pail was taken, weighing 8 lbs. when empty, and a black mark was burnt in horizontally around the inside of the pail two inches below the rim, up to which mark it held 20 lbs. of water. The specific gravity of lead sulphate being 6·3, the pail, if filled up to the mark, would hold 126 lbs. of pure lead sulphate. The specific gravity of water being 5·3 less than that of lead sulphate, it followed that if there were 1 lb. of water in the pailful of moist sulphate, the pail would weigh 5·3 lbs. less than 126 (+8, the tare of the pail)=120·7(+8); if there were 2 lbs. of water present, the weight would be 115·4 (+8), and so on. This enabled a table to be calculated giving in one column the actual weight of the pail when filled with moist sulphate, and opposite, in a second column, the amount of dry sulphate corresponding to the gross weight. The weight of dry sulphate was thus found as accurately as could be desired, although the amounts varied in practice from 30 to 105 lbs.

This is nothing but an application of the Archimedean theorem, that when a solid body is immersed in a liquid it loses a portion of its weight equal to the weight of the fluid which it displaces, or to the weight of its own bulk of the liquid.

This is precisely the principle applied by Mr. Mène. The precipitate he obtains by a certain chemical manipulation is a substance of known composition and specific gravity. Supposing it to be lead sulphate, and the bottle when filled with water at the normal temperature to weigh 70 grammes = 50 grammes of water and 20 for tare. After introducing the precipitate and filling again with water, it weighs 71·06 grammes. Now as the specific gravity of lead sulphate is 6·3, or as the weight of a cubic measure of lead sulphate is 6·3 times that of a cubic measure of water, and as the space of one part by weight of water, is taken up by 6·2 parts by weight of lead sulphate, it follows that the quantity of the lead sulphate in the bottle, which has taken up the space of one part by weight of water, increases the original weight of the bottle (filled with pure water) by 5·3. To find the amount of water displaced it is only necessary to divide the overweight (1·06 grammes) by 5·3=0·2, which, added to the overweight (1·06+0·2), gives 1·26 grammes as the weight of the precipitate.

Hence the rule, which is of great convenience in volumetric analysis, that to find the weight of a moist precipitate which is a compound of known specific gravity, weigh it in a specific gravity bottle or some other vessel of known weight when filled with water or any other liquid at the normal temperature; again fill it with the water or other liquid, divide the excess of the new weight by the specific gravity of the substance, less that of the water or other liquid (that of water being =1), and add the quotient to the overweight, which gives the weight of the precipitate.

The principle exemplified by Mr. Mayer may not be novel; but as it has never been fully exemplified before, chemists and assayers will probably also find it of interest, and certainly highly practicable and easy of execution.

Dr. F. Muck ('Zeitschrift für Analytische Chemie,' vol. xix. p. 131) remarks that a previous complete drying of the precipitate, as Bunsen has proved, is not merely a loss of time but a disadvantage; whilst introducing the still moist precipitate into the crucible requires the application of a very gentle heat at the outset, and thus insures the most favourable conditions for the easy and complete incineration of the filter-paper. Precipitates not washed upon the filter-pump can be readily brought to a sufficient degree of dryness if laid for a short time upon blotting-paper or unglazed earthenware.

Dry filters may be also much better incinerated after previous charring at the lowest possible temperature than by rapid carbonisation or direct ignition in the flame. How advantageous it is to char previously very slowly may best be seen on incinerating filters whose contents impede the complete combustion of the paper by the old process, *e.g.* silicic acid, ammonio-magnesium phosphate, &c. Charred paper obtained by rapid heating is deep black and of a silky lustre, whilst if slowly carbonised it is brownish-black, dull, and smoulders away like tinder. Charred paper of the first kind appears under the microscope perfectly amorphous, whilst the other displays the carbonaceous skeleton of the fibre.

A careful removal of precipitates from the filter—with the exception of cases like zinc and cadmium, where volatile reduction-products may be formed—is quite useless, since the errors which it was hoped to obviate are not really avoided. On incineration with the filter, wet or dry, an error due to reduction may be easily corrected, *e.g.* in barium sulphate with sulphuric acid; in lead sulphate with nitric and sulphuric acid; in iron and copper oxides with nitric acid; in silver chloride with nitric and hydrochloric acids, &c.

CHAPTER III.

GENERAL PREPARATORY CHEMICAL OPERATIONS.

Calcination.—Strictly speaking the term calcination means the production of an oxide or *Calx* by combustion, and it necessarily involves the intervention of atmospheric oxygen. But in a metallurgical sense the term is restricted to the separation of any volatile matter from a mineral substance by the aid of heat alone, the atmosphere being totally or partially excluded; or the production of rapid changes of temperature, so as, for instance, to render minerals more fragile by heating and then quenching in water &c.

Thus we speak of the calcination of minerals, as iron or zinc ores, &c., whose matrices are argillaceous, to expel water, and also of gypsum to expel water; the carbonates of lime, iron, copper, and lead are calcined to separate carbonic acid; the hydro-carbonates of zinc and iron, to get rid of both water and carbonic acid; cobalt and nickel ores, &c., to separate arsenic and sulphur. The iron ores found in the vicinity of collieries are calcined to expel bituminous matter, and wood and bones to expel volatile organic matter. Where the operation is accompanied by combustion, and requires the oxygen of the atmosphere, it is termed roasting.

Crucibles are conveniently used in calcination, as no stirring of the mass is required. They may be made of various materials, as clay, plumbago, platinum, silver, and iron. Silver must not be employed when sulphur is present or at a heat greater than dull redness. The selection of the crucibles must depend upon the substance under operation; they must all be furnished with covers.

In almost all operations in assaying it is necessary to estimate the amount of volatile matter lost by calcination. A very high temperature is seldom required in calcination; usually an air-furnace will give enough heat. When the operation is finished the crucible must be removed from the fire and allowed to cool gradually. When completely cold, remove the cover and take out the contents by means of a spatula. If any adhere, a small brush will be found very useful for its removal. The difference in weight before and after calcination will represent the volatile matter.

When the subject to be calcined is fusible, the crucible and contents must be weighed before ignition; the loss of weight is equal to the quantity of volatile matter expelled; in fact, this latter is usually the most satisfactory method of conducting the experiment.

If the ignited substance be soluble in water, it can be removed from the crucible by that menstruum, employing heat if required; if not, any suitable acid may be used.

If the substance to be calcined decrepitates on heating, it must be previously pulverised, and heated slowly and gradually in a well-covered crucible.

Certain substances, as lead carbonate, undergo a material alteration by contact with the gases given off during the combustion of the fuel in the heating furnace; others, such as carbonaceous matters, are consumed by the introduction of atmospheric air. All such substances must be calcined in a closely covered crucible placed in a second crucible (also covered) for further protection.

In some rare cases, however, these precautions are not sufficient. In such, either a weighed porcelain or German glass retort must be employed.

Sometimes earthenware crucibles lined with charcoal are employed in calcination; for even if the substance be fusible it may generally be collected and weighed without loss, as very few bodies either penetrate into or adhere to a charcoal lining. In this way grey cobalt and other arsenio-sulphides are calcined at a high temperature to expel the greatest possible amount of arsenic and sulphur.

The selection and proper management of crucibles will be given in the next chapter.

Roasting.—In this operation carbon, sulphur, selenium, antimony, and arsenic are separated from certain metals with which they were combined. Roasting differs from calcination in this particular: the latter is carried on in close vessels, independent of the atmosphere; the former, in open vessels by the aid of the atmosphere. It is thus we are enabled to separate the bodies just mentioned by this process; for the oxygen of the air, by combining with them, forms a volatile substance which the heat expels. Thus, in roasting copper and iron sulphide (copper pyrites), the sulphur, copper, and iron mutually combine with oxygen to form sulphurous anhydride (volatile), copper protoxide, and iron peroxide, thus:—

$$2\,(FeS + CuS) + 13O = Fe_2O_3 + 2(CuO) + 4(SO_2).$$

This is the final change in this case. During the process, however, some copper and iron sulphates and sub-sulphates, are formed. This change will be explained under the head of Copper Assay.

When carbonaceous matters are roasted, the operation also takes the name *combustion*, or incineration; because the object of roasting a fuel, for instance, is generally to ascertain the amount of ash left.

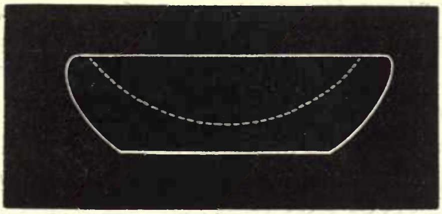
In roasting, in the ordinary acceptation of the term, the body must not be fused, but kept in a pulverulent state; there are, however, some cases in which fusion is allowable, as in *cupellation* and *scorification*.

The process of roasting is performed in different ways. In one, a small flat vessel, called a roasting-test (fig. 14), is employed, made of the same material as the earthen crucibles, and similar to a saucer. It is most conveniently heated in a muffle. The substance to be roasted must be finely pulverised, placed in the roasting vessel, and constantly stirred with an iron or glass rod until no fumes are given off, or until it ceases to evolve the odour of sulphurous acid if sulphur is one of the constituents to be eliminated.

The operation may also be performed in a crucible, in which case it must be inclined to the operator, so that the draught of air passing to the furnace flue may impinge as much as possible on the substance under manipulation.

During roasting the heat must be carefully regulated for some time. At first it ought only to be the dullest red; and the substance must be assiduously stirred in order to present the largest possible surface to the action of the atmosphere and prevent fusion, for some assays, when roasting, will fuse readily at a low temperature unless the surface be continually renewed. Even by paying the utmost attention to this point it cannot be always prevented, as for instance when antimony sulphide is being roasted. In these cases the assay must be mixed with its own weight of powdered quartz or fine white sand (silver sand); the operation will then proceed steadily.

FIG. 14.



If the assay at all agglutinates it must be taken from the fire and rejected if the substance be plentiful; if not, the fused mass must be carefully removed from the crucible or test, pulverised, and the roasting recommenced. In this case, however, the operation is always very tedious, and the final result less exact, so that great care ought to be taken at the commencement of the roasting.

When the assay has been kept at a dull red heat for some time, and shows no signs of agglutination, the heat may be slightly increased; at the same time stirring must be diligently pursued. After the heat has arrived at full redness there is little fear of fusion; and as the operation proceeds more rapidly at a high temperature than at a low one, it is well now to increase the heat to a yellowish red, and even in certain cases to nearly a white heat. If the stirring of the assay has been constant during the various gradations of heat, the roasting at this point will be accomplished; and the remaining operations of the assay may be proceeded with.

This is the general plan of operation, but different substances require for roasting a different degree of heat; for instance, copper pyrites require a higher temperature than grey copper ore, and the heat employed must in every case be adapted to the substance to be roasted. Some substances, for instance, arseniates, lead sulphate, &c., cannot be roasted by heat alone. These require the addition of a carbonaceous body to remove the combined oxygen, and allow the arsenic, sulphur, &c., to be completely roasted off. Ammonium carbonate in some cases is also added to the mixture to separate the sulphates formed during the roasting of sulphides.

In cases where the metallic bases of the sulphides are volatile, either as such, or as oxides, as for instance galena, antimony sulphide, &c., a loss of metal will always result during the roasting process.

It may be as well to mention here that platinum capsules are useful in certain roasting operations. The copper, iron, and molybdenum sulphides are conveniently oxidised in this kind of vessel, without much fear of injury, provided fusion of the roasting substance be carefully avoided. Platinum vessels should also be used in ascertaining the amount of ash in coal.

Reduction.—The process of reduction consists in removing oxygen or an analogous element from any body containing it, usually by means of either carbonaceous matter, hydrogen, or a body containing both these elements, and leaving the metal behind, usually in the form of a melted button. The *rationale* of the operation is as follows, when lead oxide is reduced with carbon:—

$$2(PbO) + C = 2Pb + CO_2.$$

In this case we start with lead oxide and carbon, and as a result we obtain metallic lead and carbonic acid.

The reaction between nickel oxide and hydrogen is thus expressed :—

$$NiO + 2H = Ni + H_2O.$$

Here we have at the commencement nickel oxide and hydrogen; and after the conclusion of the operation there remains metallic nickel, and water which has volatilised. If the reducing substance contain both carbon and hydrogen the action will be thus, when a metal (*e.g.* lead) is reduced from its oxide, carbonic acid and water being formed :—

$$3(PbO) + CH_2 = 3Pb + CO_2 + H_2O$$

In the operation of reduction by the aid of carbonaceous matters two methods are employed: in the one, charcoal, coal, sugar, starch, or any carbonaceous or hydro-carbonaceous body, as argol, is mixed with the substance to be reduced; in the other, the process of cementation is employed. Where sulphides are to be reduced, metallic lead or iron is usually employed to remove the sulphur. Generally, however, the sulphides are previously converted into oxides by the operation of roasting, and the reduction is then effected by means of carbonaceous matter.

The process of cementation is conducted by placing the oxide to be reduced in a crucible lined with charcoal, and covering it closely while it is in the furnace; the reduction proceeds gradually from the outside of the oxide to the centre of the mass. The time requisite for this operation depends on three circumstances—viz. the nature of the oxide, the degree of temperature, and the mass acted on.

Some oxides treated this way are reduced very readily; others, again, take a considerable time; while certain of them do not appear to be acted on beyond the outermost layer. Of the first class is nickel oxide; of the second, manganese oxide; and of the third and last, chromium oxide.

Each of these classes of reduction has its advantages. The former, or reduction by *mixture* with carbonaceous matter, takes place very quickly and completely, but the reduced metal is often mixed with carbon; in the latter process the residue is comparatively pure, but it is not generally preferred, on account of the time and high temperature necessary.

Reduction by hydrogen gas is very seldom employed; it is, however, necessary in some cases, as for instance in the determination of the percentage of cobalt or nickel in a sample, where perfect accuracy is desirable. The operation is carried on in a tube of hard German glass, having a bulb blown in its centre, which is heated either by a spirit or gas lamp. Attached to it is a tube full of dried calcium chloride, through which the hydrogen gas effecting the reduction passes to perfectly dry it.

The bulb tube is weighed and the oxide introduced into it; it is again weighed, and the apparatus united by caoutchouc tubes; hydrogen gas (see Reducing Agents) is then passed through it until the whole of the atmospheric air is expelled. Heat is afterwards applied till the bulb is bright red, and the current of gas continued until no more water from the decomposition of the oxide is formed; the source of heat is then removed, and the current of gas continued until the apparatus is cold. The bulb tube, with the reduced metal, is then weighed, and the amount which it has lost represents the oxygen which the hydrogen has removed. By subtracting this oxygen from the original weight of the substance, the difference gives the amount of metal in the amount of oxide operated on.

Fusion.—This operation is sufficiently simple, and is employed in all assays by the dry way, in order to obtain, in conjunction with the last process, a button or prill, as it is termed, of the metal whose assay is in progress. It is also a necessary step in the granulation of metals, the preparation of certain fluxes and alloys, also lead for the assay for silver, in order that a homogeneous ingot may be obtained. Some ores, such as those of copper, are melted instead of being roasted or calcined, in order to prepare them for reduction. Minerals are also melted *per se*, or with the addition of borax or sodium carbonate, in order to ascertain the best treatment to be adopted in a subsequent operation. Metals too are frequently melted to drive off other volatile metals; in this case the heat should be continued for some time, and should be very high, as it is difficult to remove the last traces of volatile metals. Thus, in melting the spongy gold left behind in the retort after the distillation of gold amalgam, the ingot of gold almost always retains mercury, which can only be removed by repeated meltings at a very high temperature. In some cases the fusion is intended to be only partial, the object being to melt out an easily fusible part of the mineral—for instance, in assaying grey antimony ore and different bismuth ores.

SOLUTION.—In all cases where analysis in the wet way is required, the mineral must be either wholly or partially brought into the state of solution. The choice of a solvent necessarily depends upon the nature of the material under treatment. In some few cases water will be sufficient; but in the majority acids are required. Sometimes advantage will be derived by first extracting all that water will dissolve, and then applying acids to the residue. In speaking of the minerals, &c., which require solution for their assay, the most appropriate solvents will be pointed out. In all cases heat promotes solution.

Solution is best effected in glass flasks; clean Florence oil flasks are very appropriate for most purposes. They may be supported on a hot sand bath, or on a metal ring or coarse wire gauze, over the naked gas or spirit-flame. The flask should then be placed in a sloping position, so that when the liquid boils or effervesces from the escape of gas, the drops spirted up may strike against the sloping side, and run back into the liquid instead of being thrown out of the mouth.

A porcelain dish may also be used, although from the great surface exposed these vessels are more appropriate for evaporation than solution. Beakers may likewise be employed, but they should be covered over with an inverted funnel sufficiently large to rest within the top edge without slipping down more than about half an inch; or a large watch-glass or dial-plate turned concave side upwards may be used as a cover. Both the funnel and dial-plate serve the double object of keeping out dust and preventing loss of the liquid by projection of fine drops during ebullition.

In many cases solution of the whole or part of a mineral must be preceded by its fusion at a high temperature with sodium carbonate, nitre, or some other flux. The fused mass must then be well extracted by boiling water, when the residue will usually be found soluble in hydrochloric or other acid. Special instructions in this method of effecting solutions will be given in those cases where it is necessary.

FIG. 15.

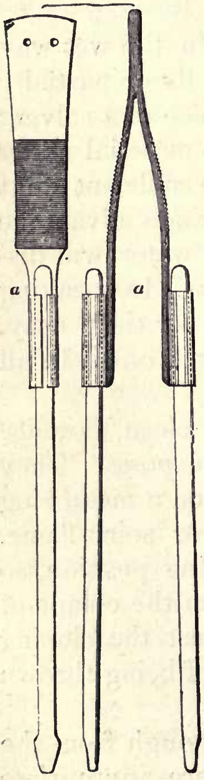
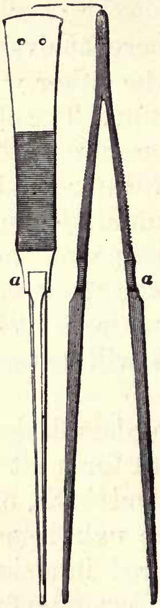


FIG. 16.



Where it is necessary to manipulate in acid or other solutions, the glass and platinum forceps described by David Forbes, F.R.S., in the 'Chemical News' for October 2, 1868, will be found useful.

The accompanying woodcut, Fig. 15, shows them in front and side view, and will require but little explanation. They are made as follows: an ordinary pair of strong surgical forceps are taken and the points cut off; a small piece of sheet brass, bent into a cylinder, is then soldered to each arm as shown at *a*; these cylinders being formed by merely bending the brass round, so as to leave an open slit about one twentieth of an inch wide in front. Two glass rods, such as are used for stirrers, as long as the glass arms of the forceps are intended to be, and just as thick as will enter these brass cylinders when pressed with some force, are rounded by the blow-pipe at the one end, whilst the other, when softened, is somewhat flattened between the glassblower's pliers, as seen in the woodcut. In order to complete the forceps it is now only necessary to push each of these rods into its corresponding brass cylinder or socket, the longitudinal slits of which, by imparting a certain amount of elasticity to the sockets, cause them to grasp the glass rods firmly, and retain them without any cement or other fixing. The relative lengths of the arms are easily adjusted by slipping one rod more or less forward, whilst the points can be made to hold and meet accurately, by rubbing them down on a piece of sandstone.

Such forceps may, of course, be made to any convenient size; the one figured in the woodcut is drawn to exactly half-size, and is found to be of very useful dimensions for general analytical work, especially when manipulating in nitro-hydrochloric acid, nitrate of silver, and other solutions which would have acted upon metals, horn, ivory, &c.

Fig. 16 represents another convenient form of forceps, also drawn to one half the real size, with long platinum points soldered to the steel body at *a*; these have been also found of great service in general laboratory operations, especially when hydrofluoric acid is in question.

Distillation.—There are two distinct classes of this operation: in the one, liquids are submitted to experiment with the object generally of separating them from substances which are non-volatile, and will consequently be left behind when the liquid comes over. Belonging to this class may be mentioned the distillation of nitric acid, the preparation of distilled water, and the separation of mercury from gold and silver amalgam. In the other kind of distillation, which goes by the name of *dry distillation*, solid bodies, as wood, coal, &c., are subjected to heat in order generally to ascertain the amount of gas or other volatile matter given off in the course of an experiment, from a certain quantity of the coal or other substance operated upon.

In liquid distillation (as in the purification of nitric acid, &c.), retorts are used. The best form for general use is that which is furnished with a stopper at the upper part of the body, *a* (fig. 17), through which the liquid is introduced; the neck of the retort is then placed in that of a receiver, *b*, over which a piece of wet cotton or woollen cloth is placed, and which must be kept cold by means of a stream of water from a funnel, *c*, the shaft of which is partially plugged up with cotton wool. Heat is then applied to the retort, and as much of the liquid as is desired is distilled over into the receiver. It is advisable not to fill the retort more than two thirds full, and to apply the heat at first very gently, otherwise there is a risk of breaking the vessel.

FIG. 17.

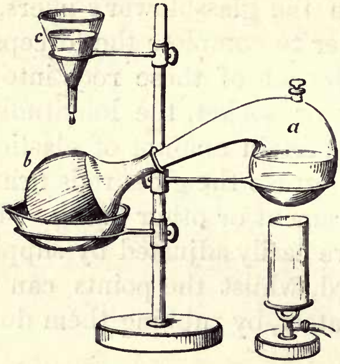
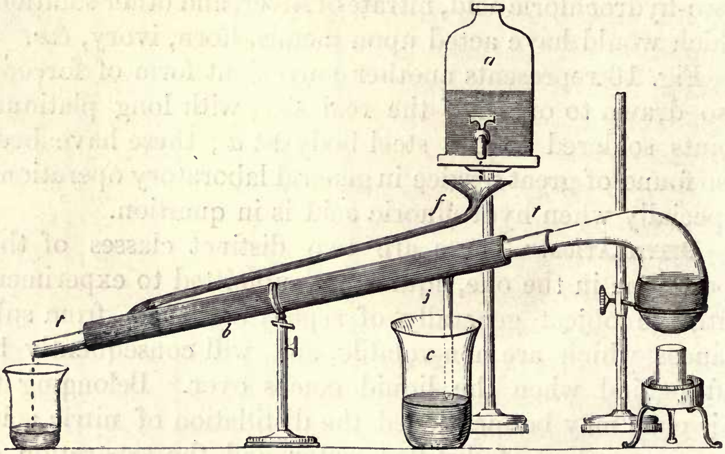
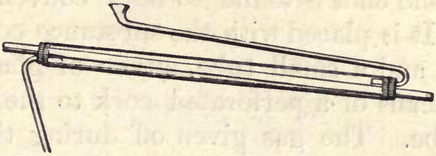


FIG. 18.



A more convenient form of apparatus for distillation and condensation is shown at fig. 18, in which a Liebig's condenser is attached to the retort. Fig. 19 will show the construction of the condensing apparatus. The cold

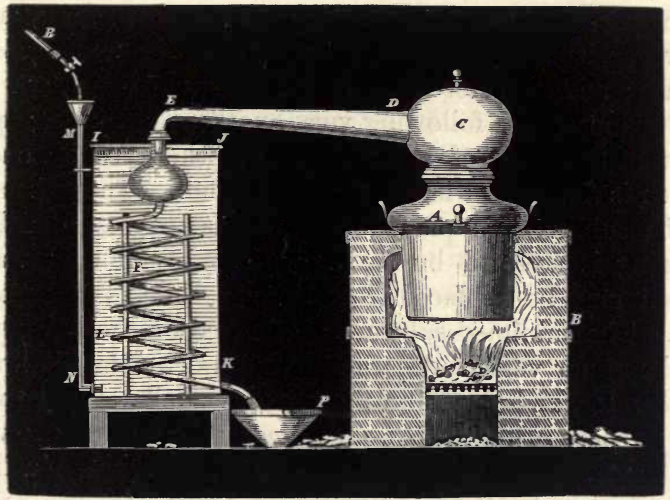
FIG. 19.



water passes into the funnel above, is conveyed at once to the lowest end of the condenser, whilst the heated water passes off by the upper tube.

Distilled water is a most important agent in the laboratory; and, as much is needed, it is better to have a still

FIG. 20.



specially adapted for its production. Such a one is depicted at fig. 20, where *A* is the body of the still; *B* the furnace in which it is set (the still may also be placed in the portable furnace, fig. 25, p. 63); *C* the still head; *D E* the neck; *F* the worm; *I J K L* worm-tub containing cold water to condense steam generated in still; *M N* pipe to lead fresh cold water to bottom of worm-tub, while the warm water runs off at the top, as in Liebig's condenser; and *P* the vessel in which the distilled water is received.

In the dry distillation of bodies, earthenware, glass, or iron retorts are employed; but for small operations a tube of wrought-iron, about one inch internal diameter, and plugged at one end, is found to be a convenient form of apparatus. It is placed with the substance contained in it in a furnace, and a small tube, either of glass or pewter, is fixed by means of a perforated cork to the open end of the large tube. The gas given off during the operation may be collected by the aid of the pneumatic trough.

Sublimation.—This operation is a kind of distillation in which the product is obtained under the solid form. The apparatus which may be employed for this purpose are tubes, flasks, capsules, or crucibles. Florence flasks are exceedingly useful; they may be sunk in a sand-bath, and the sublimed substance received directly into another flask, or by passing through an intermediate tube. Sometimes, however, it is difficult to entirely remove the sublimed substance; and in order to avoid this inconvenience, Dr. Ure has proposed the following very excellent subliming apparatus: It consists of two metallic or other vessels, one of which is flatter and larger than the other. The substance to be sublimed is placed in the smaller vessel, and its opening is covered by the larger filled with cold water, which may be replaced from time to time as it becomes hot. The sublimed substance is formed on the lower part of the upper vessel. A large platinum crucible, filled with cold water, and placed on the top of a smaller one, answers the purpose of the before-mentioned apparatus very well.

Scorification—Cupellation.—These operations will be described under the head of Silver Assay.

CHAPTER IV.

PRODUCTION AND APPLICATION OF HEAT.

FURNACES for assay purposes may be heated either by solid fuel, oil, or gas, and they may be divided into *wind* and *blast* furnaces. In the former the fire is urged by the ordinary draught of a chimney, and in the latter by means of bellows or artificial blast. We shall commence with the former, as they are in most common use. They are of various kinds, according to the purposes for which they are required. The three principal kinds are those for fusion, calcination, and cupellation. Coal, coke, and charcoal are the fuels employed, and the merits of each will be particularly discussed. Blast furnaces are only employed for the purpose of fusion, although their forms are various; charcoal and coke are the fuels most in use, but oil and gas blast furnaces are used in small laboratory operations, and for many purposes they are preferable to other furnaces, on account of their freedom from dust and dirt, and the perfect control the operator possesses over the heat.

Furnaces consist of certain essential parts—viz. first, the ash-pit, or part destined to contain the refuse of the combustible employed; secondly, the bars on which the fuel rests; these are sometimes made movable, or are fixed to a frame; the former arrangement is more convenient, as it allows clinkers and other refuse matters to be readily removed; thirdly, the body of the furnace in which the heat is produced; and lastly, in wind furnaces, the chimney by which the heated air and gaseous products of combustion are carried off.

CALCINING FURNACE.—Calcining furnaces are small and shallow, because a high temperature is not required. They may be made square or circular; the former are most readily constructed, and, where many crucibles are to be heated at once, they are preferable to the circular; but the latter give the greatest degree of heat with the least possible consumption of fuel, and are to be preferred on that account where one crucible only is to be ignited.

The body of the furnace is best made with good bricks, lined with Welsh lump, fire-bricks, or a mixture of Stourbridge clay and sand. It is also desirable that a plate of iron with a ledge be placed over the upper part of the furnace to protect the brickwork from blows with crucible tongs, &c., and to keep it in its place when disturbed by sudden alterations of temperature. The bars of the furnace may be either in one single piece, or made up of several bars of iron fastened to a frame. They ought to be as far as practicable from each other, and must not be too large, although large enough not to bend under the weight of the fuel and crucibles when they become hot, and they must not be so far removed from each other as to allow the coke or charcoal to fall through easily. Lastly, the more readily the air can find access to the centre of the fuel, the higher will be the temperature produced in the furnace; very simple assays occasionally fail, only because the bars are either too large or too close together.

Chimney.—Calcining furnaces generally have no fixed chimney, but are covered with a movable one when a greater degree of heat is required. This chimney may be about five feet high, the diameter of the furnace at the bottom, and tapering off to about two thirds of that diameter at the top. It is made of strong plate iron, furnished with a wooden handle. The lower part is provided with a door, by means of which the interior of the furnace may be examined without disturbing the whole arrangement of the chimney, and consequent cooling of the contents of the furnace.

If, during the course of any experiment, noxious or offensive vapours are expected to be given off, the furnace must be so arranged that they may be introduced into a flue, by fastening a piece of iron plate pipe, furnished with an elbow joint, on to the movable chimney before spoken of.

Evaporating Furnaces.—The furnaces just described answer exceedingly well in the absence of gas, for heating small flasks, evaporating basins, &c., when surmounted by a tripod stand or sand-bath. This is necessary, as many assays by the dry way are preceded and followed by certain operations in the wet way.

The Hood.—In order to prevent certain gases or vapours from fires, evaporating basins, &c., from entering into the laboratory, a large metal covering, termed a hood, is employed, terminating in a chimney having a good draught. It is best made of plate or galvanised iron.

Fusion Furnace—Wind Furnace.—The wind furnace, properly so called, is a furnace provided with a chimney, and capable of producing a very high temperature.

Wind furnaces are generally square, but, if more than four crucibles are to be heated at one time, they may be made rectangular, the chimney being placed at one of the long sides. When the furnace is required to hold but one pot, it may, however, be made circular.

The body of the furnace ought to be made of good bricks, solidly cemented with clay, and bound by strong iron bands. The bricks must be very refractory, and capable of sustaining changes of temperature without cracking. They are ordinarily made with the clay used in the manufacture of crucibles. In some cases bricks are not used for the lining of this kind of furnace; for instance, a mould of wood is placed in the centre, and the open space between the surface of that and the outer brickwork is filled with a paste of very refractory clay, each layer being well beaten down. When the space is filled the case is withdrawn, and the crust of clay dried with much precaution, every crack that may be caused by unequal desiccation being filled up as fast as formed. This method of manufacture is very applicable to circular furnaces. In every case, however, it is necessary to border the edge with a band of iron to prevent injuries from tongs or pots.

By using a mixture of 1 part of refractory clay and 3 to 4 parts of sifted quartz sand, no cracks are formed during desiccation. This mixture is used on the Continent for the interior fittings of Sefström's blast furnace, as well as for larger blast furnaces for manufacturing purposes. It is said to stand a high temperature exceedingly well.

Makins * recommends for small furnaces the second kind of bricks, known as Windsor, or in the trade P.P bricks. 'These are of a red colour, very siliceous, but soft, easily cut and shaped, and yet standing heat very well. The best method of cutting them is by a piece of zinc roughly notched out as a saw, and then the more accurate figure required may readily be given them by grinding upon a rough flat stone. In this way the small circular furnace formerly made by Newman, and sold by him as his "universal furnace," is lined by cutting the bricks with care to the radii of the circle they are to form, when they key in, like an arch, and so need no lining whatever.'

The Ash-pit is an open space under the bars, which serves as a receptacle for ashes, clinkers, &c., produced during the time the furnace is in use. It should have the same area as the furnace, and be completely open in front, so that the air may have free access; it is well, however, for the sake of economy, to furnish this opening with a hinged door, having a register plate fixed in it, so that the draught may be reduced, or entirely shut off, in order that the fire may be extinguished when desirable, and fuel saved which would otherwise be burnt in waste.

On the one hand, it is well to have the power of cutting off access of air into the body of the furnace by the lower part, either to put out the fire entirely, or to deaden it whilst putting in a pot; and, on the other, to attain the maximum of temperature, we must have the means of allowing the air to pass with the greatest possible facility into the furnace. In order to do this it is necessary to furnish the ash-pit with doors, or valves, whereby the quantity admitted may be regulated as desired. It is advantageous to lead the air to the ash-pit from a deep and

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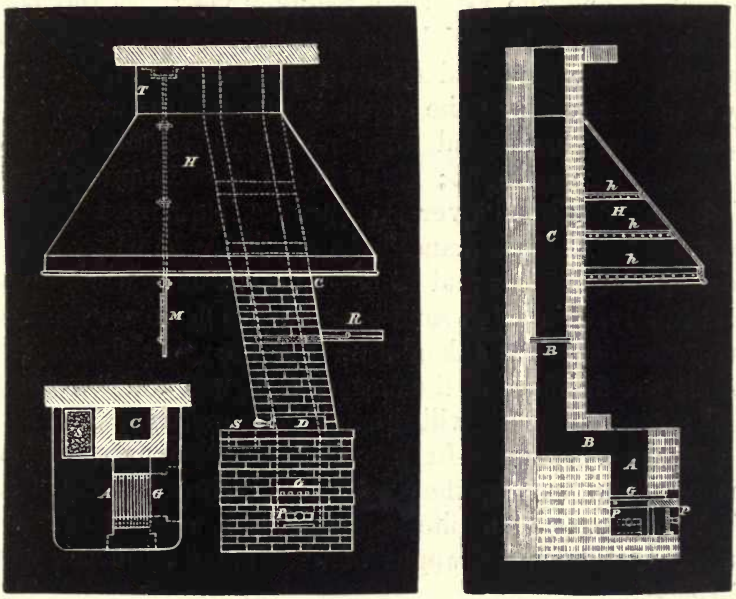
* Makins's *Metallurgy*, p. 88.

cold place, by means of a wide pipe. A chimney of less height will then be required.

The Bars are made in one piece, or are made up of movable pieces of metal; the latter arrangement is the most convenient. Wherever a wind furnace is in use, the superior opening is closed by a cover made of a fire-tile, encircled with iron.

The Chimney is a very essential part of a wind furnace: it is on its height and size that the draught depends, and, in consequence, the degree of heat produced within the furnace. In general, the higher and larger the chimney, the stronger is the draught; so that, by giving it a great elevation, exceedingly high temperatures may be obtained. But there is a limit which it is useless to pass in a furnace destined for operations by the dry way; and, besides this, the building a very high chimney presents many difficulties and much expense, so that in laboratory operations, where a very strong current of air is required, recourse is had to a pair of double bellows. A temperature can be produced in a wind furnace sufficiently strong to soften the most

Fig. 21.



refractory crucibles, by means of a chimney from thirty-six to forty feet high.

Chimneys are generally made square or rectangular, and have interiorly the same dimensions as the body of the furnace. About two feet above the upper part of the furnace they are furnished with a register or damper, by means of which the current of air may be regulated or entirely stopped at will. The damper is a plate of iron sliding into a small opening across the chimney.

A wind furnace of the kind above described is represented by fig. 21.

The left-hand figure in 21 is the plan, the middle and elevation, and the right is a sectional view. *A* the body of the furnace in which the crucibles to be heated are placed, *G* the bars, and *P* the ash-pit; the cover is formed of a thick fire-tile of the requisite size, firmly encircled by a stout iron band, and furnished with a handle for convenience in moving it; *B* the flue, *C* the chimney, *R* the damper; *H* a hood over the furnace, supported by iron bands *h h h*; *M* the handle of a ventilator *T*, which serves to carry off hot air and fumes from furnace when open; and finally, *S*, a small sand-bath, in which to set the red-hot crucibles when taken from the fire; one foot square inside the fireplace of the furnace is a good and convenient size; the remainder will then be in proportion.

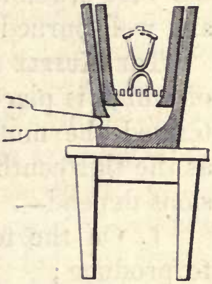
Blast Furnaces.—In this species of furnace the air necessary to keep up the combustion is forced through the fuel by means of a blowing apparatus, instead of being introduced by the draught of a chimney as in the wind furnace.

The most convenient apparatus for forcing air into a furnace is a double bellows; a fan may be used, but it is not so powerful.

The quantity of air passing into a furnace varies with the length of the assay, and ought to increase gradually as the temperature becomes higher.

The following is the description of a most excellent blast furnace which has been in use for some years in the laboratory of the Royal Institution: The temperature produced by it is extraordinary, considering the small amount of time and fuel employed. It is sufficiently powerful to melt pure iron in a crucible in ten to fifteen minutes, the fire having been previously lighted. It will effect the fusion of rhodium, and even pieces of pure platinum have sunk together into one button in a crucible subjected to its heat.* All kinds of crucibles, including the Cornish and Hessian, soften, fuse, and become frothy in it; and it is the want of vessels which has hitherto put a limit to its application. The exterior (fig. 22) consists of a black-lead pot, eighteen inches in height, and thirteen inches in external diameter at the top; a small blue-pot of seven and a half inches external diameter at the top has the lower part cut off so as to leave an aperture of five inches. This, when put into the larger part, rests upon its lower external edge, the tops of the two being level. The interval between them, which gradually increased from the lower to the upper part, is filled with pulverised glass-blowers' pots, to which enough water has been added to moisten the powder, which is pressed down by sticks, so as to make the whole a compact mass. A round grate is then dropped into the furnace, of such a size that it rested about an inch above the lower edge of the inner pot; the space beneath it, therefore, constitutes the air-chamber, and the part above, the body of the furnace. The former is 7½ inches from the grate to the bottom, and the latter 7½ inches from the grate to the top. Finally, a longitudinal hole, conical in form, and 1½ inch in diameter in the exterior, is cut through the outer pot, forming an opening in the air-chamber at the lower part, its use being to receive the nozzle of the bellows by which the draught is thrown in.

FIG. 22.



Sefström's blast furnace, obtainable at most chemical-instrument makers, is also very powerful and convenient; it consists of a double furnace. It is made of stout sheet-

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* Faraday.

iron, lined with fire-clay, and is used with coke, or charcoal and coke, broken into pieces of about a cubic inch in size. The blast of air is supplied by a powerful blowing-machine. It will readily produce a white heat. Indeed the limit to its power seems to be the difficulty of finding crucibles or interior furnace fittings which will stand the temperatures produced in it without softening. Kersten states that he increases the heat in Sefström's blast furnace by using a hot blast.

H. Ste-Claire Deville has employed for melting platinum a furnace of 30 centim. height, and 28 centim. wide, which rests upon a cast-iron plate full of holes. This is connected with a forge bellows. After blowing for a few minutes, the temperature of the furnace will have reached the highest possible degree, but this zone of maximum heat only extends to a small height above the bottom of the furnace. Above this point a considerable quantity of carbonic oxide gas is formed, which burns with a very long flame. The heat produced in this furnace is so high that the best crucibles melt, and only crucibles made of good and well-burned lime can be used.

The Muffle or Cupel Furnace is a furnace in the centre of which is placed a small semi-cylindrical oven, which is termed the muffle. These furnaces were in use as early as the thirteenth century. Their construction and dimensions depend—

1. On the temperature which the furnace is intended to produce;
2. On the number of cupellations required to be performed at one time; and
3. On the kind of fuel to be used.

The muffles are mostly made of refractory clay, generally of one piece, but it is best to make them of two pieces; the bottom being one, and the cover or vault the other.

Muffles are sometimes made of cast-iron, cast in one piece. They are useful in small furnaces intended for cupellations only.

Muffle furnaces must always be provided with a good chimney to carry off the hot gases.

The muffle, being completely surrounded by ignited fuel, acquires a very high temperature, and in its interior all operations requiring the presence of air, and which cannot be carried on in contact with carbonaceous matters, may be performed—such as roastings, scorifications, and cupellations.

When from ten to twenty cupellations have to be effected at one time, large brick furnaces are employed; and, in consequence, much fuel is consumed to waste in these when only a few cupellations are required. This has occasioned many persons to endeavour to form small furnaces, where one or two cupellations may be carried on with the smallest possible quantity of fuel.

MM. Aufryé and d'Arcet have contrived a furnace which is capable of fulfilling all these conditions.

The furnace is elliptical, about 7 inches wide and 18 high; its ash-pit has but one circular opening, and its height is such that, when the furnace is placed upon it, and the whole upon a table, the assayer can, when seated, readily observe the course of the assay within the muffle. The hearth has five openings, in one of which the muffle is placed; in another a brick to support it; a third is for the purpose of introducing a poker to stir the ashes, and make them fall through the grate-holes: this can be closed with a small earthen plug; and lastly, there are two round holes, placed in its largest diameter, to facilitate the introduction of air, either by draught or a pair of bellows, as the case may require. The support for the fuel is generally a plate of earthenware, pierced with holes, and bound round with iron wire to keep it together in case it cracks by changes of temperature; but it is better to use an iron grating.

The dome of the furnace has a circular opening, which can be closed by a plug of earthenware; this opening serves for the introduction of the fuel. A chimney is necessary to increase the draught; it is made of sheet-iron, and may be from 1½ to 2 feet in height, and ought to fit the upper part of the dome very exactly. At its base there is a small gallery, also of sheet-iron, in which it is intended to place the new cupels, so that they may be strongly heated before introduction to the muffle. This saves many of them from fracture.

MM. Aufryé and d'Arcet have estimated the quantity of charcoal necessary to heat this furnace. The following are comparative experiments :—

No.	Silver employed, grains	Lead employed, grains	Time of assay, minutes	Standard thousandths	Charcoal used, grains
1	1	4	12	947	173
2	1	4	11	950	86
3	1	4	13	949	93
4	1	4	10	949	60

Coke or charcoal may be used in this furnace, but the fire must be lighted by means of charcoal alone, as coke is very difficult to inflame in a cold furnace. When it is red-hot it may be fed with coke, or, better still, a mixture of coke and charcoal.

Where great numbers of cupellations have to be made at once, the following form of brick furnace is requisite :—

Fig. 23 shows an elevation of the furnace; fig. 24 shows a section. The interior of the furnace is of fire-brick; the exterior, of common brick. The upper part is protected by a plate of iron, and the superior opening, through which the fuel is introduced, is covered, when necessary, by a large fire-tile strongly encircled with an iron band, to which are attached two handles, by which the whole can be moved.

The muffle opening, as seen partially open in the diagram, can be entirely closed by means of two sliding doors, made of sheet-iron, running in a stout wrought-iron frame, built into the brickwork. Immediately below the muffle entrance are two movable bricks; these close the openings through which the fire-bars are introduced; and still lower down is the ash-pit door, furnished with a register for the better regulation of the current of air required by the furnace. In fig. 24 is shown a brick built into the back of the furnace, on which the close end of the muffle is supported. This brick may, however, be replaced by a crucible or fire-brick standing on the bars of the furnace.

A very useful furnace for small operations is one which has been aptly termed the 'universal furnace,' as it is capable of performing all that is required of any furnace in an assay (see figs. 25 and 26, elevation and section). It is much to be recommended for its durability, cheapness, and its small size compared with the heat it can produce. It is constructed externally of sheet-iron, very stout, and

FIG. 23.

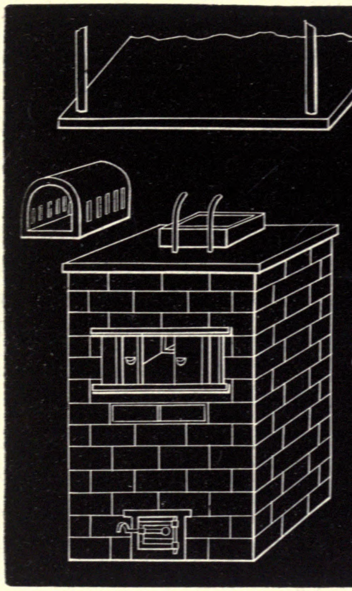


FIG. 24.

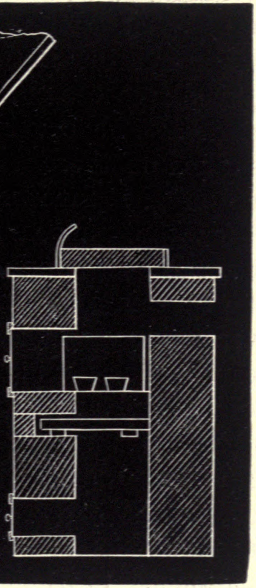


FIG. 25.

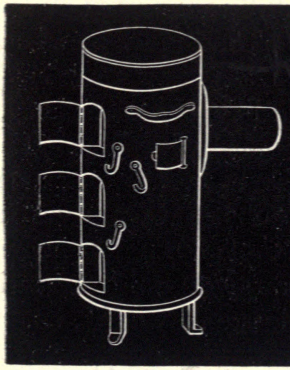
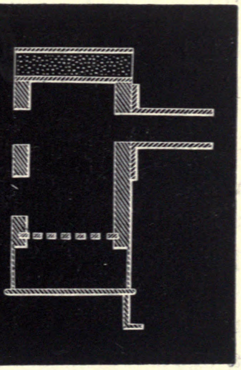


FIG. 26.



is lined with fire-brick, not cemented together, but ground and keyed as an arch, so that it can never fall out till it is completely useless. Its height is about 2¼ feet and diameter 1 foot; internal diameter 8 inches and depth of fireplace 1¼ feet. It is furnished with five doors, one in the ash-pit and four in the body of the furnace, two in the front, one above the other, and two opposite each other, at the sides. The cover serves as a sand-bath, and when that is taken off there is a series of cast-iron rings, fitting the top of the furnace, where basins can be placed either for the purpose of evaporation, calcination, or roasting. The two opposite holes serve for the introduction of a tube in operations where it is requisite to pass a gas over any body at a red heat. In the lower hole in front can be placed a muffle for roastings and cupellations, introducing fuel and crucibles by the upper one; it also serves as an opening through which the state of the furnace can be seen, or the progress of any assay observed.

Iron, manganese, nickel, and cobalt can be fused in this furnace when it has a flue of about thirty feet in height attached to it, and by closing the ash-pit door, the dullest red-heat, for gentle roastings, can be obtained.

FURNACE OPERATIONS.

Crucibles must be carefully supported in the fire, and must always be covered. They must stand solidly, and be at equal distances from the sides and bottom of the furnace, so as to receive a like share of heat, and they must be completely surrounded with fuel. If a crucible is supported on the grate-bars of a furnace, the draught of cold air will prevent the bottom from getting hot. If it is supported on the fuel, the bottom gets heated quickly, but the fuel on burning away allows the crucible to fall down, and may cause the loss of the contents. For these reasons a crucible should always be supported on a piece of fire-brick about three or four inches high. In many cases an old crucible inverted will serve as a convenient support. The fire must be got up gradually, so as to prevent the sides of the furnace and the crucibles within from cracking from the sudden increase of heat. No time is saved by urging the fire strongly at first, for crucibles are bad conductors of heat, and a high temperature at the commencement scarcely causes the heat to penetrate to the interior faster than a moderate redness. After the furnace has arrived at a full red heat, more air may be given, and in from about twenty minutes to one hour the assay will be finished. During the time that the furnace is in full action, the cover must be occasionally removed to add more fuel, if any open spaces occur round the crucibles, also to press the fuel close to the pots. When the pots are taken out they may be placed on the anvil or in a sand-bath, and allowed to cool gradually before they are broken to examine their contents.

In commencing a second assay immediately in the same furnace, certain precautions must be taken to insure success. In the first place, all ash and clinker must be removed from the grate by means of a crooked poker; secondly, the fuel must be pressed down firmly; and lastly, a layer of fresh combustible must be placed on the fire, and before that is ignited the crucibles must be arranged upon the support and the spaces about them be filled with coke or charcoal, as the case may be, and the assay be proceeded with as before.

In executing many assays, one after the other, a great saving of fuel is effected, for the furnace is not allowed time to cool.

Auxiliary Apparatus.—Ordinary assay furnaces require very few instruments; they are, firstly, pokers or stirring rods, made of stout bar-iron: these may be straight, as for stirring the fuel from the top of the furnace, so as to fill up cavities formed by uneven combustion; or curved, for clearing the bars from below from clinkers and ashes. Straight and curved tongs are also required; for small crucibles the blacksmith's common forge tongs are the most suitable; tongs with semicircular ends (see fig. 27) are very serviceable for larger crucibles. The tongs *a* are particularly adapted for removing large cupels or calcining tests from the muffle; the tongs *b* and *c* are used for lifting heavy crucibles from the wind or blast furnace. In case the eyes of the operator are weak, it is advisable to make use of a pair of deep neutral-tint spectacles. Most of the radiant heat from the interior of a furnace may be cut off by holding before the face a large sheet of window glass; or the operator may look at the reflected image in a looking-glass, instead of looking direct into the furnace itself. Some assayers recommend the use of masks for the face and gloves for the hands, but these are not needed. In cupel furnaces, both curved and straight pokers or stirring rods are required; also a curved rod made of lighter iron, to be used in closing the sliding doors, slightly moving cupels, &c. The tongs used vary in form (see fig. 28). *a* represents very light elastic tongs or pincers

FIG. 27.

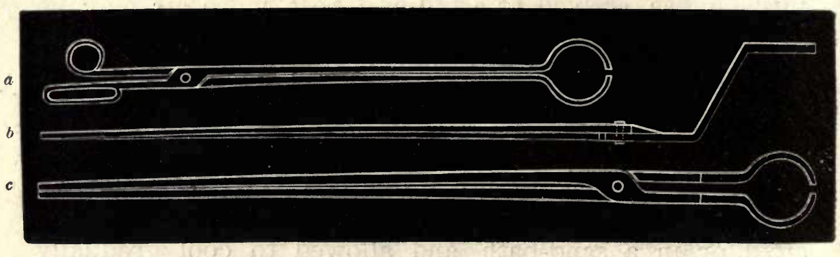
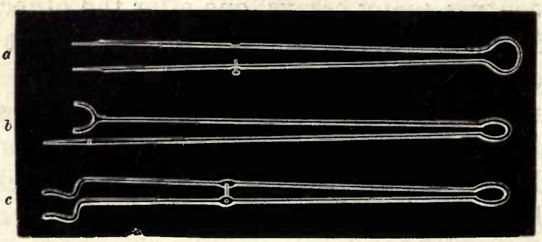


FIG. 28.



employed in the introduction of lead and other matters to the cupel; *b* shows the tongs for holding the scorifier; the curved part fits the lower part of the scorifier, and the upper or single part passes over the upper part of the scorifier, so that its contents may be emptied into the proper mould without fear of its slipping from the operator's grasp; *c* represents the tongs used in moving cupels; they are slightly curved, so that the cupels from the back part of the muffle may be removed without disturbing those in front. Fig. 29 shows the plan and section of the ingot mould, into which the contents of the scorifiers are poured; it is made of thin sheet iron, and the depressions for the reception of the fused lead slag and ore are hammered out.

FIG. 29.

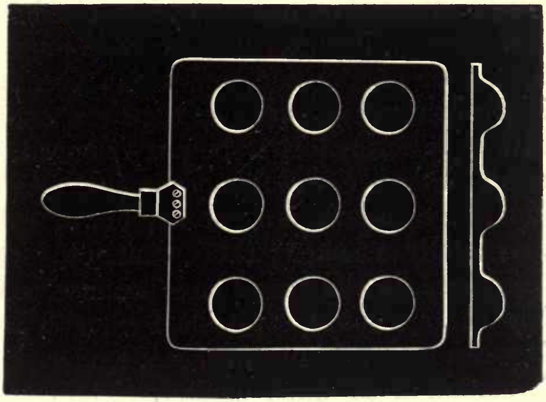


FIG. 30.

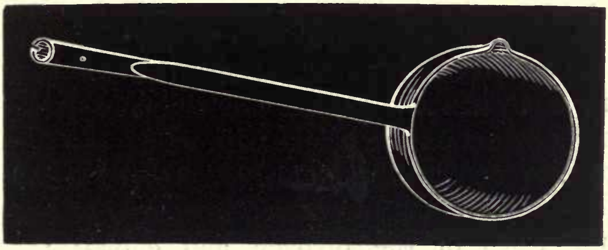
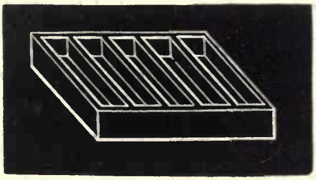


Fig. 30 is a wrought-iron ladle, in which lead clippings, &c., are melted, in order to obtain a fair average of a large quantity; and fig. 31 represents the ingot mould into which the fused lead or other metal is poured. Other special apparatus will be described under the assay in which they are required.

FIG. 31.



Furnaces are heated with anthracite, coke, and charcoal, and sometimes with a mixture of the two latter; coal is very seldom employed, and therefore will not be much spoken of; coke is the principal combustible used in assaying. Calcining furnaces ought to be heated with charcoal alone, because coke employed in small quantities ignites and burns with too much difficulty. All fuel contains certain fixed matters which remain after combustion, and which constitute the ash. This ash fuses or agglutinates together, and when a certain quantity is formed, if it be not removed, the fire will decrease in intensity, and finally die out. As all combustibles do not contain the same amount of ash; they should be carefully selected; those containing the least are to be preferred, in the first place because, weight for weight, they contain more available fuel, and secondly, because they can be used in a furnace a longer time without the formation of so much clinker. The composition of the ash likewise merits much attention.

Charcoal contains, in general, from 3 to 4 per cent. of ash, the chief components of which are lime and potash carbonates. Certain other matters are also present, as phosphoric acid, iron oxide, manganese, &c., but these are in very minute proportions. The ash is not fusible *per se*, and, if it does not meet with any substance capable of combining with it, it passes through the bars as a white powder; but when the potash predominates, it exercises a corrosive action on the bricks with which the furnace is lined, as also on crucibles, lutes, &c., by the formation of a fusible potassium silicate, which in course of time runs down the sides of the furnace, and chokes the bars. Whenever the ash is in very small proportion to the charcoal, its fusion is rather useful than otherwise, because it forms a species of varnish, which, penetrating the surface of the bricks and lutes, gives them solidity by binding them together with a cement, forming part of their substance.

The proportion of ash which coke contains is very variable; some commercial samples contain from 8 to 10 per cent., while others, made from very pure coal, give but 2 to 3 per cent.; so that this fuel also ought to be carefully chosen. The nature of this ash is different from that of charcoal; it consists principally of iron oxide and clay. The former is produced from the pyrites which coal generally contains. The clay is similar to the carbonaceous schists, not very fusible by itself, but nevertheless capable of softening. When pure, it forms a slag, which attacks neither the bricks nor crucibles. This happens very rarely; it is more often that iron oxide predominates, and this by contact with the carbonaceous matter becomes reduced to the state of protoxide, and is then not only very fusible, but exercises on all argillaceous matters a very corrosive action, so that crucibles are very seriously injured, and the sides of the furnace require frequent repairs.

Weight for weight, coke and charcoal give out nearly the same quantity of heat; but in equal bulks, the former develops much more heat, because its density is greater. From this difference in the calorific power of coke and charcoal, it results that in the same furnace the former produces a greater degree of heat than the latter; and at high temperatures the difference has been proved to be nearly 10 per cent. In order to account for this, we must consider, firstly, that in a given space the quantity of heat produced in a certain time (and, in consequence, the temperature) depends on the amount of fuel burnt, and increases with its weight; secondly, that combustion takes place but at the surface of the masses, whatever may be the nature of the fuel; from which may be deduced, that the weight of fuel burnt in an unit of time ought to be exactly proportionate to its density; and in consequence, the densest fuels, furnishing the most food for combustion, ought to give out the greatest heat. But, as for the same reason they consume a larger proportion of oxygen, they require, in order to produce the maximum effect, a more rapid and stronger current of air.

It is clear, from what has been stated concerning the relative properties of coke and charcoal, that when the former can be procured of good quality, and especially when the ash contains but little oxide of iron, it ought to be preferred to charcoal, for assays requiring a high temperature.

This being an important subject, it has been thought advisable to devote a special chapter to the assay of fuel.

A very essential condition in obtaining the maximum effect of a furnace, the importance of which can alone be appreciated by experience, is to choose pieces of fuel of a suitable size. If, on the one hand, a shovelful of coke or charcoal be taken at random, it generally contains the dust and dirt found in most fuel, and which, by filling the interstices, prevent the air from passing as required, and consequently render the combustion slow. On the other hand, if a furnace be filled with large pieces, considerable spaces are left between them, so that but a comparatively small surface is exposed to the action of the atmospheric oxygen, and a correspondingly small quantity of fuel is consumed in a given time; so that the maximum heat can never be obtained. In order to produce the desired result, it is necessary that the pieces shall have a certain mean size, and experience has proved that pieces about 1 inch to 1¼ inch diameter produce the best effect. These may be selected by sifting the coke through two strong wire sieves, one of which has meshes about 1¼ inch square, and the other about 1 inch square. The coke which passes through the larger one, but will not go through the smaller sieve, will be the right size for the furnace.

The Effects produced by Wind and Blast Furnaces.—Assays by the dry way can be made either in wind or blast furnaces. In either of them, the degree of heat depends upon the volume of air which passes through the fuel in the same time; but, *cœteris paribus*, large furnaces produce more heat than small ones, because comparatively less heat is lost by radiation in the former than the latter.

In a wind furnace, the maximum of heat is limited by the size of the chimney, and in a blast furnace by the dimensions of the bellows; but by weighting the latter, more or less, the force of the blast can be increased, and, in consequence, the temperature to a considerable extent. In this respect blast have the advantage over wind furnaces.

In the latter, the draught increases in proportion as the heat becomes more intense in the furnace, so that the temperature producible increases progressively. In a blast furnace, the bellows can be weighted and worked as heavily as possible at once, and, by opening all the apertures for receiving air, the maximum temperature can be produced *more rapidly* than in a wind furnace; but this is of little use, because, as heat passes very slowly through the substance of a crucible, when the object is to fuse its contents it must be heated gradually, so as to avoid running the risk of softening the crucible before its contents are acted upon, or even scarcely made warm.

Wind furnaces are, however, much more serviceable and economical than blast, because they work themselves, and do not require the service of a man to attend to the bellows. A blast furnace is used in a laboratory, in certain cases; for instance, when a single crucible has to be submitted to an intense heat, and when the furnace is small, and the bellows large, in which case the operation resembles a blow-pipe assay.

In whatever manner the air is introduced into any kind of furnace, whether wind or blast, it is evident that the quantity of heat developed in equal-sized furnaces depends upon the quantity of air introduced in the same time; but the degree of temperature is not the same in different parts of the furnace, and the distribution of heat varies according to the manner in which the air is introduced into the midst of the fuel. The side over which the air passes is kept cold by the current, on which account fire-bars last a long time without becoming oxidised, but the heat rapidly augments up to a certain distance from the bars, at which place it arrives at its maximum; above that it diminishes rapidly, because the air is nearly deprived of its oxygen. Experiment has proved that this maximum is about 2½ to 3 inches above the bars or tuyeres.

In common wind furnaces the air enters through the spaces between the horizontal bars which form the bottom of the furnace, and the crucibles are placed on a stand which rests on these bars. By this means the lower and centre part of the crucibles, in which parts the matter to be fused is placed, are exactly situated in the maximum of heat; but the stand being constantly kept cold, by the contact of a current of air, establishes a continual draining or carrying away of heat from the interior of the crucibles outwards, so that the substance submitted to assay can only arrive at the maximum temperature after a length of time, and the maximum then is always inferior to that in the mass of fuel. It is on this account that assays in a blast or wind furnace generally occupy from one hour to two hours. The author has found that the time may be reduced to half that just stated, if a good solid foundation of fuel be made, and the crucible placed on that, and well surrounded by coke, constantly kept close to the pot and the sides of the furnace; in this manner the cooling effect of the stand is removed, and the consequent maximum effect of the furnace is produced, but then there is danger of the supporting fuel being burnt away from the crucible and the latter getting upset.

OIL AND GAS BLAST FURNACES.

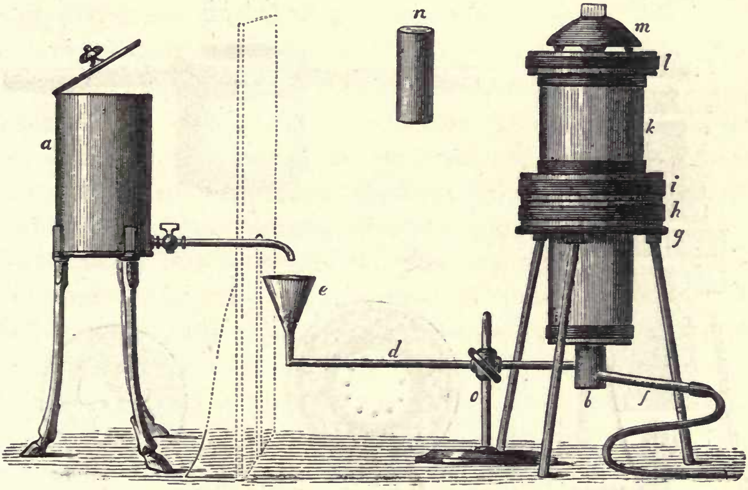
It sometimes happens that metallurgists and assayers have occasion to melt metals at a white heat, but do not wish to heat a large furnace for the purpose. In these cases either the gas or oil furnaces now to be described will prove very useful.

Oil Furnaces.—Mr. Charles Griffin, the well-known chemical instrument maker, has described an oil lamp, which is not only as powerful in action as the best gas furnaces, but almost rivals them in handiness and economy.

Description of the Apparatus.—The oil-lamp furnace is represented in perspective by fig. 32, and in section by fig. 33. It consists of a wick-holder, an oil-reservoir, and a fire-clay furnace; to these must be added a blowing-machine for the supply of atmospheric air.

The oil-reservoir is represented at *a*, fig. 32; it is made of japanned tin-plate, mounted on iron legs, and fitted with a brass stop-cock and delivery-tube. Its capacity is a little more than a quart. The wick-holder is represented at *b*, and the upper surface of it by the separate figure *c*, fig. 34. The wick-holder and the oil-reservoir are consequently detached. *d* is a tube which brings oil from the funnel *e*, and *f* is a tube to be placed in connection with the blowing apparatus. The wick-holder contains three concentric wicks, placed round the multiple blowpipe *c*, which is in communication with the blowing-tube.

FIG. 32.



The crucible furnace consists of the following parts, shown in figs. 32 and 33: *g* is an iron tripod; *h* is a flue for collecting and directing the flame. The flue is of such a width that when the wick-holder, *b*, is pushed up into it until the top of the wick is level with the top of the clay cone, there remains a clear air-space of about $\frac{1}{8}$ inch all round between the wick-holder and the cylindrical walls of the flue. *i* represents a fire-clay grate having three tongues, shown by *i* (fig. 34), on its upper surface. These tongues support the crucible, without stopping the rising flame. *k* is a fire-clay cylinder which rests upon the grate *i*, and incloses the crucible, forming, in fact, the body of the furnace. Of this piece there are three sizes: the smallest is of 3 inches bore, and works with crucibles that do not exceed $2\frac{3}{4}$ inches diameter; a middle size, 4 inches bore, for crucibles not exceeding $3\frac{3}{4}$ inches diameter; the largest size, 5 inches bore, for crucibles not exceeding $4\frac{3}{4}$ inches diameter. This piece, being heavy, is provided with handles, as represented in *p*, fig. 34. The walls of the cylinders are from 1 inch to $1\frac{1}{2}$ inch thick. *l* is a flat plate of fire-clay with a hole in the centre, used to cover the cylinder *k*, so as to act like a reverberatory dome; *m* is a cover which prevents loss of heat from the crucible by radiation, but gives egress to the gaseous products of the combustion of the oil; *n* is an extinguisher to put over the wick-holder when an operation is ended; and *o* is a support for the wick-holder. No chimney is required.

FIG. 33.

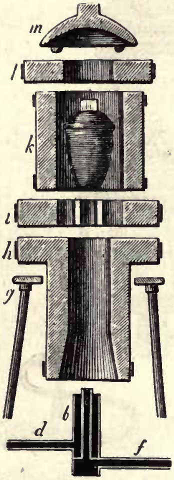
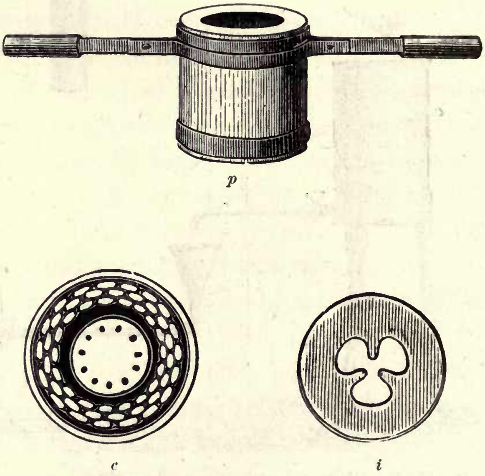


FIG. 34.



Management of the Oil-lamp Furnace.—The apparatus is to be arranged for use as it is represented by fig. 32. The cylinder, *k*, is to be selected to fit the crucible, and the crucible of a size to suit the quantity of metal that is to be melted: 1 lb. of iron requires the smallest of the three cylinders, described above; 1½ lb. the middle size; 5 lbs. the largest size. The air-way between the crucible and the inner walls of the cylinder should never exceed ¼ inch nor be less than ⅛ inch.

The cotton wicks must be clean, and be trimmed a little below the level of the blowpipe *c*. If properly managed, they do not readily burn away, but can be used for several fusions. The reservoir should be filled with oil for each operation. The proper sort of oil for use is the more volatile kind of mineral oil, of the specific gravity of ·750, which is now easily procurable at about three shillings per gallon. The variety known by the commercial name of turpenzine answers well. The combustion of a quart of this oil, costing ninepence, gives heat sufficient to melt 5 lbs. of cast iron. Probably the lighter kinds of paraffin oil may be suitable. Liquids of the alcoholic class, spirits of wine, and pyroxylic spirit can be used; but they are less effective and more expensive than turpenzine. Care must be taken not to spill the oil on the table or floor, and not to decant it carelessly in the neighbourhood of a light, because atmospheric air strongly charged with the vapour of these light oils is explosive. When the oil is burnt in the furnace in the manner described below, there is no danger. During an operation, a wooden screen, as represented by the dotted lines in fig. 32, should be placed between the oil-reservoir and the furnace, to prevent the vaporisation of the oil by radiant heat. As the wick-holder *b*, and the supply pipe *d*, contain only about one fluid ounce of oil, the oil must run continuously during a fusion, from the reservoir *a*, into the funnel *e*, in order that the cotton may be always flooded. The success of the fusion depends upon the due supply of oil, to which point the operator must pay attention. At the commencement of a fusion, the oil must be run from the reservoir until the surface of the oil in the funnel has a diameter of about an inch. The wicks will then be flooded, and a light may be applied, and a gentle blast of air then turned on. The oil immediately sinks in the funnel, and the stop-cock must be opened and so regulated as to keep the oil barely visible at the bottom of the funnel. If too much oil is supplied it immediately rises in the funnel, and simultaneously overflows the wick-holder. Too much vapour is then thrown into the furnace, and the heat is immediately lowered, especially at the beginning of an operation, before the fire-clay portions of the furnace are well heated. If, on the contrary, too little oil is supplied, the wicks burn, and the operation is spoilt. The demand of the wick-holder for oil depends upon the condition of the furnace and the character of the fusion in progress. When the lamp is newly lighted and the furnace cold, the oil should be passed slowly in distinct drops; but as the furnace becomes heated the rapidity of the supply of drops should be increased; and finally, when the furnace is at a white heat, the oil should be supplied in a thin continuous stream. When the fusion to be effected is that of only a small quantity of metal, such as 1 lb. of iron, a rapid supply of drops of oil is sufficient even to the close of the operation. At that rate the burner consumes about 1¼ pint of oil in an hour. When the fusion to be effected is that of 4 lbs. or 5 lbs. of iron and the large furnace is in action and has been brought to a white heat, the supply of oil must, as stated above, be in a thin continuous stream, and the operation will then consume two pints of oil in an hour. And here it requires remark that, with that continuous supply, when the furnace is large and is at a white heat, the oil does not rise in the funnel, being instantaneously converted into gas at the mouth of the burner, and thrown up in that state into the furnace for combustion. The operation, indeed, consists at that point of a rapid distillation of oil-gas, which is immediately burnt, in the presence of air supplied at a suitable pressure by a dozen blowpipes, in effective contact with the crucible to be heated.

The flame produced in this furnace is as clear as that produced by an explosive mixture of air and coal-gas. It is perfectly free from smoke, and the consumed vapours which occasionally escape with gaseous products of a combustion, are even less unpleasant to smell and to breathe in than are those which are usually disengaged by a blast gas furnace, or by an ordinary lamp, fed with pyroxylic spirit.

The contents of a crucible under ignition in this furnace can at any moment be readily examined, it being only necessary to remove the pieces *l* and *m* with tongs, and to lift the cover of the crucible, during which the action of the furnace need not be interrupted.

When the operation is finished, the blast is stopped, the stop-cock is turned off, the oil-reservoir is removed, the wick-holder is lowered on the support *o*, withdrawn from the furnace, and covered with the extinguisher *n*. The quantity of oil which then remains in the lamp is about one fluid ounce.

Power of the Oil-lamp Furnace.—The furnace being cold when an operation is commenced, it will melt 1 lb. of cast iron in 25 minutes, 1½ lb. in 30 minutes, 4 lbs. in 45 minutes, and 5 lbs. in 60 minutes. When the furnace is hot, such fusions can be effected in much less time; for example, 1 lb. of iron in 15 minutes. It need scarcely be added that small quantities of gold, silver, copper, brass, German silver, &c., can be melted with great ease, and that all the metallurgical and chemical processes that are commonly effected in platinum and porcelain crucibles can be promptly accomplished in the smallest cylinder of this furnace; and in the case of platinum vessels, with this special advantage, that the oil-gas is free from those sulphurous compounds the presence of which in coal-gas frequently causes damage to the crucibles.

Requisite Blowing Power.—The size of the blowing-machine required to develop the fusing power of this oil-lamp furnace depends upon the amount of heat required or the weight of metal that is to be fused. For ordinary chemical operations with platinum and porcelain crucibles, and even for the fusion of 1 lb. of cast iron in clay or plumbago crucibles, a blowing power equal to that of a glass-blower's table is sufficient, provided the blast it gives is uniform and constant. But the fusion of masses of iron weighing 4 or 5 lbs. can be effected by the gas which this oil-lamp is capable of supplying, provided a sufficiently powerful blowing-machine supplies the requisite quantity of air. When more than a quart of oil is to be rapidly distilled into gas, and the whole of that gas is to be burned with oxygen, it is evident that effective work demands a large and prompt supply of air.

As in all practical matters of this sort the *cost* is a main question, it may be useful to state that the price of this apparatus complete, without the blowing-machine, but including every other portion necessary for heating crucibles up to the size sufficient to fuse 1 lb. of cast iron, is one guinea; and that with the extra furnace-pieces for crucibles suitable for 5 lbs. of iron, or any intermediate quantity, the cost is one guinea and a half.

Mr. Griffin has described before the Chemical Society an improved gas furnace for chemical operations at a white heat without the aid of a blowing-machine, and a new method of supporting crucibles in gas furnaces. The following extracts from his paper are taken from the *Journal of the Chemical Society*:—

"On a former occasion I introduced to the notice of the Chemical Society a gas furnace for operations at a white heat in crucibles, or a copper-melting heat in muffles. A detailed description of that furnace is given in the Journal of the Society for August 1870. The crucibles are either suspended in a pierced plumbago cylinder, or supported on a trivet grate, both of which are liable to break when white hot, and therefore cause trouble and expense. Crucibles vary so much in form and size that they are often not suspended from these cylinders exactly in the focus of the heating power. Trivet grates have the disadvantage that they interfere with the direct action of the flame upon the crucible, and if made slightly they break when heated to whiteness. I desire now to place before you a new form of burner by which these defects are remedied. In the new burner the circle of gas-jets is enlarged so as to leave a space round the central jet. An atmopyre similar to those used in Hofmann's combustion furnace, but of greater bulk and strength, is dropped over this central jet, and forms a solid support for the crucible. This support does not readily break, but, should an accident happen, it can be replaced at the cost of a few pence. It brings the bottom of the crucible exactly into the focus of heat, and itself supplies a portion of the heating power of the burner. It also enables one to use any crucible at hand, independent of its form or size. A strong lateral arm cast on the body of the burner supports an upright iron rod, which carries the chimney of the furnace. By prolonging the legs of the burner upwards they are made to carry the clay furnace, and thus, by doing away with a stool or other support, the construction is simplified and the cost lessened. A plumbago cylinder, to deflect the flame and entrap the heat, is placed round the crucible, and is covered with an ordinary crucible cover, by removing which the crucible can be inspected. These fittings, however, present nothing new, being adapted from Griffin's blast gas furnace, which was introduced sixteen years ago. Access to the crucible in the furnace is gained by turning aside the chimney and lifting the top plate of the furnace, which is provided with handles for this purpose. These handles do not become very hot, even when the furnace is at a white heat. The power of these new burners is very remarkable, one of small size consuming only 20 feet of gas per hour, and having a chimney 4 feet high, being capable of fusing half a pound of cast iron in 35 minutes from the time of lighting the gas; or of melting gold, silver, or copper in crucibles placed within a muffle measuring 5 inches long by 3 wide. If a chimney 6 feet high be employed, cast iron can be melted in crucibles placed within the muffle. A burner of larger size, consuming 40 feet of gas per hour, will melt cast iron in crucibles placed within a large muffle measuring 8 inches long by 4 inches wide. In the crucible furnace it will melt 1 lb. of cast-iron in 35 minutes, 2 lbs. in 45 minutes, 3 lbs. in 55 minutes, and 4 lbs. in 65 minutes, from the time of lighting the gas. It is thus seen that, when a white heat has been once obtained, 10 minutes' time is required for the fusion of every additional pound of iron. These results, attainable with certainty and rapidity, are, I believe, the highest that have hitherto been placed at the command of the chemist. As in my former furnace, the proper admixture of gas and air is judged of from the colour and quantity of flame which passes up the chimney. To enable the operator to see this flame, three small holes are bored in the chimney.

Fig. 35.

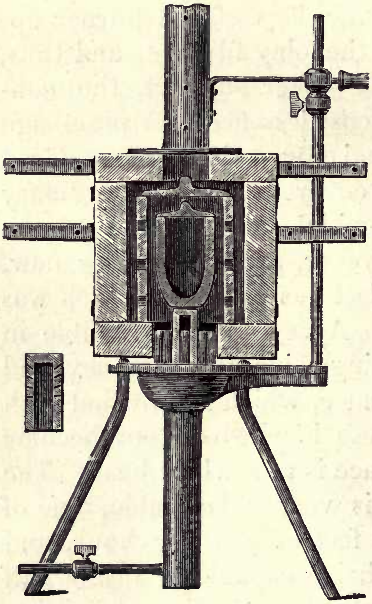
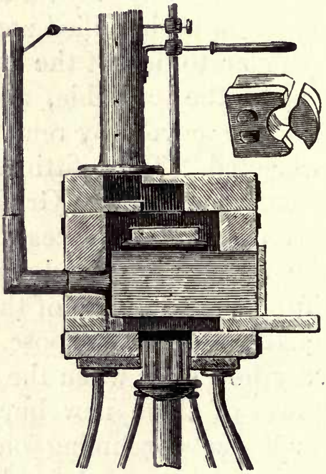


Fig. 36.

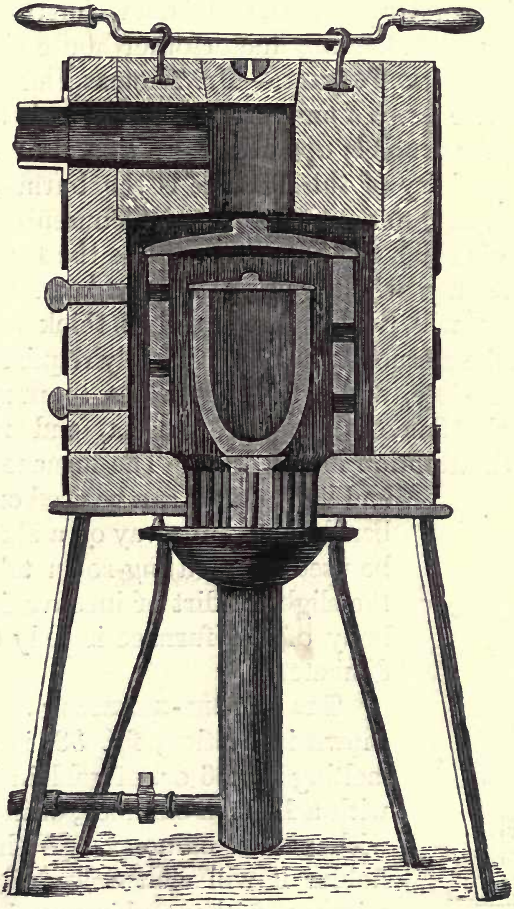


The flame is not seen at the upper hole, unless the supply of gas is too large, but it is always visible at both the lower holes."

In the above figure the muffle is provided with a small draught flue, having a regulating cap on its upper end. In the small furnaces this is omitted, and the muffle is slotted in the usual manner. The cover of the furnace is now made without the zigzag opening in the roof. The burner of the muffle furnace is the same as that used in the crucible furnace, fig. 35.

Skittle pots up to 8 inches can be used in these furnaces for collecting and burning waste with fluxes, &c., and in much less time than is required by a coke fire. An 8-inch pot can be worked in half an hour from lighting the gas. Two of the outer cylinders are used, placed one on the top of the other.

FIG. 37.



With a 4-foot flue the muffle furnace melts gold, silver, and copper; with a 6-foot flue it melts cast-iron placed in crucibles within the muffle. The consumption of gas is 20 cubic feet per hour.

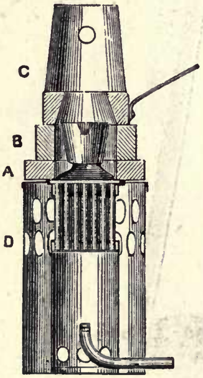
The *Distillation of Pure Zinc, per descensum*, can be performed in one of these gas furnaces by passing a tube from the top of the crucible downwards through the burner to the table.

Fig. 37 shows one of Griffin's extra large gas furnaces, capable of raising a No. 12 plumbago pot, measuring 8 inches high by 6 inches wide, to a white heat. The cover of this furnace is let into the body, which rises higher than in the smaller patterns, and from which the flue passes off laterally to a standing flue or other house chimney.

Universal Gas Furnace.—Mr. Thomas Fletcher has devised what he terms a universal gas furnace; it works without blast, for crucible operations, up to a clear white heat.

The specialty of this furnace is the burner. It is as simple and easy to use as an ordinary Bunsen's burner, but the flame is solid to the centre, unlike the flame of every heating burner which has previously been made. The open flame will readily fuse a coil of thick copper wire, and to make a crucible furnace it simply requires a support for the crucible, and a fire-clay jacket to prevent radiation, as the flame is in itself perfect, and requires no blowing or attention in any way. The furnace is so small and light that it can be used on the work-bench, and put away on a shelf, and can be used on a sitting-room table without the slightest dirt or inconvenience. The body of the furnace is only 6 inches in diameter.

Fig. 38.



The Single-jacketed Arrangement, shown in section, fig. 38, is capable of melting 5 or 6 oz. of gold in 15 minutes with a 10-inch chimney, or in 10 minutes with a 2-ft. chimney. With the ladle-holder it will melt 8 lbs. of zinc in 15 minutes, without chimney, in an ordinary iron ladle, and lead, tin, &c., in a proportionately shorter time.

The Double-jacketed Chemical Furnace, shown in section, fig. 39, having the same burner as above, and requiring no more gas, will melt 3 or 4 oz. of cast-iron in 35 minutes, if used with a 3-ft. chimney, or, if with a longer chimney, in a proportionately shorter time, and will give any required temperature in proportion to the length of chimney used, provided the gas is turned on sufficiently just to cover the crucible with flame when the chimney is in its place.

In case of the fusion of a crucible, or its penetration by fluxes when the furnace is used for extremely high temperatures, no damage can be done to the furnace, except perhaps the destruction of a few of the burner tubes, which can be replaced at a trifling expense. No part of the furnace is liable to injury with constant use

FIG. 39.

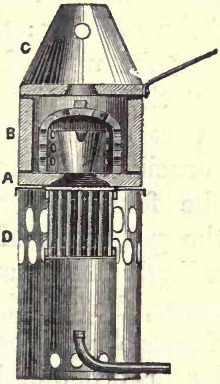
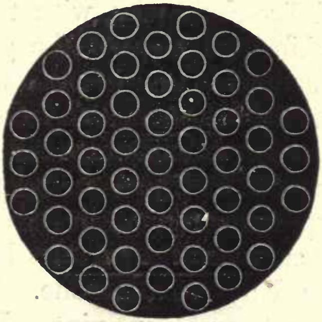


FIG. 40.



The burner is shown in plan in fig. 40. The lower part is a chamber 6 in. × 3 in., open at the bottom, in which the gas is partially mixed with air. This mixture is conducted to the top of the burner through a mass of fine tubes, 55 in number, with an arrangement to supply between each exactly the amount of air necessary to consume it instantly. A flame produced by this means, consuming 20 feet of gas per hour, is only about 2 inches high, and almost colourless. The whole of the available heat is generated in the proper place, viz. below the object to be heated, which, therefore, is not also cooled by the passage of unburnt gas and air. The flame is very similar in appearance to a mass of blowpipe jets, and has the same heating power. The point of greatest heat commences, as with a blowpipe, at the point of the blue cones, about $\frac{1}{2}$ in. or $\frac{3}{4}$ in. above the tubes.

The Double-jacketed Chemical furnace is made to take crucibles not exceeding in size No. 00 of the Plumbago Crucible Co., which are the most convenient for melting quantities not exceeding 5 or 6 oz. of gold, &c.

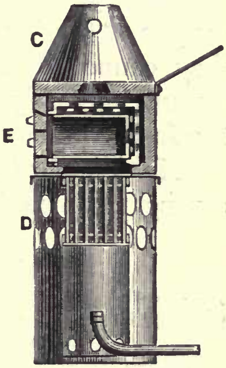
For crucibles put the flat plate *A* (see fig. 38) over the centre of the burner, with the three inner projecting points upwards. Place the crucible on the projecting points. Be careful that the points are upwards, or the crucible will be too low. Light the gas, and then put on the large fire-clay ring *B*, to surround the crucible, which must be exactly in the centre of the opening: then the small fire-clay cover, with the iron tube upward, *C*, and the chimney if used. The gas must then be turned very gradually down until the white part of the flame disappears, and the flame covers the crucible. If the supply of gas is not sufficient, it will be found necessary to examine the tap which supplies the gas, many of which, as supplied by gasfitters, are exceedingly faulty, and partially stopped up. If this be the case, the tap should be replaced by a better one. The furnace requires supply from a $\frac{3}{8}$ or $\frac{7}{16}$ in. pipe. If a larger crucible be used than the one supplied, an extra fire-clay ring must be obtained of the same proportionate width, and half an inch higher than the top of the crucible.

When a white heat is required, the crucible must be covered with the inner perforated plumbago dome, as shown in fig. 45, and which forms the inner jacket, with the perforations in such a position that the crucible can be seen through the hole in the lower part of the chimney; a chimney not less than 3 feet high must be used. If a greater heating power is required, a longer chimney will enable it to be obtained in the same or a shorter time, but under all circumstances the flame must just cover the crucible to obtain proper results.

Where the gas supply is more than necessary, a longer chimney may be used with advantage, but as the furnace itself is too small and light to form a steady support for a longer chimney, it will be necessary to suspend the upper part with a wire, or to support it with a bracket from the wall. The furnace requires the following supply of gas: Without chimney, 18 cubic feet; with 10-inch do., 22 cubic ft.; with 36-inch do., 28 to 30 cubic ft. per hour. If the gas supply is deficient, the wire should in all cases be removed from india-rubber tubing, as it interferes seriously with the passage of gas.

The addition of the small muffle (*E*, fig. 41) for high temperatures makes this furnace complete for all purposes. The clear working space, which is equally heated in every part, measures 2¼ × 2¾ × 2¼ in. It will be seen from the engraving that the muffle is not in contact with the outer casing in any part, and therefore all parts are equally heated. The temperature obtained depends on the length of chimney used, provided the gas supply is sufficient to cover the muffle with flame when the chimney is on. For silver assays about 4 feet of chimney should be used, which gives the melting point of fine silver in 16 minutes from the time the gas is lighted; the same temperature being always obtained in exactly the same time, within a few seconds; and after the first trial the operation does not require watching. With this furnace there will be found no variation in a number of assays done at different times.

FIG. 41.

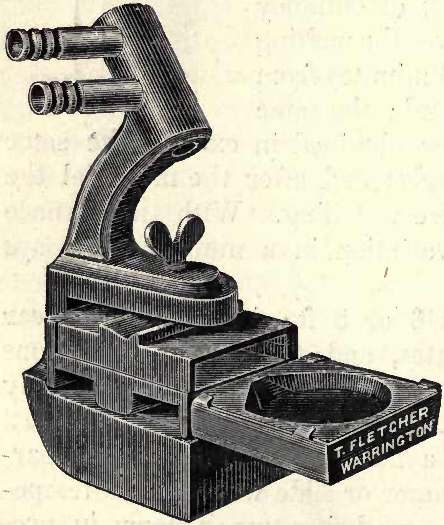


A chimney of about 6 or 8 ft. gives nearly a clear white heat in 30 minutes, and for special operations requiring very high temperatures a longer chimney may be used as required. A chimney or stove pipe 10 or 12 ft. long may be used as a fixture, and the draught partially stopped with a damper or slide when lower temperatures are required, the gas being turned down in proportion; the guide for the proper adjustment being that under all circumstances the flame must just cover the muffle, but must not extend into the chimney so as to make it red hot.

It will not be found necessary in practice to partially close the chimney for lower temperatures, as the same effect may be produced equally well by simply turning the gas lower; but it is more economical to partially stop the draught, so as to prevent excess of cold air being drawn in. When the flame covers the muffle, the gas is doing its extreme duty under the most favourable circumstances, without waste. The same rule applies also to the crucible arrangement. Particles of flux should not be allowed to fall on the fire-clay casing, where the parts touch each other; and the power of the furnace should not be urged too far by the use of very long chimneys, as there is danger of the fusion of the fire-clay parts together so that they cannot be separated. Fire-clay fittings, as a rule, cannot be safely used for temperatures much exceeding the fusing point of cast iron.

Mr. Fletcher has recently brought out a new melting arrangement for melting up to 3 oz. of gold or silver, rapidly, without the use of a furnace.

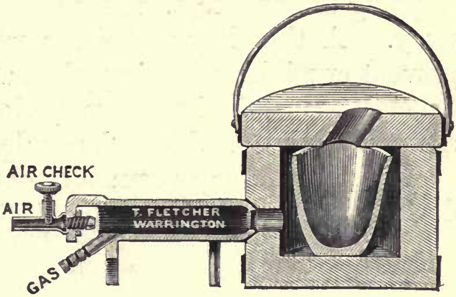
FIG. 42.



The figure (42) is slightly under half-size. In this arrangement the two parts of the ingot-mould slide on each other, to enable ingots of any width to be cast. And the blowpipe is part of the rocking-stand. Connect the blower to the upper tube, and the gas to the lower. When the metal is melted in the shallow crucible of compressed charcoal, tilt the whole apparatus over so as to fill the ingot-mould. A sound ingot can be obtained in about 2 minutes. Very bulky scrap should be run into a mass in one of the moulder carbon blocks before being placed in the crucible. No flux must be used with the *charcoal* crucibles.

Mr. Fletcher has also devised an injector gas furnace (fig. 43) for metallurgists, jewellers, chemists, iron, brass, and nickel castings, manufacturers of artificial gems, and other purposes where an ordinary furnace is useless or unreliable.

FIG. 43.



It has been found that in working at extremely high temperatures, the ring which holds the gauze is liable to be fused. To prevent this, a new burner has been designed, in which the ring is entirely dispensed with, and the gauze cap is pushed up from the back of the burner against a small shoulder inside the nozzle of the burner. The burner is in one casting, and therefore there is no tendency for the nozzle to get hot, as in the former pattern. See that the gauze is pushed up from behind to within about $\frac{1}{4}$ inch of the nozzle. The power and speed of working are practically without limit, depending only on the gas and air supply, and are under perfect control. With $\frac{1}{2}$-inch gas-pipe and the smallest foot-blower, the small furnace will melt a crucible full of cast-iron scrap in 7 minutes; and steel in 12 minutes, starting with all cold.

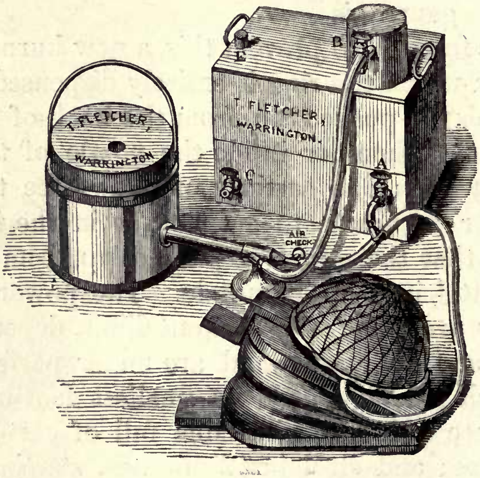
To adjust a new furnace to its highest power, put the nozzle of the burner tight up against the hole in the side of the casing, turn on the full gas-supply, with the air-way full open. If the flame comes out of the lid about 2 inches the adjustment is right. If the flame is longer, enlarge the hole in the air-jet until the proper flame is obtained, or reduce the gas-supply; if smaller, or not visible, turn the air-check until the flame appears.

Keep all fluxes away from the furnace jacket. Before stopping the blower, draw the burner back from the hole. Commence blowing before the lid is put on the furnace.

The old pattern blower is liable to pick up dirt from the floor, throwing it against the gauze of the burner, and stopping the proper working of the furnace until cleared away. A thin layer of silver sand on the bottom will prevent crucibles adhering when at a white or blue heat. Crucibles must be heated very slowly the first time they are used, unless of the 'Salamander' brand.

In cases where gas cannot be obtained, Mr. Fletcher has devised a simple furnace (fig. 44) for high temperatures, working with either gas or spirit-petroleum without alteration, and with perfect results with either fuel. This furnace is supplied with a small, simple, and perfectly safe arrangement for burning the vapour of gasoline or benzoline, giving a power and efficiency fully equal to that which can be obtained by a larger gas-supply. The arrangement is in every way as simple as when gas is used, requiring no more trouble or attention.

FIG. 44.



It equals a gas-furnace in every respect, and, in addition, gives a heat of absolute purity, fitting it for the most delicate chemical operations where gas cannot be used owing to the presence of sulphur and other matters.

The ordinary pattern of injector furnace is used in precisely the same way as with gas, the only difference being that a branch pipe is taken out of the air supply and connected to the lower tap *A* on the generator, and a tube is carried from the upper tap *B* to the side tube of the injector-burner marked 'gas.' The quantity of vapour required is adjusted by the lower tap *A* when the furnace is working, and the flame must be just visible at the hole in the lid, exactly as when gas is used, the instructions being precisely the same for both fuels.

To charge the generator, pour benzoline or gasoline in the top hole until it overflows at the small tap *C* in the side, replace the cork firmly, and close the overflow tap. It will then work for about 10 to 12 hours at the full power of the furnace.

Benzoline varies much in quality; it must, when a few drops are poured on a plate or the hand, evaporate quickly and completely, leaving no greasy stain, and if good will produce more vapour than the furnace can burn at its maximum power. All the tubing used must be perfectly smooth inside, or the power of the furnace is greatly reduced.

At the conclusion of an operation, close both taps on the generator. It can then be left for any length of time ready for instant use. For ordinary meltings, the generator can be used about thirty or forty times without refilling.

The No. 3 size will refine and perfectly fuse 6 lbs. of chemically pure nickel so that it can be poured clean, using an open crucible, a feat beyond the capabilities of any other known furnace.

Benzoline often contains heavy oils. If the generator works badly, empty it and refill with fresh.

G. Gore, Esq., F.R.S., has devised a gas furnace which will fuse cast iron, &c., and still allow the melted substances to be perfectly accessible to be manipulated upon for a continuous and lengthened period of time, without contact with impurities or with the atmosphere, and without lowering their temperature sufficient to cause them to solidify. These conditions Mr. Gore has obtained by means of ordinary coal-gas and atmospheric air, without the use of a bellows or lofty chimney, or of regenerators or valves requiring frequent attention. The arrangement is as follows: *A* (figs. 45 and 46) is a cylinder of fire-clay about 9 inches high and 6 inches diameter, open at both ends, with a hole in its side near the bottom to lead into the chimney; it is covered by a movable plate of fire-clay, *B*, with a hole in its centre for introduction or removal of the crucible, &c.; this hole is closed by a perforated plug of clay, *C*, for access to the contents of the crucible, and that again is closed by another clay stopper *D*; *E* is a chimney of sheet iron about 5 or 6 feet high, kept upright by a ring of iron *F* attached to the top of the furnace. The fire-clay cylinder is enclosed in a sheet of

FIG. 45.

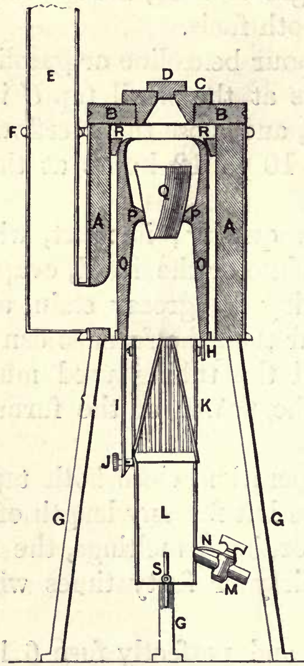
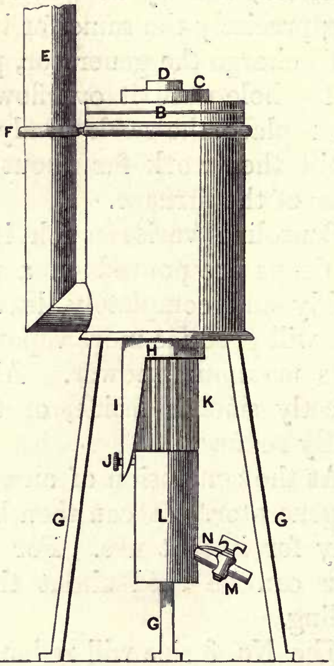


FIG. 46.



iron casing with a bottom of iron, to which are fixed three iron legs *G*. An iron tube *H*, with a prolongation *I*, supports by means of the screw *J* the burner *K* and its tube *L*, which is open at both ends. Gas is supplied to the burner by means of the tap *M*, which has a small index *N* attached to it for assistance in adjusting the gas. Inside the large cylinder is another fire-clay cylinder or cupola *O*, with open ends, and with three projections of fire-clay *P*, for supporting the crucible *Q*; it is kept steady by means of three clay wedges *R*; *S* is an air-valve for closing the bottom of the tube *L*. The gas-burner is a thin metal cylinder, deeply corrugated at its upper end, with the corrugations diminishing to nothing at its lower end, as shown in the engravings. The action of this furnace is as follows: Gas is admitted to the open tube *L* by the tap *M*; it there mixes with air to form a nearly combustible mixture, which ascends through the burner, and burns in the clay cylinder *O*, being supplied with the remainder of air necessary to combustion through the tube *H* to the outer surface of the flame; the products of combustion pass up through the cylinder *O*, and then downwards outside of it to the chimney, the point of greatest heat being at *Q*.

It is important in using this furnace that the burner be placed quite in the centre of the bottom of the tube *O*; also that a crucible of not too large nor too small dimensions be selected. The most suitable way of supporting a smaller crucible is by placing it in a larger one that has had its upper part broken off. If desirable, a little clay luting may be placed round the top edge of the iron casing to exclude air entering between it and the cylinder; also a little thin clay luting upon the part of the bottom of the furnace where the inner cylinder *O* rests.

In lighting the furnace, the plugs *C* and *D* are removed, a light held *inside* the opening, and the gas turned on full. Should the flame blow down to the bottom of the tube *L* on lighting (which, however, rarely occurs unless the furnace is already hot), the gas must be turned off, and the bottom of *L* momentarily closed whilst lighting the gas as before. Should the flame not burn down to the burner, but only burn to the orifice in the clay plate *B*, it must at once be extinguished and relighted, otherwise some of the gaseous mixture will pass into the chimney unburned, and subsequently ignite and cause an explosion. A large flame now issues from the top orifice, and is white if too much gas is on, and chiefly violet or red with the proper quantity; it should now be coarsely adjusted until these appearances are represented. The annular plug *C* should now be inserted, which will compel it to pass downwards to the chimney, and as soon as the small remaining flame now issuing disappears, or nearly disappears, as it will in a few seconds, the smaller stopper *D* should also be inserted. In lieu of this, the large flame may be deflected against the chimney by means of a piece of sheet iron until it withdraws inwards as before mentioned; the two plugs may then be reinserted. The gas tap may now be partly adjusted. The crucible should be placed in the furnace after the act of lighting the gas, but not immediately after if the furnace is cold, or explosions may occur by unburned gaseous mixture passing the crucible into the chimney, and igniting afterwards.

After about five minutes the gas should be slowly adjusted, until a sound is heard inside like a series of small explosions. This sound is sometimes not very distinct, especially at high temperatures, and therefore requires a little experience in the use of the furnace in order to be detected. It is, however, a chief guide in determining the proper amount of gas, and should therefore be carefully studied. To assist in adjusting the gas it will be found very useful to place a small piece of looking-glass beneath the tube *L*, and to adjust the gas tap until the flame between the burner and crucible appears wholly violet or slightly white; but this test is liable to fallacy if employed when the gas is first lighted, because the coldness of the parts makes the flame much whiter than it otherwise would appear. It is also fallacious, the flame appearing whiter than it really is when the crucible is very hot. It is, however, of great assistance, especially at intermediate temperatures. A rough deposit upon the outer edge of the crucible indicates an excess of gas; the deposit is carbon. Less gas is required with a crucible in the furnace than without one: also less is required when the small hole at the top of the furnace is open than when it is closed; and less is also required when the furnace is cold than after it has been lighted some time, because the draught gradually increases and draws in more air. After having accurately adjusted the gas, no further attention to the furnace is requisite.

Having once found the proper adjustment of gas under certain known conditions, it is well to notice the position of the index pointer *N*, in order to be able at once to adjust it to about the right point on other occasions. Under ordinary circumstances, during daylight it is best to set the gas nearly full on at first, and fully on at about five minutes afterwards when the draught has become more powerful; but during twilight, when the supply of gas from the gas works is more free, the index pointer may be set at the numbers 2½ or 3. The gas should be supplied by a pipe of not less than ⅜-inch bore, with a main pipe of ½ an inch; but all depends on the pressure of gas at the particular locality, which is very variable. The consumption of gas varies from 30 to 40 cubic feet per hour, the value of which is about twopence.

The top of the chimney should be placed in a position where the products of combustion can pass freely away. If it is placed in an opening or pipe leading to another chimney, care must be taken not to have the draught too powerful, otherwise the heat will be drawn more into the chimney, and the supply of gas in the daytime may be found rather deficient. The furnace will act satisfactorily though less powerfully, with the chimney standing in an open room without any special outlet for the products of combustion, provided the full height (6 feet) of chimney is employed. Under other circumstances a chimney 4½ or 5 feet high may be used.

This furnace will produce what is generally called a white heat; it will readily melt half a pound of copper, or six ounces of cast iron; it will melt as large a quantity of those substances as the largest-sized crucible that can be introduced into it will contain, sufficient space being reserved around the crucible for draught. It requires from 20 to 30 minutes to acquire its highest temperature, and then the entrance part of the chimney exhibits a faint red heat in daylight. If it exhibits much more than this, the draught is too powerful, and, if less, there is not sufficient gas.

With one ounce of copper put into the cold furnace, and the gas lighted and properly adjusted, the copper generally begins to melt at about the tenth or twelfth minute, and is completely melted by the fifteenth. With the heat well up, 1 ounce of copper has been melted in it in 2¼ minutes, 1 ounce of cast iron in 3 minutes, 5 ounces of copper in 4¼ minutes, and 3 ounces of cast iron in 5 minutes. With the smaller hole in the top of the furnace open, 1 ounce of copper has been melted in 3½ minutes, and several ounces of copper have been kept in fusion for upwards of half an hour, and may be kept so for any length of time; cast iron has also been fused and kept melted under the same conditions. These various effects have also been obtained in a somewhat diminished degree with the chimney standing in an open room.

When the small hole *D* is open some air is drawn in that way, and less air passes up with the gas through the tube *O*, but the cold air does not much diminish the temperature of the crucible, because it combines with the excess of gas now passing over the edge of the inner cylinder; it, however, renders the flame round the crucible white by deficiency of air, and this should be partly corrected by lessening the gas. An excess of either gas or air renders the surface of melted copper dull.

When it is desirable to perfectly avoid contact of air with the fused substance during manipulation, a narrow crucible should be employed, and a thin narrow ring of fire-clay should be placed upon the top of the tube *O* to contract its opening; the flame then closes completely over the top of the crucible and prevents access of air; a proper adjustment of gas, together with exclusion of air in this manner, enables a perfectly bright surface of melted copper or even tin to be continuously maintained from which the images of parts above are clearly reflected. The clay ring may be withdrawn by lifting the plate *B*. A less perfect exclusion of air may be obtained by employing a narrow crucible placed rather low down in its support. A small iron dish should be placed beneath the tube *L*, to receive any melted substance that may fall. The chief conditions of success in the use of this furnace are sufficient gas, a suitable degree of draught, and proper regulation of gas to air.

Mr. Griffin has devised what he calls a *Reverberatory Gas Furnace*, which also produces a high temperature without the use of a blowing-machine. It is especially suitable for assay purposes on a small scale, and for the decomposition of siliceous minerals by fusion with alkaline carbonates in platinum crucibles, being capable of fusing 1,000 grains of anhydrous sodium carbonate in ten minutes.

The different parts of this furnace are also arranged in a very convenient manner, so as to admit of its being employed for various purposes in a chemical or assay laboratory. It is based upon a new form of gas-burner which, aided by suitable bellows, can be used as a convenient source of heat for most operations of the chemical laboratory and lecture table. It will boil a quantity of liquid, exceeding two gallons, at once; it will raise a 4¾-inch fire-clay crucible to full redness; it will fuse anhydrous sodium carbonate in greater quantity than is required for the analysis of a siliceous mineral; and it will melt small quantities of sterling silver. This amount of power is sufficient for most chemical and many metallurgical operations.

Fig. 47 represents the gas-burner of this apparatus. The gas is supplied by the horizontal tube, whence it passes through a set of small holes into the box *a*, in which it mixes with atmospheric air that enters freely by the holes shown in the sketch. The gaseous mixture passes up the vertical tube *b*, and is inflamed at the top, where it burns with a single tall blue flame, which gives no smoke, very little light, but much heat. In this condition the apparatus differs from 'Bunsen's gas-burner' only in size. *c* represents a thin brass cap, which fits the air-box *a*, but moves easily round it; *d* is a flat cast-iron box with many holes around the margin, and a few small ones on the top. This box fits loosely on the upper part of the tube *b*, and when it is placed on it and the gas is lighted the flame produced consists of a series of radiating jets, forming a horizontal circular flame of about seven inches in diameter. Fig. 48 shows a ring of horizontal flame produced; 47 *b* gives a single vertical flame.* The ring of flame is suited to the purposes of boiling and evaporation; the single flame, to ignition and fusion. The height of the apparatus represented by fig. 47 is twelve inches; the bore of the tube *b* is one inch; and the diameter of the fire-box *d* is four inches.

When a large crucible is to be heated to redness, the gas-burner is to be used without the rose, and is to be arranged with the furnace fittings that are represented in perspective by fig. 49, and in section by fig. 50, and the lower part of fig. 51, *a*, *b*, *c*, *d*. Letter *a* represents the gas-burner; fig. 49 *b* is a tall iron stool; *c* a chimney which collects atmospheric air to feed the flame, and leads it up close to the vertical tube of *a*, by which contrivance the air is warmed and the tube cooled; *d* is a furnace-sole or plate of fire-clay; *f* is a reverberatory dome, the interior of which is best shown in the section fig. 50; *e* is a cast-iron ring or trivet, represented more clearly in fig. 52; *g* is an iron chimney 24 inches long and 3¼ inches wide; and *h* a damper to lessen the draught when small crucibles are to be heated. The height of

FIG. 47.

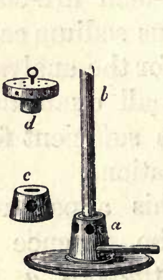
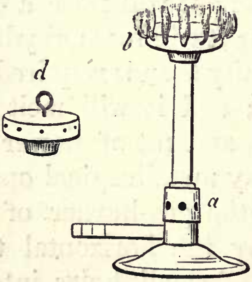


FIG. 48.



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* Fig. 48 represents a small variety of this gas-burner, in which the head is not removable, but the efflux of the mixed gases is regulated by a sliding valve, which is represented by *b*.

this apparatus from *a* to the top of *f* is 24 inches ; and the external diameter of the dome *f* is about 8 inches. The crucible, which may be from 4¼ to 4¾ inches in height, is placed on the iron ring *e*, fig. 51, and that on the clay sole *d*, and it is then covered by the dome *f*. The gas should be lighted after the crucible is placed in its position and before the dome is put on. The dome

Fig. 49.

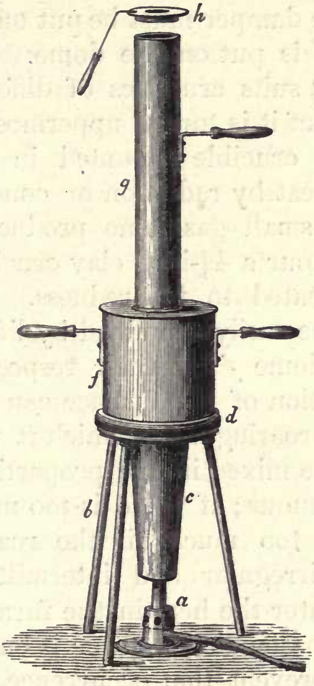


Fig. 50.

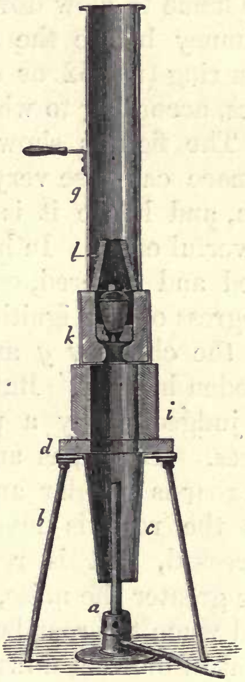


Fig. 51.

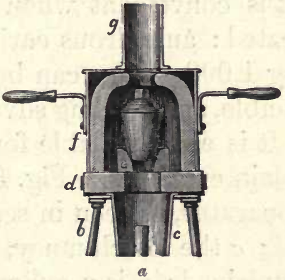


Fig. 52.

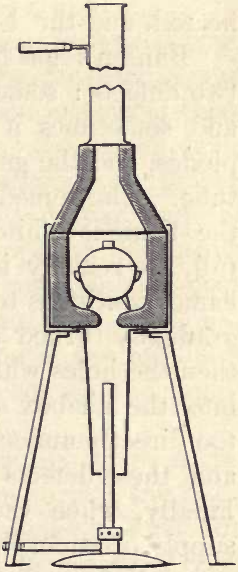
and the chimney are then to be added and the operation allowed to proceed. With a crucible of the above size the damper *h* is not required; but it must be used when the crucible is under 4 inches in height, otherwise the draught occasioned by extra space within the dome causes the flame to blow down. The damper must be put on the chimney before the chimney is put on the dome. The iron ring (fig. 52 or *e* fig. 51) suits crucibles of different sizes, according to which side of it is turned uppermost.

The figures show that a crucible mounted in this furnace can lose very little heat by radiation or conduction, and hence it is that a small gas flame produces a powerful effect. In half an hour a $4\frac{3}{4}$-inch clay crucible, filled and covered, can be heated to full redness. The progress of the ignition can be easily examined by lifting up the chimney *g* and the dome *f* by their respective wooden handles. But the action of the furnace can also be judged of by a peculiar roaring noise which it produces. If the gas and air are mixed in due proportions, the roar is regular and continuous; if there is too much gas the roar is lessened, if too much air the roar is increased, but is rendered irregular and intermittent. The greater the noise, the greater the heat in the furnace. And when the roar becomes spasmodic the flame is on the point of blowing down. To prevent that occurrence, the proportion of air must be lessened or that of gas increased.

The following arrangement is convenient when small crucibles are to be strongly heated: anhydrous carbonate of soda in quantities exceeding 1,000 grains can be thus readily fused in a platinum crucible, and sterling silver can be melted in a clay crucible. It is also available for ignitions or fusions in small porcelain crucibles. Fig. 50 represents the arrangement of apparatus, as seen in section: *a* is the gas-burner; *b* the stool; *c* the air chimney, and *d* the furnace-sole, as already explained; *i* is a cylinder of fire-clay, 4 inches high, and $4\frac{1}{2}$ inches diameter; *k* is a fire-clay furnace, in which is placed a small cast-iron ring about 2 inches in diameter, similar in form to that represented by fig. 52, and on this ring the platinum crucible is adjusted; *l* is a fire-clay or plumbago reverberatory dome; and *g* is the chimney that forms part of the furnace represented by fig 48. The crucible being adjusted, the gas lighted, and the dome and chimney put on, the lapse of twelve or fifteen minutes, according to the quality and pressure of the gas, suffices for the fusion of 1,000 grains of carbonate of soda in a platinum crucible. At the heat which this furnace produces, the cast-iron ring does not melt nor alloy with the platinum crucible placed upon it.

By a modification of these arrangements, Mr. Griffin has made a gas furnace for melting quantities of lead, zinc, antimony, &c. This is represented by fig. 53. The iron crucible will contain nearly 30 lbs. of lead and about 24 lbs. of zinc. The burner readily melts these quantities, and then, with a diminished quantity of gas, will keep the metals fluid. The metals being protected from the air suffer little loss by oxidation. Such operations as the granulation of zinc are performed with this apparatus with great facility; it serves also for baths of fused metal. In a large furnace of this kind, made for a special operation, 60 lbs. of zinc have been melted with ease, and the inventor believes that, used in this manner, the burner is powerful enough to melt a hundredweight of zinc.

FIG. 53.



The principles of heating by gas, which have led Mr. Griffin to the construction of these gas furnaces, may be summed up as follows: When a crucible or other solid body is to be heated, it is to be wrapped in a single flame at the point of maximum heat, and loss of heat by radiation and conduction is to be prevented by the interposition of non-conducting materials (plumbago or fire-clay); and when liquids are to be boiled or evaporated, particularly when they are contained in vessels of glass or porcelain, the flame is to be broken up into numerous horizontal jets, and these are to be made to supply a large and regular current of highly heated air, by which alone, and not by the direct application of the flame, the vessel that contains the liquid is to be heated. In both cases provision must be made to secure a sufficient draught of air through the furnace, because every cubic foot of gas requires for combustion 10 or 12 cubic feet of air, and the gases which have done their duty must be rapidly carried away from the focus of heat. If the steam, the carbonic acid gas, and the free nitrogen which constitute the used-up gases are not promptly expelled, fresh gaseous mixture in the act of producing additional heat by combustion cannot get near the object that is to be heated, and the heat so produced out of place is wasted.

Bunsen's gas-burner, whatever its size, is subject to two defects: sometimes the flame burns white and smoky, and sometimes it blows down, the gaseous mixture explodes, and the gas then burns with a smoky flame in the tube. The remedies for these defects are as follows: If the flame is white only when the gas is turned on very full, the remedy is to lessen the supply of gas; but if the flame continues to burn white at the top when the gas is gradually turned off and the mass of flame slowly sinks, then the holes which deliver the gas from the supply pipe into the air-box *a* (fig. 47) are too large, and are placed too directly under the centre of the vertical tube *b* (fig. 47), and these defects must be corrected in the instrument. Finally, when the flame blows down, it is because the supply of atmospheric air is too large in proportion to the supply of gas, and their relative proportions must be altered. To effect this alteration the cap *c* is to be turned round on the air-box *a* so as partially to close the holes, and thus lessen the supply of air. If, when the gas is alight, the flame needs to be lowered, first the supply of air is to be lessened and then the supply of gas. If the flame is to be enlarged, first the supply of gas must be increased and then the supply of air. In short, to prevent the flame blowing down, the gas must always be placed in excess, and then have the proper quantity of air adjusted to suit it by means of the regulator *c*. When gas-burners of this description have to be used in a locality where the pressure of the gas is slight, especially in the daytime, there is a constant tendency in the flame to blow down. The best way to prevent that occurrence is to supply the gas by a pretty wide tube, and to see that the current of gas is not checked by a very narrow bore in the plug of an intervening stop-cock, which is often the unsuspected cause of want of pressure in the supply of gas. If this does not suffice to prevent the blowing down of the gas, the holes which admit the gas from the supply pipe into the box *a* of the burner should be enlarged, more or less according to necessity. A large supply of gas compensates, to some extent, for want of pressure.

When a steady and long-continued heat is desired from a Bunsen's burner, it is proper to use two stop-cocks and a length of caoutchouc tube between them. One of these stop-cocks is to be affixed to the burner, and the other to the supply pipe. The latter is to be opened *wider* than is necessary to supply the required quantity of gas, and the former is to be used to regulate the supply to the burner exactly; under these circumstances, if another stop-cock is opened and gas burnt in the immediate neighbourhood, the flame does not so readily blow down in the regulated burner as it does when only the stop-cock on the supply pipe is used.

When a crucible is suspended by wires or by a ring over the flame of a spirit lamp or gas-burner, the flame and the hot air supplied by the flame strike the crucible for an instant and then pass away to do no more good. At the same time, the effect of the heating power on the crucible is lessened by other circumstances; namely, by radiation on all sides, by a mass of cold air which constantly rises around and in contact with it, and by the conducting power of the metallic apparatus which supports both the crucible and the lamp. These losses are avoided if the crucible is inclosed in a furnace made of a non-conducting material, such as fire-clay, which can absorb and retain heat. In the descriptions of the gas furnaces, and in that of Mr. Charles Griffin's oil-lamp furnace, several methods of mounting crucibles in fire-clay jackets have been shown; and we will now describe some of Mr. Griffin's fittings that may be used to construct temporary table furnaces for crucibles that are to be exposed to the flame produced by gas, oils, or spirit up to a temperature close upon, but not quite up to, a white heat; that is to say, up to a heat that will readily melt anhydrous carbonate of soda and small quantities of silver, and so be fit for many metallurgical operations, but which will not melt copper nor cast iron.

Fig. 54 represents sections of cylinders of fire-clay which are drawn on a scale of 1 to 8, and have the relative heights and bores represented in the figures. The clay pieces, that is to say, as many of them as are necessary for a given purpose, can be adjusted over a gas-flame by means of a tripod (fig. 49) or a clay support.

The crucible to be operated upon is to be supported on a toothed ring made either of cast iron or fire-clay, such as are represented by figs. 52 and 55. Fig. 52 is a ring of cast iron, *h* representing it in section and *i* as seen from above. It is about two inches in diameter, and has three teeth projecting towards the middle of the ring. This ring can be supported by any of the clay cylinders whose bore does not exceed two inches. Fig. 55 is a ring of fire-clay of 4 inches external diameter, and 1 inch in thickness, provided with three teeth that project inwards, and upon which a crucible can be supported without injuring the draught of the gas furnace.

Both these grates will support crucibles at the highest temperature which can be produced by spirit, oil, or gas, without a blast of air; but at a white heat produced by any of these fuels with a blast of air, the iron ring melts, and, if the heat is long continued, those of fire-clay soften and partially give way. When the fire-clay grate (fig. 55) is required to sustain a very high temperature for a considerable time, it is proper to have it made of 6 inches diameter, as represented by fig. 54 *p*, the air-way in which is the same as that of the small grate, but the clay ring is much stronger.

FIG. 54.

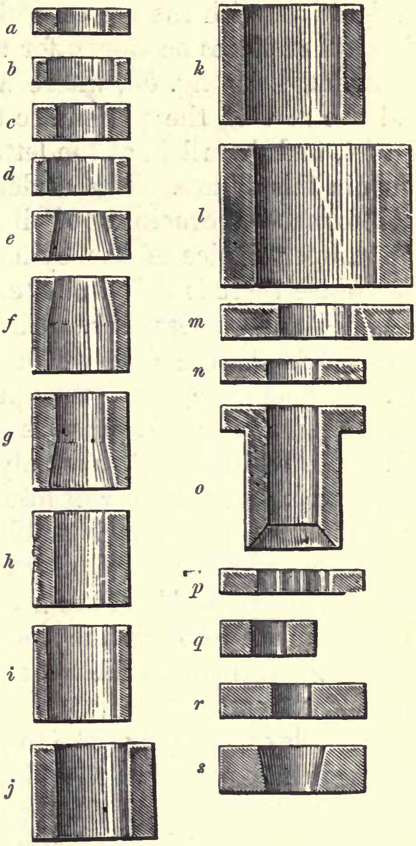


FIG. 55.

The grate is fixed above the flame at a distance which is found by trial to place the crucible on the point of greatest heat. Commonly a 4-inch cylinder (54, *h* or *g*) placed upon a suitable support serves the purpose. The bore of the cylinders at the bottom must be wider than the burner, to allow of a considerable influx of atmospheric air around the flame. The grate is placed on this cylinder, the crucible on the grate, and then another cylinder around the crucible. The choice of this upper cylinder depends entirely upon the size of the crucible that is to be heated. Whatever the size of the crucible, the cylinder must be so chosen as to fit the crucible as accurately as possible, leaving between it and the furnace walls an open space of not less than $\frac{1}{8}$ inch, nor more than $\frac{1}{5}$ inch all round. If the upper cylinder is not contracted at top like 54 *e f g*, then a cylinder of narrow bore, such as 54 *a* or *c*, must be put upon it, in order to deflect the flame and the rising current of hot air upon the top of the crucible, and thus produce a reverberatory furnace. Finally, an iron chimney, 2 or 3 feet long, must be put upon the furnace, to force up a draught of air sufficient to feed the flame.

Suppose a small rose gas-burner is to be arranged for an ignition, with the use of a fire-clay support, the combination of pieces necessary for the purpose may be those represented by fig. 56, where A is the fire-clay support, and the rest of the pieces are those which are shown at fig. 54, and described at the letters placed against each of them in this figure. It is evident that the application of this furnace to crucibles of different sizes depends upon the proper choice of the cylinders here marked *i* and *e*. Of course there is only a limited choice of crucibles suitable for such operations. Three inches is the extreme width between the furnace walls of any of the pieces in fig. 54, from *a* to *g*, and though larger cylinders could be used, such as *i* to *o*, it must be remembered that the flame of a lamp without blast has only a limited power, and that although a given flame will fuse 1,000 grains of carbonate of soda in a platinum crucible, it may only heat to a moderate redness a large clay crucible. Yet, considering that low degrees of heat are suitable for many purposes, it is convenient to have the power of readily adjusting a temporary furnace to the bulk of any crucible which it is desired to heat.

The clay pieces (fig. 54 *i* to *p*) are those that have been expressly designed for the blast oil furnace already described; but these can also be used for spirit and gas furnaces, the respective sizes being chosen in each case according to the size of the crucible that is to be ignited.

In respect to the *means of supporting* a crucible, it has been shown that clay trivets with a wide flange, namely, the 6-inch trivets fig. 54 *p*, will support a crucible containing 5 lbs. of iron until that quantity of iron is melted, even under the operations of a blast; so that it is evident that this method of supporting a crucible in a gas flame may be always depended upon when no blowing-machine is employed.

Fig. 57 represents the gas furnace arranged for boiling or evaporating: *a* is the gas-burner; *b* an iron stool with three legs; *c* a furnace body or iron jacket lined with plumbago or fire-clay. This furnace may be 14 inches high and 9 inches in diameter. The three brackets fixed on the upper part of the jacket serve to support the vessel that contains the liquid that is to be boiled or evaporated. A porcelain basin of 16 or 18 inches in diameter can be thus supported. It is important to allow between the jacket *c* and the evaporating basin plenty of space for the escape of the heated air, which ascends from the interior of the furnace. When the evaporating basin is of small diameter, it may be supported on iron triangles, placed in the furnace *c*. The section shows that around the vertical tube of the gas-burner *a* there is in the bottom of the furnace *c* a circular opening which is of 2 inches diameter, and through which air passes freely, partly to feed the flame and partly to be heated by the flame and be directed upwards in a continuous current upon the lower surface of the basin that is to be heated. The flame within the furnace burns steadily. No side currents of air agitate it. No part of it touches the basin, which should receive its heat solely from the mass of ascending hot air. The gas-burner thus arranged and supplied by a gas-pipe of $\frac{1}{4}$-inch bore, burns about 3 cubic feet of gas in an hour, and the flame which it produces, acting upon water contained in

FIG. 56.

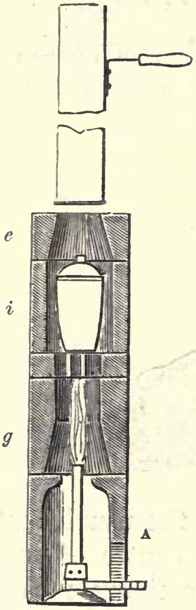
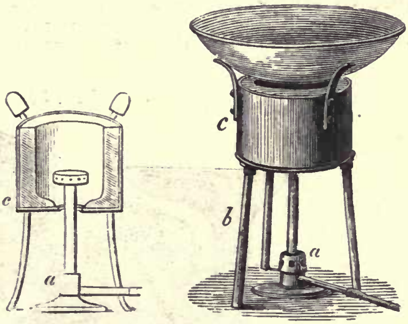


FIG. 57.



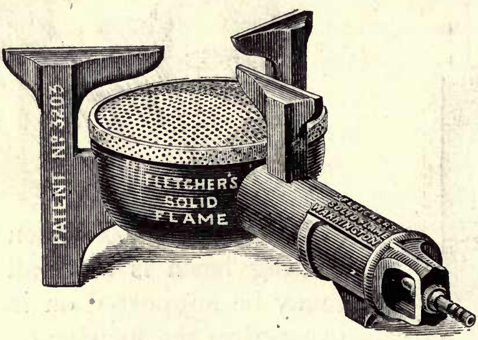
an open porcelain evaporating basin, will heat from 60° to 212° F.—

1 quart in	5 minutes
1 gallon in	15 „
2 gallons in	30 „

and when the water boils it is driven off in steam at the rate of more than a gallon of water per hour. The method is consequently applicable to distillation on a small scale, and to numerous other laboratory operations.

An excellent gas-burner for general laboratory use is Mr. Fletcher's solid-flame burner, shown in fig. 58. This is one of the very best heating burners which has yet been made. The flame is of a brilliant green colour, solid, and of the same temperature throughout; the usual heating burners having a flame with a hollow centre of unconsumed gas. The pattern shown in the figure measures only 3½ inches in height, and it will melt half a hundredweight of lead in an iron pot. It will boil half a gallon of water in a flat copper kettle in five minutes, and will melt 6 lbs. of lead or solder in an iron ladle in seven minutes. The burner can be adapted for a blast where very high power is required in a small burner. With a blast it can be made to consume any gas supply up to 200 cubic feet per hour, giving a very high duty. One advantage which this burner possesses over those of the ordinary kind with wire-gauze tops, is that it cannot be spoiled by any accident. In case a solution boils over, and chokes the holes

FIG. 58.



in the perforated copper dome, the latter can be lifted off (when the burner is warm) and cleaned. The whole burner is designed to stand the roughest and heaviest work without injury.

A smaller size of this burner, of little less than half the power, is shown in fig. 59.

The india-rubber tubing for these burners must be of good size, and smooth inside, made without wire.

Fig. 59.

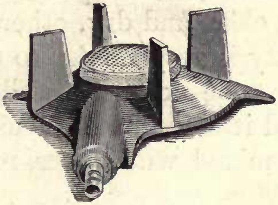


Fig. 60.

The burner shown in fig. 60 is a very excellent evaporating burner for glass and porcelain vessels and general laboratory work. It is a great improvement on the ordinary coil burners in use, owing to the fact that no currents of cold air, which are so fatal to glass and porcelain dishes, can reach the vessel, as is the case with all coil burners. The flames are blue and smokeless, and are not liable to be extinguished with a splash, being raised above the body of the burner. Vessels must not be put in contact with the flame; half the diameter of the burner must be taken as the nearest distance at which a vessel can be placed above the top of the burner.

LUTES AND CEMENTS.

It may be as well to mention in this part of the work the various lutes and cements which may be employed, either in fire operations or in making good joints in experiments with gases or liquids. The following are the principal kinds.

Fire Lute is composed of good clay two parts, sharp washed sand eight parts, horse-dung one part. These materials are to be intimately mixed; and afterwards the whole is to be thoroughly tempered like mortar. Mr. Watt's fire lute is an excellent one, but is more expensive. It is made of finely powdered Cornish (porcelain) clay mixed to the consistence of thick paint, with a solution of borax in the proportion of 2 ounces of borax to a pint of hot water.

Fat Lute is prepared by mixing fine clay, in a fine powder, with drying oil, so that the mixture may form a ductile paste. When this paste is used, the part to which it is applied ought to be very clean and dry, otherwise it will not adhere. Glazier's putty is very similar to this.

Roman Cement.—This must be kept in well-closed vessels, and not moistened until it is required for use.

Plaster of Paris.—This is mixed with water, milk, or weak glue, or starch water.

These three lutes stand a dull red heat: the two latter may be rendered perfectly impermeable to gaseous bodies by being smeared over with oil, or a mixture of oil and wax.

Linseed or Almond Meal, mixed to the consistence of a paste with water, milk, lime water, or starch paste. This lute is very manageable and impermeable, but does not withstand a heat greater than about 500° F.

Lime and Egg Lute.—If just the sufficient quantity of water be added to quick lime to reduce it to a dry powder, and that is mixed well and rapidly with white of egg diluted with its own volume of water, and the mixture spread immediately on strips of linen and applied to the part, then powdered with quick lime, it forms a good cement. Instead of white of egg, lime and cheese may be used, or lime with weak glue water. This lute dries very rapidly, becoming very hard and adhering strongly to glass; but its great inconvenience is the want of flexibility.

White Lead mixed with Oil.—If this mixture be spread upon strips of linen, or bundles of tow, it acts much in the same manner as the lime lutes.

Yellow Wax is often used as a lute, but it becomes very brittle at a low temperature. It may be rendered less brittle, and at the same time more fusible, by an admixture of one eighth crude turpentine.

Soft Cement is prepared by fusing yellow wax with half its weight of crude turpentine and a little Venetian red in order to colour it. It is very flexible, and takes any desired form under the pressure of the fingers.

Waterproof Cement.—Mr. Edmund Davy, F.R.S., described a cement made by melting in a saucepan two parts by weight of common pitch, and adding to it one part by weight of gutta-percha, stirring and mixing them well together until they were completely incorporated with or united with each other. The mixture then forms a homogeneous fluid which may be used in this state for many purposes, and is remarkable on account of the facility and tenacity with which it adheres to metals, stones, and glass. It may be poured into a large basin of cold water, in a thinner or thicker stream, or as a cake. In this state, while warm, it is quite soft, but may be soon taken up out of the water and drawn out into longer or pressed into shorter pieces, or cut or twisted into fragments, which may again be readily reunited by pressure. When the cement is cold, or before, it may be removed from the water and wiped dry, when it is fit for use. It is of a black colour; when cold, it is hard. It is not brittle, but has some degree of elasticity, which is increased by a slight increase of heat. It appears to be not so tough as gutta-percha, but more elastic. Its tenacity is very considerable, but inferior to gutta-percha. It softens when put into water at about 100° F.; when heated to above 100° F. it becomes a thin fluid; and if the heat is gradually increased it passes through intermediate stages of softness, becomes viscous like bird-lime, and may be extended into threads of indefinite length: it remains in this state even when exposed for some time in a crucible to the heat of boiling water, 212° F. Water appears to have no other action upon it but that of softening it when warm or hot, and slowly hardening it when cold. The cement adheres strongly, if pressed on metal or other surfaces, though water be present, provided such surfaces be warm. This cement is applicable to many useful purposes. It adheres with great tenacity to metals, wood, stones, glass, porcelain, ivory, leather, parchment, paper, hair, feathers, silk, woollen, cotton, linen fabrics, &c. It is well adapted for glazing windows, or as a cement for aquariums. This cement does not appear to affect water, and it will apparently be found applicable for coating metal tanks; to secure the joints of stone tanks; to make a glue for joining wood, which will not be affected by damp; and to prevent the depredations of insects on wood.

Resinous or Hard Cement is made by fusing together at the lowest possible temperature one part of yellow wax and five or six of resin, and then adding gradually one part of red ochre or finely powdered brickdust (plaster of Paris succeeds very well), and then raising the temperature to 212° at least, until no more froth arises or agitation takes place, and stirring it continually until cold. This cement is employed in a hot state. This lute is much used for fixing brass caps, &c., to air-jars.

Caoutchouc.—Tubes of vulcanised caoutchouc form a very ready means of attaching one piece of apparatus to another, and they possess the peculiar advantage of flexibility, which allows the various parts of the apparatus which they connect to move in different directions to a slight extent, so that the whole is not so likely to be fractured as when connected in an inflexible manner. Caoutchouc is also less acted upon by gases and vapours than almost any other substance we know; even chlorine attacks it but slowly, and when unvulcanised it possesses the valuable property of forming a perfect joint when freshly cut edges are brought and pressed together, hence the facility with which it is manufactured into tubes. The mode of manufacturing small connecting tubes, which are often required to be of unvulcanised caoutchouc, is as follows: Take a piece of the sheet caoutchouc of the required size, and warm it either in the hand or before a fire, until it is perfectly soft; then place it around a glass rod of the requisite size, pressing the edges close together with the fingers; when close together cut off the superabundance with a sharp pair of scissors, and the newly cut edges will unite by simple pressure of the nail. When well executed the joint is scarcely apparent. In order to prevent the caoutchouc from adhering to the rods on which the tube is formed, a little moisture or dry starch may be employed. When caoutchouc is not at hand, oiled paper may be substituted, the joint being made of wax.

Faraday gives the following directions for luting iron, glass, or earthenware retorts, tubes, &c., for furnace operations. When the lute has to withstand a very high temperature it should be made of the best Stourbridge clay, which is to be made into a paste varying in thickness according to the opinion of the operator. The paste should be beaten until it is perfectly ductile and uniform, and a portion should then be flattened out into a cake of the required thickness, and of such a size as shall be most manageable with the vessel to be coated. If the vessel be a retort or flask, it should be placed in the middle of the cake, and the edges of the latter raised on all sides and gradually moulded and applied to the glass; if it be a tube it should be laid on one edge of the plate, and then applied by rolling the tube forward. In all cases the surface to be coated should be rubbed over with a piece of the lute dipped in water for the purpose of slightly moistening and leaving a little of the earth upon it; if any part of the surface becomes dry before the lute is applied, it should be re-moistened. The lute should be pressed and rubbed down upon the glass successively from the part where contact was first made to the edges, for which purpose it is better to make them thin by pressure and also somewhat irregular in form, and if at all dry they should be moistened with a little soft lute. The general thickness may be about $\frac{1}{4}$ to $\frac{1}{3}$ of an inch.

Being thus luted, the vessels are afterwards to be placed in a warm situation, over the sand-bath or near the ash-pit, or in the sun's rays. They should not be allowed to dry rapidly or irregularly, and should be moved now and then to change their positions. To prevent cracking during desiccation, and the consequent separation of the coat from the vessel, some chemists recommend the introduction of fibrous substances into the lute, so as mechanically to increase the tenacity of its parts. Horse-dung, chopped hay and straw, horse- and cow-hair, and tow cut short, are amongst the number. When these are used, they should be added in small quantity, and it is generally necessary to add more water than with simple lute, and employ more labour to insure a uniform mixture. It is best to mix the chopped material with the clay before the water is put to it, and, when adding the latter, to mix at first by stirring up the mass lightly with a pointed stick or fork; it will then be found easy, by a little management, to obtain a good mixture without making it very moist.

The luting ought to be made as dry as possible consistent with facility in working it. The wetter it is, the more liable to crack in drying, and *vice versâ*.

Mr. Willis recommends, when earthenware retorts, &c., are to be rendered impervious to air, the following coating: One ounce of borax is to be dissolved in half a pint of boiling water, and as much slaked lime added as will make a thin paste. This composition is to be spread over the vessel with a brush, and, when dry, a coating of slaked lime and linseed oil is to be applied. This will dry sufficiently in a day or two, and is then fit for use.

Iron Cement.—This mixture is used for making permanent joints generally between surfaces of iron. Clean iron borings or turnings are to be slightly pounded, so as to be broken but not pulverised: the result is to be sifted coarsely, mixed with powdered sal-ammoniac and sulphur, and enough water to moisten the whole slightly. The proportions are—1 sulphur, 2 sal-ammoniac, and 80 iron. No more should be mixed than can be used at one time. Mr. Cooley states that he is informed by one of the first engineers in London that the strongest cement is made without sulphur, and with only one or two parts of sal-ammoniac to 100 of iron borings: but that when the work is required to dry rapidly, as for the steam joints of machinery wanted in haste, the quantity of sal-ammoniac is increased a little, and a very small quantity of sulphur is added. This addition makes it set quicker, but reduces its strength. Several excellent cements are described in Cooley's 'Cyclopædia of Practical Receipts.' From these the following are selected:—

Beale's Cement.—Chalk, 60 parts; lime and salt, of each 20 parts; Barnsey sand, 10 parts; iron filings or dust, and blue or red clay, of each 5 parts. Grind together and calcine. This is patented as a fire-proof cement.

Boiler Cement.—Dried clay in powder, 6 lbs.; iron filings, 1 lb., made into a paste with boiled linseed oil. This is used to stop leaks and cracks in iron boilers, stoves, &c.

Bruyère's Cement.—Clay, 3 parts; slaked lime, 1 part; mix and expose them to a full red heat for 3 hours, then grind to powder.

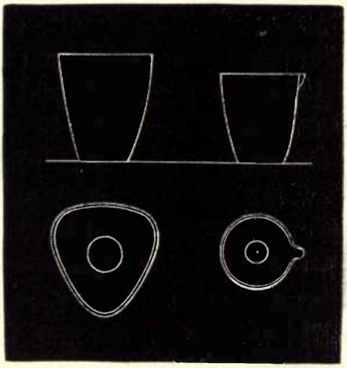
This makes a good hydraulic cement.

Oxychloride of Zinc Cement.—In solution of zinc chloride, of 1·49 to 1·65 specific gravity, dissolve 3 per cent. of borax or sal-ammoniac, and then add zinc oxide, which has been heated to redness, until the mass is of a proper consistency. This cement becomes as hard as marble. It may be cast in moulds like plaster of Paris.

CRUCIBLES, CUPELS, ETC.

The crucibles best known in commerce are the Hessian, the Cornish, the Stourbridge, and the London clay crucibles; charcoal, plumbago, iron, porcelain, platinum, silver, and gold crucibles are also required in small operations. Of the clay crucibles, the London pots are much to be preferred, on account of their very refractory nature. They resist the action of fused oxide of lead better than most clay crucibles, and they are also better made than the two other kinds, being much smoother and more regularly formed. They have the form of a triangular pyramid (see fig. 61, crucibles and cover), and are made in such sizes that they fit one into the other, forming nests. The triangular form is very convenient, because there are three spouts, from either of which can be poured the fused contents of the pot. The Cornish crucibles are circular, and do not stand changes of temperature so well as the London pots, neither can they endure such an extreme of heat, for they agglutinate and run together at a temperature which does not touch the others. Dr. Percy says they are more generally useful than any other crucible. The Hessian pots are the worst of all; they do not stand moderate change of temperature without risk of fracture, so that they require to be very carefully used. There is also another kind of pot in use, made of the same material as the London crucibles, termed a 'skittle pot,' from its resemblance to the ordinary wooden skittle or ninepin. They are exceedingly useful for the fusion of large masses of matter, or such substances as boil or bubble much when heated. Plumbago or graphite crucibles are rapidly superseding all other kinds when metals have to be melted. They possess many advantages over clay crucibles. Their surface is very smooth; they are not liable to crack, however violent the changes of temperature may be to which they are subjected; they bear the highest heat without softening, and can be used repeatedly. Owing to the reducing property of the carbon they contain, they must not be employed when oxidising actions are required.

FIG. 61.



Crucibles and all plumbago fittings for furnaces should be of the 'Salamander' brand. These require no annealing or care in heating up, and stand strong fluxes better than the ordinary make.

The Patent Plumbago Crucible Company have recently introduced a very excellent fluxing crucible. It is made of fine white china clay, is perfectly smooth inside and out, and will stand very high temperatures without softening.

Stourbridge clay crucibles are not much used. They require the greatest care in using them, and are spoilt after the first operation.

Porcelain crucibles are not used in large assaying or metallurgical operations, but they are invaluable in small laboratory experiments. They are practically infusible, are little liable to crack, and are almost unacted on by reagents and fluxes. In many cases they will replace the more expensive platinum crucibles, and where easily reducible metals are under treatment they must be used in preference to platinum.

Crucibles, in order to be perfect and capable of being used indifferently for any operation, ought to possess the four following qualities: first, not to break or split when exposed to sudden changes of temperature; secondly, to be infusible; thirdly, to be only slightly attacked by the fused substances they may contain; fourthly and lastly, to be impermeable, or nearly so, to liquids and gases. But as it is very difficult to unite all these qualifications, various kinds of pots are made to fulfil one or more of them.

In order to render crucibles capable of withstanding changes of temperature without breaking, a certain proportion of substances infusible by themselves is mixed with the pasty clay; sand, flint, fragments of old crucibles, black-lead, and coke are used for this purpose. They are reduced to a state of division more or less fine, according to the grain of the clay paste. For ordinary pots the powder ought not to be very fine; but for porcelain crucibles it ought to be as fine as flour. The choice of these various bodies depends upon the use for which the crucible is intended.

The most refractory crucibles are those made with the pure clays, or such as contain little or no oxide of iron, and especially those free from calcareous matters. Amongst clays, the best are those which contain most silica ; nevertheless, these are not absolutely infusible, and in the high temperature of a wind furnace they sometimes soften so much as actually to fall into a shapeless mass. This defect, as before stated, can be in some measure diminished by mixing with the clay a quantity of graphite or coke ; either of these substances forms a kind of solid skeleton, which retains the softened clay, and prevents its falling out of shape.

Coke and black-lead are more efficacious than sand, because they have no action on clay, whilst sand forms a fusible compound with it. If too large a quantity of black-lead or coke be employed, it gradually consumes in the fire, and the pots become porous, and break at the least movement. Wood charcoal can be used instead of black-lead or coke, but is not so good, as it burns more readily.

Black-lead crucibles are generally composed of 1 part of refractory clay, and from 2 to 3 of black-lead. These pots withstand all possible changes of temperature without cracking, and their form is rarely changed by the heat ; not because they are absolutely infusible, but because they are supported by the skeleton of graphite.

Crucibles into whose composition carbonaceous matters enter, reduce any oxides that may be heated in them, and hence are inconvenient in certain cases. They can, nevertheless, be employed in all cases by giving them a lining of clay, which must be tolerably thick, and well dried before use.

Earthen crucibles which have not been baked at a white heat are more or less permeable to liquids and gases, according to the grain. In order to render them impermeable to liquids, they must be heated to such a temperature as will suffice to fuse the outside. When treated in this way, however, they are very liable to crack with sudden changes of temperature: the best method, therefore, of rendering them capable of containing water, &c., is to coat them with the mixture of borax and lime described as Willis's lute.

In order that crucibles may resist the corrosive action of the fused substances contained within them, they must be as compact as possible, and the substance of which they are made must have little or no tendency to combine with the fused contents. The metals and their non-oxidised compounds attack neither clay nor black-lead; but there are, nevertheless, some metallic substances—galena, for instance—which, without exercising any chemical action, on earthy matters, have the property of filtering through their pores.

The readily reducible oxides gradually corrode black-lead crucibles and those pots into the composition of which coke enters, by burning the carbonaceous matter. The greater number of these oxides, the alkalies, earths, and glasses (which are fusible silicates, borates, &c.), act more or less powerfully on the earthy base of all crucibles; so that these substances are most difficult to keep in fusion for any length of time. They attack the crucible layer by layer, dissolving the substance of which it is composed, and after a lapse of time rendering it so thin that it cannot withstand the pressure of the molten mass within it; and the fracture of the pot, and consequent loss of contents, is inevitable.

Under the same circumstances, all those crucibles whose texture is loose are more readily corroded than those with a firm, compact body; because the corrosive substance filters to a certain depth in the former crucibles, and in consequence has a larger surface to act upon than when it is contained in a compact pot.

Earthen crucibles may be assayed by noticing the time they will contain fused litharge, which exercises a very corrosive action on them, honeycombing them in all directions; and those pots which contain it longest without undergoing much damage, may be considered the best. However, this method of assay is not exact, even by taking into account the thickness of the pot, for litharge runs through crucibles: first, because it is very fusible, and easily filters through their pores; and secondly, it has the property of forming fusible compounds with all the silicates by combining with them. From these remarks it will be evident that a crucible whose grain is loose will readily allow litharge to pass through it, however slightly its substance may be fusible or acted on; or, on the contrary, it may be very easily acted on (even when infusible) when it has an extremely fine grain; so that the promptitude with which a crucible is pierced by litharge bears no relation to its fusibility. A crucible of pure quartz will be very readily attacked by litharge, because the latter has much affinity for silica, and the simple silicates of lead are all very fusible; whilst a crucible composed of silica, alumina, and lime, which by itself is very fusible, would be corroded less rapidly, because the oxide of lead has much less affinity for the earths than it has for the silica; moreover, it forms less fusible compounds with the earths than with silica alone. The assay of crucibles with litharge, if not of use in ascertaining their degree of fusibility, fulfils perfectly its object when it is wished to prove the resistance a crucible has to the corrosive action of various bodies in a state of fusion; for of all fusible substances, none exercise such a powerful action on earthy matters as litharge.

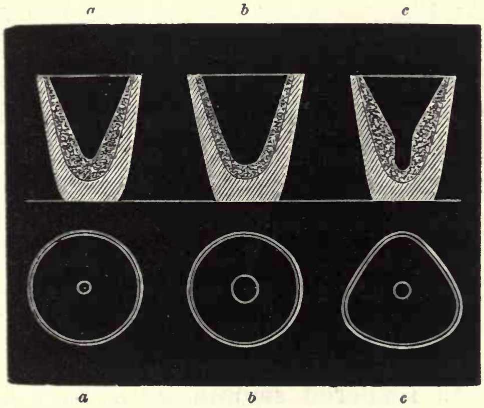
Crucibles ought not only to resist the corrosive action of those bodies they may contain, but also that of the ash produced by the combustion of the fuel in which they may be placed. These ashes being often calcareous, alkaline, or ferruginous, act on the clayey part of the crucibles exactly as the fluxes. Whence it follows, that those crucibles which contain litharge longest will also resist the action of the fluxes best.

In order to ascertain the fusibility of a crucible, a direct experiment must be made, either by heating a piece in a crucible lined with charcoal, and ascertaining if its angles be rounded, if its substance has become translucent, &c.; or, better still, by heating the crucible to be assayed with another whose properties are well known.

As to permeability, it may approximately be ascertained by filling two crucibles with water, and noting what length of time is required to empty them completely; the crucible which contains it longest being, of course, the least permeable.

To prove if a crucible be able to sustain great changes of temperature without breaking, introduce it, perfectly cold, into a furnace full of lighted coal: take it out when reddish white, and expose it to a current of cold air produced by a bellows or otherwise: if it stand these trials, it may be heated afresh and plunged red-hot into water, and, if it be not broken, placed immediately in the fire. The best pots support all these operations without breaking; but it often happens that they are filled with innumerable small fissures, through which fused matters can pass. This can be ascertained by fusing rapidly in the assay pot a quantity of litharge: if these fissures be present, the fused oxide will readily filter through them.

FIG. 62.



CHARCOAL CRUCIBLES.—As all oxidised matters act readily on clay pots, and a great number of the metals and their compounds adhere to them, they have long since been replaced, under certain circumstances, by charcoal crucibles, which do not possess these disadvantages. The older assayers used merely a piece of charcoal, with a hole made in it, and then bound round with iron or other wire. The use of these has, however, been abandoned for some time, and earthenware crucibles lined with charcoal have been substituted (see fig. 62, *a*, *b*, and *c*). These may be considered as charcoal pots enveloped with refractory clay; they are solid, always free from cracks, and easy of preparation, and they have the same properties as the solid charcoal crucibles without their inconveniences.

In order to prepare these crucibles, the charcoal must be chosen carefully, so as to contain no foreign substances; it must be pulverised and passed through a sieve; the powder moistened with water or treacle, mixed with a spatula, and then kneaded with the fingers until it just adheres, and forms adhesive lumps without being sufficiently wet to adhere to the hand. Some advise the addition of gum to the water with which the charcoal is moistened. The crucible is moistened slightly by being plunged into water, and withdrawn as speedily as possible, and about half an inch in depth of the charcoal paste, prepared as above, is placed in it; the paste is then pressed firmly down, by means of a wooden pestle: the blows are to be slight at first, and then increase in force until it is as firm as possible: another layer is then applied and pressed as before, and the process repeated until the crucible is quite full, taking great care to render all as firm as possible, especially at the sides. In order to make each layer adhere firmly to the other, the surface must be scratched rather deeply with the point of a knife before a new layer is applied. When the crucible is completely filled, a hole is to be scooped in the charcoal of about the form of the pot. The sides are then rendered smooth by friction with a glass rod. This is absolutely necessary, so that the metallic globules produced in an assay may not be retained by the asperities of the lining, but may be readily enabled to unite into one button. When a lined charcoal pot is well made, its sides are very smooth and shining. For ordinary use, the lining may be $\frac{3}{8}$ths of an inch thick at the bottom and $\frac{1}{8}$th or so at the sides: but in some cases, for instance, when the substance to be fused is capable of filtering through the lining and attacking the pot as a flux, it must be at least twice the above thickness in every part.

Lined crucibles have many advantages over plain crucibles. The lining gives them greater solidity, and prevents a loss of shape when softened; for plain crucibles are always three-fourths empty when their contents are fused, on account of contraction in volume: the pots then have nothing to sustain their sides when they soften towards the end of the assay, at which period the highest temperature is employed. Besides, vitreous matters do not penetrate the lining, and exercising no action on it, can be obtained in a state of purity, and the exact weight determined: if fused in a plain pot, the weight could not be ascertained, because a portion would adhere to the sides, and the resulting mass would not be pure, having taken up a portion of the crucible in which the fusion was effected.

The lining, too, effects the reduction of certain metallic oxides by cementation, and does away with the necessity of adding powdered charcoal to the body to be reduced. This property is very valuable, because, when an oxide is reduced by mixing it with charcoal, an excess must always be employed, and this excess remains with the metal, and prevents its exact weight from being ascertained. No oxidising substances or bodies which readily part with oxygen (oxide of copper, for example) must be calcined in a plumbago or charcoal-lined crucible, unless indeed the chemical union of the charcoal with the oxygen is desired.

Lime Crucibles.—Some years ago Deville proposed the use of crucibles cut out of solid blocks of pure lime, in order to prevent the introduction of carbon and silicon into metals and alloys during the process of fusion.

The results of experiments made with such crucibles were found to be extremely satisfactory, and metals fused therein, as iron, manganese, nickel, cobalt, &c., were obtained far purer and more malleable and ductile than when fused in the usual clay or brasqued crucibles. Unless, however, the crucibles required were of very small size, it was found difficult to obtain blocks of lime for shaping them sufficiently large and free from flaws; and experiment showed a considerable loss, both by breakage when shaping them, and by their cracking when in the furnace. In order to obviate this, trials were made with clay crucibles lined with lime, but ineffectually, as these crucibles invariably melted down before the requisite heat was arrived at—a result due to the action of the lime itself upon the outer clay crucible.

Mr. David Forbes, F.R.S., has published in the 'Chemical News' the result of some very valuable experiments on this subject. The arrangement he proposes fully answers the purpose, the crucibles being capable of standing the heat of melted wrought iron or cobalt without fusion or cracking, as well as of being made of any reasonable size.

A clay crucible of somewhat larger capacity than the desired lime one, is filled with common lamp-black, compressing the same by stamping it well down. The centre is then cut out with a knife until a shell or lining of lampblack is left firmly adherent to the sides of the crucible, and about half an inch or less in thickness, according to the size of the crucibles; this lining is now well rubbed down with a thick glass rod until its surface takes a fine glaze or polish, and the whole cavity is then filled up with finely powdered caustic lime, thoroughly pressed down, and a central cavity cut out as before; or the lime powder may be at once rammed down round a central core of the dimensions of the intended lime crucible.

This lime lining is naturally rather soft before being placed in the furnace, but upon heating, it agglutinates, and forms a strong and compact crucible, which is prevented from acting upon the outer one by the interposed thin layer of lampblack, and at the end of the experiment it generally turns out as solid and compact as those made in the lathe.

Experiments made with such crucibles, even up to dimensions containing several pounds of metal, have proved them extremely well suited for these operations, and doubtless similar crucibles could be made, lined with magnesia or alumina as required. In some cases ordinary black-lead crucibles, lined with powdered lime, magnesia, or alumina, might possibly be found to answer.

Having frequently used lime crucibles in metallurgical operations, and having met with the inconvenience pointed out by Mr. Forbes, the editor can appreciate the great value of his improvement. It is one which cannot fail to be extensively adopted in metallurgical laboratories.

In certain particular experiments, crucibles are lined with other bodies besides charcoal and lime, such as silica, alumina, magnesia, or chalk, by merely moistening their respective powders with water, and applying the paste as above described for the charcoal. A slight layer of chalk lessens the liability of attack from fused litharge.

Alumina Crucibles are strongly to be recommended in many metallurgical operations. They are made in the following manner. Ammonia alum is ignited at a full red or white heat, when it leaves behind pure alumina in a dense compact form: this is to be finely powdered. To a solution of another portion of ammonia alum in water, ammonia is added, when alumina is precipitated in a gelatinous state: this is to be washed until free from sulphate of ammonia. The dense alumina is then mixed with water and worked up into a paste, the precipitated gelatinous alumina being kneaded in from time to time; this gives coherency: and when sufficient has been added (which must be ascertained experimentally), the mass may be moulded into shape. These crucibles require slow and careful drying; but they well repay all the care which is bestowed on them, for they do not readily crack, are attacked by very few fluxes, give out no impurities to metals which are melted in them, and are infusible at the highest heat of the furnace.

Magnesia Crucibles and Bricks.—M. H. Caron has pointed out the advantages which would accrue to metallurgy from the employment of magnesia as a refractory material. Formerly the high price of this earth appeared likely to confine it to the laboratory. Now, circumstances have happily changed; recent modifications introduced into the manufacture of cast steel, and especially the employment of Siemens's furnace and Martin's process, absolutely demand more refractory bricks than those at present in use, irrespective of price. On the other hand, native carbonate of magnesia, which formerly cost 10*l.* the ton, may now be obtained at the price of 2*l.* 15*s.* delivered at

Marseilles, or delivered at Dunkirk. Calcination at the place where the carbonate is obtained may still further reduce its price.* The following is M. Caron's process for its agglomeration, which may be employed by the chemist for the ready preparation of refractory vessels of all forms; by the physicist to obtain pencils for oxyhydrogen lighting purposes; and also by the manufacturer, to replace, in some cases, fire-bricks which have become insufficient in carrying out different processes of heating.

The magnesia which he employs comes from the island of Elba, where it is found in considerable quantities as a native carbonate, white, very compact, and of great hardness. This carbonate contains traces of lime, silica, and iron; it is, besides, interspersed sometimes with serpentine and large plates of silica, which would diminish the infusibility of the substance, and render it especially unfit for oxyhydrogen illumination if their removal is neglected. These plates are, however, easily recognised, and may be readily separated, even in working on the large scale. In the case of refractory bricks, the presence of a small quantity of these foreign bodies would, at the most, give rise, under the influence of the highest temperatures, to a slight vitrification, offering no serious inconvenience.

Before powdering the carbonate, it is advisable to bake it at the temperature necessary for the expulsion of the carbonic acid; the material then becomes very friable, and may be pulverised more easily. It is then possible to separate the serpentine and silica, which do not become friable under the influence of heat. This preliminary treatment does not permit of the agglomeration of the magnesia, and, even were this difficulty to be overcome, a temperature higher than that of the original calcination would cause an enormous contraction, producing fissures and alterations in shape which would interfere with the use of this substance. It is therefore indispensable, before moulding the magnesia, to submit it to a very intense heat,

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* This preliminary calcination requires less heat than burning lime, and diminishes the weight of the carbonate one-half.

at least equal to that which it is intended to support subsequently.

Thus calcined it is not plastic, its appearance is sandy, and compression does not cause it to acquire any cohesion; a mixture of magnesia, less calcined, imparts to it this quality. The quantity of the latter to be added necessarily varies with the degree of calcination of the two magnesias; it is scarcely one-sixth of the weight of that which has been exposed to the temperature of melting steel. It only now remains to moisten it with 10 or 15 per cent. of its weight of common water, and strongly compress it in iron moulds, as adopted in making artificial fuel. The brick produced in this operation hardens on drying in the air, and becomes still more resisting when it is subsequently calcined at a red heat. The same process would appear practicable, varying the form of the moulds, for obtaining crucibles of great capacity; but compression is difficult in large masses, as well as when the moulds have a large surface, as the magnesia adheres strongly to the sides. Although M. Caron has been able to obtain small crucibles for the laboratory, he does not consider this process adapted to make the large crucibles employed in steel melting. In this and other cases it is preferable to agglomerate the magnesia in the humid way.

To endow magnesia with a sort of plasticity, advantage is taken of a property of this earth pointed out in 'Berzelius's Chemistry.' When strongly calcined and then moistened, it hardens in drying. This fact is doubtless due to a hydration which takes place without sensible increase of temperature. When solidified in this manner the magnesia only loses the assimilated water at a high temperature. Then calcination not only does not disintegrate it, but, on the contrary, confers upon it a hardness and resistance comparable to those of ordinary crucibles after their baking. This being understood, the application of this fact is obvious. Thus, the magnesia to be employed in the manufacture of crucibles should only be moistened, moulded into shape, dried, and then ignited. For the construction of steel melting furnaces, a paste of moistened magnesia should be plastered over the walls; it will become ignited in due course without any particular precautions being taken. It sometimes happens, however, either owing to the magnesia being too much or too little hydrated, or owing to its containing siliceous matter, that the vessels before or after firing do not possess quite the desirable solidity; they should then, to acquire this, be simply moistened in a cold saturated solution of boracic acid, dried, and then fired as before. This operation does not render the magnesia more fusible; it only causes the grains of the substance to cohere more strongly together.

Magnesia, very pure, strongly calcined and finely pulverised, may be employed in the form of paste (*barbotine*) and yield the most delicate and translucent crucibles, as well as the sharpest and most complicated impressions.

Malleable Iron Crucibles are often very serviceable in assays of fusibility, and of certain selinides and sulphides, as in assays of galena or ordinary lead ore. They are either made of hammered sheet iron, or by plugging up small iron tubes, as gun-barrels, &c. The latter are preferable, because thick solid crucibles can be used a number of times, whilst the others are necessarily very thin and can be used only once. Whenever iron crucibles are employed at a very high temperature, they must be placed in those of earthenware, which protect them from the oxidising action of the air; but when they are not heated above the temperature of a copper assay, they may be used naked, if tolerably thick.

For assays at the above temperature, cast-iron crucibles may be employed with advantage, instead of wrought-iron, because they are very nearly as good, and much less expensive.

Platinum Crucibles.—Platinum crucibles are invaluable in a laboratory. Few pieces of apparatus are used so frequently by the chemist. Their chief use is in the ignition of precipitates and the decomposition of siliceous minerals by fusion with alkaline carbonates. They are preferable to porcelain, as not being fragile and being more readily heated to redness over the gas or spirit flame.

Their most convenient size is $1\frac{1}{2}$ inch high and $1\frac{1}{4}$ inch wide at the top.

In employing a crucible for the incineration of filters in quantitative assays by the wet way, it sometimes happens (as, for instance, with chloride of silver or sulphate of lead) that the employment of platinum is inadmissible. In these cases thin porcelain crucibles must be used. The analyst will, however, frequently experience difficulty, owing to the extreme slowness with which, in many cases, the last portions of the carbon of a filter are consumed when ignited in a porcelain crucible. It does not appear, however, that the following simple method of obviating the difficulty, as practised in the laboratory of Professor Sheerer, in Freiburg, has ever received the publicity which it deserves. Whenever a filter upon which a substance capable of injuring platinum has been collected, has to be incinerated, the porcelain crucible or capsule in which the process is to be conducted should be placed within a vessel of platinum of similar form, and the whole ignited in the usual way. Whether the greatly accelerated rapidity of combustion of the carbon which ensues depends upon a more equal distribution of heat brought about by the greater conducting power of the metal—an explanation which is current for the somewhat analogous case of copper-coated glass flasks—or whether, as seems probable, the power of the porcelain vessel to absorb heat be really increased by the interposition of the platinum; whether both these causes be of influence, or, the result depends upon another less apparent reason; or finally, whether vessels of some other metal would not be preferable to those of platinum, are questions which are open to discussion.

Fresenius gives the following excellent directions as to the preservation of platinum crucibles. The analyst should acquire the habit of cleaning and polishing the platinum crucible always after using it. This should be done, as recommended by Berzelius, by friction with moist sea-sand, whose grains are all round, and do not scratch. The writer has found this method to answer extremely well.

The sand is rubbed on with the finger, and the desired effect is produced in a few minutes. The adoption of this habit is attended with the pleasure of always working with a bright crucible, and the profit of prolonging its existence. This mode of cleaning is all the more necessary when one ignites over gas-lamps, since at this high temperature crucibles soon acquire a grey coating, which arises from a superficial loosening of the platinum. A little scouring with sea-sand readily removes the appearance in question, without causing any notable diminution in the weight of the crucible.

The ordinary Bunsen burner is known to act upon the surface of platinum vessels brought into contact with the inner line of the flame; the metal loses its polish, becoming superficially porous and spongy, and requires the use of the burnisher to bring it back to its original state. This alteration of the surface Mr. Dexter has found to be attended with a change of weight, so that for some years he has used a lamp of different construction for the heating of platinum crucibles in analytical operations. Such a lamp may be made by removing the air-tube of a common Bunsen lamp, and putting in its place a somewhat longer one of glass or iron of about 12 millimètres internal diameter. The gas jet should have a single circular aperture, and be in proper proportion to the diameter of the tube, which may be held in any of the ordinary clamp supports. The tube being raised sufficiently above the jet to allow free entrance of air, and a full stream of gas let on, a 'roaring' flame is produced, of which the interior blue cone is pointed, sharply defined, and extends only about half an inch from the top of the tube. A polished platinum surface is not acted upon by this flame, provided it be not brought into contact with the interior cone. In the Bunsen burner, as usually made, the supply of air depends upon the diameter of the tube, the holes at its base being more than sufficient to supply the draught. With the wider tube it is necessary to limit the admission of air by depressing the tube upon the lamp when the force of the gas is diminished. Otherwise the proportion becomes such that an explosive mixture is formed; for this reason it is more convenient to use an arrangement in which the access of air can be regulated by an exterior tube sliding obliquely downward over the air-apertures. The gas jet should be on a level with the top of these apertures, which must be much larger than those of the ordinary Bunsen's burner. On account of the liability to explode and burn at the jet inside, the lamp is not well adapted for ordinary use; but for ignition of crucibles, working of glass, &c., it has proved efficient and practical.

In connection with some sensible remarks upon the before-mentioned use of sand in cleaning platinum crucibles, Erdmann explains in the following way the cause of this grey coating which forms upon platinum crucibles whenever they are ignited in the flame of Bunsen's gas-burner. This coating has given rise to much annoyance and solicitude among chemists. Indeed it has often been asserted that the use of Bunsen's burner is unadvisable in quantitative analysis, since by means of it the weight of platinum crucibles is altered and the crucibles themselves injured. The coating is produced most rapidly when the crucible is placed in the inner cone of the flame, and the more readily in proportion as the pressure under which the gas is burned is higher. Having found it advantageous to maintain, by means of a special small gas-holder, a pressure of four or five inches upon the gas used in his own laboratory, Erdmann observed that the strong gas-flame thus afforded immediately occasioned the formation of a dull ring upon the polished metal placed in the inner flame, this ring being especially conspicuous when the crucible becomes red-hot; it increased continually, so that after long-continued ignition the whole of the bottom of the crucible was found to be grey and with its lustre dimmed.

The ring is caused neither by sulphur, as some have believed, nor by a coating of inorganic matter, but is simply a superficial loosening of the texture of the platinum, in consequence of the strong heat, whence it first of all appears in the hottest part of the flame. In consequence of the serious damage which the gas furnace causes, many chemists now discard gas and ignite platinum crucibles over specially constructed spirit lamps.

In conjunction with Pettenkofer, Erdmann instituted several experiments, which have left but little doubt that the phenomenon depends upon a molecular alteration of the surface of the metal. If a weighed polished crucible be ignited for a long time over Bunsen's lamp, the position of the crucible being changed from time to time, in order that the greatest possible portion of its surface shall be covered with the grey coating, and its weight be then determined anew, it will be found that this has not increased. The coating cannot be removed either by melting with bisulphate of potash or with carbonate of soda. It disappears, however, when the metal is polished with sand; the loss of weight which the crucible undergoes being exceedingly insignificant, a crucible weighing 25 grammes having lost hardly half a milligramme. When the grey coating of the crucible is examined under the microscope, it may be clearly seen that the metal has acquired a rough, almost warty, surface, which disappears when it is polished with sand. Platinum wires, which are frequently ignited in the gas-flame—for example, the triangles which are used to support crucibles—become, as it is known, grey and brittle. Under the microscope they exhibit a multitude of fine longitudinal cracks, which, as the original superficial alteration penetrates deeper, become more open, or, as it were, spongy, until finally the wire breaks.

If such wire is strongly and perseveringly rubbed with sand, the cracks disappear, and the wire becomes smooth and polished; for the grains of sand, acting like burnishers, restore the original tenacity of the metal, very little of its substance being rubbed off meanwhile. The loosening effect of a strong heat upon metals is beautifully exhibited when silver is ignited in the gas-flame, a thick polished sheet of silver immediately becoming dull white when thus heated. Under the microscope the metal appears swollen and warty. Where it has been exposed to the action of the inner flame along its circumference, this warty condition is visible to the naked eye. A stroke with the burnishing stone, however, presses down the loosened particles, and reproduces the original polish. This peculiar condition which the surface of silver assumes when it is ignited, is well known to silversmiths; it cannot be replaced by any etching with acids, and it must be remembered that what is dull white in silver appears grey in platinum.

If each commencement of this loosening is again destroyed, the crucibles will be preserved unaltered, otherwise they must gradually become brittle. Crucibles of the alloy of platinum and iridium are altered like those of platinum, when they are ignited. It is, however, somewhat more difficult to reproduce the original polish of the metal by means of sand, as might be expected, from the greater hardness of the alloy.

The sand used should be well worn. When examined under the microscope no grain of it should exhibit sharp edges or corners; all the angles should be obtuse.

If there are spots on the platinum crucibles which cannot be removed by the sand without wearing away too much of the metal, a little potassium bisulphate is fused in the crucible, the fluid mass shaken about inside, allowed to cool, and the crucible finally boiled with water. There are two ways of cleaning crucibles soiled outside; either the crucible is placed in a larger one, and the interspace filled with potassium bisulphate, which is then heated to fusion, or the crucible is placed on a platinum-wire triangle heated to redness, and then sprinkled over with powdered potassium bisulphate. Instead of the bisulphate, borax may be used. Never forget at last to polish the crucible with sea-sand again.

A remarkably rapid and perfect method of cleaning platinum apparatus consists in gently rubbing upon the dirty metal a small lump of sodium-amalgam. Sodium has the curious property of lending to mercury the power of 'wetting' platinum in so complete a manner that the positive capillarity between platinum and an amalgam containing even only one per cent. of sodium appears to be as great as that between mercury and zinc, with this important difference, however—in the former case, the 'wetted' metal does not suffer the least trace of amalgamation. Even when foreign metals, such as lead, tin, zinc, silver, are purposely added to the sodium-amalgam, the platinum surface suffers no disintegration.

When the amalgam has been rubbed on with a cloth until the whole surface is brilliantly metallic, water is applied which oxidises the sodium and allows the cohesion of the mercury to assert itself. On wiping the mercury off, the platinum surface is left in admirable condition for the burnisher.

When the crucible is clean it is placed upon a clear platinum-wire triangle, ignited, allowed to cool in the desiccator, and weighed. This operation, though not indispensable, is still always advisable, that the weighing of the empty and the filled crucible may be performed under as nearly as possible the same circumstances.

In using platinum crucibles, it must be remembered that certain substances must not be ignited in them. Berzelius says that 'it is improper to ignite in platinum vessels the caustic alkalies or the nitrates of any alkaline base, such as lime, baryta, or strontia, because the affinity of the alkali for platinum oxide causes a very considerable oxidation of the metal; and after the saline matter is removed, the surface of the metal is found to be honeycombed.'

The alkaline sulphides or the alkaline sulphates mixed with charcoal are inadmissible, because the sulphides so formed attack platinum even more energetically than the caustic alkalies; so are metals whose fusing-point is lower than that of platinum, because an alloy would be formed. Gold, silver, and copper may be heated to dull redness in platinum vessels without danger; but fused lead cannot come in contact with platinum without destroying it. A drop of fused lead, tin, zinc, or bismuth, placed on red-hot platinum, always produces a hole. Neither can a phosphide or phosphoric acid mixed with charcoal be ignited in vessels of platinum, because a platinum phosphide is produced, which is an exceedingly brittle compound.

In analyses by the humid method, nitro-hydrochloric acid (*aqua regia*), even when very dilute, must not be allowed to come in contact with platinum, and, as a general rule, liquids containing either free chlorine, bromine, or iodine must not be boiled in platinum capsules.

Silver Crucibles can only be used at temperatures below full redness. They are not affected by caustic alkalies, but must not come in contact with sulphur or be heated over coke, coal, gas, or other fuel containing sulphur.

Cupels.—These are vessels in which the operation termed cupellation is carried on. They must be made of such substances as are not acted upon by certain fused oxides, as those of lead or bismuth, and their texture has to be sufficiently loose to allow of the oxides penetrating their substance readily, and yet be sufficiently strong to bear handling without breaking.

There are several substances of which cupels might be made, which will fulfil all these conditions, but only one is in general use, viz. the ash of burnt bones. This consists principally of calcium phosphate, with a little calcium carbonate and fluoride. Berzelius found that bones of oxen contained 57 parts of calcium phosphate for every 3·8 parts of calcium carbonate, whilst, according to Barros, sheep bones contain 80 parts of calcium phosphate to 19 parts of calcium carbonate. When bones are burnt whole they likewise contain mineral matter derived from the cartilage, such as alkaline sulphates and carbonates. The greater part of the calcium carbonate is likewise converted into caustic lime.

The bones of sheep and horses are best for cupels. In getting rid of the organic matter, it is advisable to boil them repeatedly in water before burning them. This dissolves a great part of the organic matter. If the bones are not rendered quite white by the first ignition, but contain a little carbon, they should be ground up, moulded into shape, and burned again.

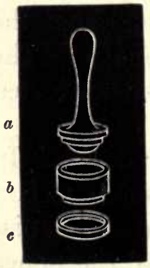
Care should be taken not to heat the bone earth too strongly. In this case the bones will have a smooth, glassy fracture, and will not be sufficiently spongy or absorbent to make good cupels.

When the bones are burnt white throughout, they must be finely ground, sifted, and washed several times with boiling distilled water till all soluble salts are removed. The finest particles of the powdered bone earth will remain longest suspended in the washing waters. This must be allowed to settle separately, and should be reserved for giving a final coating to the surface of the cupels; this coating acts, to a certain extent, like a fine filter, and may be applied to all cupels, although the body of the cupel is made of different materials.

For the body of the cupels, the bone-ash should be about as fine as wheat flour. If too coarse, litharge containing silver will be absorbed into its pores, and will occasion a loss of silver.

Cupels must neither crack nor alter in texture at a white heat. It is very important that they should not contain carbon, and therefore, in making them, the bone earth must not, as sometimes recommended, be mixed with beer, or water containing adhesive substances. Nothing but pure water should be used, and the mixture should be just sufficiently moist to adhere strongly when well pressed, but not so moist as to adhere to the finger or the mould employed to fashion the cupels. The mould (fig. 63) consists of three pieces: one a ring, *b*, having a conical opening; another a pestle, *a*, having a hemispherical end fitting the larger opening of the ring: and the third, *c*, a piece of turned metal, into which *b* fits; *c* serves to form an even bottom to the cupel. In order to mould the cupels, proceed as follows: Place the ring on the lower piece *c*, and fill it with the composition; then place the pestle upon it, and force it down as much as possible: by this means the moistened bone ash will become hardened, and take the

Fig. 63.



form of the pestle; the latter must then be driven as much as possible by repeated blows from a hammer, until quite home. The surface of the cupel may then have sifted over it a little of the very fine levigated bone-ash, and the pestle hammered again on it. It is then to be turned lightly round, so as to smooth the inner surface of the cupel, and withdrawn: the cupel is removed from the mould by a gentle pressure on the narrowest end. When in this state, the cupel must be dried gently by a stove; and lastly, ignited in a muffle, to expel all moisture. It is then ready for use.

There are two or three points to attend to in manufacturing the best cupels. First, the powdered bone-ash must be of a certain degree of fineness; secondly, the paste must be neither too soft nor too dry; and thirdly, the pressure must be made with a certain degree of force. A coarse powder, only slightly moistened and compressed, furnishes cupels which are very porous, break on the least pressure, and, as before mentioned, allow small globules of metal to enter into their pores.

When, on the contrary, the powder is very fine, the paste moist, and compressed strongly, the cupels have much solidity, and are less porous; the fine metal cannot penetrate them, but the operation proceeds very slowly: besides, the assay is likely to become dulled, and incapable of proceeding without a much higher degree of temperature being employed.

Cupels for assaying silver bullion are sometimes made of equal parts of bone-ash and beechwood-ash; and for assaying gold, 2 parts of beechwood-ash and 1 part of bone-ash are used. The hemispherical cavity of both these kinds are coated with the fine levigated powder of bone-ash.

Beechwood-ash is preferred for the manufacture of cupels on account of the larger proportion of phosphoric acid it contains.

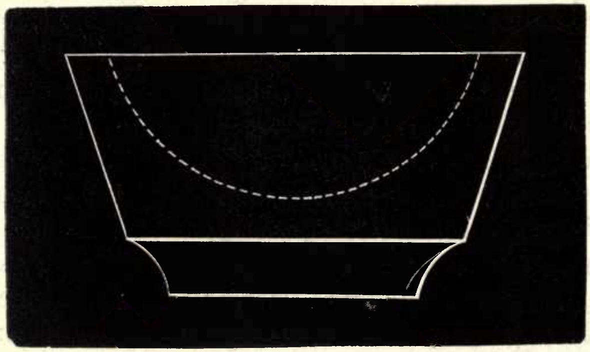
According to Hertwig, beechwood-ash contains in 100 parts:—

Potassium carbonate	11·72
Sodium carbonate	12·37
Potassium sulphate	3·49
Calcium carbonate	49·54
Magnesium carbonate	7·79
Calcium phosphate	3·32
Magnesium „	2·92
Iron „	0·76
Aluminium „	1·51
Manganese „	1·59
Silica	2·46

Scorifiers.—A scorifier (fig. 64) is a vessel made much in the shape of a cupel, but of crucible earth. The proper use both of cupels and scorifiers will be explained under the head of silver-assaying.

Methods of Measuring the Heat of Furnaces.—As much of the accuracy of an assay depends on the temperature at which it is made, and as the temperature required varies with each metal, it is very desirable to possess some means of ascertaining the heat of the furnace more accurately than by the eye. Many persons have devised instruments, called pyrometers, for this purpose; the earliest being those of Mr. Wedgwood and the late Professor Daniel, of King's College.

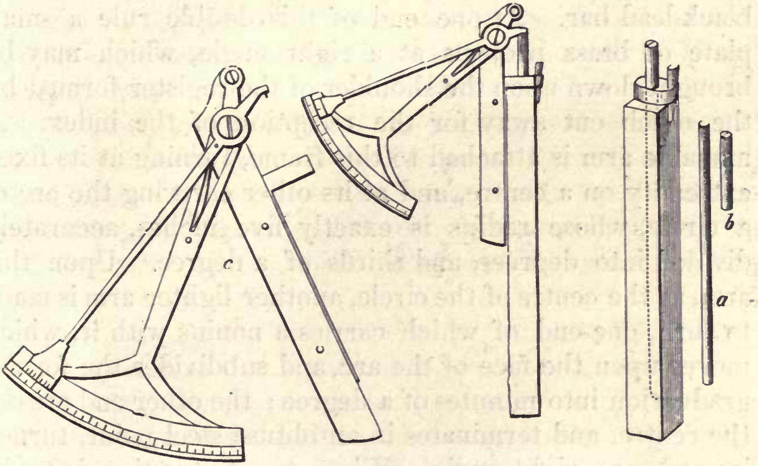
Fig. 64.



We shall not give a description of Wedgwood's pyrometer, as its indications are inaccurate, from the fact that the clay cylinders, whose contraction serves to measure the temperature, will contract as much by the long continuance of a low heat as by the short continuance of a high one. Hence the degrees of heat measured by Wedgwood's pyrometer have been enormously exaggerated. It was long since noticed that it did not produce comparable effects; and this was supposed to proceed wholly from the impossibility of obtaining clay perfectly alike for each experiment.

Daniel's pyrometer is composed of a rod of platinum simply laid in a groove made of refractory clay, and baked in the highest degree of heat. This rod rests at one end on the edge which terminates the groove, and at the other on a lever with two arms, the larger of which forms a needle on a graduated arc of a circle; so that the removal of this needle from its position marks the additional length which the metal acquires by the heat. The following is Daniel's description of his pyrometer: 'It consists of two parts (see fig. 65), which may be distinguished as the register and the scale. The register is a solid bar of black-lead or earthenware highly baked. In this a hole is drilled, into which a bar of any metal, *a*, six inches long, may be dropped, and which will then rest upon its solid end. A cylindrical piece of porcelain, *b*, called the index, is then placed upon the top of the bar, and confined in its place by a ring or strap of platinum passing round the top of the register, which is partly cut away at the top, and tightened

FIG. 65.



by a wedge of porcelain. When such an arrangement is exposed to a high temperature, it is obvious that the expansion of the metallic bar will force the index forward to the amount of the excess of its expansion over that of the black-lead, and that when again cooled it will be left at the point of greatest elongation. What is now required is the measurement of the distance which the index has been thrust forward from its first position, and this, though in any case but small, may be effected with great precision by means of the scale, *c.*' *

This is independent of the register, and consists of two rules of brass accurately joined together at a right angle by their edges, and fitting square upon the two sides of the black-lead bar. At one end of this double rule a small plate of brass projects at a right angle, which may be brought down upon the shoulder of the register formed by the notch cut away for the reception of the index. A movable arm is attached to this frame, turning at its fixed extremity on a centre, and at its other carrying the arc of a circle, whose radius is exactly five inches, accurately divided into degrees, and thirds of a degree. Upon this arm, at the centre of the circle, another lighter arm is made to turn, one end of which carries a nonius with it, which moves upon the face of the arc, and subdivides the former graduation into minutes of a degree; the other end crosses the centre, and terminates in an obtuse steel point, turned inwards at a right angle. When an observation is to be made, a bar of platinum or malleable iron is placed in the cavity of the register; the index is to be pressed down upon it, and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross piece upon the shoulder, and placing the movable arm so that the steel part of the radius may drop into a small cavity made for its reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted which the nonius indicates upon the arc. A similar observation must be made after

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* Daniel's 'Chemical Philosophy,' p. 111.

the register has been exposed to the increased temperature which it is designed to measure, and again cooled, and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of this pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, whose temperature is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of degrees is thus determined, and the value of all other expansions may be considered as proportionate.

By Daniel's pyrometer the melting point of cast iron has been ascertained to be 2,786°, and the highest temperature of a good wind furnace 3,300° Fahrenheit—points which were estimated by Mr. Wedgwood at 17,977° and 21,877° respectively.

The following is a list of the melting points of some of the metals as ascertained by Professor Daniel; and it is obvious that in an assay of each particular metal the temperature employed must exceed by a considerable number of degrees its melting point. The table is, therefore, very useful.

	Fahr.
Tin melts at	422°
Cadmium	442
Bismuth	497
Lead	612
Zinc	773
Silver	1860
Copper	1996
Gold	2016
Cast iron	2786

Cobalt and nickel rather less fusible than iron.

Mr. S. Wilson* has described an ingenious process of measuring high temperatures. He exposes a given weight of platinum or Stourbridge clay to the action of the heat which is to be measured, and then quenches it in a definite weight of water at a certain temperature. Thus, if the piece of platinum weigh 1,000 grains and the water 2,000 grains at 60° F., and should the heated platinum when dropped into the water raise its temperature to 90°, then,

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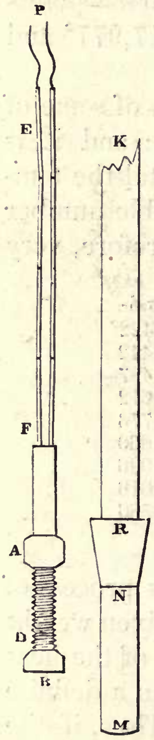
* 'Philosophical Magazine,' ser. iv. vol. iv. p. 157.

$90° - 60° = 30°$; which, multiplied by 2 (because the weight of the water is twice that of the platinum), gives 60°—the temperature to which a weight of water equal to the platinum would have been raised. To convert this into Fahrenheit degrees we must multiply by $31\frac{1}{4}$, which is the specific heat of water as compared with platinum, that of the latter being 1. Therefore, $60° \times 31\frac{1}{4} = 1875°$, which will be the temperature of the furnace.

One or two other methods of measuring high temperatures applicable to special cases may here be mentioned.

Fig. 66.



Mr. C. W. Siemens, C.E., F.R.S., has invented an ingenious pyrometer, the principle of which is, that as the electrical conductivity of platinum, iron, and other metals decreases as they rise in temperature, their increase of resistance to the passage of the current is a measure of the heat to which the metals are subjected.

The principle of construction may be explained by the aid of fig. 66, in which F A B is a tube of pipe-clay, and the length between the projections, A and B, has a screw-shaped spiral groove cut on its outer surface; the length of this part of the tube is about 3 inches. A spiral of fine platinum wire lies in the groove, each turn of the platinum spiral being thus protected from lying in contact with its neighbour by the projecting edges of the groove, by which plan of insulation the current is forced to pass through the whole length of the fine wire. D is a little platinum clam, connected with one pole of the battery, and the position of this clam on the spiral regulates the length of platinum wire through which the current shall pass. By this plan of adjustment, all the pyrometers constructed by Mr. Siemens are made to agree with each other.

At F, the ends of the thin platinum wire are connected with very thick platinum wire, and higher up, near E, where the heat of the furnace is less felt, the thick platinum wires are connected with thick copper wires, shown at P; from E to F, these connecting wires are protected by clay pipes, as shown in the cut.

When this arrangement has to be used, the whole of it is dropped into a thick metal pipe made of iron, copper, or platinum, according to the heat of the furnace to be tested. The lower end of this outer pipe is shown at K M, and when it is used the spiral, A B, lies inside it at N M. At R there is a very thick collar of metal in which the heat accumulates, and this prevents the cooling action of the length K R (most of which does not enter the furnace) from interfering with the accuracy of the indications. The ends of the wires, P, are connected with suitable and very delicate electrical apparatus, by which the increasing electrical resistance of the hot spiral is measured.

A good plan for comparing the temperatures of two furnaces is to prepare alloys of platinum and gold, containing definite quantities, say, 5, 10, 15, 20 per cent. &c., of gold. These fuse at intermediate temperatures between gold and platinum. By placing small angular chips of these alloys separately in muffles, and noticing which are melted, which softened only, and which resist the action of the heat, an idea of the power of the furnace is obtained. In this way the amount of heat required to perform any operation may be registered for future reference, by simply recording that it was sufficient just to melt, say, a 20 gold 80 platinum alloy.

CHAPTER V.

FUEL: ITS ASSAY AND ANALYSIS.

Before treating of the assay of metals and metalliferous ores, it is advisable to devote some space to the important subject of fuel. The substances employed as fuel, although all of vegetable origin, are derived either from the vegetable kingdom (wood), or from the mineral kingdom (peat, brown coal, coal, anthracite). These natural fuels can be converted into artificial fuels by heating them more or less out of contact with the air (charcoal, turf-charcoal, coke).

The essential elements of combustible matters are carbon, oxygen, and hydrogen; nitrogen being present sometimes, but only in small proportions. These constitute the organic part; various salts and silica constitute the inorganic part, or ash. The valuable constituents of fuel, on which its calorific and reducing powers depend, are the carbon and hydrogen, and it is upon the combustion or union of these elements with oxygen to form carbonic acid and water, that the heating effect of the fuel depends.

The more oxygen a fuel contains, the less carbon and combustible gases it will yield, and the more hydrogen, the more combustible gases.

The proportion of hydrogen to oxygen in	wood .	is	1 : 7
” ” ”	turf .	”	1 : 6
” ” ”	fossil-wood	”	1 : 4
” ” ”	coal .	”	1 : 2–3
” ” ”	anthracite	”	1 : 1

The more oxygen, the less carbon the fuel contains, thus:—

Anthracite	contains	about	90	per cent.	carbon
Coal	”	”	80	”	”
Brown coal	”	”	70	”	”
Fossil-wood and turf		”	60	”	”
Wood	”	”	50	”	”

The more carbon a fuel contains, the greater heat it produces, and the more difficult it is to ignite.

The greater the amount of hydrogen in a fuel, the more inflammable it will be, and the larger flame it gives, the hydrogen being evolved below a red heat. But the more carbon present, the less flame. These differences are shown in a blazing fire and a glowing fire. In a flame the hottest part is at the periphery, whilst in a glowing fire the greatest heat is in the immediate contact of the burning surface.

An elementary analysis of coal teaches little with regard to the nature or practical value of the combustible. A proximate analysis, on the contrary, enables us to learn something in regard to the real nature of the coal. The moisture and ash are not only diluents of the fuel, but are in themselves obstacles to its effectiveness; the vaporisation of the moisture causes a serious loss of heat, whilst the ashes, by hindering complete combustion and by the heat they contain when dropped through the grate, constitute another loss. By furthermore determining the total amount of volatile matter we learn both the percentage of coke in the fuel and the amount of carbon (fixed combustible) and bitumen (volatile combustible matter). Although neither of these two products can be considered as simple chemical compounds, it is nevertheless of the utmost practical importance to know these two quantities, because of the great value of coke and gas in manufactures.

The assay of fuel comprises the following examinations:

1. The examination of the external appearance of the fuel, its porosity or compactness, its fracture, the size and shape of the pieces composing it.
2. Determination of the adhering water.
3. Determination of the specific gravity.
4. Determination of the absolute heating power.
5. Determination of the specific heating power.
6. Determination of the pyrometric heating power.
7. Determination of the volatile products of carbonisation.

8. Examination of the coke or charcoal left behind on carbonisation, both with regard to quality and quantity.

9. Determination of the amount of ash, and its composition.

10. Determination of the amount of sulphur.

11. Examination of any other peculiarity which may be noticed during the burning or carbonisation of the fuel.

1. **External Appearance of the Fuel, its Porosity, Compactness, Fracture, Size, and Shape of Pieces.**—From the outward appearance of a fuel, its cleavage, and an examination of the embedded earthy matter, iron pyrites, gypsum, &c., its applicability to any special purpose may be judged. Its degree of inflammability, together with the pressure of blast which it will bear in the furnace, partly depend on the more or less compactness of the fuel. The amount of loss which it will suffer in transport depends upon its friability. Playfair and De la Beche * determined the amount of this loss in coal by rotating in a barrel different qualities of coal for the same time. The powder produced was separated and weighed, and in this way the friability or cohesion of a fuel could be expressed in percentages. Schrötter † made the same experiments with brown coal.

The size and form of the pieces composing the fuel is important, as on this depends the space occupied in its stowage—an important point for steam-vessels. This space cannot be calculated from its specific gravity, but must be ascertained by direct measurement. The space occupied will be smallest when the form of the lumps is cubical. Playfair and De la Beche have also investigated this subject.

2. **Determination of the Adhering Water.**—The water contained in a fuel exerts great influence on its heating power. It not only increases its bulk, but it acts injuriously by abstracting a certain quantity of heat required for its evaporation, and it also causes imperfect combus-

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* Dingl. cx. 212, 262; cxiv. 346. Liebig's 'Jahresber.,' 1847–1848, p. 1117; 1849, p. 708.

† Wien. Akad. Ber. 1849, Nov. and Dec. p. 240. Liebig's 'Jahresber.' 1849, p. 709.

tion. For this reason, wood, turf, and brown coal never give so high a temperature as coal, anthracite, and coke.

The determination of the adhering water is effected by drying a certain weight of the pounded fuel in a water-bath at 212° F., or in an air-bath at 220°. It may also be ascertained by placing a certain weight of the powdered fuel in a glass tube, heating to 212°, and passing over it air dried by means of chloride of calcium, till the fuel no longer loses weight. The amount of water which the dried fuel will absorb from the atmosphere in twenty-four hours should also be determined, in order to ascertain its hygroscopic qualities.

3. **Determination of the Specific Gravity.**—The specific gravity of a fuel depends on its density and the amount of ash, and it appears also to be in proportion to its greater or less inflammability. Of two equal volumes of carbonised fuel, the one will produce the greatest heating effect which has the greatest specific gravity, provided the density is not produced by mineral constituents.

The determination of the specific gravity is difficult, and sometimes uncertain, owing to the cleavage of the fuel, and the entanglement of air in its pores. The best way of obviating this difficulty is as follows:—

Coarse fragments, freed by means of a sieve from all small particles, and averaging 1-10th c.c. in volume, are introduced into a fifty-gramme flask provided with a thermometer stopper. The constants for this flask for temperatures varying from 50° to 80° F. are previously carefully determined.

The given sp. gr. corresponds to the coal perfectly soaked, so that all its pores are filled with water. That requires, on the average, 12 hours, permitting two determinations per day, one in the morning, another in the evening.

That this precaution is important may be seen from the following example: 2·760 grms. coal gave the sp. gr. 1·309 at 64° F., immediately after filling the flask with water: after about 12 hours' soaking, the sp. gr. had increased to 1·328, for the same temperature. According to this latter determination, a cubic foot of this coal would weigh 82·76 lbs.; according to the former, only 81·58, or 1·18 lbs. less. This shows a considerable degree of porosity of the coal, and indicates the absurdity of giving the weight in pounds of a cubic foot of coal with four decimals, although no statement in regard to temperature or time of weighing is made.

4. **Determination of the Absolute Heating Power.**—The value of a fuel for any purpose depends chiefly on its price and the quantity required for that purpose. The *quantity* required depends on the heating power possessed by a certain *weight* of fuel (its *absolute* heating power) or that possessed by a certain *volume* (its *specific* heating power).

The less oxygen, ash, and water the fuel contains, the greater its heating power will be, and this will also increase in proportion to the carbon and hydrogen present.

Whether the combustion is effected quickly or slowly, the amount of heat produced will be the same, but the degree of temperature attained will be very difficult. This latter constitutes the *pyrometric* heating power.

The determination of the absolute heating power of a fuel may be effected—

a. By heating a definite quantity of water from 32° F. to 212°;

b. By ascertaining how much fuel is required to melt a known weight of ice;

c. By ascertaining how much water may be evaporated by 1 lb. of different kinds of fuel;

d. By ascertaining how much the temperature of a room increases by burning a certain weight of a fuel in a stove.

e. By ascertaining the elementary composition of the fuel, and calculating how much oxygen will be required to convert the carbon and hydrogen into carbonic acid and water; the quantity of heat produced will be in proportion to the amount of oxygen consumed.

f. By Berthier's method.

g. By Dr. Ure's method.

According to Berthier, the most convenient method for ascertaining the comparative calorific power of any combustible matter is by means of litharge. He says: It has been proved by the experiments of many philosophers that the quantities of heat emitted by combustible substances are exactly proportioned to the amounts of oxygen required for their complete combustion. Whence, after the elementary constitution of any combustible is known, its calorific power is easily determined by calculation. For instance, it is only necessary to ascertain the quantity of oxygen absorbed in the conversion of all its carbon into carbonic acid, and all its hydrogen into water, and compare that quantity with that which is consumed in burning a fuel whose calorific power is well ascertained. Such a fuel is pure charcoal.

By adopting the principle just pointed out, it may be conceived that, without knowing the composition of a fuel, its heating power may be ascertained by determining the amount of oxygen it absorbs in burning. This can be done in a very simple and expeditious manner, if not exactly, at least with sufficient exactitude to afford very useful results in practice. It is as follows: many metallic oxides are reduced with such facility that when heated with a combustible body, the latter burns completely, without any of its elements escaping the action of the oxygen of the oxide, if the operation be suitably performed. The composition of the oxide being well known, if the weight of the part reduced to the metallic state be taken, the quantity of oxygen employed in the combustion can be ascertained. In order to collect the metal and separate it from the non-reduced mass, it must be fusible as well as its oxide. Litharge fulfils these conditions, and experiment has proved that it completely burns the greater part of all ordinary fuels; the only exceptions are some very bituminous matters containing a large proportion of volatile elements, a portion of which escapes before the temperature is sufficiently high to allow the reduction to take place. The experiment is made as follows: 10 grains of the finely powdered or otherwise divided fuel is mixed with about 400 grains of litharge. The mixture is carefully placed in an earthen crucible, and covered with 200 grains more litharge. The crucible is then placed in the fire and gradually heated. When the fusion is perfect, the heat is urged for about ten minutes, in order that all the lead may collect into a single button. The crucible is then taken from the fire, cooled, broken, and the button of lead weighed. Sometimes the button is livid, leafy, and only slightly ductile; in which case it has absorbed a little litharge. This can be partially prevented by fusing slowly, and adding a little borax.

Two assays, at least, ought to be made, and those results which differ more than a grain or two ought not to be relied on. The purer the litharge, the better the result; it ought to contain as little minium as possible. It is an excellent plan to mix up the litharge of commerce with one or two thousandths of its weight of charcoal, and fuse the whole in a pot; when cold, pulverise the litharge, which will now be deprived of minium.

Pure carbon produces, with pure litharge, thirty-four times its weight of lead, whilst hydrogen gives 103·7 times its weight of lead; that is to say, a little more than three times as much as carbon. We can, therefore, from these data, find the equivalent of any fuel, either in carbon or hydrogen.

When a fuel contains volatile matters, the quantity can be ascertained, as before pointed out, by ignition in a close tube or crucible. If, further, we ascertain the proportion of lead it gives with litharge, it is easy to calculate the equivalent in carbon of the volatile matters, and, in consequence, to ascertain its calorific value.

Supposing that a substance gives by distillation C parts of coke, or carbon, having deducted the weight of the ash and of volatile substances, and that it produces P parts of lead with litharge. The quantity C of carbon would give $34 \times C$ of lead; the quantity of volatile matter would give but $P - 34 \times C$; it would be equivalent to $\frac{P - 34 \times C}{34}$ of carbon: whence it follows that the quantity of heat developed by the charcoal, the volatile matter, and the unaltered combustible, will be to each other as the numbers $34 \times C$, $P - 34 \times C$, and P.

Dr. Ure[*] says, speaking of the above method of assay, 'On subjecting this theory to the touchstone of experiment, I have found it to be entirely fallacious. Having mixed very intimately 10 grains of recently calcined charcoal with 1000 parts of litharge, both in fine powder, I placed the mixture in a crucible, which was so carefully covered as to be protected from all fuliginous fumes, and exposed it to distinct ignition.

'No less than 603 grains of lead were obtained, whereas, by Berthier's rule, only 340 or 346·6 were possible. On igniting a mixture of 10 grains of pulverised anthracite with 500 grains of pure litharge previously fused and pulverised, I obtained 380 grains of metallic lead. In a second experiment, with the same anthracite and the same litharge, I obtained 450 grains of lead; and in a third, only 350 grains. It is therefore obvious that this method of Berthier's is altogether nugatory for ascertaining the quantity of carbon in coals, and is worse than useless in judging of the calorific qualities of different kinds of fuel.'

This discrepancy in the results obtained by Dr. Ure is very perplexing, and does not at all accord with Berthier's experience, as shown by his experiments, or by the author's on the subject. The latter never had a difference of more than 50 grains, and in general only two or three, which latter result is satisfactory. The only precaution he found necessary was to heat very gradually until the mixture was fully fused, and then to increase the fire to bright redness for a few minutes.

Further experiments have been made by the author on this subject, and he has succeeded most perfectly in estimating the value of a fuel. With the litharge of commerce, which contains much minium, the process is never exact: results have been obtained differing as much as 40 or 50 grains when the litharge employed had not been purified, and to purify it completely is a troublesome

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[*] 'Supplement to the Dictionary of Arts, Mines, and Manufactures.'

process. This difficulty may be completely obviated, however, by substituting for litharge, white lead, using for each 10 grains of fuel 700 grains of white lead, which are well mixed with it, and 300 grains of pure white lead to cover the mixture.

When the whole is heated, the carbonate of lead decomposes, forming pure lead oxide, which is then reduced, as in the former case. By this process the results correspond to 1 grain in the quantity of lead produced from a given sample of fuel. Of course great care must be taken that the white lead is genuine.

Commercial samples are frequently adulterated with lead sulphate and barium sulphate, lead oxychloride, zinc oxide, &c. This is a serious drawback to this otherwise excellent modification.

The following is the method of ascertaining the calorific power of fuel, employed by Dr. Ure, and described in his 'Supplement.'

'The following calorimeter, founded upon the same principle as that of Count Rumford, but with certain improvements, may be considered as an equally correct instrument for measuring heat with any of the preceding (Lavoisier's, Meyers', and others), but one of much more general application, since it can determine the quantity of heat disengaged in combustion, as well as the latent heat of steam and other vapours.

'It consists of a large copper bath capable of holding 100 gallons of water. It is traversed four times backwards and forwards in four different vessels, by a zigzag horizontal flue or flat pipe, nine inches broad and one deep, ending below in a round pipe, which passes through the bottom of the bath and receives there into it the top of a small black-lead furnace, the innermost crucible of which contains the fuel. It is surrounded at the distance of an inch by a second crucible, which is inclosed at the same time by the sides of the outermost furnace, the stratum of stagnant air between the crucibles serving to prevent the heat being dissipated into the atmosphere by the body of the furnace. A pipe from a double pair of bellows enters the ashpit of the furnace at one side, and supplies a steady but gentle draught to carry on the combustion kindled at first by half an ounce of burning charcoal. So completely is the heat which is disengaged by the burning fuel absorbed by the water in the bath, that the air discharged at the top pipe is generally of the same temperature as the atmosphere. The vessel is made of copper, weighing 2 lbs. per square foot; it is 5½ feet long, 1½ wide, 2 deep, with a bottom 5½ feet long, and 1¾ broad upon an average. Including the zigzag tin-plate flue, and a rim of wrought iron, it weighs altogether 85 lbs. Since the specific heat of copper is to that of water as 94 to 1,000, the specific heat of the vessel is equal to that of 8 lbs. of water; for which, therefore, the exact correction is made by leaving 8 lbs. of water out of the 600 or 1,000 lbs. used in the experiment.

'In the experiments made with former calorimeters of this kind, the combustion was maintained by a current or draught of a chimney open at bottom, which carried off at the top orifice of the flue a variable quantity of heat, very difficult to estimate.

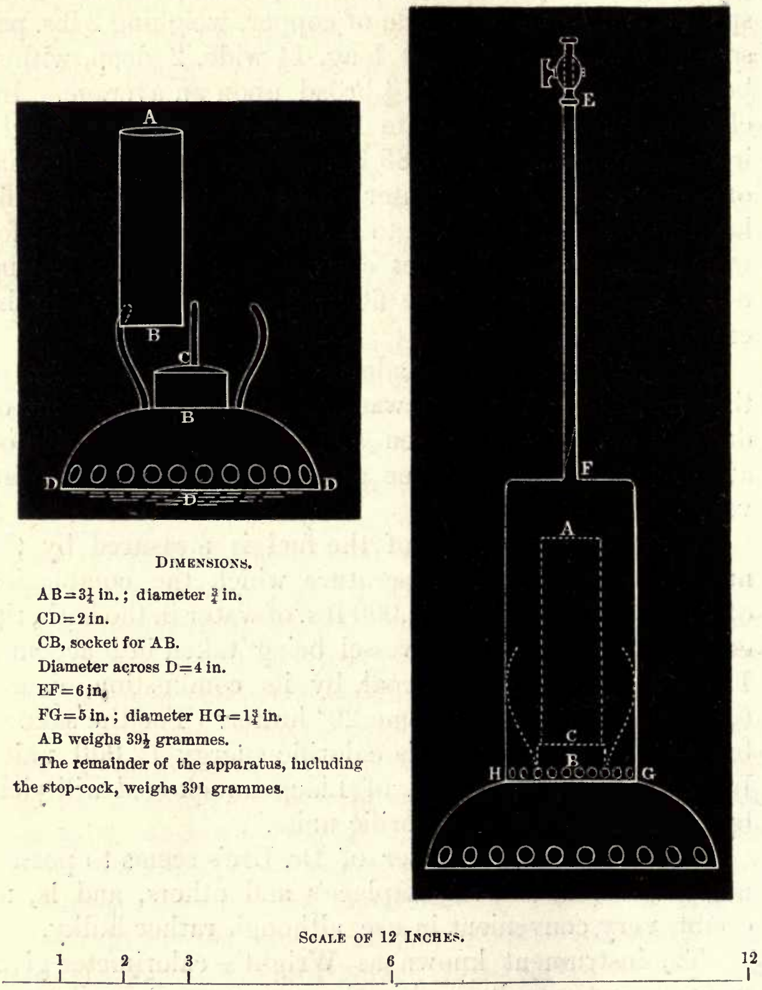
'The heating power of the fuel is measured by the number of degrees of temperature which the combustion of 1 lb. of it raises 600 or 1,000 lbs. of water in the bath, the copper substance of the vessel being taken into account. 1 lb. of dry wood charcoal, by its combustion, causes 6,000 lbs. of water to become 20° hotter. For the sake of brevity, we shall call this calorific energy 12,000 units. In like circumstance, 1 lb. of Llangennock coal will yield by combustion 11,500 calorific units.'

This form of calorimeter of Dr. Ure's seems to possess many advantages over Laplace's and others, and is, no doubt, very convenient in use, although rather bulky.

The instrument known as Wright's calorimeter gives very accurate results, and is the one most generally used now in experiments on the heating power of fuel, in all but the most refined investigations. It is shown in the accompanying figure (fig. 67).

The copper cylinder A B is filled with a mixture of 20 grains of the combustible, and 240 of the deflagrating compound, which is composed of three parts of potassium chlorate, and one of potassium nitrate. A little piece of cotton soaked in potassium chlorate is placed partly in the mixture, the other end projecting above the top of the cylinder; this is ignited, quickly covered with the bell-shaped part of the apparatus, and immersed in a measured quantity of water. As constructed, the whole metallic

FIG. 67.



DIMENSIONS.

AB=$3\frac{1}{4}$ in.; diameter $\frac{3}{4}$ in.
CD=2 in.
CB, socket for AB.
Diameter across D=4 in.
EF=6 in.
FG=5 in.; diameter HG=$1\frac{3}{4}$ in.
AB weighs $39\frac{1}{2}$ grammes.
The remainder of the apparatus, including the stop-cock, weighs 391 grammes.

SCALE OF 12 INCHES.

apparatus weighs 6,642·7 grains, and with this weight 290·1 grains of water are used. The temperature is recorded before and after making the experiment. During the deflagration the stop-cock is closed; it is, however, opened before taking the temperature the second time. A tenth of the temperature that the water is raised by the combustion is added for errors that are incidental to the use of the instrument.

If the instrument is made of the weight above given, the result is obtained by a very simple calculation. Each Fahrenheit degree by which the temperature of the water has been augmented corresponds to a pound of water converted into steam.

EXAMPLE.

Fahr.
Temp. of water before making experiment = 56°
„ „ after the combustion . = 65
9° + $\frac{1}{10}$th
„ produced by the combustion = 9·1

20 grains of the coal will convert into steam (maximum effect) 9·1 lbs. of water

$$\frac{9{\cdot}1 \times 7000 \times 2240}{20} = \text{Effect of a ton.}$$

5. **DETERMINATION OF THE SPECIFIC HEATING POWER.**—This represents the heat produced from a certain volume of fuel. It may be ascertained by multiplying the absolute heating power by the specific gravity.

6. **DETERMINATION OF THE PYROMETRIC HEATING POWER.**—By pyrometric heating power is meant the degree of temperature which may be obtained by completely burning the fuel. This heating power not only depends upon the composition of the fuel, but chiefly on the time required for its combustion, and this again depends on the looseness and inflammability of the fuel. The absolute heating power of hydrogen is greater than that of carbon, but with regard to the pyrometric heating power it will be found that the reverse is the case.

Carbon burned in contact with the air to carbonic acid will produce a heat of 2,558° C.; if burned to carbonic oxide it only produces 1,310°; hydrogen burning to water will produce a heat of 2,080°. From this we learn that fuel rich in carbon, such as anthracite, coal, and coke, will produce a greater pyrometric effect than fuel rich in hydrogen, as wood, &c.

Density is an essential quality of fuel required to produce great pyrometric effect. This is proved in the following way.

When atmospheric air first acts on the carbon contained in fuel, carbonic acid is formed, and the temperature rises to a certain degree, but on passing over glowing coal, carbonic acid becomes converted into carbonic oxide, and this causes a portion of the heat at first produced to become latent. This conversion of carbonic acid into carbonic oxide is more easy and complete as the fuel used is more inflammable; and as a greater quantity of heat is thereby rendered latent, it follows that the heating power of such a fuel is inferior. This accords with general experience; for it is well known that coke is able to produce a greater heat than charcoal.

Several good methods for determining pyrometric heating power were given in the last chapter.

7. **Determination of the Volatile Products of Carbonisation.**—The amount of volatile matter yielded on carbonising a fuel depends partly on the composition of the fuel, and partly on the temperature employed. If a fuel rich in oxygen and hydrogen is quickly heated, it will yield the greatest amount of volatile products. These are partly liquid (tar, naphtha, and acetic or ammoniacal water), and partly gaseous (carbonic oxide, carbonic acid, and light and heavy carburetted hydrogen). The more oxygen a fuel contains, the more carbonic acid and carbonic oxide it will produce; the more hydrogen it contains, the more illuminating gas it yields. The applicability of a sample of coal to the production of illuminating gas depends on these conditions.

Coal distilled at a low temperature yields much tar and comparatively little gas, and, when a very high temperature has been used, less tar and more gas is produced, but the great heat will have reacted on the gas and injured its illuminating qualities. If the coal contains pyrites, the gas will contain sulphur compounds. The amount of water produced is generally larger than that of the tar.

In order to estimate the amount of volatile matter given off from any particular sample of coal, proceed in the following manner: Place a given weight, say 200 grains, of the coal in an iron tube, closed at one end, to the other end of which adapt, by means of a cork, a glass or other tube, which must be conducted into an inverted jar full of water standing in the pneumatic trough. Raise the temperature very gradually to redness, and continue the heat until no more gas is given off, then ascertain its quantity in cubic inches, with due correction for temperature and pressure.

8. **Examination of the Coke or Charcoal left behind on Carbonisation.**—The amount of coke or charcoal yielded by a sample of fuel is found by the last operation. This residue is the amount of coke which that particular sample of coal produces; and its weight, divided by two, gives the percentage of coke.

The process of coking, charring, or carbonising fuel, whilst it drives off some of the valuable hydrocarbon constituents, also gets rid of all the aqueous elements. And therefore, the coke or charcoal which is left behind has its value greatly increased when high temperatures are required, although, from the absence of flame-yielding constituents, it is much more difficult to ignite.

The degree of inflammability of coke or charcoal is relatively the same as that of the raw fuel from which they were produced. The more inflammable a fuel has been, the more inflammable will be the coke or charcoal produced from it.

The temperature employed in the carbonisation, as has been already explained, exerts great influence on the yield of coke.

If the fuel contains iron pyrites, part of the sulphur goes off in the volatile portion, but from $\frac{1}{4}$ to $\frac{1}{2}$ is retained in the form of FeS.

9. **Determination of the Amount of Ash.**—In order to ascertain the amount of ash: Fully ignite about 50 grains

of coal in a platinum capsule, allowing the air to have free access all the time until nothing but ash is left. Its amount may then be ascertained by weighing: good fuel should contain little ash. It may vary from 1 to 10 per cent., but if it exceeds 5 per cent. it becomes deleterious. The chemical composition of the ash also influences the quality of the fuel to some extent.

10. **Determination of the Amount of Sulphur.**—This is an important operation in the assay, as a coal containing sulphur cannot be employed for particular operations, and, indeed, those which contain much sulphur ought only to be used for the commonest purposes. This assay is most important to ironmasters as well as to steamboat and other companies, who consume fuel under steam-boilers; and the coal they purchase should always be subjected to this particular test, as sulphur has a corroding and destroying action on iron and copper. Where sulphurous coals are continually burnt under boilers, the metal of the latter becomes deteriorated, and the boiler is rapidly rendered useless. Sulphur exists in coal in the form of iron pyrites; this can generally be detected by its brassy colour. Some coals and lignites also contain calcium sulphate, and in rare cases barium sulphate.

The process for the determination of the amount of sulphur in coal is not difficult. 1 part of the coal is to be finely pulverised, and then mixed with 7 or 8 parts of potassium nitrate, 16 parts of common salt, and four parts of potassium carbonate, all of which must be perfectly pure; the mixture is then placed in a platinum crucible and gently heated. At a certain temperature, the whole ignites and burns quietly. The heat is then increased until the mass is fused: the operation is finished when the mass is white. It must, when cold, be dissolved in water, the solution slightly acidulated by means of hydrochloric acid, and barium chloride added to it as long as a white precipitate forms. This precipitate is barium sulphate, which must be collected on a filter, washed, dried, ignited, the filter burnt away, and the remaining barium sulphate weighed: every 116 parts of it indicate 16 of sulphur.

Dr. Price has drawn attention to a source of error which has hitherto escaped notice in the estimation of sulphur, where fusion of the substance with nitre is the process employed. This author has found that unless great care be taken to prevent the fused mass passing over to the outside of the vessel, and so coming in contact with the flame, or products of combustion, an appreciable and, in some cases, serious error will arise, owing to the sulphuric acid produced from the sulphurous acid in the flame—a product of the oxidation of the sulphide of carbon contained in the gas—combining with the potash of the fused salt. Several experiments have been made to ascertain the amount of error that may be occasioned from the above cause. In one instance, the flame issuing from a Bunsen's burner was made to strike against a little fused nitre on the under-side of a small platinum dish, when, in three quarters of an hour, as much sulphuric acid was obtained as is equivalent to 12 milligrammes of sulphur. As a check on these experiments, nitre was fused by the flame of the spirit lamp, when, as was to be anticipated, not a trace of sulphuric acid could be detected upon the addition of a barium-salt to the aqueous solution of this fused mass, rendered acid by hydrochloric acid. In determinations of sulphur in coke or coal, great care should, therefore, be taken to prevent any of the fused saline contents of the crucible from getting on to the outside. In fusing pig-iron with nitre, a process recommended by some for the estimation of the sulphur it contains, the mass, especially if the iron be rich in manganese, invariably creeps over to the outer wall of the crucible; and it is, therefore, impossible to obtain correct results when the operation is conducted over the gas flame. The assayist should for these reasons always employ a spirit flame in preference to gas in sulphur determinations.

Teikichi Makamura recommends the following procedure: 3 or 4 parts of the mixed alkaline carbonates, or of sodium carbonate, are intimately mixed with one part of coal in very fine powder in a large platinum dish. The mixture is heated at first very gently, a spirit lamp being used instead of a Bunsen, to prevent possible absorption of sulphur; the heat is then raised slowly without attaining that of visible redness, until the surface becomes only faintly grey. No smoke or odorous gases should escape during the whole of the oxidation. The temperature is now raised to a faintly red heat for sixty minutes, at the end of which time the mass is perfectly white or reddish if iron be present. The mass is not to be stirred during the ignition. The residue is heated with water, filtered, and the sulphates determined in the ordinary way.

11. **Examination of other Peculiarities of Fuel.**—Besides the above-named examinations, the assayist should notice the degree of inflammability of the fuel, and whether any particular smell is evolved during combustion; whether the coal is good for coking purposes; whether it burns with a large smoky flame or a luminous flame; whether it burns quietly or with decrepitation; and whether the ash is dusty or fusible, and likely to accumulate and clog up the grate-bars.

Calculation of Results.—It may be sufficient here to state that, beside the percentage composition of the coal, it is proper to reduce the composition to the combustible =100, in order to obtain a proper comparative estimate of the character of the fuel itself (in regard to the proportion of bitumen and carbon), and of the amount and quality of the impurities (ash and moisture). It has also been shown that, for considerable areas of the coal-field, the sum of the constituents on the scale of combustible=100 is the proper calorific equivalent, and that the percentage of the combustible in the fuel gives a proper estimate of its value.

Assay of Coal before the Blowpipe.—The blowpipe method is well adapted to the assaying of coal. Not only does the portableness of the apparatus make it very convenient for use away from home, wherever the balance can be set up; but its use at home is quite as satisfactory on the score of exactness as the assay with the muffle or retort, or large platinum crucible and large balance. Mr.

B. S. Lyman gives the following directions for carrying out this assay:—

Besides the ordinary pieces of the blowpipe apparatus, as made at Freiburg, all that needs to be made expressly for the coal assay is a small covered platinum crucible of the same size and shape as the clay crucibles of that apparatus; and there must be a little ring for the crucible to stand on, of German silver, about three-eighths of an inch across and half that in height. Such a crucible cover and ring weigh about 2½ grammes more than the ordinary metallic cup that rests on the pan of the balance; the crucible and ring with the cover weigh less than 2 grammes more than the cup. If it be desired to determine the amount of hygroscopic moisture in the coal, a small drying bath must be made too; but the hygroscopic water in ordinarily well-dried coals (not brown coals) is of little importance.

The size of the crucible allows the coking of 200 to 600 or more milligrammes of coal, according to the dryness of the coal and the extent of its swelling up when heated; and as the blowpipe balance weighs within 1-10th of a milligramme, it is easy to weigh within much less than 1-10th of one per cent. of the amount of coal assayed, much nearer, in fact, than the exactness of the coke assay in other respects. On this point, indeed, the blowpipe assay is quite as good as the assay with the larger balance, especially the muffle assay, where the coal must be brushed into a clay receptacle after weighing, and the coke or ashes brushed off from it before weighing; while here the crucible is weighed each time without removal of its contents, and without danger, therefore, of losing anything or adding any dust. It may be objected that the smallness of the amount of coal that can be assayed with the blowpipe makes it a less trustworthy indicator of the general composition of the coal than a larger assay; but the size of the lumps or powder assayed may be made finer accordingly, so that, when mixed up, an equally just sample of the whole mass would be got for the small assay as for the large.

Anyone who has had a little experience, both in the use of the blowpipe and in the ordinary muffle assay of coal, will scarcely need any further teaching for the coal assay with the blowpipe. For others it is worth while to say that the coal may be assayed either in a fine powder or in little lumps, and either with a slowly increasing or with a quickly increasing heat. A quick heat will give less coke by several per cents., but will often make a dry coal cake together that would not cake with a slow heat. The cover of the crucible should be left open a little, for the easy escape of the gas, but covered enough to prevent any flying off of solid material. The heat should increase to redness, and as soon as the escaping gas stops burning the heat should be stopped. As some coals part with their gas more quickly than others, of course no definite time can be fixed for heating all coals ; but the burning of the gas is a good enough sign. Care should be taken not to let the coke take up moisture from the air before weighing, as it will quickly do if it has a chance. Of course, owing to the different effects of quick or slow heating, a certain uniformity of result, even with perfectly uniform samples of coal, can only be got without error by practice and by mechanical skill, by reproducing with nicety the same conditions in successive assays.

After the coke has been weighed, it can be heated again with very free access of air, say with the crucible tilted to one side, and the cover off, until everything is thoroughly burnt to ashes ; and these should be re-heated until no change for the less is made in the weight. With free burning, soft (semibituminous) coals this burning to ashes is very slow, so that it is very fatiguing or even impossible to carry it out with a blowpipe ; but in that case the crucible may be heated over a Bunsen gas-burner or an alcohol lamp, and left to glow for hour after hour. The coking is far more conveniently done in the same way than by blowing with the mouth.

As an illustration of the degree of accuracy which this method may be expected to give, the author adduces a pair of blowpipe assays, made five years ago, of some West

Virginia asphaltum, that seemed itself to be much more uniform in composition than coal from different benches in one bed is apt to be :—

	Volatile Matter	Coke	Ashes
No. 1 . .	47·29 per cent.	52·71 per cent.	1·65 per cent.
No. 2 . .	46·93 „	53·07 „	1·81 „
Mean . .	47·11 „	52·89 „	1·73 „

Valuation of Coal for the Production of Illuminating Gas.—Take 100 grs. of the coal in small lumps, so that they may be readily introduced into a rather wide combustion-tube. This is drawn out at its open end (after the coal has been put in) so as to form a narrow tube, which is to be bent at right angles; this narrower open end is to be placed in a wider glass tube, fitted tight into a cork fastened into the neck of a somewhat wide-mouthed bottle serving as tar vessel (hydraulic main of the gasworks). The cork alluded to is perforated with another opening, wherein is fixed a glass tube, bent at right angles for conveying the gas first through a chloride of calcium tube, next through Liebig's potash bulbs containing a solution of caustic potash, having lead oxide dissolved in it. Next follows another tube, partly filled with dry caustic potash, and partly with calcium chloride; from this last tube a gas-delivery tube leads to a graduated glass jar standing over a pneumatic trough, and acting as gas-holder. Before the ignition of the tube containing the coal is proceeded with, all the portions of the apparatus are carefully weighed and next joined by means of india-rubber tubing. After the combustion is finished, which should be carefully conducted, so as to prevent the bursting or blowing out of the tube, the different pieces of the apparatus are disconnected and weighed again. The combustion-tube has to be weighed with the coal after it has been drawn out at its open end, and with the coke after the end of the combustion when it is again cold; and for that reason care is required in managing it. We thus get the quantity of tar, ammoniacal water, carbonic acid, and sulphuretted hydrogen (as lead sulphide); and the gas is measured by immersing the jar in water, causing it to be at the same level inside and out. Empty the Liebig's bulbs into a beaker, and separate the lead sulphide by filtration, wash carefully, dry at 100° C., and weigh. From the lead sulphide the sulphuretted hydrogen present is calculated. This process, devised by the late Dr. T. Richardson, of Newcastle-on-Tyne, was found by him to yield very trustworthy results, so as to be suitable for stating what quantity of gas a ton of coal thus analysed would yield.

CHAPTER VI.

REDUCING AND OXIDISING AGENTS—FLUXES, ETC.

In some assay operations in the dry way, bodies are heated in suitable vessels *per se*; but it is more often necessary to add to the bodies submitted to assay other substances, which are varied according to the nature of the change to be effected. These substances may be divided into five classes: I. reducing agents; II. oxidising agents; III. desulphurising agents; IV. sulphurising agents; and lastly, V. fluxes properly so called.

I. REDUCING AGENTS.

The substances belonging to this class have the power of removing oxygen from those bodies with which it may be combined. In assaying, the substance under examination is generally fully oxidised either naturally or artificially before reduction is required to be effected. The most common reducing agents are as follows:—

1. Hydrogen gas.
2. Carbon.
3. The fatty oils, tallow, pitch, and resins.
4. Sugar, starch, and gum.
5. Tartaric acid.
6. Oxalic acid.
7. Metallic iron and lead.

Hydrogen Gas.—The most common method of preparing this gas consists in dissolving zinc in dilute sulphuric acid. But as this plan gives the gas in the moist state, it must be dried by being allowed to bubble through oil of vitriol or by being passed through a bottle containing fragments of dried calcium chloride before it is used for assaying purposes. This gas will only be required in very accurate assays, which are generally performed where there are ample conveniences for generating pure hydrogen gas. The gas is inodorous, invisible, and colourless when absolutely pure. It is a most powerful reducing agent, and reduces a great number of metallic oxides at a red or white heat, viz. the oxides of lead, bismuth, copper, antimony, iron, cobalt, nickel, tungsten, molybdenum, and uranium. When any metal is required in a state of absolute purity, this is the only reducing agent admissible, as others give the metal combined with a certain proportion of carbon.

Carbon.—Found in large quantities in the mineral kingdom, but generally combined with other bodies. In a state of purity it constitutes the diamond. The diamond, like all other species of carbon, is unacted on by the highest possible temperature when in close vessels. It burns in atmospheric air and oxygen gas, but requires for combustion a higher temperature than ordinary charcoal. After the diamond, the varieties of carbon found in nature or artificially prepared, are:—

1. **Black-lead** or **Graphite.**—This is a mineral found in beds in the primitive formations, principally in granite and mica-schist. It is generally mixed with earthy substances, and rarely yields less than 10 per cent. of ash. Before employing it for reduction purposes it should be purified. Lowe * has given an excellent plan for effecting this object.

Determination of the Value of Graphite.—G. C. Wittstein † heats a gramme of the sample to dull redness, and takes the loss as water. The residue is ground up with 3 grammes of a mixture of equal equivalents of potassium and sodium carbonates, introduced into a platinum crucible, covered with one gramme of potash or soda, and slowly heated to redness. The crust which is formed

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* Polyt. Centr. 1855, p. 1404.

† Dingler's Polyt. Journal, 216, 45.

must be from time to time pushed down with a platinum wire. After fusion for half an hour it is let cool, softened with water, heated almost to a boil for a quarter of an hour, filtered, washed well, and the liquid set aside.

The residue on the filter is dried, placed in a small flask, the ashes of the filter added, and about three grms. of hydrochloric acid (sp. gr. 1·12) poured in. On the mixture becoming slightly gelatinous a few more drops of the acid are added, the digestion is continued for an hour, the mixture diluted with water, filtered, and washed. Pure graphitic carbon remains on the filter, and is dried, slightly ignited, and weighed. The acid filtrate mixed with the former one of an alkaline character is evaporated to dryness, and in it silica, alumina, ferric oxide, &c., are determined in the usual manner.

2. **Anthracite.**—This is another species of fossil carbon much resembling ordinary coal, but differing from it by burning with neither smell, smoke, nor flame.

3. **Coke.**—This is the residue of coal after all the volatile matter is expelled. It is generally iron-black, and has nearly a metallic lustre; it is difficult to inflame, and burns well only in small pieces, but gives a very intense heat. Oven or furnace coke is preferable, as it is harder, lasts longer, and is more economical in use.

4. **Wood Charcoal.**—This is obtained by burning the woody part of plants, with a limited supply of air, so as to drive off all their volatile matters, and leave merely their carbon. It is this kind that is generally employed in assays. It ought to be chosen with care, well pulverised, passed through a sieve, and preserved in well-stopped vessels. Wood charcoal is never perfectly pure, generally containing, besides ash, a proportion of hydrogen and watery vapour; these bodies are not generally prejudicial, but in some experiments ash must not be present: in that case pure charcoal may be procured by heating sugar to redness in a closed crucible.

The advantage of carbon as a reducing agent consists in its great affinity for oxygen, which at a red heat surpasses that of most other substances. Charcoal by itself possesses two inconveniences: first, it has the property of combining with many metals; and in the second place, it is infusible, and cannot combine with vitreous substances. The property it possesses of combining with iron, nickel, cobalt, &c., is of no consequence to the assayer, for the increase of weight it gives is not material, excepting under the circumstances to be hereafter pointed out; but its infusibility and inability to combine with fluxes is a very serious inconvenience; for after the reduction, that portion which has not been consumed remains disseminated with the grains of metal in the fused slag, and prevents the separation of all the metal, and the consequent formation of a good button; a large quantity of charcoal can thus irreparably injure an assay. This inconvenience does not happen, however, when an oxide is reduced by cementation in a lined crucible, but there are some cases in which this mode of reduction is inadmissible.

Coke should never be used as a reducing agent in assays when it is possible to avoid it. It often contains a very large proportion of earthy and other extraneous matters (more particularly sulphur, which is very injurious). Coke is never so good as wood charcoal as a reducing agent, because it burns more slowly. When it is used, the temperature employed for an assay must be much increased.

Coal is nearly always inconvenient, because it swells by heat; nevertheless, as it is not required in very large quantities, it is sometimes employed, being finely powdered and sifted previous to use.

The Fatty Oils.—The name oil is generally given to those bodies that are fat and unctuous to the touch, more or less fluid, insoluble in water, and combustible. They all become solid at various degrees of temperature. There are some which, at the temperature of our climate, have constantly a solid form, as butter, palm-oil, cocoa-nut-oil, &c.

Tallow is an animal product analogous to the fatty oils in properties.

Resins.—The greater part of the resins are solid, but some are soft. They are brittle, with a vitreous and shining fracture, and are often transparent. They are very fusible, but cannot be raised to their boiling point without partial decomposition.

Although all the bodies just mentioned consume in their combustion a large quantity of oxygen, they cannot generally effect the total reduction of an oxide on account of their volatility; so that, before the temperature at which the reduction takes place can be attained, the greater part of the reducing agent has been expelled. They generally act only by virtue of the small carbonaceous residue produced by the action of heat; so that their use is very limited and uncertain. Whenever they are employed as reducing agents, without covering the substance, a loss is experienced, on account of the bubbling and boiling caused by their decomposition: this will always take place unless the contents of the crucible be covered with charcoal powder. Oils are very serviceable in the reduction of a large mass of oxide by cementation; in this case, after the oxide has been placed in the crucible, as much oil is added as the oxide and the lining of the crucible will soak up. Fat or resin is also used to prevent the oxidation of the surface of a metallic bath (as in the fusion of bar-lead samples), by coating the metal, and preventing the action of the atmospheric oxygen.

Sugar in its decomposition by heat leaves a much larger proportion of carbon than the oils, fats, or resins; so that it would appear serviceable as a reducing agent. There are some cases in which it may be used with advantage, but it undergoes a great increase in volume when heated; so that losses in an assay may occur by the use of this agent. To purify sugar from mineral ingredients it should be recrystallised from alcohol. It then may be used as such, or after carbonisation. It yields about 14 per cent. of charcoal: this is pure carbon, and leaves no residue when burnt; it is, therefore, preferable to wood charcoal in cases where no foreign matter should be introduced into the assay.

Starch, well dried, and, better still, torrified, is employed with advantage as a reducing agent, and is better than sugar, as it neither fuses, swells up, nor spirts, and in many cases is even preferable to charcoal, because it is in such a fine state of division that it can be more readily and intimately mixed with the substance to be reduced. Wheat and rye flour have nearly the same qualities as starch. They are sometimes used.

Gum decrepitates slightly by heat, softens, agglomerates, and boils, without spirting. The gums can be employed as reducing agents under the same circumstances as sugar and starch, but the two latter are preferable, because they contain no earthy substances.

Tartaric Acid is the reducing agent in cream of tartar, or argol, of which so frequent use is made; but the acid is never employed by itself. When heated in close vessels, it fuses and decomposes, giving off combustible gases, leaving a little charcoal. It burns when heated in contact with air, giving rise to a peculiar and not unpleasant odour.

Oxalic Acid fuses at a temperature of 208° without decomposing, but when heated to 230° it is decomposed, giving rise to carbonic acid, carbonic oxide, and a little formic acid vapour, and when heated strongly some portions volatilise without decomposition; it does not leave a carbonaceous residue.

The property which oxalic acid possesses of not leaving a residue would render it remarkably valuable for the reduction of the metallic oxides in cases where the slightest trace of carbon is to be avoided, if its reducing power were greater; but it decomposes at a low temperature, and in burning absorbs but a small quantity of oxygen, especially when it has not been dried; so that even for the most easily reducible oxides a large proportion must be employed. When it is combined with a base, as potash in potassium binoxalate, its reducing power is much augmented.

Ammonium Oxalate, when heated in close vessels, is decomposed. Its reducing power is nearly double that of oxalic acid.

Comparative Reducing Power of the above Agents.—In order to give an idea of the comparative reducing power of the agents just described, the result of some assays made on them by Berthier, by means of litharge, are given below.

By heating the same weight of each reducing agent with an excess of litharge, buttons of lead were obtained, whose weights were proportional to the quantity of oxygen absorbed, and by comparing them with each other the reducing power of each flux is given; by taking for unity the weight of the reagent, calculation has proved that 1 part of pure carbon reduces from litharge 34·31 of lead. The following are the results of Berthier's experiments:—

Hydrogen	104·00
Pure carbon	34·31
Calcined wood charcoal	31·81
Amber resin	30·00
Ordinary wood charcoal	28·00
Animal oil	17·40
Tallow	15·20
Resin	14·50
Sugar	14·50
Torrified starch	13·00
Common starch	11·50
Gum-arabic	11·00
Tartaric acid	6·00
Ammonium oxalate	1·70
Oxalic acid	·90

It must be borne in mind that these numbers do not represent the quantities of oxygen each reagent would absorb in complete combustion; but that it only indicates the quantity of metal produced by equal weights of the reagents.

In assaying, however, it is rarely that these agents are used by themselves; they are generally mixed with a flux properly so called, which will be more particularly described under the head of Fluxes.

Metallic Iron removes oxygen from the oxides of lead, bismuth, copper, &c., but is rarely added for that especial purpose; and when it does produce this effect, it is generally secondary, because it previously existed in the matter subjected to assay, or was added for some other purpose.

Metallic Lead reduces but a very small number of oxides, but it reduces many to the minimum of oxidation; it also decomposes some sulphates and arseniates.

II. OXIDISING AGENTS.

The oxidising agents in general use are as follows :—

1. Oxygen, atmospheric or combined.
2. Litharge and ceruse.
3. Lead silicates and borates.
4. Potassium nitrate.
5. Lead nitrate.
6. Manganese peroxide.
7. Copper oxide.
8. Iron peroxide.
9. The caustic alkalies.
10. The alkaline carbonates.
11. Lead, copper, and iron sulphates.
12. Sodium sulphate.

Oxygen is a gas which has neither smell nor taste, and is about one-tenth heavier than atmospheric air. It has the property of forming compounds with nearly every element, and its affinities are very energetic. Atmospheric air consists of four-fifths nitrogen and one-fifth oxygen.

Litharge is a fused protoxide of lead, and is generally obtained from the silver-lead works. When melted, it oxidises nearly all the metals, except mercury, silver, gold, palladium, platinum, &c., and generally forms very fusible compounds with the oxides. These two properties cause it to be a very valuable agent in separating silver and gold from all the substances with which they may be mixed.

Litharge is occasionally mixed with a little of the red oxide of lead; the presence of this in large quantities becomes injurious, as it has the property of oxidising silver. Ordinary litharge can be easily freed from this oxide by fusing it and pouring it into a cold ingot mould, then pulverising, and carefully keeping it from contact with air, as it readily absorbs oxygen, and if it be allowed to cool in the atmosphere it will nearly all be converted into the red oxide.

Ceruse, or **White Lead,** is a carbonate of lead protoxide. As it does not contain the slightest traces of red oxide, it may be used where the presence of that substance may be inconvenient; but it is troublesome to use, as it is much less dense than litharge; large vessels must be employed in consequence; besides, it generally contains a small quantity of lead acetate or subacetate, and sometimes metallic lead separates from it on ignition, which is, in some cases, disastrous to the result of an experiment. When ceruse is employed, a certain quantity must be fused, to ascertain if any metallic lead be produced; and, on the other hand, it must be examined to ascertain if it be adulterated with barium sulphate. When it is pure, it dissolves completely in acetic or nitric acid.

Action of Oxide of Lead on the Metals.—The following are the results of the experiments of Berthier on the action exercised by oxide of lead on sulphur, selenium, tellurium, arsenic, and the most common of the metals. The experiments were made in a furnace capable of producing heat enough for a copper assay.

Sulphur.—Lead oxide is completely reduced by sulphur with the formation of sulphurous acid, but not a trace of sulphuric acid: thus $S + 2PbO = 2Pb + SO_2$.

Selenium is dissolved by oxide of lead in all proportions; but these bodies exercise no action on each other.

Tellurium is strongly attacked and converted into telluric acid, which combines with the oxide of lead when the latter is in excess ($Te + 4PbO = 3Pb + PbO,TeO_3$). If the contrary be the case, the excess of acid is volatilised and telluride of lead produced ($2Te + 3PbO = TePb_3 + TeO_3$).

Arsenic.—When metallic arsenic is heated with litharge, if the latter be employed in great excess, all the arsenic is oxidised ($As_2 + 3PbO = As_2O_3 + 3Pb$); if not, a part only is oxidised, and lead produced; the remainder volatilises, or forms a lead arsenide. (For nature of reaction, refer to the preceding metal, Tellurium.) Mixtures of

Arsenic	75·24	37·60	9·40
Litharge	111·60	111·60	111·60

gave: No. 1, a lamellar metallic button, and a compact vitreous slag of a fine orange-colour. The fusion was accompanied by a considerable amount of arsenical smoke.

No. 2 gave a semi-ductile metallic button, with a lamellar fracture, like galena, but not so blue, and a transparent vitreous orange-coloured slag.

No. 3 yielded a button of lead and a deep olive-green slag, very crystalline, and in large plates. This fusion was not accompanied by smoke. It is probable that arsenious acid is formed in these reactions: the last slag contained about a fifth of its weight of this acid.

Lead reduces, in part, arsenious acid; in the same manner, arsenic partly reduces oxide of lead. A mixture of

Arsenious acid	12·40
Lead	38·80

produced on fusion a very arsenical vapour, and yielded 32 parts of arsenide of lead, which was deep-grey, semi-ductile, and had a granular fracture; a fine orange-yellow vitreous lead arsenite was also produced.

Antimony.—The two following mixtures of antimony and litharge:—

Antimony	10	10
Litharge	40	80

gave (No. 1) 23 parts of lead, and a compact, well-fused slag, of a topaz yellow colour, which contained more than one-third of its weight of antimony protoxide ($Sb + 3PbO = SbO_3 + 3Pb$). The second gave 26 parts of lead, and a very fluid glass, which cooled rapidly, and was opaque, like yellow wax; it contained

Lead oxide	52
Antimony protoxide	11·86

Tin.—This metal, cut into small fragments, was heated with the following quantities of litharge:—

Tin	10	10	10
Litharge	37·5	80	120

The first mixture gave a slaggy substance, of dull grey colour, not well fused, with globules of lead at the lower part.

The second mixture gave 26 parts of lead, and a semi-fused slag, compact and opaque, the colour yellowish-grey. It contained

Lead oxide	52
Tin protoxide	11·4

The third mixture produced 26·3 of lead, and a very fluid slag, which was compact, opaque, and greyish-yellow with a granular fracture ($Sn+PbO=SnO+Pb$). It contained

Lead oxide	97·0
Tin oxide	11·4

Zinc.—Ten parts of zinc filings and 100 of litharge were heated together; as soon as the latter softened, action commenced. A slight bubbling and flaming, occasioned by the combustion of a portion of the zinc, took place, and on increasing the heat the mixture fused completely. The result was a button of lead equal to 13 parts; it was pure and ductile, and was covered with a crystalline slag, like litharge, opaque and yellowish, but in small plates. This experiment proves that about one-fifth of the zinc employed is volatilised, whilst the remainder reduces the litharge ($Zn+PbO=ZnO+Pb$). The slag contains

Lead oxide	877
Zinc oxide	123

Bismuth.—Twenty parts of bismuth heated with 40 of litharge gave a ductile metallic button, tin-white, and weighing 24·3 parts, and a crystalline slag, like litharge.

Iron.—M. Berthier heated metallic iron with litharge in the following proportions—

Iron wire	10	10
Litharge	100	160

The first mixture gave 40 of lead, and a pasty, compact, opaque slag of a deep metallic-black colour, and very magnetic ($Fe+PbO=FeO+Pb$). There was no metallic iron, but some globules of lead were present. The slag contained about

Lead oxide	55·9
Iron oxide	13·4

The second mixture gave a button of lead, weighing 46·6, and a very fluid, compact, opaque slag, with an unequal shining lustre, deep-brown, and very magnetic. The slag contained nearly

Lead oxide	110
Iron oxide	13·4

Copper.—The following are the results obtained with different mixtures:—

Copper	15·8	15·8	15·8	15·8	15·8
Litharge	13·9	27·9	55·8	167·4	334·8

With the first mixture a button was produced, copper-red on the exterior, grey in the interior, weighing 17 parts; and a compact, opaque, deep-red slag. The slag contained

Lead oxide	10·3
Copper suboxide	2·4

and the button—

Copper	13·6
Lead	3·4

The button produced by the second mixture was exteriorly copper-red, and interiorly grey, spotted with red; it weighed 17·8, and the slag was compact, reddish-brown, and opaque. The slag contained

Lead oxide	22·3
Copper suboxide	3·6

and the button—

Copper	12·4
Lead	5·2

The third mixture gave a button similar to the last, weighing 18 parts, and a compact, opaque, reddish-brown slag. It contained

Lead oxide	49·8
Copper suboxide	3·8

The button was composed of

Copper	12·4
Lead	5·6

With the fourth mixture, a button weighing 25·6 was produced, and a slightly crystalline, reddish-brown slag, which contained

Lead oxide	151·28
Copper suboxide	10·32

and with the fifth, a grey metallic button, weighing 23·6, and a crystalline slag in large plates, like litharge, yellowish green and reflecting green. The analysis of the button gave

Copper	3·6
Lead	20·0

and the slag contained

Lead oxide	313·28
Copper suboxide	13·72

Action of Copper Oxides upon Lead.—Copper oxide is speedily reduced to the state of suboxide by excess of lead. If the lead be not in excess, it is totally oxidised, reducing a corresponding quantity of the copper to the minimum of oxidation.

The oxide is reduced to the metallic state by lead, but not completely, because a certain quantity is taken up by litharge. The following mixtures have been made the subject of experiment:—

Metallic lead	25·9	25·9	25·9	38·8	51·8
Copper suboxide	19·8	14·9	9·9	9·9	9·9

All of these gave an imperfect alloy of copper or lead, and a very fusible slag composed of lead oxide and copper suboxide. The first produced a very small globule of copper and a very fluid slag, having a much greater tendency to run through the body of a crucible than litharge. Cooled slowly, it was reddish-brown, opaque, and had a finer texture. It was composed of

Lead oxide	27·9
Copper suboxide	17·8

The second mixture produced a button of copper weighing 4·4, and a deep reddish-brown slag, composed of

Lead oxide	27·7
Copper suboxide	8·7

The button gave—

Copper	4·1
Lead	0·3

The third gave a metallic button weighing 8·8, and a deep red, opaque slag, which contained

Lead oxide	24·89
Copper suboxide	2·11

The button contained

Copper	5·9
Lead	2·9

In the fourth and fifth mixtures, buttons weighing 21·2 and 34·8 were produced, together with slags similar to the preceding, and containing about 1 per cent. of copper suboxide.

Lead Silicates and Borates behave as litharge, but they oxidise less rapidly.

They may be prepared by fusing together 1 part of silica or boracic acid with 1 part of litharge. The borates are more fusible than the silicates, but their use is attended with inconvenience, as they swell very much in fusing.

Potassium and Sodium Nitrates fuse at a temperature below redness, without alteration, but when heated more strongly they give up oxygen. The action of these salts, when fused, is very energetic, because they have a great tendency to decompose, and because they contain a large quantity of oxygen. They are used as oxidising agents in the purification of the noble metals, and for preparing some fluxes. They ought always to be employed in a state of purity.

Saltpetre often contains impurities. On this account a determination of the real amount of potassium nitrate often becomes necessary, not only in cases where saltpetre is to be used for docimetric purposes, but also when used in certain technical operations, viz. the manufacture of gunpowder, enamel, &c.

If saltpetre is very impure, it may easily be purified by recrystallisation to such a degree that it will only contain 2 to 3 per cent. foreign substances (chiefly sodium chloride).

An exact assay of saltpetre is most difficult, and the different modes in use are not quite accurate, on account of the chemical properties of the nitric acid, potash, and soda, which substances are generally contained together in saltpetre, and cannot be perfectly estimated by means of reagents. This is chiefly the case with the nitric acid and soda.

Soda is frequently found in saltpetre, as the manufacturers often intentionally mix the raw saltpetre with soda-saltpetre, and it is also often manufactured from a mixture of soda-saltpetre and potassium carbonate.

Assay of Saltpetres.—The following are the different modes of assaying saltpetre.

a. To determine the nitric acid directly, 150 grains of the well-ground sample are mixed with six times the weight of well-powdered silica, placed in a platinum capsule and dried in the water-bath till there is no further loss of weight. The temperature is then raised to dull redness for about half an hour, by which the whole of the nitric acid is expelled. Its quantity is found by weighing the cold crucible.

Sodium nitrate may be treated in the same manner.

The most usual, though not the most satisfactory, process for the assay of potassium and sodium nitrates is to determine the total impurities, viz. water, insoluble matter, alkaline chlorides and sulphates, and the residue being taken as pure nitrate.

b. **Gay-Lussac's Mode** of assaying saltpetre consists in converting the potassium nitrate into potassium carbonate, and in determining its amount volumetrically by means of standard sulphuric acid. 2·639 grs. of saltpetre are mixed with 1 gr. of ignited pine-root, and 12 grs. of ignited and finely pulverised sodium chloride (the latter is added in order to moderate the combustion), and this mixture is heated in a platinum crucible. After cooling, the mass is extracted by water, and either a standard solution of sulphuric acid or oxalic acid is added to the solution. The sulphuric acid is prepared by mixing 70 grs. of sulphuric acid, sp. gr. 1·84, with 600 grs. of water, and to this mixture so much water is added again that 100 measures of it will saturate 6,487 grs. of potassium carbonate. The number of measures used for saturation will then indicate directly the percentage of potassium carbonate.

The following foreign substances in raw saltpetre should be determined.

Water.—Twelve to 20 grammes of air-dried, finely pulverised saltpetre are heated in a porcelain crucible to 120° C., and the resulting loss is calculated as water.

Mechanically mixed Impurities.—The substance obtained in the former assay is dissolved in hot water, and filtered through a dried and weighed filter. The residue is well washed with hot water, dried on the filter at 120° C., and weighed. On deducting the weight of the filter, there will be left the weight of the mechanically mixed impurities (alumina, silica, calcium carbonate, iron peroxide, &c.), which usually amount to 2 to 5 per cent.

Lime and Magnesia.—These substances are precipitated as carbonates, in the former filtered solution raised to the boiling-point, by sodium carbonate; the carbonates are then dissolved in hydrochloric acid, and neutralised with ammonia. The lime can be precipitated by oxalic acid, and filtered off; the magnesia which remains in solution may then be precipitated by sodium phosphate.

The amount of lime in East Indian raw saltpetre which has been once crystallised varies between 0·216 and 0·265 per cent., the amount of magnesia between 0·263 and 0·28 per cent.

Chlorine.—Two to 3 grammes of raw saltpetre are dissolved in about 30 grammes pure warm water, in a flask furnished with a tight-fitting stopper, and the amount of chlorine is determined by a standard solution of nitrate of silver. The latter is prepared by dissolving 4·793 grammes of silver nitrate in 1,000 burette divisions of water; each division of the burette will then indicate 0·001 gramme of chlorine. The solution, after being warmed and acidulated with nitric acid, is mixed gradually with the solution of silver; after each addition of the latter, it is to be shaken and then allowed to rest.

The amount of chlorine determined by this assay is calculated as being derived from $\frac{2}{3}$ potassium chloride, and

$\frac{1}{3}$ sodium chloride, so that 1 part of chlorine corresponds to 1·927 part of metal (1·285 potassium, 0·642 sodium). Experience has proved that East Indian saltpetre contains potassium and sodium chloride in these proportions.

Sulphuric Acid.—Six to 8 grammes of raw saltpetre are dissolved, and from this solution diluted and heated to the boiling-point, the sulphuric acid is precipitated by means of a standard solution of baryta. By using a solution of 3·26 grammes of barium nitrate in 2,000 parts of the burette, each division of the latter will correspond to 0·0005 gramme sulphuric acid. The amount of sulphuric acid in East Indian raw saltpetre varies between 0·05 and 0·11 per cent.

Sodium Nitrate.—This determination is most difficult, and the following modes are recommended.

α. Perfectly pure potash-saltpetre is mixed with different quantities of soda-saltpetre. These mixtures are put under a glass bell-jar, together with a quantity of the raw saltpetre to be assayed. The glass bell must contain also a vessel with water. After a certain time, it is ascertained which of the standard samples corresponds in weight with the raw saltpetre.

The results so obtained are of value only if no other hygroscopic salts (magnesium, chloride, &c.) are present.

β. Longchamps' mode is based upon the decomposition of soda-saltpetres by potassium chloride, producing sodium chloride and potassium nitrate. The saltpetre is mixed with potassium chloride, and the solution evaporated down. By this operation, first sodium chloride and afterwards saltpetre become separated. The latter is washed, dried at 150° C., and weighed. Werther has recommended a similar mode.

If the saltpetre does not contain certain oxides, such as alumina, lime, &c. (or if, previously present, they have been precipitated), a solution of potassium antimoniate will precipitate the soda contained in the saltpetre solution. The precipitate consists of sodium antimoniate, 100 parts of which contain 84·39 antimonious acid, and 15·61 soda.

The presence of soda is also to be ascertained by washing saltpetre with a saturated solution of pure potash-saltpetre. This saturated solution will then contain a proportionally large amount of sodium nitrate. If a small quantity of the solution is made to crystallise upon a watch glass, soda-saltpetre, showing a rhombohedric form, may be detected by means of a microscope, while potash-saltpetre crystallises in prisms, and sodium and potassium chlorides in cubes arranged in the form of steps.

Soda-saltpetre (*Chili- or cubic-saltpetre*) may, in many cases, be substituted for potash-saltpetre.

Lead Nitrate acts in a similar way to the two last-mentioned salts. It is prepared by dissolving litharge in nitric acid, and crystallising the solution.

Manganese Peroxide is easily reduced to the state of protoxide by many metals, and is a very powerful oxidising agent; but is rarely employed, because its compounds are very infusible. It is employed occasionally in the purification of gold and silver.

Copper Oxide is not much employed as a flux, but is often contained in substances submitted to assay; it then acts as an oxidising agent. A great number of metals, even silver, reduce it to the minimum of oxidation: and other metals, as iron, for instance, totally reduce it.

Iron Peroxide.—This, like copper oxide, sometimes acts incidentally as an oxidising agent.

The Caustic Alkalies, Potash and Soda, fuse below a red heat, and volatilise sensibly at a higher temperature. Charcoal, at a high temperature, decomposes the water combined with the hydrates of potash and soda, converting them into carbonates, but an excess at a white heat decomposes the carbonate, and potassium or sodium is the product.

Potassium and Sodium Carbonates are very much employed as agents in the assay by the dry way. They have the power of oxidising many metals, as iron, zinc, and tin, by the action of the carbonic acid they contain; part of it being decomposed, with the formation of carbonic oxide.

Lead, Copper, and Iron Sulphates.—These three salts at a high temperature oxidise the greater number of the metals, even silver, the sulphuric acid giving off oxygen and sulphurous acid. They are used in the assay of gold.

Sodium Sulphate is not used by itself as a reagent, but is a product in many operations; it is either formed in the course of an assay, or is contained as an impurity in some of the bodies used.

III. DESULPHURISING REAGENTS.

1. The oxygen of the atmosphere.
2. Charcoal.
3. Metallic iron.
4. Litharge.
5. The caustic alkalies.
6. The alkaline carbonates.
7. Nitre.
8. Lead nitrate.
9. Lead sulphate.

1. **The Oxygen of the Atmosphere** acts as a desulphurising agent in roasting, combining with the sulphur present, forming sulphurous acid ($2FeS_2 + 11O = Fe_2O_3 + 4SO_2$) or sulphuric acid ($CuS + 4O = CuO,SO_3$), sometimes both.

2. **Charcoal** decomposes many sulphides by taking their sulphur to form sulphide of carbon. It acts in this manner with the mercury, antimony, and zinc sulphides ($2ZnS + C = 2Zn + CS_2$). It is only employed as an auxiliary to the desulphurising power of the alkalies and their carbonates.

3. **Iron** separates sulphur from lead ($PbS + Fe = Pb + FeS$), silver, mercury, bismuth, zinc, antimony, and tin, but only partially decomposes copper sulphide. It is generally used in the state of filings, or nails; the latter are preferable, and ought to be kept free from rust. Oxide of iron may be used if it be mixed with the requisite quantity of charcoal to reduce it. Cast iron must not be employed, as it has very little affinity for sulphur.

4. **Litharge** (PbO) exercises a very energetic action on sulphides, even at a low temperature. If it be employed in sufficient proportion, the sulphide acted on is wholly decomposed. The sulphur is often disengaged as sulphurous acid, and the metal remains alloyed with the lead proceeding from the reduction of a portion of the litharge, or combines as oxide with that portion of the litharge which is not reduced. The quantity of litharge requisite for the decomposition of a sulphide is considerable, and varies according to its nature; some sulphides require 34 times their weight. When less than the requisite quantity is used, only a portion of the sulphide is decomposed, and a corresponding quantity only of lead reduced, whilst the remainder of the sulphide forms, with the litharge and the metallic oxide which can be produced, a compound belonging to the class of oxysulphides, which is generally very fusible.

When the sulphides have a very strong base, as an alkali or alkaline earth, no sulphurous acid is given off by the action of litharge, but all the sulphur is converted into sulphuric acid.

Litharge is a very valuable reagent, and its use is nearly exclusively confined to the assay of sulphides containing the noble metals, as these metals are thus obtained as alloys of lead, which are afterwards assayed by cupellation.

The following is an account of the behaviour of this reagent with the ordinary sulphides.

Manganese Sulphide requires at least six times its weight of litharge to produce a fusible compound, and thirty times its weight to desulphurise it completely. The sulphur and metal oxidise simultaneously ($MnS + 3PbO = MnOSO_2 + 3Pb$), and a manganese protoxide is formed, which partly peroxidises, taking a brownish tint in contact with the atmosphere. Berthier assayed the four following mixtures:—

Manganese sulphide . .	5	5	5	5
Litharge	20	30	100	150

The first produced an infusible, greyish-black, scoriform mass, in which small plates, having the look of galena, could be discovered. It was composed of the sulphides and oxides of manganese and lead. Much sulphurous acid was given off during the operation.

The second fused to a soft paste, and gave 17·5 of lead, and a compact, vitreous, opaque slag, of a very deep brown colour. The slag contained about half its weight of manganese sulphide.

The third fused readily, and produced 31·5 of ductile lead, and a transparent, vitreous slag, of a deep hyacinth red.

The fourth produced 33·7 of lead, exceedingly ductile, and the desulphurisation was complete.

Iron Sulphide.—Thirty parts of litharge are sufficient to scorify iron protosulphide; the metal is converted into the protoxide ($FeS + 3PbO = FeO + SO_2 + 3Pb$).

The four following mixtures—

Iron protosulphide . . .	10	10	10	10
Litharge	60	125	250	300

gave, the first a pasty, scoriform mass, colour metallic grey, and very magnetic. It was composed of the sulphides and protoxides of iron and lead.

The second gave a very fluid metallic black slag, very magnetic, opaque, and possessing great lustre, and 36 of lead.

The third gave a compact vitreous transparent slag of a fine resin-red, and 67 of lead.

The last yielded a similar slag to the former, but containing no sulphur, and 70 of lead.

Native iron pyrites was treated with the following proportions of litharge:—

Iron pyrites . .	10	10	10	10	10	10
Litharge . .	60	125	200	300	400	500

The mixtures fused very readily with an abundant disengagement of sulphurous acid.

The first produced only a metallic button, divisible into two parts: the lower was the largest, and was a lead subsulphide; the other looked like the compact galena, but was magnetic; it was composed essentially of the sulphides of iron and lead, but probably contained a small quantity of their oxides.

The second and third gave black vitreous opaque slags which stained the crucibles brown, together with lead, having a granular fracture, and a deep grey colour: the first button weighed 35, and the second 40. Both samples of lead were contaminated with a small quantity of slag, and contained from $\frac{8}{1000}$ths to $\frac{1}{100}$th of sulphur, and a small quantity of iron.

The slags from the three last mixtures were vitreous, transparent, and of a fine resin-red colour: the buttons of lead weighed 45·4, 54·8, and 86 parts. A much larger proportion of litharge does not produce more than 86 of lead, proving that 50 parts of litharge completely effect the desulphurisation of iron pyrites.

Copper Sulphide.—The following mixtures of sulphide of copper and litharge—

Copper sulphide . . .	10	10	10	10	10
Litharge	20	30	50	100	250

fuse very readily, giving off an abundance of sulphurous acid.

The slags formed were compact, vitreous, opaque, or translucid, and more or less bright red. The copper which they contained was at the minimum of oxidation.

The three first mixtures gave metallic buttons, composed of uncombined lead and sulphide of copper.

The fourth gave 28 of lead, with a little adhering sulphide of copper.

The fifth gave 38·5 of pure ductile lead, the exact quantity that ought to be reduced from litharge by the transformation of the above quantity of copper sulphide into suboxide and sulphurous acid ($2CuS + 5PbO = Cu_2O + 2SO_2 + 5Pb$).

Copper sulphide does not combine with litharge; this is an exception to the general rule. It requires about twenty-five times its weight of litharge to decompose it completely. When litharge is combined with a certain quantity of copper protoxide, it has no action on the sulphide of that metal.

The desulphurisation of copper pyrites requires about 30 parts of litharge.

Copper pyrites	10	10	10	10
Litharge	50	100	200	300

were fused together.

In the first assay the fusion was accompanied with much ebullition, and the mass remained pasty: 6 parts of ductile lead were produced, and a matt similar to galena, but deep grey, with small facets, and a brownish-black vitreous slag.

In the second, much ebullition and swelling up took place: 35 of lead, 45 of matt, and a deep brown vitreous slag, were produced.

In the third assay, 49 of lead was the result. It was covered by a thin layer of matt, and a very shining, deep brown, vitreous, translucid slag.

The last mixture fused readily, almost without ebullition, and gave 72 of lead, and a compact shining slag, of a bright grey, and without the least trace of matt; the desulphurisation was complete ($CuS,FeS + 6PbO = CuO + FeO + 2SO_2 + 6Pb$).

Antimony Sulphide has a great tendency to combine with litharge, and it must be heated with at least 25 parts to effect its desulphurisation. By mixing these two substances in the following proportions:—

Antimony sulphide	10	10	10	10	10
Litharge	38	60	100	140	250

the first three mixtures afforded very fluid slags, compact, deep black, and slightly metallic, and buttons of ductile lead, weighing 2, 9, and 26 parts. These slags resemble the black litharge produced at the commencement of a cupellation.

The fourth mixture gave a transparent compact slag, vitreous and shining, having a splendid hyacinth-red colour, and 50 parts of lead.

The last produced 57 of lead, proving the desulphurisation to be complete ($Sb_2S_3 + 9PbO = Sb_2O_3 + 3SO_2 + 9Pb$). The antimony, in this case, exists as protoxide in the slag.

M. Fournet has observed that antimony sulphide has the property of carrying copper sulphide, and even silver-sulphide, into the compounds formed with litharge. In one of the experiments which he made, a double sulphide, composed of equal parts of silver sulphide and antimony sulphide, was fused with three times its weight of litharge, and gave, first, a button of lead, mixed with silver; secondly, a matt like galena; and thirdly, a black slag. This slag was analysed, and found to contain from 8 to 9 per cent. of silver.

It is probable that all the sulphides, having a strong tendency to combine with lead oxide, have, like antimony sulphide, the property of determining the scorification of a certain quantity of silver sulphide; like all the sulphides, which, in a state of purity, are completely decomposed by lead oxide.

Zinc Sulphide must be fused with twenty-five times its weight of litharge to be decomposed. The following mixtures were heated together:—

Blende	24·08	12·08	10	10
Litharge	55·78	83·68	100	250

However strongly the first mixture was heated, it always remained pasty; 29·2 of a greyish-black lead were produced, which contained ·018 of sulphur and ·008 of zinc. The button was covered by a metallic-looking black substance, intermediate between a matt and a slag; it was composed of zinc and lead sulphides and oxides.

The second mixture gave 35·5 of lead and a fluid slag, which was compact, opaque, and black.

The third gave 43 of lead, and a deep grey slag.

The last produced 65 of pure lead ($ZnS + 3PbO = ZnO + SO_2 + 3Pb$), and a vitreous slag, of an olive-colour, and translucid on the edges.

Lead Sulphide.—Galena and litharge, at a heat just sufficient to fuse them, combine and form an oxysulphide; but if the temperature be increased, the two bodies react on each other, and are mutually decomposed ($PbS + 2PbO = 3Pb + SO_2$). If 2,789 parts of litharge be employed to 1,496 of lead, or 1,865 of litharge to 1,000 of galena, nothing but pure lead is obtained. If more litharge be employed, a portion is not decomposed, and covers the lead. If less be employed, the galena is not completely decomposed, and the lead is covered by a matt of sub-sulphide.

But when litharge is combined with a certain proportion of sulphides or metallic oxides, it completely loses its oxidising power on galena, even at a white heat; so that it can be combined with this substance as with the other sulphides, without effecting its total decomposition.

5, 6. **Caustic Alkalies and their Carbonates.**—All the sulphides are decomposed by caustic alkalies, and their carbonates; but in the latter case carbonaceous matter must be present. In the absence of charcoal, there are some sulphides, as of copper, on which they have no action. In these decompositions alkaline sulphides are formed, and combine with and retain a certain quantity of the sulphide submitted to experiment. The proportion of the sulphide which remains in combination with the alkaline sulphides depends on many circumstances. It is always less when a large proportion of alkali or carbonate has been employed; as it is also when a high degree of temperature has been employed; and the presence of charcoal always much diminishes the proportion. When the metal of a sulphide is very volatile, as mercury or zinc, the decomposition may be perfect.

Potash, as it is sold in commerce, always contains foreign substances, viz. silica, peroxide of iron, potassium sulphate, muriate, phosphate, and silicate, soda-salts, &c., and also water.

A partial purification of the potash may be effected by dissolving it in boiling water, which will not dissolve some of the above-named foreign substances.

The amount of potassium carbonate contained in potash may be ascertained by a standard solution of oxalic acid, or by tartaric acid. Mohr* recommends for this purpose the use of oxalic acid.

Soda also is never free from foreign substances.

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* Mohr, Lehrb. d. Titriermethode, 1855.

The determination of sodium carbonate may be effected also by tartaric acid, or by a salt of oxalic acid.

When employing a standard solution, sulphuric acid is taken, or sometimes oxalic acid, while for the determination of potash a standard solution of oxalic acid is always used.

Ammonium carbonate is used for decomposing metallic sulphates which are formed during the roasting process of several sulphur minerals. Ammonium sulphate is then formed, which is volatile when slightly heated.

7. **Nitre, Saltpetre, or Potassium Nitrate** has a very powerful action on the sulphides : in fact, if not modified by the addition of some inert substance, as an alkaline carbonate or sulphate, explosion may take place, and a portion of the contents of the crucible be thrown out. Where an excess of nitre is used, all the sulphur is converted into sulphuric acid, and every metal but gold and silver is oxidised. When only the exact quantity of nitre is employed, that is to say, just as much as is sufficient to burn all the sulphur in the sulphides of those metals which are not very oxidisable, as those of copper, silver, and lead, the metal is obtained in a state of purity, and the whole of the sulphur converted into sulphuric acid ; but with the sulphides of the very oxidisable metals, the oxygen of the nitre is divided between the sulphur and the metal.

8. **Lead Nitrate** possesses the combined properties of nitre and litharge. It is not much used.

9. **Lead Sulphate** is not used as a reagent, but is often formed in the assay of lead ores. It decomposes lead sulphide by burning the sulphur ($PbO,SO_3 + PbS = 2Pb + 2SO_2$). It acts on many other sulphides in a similar manner.

IV. SULPHURISING REAGENTS.

1. Sulphur.
2. Cinnabar, or mercury sulphide.
3. Galena.
4. Antimony sulphide.
5. Iron pyrites.
6. The alkaline persulphides

1. **Sulphur** fuses at 226°, and at 284° is very liquid. It has very powerful affinities, and combines with the greater number of the metals. That kind generally known as flowers of sulphur ought to be employed; and before use, the presence or absence of earthy matters should be ascertained, by exposing it to a dull red-heat in a crucible. The sulphur will go off, and the earthy impurities will be left behind.

Sulphur is principally used in the preparation of the alkaline sulphides and in the assay of some of the noble metals.

2. **Cinnabar** is decomposed by many of the metals, and is a better sulphurising agent than sulphur itself, as it is less volatile.

3. **Galena.**—Many metals, as iron, copper, &c., separate sulphur from lead, while some others, as silver, gold, &c., do not; so that if galena be heated with an alloy of various metals, some of which decompose it, and some do not, the former are transformed into sulphides, and the latter combine with the metallic lead which is produced. It is often employed for this purpose. It is a common ore, and readily procured.

The samples employed must contain no antimony sulphide, and all the matrix must be carefully separated by sifting and washing.

4. **Antimony Sulphide** yields its sulphur to many of the metals, but it is only used in the separation of gold from some alloys. In this operation the sulphur combines with the alloyed metals, and the antimony with the gold, for which it has much affinity.

5. **Iron Pyrites** is a persulphide which loses half its sulphur at a white heat. It is much employed in metallurgical operations, but not in assaying.

6. **Alkaline Persulphides** can support a tolerably elevated temperature without losing sulphur, but they have a great tendency to do so, and to this is due their sulphurising power. By their means almost every metal can be made to combine with sulphur. When an alkaline persulphide is heated with a metal, or an oxide of a metal

mixed with charcoal, a fused compound, a mixture of the sulphide of the metal and an alkaline sulphide, is obtained.

When they are in combination, they are held together by very feeble affinities, and their decomposition is generally effected by the mere action of water, which dissolves the alkaline sulphide and leaves the other perfectly pure. But with gold, molybdenum, tungsten, antimony, &c., the compound is stable and soluble in water; and it is from this fact that the alkaline sulphides are sometimes employed in the assay of auriferous substances.

In order to effect a sulphurisation by means of the alkaline sulphides, it is much better to use equivalent mixtures of sulphur and alkaline carbonates than to prepare them beforehand. To obtain potassium persulphide, 46 parts of potassium carbonate, and 54 of flowers of sulphur, must be fused together; and for sodium persulphide, 40 parts of dry sodium carbonate must be heated with 60 parts of sulphur.

When the mixture is fused in a plain crucible, potassium sulphate, or sodium sulphate is formed, because part of the alkali gives up its oxygen to a portion of the sulphur, which becomes sulphuric acid; but when charcoal-lined crucibles are used, the carbon combines with the oxygen of the alkali, and no sulphate is produced.

V. FLUXES.

Fluxes are used in the following cases:—

1st. To cause the fusion of a body, either difficultly fusible, or infusible by itself.

2ndly. To fuse foreign substances mixed with a metal, in order to allow the latter to separate by its difference of specific gravity.

3rdly. To destroy a compound into which an oxide enters, and which prevents the oxide being reduced by charcoal. Zinc silicate, for instance, yields no metallic zinc with charcoal, unless it be mixed with a flux capable of combining with the silica.

4thly. To prevent the formation of alloys of some metals with others, as, for instance, in the case of a mixture of the manganese and iron oxides; when a suitable flux is employed, the iron is obtained in a state of purity, whereas if no flux had been added an alloy would have been obtained. Gold and silver can be separated from many other metals by means of a flux.

5thly. To scorify some of the metals contained in the substance to be assayed, and obtain the others alloyed with a metal contained in the flux, as gold or silver with lead.

6thly. A flux may be employed to obtain a single button of metal, which otherwise would be obtained in globules.

Fluxes are divided into non-metallic and metallic; the non-metallic fluxes are—

1. Silica.
2. Lime.
3. Magnesia.
4. Alumina.
5. Calcium and aluminium silicates.
6. Glass.
7. Borax (sodium biborate).
8. Fluor-spar (calcium fluoride).
9. Potassium carbonate.
10. Sodium carbonate.
11. Nitre (potassium nitrate).
12. Common salt (sodium chloride).
13. Black flux and its equivalents.
14. Argol (potassium bitartrate).
15. Salt of sorrel (potassium binoxalate).
16. Soap.

The metallic fluxes are—

17. Litharge (lead oxide) and ceruse (lead carbonate).
18. Glass of lead (lead silicate).
19. Lead borate.
20. Lead sulphate.
21. Copper oxide.
22. Iron oxides.

1. **Silica** is employed frequently to cause the fusion of some gangues in assays made at an elevated temperature. Silica combines with all the bases, and forms with them bodies termed silicates, which are more or less fusible.

Quartz is the best form of silica to use. For that purpose it must be strongly heated, and then quenched in cold water. It can then be easily pulverised. In case the quartz takes a yellow or reddish colour on ignition, it must be digested with hydrochloric acid.

2, 3, 4, 5. **Lime, Magnesia, Alumina, and their Silicates.** No simple silicate is readily fusible, so that lime, magnesia, or alumina are employed, according to circumstances, to reduce a simple silicate to such a condition that it will readily fuse in an assay furnace. Sometimes it may be requisite to use all the above-mentioned earths.

Pure lime, when exposed to atmospheric air, attracts carbonic acid and water so quickly that, in practice, pure calcium carbonate is used in the form of chalk, calcareous spar, or marble, if they are pure. Calcium carbonate frequently contains foreign substances, viz. iron, manganese, alumina, silica, and also magnesium carbonate. A certain quantity of magnesium carbonate is, in many cases, advantageous, and alumina and silica are not disadvantageous.

Alumina is never used in the pure state. Washed china-clay which, on burning, becomes white, is used instead. Clay generally contains from 20 to about 40 per cent. alumina, and, if it is used for the formation of silicates, a quantitative analysis of its components should first be performed.

6. **Glass** is a very useful flux in certain assays, and, being a saturated silicate, it will serve by itself either as a slag or merely as a covering. The kind employed must contain no easily reducible metallic oxides, and it must especially be free from arsenious acid and lead oxide.

The subjoined analyses of glass from *Bödemann Kerl's Probierkunst* will be found useful. (See p. 193.)

7. **Borax** ($Na_2B_4O_7 + 10H_2O$ and $Na_2B_4O_7 + 5H_2O$).—That kind with 10 atoms or 47·1 per cent. water effloresces when exposed to atmospheric air, and the other

ANALYSES OF DIFFERENT KINDS OF GLASS.

	SiO_3	KO	NaO	CaO	MgO	MnO	Al_2O_3	Fe_2O_3
1–2. French green bottle-glass (Dumas and Berthier)	53·55	5·48	...	29·22	...	...	6·01	5·74
	60·0	3·1		22·3	...	1·2	8·0	4·0
3–5. „ „ medicine bottle-glass (Berthier)	62·0	...	16·4	15·6	2·2	...	2·4	0·7
	71·6	10·6	...	10·0	...	0·3	3·0	1·5
	69·6	8·0	3·0	13·0	0·6	...	3·6	1·6
6–7. English green bottle-glass, decomposable by wine (Warrington)	59·0	1·7	10·0	19·9	0·5	...	1·2	7·0
	49·0	2·0	7·2	24·7	2·0	...	4·1	10·1
8–9. Bohemian white hollow wine-glass (8 by Peligot)	76·0	15·0	...	8·0	...	...	1·0	...
	71·7	12·7	2·5	10·3	...	0·2	0·4	0·3
10. „ plate (mirror) glass (Peligot)	67·7	21·0	...	9·9	..	...	1·4	...
11. „ glass goblet, not decomposable by acids (Struve)	77·25	10·73	3·13	8·71	...	...	trace	trace
12. „ „ (Peligot)	77·0	14·0	8·0	...	...	...	1·0	...
13–14. „ combustion-tubes for organic analysis (Rowney and Otto)	73·13	11·49	3·07	10·43	...	...	0·30	0·13
	74·0	18·5	...	7·2	...	...	0·1	
15. Glass goblet from Petersburg, of which 8 per cent. alkalies have been extracted by muriatic acid at the boiling-heat (Struve)	67·85	29·98	2·06	9·41	...	...	0·88	
16. French hollow wine-glass	69·2	15·8	3·0	7·6	2·0	...	1·2	0·5
17. French glass for the apparatus of the laboratories in Paris (Salvetat)	70·5	2·1	17·20	8·7	0·2	...	0·5	0·3
18–19. French window-glass	68·55	...	12·88	16·17	...	...	2·4	...
	69·6	...	15·2	13·3	...	...	1·8	...
20. French mirror-glass (Berthier)	72·0	...	17·0	6·4	...	...	2·6	1·9
21–23. English mirror-glass	77·4	3·0	13·0	5·3	..	...	...	0·9
	78·7	1·3	11·6	6·1	...	...	2·7	...
	77·9	1·7	12·4	4·8	...	...	3·6	...
24. Venetian mirror-glass	69·6	6·9	8·1	11·0	1·1	0·1	1·2	0·5

kind with 5 atoms or 30 per cent. water, does not effloresce, and crystallises in octahedrons. This difference is immaterial for assaying purposes, but it is of importance in purchasing borax.

When borax is heated, it loses its water of crystallisation and undergoes an enormous increase of volume ; at a higher temperature, it fuses and forms a transparent glass, which becomes dull on the surface by exposure to air. Only the fused vitrified borax ought to be used in assays. It must be reduced to powder, and kept in well-closed vessels.

Borax may be regarded as containing free boracic acid; it is an excellent and nearly universal flux: it has the property of forming, like boracic acid, fusible compounds with silica and nearly all the bases, and is preferable to boracic acid because it is much less volatile. It may be used at a high or a low temperature. It is employed in the assay of gold and silver, because it fuses and combines with most metallic oxides, or in obtaining a *regulus* —that is to say, to separate the metals, their arsenides and sulphides, from any stony matter with which they may be mixed; because this salt is neither oxidising nor desulphurising. It is also employed in the assay of iron and tin ores, as in the presence of charcoal it retains but traces of their oxides, and, indeed, much less than generally remains with the silicates.

8. **Fluor-spar** or **Calcium Fluoride** is rarely employed in assays, but in certain cases is an excellent flux; as will be hereafter shown.

9, 10. **Potassium Carbonate** and **Sodium Carbonate.**—It has been already shown that they possess oxidising and desulphurising power: they will now be considered as fluxes.

They are decomposed in the dry way by silica and the silicates, with the separation of carbonic acid. The presence of charcoal much facilitates this decomposition.

They form fusible compounds with many metallic oxides. In these combinations the oxide replaces a certain quantity of carbonic acid ; but they are not stable—

they are decomposed by carbon, which reduces the oxides, or by water, which dissolves the alkali.

On account of their great fusibility, the alkaline carbonates can retain in suspension, without losing their fluidity, a large proportion of pulverised infusible substances, as an earth, charcoal, &c.

The alkaline carbonates ought to be deprived of their water of crystallisation, for assaying purposes; in fact, it would be better to fuse them before use. They must in all cases be kept in well-stopped vessels.

They may be used indifferently, but sodium carbonate is to be preferred, as it does not deliquesce, and is generally much cheaper.

The alkaline carbonates of commerce always contain sulphates and chlorides. In some cases this causes no inconvenience, but there are many circumstances in which the presence of sulphuric acid would be injurious.

Potassium carbonate can readily be procured free from sulphate and chloride by means of nitre and charcoal, as follows: Pulverise, roughly, 6 parts of pure nitre, and mix them with 1 part of charcoal; then project the mixture, spoonful by spoonful, into a red-hot iron crucible. The projection of each spoonful is accompanied by a vivid deflagration, and potassium carbonate is found in a fused state at the bottom of the crucible. It must be pulverised, separated from excess of charcoal, and kept in a dry state for use.

Sodium carbonate may be obtained in much the same way, substituting sodium nitrate for potassium nitrate. Either carbonate may also be obtained in a sufficient state of purity by repeatedly crystallising the commercial carbonates.

11. **Potassium Nitrate.**—Its properties have already been pointed out. The presence of silica or of silicates much assists its decomposition.

12. **Common Salt (Sodium Chloride)** is recommended either mixed with flux, or placed above it, for the purpose of preserving the substance beneath from the action of the atmosphere, or to moderate the action of such bodies

as cause much ebullition. It is very useful in lead assays, and is much used in the assay of silver by the wet way. It must be previously pounded, and heated to dull redness in a crucible, to prevent its decrepitation.

Common salt, though containing calcium and magnesium sulphates and chlorides, is in most cases sufficiently pure for assaying purposes. If intended for copper assays, it must be previously purified from sulphates.

Plattner * has examined the influence of common salt upon different oxides and sulphates. It does not act upon uncombined lead and zinc oxides. Lead sulphate, when melted with it at a dull red heat, becomes liquid, and evolves vapour of lead chloride. By raising the temperature, and by giving more draught of air, the evolution of such vapour is increased. Common salt acts upon zinc sulphate in the same way. Antimony oxide and antimonious acid heated with it at a dull red heat evolve vapour of antimony chloride, though not in a great quantity. Copper sulphate melted with salt at a red heat becomes converted into copper chloride and sodium sulphate. Copper chloride becomes vaporised if air is admitted, and it becomes converted into copper subchloride by raising the temperature a little, chlorine being then evolved.

13. **WHITE FLUX, BLACK FLUX, and RAW FLUX.**— *White flux* is produced by deflagrating together equal parts of saltpetre and argol (crude potassium bitartrate); *black flux*, by deflagrating one part of saltpetre with two or three or more parts of argol. Generally one part of saltpetre and two and a half parts of argol are taken. The finely pulverised and intimate mixture for either flux, before it is deflagrated, is called *raw flux*.

After the saltpetre and argol have been finely pulverised and sifted separately, they are intimately rubbed together, and then deflagrated by throwing the mixture little by little into a low-red-hot crucible, which after each addition is lightly covered over. The deflagration may also be conducted, though less advantageously, by filling the crucible about two-thirds full of the raw flux and then

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* 'B. u. h. Ztg.' 1854, p. 126.

touching it with a red-hot coal or iron. It can only be performed in the open air or under a flue with a strong draft, as the tartaric acid evolves various empyreumatic volatile matters in considerable quantity during its decomposition.

With *white flux* the saltpetre suffices to burn all the charcoal produced by the carbonisation of the tartaric acid, and the result is therefore almost pure potassium carbonate, if pure saltpetre and pure argol have been used. If the latter were impure, the resulting neutral potassium carbonate may contain much, perhaps 10 per cent., of calcium carbonate. White flux works like ordinary potassium carbonate, which is therefore almost always preferred to the far more expensive *flux*.

With the *black flux* the quantity of saltpetre is not sufficient to burn all the carbon from the argol, and there remain therefore in the black flux, according as two, two and a half, or three parts of argol were taken, about 5, 8, or 12 per cent. of free carbon, which is mixed in the most intimate manner with the resulting neutral potassium carbonate—more intimately indeed than would be possible by any mechanical means. This charcoal does not hinder the fusing of the assay when the flux is used, and effects or promotes the reduction of the metallic oxides.

Fusion and reduction, sometimes also desulphurisation, are the purposes for which black flux is used, and, according to the special character of the assay, a greater or a less proportion of charcoal to the carbonate of potash may be desirable, and this is to determine whether two, two and a half, three, or more parts of argol are to be used, to one of saltpetre. As a general rule it may be stated, the more difficultly fusible is the assay, the more potash; and the more metallic oxide is to be reduced, the more charcoal; and the more also of the latter, the more oxygen the oxide contains.

In many cases, instead of black flux, a *mixture* of potassium carbonate and powdered charcoal, in a suitable ratio to each other, suffices, especially if the mixture, before use, is passed through a sieve, or otherwise very intimately mingled. Instead of the powdered charcoal, also, a corresponding (about twice or four times as large) quantity of flour, sugar, or starch may be mixed with the potassium carbonate. Lampblack is, however, the best form of carbon. The three following fluxes are very useful:—

Sodium carbonate	94	88	816
Charcoal	6	12	184

The second is very nearly equivalent to sodium and carbonic acid, and the third to sodium and carbonic oxide; but it must be observed that, whatever precautions be taken, these mixtures never become so liquid as black flux, because the charcoal tends very much to separate and rise to the surface.

A mixture of 100 parts of pure potassium carbonate and 10 to 15 parts of wheat or rye flour is to be preferred to black flux in case the argol contains gypsum, or the saltpetre, sulphates, which in many cases might work injuriously upon the assay. If this is the case, then, in the presence of a reducing flux, sodium sulphide is apt to form, which, for example in the copper assay, occasions the slagging of copper.

Cream of tartar, carbonised by a semi-combustion until it is reduced to half its weight, is a very good substitute for black flux; it contains about 10 per cent. of charcoal.

As a perfectly general rule for the use of black flux, and of mixtures similar to it, it is to be observed that the crucible should never be more than two-thirds filled, as the assay always intumesces, *i.e.* evolves gaseous matters, when free carbon is present.

14. **Argol, Cream of Tartar,** or **Potassium Bitartrate.**—When potassium bitartrate is heated in a covered crucible, a rapid decomposition takes place, accompanied by a disengagement of inflammable gases: the substance agglomerates, but without fusing or boiling up. The residue is black and friable, and contains 15 per cent. of carbon when produced from rough tartar or argol, and 7 per cent. from cream of tartar.

These reagents produce the same effects as black flux, and possess more reducing power, because they contain more combustible matter: but this is an inconvenience, for the excess prevents their entering into full fusion when the substance to be assayed requires but a small proportion of a reducing agent. They can be used with success in assays requiring much carbonaceous matter.

15. **Salt of Sorrel,** or **Potassium Binoxalate,** when heated, is decomposed. It decrepitates feebly, and during its decomposition is covered with a blue flame; it at first softens, and when fully fused is wholly converted into carbonate. When the oxalate is very pure, the resulting carbonate is perfectly white, and free from charcoal: but very often it is spotted with blackish marks. It has no very great reducing power.

16. **White** or **Mottled Soap** is a compound of soda with a fatty acid. When heated in closed vessels it fuses, boiling up considerably, and during its decomposition gives off smoke and combustible gases, and leaves a residue composed of sodium carbonate with about 5 per cent. of charcoal. Of all reducing agents, soap absorbs the greatest quantity of oxygen; and as the residue of its decomposition by heat affords but little charcoal, it has the property of forming very fluid slags. Nevertheless, it is rarely employed, because certain inconveniences outweigh its advantages. These inconveniences are, its bubbling up, and its extreme lightness. It also requires to be rasped, in order to mix it perfectly with the substances it is to decompose, and it then occupies a very large volume, and requires correspondingly large crucibles. By mixing rasped soap with potassium binoxalate or sodium carbonate excellent reducing fluxes may be made.

Reducing Power of the various Fluxes.—By fusing equal weights of each of the above-mentioned reducing fluxes with an excess of litharge, the following quantities of lead were yielded:—

Common black flux, made with two parts of tartar		1·40
Ditto, with 2½ of tartar		1·90
Ditto, with 3 of tartar		3·80
Sodium carbonate	94	1·80
Charcoal	6	
Sodium carbonate	88	3·60
Charcoal	12	

Sodium carbonate	90	1·40
Sugar	10	
Sodium carbonate	80	2·80
Sugar	20	
Sodium carbonate	90	1·15
Starch	10	
Sodium carbonate	80	2·30
Starch	20	
Crude tartar, argol		5·60
Cream of tartar		4·50
Salt of sorrel	85	3·35
Soap	15	
Sodium carbonate	85	2·40
Soap	15	
Cream of tartar, carbonised		3·10
Ditto, ditto, calcined		2·20
Potassium binoxalate		·90
White soda soap		16·00

All fluxes containing alkaline and carbonaceous substances are reducing and desulphurising, besides acting as fluxes, properly so called. They also produce another effect which it is useful to know, viz. they have the property of introducing a certain quantity of potassium or sodium into the reduced metal. This was first pointed out by M. Vauquelin.* He found that when antimony, bismuth, or lead oxide was fused with an excess of tartar, the metals obtained possessed some peculiar characters, which they owed to the presence of potassium.

METALLIC FLUXES.

17. **Litharge and Ceruse.**—These bodies always act as fluxes, but at the same time often produce an alloy with the metal contained in the ore to be assayed. Ceruse produces the same fluxing effect as litharge. The former is the better flux, and is very useful in a great number of assays.

18. **Glass of Lead (Lead Silicate).**—Lead silicates are preferable to litharge in the treatment of substances containing no silica, or which contain earths or oxides not capable of forming a compound with lead oxide, excepting by the aid of silica. It may be made by fusing 1 part of sand with four parts of litharge: if required more fusible, a larger proportion of litharge must be added.

* 'Annales des Mines.'

19. **Lead Borate.**—The lead borates are better fluxes than the silicates when the substance to be assayed contains free earths; but in order to prevent them swelling up much when fused, they must contain an excess of lead oxide. The lead borate containing 90·56 of lead oxide and 9·44 of boracic acid, is very good. Instead of lead borate, a mixture of fused borax and litharge may be employed; it is equally serviceable.

20. **Lead Sulphate** is decomposed by all siliceous matters, and by lime, so that when these substances are present litharge is produced, which fluxes them.

21. **Copper Oxide** is rarely used as a flux for oxidised matters, but is sometimes employed in the assays of gold and silver, to form an alloy with those metals. In this case a reducing flux must be mixed with the oxide. Metallic copper may be used, but is not so useful, as it cannot be so intimately mixed with the assay.

22. **The Iron Oxides** are good fluxes for silica and the silicates. They are, however, rarely employed for that purpose; they are more often used to introduce metallic iron into an alloy to collect an infusible, or nearly infusible, metal, by alloying it with iron; such as manganese, tungsten, or molybdenum.

CHAPTER VII.

THE BLOWPIPE AND ITS USE.

The blowpipe was formerly only used by jewellers and workers of metal for producing sufficient heat for soldering certain small portions of their work; and it was not till about the year 1733 that Anton Swab applied it to the analysis of mineral substances. Cronstedt used the blowpipe to ascertain the difference between various mineral substances as to fusibility, &c. In 1765 Von Engeström published Cronstedt's System of Mineralogy, and added to it a Treatise on the Blowpipe, in which he pointed out the processes of Cronstedt.

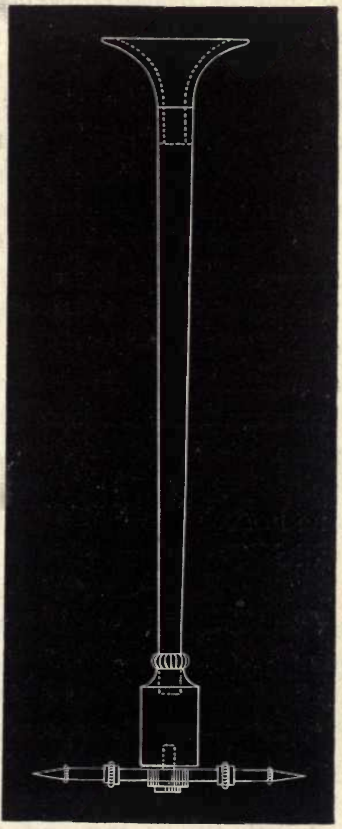
This work attracted the attention of philosophers to this valuable instrument, and its use became more general, and was further developed by Bergman and Gahn.

Berzelius, after Gahn, was particularly famed for his skill with the blowpipe, and for his improvements in the form of apparatus; and from his excellent work on this subject some of the following descriptive part of Blowpipes, Lamps, Tongs, &c., is derived.

The common blowpipe of gasfitters, jewellers, &c., is a tube of brass, tapering towards one end, and curved at that extremity, which has an opening as fine as that made by the finest needle; it is this opening which is held against the flame of the lamp, and air is blown to it to increase the amount of heat. In all ordinary operations, the blast is required to be kept up not more than a minute, so that the quantity of moisture exhaled from the lungs produces no inconvenience by stopping up the tube. But in certain chemical operations, this is exceedingly troublesome, as a continuous blast is required, and a large quantity of water collects in consequence, generally sufficient to mar the success of an experiment. In order to obviate this, Cronstedt placed in the centre of his blowpipe a bulb, in which the greater part of the water collected. This form was, however, inconvenient, because if the jet of the blowpipe were at all inclined, even for an instant, the water ran from the bulb and filled it. In a series of articles communicated to the 'Chemical News,' Mr. David Forbes, F.R.S., has given directions which are invaluable to all who practise with this instrument. From these we quote the following.

'**Blowpipe.**—The form adopted long ago by Gahn is considered as the most convenient. Fig. 68 shows an improvement made by the author upon this form.

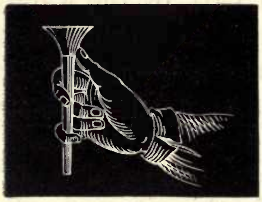
Fig. 68.



'In this figure it will be seen that the arm of the jet is double, turning upon a central hollow axis, which allows the blast to be directed at will through either half of the arm, merely by rotating the arm itself half round; by having consequently the two holes with respectively a large and small orifice, a corresponding blast may be obtained at pleasure, without suspending the operation.

'As a more steady and long-continued blast is required in quantitative operations than could be kept up by using a blowpipe provided with an ordinary mouthpiece held between the lips without seriously distressing the muscles of the cheeks, it is quite essential that the trumpet mouthpiece shown in fig. 68 be adopted; for the same reasons also the mode of holding the blowpipe represented in fig. 69 is recommended, as securing the greatest steadiness from motion, and as greatly assisting the muscles of the cheeks by the external support afforded them by the position of the thumb pressing against the trumpet mouthpiece.

FIG. 69.



'The nipples are turned, and bored of three different sizes, and are made both of platinum and of brass. The first, of platinum, contains the smallest aperture, and is employed for qualitative analysis; the second, of brass, is used for such qualitative experiments as require a strong oxidising flame, and for heating silver, gold, and copper, in quantitative assay; also for roasting copper, lead, and tin ores, the metallic contents of which are to be accurately determined; and the third, which is also manufactured of brass, has the largest bore, and is used for the quantitative estimation of lead and tin.

'Platinum nipples are, however, always preferable to those of brass, because by exposure to a moderate red heat on charcoal before the blowpipe, they are more easily cleaned from the sooty particles which obstruct the aperture. This method of cleansing cannot be applied to brass nipples, owing to their rapid oxidisation; to clean these the operator must adapt in the opening a sharp-pointed fragment of horn, or a small needle, ground along one half of its length; by this means the aperture through which the air passes may be readily cleansed.'

The power and perfection of the blowpipe flame greatly depends upon the internal construction of these jets or nipples. The current of air for at least three-quarters of an inch of the orifice should meet with no obstruction or roughness such as a screw thread or angle so frequently met with in blowpipes having removable nozzles. The most perfect form for the blowpipe jet is that obtained by slightly thickening and drawing down a piece of glass tubing of about 5 millims. internal diameter to the required size for the jet, then cutting the contracted part cleanly across at a point about half an inch from one of the shoulders. We then have a jet of the shape shown in

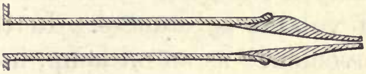
FIG. 70.

fig. 70, with which the most beautiful flame can be produced, and almost any desired pressure of air used without hissing.

It is needless, however, to remark that the liability of glass jets to crack and fuse render their use impracticable except for an oxidising flame, where the jet need not be inserted in the flame of the lamp. Metal therefore must be resorted to, and, as the superiority of the glass jets solely depends on their internal shape and smoothness, the nearer the metal jets can be made to approach them the greater will be the satisfaction in using the blowpipe.

The jets should be at least half an inch long and

FIG. 71.



coned into the blowpipes, as shown in fig. 71, not screwed as is generally the case.

To obtain, therefore, the necessary internal shape for satisfactory blowpipe jets, too much care cannot be taken over the work of drilling, which operation can only be successfully performed by means of a specially constructed drill.

Any kind of flame may be used for the blowpipe, provided it be not too small; a candle, a lamp, or gas may be employed; Engeström and Bergman used common candles in preference. Berzelius employs a lamp, which is certainly much preferable to a candle. I have occasionally employed the flame of coal gas, which answers very well, but is not so good as that of a lamp. Berzelius says on this subject: 'Lamps have doubtless many advantages over candles, but are not so convenient in travelling, on account of the escape of oil. The oil employed ought to be the best olive or salad oil.

The lamp recommended by Mr. Forbes has the advantage of being portable, and closes in such a manner that no oil can escape. It is made of japanned tin-plate, and is about 4 inches long and 1 inch wide, furnished at one end with a wick-holder, capable of being completely closed by a screw, and at the other with a ring of tin-plate, which passes over the upright end of a support. It may be mentioned that the screw-cap is furnished with a leather washer, by the aid of which it can be rendered much tighter, and the escape of oil entirely prevented.

Mr. Forbes says that olive oil, burnt in the usual Berzelius blowpipe lamp, is probably superior to any other. Gas is not to be recommended, as it is difficult to obtain a good reducing flame when using it. For cupellation and such other operations, however, which only require an oxidising flame, it is excellent.

A spirit-lamp may sometimes be employed in blowpipe assays, particularly when glass tubes are employed, as in the detection of volatile substances. In these cases it is much more convenient; as an oil lamp, in the first place, blackens the tube; and secondly, does not yield sufficient heat, except when the blowpipe blast is employed.

It is very difficult to describe in writing a method whereby a student may acquire the practice of using the mouth-blowpipe; that given by Faraday * is perhaps the clearest and most concise. He says, 'The practice necessary, in the first place, is that of making the mouth replace the lungs for a short time, by using no other air for the blowpipe than that contained in it.' This practice is simple in itself, and easy to acquire, but, as before stated, difficult to describe. Let the student first observe that it is easy after having closed the lips to fill the mouth with air, and to retain it so, at the same time respiration may be carried on; and if, while the mouth is in this state, a blowpipe be introduced between the lips, it will be found

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* 'Chemical Manipulation.'

that the small quantity of air which its jet allows to pass through it will be amply supplied for ten or fifteen seconds by the quantity contained in the mouth ; and this being repeated a few times, a ready facility for using the blowpipe, independent of the lungs, will be acquired.

This step being taken, the next is to combine this process with the ordinary one of propelling air directly from the lungs through the mouth, in such a way that when the action of the lungs is suspended during inspiration, the blast may be continued by the action of the mouth itself, from the air contained within it. The time of fourteen or fifteen seconds, during which the mouth can supply air independently of the lungs, is far more than that required for one or even many more inspirations ; and all that is required to acquire the necessary habit is the power of opening and closing the communication between the mouth and the lungs, and between the air and the lungs, at pleasure.

The capability of closing the passages to the nostrils is very readily proved : everyone possesses and uses it when he blows from the mouth, and that of closing or opening the mouth to the lungs may be acquired with equal readiness. Applying the blowpipe to the lips as before, use the air in the mouth to produce a current, and, when it is about half expended, open the lungs to the mouth, so as to replace the air which has passed through the blowpipe ; again cut off the supply, as at first, but continue to send a current through the instrument, and, when the second mouthful of air is gone, renew it as before from the lungs.

To some this may be difficult ; but if the preceding instructions be followed and persevered in for a short time, the learner will soon find that he can keep up a continuous blast from ten minutes to a quarter of an hour, without any other inconvenience than the mere lassitude of the lips, caused by compressing the mouthpiece of the instrument, and this may be avoided by using the trumpet mouthpiece as recommended by Mr. Forbes.

After having conquered the difficulty of keeping up a continuous blast, the student must learn how to attain the maximum of heat with the least exertion to himself. The chief points to be observed are, neither to blow too fiercely nor too gently; in the first case, the force of the blast would carry away heat by the quantity of cold air thrown into the flame, and, in the second, a sufficient amount of heat would not be obtained; because a less amount of air would pass into the flame than that required for perfect combustion.

The highest degree of temperature is required in testing the fusibility of many bodies, as also in the reduction of certain oxides, as those of iron, tin, &c. We have yet another class of phenomena to describe, which do not essentially depend on a high temperature; these are the processes of *reduction* and *oxidation*. In order to explain and point out the best methods of effecting these two objects, it will be necessary to enter somewhat into the nature of flame: this will be done as briefly as is consistent with perspicuity. The species of flame examined will be that of a candle, as it is a similar one to that with which the blowpipe operator will have to experiment.

On careful examination, it will be found that the flame of a candle or lamp may be divided into four distinct portions: first, a deep blue ring at the base; this consists of the vapour of the combustible, which can hardly burn because it has not acquired a sufficient temperature; secondly, a dark cone in the centre; this is also the vapour, but heated intensely, not, however, in a state of combustion, on account of the absence of air; thirdly, of a very brilliant envelope, which surrounds the dark parts just mentioned; this is the partially consumed vapour at a very high temperature; the luminous property it possesses is due to the precipitation and subsequent ignition of particles of solid carbon; and fourthly, of an almost invisible envelope which surrounds the luminous portion; this is the substance of the combustible in full ignition, it here mingles with the atmospheric oxygen, and is consumed. The highest degree of temperature in the whole flame is to be found at the point of contact between the luminous and this part. It must be particularly borne in mind that the inner portions of the flame have an excess of carbonaceous matters, and the outer an excess of oxygenated matters.

Having premised this much, we will examine the nature of the flame of a candle when acted on by the blowpipe blast, and ascertain how far it is altered, and what are the properties of its separate parts in relation to their oxidising and reducing powers. Supposing the lighted lamp or candle be ready and neatly snuffed, place the nozzle of the blowpipe just in the edge of the flame, and about the sixteenth of an inch above the level of the wick: when things are in this state, blow gently and evenly through the blowpipe, and a conical jet or dart of flame will be produced, which, when formed in a steady atmosphere, free from accidental draughts and currents, will be found to consist of two essential parts—the inner cone, blue, small, and well-defined; the outer, brownish and vague. The greatest intensity of heat is found a little beyond the apex of the blue flame; it is there, also, *reduction* takes place. The outer flame is formed by the complete combustion of the combustible matter of the inner; and at that place, and just beyond it, *oxidation* takes place.

Oxidation, as before stated, takes place at the extremity of the outer flame, hence it is termed the *oxidising* flame; in it all the combustible portions are supersaturated with oxygen. In general the further the substance to be oxidised can be placed from the extremity of the flame, the better the operation proceeds, provided always that the necessary temperature be maintained. Dull redness is the best suited for oxidation.

Reduction.—In this operation the jet of the blowpipe must be introduced into the body of the flame, so as only to produce a small dart; and a jet having a smaller hole than that used for oxidation ought to be employed. By operating thus, a more brilliant flame than the last is produced; it is the result of a less perfect combustion, and therefore contains a large amount of carbonaceous matter, fitting it more especially for the purpose of separating oxygen from all metallic bodies.

Berzelius says, ‘the most important point in blowpipe assays is the power of producing *oxidation* and *reduction* at will.’ Oxidation is so easy, that to do it requires only to read a description of it; but reduction requires some practice, and a certain knowledge of producing various kinds of blasts. One of the best methods of exercise in this operation is to take a small grain of tin, and place it on charcoal; then direct the blowpipe dart upon it—it will soon fuse; and if the operator has not produced a good reducing flame, it will become covered with a crust of oxide; so that it becomes a witness against him each time this happens. The nature of the flame must be altered until, by observation, the proper kind is produced at will. The longer the button of tin is kept bright, the better and more expert the operator.

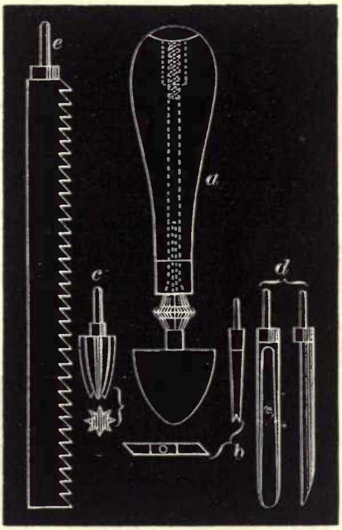
AUXILIARY BLOWPIPE APPARATUS, ETC.

Supports.—The support is the substance destined to hold the material to be assayed whilst under the influence of heat. From this it will be seen that an exceedingly refractory body must necessarily be employed, so as not to give way under the excessive heat; and also (with the exception of charcoal), it ought to have no chemical action on the substances placed in contact with it. Supports may be divided into combustible and incombustible; the former is charcoal, and for the latter, metal, glass, and earthenware, and in some cases certain minerals have been employed.

Charcoal.—Mr Forbes gives the following excellent description of the preparation of charcoal for blowpipe purposes. ‘It is extremely difficult to obtain, in England, charcoal fit for blowpipe operations, without special preparation. The charcoal sold is generally of hard wood, badly burnt, full of cracks, and decrepitating upon application of heat. Good charcoal should be soft, yet compact, and without cracks, and is best made from fir or pine. Where good charcoal cannot be obtained it can be made artificially by moulding charcoal powder agglutinated by some starch paste, and, after desiccation, burning the pieces in a crucible filled with sand.

‘For the preparation of the charcoal used as a support for the assays, the instruments represented in fig. 72 are required, all of which are fitted in the universal handle *a*, which is shown in this figure as holding the largest charcoal borer, a section and plan of which are shown in *b*. This large borer is employed for forming the deep holes in the charcoal used in the blowpipe furnace, and which serve to contain the clay crucibles or capsules in which the assays are fused. The blast holes in the charcoal inside the blowpipe furnace are bored out by the gouge-shaped borer *d*, which also serves for making small holes or grooves in charcoal for general purposes. The smaller borer *c*, is most useful, particularly in boring out the holes for receiving the soda paper cornets containing the assay for reduction. The saw-knife *e* also fits into the same handle, and is used for trimming and sawing across the charcoal pieces, having coarse saw-teeth in front, whilst the back presents a sharp knife-edge. The figures are all drawn to one-half of the real size.’

FIG. 72.

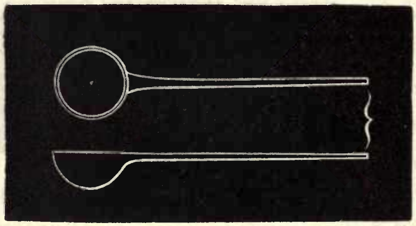


Platinum.—This metal is much employed as a support in cases where charcoal would be injurious by its reducing power. It is used in three forms, viz. wire, foil, and as a spoon, or small capsule.

Wire.—A moderately strong wire of platinum, about 2 inches long, and curved at one end, is used with great advantage in many quantitative examinations. The curve serves as a support in all experiments on tests of oxidation and reduction, where alteration of colour only is to be observed. This support can be relied on, for it is totally free from the false varieties of colour which are too often perceptible when the assay rests on charcoal. In the treatment of metals, or in reduction tests, where an easily melted body is to be operated upon, charcoal must, however, be used. It is necessary to have at hand several platinum wires, so as to proceed to another experiment without being obliged to forcibly remove the adhering borax glass, or to wait for its solution in hydrochloric acid, which is the better mode. If the platinum loop melts with the reagent, it must be cut away, and a new one formed. A wire can be used for a very long time, and when it becomes too short to be held between the fingers the straight end may be fastened into a cork, or a piece of glass tubing.

The platinum spoon (see fig. 73) and foil are used in much the same way; but as charcoal and the platinum wire answer every purpose, it will be unnecessary to describe their use further: small iron spoons of the above form are also made, and are very useful in cases where the presence of iron is not objectionable.

Fig. 73.



Other instruments, as forges, hammer, anvil, agate mortar, scissors, &c., are sufficiently familiar to everybody not to require description. Special apparatus required for any operation will be described in the course of the processes.

Colonel Ross recommends as a support in certain cases a thin rectangular slip of aluminium plate, 4 inches by 2, half an inch of the lower end of which is turned up at an angle of 80° as a rest for the assay. A fragment of the substance of the size of a pea is laid upon the edge close to the angle, and heated very slightly about half an inch from the top of a pure blue flame. The sublimate obtained should be examined from time to time, increasing the heat after each examination, till nothing more is obtained.

For a full description of this method, by means of which substances existing in mixture or combination may be usefully separated by taking advantage of their different degrees of volatility, the reader is referred to 'Alphabetical Manual of Blowpipe Analysis' (Trübner & Co.).

Asbestos card-board, according to Mr. W. M. Hartley, may also serve for supports. This substance resembles greyish cardboard, but has a soapy feel, like steatite; it can be used for making crucible-supports, sand-baths, muffles, retort-supports, etc.; it can be cut with cork borers or scissors; by moistening with water it can be moulded to any shape. After moistening it should be gradually dried and ignited, to get rid of organic matter. It stands the ordinary wear and tear of the laboratory well. It is formed principally of asbestos fibres. It can be obtained from the manufactory, 31, St. Vincent Place, Glasgow, at 4*s.* a pound.

REAGENTS AND FLUXES.

Blue Litmus Paper is used for detecting free acid in solution, its colour being changed to red.

Reddened Litmus Paper is used for the detection of free alkali, its colour being restored to blue.

Brazil-wood Paper is used for detecting hydrofluoric acid, being tinged straw-yellow when immersed in a very dilute solution of this acid.

Turmeric Paper is used for detecting free alkalies: the change produced is very characteristic, its bright yellow colour becoming dark brown.

Nitric Acid is employed in the solution of various metals, alloys, and ores, and for the discrimination of certain precipitates; also as an oxidising agent.

Zinc is principally employed for the reduction of antimony and tin.

Copper is used for the reduction of mercurial salts and for the detection of arsenious acid. It is also used to detect the presence of nitric acid.

Iron Wire is employed to precipitate many metals, and in the separation of sulphur and the fixed acids from any substance with which they may be combined. The metals which can thus be precipitated, or deprived of sulphur, are copper, lead, nickel, and antimony. For instance, if a small piece of iron (pianoforte) wire be placed in a substance in fusion, and acted upon by the blowpipe, it becomes covered with the reduced metal. The latter sometimes appears as small globules.

Iron has the property of reducing phosphorus from phosphoric acid or the phosphates, giving rise to a phosphide of iron, which forms on fusion a white, brittle, metallic globule.

Potassium Cyanide.—This is a most useful flux. MM. Haidlen and Fresenius say: 'We have examined its action on many oxides, sulphides, salts, &c., in reference to its use as a reagent combined with the blowpipe. We prefer, in general, a mixture of equal parts of anhydrous soda and potassium cyanide. This mixture was employed on account of the great facility with which the pure cyanide fuses. It acts, in general, so very similarly to pure soda, that it would be superfluous to describe singly the changes which each individual body appeared to undergo when exposed to its action. We cannot, however, pass over the following especial advantages which it possesses as compared with soda. First, reductions are obtained with such great facility that the least practised operator may execute reductions which would otherwise be very difficult; for instance, the reduction of tin from either its oxide or sulphide; and, secondly, that the fused mixture of potassium cyanide with soda is so easily absorbed by the charcoal, that the grains of reduced metal can always be most distinctly perceived, and may be most easily separated therefrom for further examination.'

Sodium Carbonate, called, for the sake of brevity, Soda.—The plain carbonate or the bicarbonate may be indifferently employed; but in either case it is absolutely necessary that it be free from sulphates.

There are two objects in view in the employment of soda as an auxiliary to the blowpipe; first, to ascertain if the substances combining with this body be fusible or infusible; and secondly, to facilitate the reduction of certain metallic oxides.

In the fusion of substances with Soda there are many things to observe. The necessary quantity must be taken on the moistened point of a knife, and kneaded in the palm of the hand, so that it may form a coherent mass. If the body under examination be pulverulent it must be incorporated with it, but if in lump it must be placed upon it, forcing it slightly into the moistened soda; then carefully heated on the charcoal with a gentle flame, until thoroughly dry; and lastly it may be fused. It generally happens that the soda, at the instant of fusion, is absorbed by the charcoal; but this does not hinder its action on the assay; for if it be fusible with soda, the latter comes to the surface and attacks it, finally forming a liquid globule. If the substance be infusible in soda, but decomposable by it, it alters its appearance without entering into fusion. But, however, before pronouncing any substance to be infusible by soda, the flux ought to be mixed with the pulverised substance. If in these trials too little soda be taken, a portion of the substance remains solid, and the rest forms a covering of transparent glass; if too much, the bead of glass becomes opaque on cooling. It sometimes happens that the assay contains a substance which, being insoluble in the glass of soda, prevents it becoming transparent. Then, in order that we may fall into no error respecting the nature of the glass, it becomes necessary in the two last-mentioned cases to add a new quantity of the body under examination, and then ascertain if a limpid globule cannot be obtained. In general it is the best method to add the soda by successive small doses, and note the changes produced by each addition. It sometimes happens, in this kind of assay, that the glass becomes coloured at the moment of cooling, and finally takes a yellow or deep hyacinth red; it even becomes occasionally opaque and yellowish-brown. These phenomena indicate the presence of sulphur, either in the assay or the soda employed. If the same colour be constantly produced by the same soda, it is a proof that it contains sulphate of soda; it must then be discarded, but if it gives generally a colourless glass, it is the substance under assay that contains sulphur or sulphuric acid.

Reduction of Metallic Oxides.—This species of assay, by which quantities of reducible metals, so small as to escape ordinary wet analyses, can be detected, is the most important discovery Gahn made in the application of the blowpipe.

If a small quantity of native or artificial oxide of tin be placed on charcoal, it requires a long blast and a skilful operator to produce a grain of metallic tin; but if a small quantity of soda be added, the reduction takes place readily, and so completely with pure oxide, that the whole is transformed into a button of tin. From this it is certain, that the presence of soda favours the decomposition.

The action, however, can be explained thus, as Berzelius himself hints: the red-hot charcoal reacts upon the sodium carbonate, producing by its reduction a certain amount of sodium, which by its strong attraction for oxygen seizes on that contained by the metallic oxide which is required to be reduced. If the metallic oxide contain an unreducible substance, the reduction of the former becomes difficult; but if a little borax be added, the reduction takes place as usual.

This assay is very easy of execution, and the metal is readily recognised, as by previous assays the nature of it is somewhat ascertained, and the reduction but confirms the previous idea.

If the metallic oxide be mixed with such a quantity of non-reducible substances that its nature cannot be ascertained by previous experiment, how can it be proved that a reducible metal is present?

Gahn has solved this question in a very simple manner. 'After having pulverised the substance to be assayed, it is kneaded in the palm of the hand with moistened soda, and the mixture placed on charcoal and exposed to a good reducing flame; a little more soda is then added, and the blast recommenced. As long as any portion of the substance remains on the charcoal, soda is added in small portions, and the blast continued until the charcoal has absorbed the whole of the mass. The first quantities of soda serve to collect the metallic particles scattered in the substance to be assayed, and the final absorption of the latter completes the reduction of any that may remain in the state of oxide.

'This done, the burning charcoal is extinguished with a few drops of water; then having cut out the part which absorbed the soda and assay, grind it to a very fine powder in an agate mortar. This powder is then washed with water to carry away the finest portion of the charcoal. The grinding and washing are repeated until all the charcoal is washed away. If the substance contained no metallic body, nothing will remain in the mortar after this last washing. But if it contained the smallest quantity of reducible matter, it is found at the bottom of the mortar, as small brilliant plates if it be malleable, or as a fine powder if it be brittle or not fusible. In either case, the bottom of the mortar is covered by metallic traces, resulting from the friction of the particles of metal against its sides (provided that the quantity of metal contained in the sample be not too small). The flattening of almost imperceptible globules of any malleable metal converts them into shining discs of a perceptible diameter. In this manner may be discovered by the blowpipe, in an assay of ordinary size, less than a half per cent. of tin, and even less than that of copper.'

The following points in this class of assay ought to be particularly attended to. First, to produce the strongest possible flame, taking care that it covers every part of the assay. Secondly, to leave none of the metal in the charcoal, or lose the smallest quantity in the collection. Thirdly, to well grind the carbonaceous mass. Fourthly, to decant very slowly, so that only the lighter parts may be carried away by the water. Fifthly, not to judge of the result until the whole of the charcoal has been removed, for a small quantity remaining suffices to hide the metallic particles; and, moreover, the particles of charcoal, viewed in a certain light, have themselves a metallic lustre, which will deceive an inexperienced eye. Sixthly, and lastly, not to trust to the naked eye, however plain the sample may be, but always examine by the aid of a good microscope.

The metals reducible by this process are (besides the noble metals), molybdenum, tungsten, antimony, tellurium, bismuth, tin, lead, thallium, copper, nickel, cobalt, and iron. Amongst these, antimony, bismuth, thallium, and tellurium volatilise easily when they are exposed to a strong heat. Selenium, arsenic, cadmium, zinc, and mercury volatilise so completely that they cannot be collected except by means of a small subliming apparatus.

The reduction can always be effected the first time when the assay contains from 8 to 10 per cent. of metal; but in proportion as the standard decreases more attention and care must be paid to the washing and recognition of the reduced metal in the mortar. A good system of practice in this experiment is to employ any cupreous substance, and make on it a great number of experiments, taking care to mix it each time with a substance containing no copper; thus the metallic value will diminish at each new assay, until at last no copper can be found.

If the substance to be assayed contains several metals, the reduction of their oxides must be made *in globo*, and a metallic alloy obtained. Some, small in number, are reduced separately. For instance, copper and iron give a regulus of each metal; copper and zinc, the first gives a regulus of copper, whilst the latter volatilises. But when the result of the operation is an alloy, recourse must be had to the reactions produced by other fluxes to ascertain its constituents.

BORAX (SODIUM BIBORATE).—The borax of commerce must be dissolved in hot water and recrystallised, before it can be used in blowpipe analysis.

Borax may be employed either in crystals, the requisite size for an assay, or in a pulverulent form; in this case it may be taken up on the moistened point of a knife. Some operators prefer fusing the borax before use, in order to drive off its water of crystallisation, and thus avoid the tumefaction of the crystal on charcoal.

Borax is employed in the solution or fusion of a variety of substances. It is best to commence by acting upon a scale of the substance to be examined; because if a powder be employed the resulting action cannot be so well ascertained. The following phenomena are to be carefully watched, for in treating any substance with borax it must be particularly noted whether the fusion takes place rapidly or otherwise; without motion or with effervescence; if the glass resulting from the fusion is coloured, and if that colour changes in the oxidising or reducing flame; and, lastly, if the colour diminishes or increases on cooling, and if, under the same circumstances, it loses or retains its transparency.

Some substances possess the property of forming a limpid glass with borax, which preserves its transparency on cooling, but which, if slightly heated in the exterior (oxidising) flame, becomes opaque and milk-white, or coloured when the flame strikes it in an unequal or intermittent manner. The alkaline earths, as yttria, glucina, zirconia; the oxides of cerium, tantalum, titanium, &c., belong to this class. In order to be certain of this result we must assure ourselves that the glass is saturated to a certain point with either of the above class of bodies. The same thing, however, does not happen with silica, alumina, iron, manganese, &c., oxides, and the presence of silica prevents the production of this phenomenon with the earths; so that alone they present this peculiar appearance with borax; but when combined with silica (as natural silicates, for instance), no such effect is produced. This operation has received the name of *flaming*, and any substance thus acted upon is said to become *opaque by flaming*.

Sodium Ammonia-phosphate (Microcosmic Salt) is obtained by dissolving 16 parts of sal-ammoniac in a very small quantity of boiling water, and mixing with it 100 parts of crystallised sodium phosphate, dissolving the whole with heat, filtering the boiling liquid; during cooling the double salt crystallises. When microcosmic salt is not pure it forms a glass which becomes opaque by cooling. It is then necessary to dissolve it in a small quantity of water and recrystallise it.

It may be collected in large crystals, or in a pulverulent state. The crystals are in general of a suitable size for ordinary assays. Placed on charcoal, and submitted to the blowpipe flame, it bubbles and swells up, giving off ammonia; that which remains after this treatment is an acid sodium phosphate, which fuses readily, and forms on cooling a transparent and colourless glass. As a reagent, it acts principally by its free phosphoric acid; and if the salt be employed in preference to the acid, it is because it is less deliquescent, costs less, and passes readily into the charcoal. By means of microcosmic salt we ascertain the action of free acids on any substance we may wish to assay. The excess of acid it contains combines with all bases, and forms a class of double salts, more or less fusible, which are examined as to their transparency and colour. In consequence, this flux is used more particularly in the detection of the metallic oxides, most of which impart to it very characteristic colours. This flux exercises on acids a repulsive action. Those which are volatile, sublime; and those which are fixed remain in the mass, dividing the base with the phosphoric acid, or yielding it up entirely; in which case they are suspended in the glass without being dissolved. In this respect, microcosmic salt is a good test for silicates; for by its aid silica is liberated, and appears in the glass as a gelatinous mass.

Potassium Nitrate (Nitre), in long and thin crystals, is employed in hastening the oxidation of those substances which do not readily combine with oxygen in the exterior flame. It is used as follows; the point of a crystal is thrust into the fused bead; but in order to prevent the cooling of the latter the crystal is held by a pair of pliers, so that when the bead begins to cool it may be withdrawn, the bead reheated, and the crystal employed as before, until the desired effect is produced.

Potassium Bisulphate is employed in the detection of lithia, boracic acid, nitric acid, hydrofluoric acid, bromine, and iodine. It separates baryta and strontia from the earths and metallic oxides.

Sodium Bisulphate.—Professor J. Lawrence Smith * has suggested the use of sodium bisulphate as a substitute for the potassium bisulphate in the decomposition of minerals, especially the aluminous minerals. He finds that 'while the soda salt gives a decomposition at least as complete as the potash salt, the melted mass is very soluble in water, and in the future operations of the analyses there is no embarrassment from a deposit of alum.

'The ordinary commercial article is not sufficiently pure for use, and he prepares it from pure sodium carbonate, or sodium sulphate that has been purified by recrystallisation. In either instance pure sulphuric acid is added in excess to the salt in a large platinum capsule, and heated over a flame, until the melted mass, when taken up on the end of a glass rod, solidifies quite firmly. The mass is then allowed to cool; moving it over the sides of the capsule will facilitate this operation. When cool it is readily detached from the capsule, is then broken up, and put into a glass stoppered bottle. In almost every instance where we have been in the habit of using potassium bisulphate the sodium bisulphate can be substituted.'

Vitrified Boracic Acid is used to ascertain the presence of phosphoric acid and small portions of copper in lead alloys. For quantitative analysis, it is generally used to ascertain the quantity of copper contained in a lead ore, and also the amount of copper united with various metals.

Cobalt Nitrate in solution ought to be free from arsenic and nickel, and the solution must be moderately strong. It is used as a test for alumina, magnesia, tin, and zinc, by the blowpipe.

Nickel Oxalate is used in qualitative examinations for the detection of potash in a salt which also contains soda and lithia.

Copper Oxide is employed to detect the presence of hydrochloric acid and chlorine.

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* 'American Journal of Science and Arts.'

Silica is, with soda, an excellent test for the presence of sulphuric acid ; and when in combination with borax or soda, separates tin from copper.

Turner's Flux.—This is a mixture of potassium bisulphate and fluor-spar. It is used for producing coloured flames before the blowpipe.

Calcium Fluoride (Fluor-spar), and Lime Sulphate (Gypsum).—These two bodies (deprived of water) are used to indicate the presence of each other. If a small piece of gypsum be ignited in contact with a similar piece of fluor-spar, they soon liquefy at their points of contact ; they then combine, and form, by fusing, a colourless and transparent bead of glass, which becomes enamel-white on cooling. Fluoride of calcium is thus employed as a test for gypsum, and *vice versâ*.

Mr. S. D. Poole prefers a mixture of calcium sulphate (selenite) and fluor-spar (in the proportions of two parts of the former to one of the latter) to Turner's flux described above. It forms an easily fusible bead, which by itself gives only a very faint dull red tint (lime) to the flame, but which renders the presence of many elements which give colour most beautifully evident. Thus small portions of lepidolite, petalite, &c., mixed with this flux impart the fine carmine tint of lithia ; copper or strontium their well-known colours, especially after continued blowing. Potash and soda minerals (felspar and albite) are at once distinguished.

This flux is of more limited applicability than that of Turner, because there is no provision in it for the liberation of hydrofluoric acid.

It serves, when mixed with bisulphate of potash, to detect lithia and boracic acid in their various combinations.

Bone Ashes are employed in the cupellation of gold and silver. Harkort reduced them to many states of minute division by the processes of sifting and washing. The bones are burned until they become perfectly white, and then freed from any carbonaceous matter that may have adhered to them. This being done, they are pulverised in a mortar, and the finer portions separated by a sieve. The remaining powder is then thrown upon a filter, and treated with boiling water, which extracts the soluble matter. The washing, which is then resorted to, is for procuring the bone ashes of a more uniform degree of fineness. The mass from the filter is mixed with water in a cylindrical glass, allowed to settle for a few minutes and then decanted; the coarser powder is deposited at the bottom of the vessel, while the finer passes over suspended in the water. By repeated decantations in this way, deposits are obtained of different degrees of fineness; the last, or that which remains longest floating through the liquid, being the finest. The resulting powders must be kept in separate bottles. The coarser ashes are used for the cupellation of rich silver ores, and the finer for assaying ores in which only a minute quantity of gold or silver is present.

Proof Lead is made use of in cupelling argentiferous or auriferous substances; it must be free from silver. Dumas states that the best method of obtaining lead in this desirable state is to decompose the best white-lead by means of charcoal, as it is then impossible for it to contain any other metal.

Tinfoil is employed to reduce certain peroxides to the state of protoxide. When it is used, a small roll, about a quarter of an inch long, is plunged into the fused button, and heated strongly in the reducing flame: the desired effect is then produced.

Dry Silver Chloride.—Herr H. Gericke proposes the employment of this compound in qualitative blowpipe assays. In an elaborate paper on this subject, communicated to the 'Chemical Gazette' (vol. xiii. p. 189), he says:—

'Amongst the phenomena which characterise different bodies before the blowpipe, and serve for their distinction, the colour of the flame is of no small importance. This power of colouring the blowpipe flame is not, however, exhibited by all bodies with sufficient intensity to enable them to be distinguished by it with certainty; and certain substances are consequently usually employed, such as muriatic acid with baryta, strontia and lime, or sulphuric acid, partly to form and partly to set free volatile compounds. By this means, however, although the intensity of the coloration is heightened, its duration is not increased, as these acids, and particularly muriatic acid, evaporate for the most part before they have acted sufficiently, so that the coloration lasts only for a few moments. This defect may be got over by the employment, instead of the volatile muriatic acid, of a chloride, which will retain the chlorine at a high temperature, so that it may only be set free by degrees in small quantities, while the body forming its base may be without action upon the colouring power of the body under investigation. For this purpose chloride of silver appears to be the best, especially as it may readily be prepared in a state of purity. The best plan is to stir it with water into a thick paste, and keep it in a bottle.

'In regard to the action of chloride of silver upon the coloration of the blowpipe flame, I have investigated several compounds of potash, soda, lithia, lime, baryta, strontia, copper, molybdenum, arsenic, antimony, and lead, and mixtures of these substances. Chloride of silver, of course, has no action upon borates and phosphates, both of these acids being amongst those which offer the most resistance to the action of heat.

'For a support, I employed first of all platinum wire, but this is soon alloyed by the metallic silver which separates, and thus rendered useless in testing metals. Silver wire is too readily fusible, and also difficult to obtain free from copper, which may give rise to errors when in contact with chloride of silver. For these reasons, iron wire is best fitted for experiments with chloride of silver, as from its cheapness a new piece may be employed for each experiment, while the silver may readily be obtained in the form of chloride from the broken pieces. If the size of the fragment under examination be sufficient, the platinum forceps may be employed.

'The results at which I arrived, by the employment of chloride of silver, in comparison with those obtained without this reagent, are as follows:

'With potash compounds, such as saltpetre, potashes, &c., the flame is decidedly of a darker colour with chloride of silver; and even in ferrocyanide of potassium, which, when treated by itself with the blowpipe, colours the flame blue, the addition of chloride of silver produces a distinct potash coloration.

'The action of chloride of silver upon soda salts is not so favourable; for although with some, as nitrate of soda, common soda, and labradorite, the flame acquires a more intense yellow colour by the addition of chloride of silver, this reagent produces no observable difference with other soda compounds, such as sulphate of soda and analcime. This also applies to the compounds of lithia, some of which give a finer purple-red colour on the addition of chloride of silver, whilst upon others it has no such effect.

'With lime compounds chloride of silver acts favourably upon the colouring power. Thus the addition of chloride of silver to calcareous spar or gypsum (in the reduction flame) gives the flame a more distinct yellowish-red colour, but stilbite gives no coloration either with or without chloride of silver. With fluor-spar the coloration cannot well be observed, as this decrepitates too violently under the blowpipe.

'The action of chloride of silver upon compounds of baryta and strontia is decidedly advantageous, as both the intensity of the coloration and its duration leave nothing to be desired. Siliceous celestine, which, when heated by itself in the forceps, scarcely coloured the flame, immediately produced a permanent red coloration when heated with chloride of silver.

'Although it appears from the preceding statements, that the employment of chloride of silver presents no advantage with some substances, it may be used with good results in the treatment of mixtures of alkalies and earths.

'Thus, with *petalite* alone the lithia coloration is first produced, and a slight soda coloration is afterwards obtained; whilst with chloride of silver the soda coloration appears very distinctly after that of the lithia. With *lithion-mica* alone a very distinct lithia coloration is presented; but in the presence of chloride of silver a colour is first produced which may lead to the conclusion that potash is present, but the lithia coloration is weakened. *Ryacolite*, heated by itself in the blowpipe flame, only gives a distinct soda coloration; but with chloride of silver a slight potash coloration is first produced, and the colour of soda then appears very distinctly; the lime contained in it cannot, however, be detected by the coloration of the flame.

'Chloride of silver may be employed with still greater advantage with the following metals, but in these cases it is particularly necessary that the operator should become familiar with the colour produced by each individual substance.

'With copper compounds, such as red copper ore, malachite, copper pyrites, sulphate of copper, &c., when contained in other minerals so as to be unrecognisable by the eye, the employment of chloride of silver may be of the greatest service, as the smallest quantities of copper, when treated with chloride of silver under the blowpipe, give a continuous and beautiful blue colour to the flame. With chloride of silver the presence of copper may be distinctly ascertained by the blowpipe, even in a solution which is no longer coloured blue by the addition of ammonia.

'The employment of chloride of silver will be equally advantageous with molybdenum, as in this case also the flame gains greatly in intensity. Arsenic, lead, and antimony are already sufficiently characterised, the former by its odour, the two latter by their fumes; but even with these metals chloride of silver may be employed with advantage to render their reactions still more distinct. It is only necessary to observe, that the greenish-blue flame of antimony appears greener and more like that of molybdenum under the influence of chloride of silver.

'Chloride of silver may also be employed with compounds containing several of the above-mentioned metals.

'If *bournonite* be heated in the oxidation flame of the blowpipe, a fine blue flame is first produced, which indicates lead with certainty; if chloride of silver be now applied, copper is also readily shown. The antimony contained in *bournonite* cannot be ascertained by the coloration of the flame; but this may easily be detected upon charcoal, or in a glass tube open at both ends.

'Native molybdate of lead, without chloride of silver, only gives a blue colour to the blowpipe flame; with chloride of silver this blue coloration of the lead comes out more distinctly, but at the same time the tip of the flame, particularly when the reduction flame is employed, appears of a beautiful yellowish-green colour from molybdenum.

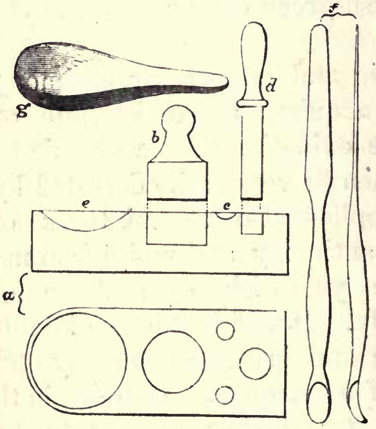
'With mixtures of arsenic and copper, or antimony and copper, the flame first acquires a greyish-blue or greenish-blue colour from the oxidation of the arsenic or antimony; the copper may then be very easily detected by chloride of silver. This applies also to mixtures of arsenic and molybdenum, or antimony and molybdenum; with chloride of silver the yellowish-green flame of molybdenum appears distinctly. It will be more difficult to analyse mixtures of arsenic and lead, or antimony and lead, in this manner; and if a compound contain both arsenic and antimony, these two bodies are not to be distinguished with chloride of silver under the blowpipe.

'From these experiments it appears that in blowpipe testing it is advantageous to employ chloride of silver instead of muriatic acid.

'Chloride of silver is particularly to be recommended in testing metallic alloys for copper. Thus, to test silver for copper, chloride of silver may be applied to the ends of silver wires, and on the application of heat the smallest quantity of copper will furnish the most distinct reaction. This is as sensitive as any of the known copper reactions, and may be performed quickly and easily. In testing metallic alloys for traces of copper, it may be advisable to submit those which contain antimony, zinc, lead, and other volatile metals to roasting, so as to drive off these metals before the addition of chloride of silver.'

Soda-Paper.—Mr. Forbes writes as follows in the 'Chemical News': 'As it would be impossible to submit any powdered substance to the direct action of the blowpipe flame without its suffering mechanical loss, some means must be employed for holding the particles together until they are so agglutinated by the heat that no such loss need be apprehended; this is secured by the use of the soda-paper envelope or cornet, as devised by Harkort. For this purpose slips of thin slightly sized writing paper, about 1¼ inch long by 1 inch broad, are steeped in a solution of one part crystallised pure carbonate of soda (free from sulphate) in two parts of water. When dried these are used for forming small cylindrical cornets, by rolling them round the ivory cylinder, fig. 74 *d*, previously described. A bottom is formed to them by folding down a portion of their length on to the end of the cylinder, which is then pressed firmly into the corresponding mould in the blowpipe anvil, and which, upon the withdrawal of the cylinder, serves as a support until they are filled with the assay from the scoop in which the assay and flux have been mixed. After pressing the assay down, the superfluous paper is cut off, leaving only sufficient when folded down upon the contents of the cornet, to form a paper cover to the top similar to the hollow of the cornet. The assay is then ready for placing in a bore in the charcoal, formed by the charcoal borer *c*, fig. 72, and is then submitted to a reducing fusion.'

FIG. 74.



GENERAL ROUTINE OF BLOWPIPE OPERATIONS.

Size of the Assay.—The morsel operated on is sufficiently large when the effect of the heat and the fluxes added can be distinctly discerned. The size of the assay-piece generally recommended is much too large; its size ought to be about that of a mustard-seed; that of the flux added, about the size of a hemp-seed. It should in general be previously reduced to fine powder.

When a large piece is employed, the experiment consumes much more time and requires much more labour than a smaller piece. It is only in reductions that a larger piece may be successfully employed, because in that case the more metal produced, the more readily can its nature be ascertained. Having thus endeavoured to fix the size of the assay, we will now lead our readers to the operations necessary in blowpipe analysis, and in the order in which they are to be performed.

First.—The substance is heated in the closed tube, or mattrass, over a spirit lamp. It may, by this treatment, decrepitate, or give off water, or some other volatile substance.

Secondly.—It is heated gently on charcoal, by aid of the blowpipe; and, as soon as warm, withdrawn from the heat, and the odour given off ascertained: volatile acids, arsenic, selenium, or sulphur, may be present. The odour thus produced by the oxidising flame must be compared with that produced by the reducing flame; if there is any difference, it must be carefully noted. Sulphur, selenium, &c., are best detected in the oxidising flame, and arsenic in the reducing flame.

Thirdly.—The substance is examined as regards its fusibility. If it be in grains, it is better acted upon on charcoal, notwithstanding its liability to escape on the first insufflation, when not very fusible. But if we can choose the form, it is better to knock off a small splinter, by means of the hammer, and hold it in the flame by the platinum-pointed pincers. A fragment with the most pointed and the thinnest edges ought to be selected. By thus acting, we can always ascertain at a glance if the substance be fusible or not. Infusible substances retain their sharp points and angles, which can be ascertained immediately by means of a microscope. The points are merely rounded in bodies of difficult fusibility, and in substances of easy fusion are rendered globular.

Certain substances, and particularly some minerals, change both aspect and form when exposed to the blowpipe flame, without entering into fusion; some swell up like borax; some of them fuse after tumefaction; others keep in that state without fusion. Some minerals give off a sort of foam on fusing, giving rise to a kind of blebby glass, which, although transparent itself, does not appear so, on account of the multitude of air-bubbles it contains.

This bubbling and tumefaction takes place in the greater part of the minerals only at that temperature at which all the water is disengaged; and these ramifications appear to proceed from a new molecular arrangement, produced by the action of heat on the constituent parts of the substance. It cannot be said that the expansion of a particular part of the substance or its formation into gas, gives rise to this, because it most often happens in those substances which contain no such substance. The minerals which generally give these indications are the double silicates of lime or alkali, and alumina. It sometimes disappears after a few instants, and occasionally lasts as long as the substance is kept in fusion. In the latter case, it seems that the assay takes carbonic acid from the flame, which carbonic acid is transformed by the charcoal into carbonic oxide, and it is that gas which causes the bubbles.

In the employment of fluxes, it is necessary to continue the blast for a sufficiently long time, because some substances appear infusible at the commencement of the operation, and gradually yield to the influence of the flux, and in about two minutes enter into full fusion. The substance is best added in small quantities, and no new dose must be introduced until the former one is acted upon, so that at last the glass arrives at that degree of saturation that it can dissolve no more: it is at this particular point that the reactions are most vivid and plain. Beads of glass, not so saturated, do not give such decided indications.

Occasionally, in operating with a flux in the reducing flame, it happens that the assay-bead reoxidises during the cooling of the charcoal, and thus the labour of a preceding operation is lost. In order to obviate this inconvenience, the charcoal is turned over, so that the bead may fall in a yet liquid state on some cold body, as a porcelain plate.

When the colour of the bead is so intense that it appears opaque, its transparency can be proved by holding it opposite to the flame of a lamp; the reversed image of the flame can then be seen in the bead, tinged with the colour imparted to the flux by the body under experiment. The globule may also be flattened by a pair of pliers before it cools, or it may be drawn into a thin thread. In either of the last-mentioned cases its colour can readily be ascertained.

Minerals exposed to the exterior and interior flame, either with or without fluxes, present a variety of phenomena, which ought to be carefully noted, and which, collectively, form the result of the assay. The smallest circumstance must not be overlooked, because it may lead us to ascertain the presence of a substance not suspected. It is necessary, in all cases, to make two assays, and compare the separate results; because it sometimes happens that an apparently trivial fact had been overlooked in the first series of operations, which materially conduces to the good result of the experiment.

DISCRIMINATION OF MINERALS.*

Selecting those minerals which are remarkable for their wide distribution, and at the same time those which are of value, whether rare or frequent, the number which it is advisable for the explorer to know is reduced to about seventy-five, and it is only to this limited number that reference will be made in this chapter.

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* This method of distinguishing the various minerals, ores, etc. which are likely to be met with during an exploration, is partly condensed from a very valuable pamphlet by Alexander M. Thompson, D.Sc., Professor of Geology at the University of Sydney, entitled 'Guide to Mineral Explorers in Distinguishing Minerals, Ores, and Gems.' The instructions given will not be found to involve greater difficulties than can be overcome by a little practice and perseverance. The appliances which are needed may be bought for a few shillings, and will be found too trifling in weight and bulk to incommode the traveller.

The distinctions in minerals lie in their chemical and physical characters; but as the appearance of a mineral may afford little or no indication of what these are, they have to be discovered by testing.

These characters will be described in detail, and the modes of testing will be indicated, where necessary.

The characters include crystalline form, mode of fracture, colour, lustre, transparency, taste, odour, feel, hardness, specific gravity, fusibility, and chemical composition.

Crystalline Form.

The crystalline form is an important guide in many cases, but crystals are subject to so many modifications, that this character ceases to be a practical one except to those persons who are familiar with its geometrical laws.

Fig. 75.

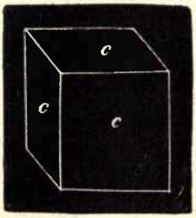


Fig. 76.

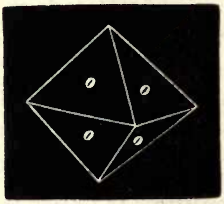


Fig. 77.

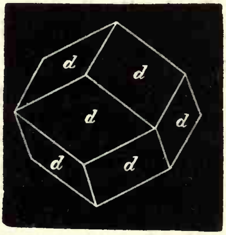


Fig. 78.

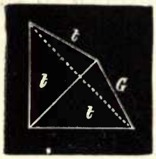


Fig. 79.

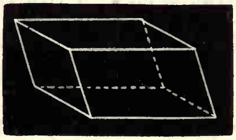


Fig. 80.

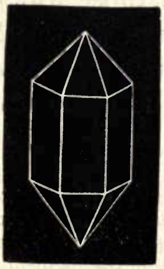


Fig. 81.

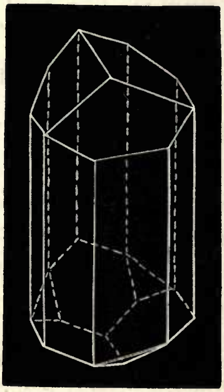
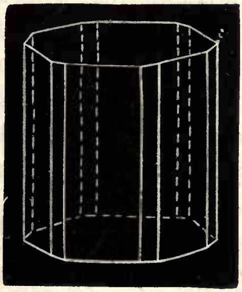


Fig. 82.



Still it is very useful to know a few common primary forms such as the following:—

CUBE.—6 sides or faces, each square (fig. 75).

OCTAHEDRON.—8 sides, each an equal-sided triangle (fig. 76).

DODECAHEDRON.—12 sides, each rhombic,—(shaped like the diamond of a pack of cards) (fig. 77).

TETRAHEDRON.—4 sides, each triangular (fig. 78).

RHOMBOHEDRON.—6 sides, each rhombic (fig. 79).

PRISM.—Any column with three or more sides; when placed on its base, it may stand *straight* or *oblique*; it may terminate abruptly with a flat face, or come off to a point, blunt or sharp, like a pyramid (figs. 80, 81, 82).

Mode of Fracture.

The mode in which a mineral breaks when smartly struck with a hammer, or pressed with the point of a knife, is a character of importance. Many can only be broken in certain directions; for instance, a crystal of calc-spar can only be split parallel to the faces of a rhombohedron; many crystals break more easily in one direction than in others. Whenever a mineral breaks with a smooth, flat, even surface, it is said to exhibit *cleavage.* Cleavage always depends upon the crystalline form. But minerals often break in irregular directions, having no connection whatever with the crystalline form, and this kind of breaking is called *fracture;* the broken surfaces are usually irregular or conchoidal (*i.e.* with concave and convex outlines, like shells).

Lustre.

Some minerals have a brilliant lustre like that of metals; in others the lustre resembles that of glass, silk, resin, or wax; while others are dull, or destitute of lustre. The lustre of the diamond is called adamantine.

Colour and Streak.

Minerals may be colourless, white, black, or of any colour, either dull or brilliant. The same mineral may present a variety of similar tints, or even distinct colours. It often happens that a mineral, which when viewed in a solid mass possesses a distinct colour, affords a powder which has a colour different from that of the solid mass, or is even destitute of colour, that is to say, white or nearly so. The dust formed on scratching a mineral with a knife, or by a splinter of quartz, or by a diamond, is termed the '*streak*': it has usually the same colour as the powder. The colour of a mineral and its streak may correspond; or the mineral and its streak may possess different colours; or the mineral may be coloured, while its streak is colourless.

For instance, cinnabar has both a red colour and a red streak.

Specular iron has a black colour, but a red streak.

Sapphire has a blue colour, but a white or colourless streak.

The streak of most minerals is dull and pulverulent, but a few minerals exhibit a shining streak, like that formed on scratching a piece of lead or copper. This kind of streak is distinguished by the name of *Metallic*.

In judging the colour of a mineral a surface quite free from tarnish should be chosen.

The colour of a transparent gem can be seen to best advantage by immersing it in water, about half an inch below the surface.

Hardness.

This character is of great importance in distinguishing minerals; it implies the degree of facility with which the particles may be separated by cutting or scratching. The diamond is the hardest substance known, as it will scratch all others. Talc is one of the softest minerals. Other minerals possess intermediate degrees of hardness. To express how hard any mineral is, it becomes necessary to compare it with some known standard. Ten standards of different degrees have been chosen, and are given in order in the following scale :—

1. Talc.
2. Gypsum.
3. Calc Spar.
4. Fluor Spar.
5. Apatite.
6. Felspar.
7. Quartz.
8. Topaz.
9. Corundum, or Sapphire.
10. Diamond.

The hardness of a mineral may often be found by drawing the point of a steel knife across it. For instance, the slightest pressure will suffice to scratch talc ; fluor-spar is not so easily scratched as calcite ; the greatest pressure is needed to scratch felspar ; and quartz does not yield to the knife at all.

The hardness may also be found by scratching one mineral with another ; thus, the diamond will scratch all other minerals ; corundum scratches topaz, topaz scratches quartz, quartz scratches felspar ; and so on.

If on drawing a knife across a mineral it is impressed as easily as calcite, its hardness is said to be 3. If a mineral scratches quartz, but is itself scratched by topaz, its hardness is between 7 and 8.

In trying the hardness of a mineral a little judgment is necessary ; for instance, a sound portion of the mineral must be chosen ; a sharp angle used in trying to scratch : a streak of dust on scratching one mineral with another may come from the waste of either, and it cannot be determined which is the softer, until after wiping off the dust, and viewing with a lens.

The use of the above scale, however, implies an acquaintance with the ten standard minerals. It is very desirable to have specimens of these minerals for reference. But a collection of the following common minerals, which can easily be procured, will be found quite enough for ordinary purposes, viz. : calc-spar, felspar, quartz, topaz (white or yellow), and corundum or sapphire.

By the test of hardness clear distinctions may be drawn between minerals which resemble each other ; for instance, iron pyrites and copper pyrites are similar in appearance, but copper pyrites can easily be scratched with a knife, whereas iron pyrites is nearly as hard as quartz and cannot be impressed with a knife at all.

In determining the hardness of small stones, it is most convenient to fasten them by heating upon a stick of sealing wax.

Specific Gravity.

By specific gravity is meant the comparative weight of equal bulks. Water is taken as the standard of comparison; the specific gravity of a mineral is a number showing how many times it is, bulk for bulk, heavier than water.

The specific gravity of water is called 1, of gold 19, implying that, if equal bulks of gold and water were taken, the gold would weigh 19 times as heavy as the water. The specific gravity of a mineral can be found by weighing it first in air in the usual manner, and then observing how much of its weight it loses, when suspended from the arm or pan of a balance, and allowed to hang freely in water. If a piece of quartz weighing 26 grains is attached by a hair or thin cotton to the scales, and weighed whilst hanging in water, it will be found to weigh only 16 grains; it thus loses 10 grains, or $\frac{10}{26}$ of its entire weight. Similarly gold would lose $\frac{1}{19}$ of its weight.

Minerals differ very widely in the proportion of weight which they lose in water, but the same mineral invariably loses the same proportion, for instance:

Quartz loses $\frac{10}{26}$ of its weight; topaz $\frac{10}{35}$; sapphire $\frac{10}{40}$; zircon $\frac{10}{45}$; tin ore $\frac{10}{70}$.

These proportions depend upon the specific gravity of these minerals. The specific gravity of water is called 1, of quartz 2·6, of topaz 3·5, of sapphire 4·0, of gold 19.

In determining how much weight a mineral loses in water, a very delicate balance is required when the weight in air is under 10 grains; but for portions weighing heavier than this, a common balance turning readily to a grain, may be used for practical purposes. The mineral must be sound throughout, and free from any pores or cracks, and its surface should be rubbed over with water, before immersing it, to prevent bubbles of air adhering, which would falsify the result. In careful trials distilled or rain water should be used. A trial of specific gravity can have no value, unless it is made on a pure portion of a mineral, quite free from any adhering foreign matter.

A rough estimate of specific gravity can be formed from the feeling of pressure in shaking any mass loosely in the palm of the hand; in this way it can be judged whether the specific gravity is high or low.

RULE.—The rule for finding the specific gravity is to divide the weight of the mineral in air by its loss of weight in water. Example: A piece of quartz weighed 1,398 grains in air, and 862 grains in water; here the loss of weight is 536, and the weight in air divided by this number is 2·6, which is the specific gravity of quartz.

For separating from each other minerals of different specific gravities R. Bréon proposes the use of melted mixtures of lead and zinc chlorides in different proportions, so as to yield liquids ranging from 2·4 to 5·0 in specific gravity.

Sonstadt* has devised a very ingenious and useful method of taking specific gravities of minerals, when a rough and ready method of discriminating between bodies of similar appearance but of different specific gravities is all that is needed. He takes a solution of potassium iodide saturated at the common temperature, and dissolves in it as much iodide of mercury as possible. It will then dissolve more potassium iodide, then more mercuric iodide, and so forth. The iodides dissolve very slowly at the last, and as it is best not to accelerate the solution by the application of heat, considerable time must be allowed when a liquid of maximum strength is required. The solution, after filtering, is fit for use, and it may be obtained without danger of its crystallising above zero, of sp. gr. 3·085 at 12° C. This liquid is transparent, very mobile, filters easily, is of an amber colour, gives no precipitate on addition of water, and does not readily lose or gain

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* 'Chemical News,' March 20, 1874, vol. xxix. p. 127.

water on long exposure to the atmosphere. The solution undergoes no perceptible chemical change by free exposure to the air for many months. It may be diluted to any extent, and then concentrated by heat without injury.

When this liquid is diluted so that quartz will just float in it, any mineral heavier than quartz will of course sink. As many minerals closely resemble quartz in external characters, and can be distinguished more readily by their specific gravity than in any other way, this method of testing the specific gravity furnishes a very quick and certain means of discrimination. A small bottle of the liquid, containing say half an ounce, and carried in the waistcoat pocket, will enable the mineralogist to make a great many examinations in his walks as to whether the specimens examined are above or below a certain specific gravity. The smallest distinctly visible particle of a mineral is enough for a determination. After the bottle becomes clogged with specimens, the liquid may be poured out for further use, and if the washings are added and the whole concentrated there need be no sensible waste.

Mr. Hardman suggests that with this liquid it would be possible to separate completely the three constituent minerals of granite—mica, felspar, and quartz—weigh them, and determine absolutely their percentage.

Professor Church has used Sonstadt's solution extensively for years in the separation of rare minerals from their siliceous gangue. He says he has often identified the minerals of a crushed fragment of rock by introducing a drop of the solution into the 'live box' under the microscope. By using solutions of increasing strength, or adding the solid salt, the felspars, the quartz, and then some of the heavier minerals may be successively brought to the surface and thus into focus.

Fusibility.

Some minerals can be easily fused; others only with difficulty, while others resist the highest heat which can be applied to them. There are such wide differences between the various degrees of fusibility of minerals, that this character helps greatly in distinguishing them. The fusibility is most readily tested by holding a small splinter of the mineral with a forceps in a candle flame, urged by the blowpipe; or the mineral may be laid upon a piece of charcoal, and the flame directed upon it by the blowpipe. Some minerals fly to pieces when heated, others swell up, or give off peculiar and characteristic odours.

Chemical Characters.

The chemical composition of a mineral is one of the most important facts to know respecting it; the various processes for determining this form a science by themselves; but only the tests depending upon the use of the blowpipe will be described here. A great deal can be learnt respecting a mineral by a few simple trials with the blowpipe. The only requirements are a common blowpipe, a candle, a forceps or pliers, a piece of No. 7 platinum wire, two inches long, dried sodium carbonate, dried borax, and potassium cyanide. The charcoal selected for these experiments should be free from cracks and openings. By dry sodium carbonate is meant not merely dry to the touch, but quite free from water; this may be prepared from recrystallised common washing soda, by expelling the water which it contains; the washing soda is put in a shallow clean iron dish, and placed over a clear fire until a white dry powder is formed; too strong a heat might fuse the dry powder. A quarter of an ounce may be kept in a well-corked bottle or tube for use. Sodium bicarbonate may be used instead without previous heating; or if the bicarbonate be moderately heated, it loses weight, and becomes sodium carbonate, quite free from water like the above.

The borax is to be dried in the same way; a quarter of an ounce will be enough; it is convenient to keep the platinum wire in the same tube. Unless these tubes are well corked these chemicals reabsorb moisture. For testing tin ore it is useful to have a little potassium cyanide kept in a bottle with the cork and rim well covered with melted bees'-wax; it would otherwise liquefy, by absorption of moisture, and become useless. It is a most dangerous poison, and the greatest caution must be observed in its use.

Three kinds of effect can be produced by the blowpipe; *first*, it can be used as a source of heat for testing fusibility; *secondly*, it can add oxygen to a mineral; *thirdly*, it can take oxygen away.

The three principal means of chemically testing minerals before the blowpipe are (1) with borax, (2) on charcoal, usually with the addition of sodium carbonate; (3) by holding in the point of oxidation.

EXPERIMENT No. 1.—Many metals impart a colour to fused borax, by which their presence can be recognised. To try this experiment a bead of fused borax must first be obtained on the platinum wire. The end of the wire is bent into a loop or ring about the twelfth part of an inch in diameter. The wire is then heated in the blowpipe flame, and dipped whilst hot into the borax; the portion of borax that adheres is then fused on to the wire in the blowpipe flame, and the hot wire is again dipped; this is repeated until the loop contains a glass-like bead of fused borax. If the bead has become cloudy, the soot causing this may be burned off in the oxidising point of the flame. Having thus obtained a clear, colourless, transparent bead, the next step is to add to it a minute portion of the mineral which is to be tested. By touching a little of the finely pulverised mineral with the borax bead, while softened by heat, enough will adhere to the bead for a first trial. The bead is then kept at a white heat in the oxidising point of the flame for a few seconds, and on removal its colour is noted, both whilst hot and when cold. If no colour is imparted a fresh trial may be made with a larger quantity of the powder; but if the bead is opaque owing to the depth of colour, as is often the case, a fresh experiment must be made, using a still smaller quantity of the powder. The colour can only be fairly judged in a perfectly transparent bead. If no colour can be obtained in the oxidising flame, further experiment with the borax bead is needless; but if a colour is obtained, it is then advisable to try the effect of the reducing flame upon the same bead. The following observations and inferences may result from this test:—

Colour of Bead in		
OXIDISING.	REDUCING.	*Presence of*
Green (hot): Blue (cold).	Red.	COPPER.
Blue (hot and cold).	Blue.	COBALT.
Amethyst.	Colourless.	MANGANESE.
Green.	Green.	CHROMIUM.
Red or Yellow (hot). Yellow or colourless (cold).	Bottle Green.	IRON.
Violet (hot); Red-Brown (cold).	Grey and Turbid, difficult to obtain.	NICKEL.

This mode of testing may often be used to prove the presence of the above-mentioned metals.

It requires some practice before trustworthy results can be obtained in reducing; the reduced bead, if brought out of the flame at a white heat into the air, may at once oxidise; but this may be prevented by placing it inside the dark inner cone of an ordinary candle flame, and allowing it to cool partially there.

EXPERIMENT No. 2.—The mode of testing with sodium carbonate on charcoal is performed as follows:—A sound piece of charcoal half an inch square is chosen, and a neat cavity is scooped out on its surface, into which is placed a mixture containing the pulverised mineral to be tested, with three or four parts of sodium carbonate, the whole not exceeding the bulk of a pea; after lightly pressing the mixture into the cavity, the blowpipe flame may be cautiously applied to it; and afterwards, when the mixture no longer shows a tendency to fly off, the charcoal may be advanced nearer to the blowpipe, and finally be kept at as high a temperature as possible in the reducing part of the flame.

In testing for tin ore, a piece of potassium cyanide about the size of a pea may be placed upon the mixture after the first application of heat, and the further application of heat may then be continued.

This treatment is designed to extract metals from minerals; it favours in the highest degree the removal of oxygen. But like the borax test, it is limited in its application; it can only be used to detect certain metals. The failure of the test, in any case, must not be looked upon as a conclusive proof of the absence of the particular metal sought: for instance, copper can be easily abstracted from copper carbonate by this test, but not from copper pyrites. Still the test is a most valuable and indispensable one to the mineralogist.

The test is complete when the metal is obtained as a globule, in the cavity of the charcoal; in many cases the globule will be found surrounded with the oxide of the metal, forming an incrustation on the charcoal; and the colour of such incrustation should be carefully noted, both at the moment of removal from the flame, and after cooling. By pressing the globule between smooth and hard surfaces, it can be determined whether the metal is flattened out (or malleable), or crushed to pieces (brittle).

The following observations and inferences may result from this test:—

GLOBULE.	INCRUSTATION.	*Presence of*
Yellow (malleable).	None.	GOLD.
White do.	Do.	SILVER.
Red do.	Do.	COPPER.
White do.	White.	TIN.
Do. do.	Red (hot); Yellow (cold).	LEAD.
Do. (brittle).	Do. do.	BISMUTH.
None.	Yellow (hot); White (cold).	ZINC.
White, brittle, giving off fumes when removed from the flame.	White.	ANTIMONY.

EXPERIMENT No. 3.—In addition to these substances there are others which occur abundantly in minerals, and which may be recognised by the blowpipe with the greatest ease; for instance, sulphur and arsenic. These may be discovered by heating a fragment of the mineral, supported on a piece of charcoal, or held in a forceps, in the oxidising point of the flame, and noticing the odour which is given off; a smell of burning sulphur indicates that the mineral contains that substance, and white fumes having a garlic odour indicate the presence of arsenic.

Mercury, antimony, and other substances may escape as fumes when heated in this manner.

Requirements for Testing Minerals.

The requirements already mentioned are blowpipe, candle, forceps, platinum wire, dried borax, dried sodium carbonate, potassium cyanide, charcoal; also the minerals for comparisons of hardness, namely, calc-spar, felspar, quartz, topaz, sapphire. In travelling it is well to dispense with the grain scales and weights for taking specific gravities. It would be dangerous to attempt to travel with nitric acid. It addition to these it will be found useful to have a steel pocket-knife, one blade of which should be kept magnetized, which may be easily done by touching it occasionally with a strong magnet; a small iron spoon for heating minerals, such as cinnabar, over a candle flame ; also a small pocket lens.

DESCRIPTION OF MINERALS.

QUARTZ AND THE SILICATES.

Perhaps no other mineral presents such a great variety of forms and colours as quartz, and no mineral occurs in greater abundance. When pure it consists of silica only, but it is usually contaminated with other ingredients, principally alumina, iron, and clay. The impure varieties of quartz compose most of the pebbles and sand of the soil.

Out of the six hundred minerals at present known, at least two hundred and fifty contain silica in greater or less proportion, and are hence termed *silicates.*

Silicates are indispensable in the manufacture of glass, porcelain, earthenware, and for other purposes; but they exist in such profusion that their economic value is exceedingly trifling. The great majority of the silicates are purely objects of scientific interest; a few forms of silica are esteemed as gems, such as the precious opal, and some varieties of quartz, the topaz, the emerald, the zircon or hyacinth, the garnet and carbuncle, the tourmaline, and some others. Handsome varieties of serpentine are often used in ornamental stonework.

1. QUARTZ.

Chemical Composition.—Silica.

Crystallized in six-sized prisms, terminated by pyramids. Sides of the crystal often marked across with fine parallel lines. Transparent or opaque. Colourless, or of various colours. Glassy lustre. Fracture irregular, conchoidal. Specific gravity, 2·6. Hardness, 7. Cannot be scratched with a knife; scratched by topaz, zircon, sapphire, and diamond, and thus easily distinguished from these gems. Quartz scratches glass with facility; felspar and many other minerals can be scratched by quartz. The irregular fracture, the fine parallel markings, and the hardness generally suffice to distinguish quartz.

Infusible in the *blowpipe flame.*

The following are the chief varieties of quartz; the differences are due either to their mode of formation or the presence of impurities. They have the same general characters as pure quartz.

1. TRANSPARENT VARIETIES :—

ROCK CRYSTAL.—Pure, transparent, colourless quartz. Used for spectacle glasses and ornaments.

AMETHYST.—Transparent. Of a rich violet or purple colour. Used as a gem.

ROSE QUARTZ.—Seldom perfectly transparent. Of a rosy tint.

CAIRNGORM, or SMOKY QUARTZ, is transparent, with a smoky tinge.

FALSE TOPAZ has a yellow pellucid colour, distinguished from topaz and oriental topaz by its inferior hardness.

2. SEMI-TRANSPARENT VARIETIES :—

CHALCEDONY.—Pale colour and waxy lustre. Resembling icicles in some instances, the frothy surface of a liquid in others.

Carnelian and **Sard** have red tints.

Agate exhibits cloudy or moss-like patches, or a number of lines arranged in circular and angular patterns.

Onyx or **Sardonyx** is made up of regular layers one above another of different colours, often black, white, and red. It is much used for cameos.

Flint or **Hornstone.**—Common dull varieties.

3. **Opaque Varieties :—**

Jasper is quartz rendered opaque by clay, iron, and other impurities ; it is of a red, yellow, or green colour ; sometimes the colours are arranged in ribands, or in other fantastic forms. It is used for ornamental work.

Bloodstone is green jasper with splashes of red resembling blood-spots.

2. OPAL.

Chemical Composition.—Silica and water.

Never crystallized. Fracture conchoidal. Specific gravity, 2·2. Hardness, 6. Can be scratched by quartz, and thus distinguished from it.

Infusible. It is generally milk-white.

Precious or Noble Opal exhibits a beautiful play of colours, and is a valuable and rare gem. The common varieties are of no value.

3. TALC.

Chemical Composition.—Silica, magnesia, water (protoxide of iron).

Usually in irregular layers. Nearly opaque. White or green ; pearly lustre ; greasy feel. Specific gravity, 2·7. Hardness, 1. Easily impressed by the nail. But impure varieties are much harder.

Infusible. [Yields no water when heated in a glass tube. Is not attacked by boiling sulphuric acid.]

Its greasy feel and pearly lustre readily distinguish it.

Mica, which is often confounded with it, is not so soft, has not a greasy feel, and can be split into very thin transparent layers. Steatite is a variety often applied to useful purposes.

4. CHLORITE.

Chemical Composition.—Silica, magnesia, alumina, protoxide of iron, water.

Often forming rocks. Opaque. Green of various shades. Lustre pearly or dull. Hardness, 1 to 2. Very easily cut with a knife.

Infusible. [In glass tube yields water.] Boiling sulphuric acid extracts from it magnesia, alumina, and ferrous oxide.

Abundant. Of no value.

5. SERPENTINE.

Chemical Composition.—Silica, magnesia, water (ferrous oxide).

Often forming rocks. Never crystallized. Opaque. Green. Lustre resinous or dull. Streak white. Hardness, 3. Can be cut with a knife. Specific gravity, 2·5.

Infusible except in thin edges ; turns white in blowpipe flame. [Powder decomposed by sulphuric acid like chlorite. Gives off water in glass tube.]

Some varieties form handsome stone for slabs and ornamental work.

Meerschaum, which is soft and earthy, and nephrite (the New Zealand Maori greenstone), which is as hard as quartz, both contain silica and magnesia.

6. AUGITE AND HORNBLENDE.

Chemical Composition.—Silica, lime, magnesia, ferrous oxide (occasionally alumina and fluorine).

In four, six, or eight-sided prisms, exhibiting cleavage in some directions. Usually opaque. Green, black, or white. Glassy, pearly, or resinous lustre. Specific gravity, 3 to 3·5. Hardness, 5 to 6. Can be scratched with a knife, using pressure. Scratched by quartz.

Dark varieties visible.

Augite usually occurs in stout six or eight-sided prisms with roof-like terminations; hornblende in long slender prisms. Asbestos is a variety composed of separable fibres like flax.

Abundant in igneous and other rocks. Of no value. Asbestos is used as a fire-proof material.

7. CHRYSOLITE, OR OLIVINE.

Chemical Composition.—Silica, magnesia, protoxide of iron.

In prisms; but usually in grains or lumps resembling bottle glass. Transparent or opaque. Green, yellow, or black. Glassy lustre. Fracture conchoidal. Hardness, 6 to 7. Cannot be scratched with a knife. Specific gravity, 3·4.

Infusible.

In appearance, hardness, and infusibility may resemble tin ore, but is very much lighter in weight. Differs from obsidian (volcanic glass) in its infusibility and superior hardness.

Occurs in basalt and lava. Of no value.

8. TOURMALINE.

Chemical Composition. — Silica, alumina, magnesia, boracic acid, fluorine, oxides of iron (lime and alkalies).

In prisms, with three, six, nine, or more sides, furrowed lengthwise, terminating in low pyramids. Commonly black and opaque; rarely transparent, and of a rich red, yellow, or green colour. Glassy lustre. Fracture uneven. Specific gravity, 3·1. Hardness, 7 to 8. Cannot be scratched with a knife. Not scratched by quartz.

Infusible.

When the smooth side of a prism is rubbed on cloth it becomes electric and can attract a small piece of paper; if the prism is as wide as a pipe-stem, when one side is heated for a moment in the blowpipe flame the opposite side becomes electric and can attract paper until the heat spreads uniformly through the crystal. (On this account tourmaline is said to be *pyro-electric*.)

Occurs in granite and slate. Of no value; except the fine-coloured transparent varieties, which are used as gems and for optical purposes.

9. GARNET.

Chemical Composition.—Silica, alumina, lime, iron, magnesia, manganese.

Crystallized in dodecahedrons, never in prisms. Transparent or opaque. Generally red; also brown, green, yellow, black, white. Glassy or resinous lustre. Fracture conchoidal or uneven. Specific gravity, 3·5 to 4·3. Hardness, 6·5 to 7·5. Cannot be scratched with a knife.

Fusible with more or less difficulty. Red varieties impart a green colour to borax bead owing to presence of chromium.

Common in gneiss and schists. Fine-coloured transparent varieties (carbuncle, cinnamon stone, almandine) are used in jewellery.

10. TOPAZ.

Chemical Composition.—Silica, alumina, fluorine.

In prisms, sometimes furrowed lengthwise, variously terminated, breaking easily across with smooth brilliant cleavage.

Transparent or semi-transparent. White, yellow, greenish, bluish, pink. Glassy lustre. Specific gravity, 3·5. Hardness, 8. Scratches quartz. Is scratched by sapphire.

Infusible, but often blistered and altered in colour by heat. When smooth surfaces are rubbed on cloth they become strongly electric and can attract small pieces of paper, but rough surfaces do not show this. The brilliant cleavage of topaz distinguishes it from tourmaline and other minerals.

Occurs in granite. Used in jewellery. The topaz becomes electric by friction much easier than other gems, such as the balas ruby, which it may resemble. The white topaz resembles the diamond; but, unlike diamond, it can be scratched by sapphire.

11. BERYL, OR EMERALD.

Chemical Composition.—Silica, alumina, glucina.

In six-sided prisms. Usually green. Transparent or opaque. Glassy lustre. Fracture uneven. Specific gravity, 2·7. Hardness, 7 to 8. Scratches quartz.

Infusible, or nearly so, but becomes clouded by heating.

Occurs in granite and schist. Valuable for jewellery when transparent and rich glass green (emerald), or sea green (aquamarine). Opaque crystals of large size, exceeding a ton in weight, have been found in North America.

12. ZIRCON, OR HYACINTH.

Chemical Composition.—Silica, zirconia.

In square prisms, terminated by pyramids, and in octahedrons. Often found in pebbles and grains. Transparent or opaque. Wine or brownish red, grey, yellow, white. Glassy lustre. Fracture usually irregular, but in one direction it can be split so as to exhibit a smooth, even cleavage face having an adamantine lustre like the diamond. Specific gravity, 4·0 to 5·0. Hardness, 7·5. Scratches quartz; is scratched by topaz.

Infusible; the red varieties, when heated before the blowpipe, emit a bluish phosphorescent light, and become permanently colourless.

Occurs in syenite, granite, basalt. Clear crystals used in jewellery, in jewelling watches, and in imitation of diamond. It may be distinguished from diamond by its inferior hardness, and in not becoming so readily electric by friction.

13. FELSPAR.

Chemical Composition.—Silica, alumina, potash or soda (lime).

Crystallized or in irregular masses. Opaque. Usually flesh-red, or white, or of various dull tints. Glassy or pearly lustre. Fracture irregular; but in some directions it splits with an even, glimmering, cleavage face. Specific gravity, 2·3 to 2·8. Hardness, 6. Easily scratched by quartz. Cannot be scratched with a knife without greatest pressure.

In thin edges fusible with difficulty.

Abundant in granitic and porphyritic rocks. No value. By its decomposition it forms porcelain clay or kaolin.

14. MICA.

Chemical Composition.—Silica, alumina, magnesia, potash, iron.

Always crystallized in thin plates, which may be split into extremely thin flexible layers. Transparent in thin layers. Brown or black. Lustre glassy, pearly, or metallic. Streak white. Specific gravity, 2·7 to 3·1. Hardness, 2 to 2·5. Very easily scratched with a knife.

Infusible. Differs from talc in not having a greasy feel, in being harder, flexible, and affording thinner layers perfectly transparent.

Abundant in granite and schist; fine particles common in sandstone. Applied to various uses when in large plates, otherwise of no value. Was formerly used instead of glass in windows.

15. ZEOLITES.

This name is used for a large class of silicates, comprising from fifty to a hundred different minerals, which all contain water as an essential ingredient, and which melt readily before the blowpipe, and boil up owing to the disengagement of steam. They occur filling pores and cavities in basalt, lava, and other rocks. They are usually white and well crystallized. Can be scratched with a knife. Of no value. Silica, alumina, lime, soda, potash, and water are the principal ingredients.

16. CORUNDUM, OR SAPPHIRE.

Chemical Composition.—Alumina.

In six-sided prisms, often irregularly shaped. Sometimes in granular masses. Transparent or opaque. Blue, black; also red, green, yellow, white. Glassy lustre, sometimes pearly. Fracture uneven or conchoidal. Specific gravity, 3·9 to 4·2. Hardness, 9. Easily scratches topaz and quartz. In hardness it is only inferior to the diamond. Infusible.

Occurs in river sands; in granite, felspar, magnetic iron, basalt. As a gem it stands next in value to the diamond, but its tint must be brilliant and clear. The blue variety is called *Sapphire*, the most esteemed shade being deep velvet blue; the blood-red variety is the *Oriental ruby*, which can be easily distinguished from other red gems by its superior hardness; the bright yellow variety is the *Oriental topaz*, distinguished by its hardness from the topaz, yellow tourmaline, and false topaz; the bright green is the *Oriental emerald*; the bright violet, *Oriental amethyst*; these varieties readily scratch the emerald (No. 11) and amethyst (see quartz, No. 1); one variety exhibits a six-rayed star inside the prism, and it is called the *Asterias*. Dull crystals are called *corundum*, and grey or black granular varieties *emery*; these two kinds are used for polishing powder. The ruby is the most highly prized form of this mineral.

17. SPINEL.

Chemical Composition.—Alumina, magnesia.

In octahedrons, occurring only crystallized. Usually red and transparent; also white, blue, green, yellow, brown, black; the dark shades usually opaque. Lustre glassy. Fracture conchoidal. Specific gravity, 3·5 to 4·0. Hardness, 8. Scratches quartz.

Infusible, and thus distinguished from garnet which it may resemble. Colour altered transiently by heat. Distinguished from zircon by its superior hardness and inferior specific gravity.

Occurs in river sand; in igneous rocks, gneiss, limestone. The bright transparent varieties are used in jewellery. When red it forms the *common* or *spinel*, or *balas-ruby*, which is distinguished from the Oriental ruby by its inferior hardness; bright green, *chlorospinel*; orange, *rubicelle*; violet, *almandine-ruby*; black, *pleonast*.

18. CHRYSOBERYL.

Chemical Composition.—Alumina, glucina.

In prisms or tables. Transparent or semi-transparent. Green. Lustre glassy. Fracture conchoidal; imperfect cleavage. Specific gravity, 3·5 to 3·8. Hardness, 8·5.

Infusible and unaltered before the blowpipe.

Distinguished from beryl by its specific gravity, its tabular crystallization, and its entire infusibility.

Occurs with beryl in river sand, gneiss and granite. Pellucid and fine opalescent varieties are used as gems.

19. DIAMOND.

Chemical Composition.—Carbon.

In octahedrons, tetrahedrons, dodecahedrons, and forms related to these; the faces of the crystal sometimes curved. Transparent. Colourless, yellow, red, green, blue, white, brown, or black. Lustre adamantine. Breaks with smooth cleavage planes parallel to the octahedral faces. Specific gravity, 3·5; loses 10-35ths of its weight in water. Hardness, 10. It is the hardest substance known, and scratches all other minerals and gems.

Infusible. It burns and is consumed at a high temperature.

Becomes strongly electric when rubbed, and can then attract light objects; other gems do not exhibit this property unless polished. Some varieties, after exposure to the sun, are said to give out light when placed in the dark.

The distinguishing characters of diamond are, its hardness, crystalline form, clean fracture, its brilliant reflection and adamantine lustre, the facility with which it may be electrified by friction, and a peculiar sound on rubbing together.

Diamonds have been found in quartz-conglomerate and micaceous sandstone, but are mostly obtained in river beds.

20. GRAPHITE, OR BLACKLEAD.

Chemical Composition.—Carbon.

In six-sided prisms; but usually in uncrystallized wavy layers. Opaque. Black. Lustre metallic. Specific gravity, 2. Hardness, 1 to 2. Very easily cut with a knife. Has a greasy feel; marks paper like a lead pencil.

Infusible. Burns slowly away.

Molybdenite and foliated tellurium resemble graphite; the former has a paler colour than graphite, and the latter is very easily fusible.

Occurs in gneiss and slate. Valuable for lead pencils and crucibles.

21. COAL.

Coal and carbonaceous shale differ from all the minerals which they may resemble by burning before the blowpipe and leaving a white or brown ash. The quantity of ash affords an estimate of the purity of the coal.

22. APATITE.

Chemical Composition.—Phosphoric acid, lime, fluorine.

In six-sided prisms. Also in masses. Transparent or opaque. Usually green. Sometimes white, yellow, blue, red, brown. Lustre resinous. Fracture conchoidal or uneven. Specific gravity, 3·2. Hardness, 5. Can be scratched with a knife, using pressure.

Infusible, except on very thin edges. Some kinds phosphoresce when heated. The pure mineral in powder dissolves slowly in nitric acid without effervescence. The crystals may resemble beryl, which, however, is too hard to be scratched with a knife.

Occurs in gneiss, slate, limestone. Of value from its use in the manufacture of artificial manures.

23. FLUOR.

Chemical Composition.—Fluoride of calcium.

In cubes or octahedrons. Also in masses. Transparent or opaque. White or light violet, blue, green or yellow; sometimes layers of different tints in the same piece. Lustre glassy. Breaks with smooth cleavage planes parallel to the octahedral faces. Specific gravity, 3·0 to 3·2. Hardness 4. Can be scratched with a knife, but not so easily as calcite.

Fusible with difficulty; generally flies to pieces when heated. Some varieties phosphoresce.

Occurs in veins with lead and silver ores. Used in etching glass, and as a flux in smelting; sometimes for ornaments, but is too brittle. Abundant in many countries, and of little value.

24. CALC-SPAR, OR CALCITE.

Chemical Composition.—Carbonic acid, lime.

In rhombohedrons and other crystalline forms. Also massive, earthy, or fibrous. Transparent or opaque. White when pure; often tinted. Lustre glassy, or dull. Breaks with smooth cleavage planes parallel to the rhombohedral faces. Specific gravity, 2·5 to 2·8. Hardness, 3. Easily scratched with a knife, streak white.

Infusible before the blowpipe, but emits a strong light. When burned, as in a kiln, it forms quicklime. Effervesces when vinegar is poured upon it. It completely dissolves in nitric acid with rapid effervescence.

Calc-spar is one of the most abundant minerals; it occurs in cavities and veins of all kinds of rock. The term calc-spar or calcite is restricted to the crystallized variety. In an imperfectly crystallized and compact form it exists in large rocky masses and beds; all marbles and limestones consist of it, mixed more or less with impurities. Chalk and stalactites are nearly pure calcium carbonate. All varieties of calcium carbonate may be easily distinguished by being scratched with a knife, giving a white streak whatever the colour of the mass may be, by effervescing with an acid, and by being infusible.

25. MAGNESITE.

Chemical Composition.—Carbonic acid, magnesia.

In rhombohedrons. Also globular, compact, earthy. Transparent or opaque. White, yellow, brown. Lustre glassy. Cleavage parallel to rhombohedral faces. Specific gravity, 2·8 to 3·0. Hardness, 4 to 5.

Infusible. Dissolves in nitric acid, with very slow effervescence. Does not yield quicklime when burnt.

Occurs with serpentine and limestone. Used in preparing Epsom salts.

26. DOLOMITE.

Chemical Composition.—Carbonic acid, lime, magnesia.

In rhombohedrons, faces often curved. Often granular or massive. White, or dull-tinted. Glassy or pearly. Specific gravity, 2·8 to 2·9. Hardness, 3·5 to 4.

Infusible. Effervesces in nitric acid, and dissolves more slowly than calc-spar. Yields quicklime when burnt. Occurs in extensive beds of various ages like limestone. Used as a building stone, and in the manufacture of Epsom salts. Difficult to distinguish from calcite without chemical analysis.

27. ARAGONITE.

Chemical Composition.—Same as calc-spar.

It differs from calc-spar in its crystalline form, which is usually difficult to discern. It often occurs in fibrous clusters or in tangled branches. Hardness, 3·5 to 4·0. Specific gravity, 2·9.

It has the general characters of calc-spar, but may be distinguished from it by falling to powder in the blowpipe flame, as well as by its superior hardness.

28. ROCK SALT.

Chemical Composition.—Sodium chloride.

Has the characters of ordinary table salt, but is more or less impure. Occurs in beds interstratified with sandstones and clays, which are usually of a red colour and associated with gypsum. In the county of Cheshire, where salt mines are worked, the surface indications are brine springs supporting a vegetation like that near the sea-coast; also occasional sinking of the soil caused by the removal of the subterranean bed of salt, by spring water in some cases, and by mining operations in others. Small and unimportant quantities of salt are often found encrusting various rocks in dry weather.

29. SOLUBLE SULPHATES.

Aluminium sulphate alone, or combined with potash (alum), and magnesium sulphate (Epsom salts), are often found encrusting rocks. They are soluble in water and easily distinguished by their taste.

30. NITRE.

Chemical Composition.—Potassium nitrate.

Nitre or saltpetre is another soluble mineral. It has a cooling taste. It can be easily distinguished by the vivid manner in which it burns on red-hot charcoal.

31. GYPSUM, SELENITE, OR ALABASTER.

Chemical Composition.—Sulphuric acid, lime, water.

In prisms with oblique terminations; sometimes resembling an arrowhead. Transparent or opaque. White or dull-tinted. Glassy, pearly, or satin lustre. Cleavage occurs easily in one direction. Specific gravity, 2·3. Hardness, 2. Very easily cut with a knife.

Fusible with difficulty. In the blowpipe flame it becomes white and opaque without fusing, and can then be easily crumbled between the fingers. Nitric acid does not cause effervescence.

Occurs in fissures and in stratified rocks, often forming extensive beds. When burnt it forms plaster of Paris; it is also used for ornaments, and as a manure.

32. HEAVY SPAR, OR BARYTES.

Chemical Composition.—Sulphuric acid, baryta.

In tabular glassy crystals. Also in dull masses. Transparent or opaque. White or tinted. Specific gravity, 4·3 to 4·8; its great comparative weight readily distinguishes it. Hardness, 2·5 to 3·5.

Splinters fly off the crystals when heated in the blowpipe flame. Fusible with difficulty. Not acted upon by acids.

Occurs with various ores. Used as a white paint.

33. SULPHUR.

Crystallized or massive. Yellow. Resinous lustre. Specific gravity, 2·1. Hardness, 1·5 to 2·5. Fusible; burns with a blue flame and well-known odour. Occurs in volcanic regions, and in beds of gypsum.

34. TIN ORE.

Chemical Composition.—Tin 78·4, oxygen 21·6.

In four-faced prisms and pyramids, having an adamantine lustre. Also in masses and grains (stream tin) usually dull; sometimes resembling wood (wood tin). Semitransparent or opaque. Brown or black; streak and powder pale brown. Fracture uneven. Specific gravity, 6·8 to 7·0; the great comparative weight is an important character to observe in distinguishing tin ore from other minerals. Hardness, 6·0 to 7·0. Cannot be scratched with a knife, and may thus be distinguished from blende, which it resembles in lustre and infusibility.

Infusible. When mixed in powder with sodium carbonate, placed on charcoal and covered with a small piece of potassium cyanide, and then heated in the blowpipe flame, a malleable globule of metallic tin is obtained.

Occurs in veins, and disseminated in granite, schist, slate, and porphyry; and in alluvial deposits. It is a valuable ore, and the sole commercial source of the metal.

35. MOLYBDENITE.

Chemical Composition.—Molybdenum 58·9, sulphur 41·1.

In thin plates, like graphite (No. 20). Lustre metallic. Colour, lead grey. Specific gravity, 4·5 to 4·6. Hardness, 1·0 to 1·5. Easily scratched by the nail.

Infusible. Tinges blowpipe flame faint green. Heated on charcoal for a long time, it gives off a faint sulphurous odour, and becomes encrusted white.

Occurs in granite, syenite, and chlorite schist. Not applied to any particular uses.

36. BISMUTH.

Chemical Composition.—Metallic bismuth.

Sometimes crystallized in rhombohedrons closely resembling cubes, but generally massive. Lustre metallic. White, with a tinge of red, liable to tarnish. Brittle. Specific gravity, 9·6 to 9·8. Hardness, 2·0 to 2·5. Easily scratched with a knife.

Easily fusible. Sometimes gives off an odour of garlic, owing to admixture of arsenic.

Occurs with cobalt, silver, and tin ores in granite and slate rocks. Bismuth is a very valuable metal.

37. ANTIMONY SULPHIDE.

Chemical Composition.—Antimony, 72·9, sulphur, 27·1.

Usually in long columnar or fibrous crystals. Also massive and granular. Lustre metallic. Lead colour. Often tarnished. Streak metallic. Specific gravity, 4·6 to 4·7. Hardness, 2. Very easily scratched with a knife.

Easily fusible. Before blowpipe gives off white vapours and an odour of sulphur, and is entirely volatilised. When the corner of a large piece of ore is fused, the border of the fused part is often tinted red. When heated on charcoal with cyanide of potassium, it gives a globule of metallic antimony, which is brittle, has a crystalline surface, burns when strongly heated, emitting white fumes, and can be entirely volatilised.

Occurs in veins in granite and slate, alone, or with ores of silver, lead, and other metals. This ore is the principal commercial source of the metal.

38. ARSENIC.

Chemical Composition.—Metallic arsenic.

Seldom distinctly crystallized. Usually in fine granular or spherical masses. Colour white, usually with a black tarnish. Streak white, metallic. Brittle. Specific gravity, 5·7 to 5·8. Hardness, 3·5.

Before the blowpipe it quickly volatilises without fusing, giving off white fumes having an odour of garlic.

Occurs in veins with lead and silver ores.

39. ARSENIC SULPHIDE.

Chemical Composition.—Sulphur, arsenic.

In crystals, or massive. Yellow or red. Semi-transparent or opaque. Resinous or glassy lustre. Specific gravity, 3·5. Hardness, 1·5. Volatilised before the blowpipe with a blue flame.

Occurs in veins with arsenical ores; in beds of clay, limestone, and gypsum, and has been observed in lava. Used as a pigment and in making fireworks, but objectionable for each of these uses, owing to its highly poisonous character.

40. NATIVE IRON.

Chemical Composition.—Iron, with a small percentage of nickel.

Occurs in meteorites. Resembles ordinary iron. Malleable. Is attracted by a magnet. Specific gravity, 7·0 to 7·8.

41. IRON PYRITES.

Chemical Composition.—Iron, 46·7; sulphur, 53·3.

In cubes and allied forms; sides often marked by fine parallel lines. Also massive. Brass yellow. Lustre metallic. Fracture irregular. Specific gravity, 4·8 to 5·1. Hardness, 6 to 6·5. Cannot be scratched with a knife; scratched by quartz; scratches glass with great facility. Strikes fire with steel (the origin of the term *pyrites*).

Before the blowpipe it burns with a blue flame, giving off an odour of sulphur, and ultimately fuses into a black magnetic globule.

Abundant. Used as a source of sulphur and sulphuric acid; occasionally auriferous. This ore and arsenical pyrites form the 'mundic' of miners. It is easily distinguished from copper pyrites by its hardness; copper pyrites being easily cut with a knife. Distinguished from gold by its hardness and in not being malleable, and in giving off sulphurous odours in the blowpipe flame.

42. ARSENICAL PYRITES (MISPICKEL).

Chemical Composition.—Iron, 34·4; arsenic, 19·6; sulphur, 46·0.

In flattened prisms. Also massive. White. Lustre metallic. Streak grey. Fracture uneven. Specific gravity, 6·0 to 6·3. Hardness, 5·5. Cannot be scratched with a knife; scratched by quartz.

Heated before the blowpipe it gives off white arsenical fumes of a garlic odour, and ultimately fuses into a black globule.

Abundant in mining districts; sometimes auriferous.

This ore and iron pyrites form the 'mundic' of miners.

43. MAGNETIC IRON.

Chemical Composition.—Iron, 72·4; oxygen, 27·6.

In octahedrons and dodecahedrons. Also in masses (*lodestone*) and in grains. Black. Lustre metallic. Streak or powder black. Fracture irregular. Specific gravity, 5·0 to 5·2. Hardness, 5·5 to 6·5. Not scratched with a knife. Magnetic; it can attract iron filings. Is itself attracted by a magnet.

Infusible. With borax bead gives the indications of iron.

Occurs in many rocks, sometimes in beds, or forming mountainous masses; common in river sands. Used as an ore of iron.

44. SPECULAR IRON, HEMATITE, OR MICACEOUS IRON.

Chemical Composition.—Iron, 70; oxygen, 30.

In tabular crystals or scales. Also fibrous, massive, granular, earthy. Colour black. Streak or powder, red. Lustre, metallic or dull. Specific gravity, 4·5 to 5·3. Hardness of crystals, 5·5 to 6·5. Not scratched with a knife. Earthy varieties softer, and can be scratched with a knife.

Infusible. With borax bead gives the indications of iron. An abundant ore of iron. Often gradually changes into red or brown ochre.

45. RED FERRIC OXIDE, OR RED OCHRE.

Chemical Composition.—Iron oxide, and more or less water.

An uncrystalline earthy variety of the preceding, often mixed with clay. Colour, bright or dull red. Can generally be scratched with a knife.

Blackens when heated, but regains its red colour on cooling. With borax bead gives the indications of iron. Abundant ore of iron.

46. BROWN FERRIC OXIDE (YELLOW OR BROWN OCHRE).

Chemical Composition.—Iron oxide, water.

Like the last, but of a brown, yellow, or black colour. Earthy, fibrous, stalactitic. Scratched with a knife.

Blackens before the blowpipe. With borax bead gives the indications of iron. An abundant ore of iron.

47. TITANIC IRON.

Chemical Composition.—Iron oxides and titanic acid in variable proportions.

In octahedrons or in tabular plates. Also in grains. Black. Lustre metallic. Streak or powder black. Specific gravity, 4·5 to 5·3. Hardness, 5 to 6·5. Not scratched with a knife.

Infusible. With borax gives the indications of iron. With microcosmic salt, which is often used instead of borax in an exactly similar way, it gives a red bead in the reducing part of the flame, but rather a large quantity of the mineral must be used to obtain this result.

It is sometimes magnetic.

Its black streak or powder distinguishes it from specular iron, which it often resembles. Common in some river sand.

48. CHROMIC IRON.

Chemical Composition.—Chromium sesquioxide, ferrous oxide (alumina, magnesia).

In octahedrons. Usually massive. Black. Lustre faintly metallic. Streak or powder dark brown. Fracture irregular. Specific gravity, 4·4 to 4·6. Hardness, 5·5. Not scratched with a knife.

Infusible. With borax bead gives the characteristic indications of chromium.

Occurs in serpentine. Used in the preparation of chromium colours.

49. GREENEARTH.

Chemical Composition.—Iron silicate, and other ingredients. Has a green earthy appearance, often resembling an ore of copper, but is readily distinguished from copper by blowpipe tests, and by not forming a blue solution in nitric acid.

50. IRON CARBONATE.

Chemical Composition.—Carbonic acid, 37·9; ferrous oxide, 62·1.

In rhombohedrons; faces often curved. Usually massive, globular, fibrous, or encrusting. Light or dark brown. Glassy or pearly lustre. Streak white. Specific gravity, 3·7 to 3·9. Hardness, 3·5 to 4·5. Scratched with a knife.

Infusible. Blackens when heated. With borax bead gives the indications of iron. Dissolves in nitric acid with effervescence when heated.

Occurs in beds and nodules in stratified rocks; in veins and cavities. It is often mixed with clay (clay ironstone). Abundant ore of iron.

51. MANGANESE ORES.

Chemical Composition.—Various manganese oxides.

Crystallized or massive. Black. Lustre unmetallic; dull or shining. Powder or streak brown or black. Specific gravity, 4 to 5. Hardness generally below 3. Very easily scratched with a knife.

Infusible. With borax bead gives the characteristic indications of manganese. Widely distributed. Used in chemical manufactures.

52. ARSENICAL NICKEL.

Chemical Composition.—Nickel 44, arsenic 56.

Usually in masses of a pale copper colour and metallic lustre. Specific gravity, 7·2 to 7·8. Hardness, 5 to 5·5. Scratched with a knife, using pressure.

Before the blowpipe on charcoal it melts, giving out white arsenical fumes having a garlic odour. It is readily distinguished by its pale copper red colour and its arsenical fumes when heated.

Occurs in veins in granite and slate, with ores of cobalt, silver, copper, bismuth, lead. A valuable source of metallic nickel.

53. SMALTINE (TIN-WHITE COBALT).

Chemical Composition.—Cobalt up to 24 per cent., arsenic.

In octahedrons, cubes, dodecahedrons, and allied forms. Also massive. Tin-white or steel-grey. Lustre metallic. Streak greyish-black. Fracture uneven. Specific gravity, 6·3 to 6·6. Hardness, 5·5.

Fusible. In the blowpipe flame gives off arsenical fumes (odour of garlic). With borax bead gives the characteristic indications of cobalt. In nitric acid forms a pink solution. Resembles mispickel and iron pyrites, but is at once distinguished by the test with borax bead. Its arsenical fumes distinguish it from iron pyrites, and its crystalline form from mispickel.

Occurs in veins in slate and gneiss. A valuable ore of cobalt.

54. COBALT BLOOM.

Chemical Composition.—Cobalt oxide, 37·6; arsenic acid, 38·4; water, 24·0.

In oblique crystals, with a highly perfect cleavage like mica. Also in incrustations. Red or pink, grey, green. Lustre brilliant pearly. Transparent or opaque. Specific gravity, 2·9 to 3·1. Hardness, 1·5 to 2. Very easily cut with a knife.

Fusible in blowpipe flame, evolving arsenical fumes. When heated on charcoal it gives off an odour of arsenic. With borax bead gives indication of cobalt.

Occurs in beds and veins with other ores of cobalt. A valuable ore of cobalt.

55. BLENDE.

Chemical Composition.—Zinc, 66·7; sulphur, 33·3.

In dodecahedrons, octahedrons, and allied forms. Also massive. Yellow, red, brown, black. Lustre adamantine, resinous, or waxy. Transparent or opaque. Breaks with brilliant cleavage faces in some directions. Specific gravity, 4·0 to 4·1. Hardness, 3·5 to 4·0. Easily scratched with a knife.

Infusible. Emits a strong light when heated, but no odour of sulphur is perceptible. It is easily distinguished by its waxy lustre, softness, infusibility, and perfect cleavage. It dissolves at once in nitric acid.

Occurs with lead and copper ores. It is the 'black jack' of miners. An ore of zinc, but more difficult to smelt than the carbonate and silicate.

56. ZINC CARBONATE (CALAMINE).

Contains 52 per cent. of zinc.

Usually in crusts or masses. White, green, or brown. Opaque. Pearly or glassy. Specific gravity, 4·1 to 4·5. Hardness, 5. Can be scratched with a knife, using a little pressure.

Infusible. On charcoal becomes yellow whilst hot, white on cooling. Dissolves rapidly with effervescence when heated with nitric acid.

Occurs with galena and blende. A valuable zinc ore.

57. ZINC SILICATE (SMITHSONITE).

Contains 53 per cent. of zinc.

In prisms, or massive. White, greenish, bluish, or brownish. Glassy lustre. Transparent or opaque. Specific gravity, 3·3 to 3·5. Hardness, 5.

Infusible. Shines with a green light in the blowpipe flame. Does not effervesce with nitric acid, but dissolves, leaving a jelly of silica.

Occurs with zinc carbonate. A valuable zinc ore.

58. GALENA.

Chemical Composition.—Lead, 86·6; sulphur, 13·4.

In cubes. Also granular, massive. Lead colour. Metallic lustre. Streak metallic. Breaks into cubical fragments with bright cleavage faces. Specific gravity, 7·4 to 7·7. Hardness, 2·5. Very easily scratched with a knife.

Easily fusible. Before the blowpipe on charcoal is reduced to a metallic globule of lead, giving off an odour of burning sulphur.

Occurs in granite and stratified rocks. Often associated with copper and other ores. The principal ore of lead. It usually contains a small quantity of silver.

59. LEAD CARBONATE (CERUSITE).

Contains 77 per cent. of lead.

In prisms, sometimes united in four or six-rayed crosses. White or grey. Transparent or opaque. Lustre glassy. Specific gravity, 6·4 to 6·6. Hardness, 3·5.

Flies violently to pieces in the blowpipe flame. If placed in a cavity on charcoal, and covered with sodium carbonate, then carefully fused by the flame, it yields a globule of metallic lead. In nitric acid it dissolves with effervescence.

Usually occurs with galena. It is a valuable lead ore.

60. LEAD SULPHATE (ANGLESITE).

Contains 68 per cent. of lead.

In slender brilliant crystals upon galena. Also massive. White or grey. Transparent or opaque. Specific gravity, 6·3. Hardness, 3.

Before the blowpipe fusible, but apt to decrepitate on charcoal; with sodium carbonate yields a globule of metallic lead. Differs from lead carbonate in not dissolving with effervescence in nitric acid.

Usually occurs with galena, and results from its decomposition.

61. PYROMORPHITE (LEAD PHOSPHATE).

Chemical Composition.—Lead oxide, 74·0, phosphoric acid 15·8, lead chloride 10·2.

In stout prisms, grouped together. Also massive.

Bright green or brown. Opaque or semi-transparent. Lustre resinous. Streak white. Fracture irregular. Specific gravity, 6·9 to 7·1. Hardness, 3·5 to 4·0. Easily scratched with a knife.

Easily fusible. With sodium carbonate on charcoal the lead is reduced. Soluble in nitric acid.

Occurs sparingly in veins with galena.

62. CINNABAR.

Chemical Composition.—Mercury, 86·2; sulphur, 13·8.

In granular, compact, and earthy masses. Sometimes in crystals, exhibiting adamantine cleavage faces. Opaque or semi-transparent. Vermilion or brownish red. Specific gravity, 8·0 to 8·2. Hardness, 2·5. Very easily scratched with a knife.

Before the blowpipe it volatilises, giving off a strong odour of burning sulphur. Mixed with dried sodium carbonate, and heated over a candle-flame, in an iron spoon, it gives off vapours of mercury, which may be condensed on a gold coin held half an inch above the mixture. The surface of the coin appears whitish at first, but when rubbed between the fingers, becomes brilliantly amalgamated. With care, this test easily detects one per cent. of cinnabar in an ore. The mercury is removed from the gold coin by gentle heating. The blowpipe tests distinguish it at once from red oxide of iron and all other red minerals.

Occurs in talcose and argillaceous rocks. It is the principal source of the mercury of commerce.

63. NATIVE MERCURY, OR QUICKSILVER.

The metal in a pure state is rarely found. It occurs disseminated in liquid globules through sandstone and other rocks, in cavities of which it may accumulate. It is easily recognised. A rock suspected to contain mercury may be tested by simply heating it as described under cinnabar; but without the addition of carbonate of soda.

64. NATIVE COPPER.

Usually in strings, plates, or irregular masses: sometimes crystalline. Like ordinary copper, but often tarnished. Specific gravity, 8·9. Easily scratched with a knife. Malleable, can be flattened out under a hammer.

Occurs with copper ores.

65. VITREOUS COPPER.

Chemical Composition.—Copper, 79·8; sulphur, 20·2.

Sometimes in prisms, but usually massive. Blackish lead grey, tarnished. Streak metallic. Specific gravity, 5·5 to 5·8. Hardness, 2·5 to 3. Very easily scratched with a knife.

Fusible. Before the blowpipe gives off an odour of sulphur. When heated on charcoal, a malleable globule of metallic copper remains, tarnished black, but rendered evident on flattening under a hammer. With borax bead gives the indications of copper. Dissolves in nitric acid, forming a blue solution. (These tests distinguish it from sulphide of silver.)

Occurs with other copper ores. A valuable ore of copper.

66. COPPER PYRITES.

Chemical Composition.—Copper, 34·6; iron, 30·9; sulphur, 34·9.

In tetrahedrons or octahedrons. Usually massive. Brass yellow, often tarnished. Lustre metallic. Streak unmetallic, blackish green. Fracture uneven. Specific gravity, 4·1 to 4·3. Hardness, 3·5 to 4·0. Easily scratched with a knife.

Fusible. Gives off an odour of sulphur before blowpipe. Does not give the indications of copper with borax bead, or when heated upon charcoal with sodium carbonate. Dissolves in nitric acid, forming a blue solution. Distinguished from iron pyrites by being easily cut with a knife; and from gold by not flattening under a hammer, and by its greenish powdery streak.

Occurs in granite and slate in lodes or veins. Valuable ore of copper.

67. GREY COPPER.

This term includes a variety of ores having a common crystalline form, generally the tetrahedron also; a definite chemical formula, though the ingredients are numerous and may be variously combined within certain limits. Sulphur is an invariable ingredient; and arsenic or antimony, one or both, must be present; the other ingredients are copper, iron, zinc, lead, silver, or mercury, in variable proportions. The copper ranges up to 40 per cent.; and in some kinds as much as 30 per cent. of silver has been found. It also occurs massive. Steel grey to iron black. Lustre metallic. Streak black, or dark red when zinc is present. Fracture uneven. Specific gravity, 4·5 to 5·2. Hardness, 3 to 4. Can be easily scratched with a knife.

Fusible. Before the blowpipe gives off an odour of sulphur, also white inodorous fumes of antimony, and occasionally arsenic.

Copper cannot be detected by the blowpipe tests. It dissolves in nitric acid, forming a greenish brown solution.

Occurs with copper pyrites, galena, and blende. This ore is wrought for copper, and occasionally for silver.

68. BLACK CUPRIC OXIDE.

Heavy black powder or mass. Soft. Easily distinguished from manganese by affording the indications of copper by the blowpipe tests. It results from the waste of various copper ores. Valuable as a source of the metal.

69. RED CUPROUS OXIDE.

Chemical Composition.—Copper, 88·8; oxygen, 11·2.

In octahedrons and dodecahedrons. Also in granular and earthy masses. Red. Lustre adamantine, metallic, or earthy. Streak red. Semi-transparent or opaque. Exhibits cleavage parallel with octahedral faces. Specific gravity, 6. Hardness, 3·5 to 4·0. Can be scratched with a knife.

Before the blowpipe on charcoal it yields a globule of metallic copper. With borax bead gives the indications of copper. Forms a blue solution in nitric acid. These tests distinguish it from red ferric oxide.

Occurs in granite and slate, with copper ores and galena. Valuable source of the metal.

70. COPPER CARBONATES, BLUE AND GREEN.

Chemical Composition.—Oxide of copper, carbonic acid, water; the percentage of metallic copper about 56.

In crystals, but usually in fibrous, silky, globular encrusting masses. Blue or green. Opaque. Glassy, silky, or dull. Specific gravity, 3·7 to 4·0. Hardness, 3·5 to 4·0; can be scratched with a knife.

Blacken when heated. On charcoal are reduced to a globule of pure copper. Give the indications of copper with borax bead. Soluble in nitric acid with effervescence, forming a blue solution.

Copper Silicate resembles the carbonate, and is distinguished by dissolving in nitric acid without effervescence.

Occur with copper ores, and result from their decomposition. Valuable sources of the metal.

71. PLATINUM.

In flattened or angular grains or nuggets, which are *malleable*. Steel-grey. Lustre metallic. Specific gravity, 17 to 19. As heavy as gold, and, therefore, easily distinguished and separated from lighter materials.

Infusible. Insoluble in nitric acid.

Occurs in quartz veins, but principally in alluvial deposits with gold. Used chiefly for chemical apparatus. Of great value.

72. GOLD.

In dust, grains, or nuggets in river sand; or in wiry, branching, and irregular forms in quartz. Pale or deep yellow. Malleable. Specific gravity, 15 to 19. Hardness 2·5 to 3·0.

Fusible without blackening, and without giving off any odour. Imparts no colour to boiling nitric acid.

The minerals commonly accompanying gold are iron pyrites, arsenical iron, iron and manganese oxides, galena, and copper pyrites in quartz veins; and magnetic iron, titanic iron, chromic iron, tin ore, quartz, zircon, topaz, corundum, diamond, in alluvial deposits.

73. SILVER.

In strings, plates, and branching forms penetrating quartz, porphyry, slate, granite. Silver white, but usually tarnished black. Malleable. Specific gravity, about 10·5. Hardness, 2·5 to 3.

Fusible without giving off any odour. Soluble in nitric acid, and on adding salt to the solution, a white curd is thrown down which blackens on exposure to sunlight.

74. SULPHIDE OF SILVER.

Chemical Composition.—Silver, 87; sulphur, 13.

In dodecahedrons or allied forms. Also massive. Black. Opaque. Lustre metallic. Streak shining. Specific gravity, 7·2. Hardness, 2·0 to 2·5. Very easily cut with a knife.

Very fusible, giving off an odour of sulphur when heated. Before the blowpipe on charcoal, with or without sodium carbonate, it yields a white globule of metallic silver which can be flattened under a hammer.

The ore is soluble in nitric acid, and on adding salt to the solution a white curdy precipitate is thrown down, which blackens on exposure to sunlight.

Occurs in veins in granite, porphyry, and slate, with arsenic, silver, and lead ores.

75. ANTIMONIAL AND ARSENICAL SILVER ORES.

Several ores of silver contain arsenic and antimony, as well as sulphur; the percentage of silver in these ores varies from 12 to 68. Red, grey, or black. Lustre adamantine or metallic. Red streak. Specific gravity, 5 to 6. Hardness, 2 to 3. Easily scratched with a knife.

Fusible. Before the blowpipe give off an odour of sulphur, or arsenical fumes of a garlic odour, or fumes of antimony. Heated on charcoal with sodium carbonate afford a globule of metallic silver.

Nitric acid extracts the silver from these ores, forming a solution in which salt throws down a white curd, blackening on exposure to sunlight.

76. HORN SILVER.

Chemical Composition.—Silver, 75·3; chlorine, 24·7. In veins with silver ores. Greenish. Waxy lustre. Hardness, 1·0 to 1·5. Cuts like wax or horn.

Very easily fusible. Heated with sodium carbonate, on charcoal, it yields a globule of metallic silver.

77. LEAD AND ANTIMONY SULPHIDES.

Lead- or steel-grey. Lustre metallic. Hardness not exceeding 3. Specific gravity about 6.

Fusible. Give off an odour of sulphur and white fumes of antimony before the blowpipe; and with sodium carbonate on charcoal afford a bead of metallic lead.

78. MERCURY, LEAD, SILVER, OR COPPER SELENIDE.

Gives off a strong odour of horseradish, due to selenium, when heated before the blowpipe. The metal may be found in some cases by sodium carbonate on charcoal, in others by the use of nitric acid.

79. MILLERITE (NICKEL SULPHIDE).

Chemical Composition.—Nickel, 64·9 ; sulphur, 35·1.

In delicate needles. Brass-yellow. Metallic lustre.

Fusible. Hardness, 3 to 5. Imparts to borax the colour of nickel.

80. WHITE NICKEL.

Chemical Composition.—Nickel, 28·3 ; arsenic, 71·7.

Same colour, hardness, specific gravity, and crystalline form as smaltine, No. 53. Often contains cobalt, and graduates into smaltine, with which it is usually found.

81. RUTILE.

Chemical Composition.—Titanium and oxygen.

In crystals and masses. Red brown. Streak paler. Lustre sub-metallic. Hardness, 6·0 to 6·5. Specific gravity, 4·2 to 4·3.

Infusible. With borax bead, yellowish-green or colourless (oxidising), dirty violet (reducing).

82. SPHENE.

Chemical Composition.—Titanic acid, silica, lime.

In thin wedge-shaped crystals. Yellow, green, brown. Transparent or opaque. Lustre adamantine. Hardness, 5 to 5·5. Specific gravity, 3·2 to 3·6. Transparent yellow bead with borax when hot.

Fusible with difficulty on edges.

83. WOLFRAM.

Chemical Composition.—Tungstic acid, iron, manganese.

Crystals or masses. Brownish black. Lustre shining or dull. Opaque. Hardness, 5·5. Specific gravity, 7 to 8.

Fusible with difficulty. With borax gives the colour of iron. Characterised by its great weight. Found often with tin ores.

84. PITCHBLENDE.

Chemical Composition.—Uranium, 84·8 ; oxygen, 15·2. Massive. Black, opaque. Resinous lustre. Streak black. Hardness, 5·5. Specific gravity, 6·4 to 6·7.

Infusible. With borax gives yellow bead. Dissolves in hot nitric acid, forming a yellow solution.

85. MAGNETIC IRON PYRITES.

Chemical Composition.—Iron, 60·5 ; sulphur, 39·5.

Usually massive. Bronze yellow, tarnished. Metallic lustre. Feebly magnetic. Hardness, 3·5 to 4·5.

Fusible.

DETERMINATION OF MINERALS.

The following scheme * will show how a mineral may be determined by means of the tests and characters already indicated.

The scheme first separates minerals into two divisions—namely, those which possess a metallic lustre, and those which do not ; and these are further subdivided into groups by means of other characters.

The various members of each group are enumerated in the tables, which also give the mode of discrimination.

In most cases it is easy to decide whether a mineral possesses a lustre like a polished metal, but where the lustre is less decided, there is room for a difference of opinion ; besides, a mineral may possess a metallic lustre in some specimens, and not in others.

To provide against this, any mineral about which difficulty may arise is placed in both divisions, and even in several groups if necessary. The mineral blende affords an instance.

From inspection of the scheme it will be observed that *valuable metalliferous minerals* possess, as a rule, a *metallic lustre*, are *heavy* in proportion to their bulk, and are *easily scratched* with a knife. The chief exception is tin ore,

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* Drawn up by Dr. A. M. Thompson.

which has not a metallic lustre, and which cannot be impressed with a knife.

In testing it is necessary to bear in mind that a piece of ore may consist of a single mineral only, either pure, or mixed with a readily distinguishable gangue; or it may be composed of finely disseminated particles of two or more metalliferous minerals. But by search in localities where such mixtures occur, pure and isolated specimens of each kind may generally be found. Moreover, after a little practice the complication of characters which mixtures present will not interfere with the recognition of their components.

The scheme is not expected to prove an infallible means of determining minerals in all possible instances, though previous experience has shown that it is of use to those who have learned to apply the tests recommended in the former part of this chapter. To avoid error, it is necessary in all cases, before coming to a decision, for the observer to be convinced that the mineral under examination actually possesses all the characters of the mineral which it is supposed to be.

Serious mistakes may arise by drawing inferences from the scheme only, and neglecting to confirm all the other characters. In performing the experiments recommended, the greatest care and accuracy are needful; to the careless and superficial observer, or whoever is not proof against self-deception, the scheme can be of little use.

The characters of each mineral have been described in the preceding pages.

SCHEME FOR THE DETERMINATION OF MINERALS.

Division I.—Minerals possessing a METALLIC lustre.

Experiment.—Heat a fragment of the mineral supported on charcoal, or held with a forceps, in the oxidising point of the blowpipe flame.

1. An odour of burning sulphur is given off. (See Group I.)

2. An odour of garlic is given off, or white fumes not having an odour of sulphur. (See Group II.)

3. No fumes or odour given off. (See Group III.)

Note.—An odour of horseradish indicates Selenium (78).

DIVISION II.—Minerals which do NOT possess a metallic lustre.

Experiment.—Scratch the mineral with a knife or sharp fragment of quartz or sapphire, according to its hardness, and observe the colour of the streak.

Note.—If the streak is metallic the unmetallic lustre is due to tarnish. See Division I.

A. The streak is black or coloured.

Experiment.—Hold a fragment of the mineral on charcoal, or with a forceps, in the oxidising point of the blowpipe flame.

1. Fumes or odour given off. (See Group IV.)
2. No fumes or odour given off. (See Group V.)

B. The streak is uncoloured,—that is to say, white, or nearly so.

Experiment.—Try to scratch a smooth surface of the mineral with a splinter of quartz.

3. The mineral *can* be scratched by quartz. (See Group VI.)

4. The mineral *cannot* be scratched by quartz. (See Group VII.)

Note 1.—The determination must always be made upon pure minerals, free from any adhering foreign matter.

Note 2.—Coal and carbonaceous shale are distinguished from minerals which they may resemble by burning in the blowpipe flame, leaving a more or less copious ash.

GROUP I.

MINERALS WHICH HAVE A METALLIC LUSTRE, AND WHICH GIVE OFF SULPHUR.

Experiment.—Try to scratch the mineral with a knife, and observe the streak.

I.—Not scratched with a knife; scratches glass with great facility.

Pale brass-yellow or white. *Iron pyrites*, 41.

II.—Scratched with a knife; does not scratch glass easily.

* Streak unmetallic.

a. Brass-yellow. Solution in nitric acid blue. *Copper pyrites*, 66.

b. Black or red. Solution in nitric acid colourless, but on adding salt water a white curd of precipitate is thrown down which *blackens* on exposure to sunlight. Mineral gives off white fumes before the blowpipe. *Antimonial or arsenical silver ores*, 75.

c. Lead- or steel-grey. Abundant white fumes before the blowpipe. On charcoal with sodium carbonate yields a globule of metallic lead. *Lead and antimony sulphides*, 77.

d. Red. Wholly volatile before the blowpipe. Mixed with carbonate of soda and heated in an iron spoon over a candle flame, white vapours are given off which may be condensed on a gold coin held a little above the mixture, covering its surface with a brilliant amalgam when rubbed. *Cinnabar*, 62.

Note.—The streak of *Grey Copper* (see below) may be *unmetallic*, often *red*.

** Streak metallic.

Experiment.—Try fusibility in blowpipe flame.

A. Infusible:—

e. Lead-grey. Very soft. In thin leaves. Tinges the blowpipe flame faint green. *Molybdenite*, 35.

Note.—Magnetic Iron Pyrites and *Vitreous Copper* are fusible with difficulty.

B. Fusible:—(Easily, except *k* and *m*.)

Experiment.—Heat a small piece (size of linseed), free from gangue, on charcoal without adding sodium carbonate, hold first in oxidising point and finish in reducing point.

f. Wholly volatile, emitting abundant white fumes. Mineral has a lead-colour. Crystallised in long prisms. *Antimony sulphide*, 37.

g. Globule of metallic lead remains. Mineral has a lead-colour. Cubical cleavage. *Galena*, 58.

h. Abundant white fumes given off. Mineral has a lead or steel colour; and when heated on charcoal with sodium carbonate affords a globule of metallic lead. *Lead and antimony sulphides*, 77.

i. Gobule of metallic silver remains (facilitated by adding a little sodium carbonate). Mineral has a black colour. Is soluble in nitric acid; on adding salt water to the solution a white curd is thrown down which *blackens* on exposure to sunlight. *Silver sulphide*, 74.

k. Globule of metallic copper remains (facilitated by adding a little sodium carbonate); discovered by crushing the residue and flattening it under a hammer. Mineral has a black colour. Does not give off copious white fumes before the blowpipe. It forms a *blue* solution with nitric acid. *Vitreous copper*, 65.

l. Slaggy globule remains, usually attracted by a magnet, not yielding copper when crushed. Mineral has a black or steel colour. It gives off copious white fumes before the blowpipe. It forms a *greenish-brown* solution with nitric acid. *Grey copper*, 67.

m. Greyish-black magnetic bead remains. Mineral has a bronze or copper colour. Can be scratched with a knife; is attracted by a magnet; does not form a blue or green solution with nitric acid. *Magnetic iron pyrites*, 85.

n. Black magnetic globule. Mineral has the form of brass yellow needles. *Nickel sulphide*, 79.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP II.

MINERALS WHICH HAVE A METALLIC LUSTRE AND WHICH GIVE OFF EITHER AN ODOUR OF GARLIC WITHOUT SULPHUR, OR WHITE FUMES WHICH HAVE NOT A GARLIC OR SULPHUROUS ODOUR.

1. The fumes evolved have an odour of garlic (arsenic).

* Not scratched with a knife. Scratches glass.

a. White metallic. Residue after roasting gives indications of iron, with borax bead. Crystallised in flattened prisms. *Mispickel*, 42.

b. White metallic. Residue after roasting gives indications of cobalt, with borax bead. Crystallised in octahedrons. *Smaltine*, 53.

Note.—White Nickel resembles *Smaltine,* and is found with it.

** Scratched with a knife. Does not scratch glass.

c. Pale copper red. *Arsenical nickel*, 52.

d. Carmine red. *Arsenical silver ore*, 75.

e. White (as streak shows), tarnished black; wholly volatilised by heat. *Arsenic*, 38.

Note.—Metallic Bismuth is frequently associated with Arsenic. Possibly Grey Copper and Arsenical Silver may be looked for here; for their characters see Group I.

2. The fumes evolved have not a garlic odour.

Possibly *grey copper*, *antimonial silver ore*, *lead and antimony sulphides*, or *cinnabar:* but these ores generally give off a faint odour of sulphur in addition to white fumes. For their characters, see Group I.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP III.

MINERALS WHICH HAVE A METALLIC LUSTRE, AND WHICH GIVE OFF NO FUMES.

I. The mineral is malleable (can be flattened under a hammer).

a. Yellow. *Gold*, 72.

b. Red. *Copper*, 64.

c. White, rusty surface; strongly attracted by a magnet. *Iron*, 40.

d. White, feebly or not attracted by a magnet. Infusible. Insoluble in nitric acid. *Platinum*, 71.

e. White, often tarnished; not attracted by a magnet. Fusible. Soluble in nitric acid; on adding salt water to the solution, a white curd is thrown down, which blackens on exposure to sunlight. *Silver*, 73.

II. The mineral is brittle (breaks to pieces under a hammer).

Experiment.—Observe the colour imparted to a borax bead in oxidising and in reducing

1. *Violet* in oxidising, *colourless* in reducing.

a. *Manganese ores*, 51.

2. *Red* (hot), *yellow* (cold), in oxidising, *bottle-green* in reducing.

Scratch the mineral with quartz and observe the colour of the streak.

b. Brown streak; mineral not attracted by a magnet. *Brown iron oxide*, 46.

c. Red streak; not attracted by a magnet. *Specular iron*, 44.

d. Black streak; not attracted by a magnet. *Titanic iron*, 47.

e. Black or brown streak; strongly attracted by a magnet. *Magnetic iron*, 43.

Note.—Possibly *Wolfram* (83); non-magnetic; streak reddish-brown or black; remarkable for its great weight.

3. *Green* (hot), *blue* (cold), in oxidising, *red* in reducing. *Red cuprous oxide*, 69.

4. *Green* in oxidising, *green* in reducing.

f. *Chromic iron*, 48.

5. *Colourless*.

* Infusible.

Minerals HARDER *than calc-spar*.

g. Readily soluble in nitric acid. Scratched with a knife. *Blende*, 55.

h. Insoluble in nitric acid. Not scratched with a knife. With potassium cyanide upon charcoal, yields a globule of metallic tin. *Tin ore*, 34.

Minerals SOFTER *than calc-spar*.

i. Black, like black-lead. Specific gravity about 2. *Graphite*, 20.

k. Lead-colour. Specific gravity about 4·5. Tinges blowpipe flame pale green. *Molybdenite*, 35.

** Fusible.

Heated on charcoal forms an incrustation which is red whilst hot, yellow when cold. *Bismuth*, 36.

6. *Note.—Green* in oxidising, *dirty violet* in reducing, indicates Rutile (81), *yellow* in oxidising, *green* in reducing (difficult to obtain in a candle flame), afforded by a black mineral, soluble in boiling nitric acid, forming a yellow solution, indicates Pitchblende (84).

Note.—Mica may possibly be sought for in this group. It is distinguished by its lightness of weight, and its capability of being split into very thin, transparent, flexible layers.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP IV.

MINERALS WHICH POSSESS AN UNMETALLIC LUSTRE, A COLOURED STREAK, AND WHICH GIVE OFF FUMES OR ODOUR WHEN HEATED BEFORE THE BLOWPIPE.

a. Colour and streak yellow, entirely volatile, burning with a blue flame and sulphurous odour. *Sulphur*, 33.

b. Colour red, orange, or yellow, entirely volatile, burns on charcoal with a blue flame and garlic odour. *Arsenic sulphide*, 39.

c. Streak red. Strong odour of garlic or white fumes (of antimony) when heated. Dissolved in nitric acid; on adding salt to the solution a white curd is thrown down which *blackens* on exposure to sun-light. *Arsenical or antimonial silver ore*, 75.

d. Streak red. Wholly volatile before blowpipe. Mixed with sodium carbonate and heated in an iron spoon over a candle-flame, vapours are given off which may be condensed on a gold coin held a little above the mixture, covering its surface with a brilliant amalgam when rubbed. *Cinnabar*, 62.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP V.

MINERALS WHICH POSSESS AN UNMETALLIC LUSTRE, A COLOURED STREAK, BUT WHICH GIVE OFF NO FUMES OR ODOUR BEFORE THE BLOWPIPE.

Experiment.—Observe the colour imparted by the mineral to a borax bead, both in oxidising and reducing.

1. *Green* (hot), *blue* (cold), in oxidising; *red* in reducing (difficult to obtain).

a. Colour of mineral blue or green. *Copper carbonate*, 70.

b. Colour of mineral red. *Red cuprous oxide*, 69.

c. Colour of mineral black. *Black cuprous oxide*, 68.

2. *Green* in oxidising, *green* in reducing.

d. Colour of mineral black. *Chromic iron*, 48.

3. *Red* (hot), *yellow* (cold), in oxidising: *bottle-green* in reducing.

e. Colour of mineral green. *Greenearth*, 40.

f. Colour of mineral brown; blackened during heating. *Brown ferric oxide*, 46.

g. Colour of mineral red; blackened during heating. *Red ferric oxide*, 45.

Note.—Iron Arseniate is green or yellow, *Iron Phosphate* is blue.

4. *Amethyst* in oxidising, *colourless* in reducing.

h. Colour of mineral brown or black. *Manganese ores*, 51.

Note.—Manganese Carbonate is rose red or brownish, streak white.

5. *Colourless* in both oxidising and reducing.

i. Easily scratched with a knife. Cleavage. Soluble in nitric acid. *Blende*, 55.

k. Not scratched with a knife. No cleavage. Heated with potassium cyanide upon charcoal yields a malleable globule of metallic tin. *Tin ores*, 34.

Note.—Cobalt Bloom (54) has a red colour and streak; it gives the indications of Cobalt with borax bead. *Rutile, Wolfram,* and *Pitchblende* might be considered to have an unmetallic lustre. See under Group III.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP VI.

MINERALS WHICH HAVE AN UNMETALLIC LUSTRE, AND WHICH ARE SCRATCHED BY QUARTZ, SHOWING A WHITE STREAK.

I.—*Minerals soluble in water* (*having a taste*).

a. Taste of common table salt. *Salt*, 28.
b. Sweetish astringent taste. *Alum*, 29.
c. Bitter taste of Epsom salts. *Epsomite*, 29
d. Cooling taste. Causes vivid combustion when thrown on a piece of red-hot charcoal. *Nitre*, 30.

Note.—*Zinc* (white), *Iron* (green), and *Copper* (blue) sulphates have a nauseous metallic taste.

II.—*Minerals insoluble in water; but soluble in nitric acid* (best determined by placing a very little of the powder in a test tube, pouring on it a few drops of the acid, and heating if requisite).

N.B.—All of these can be *scratched with a knife*.

* Easily fusible.

a. Green, yellow or brown, Hardness, 3 to 4. Globule of lead, on charcoal with sodium carbonate. No effervescence in nitric acid. *Pyromorphite*, 61.

b. White or grey. Hardness, 3 to 4. Flies violently to pieces in the blowpipe flame. Globule of lead on charcoal with sodium carbonate. Effervesces in nitric acid. *Cerusite*, 59.

Note.—White or grey. Effervesces in nitric acid. Specific gravity 4·3. Does not fly to pieces when heated; yields no metal on charcoal, WITHERITE BARIUM CARBONATE.

** Infusible.

c. Hardness, 3. Dissolves with very brisk effervescence in cold nitric acid. Does not crumble to powder in the blowpipe flame. *Calc-spar*, 24.

d. Hardness, 3·5 to 4. Dissolves like calc-spar; but crumbles to powder in the blowpipe flame. *Aragonite*, 6.

e. Hardness, 3·5 to 4. Dissolves much slower than calc-spar; but difficult to distinguish without chemical analysis. *Dolomite*, 26.

f. Hardness, 4 to 5. No effervescence in cold nitric acid, very slight in hot. *Magnesite*, 25.

g. Hardness, 3·5 to 4·5. Effervescence in hot nitric acid. The mineral blackens when heated in the blowpipe flame; it gives the indication of iron with borax. *Iron carbonate*, 50.

h. Hardness, 5. Effervescence in hot nitric acid. Heated on charcoal with sodium carbonate it forms a crust which is yellow whilst hot. *Calamine*, 56.

i. Hardness, 5. Dissolves in nitric acid without effervescence, leaving a jelly of silica. In blowpipe flame it shines with a green light. *Zinc silicate*, 57.

k. Hardness, 3·5. Effervesces in hot nitric acid. Flies violently to pieces in the blowpipe flame. On charcoal with sodium carbonate yields a globule of lead. *Cerusite*, 59.

l. Hardness, 3·5 to 4. Brilliant cleavage. Rapidly soluble in nitric acid with effervescence. Heavy (specific gravity, 4). *Blende*, 55.

m. Hardness, 4·5 to 5. Slowly soluble in nitric acid without effervescence. *Apatite*, 22.

Note.—Hardness, 3·5. Effervesces in hot nitric acid. Tinges the blow-pipe flame crimson. *Strontianite* (*Strontium carbonate*).

III.—*Minerals insoluble in both water and nitric acid.*

* Easily fusible.

HARDNESS.	
1·0 to 1·5.	Like wax. On charcoal with sodium carbonate yields a globule of silver. *Horn silver*, 76.
2·5 to 3·0.	White or grey. On charcoal with sodium carbonate yields a globule of lead. *Anglesite*, 60.
3·5 to 4·0.	Green or brown. On charcoal with sodium carbonate yields a globule of lead. *Pyromorphite*, 61.
3·5 to 6·5.	Usually white. Swell up before the blowpipe. Occur in cavities of rocks. *Zeolites*, 15.
5·0 to 6·0.	Black, green, or white. Prisms, fibrous or flaxlike. *Hornblende and augite*, 6.
6·5 to 7·5.	Usually red. Crystallised in dodecahedrons. *Garnet*, 9.

Note.—Glass (artificial) may be included here; easily distinguished by its appearance, easy fusibility, and inferior hardness, 4·5 to 5·5.

** Infusible, or not easily fusible.

1·0 to 1·5.	Light green. In layers. Unctuous. *Talc*, 3.
1·5.	Dark green. In layers or granular. Sometimes fusible to a black glassy bead. *Chlorite*, 4.
2·0 to 3·5.	Green. Turns white in blowpipe flame. Feels often greasy. *Serpentine*, 5.
2·0.	Usually white. After heating becomes opaque, and can be rubbed to powder between the fingers. Fusible with difficulty. *Gypsum*, 31.
2·0 to 2·5.	Grey or black. Can be split into extremely thin semi-transparent flexible layers. *Mica*, 14.
3·0 to 3·5.	White or grey. Tabular crystals or massive. Heavy (specific gravity, 4·3 to 4·8). Splinters fly off crystals when heated. Fusible with difficulty. *Heavy spar*, 32.

HARDNESS.	
4·0.	Cubes or massive. Octahedral cleavage. Flies to pieces when heated. Specific gravity, 3 to 3·2. Fusible with difficulty. *Fluor-spar*, 23.
5·0.	Six-sided prisms, massive. Green or white. Specific gravity, 3 to 3·3. Generally flies to pieces when heated. In fine powder, slowly soluble in nitric acid. *Apatite*, 22.
5·0 to 6·0.	Prisms, fibrous or flaxlike. Cleavage. Green, black, or white. Generally fusible. Specific gravity, 2·9 to 3·5. *Hornblende and augite*, 6.
	Note.—Possibly *Epidote.* Yellowish green. Hardness, 6·0 to 7·0.
6·0.	Prisms or massive. Flesh colour, white, or tinted. Cleavage. Specific gravity, 2·3 to 2·8. *Felspar*, 13.
6·0 to 7·0.	Masses or grains like glass. Black or green. Specific gravity, 3·3 to 3·6. *Chrysolite*, 7.
6·5 to 7·5.	Dodecahedrons. Usually red. Generally fusible. Red infusible varieties impart a green colour to borax bead. Specific gravity, 3·5 to 4·3. *Garnet*, 9.
5·5 to 6·5.	Never crystallised. White, tinted, or chatoyant. Specific gravity, 1·9 to 2·3. *Opal*, 2.
7·0.	Six-sided prisms. Specific gravity, 2·6. *Quartz*, 1.

Note.—*Sphene* (82) occurs in acute thin crystals. Yellow, green, or brown. Specific gravity, 3·2 to 3·6.

Chiastolite and other *Aluminium Silicates* occur in prisms. Brown or white. Opaque. Hardness, 6 to 7·5. Infusible. Specific gravity, 3 to 3·7.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

GROUP VII.—Including the Gems.

MINERALS WHICH HAVE AN UNMETALLIC LUSTRE, AND WHICH ARE NOT SCRATCHED BY QUARTZ.

Note.—Tin ore (34) may occur here. Hardness, 6 to 7. Remarkable for its great weight. Specific gravity, 6·8 to 7·0. Brown or black. With cyanide of potassium, on charcoal, yields a globule of Tin.

GEMS.

If crystallised, the determination is greatly facilitated, but if the crystallisation is not evident, the *hardness* will be found a sufficiently near indication in the following scheme. The requisites in determining the hardness of gems are good specimens of sapphire, topaz, and quartz possessing smooth bright surfaces, as well as sharp points or corners. The hardness is determined by drawing the sharp points of these three test-minerals over smooth bright surfaces of the mineral under trial. (See *hardness.*) Or it may be ascertained with great certainty by means of a small angular fragment, broken off the mineral to be tried. For convenience of holding, it should be mounted on a stick of sealing-wax, which is best done by previously heating the fragment, held with a forceps over a candle flame, and applying it, whilst hot, to the wax; the hardness may then be ascertained by drawing the fragment thus mounted across smooth surfaces of the sapphire, topaz, and quartz, and observing whether a scratch is thus produced. In this way the hardness of a mineral not larger than a grain of sand may be determined.

The facility of cleavage is an important character in the *topaz* and the *diamond.*

The electrical properties are characteristic in the *diamond*, *topaz*, and *tourmaline.*

The specific gravity is a most important aid in distinguishing gems, but it cannot be attempted with an ordinary pair of grain scales in the case of minerals weighing under ten grains, at the very least.

Many varieties of *zircon* and *spinel*, and in some cases the *topaz* and *emerald*, can readily be distinguished by the effect of heat, which is applied most conveniently by the blowpipe.

The *diamond* may be easily distinguished by the use of a small writing or scratching diamond, which fails to mark the faces of a real diamond when drawn lightly across, but scratches all other gems with facility. After practice, the sound caused by tapping two diamonds together becomes characteristic.

1. Crystallised in Prisms.

HARDNESS.	
7·0.	Six-sided prisms or pyramids; sides of prism finely marked across. No cleavage. Fracture conchoidal. Infusible. When two pieces are rubbed together in the dark, they emit a phosphorescent light and a peculiar odour. Specific gravity, 2·5 to 2·8. *Quartz*, 1.
7·0 to 8·0.	Prisms, three, six, nine, or more sided; furrowed lengthwise. Black or coloured. Opaque or transparent. Smooth sides of prisms become electric by friction. No cleavage. Infusible or nearly so. Specific gravity, 3·0 to 3·3. *Tourmaline*, 8.
7·5.	Prisms, four-sided, not furrowed. Wine-red, brown, or white. Decolorised permanently by heat. Adamantine cleavage, but rather difficult to obtain. Infusible. Specific gravity, 4 to 5. *Zircon*, 12.
7 to 8.	Prisms, six or more sided. Green usually. Imperfect cleavage. Fusible with difficulty in thin edges; becoming clouded by heat. Specific gravity, 2·7; its low specific gravity combined with its hardness is characteristic. *Beryl* or *Emerald*, 11.
7·5 to 8.	Sides of prisms often finely marked lengthwise. Cleavage across the prisms brilliant and easily obtained. Smooth surfaces become strongly electric by friction. Infusible, but sometimes blistered and altered in colour by heat. Specific gravity, 3·5, *Topaz*, 10.

HARDNESS.

8·5. Prisms or tables. Green. Infusible and unaltered by heat. Specific gravity, 3·5 to 3·8. *Chrysoberyl*, 18.

9·0. Prisms, six-sided or irregular. Cleavage across the prisms, but difficult to obtain. Fracture irregular. Blue, green, black, red, yellow, brown, or white. Infusible. Easily distinguished by its great hardness, scratching all other gems except diamond. Specific gravity, 3·9 to 4·2. *Sapphire, ruby, or corundum*, 16.

2. CRYSTALLISED IN OCTAHEDRONS OR DODECAHEDRONS.

HARDNESS.

7·5. See characters above. *Zircon*, 12.

6·5 to 7·5. Dodecahedrons. Usually red. Most varieties are easily fusible; red infusible varieties impart a green colour (due to chromium) to borax bead. Specific gravity, 3·1 to 4·3. *Garnet*, 9.

8·0. Octahedrons. Usually red or black, also blue, green, yellow, and brown Some red varieties become opaque and black when heated; rose-red varieties become green when heated, but regain their original colour on cooling. Specific gravity, 3·5 to 4·0. *Spinel*, 17.

10·0. Octahedrons, dodecahedrons, or modifications of these forms. Crystalline facets often curved. Cleavage perfect. Lustre, brilliant adamantine. Usually colourless, or straw-coloured. Not water-worn. Strongly electric by the slightest friction. Specific gravity, 3·5. *Diamond*, 19.

N.B.—Before determining the name of a mineral, it is necessary to compare it with the description to which the number refers.

For further particulars respecting gems and precious stones see the concluding chapter of this volume.

Coloured Flames.—There are a great number of substances best detected by the colours they impart to the flame of the blowpipe. Indeed, so important is this point that it has been thought advisable to collect all the facts known on this subject into one place, rather than scatter them over the work. These experiments are best made in a dark room, and with a very small flame.*

BLUE FLAMES.

Large intense blue	Chloride of copper.
Pale clear blue	Lead.
Light blue	Arsenic.
Blue	Selenium.
Greenish blue	Antimony.
Blue mixed with green	Bromide of copper.

GREEN FLAMES.

Intense emerald green	Thallium
Very dark green, feeble	Ammonia.
Dark green	Boracic acid.
Full green	Tellurium.
Full green	Copper.
Emerald green, mixed with blue	Iodide of copper. Bromide of copper.
Pale green	Phosphoric acid.
Very pale apple green	Baryta.
Intense whitish green	Zinc.
Bluish green	Binoxide of tin.

YELLOW FLAME.

Intense greenish yellow	Soda.

RED FLAMES.

Intense crimson	Lithia.
Red	Strontia.
Reddish purple	Lime.
Violet	Potash.

Chlorine, combined with copper, gives an intense blue flame. This phenomenon may be produced as follows:—Take a piece of thin brass wire, and bend one end of it several times upon itself; place upon this some microcosmic salt, and fuse it until it has acquired a green colour. Then add to it the substance suspected to contain chlorine, and place it in the oxidising flame, just at the point of the blue

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* Griffin's 'Blowpipe Analysis,' p. 148.

flame; if any chloride be present a splendid blue colour will be produced.

Lead.—The blue colour produced by this metal is readily obtained. Fragments of a mineral must be held in the tongs, and powder may be assayed on charcoal.

Arsenic, in the metallic state, gives rise to a light blue flame.

Selenium and *Antimony*, when treated in the same manner, afford characteristic flames.

Bromine.—If any substance containing bromine be placed in a bead of fused microcosmic salt on the brass wire, and then in the oxidising flame, a bright blue flame with emerald green edges will be produced.

Boracic Acid.—The following is Dr. Turner's process for the detection of boracic acid. The substance is to be mixed with a flux composed 1 part of fluor-spar and 4½ parts of potassium bisulphate. This mixture is to be made to adhere to the moistened end of a platinum wire, and held at the point of the blue flame; at the instant of fusion a dark green flame will be produced. It may also be produced by merely dipping the mineral in sulphuric acid, and exposing it to the blowpipe blast. In case a very small quantity of boracic acid is contained in a mineral, the following process may be employed:—The substance must be fused with potassium carbonate on charcoal, moistened with a drop or two of sulphuric acid, and then a few drops of alcohol; the latter will burn with a green flame when exposed to the flame of the blowpipe.

Tellurium.—The peculiar flame given by this metal is produced by heating a portion of its oxide on charcoal in the reducing flame.

Copper.—All the compounds of copper, except those in which bromine and chlorine enter, give a beautiful green flame. The soluble salts give it *per se*, but the insoluble require moistening with sulphuric acid.

Iodine and Copper.—To the bead of microcosmic salt on the brass wire add any compound containing iodine, and a bright green flame will be produced when the mass is heated in the oxidising flame.

Phosphoric Acid.—The phosphates, when moistened with sulphuric acid, give a light green tint to the outer flame.

Baryta.—The soluble salts of baryta give a light green colour to the outer flame when moistened with water.

Zinc, when exposed to the blowpipe flame, burns with an intense whitish-green light.

Soda.—Any salt of soda, or substance containing soda, being exposed to the outer flame, gives a brush of intensely coloured flame, of a fine amber or greenish-yellow.

Water.—Certain minerals containing water give a feeble yellowish tint to the flame.

Strontia.—All the salts of this substance which are soluble in water give a crimson tint to the flame, which does not endure after the substance is fused. Strontium carbonate must be moistened with hydrochloric acid, and strontium sulphate must be reduced to a state of sulphide by ignition with charcoal; it must then be moistened with hydrochloric acid, after which treatment it will exhibit the characteristic flame.

Lithia.—All that has been said of strontia applies to lithia, but the coloured flame given by lithia is permanent, whilst that afforded by strontia is evanescent.

Lime acts as strontia.

Potash, treated as soda, gives a purplish light. This is, however, very liable to be masked by the intense yellow communicated by small quantities of soda, which are almost always present with potash.

CHAPTER VIII.

VOLUMETRIC ANALYSIS.

The main feature of volumetry is not so much analysis in the proper sense of the term, as the quantitative determination of one principal constituent of a substance.

This determination is done by means of solutions, containing a certain quantity of reagents in a certain volume, which is called a standard solution, the quantity used of such solution being measured by graduated tubes (burettes, pipettes, &c.).

The reaction of a volumetric analysis can be of three different kinds, according to the reagent used and to the substance to be determined.

1. The substance to be analysed being an acid or a base, it can be saturated by a suitable standard solution (saturation-analysis, used for acids, potash, soda, &c.).

2. The substance to be assayed may be precipitated by the standard solution, and the completion of the process is observed when no further precipitate occurs (precipitation-analysis, *e.g.*, Pelouze's copper assay, Gay-Lussac's silver-assay).

3. The substance to be determined becomes, by the standard solution, either oxidised or reduced, and by the performance of this process certain colours will appear or disappear, from which the completion of the process is to be observed (oxidation or reduction-analysis, *e.g.*, Schwarz's copper assay).

These processes of volumetric analysis are frequently used in assaying.

The principle of volumetric analysis may be fully explained by the following examples given by Fresenius.*

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* Fresenius's 'Quantitative Analysis,' fourth edition, p. 76.

'Suppose we have prepared a solution of chloride of sodium of such a strength that 100 c.c. will exactly precipitate 1 grm. silver from its solution in nitric acid, we can use it to estimate unknown quantities of silver. Let us imagine, for instance, we have an alloy of silver and copper in unknown proportion, we dissolve 1 grm. in nitric acid, and add to the solution our solution of chloride of sodium, drop by drop, until the whole of the silver is thrown down, and an additional drop fails to produce a further precipitate. The amount of silver present may now be calculated from the amount of solution of chloride of sodium used. Thus, supposing we have used 80 c.c., the amount of silver present in the alloy is 80 per cent.; since, as 100 c.c. of the solution of chloride of sodium will throw down 1 grm. of pure silver (*i.e.*, 100 per cent.), it follows that every c.c. of the chloride of sodium solution corresponds to 1 per cent. of silver.

'Another example. It is well known that iodine and sulphuretted hydrogen cannot exist together; whenever these two substances are brought in contact, decomposition immediately ensues, the hydrogen separating from the sulphur and combining with the iodine ($I+HS=HI+S$). Hydriodic acid exercises no action on starch-paste, whereas the least trace of free iodine colours it blue. Now, if we prepare a solution of iodine (in iodide of potassium) containing in 100 c.c. 0·7470 grm. iodine, we may with this decompose exactly 0·1 grm. sulphuretted hydrogen; for 17 : 127 :: 0·1 : 0·7470.

'Let us suppose, then, we have before us a fluid containing an unknown amount of sulphuretted hydrogen, which it is our intention to determine. We add to it a little starch-paste, and then, drop by drop, our solution of iodine, until a persistent blue coloration of the fluid indicates the formation of iodide of starch, and hence the complete decomposition of the sulphuretted hydrogen. The amount of the latter originally present in the fluid may now be readily calculated from the amount of solution of iodine used. Say, for instance, we have used 50 c.c. of iodine solution, the fluid contained originally 0·05 sulphuretted hydrogen; since, as we have seen, 100 c.c. of our iodine solution will decompose exactly 0·1 grm. of that body.

'Solutions of accurately known composition or strength, used for the purposes of volumetric analysis, are called *standard solutions*. They may be prepared in two ways, viz. (*a*) by dissolving a weighed quantity of a substance in a definite volume of fluid; or (*b*) by first preparing a suitably concentrated solution of the reagent required, and then determining its exact strength by a series of experiments made with it upon weighed quantities of the body for the determination of which it is intended to be used.

'In the preparation of standard solutions by method *a*, a certain definite strength is adopted once for all, which is usually based upon the principle of an exact correspondence between the number of grammes of the reagent contained in a litre of the fluid, and the equivalent number of the reagent (H=1). In the case of standard solutions prepared by method *b*, this may also be easily done, by diluting to the required degree the still somewhat too concentrated solution, after having accurately determined its strength; however, as a rule, this latter process is only resorted to in technical analyses, where it is desirable to avoid all calculation. Fluids which contain the equivalent number of grammes of a substance in 1 litre are called *normal solutions*; those which contain $\frac{1}{10}$ of this quantity, *decinormal solutions*.

'The determination of a standard solution intended to be used for volumetric analysis is obviously a most important operation; since any error in this will, of course, necessarily falsify every analysis made with it. In scientific and accurate researches it is, therefore, always advisable, whenever practicable, to examine the standard solution—no matter whether prepared by method *a* or by method *b*, with subsequent dilution to the required degree—by experimenting with it upon accurately weighed quantities of the body for the determination of which it is to be used.

'In the previous remarks no difference has been made between fluids of known composition and those of known power; and this has hitherto been usual. But by accepting the two expressions as synonymous, we take for granted that a fluid exercises a chemical action exactly corresponding to the amount of dissolved substance it contains; that, for instance, a solution of chloride of sodium containing 1 eq. NaCl will precipitate exactly 1 eq. silver. This presumption, however, is very often not absolutely correct. In such cases, of course, it is not merely advisable, but even absolutely necessary, to determine the strength of the fluid by experiment, although the amount of the reagent it contains may be exactly known, for the power of the fluid can be inferred from its composition only approximately, and not with perfect exactness. If a standard solution keeps unaltered, this is a great advantage, as it dispenses with the necessity of determining its strength before every fresh analysis.

'That particular change in the fluid operated upon by means of a standard solution, which marks the completion of the intended decomposition, is termed the FINAL REACTION. This consists either in a *change of colour*, as is the case when a solution of permanganate of potash acts upon an acidified solution of protoxide of iron, or a solution of iodine upon a solution of sulphuretted hydrogen mixed with starch-paste; or in the *cessation of the formation of a precipitate* upon further addition of the standard solution, as is the case when a standard solution of chloride of sodium is used to precipitate silver from its solution in nitric acid; or in *incipient precipitation*, as is the case when a standard solution of silver is added to a solution of hydrocyanic acid mixed with an alkali; or in *a change in the action of the examined fluid upon a particular reagent*, as is the case when a solution of arsenite of soda is added, drop by drop, to a solution of chloride of lime, until the mixture no longer imparts a blue tint to paper moistened with iodide of potassium and starch-paste, &c.'

The only condition on which the volumetric system of analysis can be carried on successfully is, that the greatest care is exercised with respect to the graduation of the measuring instruments, and the strength and purity of the standard solutions. A very slight error in the analytical process becomes considerably magnified when calculated for pounds, hundredweights, or tons of the substance tested. The end of the operation in this method of analysis is in all cases made apparent to the eye. (Sutton.)

We will only speak here of the preparation of potassium permanganate, and will give the preparation of other solutions when describing the processes for which they are used.

STANDARD SOLUTIONS.

A very useful form of bottle for their preservation is the ordinary wash-bottle, or any common bottle fitted with the same arrangement of tubes. The mouth end of the blowing tube should be furnished with a tightly-fitting india-rubber cap to prevent alteration of the standard by evaporation. A similar cap over the point will be useful, although not absolutely necessary, or it may be closed by a small cork fitting over it. Burettes can then be filled with the solution without its frothing, and as the tube which enters the liquid does not reach the bottom of the bottle, the sediment, if any, is not disturbed; another advantage is, that the solution does not come into contact with the cork, nor can any dust enter.

The Instruments and Apparatus.

The Burette—or graduated tube for delivering the standard solution—may be obtained in a great many forms under the names of their respective inventors, such as Mohr, Gay-Lussac, Binks, &c., but as some of these possess a decided superiority over others, it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The burette, with india-rubber tube and clip, contrived by Dr. Frederic Mohr of Coblentz, shown in Figs. 83 and 84, has the preference above all others for general purposes.

The advantages possessed by this instrument are, that its constant upright position enables the operator at once to read off the number of degrees of test solution used for any analysis. The quantity of fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip, and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks' or Gay-Lussac's form of instrument. The principal disadvantage of these two latter forms of burette is, that a correct

FIG. 83.

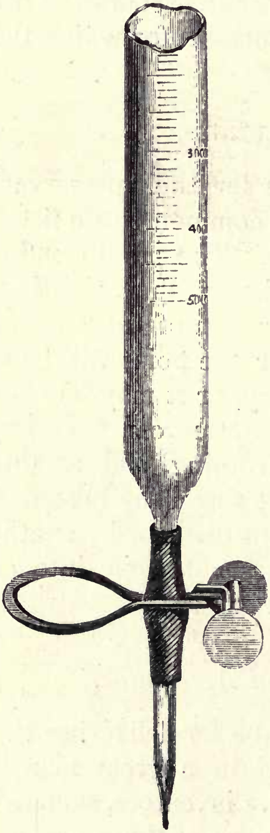
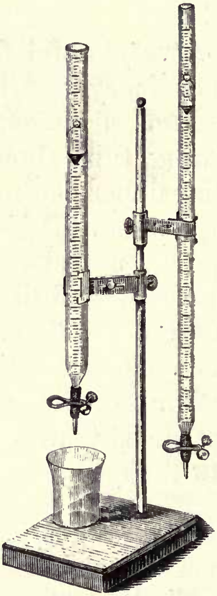


FIG. 84.



reading can only be obtained by placing them in an upright position, and allowing the fluid to find its perfect level. The preference should, therefore, unhesitatingly be given to Dr. Mohr's burette, wherever it can be used; the greatest drawback to it is, that it cannot be used for potassium permanganate, in consequence of its india-rubber tube, which decomposes the solution.

We are again indebted to Dr. Mohr for another form of instrument to overcome this difficulty, viz., the foot burette, with india-rubber ball, shown in Fig. 85.

FIG. 85.

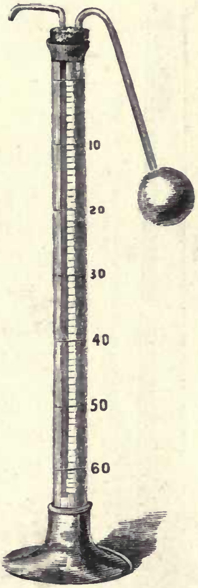
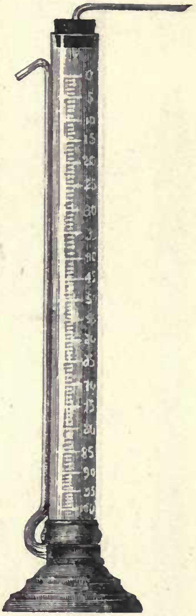


FIG. 86.



The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the elastic ball, which is of the ordinary kind sold for children, and has two openings, one cemented to the tube with shellac, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills itself with air.

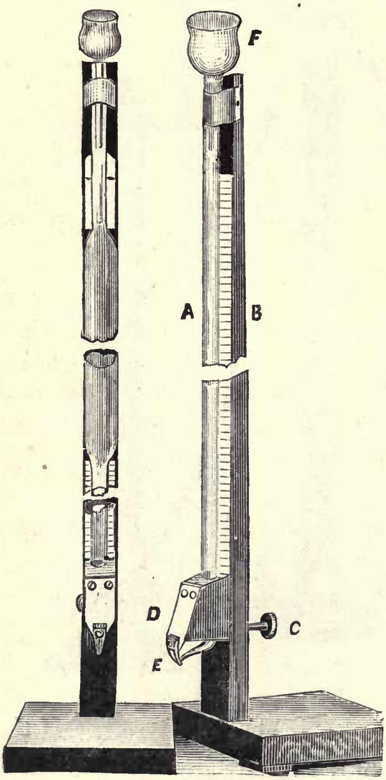
Gay-Lussac's burette, supported in a wooden foot, may be used instead of the above form, by inserting a good fitting cork into the open end, through which a small tube bent at right angles is passed. If the burette is held in the right hand, slightly inclined towards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in an horizontal position, to the great danger of spilling the contents, is avoided; at the same time the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation is more accurately determined.

Fig. 86 will show the arrangement here described.

Mr. J. Blodget Britton has described, in the 'Chemical News' for August 5, 1870, a burette for use in determining iron in metals and ores.

Figures 87 and 88 represent two of the kind, but of different patterns, mounted on walnut-wood stands; the former is for metals, and the latter, of smaller capacity, for ores.

Fig. 87. Fig. 88.



Securely fastened to the upright, B, is a graduated tube, A, having its lower part drawn out in the usual manner, but bent outwards at an angle of about 25°. E is a piece of cork riveted into a sheet-steel spring, D, which presses tightly, by means of the latter, against the vent of the tube. C is a thumbscrew passing through the frame and bearing against the spring.

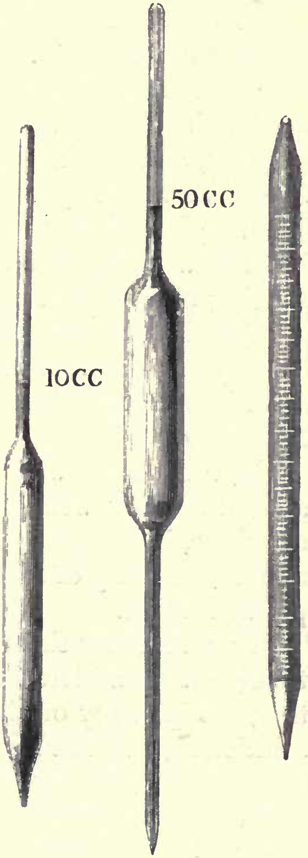
The tube of Fig. 88 has a capacity of 100 c.c. and is graduated into tenths, or 1000°; but that of Fig. 87 has a capacity of 150 c.c. and is graduated into 20ths, though only at its lower and narrow part.

Modes of operating.—Place a small narrow-necked funnel in the tube, as shown by the figures; pour in the solution to be used until it quite reaches the funnel, and then remove the latter to carry away any floating bubbles; turn the thumbscrew and bring the top line of the solution exactly to the 0 line of the scale; stop the flow, and afterwards touch the point of the cork with a glass rod to take from it any adhering drop. The instrument is then ready for use. By means of the thumbscrew the dropping may be controlled with extreme nicety or *instantly* stopped. Cork, after a little use, becomes quite inert towards potassium permanganate. The occasional application of some pure tallow to the end of the tube and cork will be quite effectual in preventing any of the fluid from running upwards by capillary attraction.

For everyday use in the laboratory, as well as for very accurate determinations, this burette will find favour.

The Pipette.—The pipettes used in volumetric analysis are of two kinds, viz., those which deliver one certain quantity only, and those which are graduated so as to deliver various quantities at the discretion of the analyst. In the former kind, or whole pipette, the graduation may be of three kinds, namely, 1st, in which the fluid is suffered to run out by its own momentum only. 2nd, in which it is blown out by the breath. 3rd, in which it is allowed to run out to a definite mark. Of these methods the last is preferable in point of accuracy, and should therefore be adopted if possible. The next best form is that in which the liquid flows out by its own momentum, but in this case the last few drops empty themselves very slowly; but if the lower end of the pipette be touched against the beaker

FIG. 89.



or other vessel into which the fluid is poured, the flow is hastened considerably, and in graduating the pipette, it is preferable to do it on this plan.

In both the whole and graduated pipettes, the upper end is narrowed to about $\frac{1}{8}$-inch, so that the pressure of the moistened finger is sufficient to arrest the flow at any point.

Fig. 89 shows two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size.

The Measuring Flasks.—These indispensable instruments are made of various capacities; they serve to mix up standard solutions to a given volume, and also for the subdivision of the substance to be tested by means of the pipettes, and are in many ways most convenient. They should be tolerably wide at the mouth, and have a well-ground glass stopper, and the graduation line should fall just below the middle of the neck, so as to allow room for shaking up the fluid.

Colorimetric Analysis is also used in assaying. It is based upon the fact that a coloured solution appears the more intense the more of the colouring substance it contains.

If, therefore, a solution containing a certain amount of a substance and being in consequence of a certain intensity of colour, is prepared, it will be possible to obtain the solution under assay of an equal intensity of colour by appropriate dilution.

By measuring the volume of the assay solution and taking into consideration the amount of the standard solution, the quantity of the substance contained in the assay solution may be readily calculated.

CHAPTER IX.

THE ASSAY OF IRON.

The ores of iron, properly so called, always contain the metal in the oxidised state, and in various degrees of purity.

The oxides and carbonates are the only minerals of iron which can be used as ores in the blast-furnace. These are associated with different impurities or foreign materials in greater or less proportion. The following is a list of the principal ores of iron, with the maximum percentage of metallic iron that could occur in each, if it were absolutely pure, as in its formula:—

Magnetic Iron Ore, $Fe_3O_4 = Fe_2O_3 + FeO$, 72·41.

Red Hæmatite and specular ore (anhydrous iron, sesquioxide or ferric oxide), Fe_2O_3, 70·00.

Brown Hæmatite, limonite (brown iron ore), $2Fe_2O_3,3H_2O$, 59·92.

Spathic Iron Ore (iron carbonate), FeO,CO_2, 48·22.

Titaniferous Ore (ilmenite), $FeO,TiO_2, + nFe_2O_3$, 36·82.

Franklinite, $3(FeO,ZnO,MnO) + (Fe_2O_3,Mn_2O_3)$, 45·16.

Besides these may be mentioned the varieties of impure iron carbonates, known as clay or clay-band ironstone and black-band ironstone. Clay-band ironstone sometimes resembles compact limestone, sometimes greyish hardened clay. Its great specific gravity, its effervescing on the addition of an acid, and acquiring a brown-red colour on roasting, are sufficient means of identifying it.

The following is the result of an analysis of this class of ore by the Author; the specimen was from Ireland, county Leitrim:—

Ferrous oxide	51·653
Ferric oxide	3·742
Manganese oxide	·976
Alumina	1·849
Magnesia	·284
Lime	·410
Potash	·274
Soda	·372
Sulphur	·214
Phosphoric acid	·284
Carbonic acid	31·142
Silica	6·640
Carbonaceous matter and loss	2·160
	100·000

Black-band is a combustible schistose variety of this ore. The following analysis is also by the Author :—

Ferrous oxide	20·924
Ferric oxide	·741
Manganese oxide	1·742
Alumina	14·974
Magnesia	·987
Lime	·881
Potash Soda	traces
Phosphoric acid	·114
Silica	26·179
Sulphur	·098
Carbonic acid	14·000
Carbonaceous matter	16·940
Water and loss	2·420
	100·000

Besides these iron ores the following substances, containing iron and used as fluxes, require assaying: Granite, Chlorite, Basalt, Pyroxene, Amphibole, and also some kind of slags (finery cinder, tap cinder, &c.).

A. THE ASSAY OF IRON IN THE DRY WAY.

Iron ores very seldom occur in a pure state, and the ores may be arranged for their assay in the dry way (and also for smelting) into five classes.

1. Iron ores containing silica, lime, and another base, which ores are fusible *per se*.
2. Iron ores containing predominantly silica.
3. ,, ,, ,, ,, lime.
4. ,, ,, ,, ,, alumina.

5. Iron ores containing a large amount of magnesia; these ores are most difficultly rendered fluid.

The flux used for assaying (and also melting) varies according to the nature of the predominant compound, and the quantity used according to the amount of that compound.

If the composition of the ore is known, it is easy to ascertain the amount of flux necessary to form a slag with the bases or silica present; in most cases an extra quantity of the flux should be added, in order to produce a sufficient volume of slag to cover the button.

According to Dr. Percy,* blast-furnace cinder of the following formula may be taken as a type of the kind of slag desirable :—

$$Al_2O_3,SiO_3\ 2(3CaO,SiO_3).$$

Its approximate composition per cent. is as under :—

Silica	38	or about	2½ parts
Alumina	15		1 ,,
Lime	47		3 ,,

The following mixtures of various fluxes, when fused, produce a slag which may be regarded as approximating to the above composition :—

Quartz . . .	1	. . . . . .		1·92	=	36·5 per cent.
China Clay .	2	Silica . .	0·92			
		Alumina .	0·82	0·82		15·5 ,,
Lime . . .	2½	. . . .		2·5		48·0 ,,
Glass . . .	2½	Silica		1·75	=	35 ,,
		Materials = Alumina		†0·75		15 ,,
Lime . . .	2½	. . . .		2·5		50 ,,
Shale or fire-clay	3	Silica		1·8	=	35 ,,
		Alumina		0·9		17 ,,
Lime . . .	2½	. . . .		2·5		48 .

According to *Bodemann* a compound of 56% silica, 30% lime, and 14% alumina forms a slag most easily rendered fluid, but as it is found that this slag itself is not sufficiently fusible in a small assaying furnace (air-furnace), an addition of fluor-spar is made to the mixture, and in some cases (the iron ore being very difficultly rendered

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[1] Percy's *Metallurgy*, p. 240.

[2] 30°/ₒ say of alkalies, lime, &c., on account of their fusibility, are taken as equivalent to so much alumina.

fluid) some borax is added, or a mixture of borax and fluor-spar.

An exact knowledge of the mineralogical properties of the iron ores, and a due experience, will enable the assayer to properly adjust the fluxes without resorting to an analysis to find what amount of silica and bases are present.

In some iron works of Germany the following proportions of fluxes are used :—

For magnetic ore, red hæmatite (very rich) . .	5 to 20%	chalk	and	25%	fluor-spar
„ argillaceous brown iron ore	20 to 40 „	„	„	30 to 40 „	„
„ bog iron ore . . .	50 „	„	„	50 „	„
„ spathose iron ore . .	10 to 15 „	china clay	„	20 to 25 „	„
„ finery cinder . . .	20 to 25 „	chalk	„	20 to 25 „	„

Air-furnaces are best adapted for assaying iron ores where many assays are required.

The furnace should have a cross section of 18 in. × 18 in., and depth to grate-bars 21 inches. Flue 7 in. × 7 in. Anthracite is the best fuel to use ; then coke.

In the assay of an iron ore it is required to reduce the oxide of iron to the metallic state, or rather that of cast-iron, to collect in a button, and to form with the foreign materials of the ore—by means of fluxes—a fusible slag that will not retain any of the iron, in combination, or in the form of pellets.

Naked crucibles, either of clay or blacklead, or crucibles lined with charcoal, are employed ; the latter are preferable. The button of metal does not adhere to naked pots, but the slag adheres very strongly ; so much so, that it cannot be detached with any degree of accuracy for weighing (which in some of M. Berthier's processes is of importance). Blacklead pots allow neither the slag nor button to adhere, but the former dissolves much argillaceous matter from the pot, so that its weight is greatly increased, and the assay cannot be verified. In naked crucibles, charcoal must always be added to the assay, to reduce the iron oxide ; in which case, if an excess be added, it prevents the button from completely forming, so that globules remain in the slag (with care this may, however, be avoided). Neither do naked crucibles resist the fire as well as those lined with charcoal, because the lining supports the sides when they soften. The charcoal lining also allows the assay to be finished without adding any reagent to the ore; the button can be readily taken out, because it does not adhere to the charcoal; and lastly, the earthy matters in the ore, which have formed a slag, may be collected and weighed. If we have added any flux to the ore, the total weight can also be ascertained.

The method of lining crucibles with charcoal brasque and conducting the assay is given as follows by Mr. Blossom: *

The brasque has a composition of four parts of finely-pulverised charcoal to one part of molasses. This must be thoroughly kneaded until a ball of it made in the hands resists, to a sensible degree, an attempt to pull it apart. The crucibles are packed full by driving the brasque in with a mallet; a conical cavity, of sufficient size for the charge, is then cut out, and the brasque dried in an oven. Care must be taken not to burn the molasses, for the brasque would in that case crumble, and be useless.

These are the best crucibles for iron assays, because they combine the following advantages:—

Being lined with charcoal, none need be mixed with the charge to reduce the oxide, whereas in naked crucibles charcoal must be added, and is liable to prevent the complete collection of the iron in a button by holding little pellets in suspension.

The slag neither adheres to a charcoal lining nor takes up any material from it, while it does adhere to ordinary naked crucibles, and dissolves argillaceous matter from blacklead crucibles. In the former case, then, the slag may be weighed as a verification of the assay, while in the latter this is, of course, impossible.

The lining serves as a support for the crucible, which, under the high heat employed, is very apt to be softened and crushed beneath the weight of the fuel.

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* *Chemical News,* April 5, 1872.

The Charge.

In making up the charge it is only necessary to consider the materials required as fluxes for the foreign matters of the ores. It may be well to sprinkle a little charcoal into the charge as a precaution, but none is absolutely required. Two cases may arise, in which we have (1) ores of unknown composition, and (2) ores previously analysed. The assay in both cases gives us a clue to the nature of the iron that may be obtained from the ore, and to the character and proportion of the fluxes to be added in the blast-furnace, in order that we may produce a fusible slag free from iron. In the former case, we obtain the additional information of the approximate percentage of iron, though the iron assay is seldom, if ever, made for this purpose. Recourse is had to the more accurate chemical analysis, which gives us the exact proportions of the substances which affect the iron injuriously or otherwise. In all the assays a constant weight of ore, 10 grammes, is taken.

1. *Ores of Unknown Composition.*

In the assay of an ore the composition of which is unknown, we employ one or more preliminary assays, and, if satisfactory results be not obtained from either, we make another assay with a charge modified according to the indications of the preliminary assay. The following charge may be used to advantage in the preliminary assay:—

Preliminary Assay—Charges.

	I.	II.	III.	IV.	
Silica	2·5	1	4·0	2·5—0	grms.
Lime	2·5	4	1·5	2·5—3	„
Ore	10·0	10	10·0	10·0	„

1. The first charge is employed for the purer ores, those containing very little gangue, such as some varieties of magnetic ore, red and brown hæmatites, specular and micaceous ores.

2. Ores containing silica; some varieties of brown hæmatite, magnetic ore, &c.

3. Ores containing lime, magnesia, or protoxide of manganese carbonates, &c.; calcareous hæmatites, spathic iron.

4. Ores containing silica and alumina; clay ironstones, black-band, &c.

The principle involved in all the charges is that of furnishing a base, lime; for an acid, silica; and *vice versâ.*

The choice of a charge, therefore, depends on the acid or basic nature of the gangue of the ore. The materials of the gangue might possibly be associated in such proportions as to flux themselves, but this would happen rarely.

Ores containing titanium require the addition of fluorspar to the charge, in quantity varying from 0·5 to 10 grms., according to the amount of titanium present.

2. *Ores Previously Analysed.*

When we know the percentage composition of an ore, it is a very simple matter to calculate a charge for the dry assay. Good results are obtained from a charge so proportioned as to yield a slag corresponding to the following formula of a blast-furnace cinder, as given by Percy :—

$$R_2O_3,SiO_3+2(3RO,SiO_3).$$

R_2O_3 represents alumina, and RO, lime, magnesia, and other bases. Its approximate percentage composition is as follows :—

Silica	38	or about	2½ parts
R_2O_3 (alumina)	15		1 „
RO (lime, magnesia, &c.) . .	47		3 „

We have, then, only to establish the latter relation between the component materials of the gangue, to obtain, on fusion, the above slag.

Let us take the following example :—

The Ore contains	Per cent.	10 grms. Ore contains	Required	Difference to be added
Silica . .	1·65	0·165	2·50	2·335 grms.
Alumina .	1·94	0·194	1·00	0·806 „
Lime, MgO, &c.	4·51	0·451	3·00	2·549 „

Silica is supplied by ground quartz. For the bases RO represented in the furnace slag and in the ore by lime, magnesia, &c., we add pure unslaked lime. The alumina is added in the form of kaolin, which may be assumed to contain equal parts of alumina and silica. Allowance must be made in adding silica for that introduced with the kaolin.

It happens sometimes that the ore contains more than is required of one of the ingredients of the slag, or the silica introduced with the kaolin may, when added to that already present, increase the quantity beyond the requirement. In either case make up a new slag with the excess. The following is an example of both cases :—

The Ore contains	Per cent.	10 grms. Ore contains	Required	Difference to be added
Silica . .	25·96	2·596	2·50	−0·096
Alumina .	6·92	0·692	1·00	0·308
Lime, MgO, &c.	7·59	0·759	3·00	2·241

Kaolin ($Al_2O_3.\frac{1}{2}$, $SiO\frac{1}{2}$) required to furnish 0·308 Al_2O_3	0·616
Silica contained in 0·616 kaolin .	0·308
Silica in excess in ore	~~6~~·096 0
Total excess of silica . . .	~~6~~·404 0

Add fluxes to make up with this excess more slag of the same composition as above.

	Excess	Required	Difference to be added
Silica	0·404	2·50	2·096
Alumina	—	1·00	1·000
Lime, magnesia, &c. . .	—	3·00	3·000

Kaolin required to furnish 1·00 Al_2O_3 . . .	2·000
Silica contained in 2·00 kaolin	1·000
Silica to be added, 2·096−1·000 . . .	1·096

Total material to be added to the charge :—

Silica		1·096
Kaolin . . .	0·616 + 2·00	2·616
Lime . . .	2·241 + 3·00	5·241

The charge having been weighed out, it must be thoroughly mixed on glazed paper; after placing it in the crucible, the conical cavity is closed with a piece of charcoal, and the whole top of the crucible is covered with a luting of fire-clay. The latter is mixed with $\frac{1}{4}$—$\frac{1}{3}$ part fine sand, and is made plastic with borax water. Hair is sometimes employed to prevent the luting from cracking off when dry; but no trouble is experienced from this source if the luting be properly made and applied. It should not be put on too thick, should be lapped over the edges of the crucible, and thoroughly dried before placing the crucible in the furnace.

Four crucibles are introduced at one time, and rest upon two fire-bricks placed one upon the other, to keep the crucibles in the very midst of the glowing coals. If the crucibles do not rest steadily on the bricks, it is well to support them with a little luting, to prevent their being knocked over in the fire. A low fire may be kindled before the introduction of the crucibles, or it may be kindled around them. The fuel is added gradually until it fills the furnace above the tops of the crucibles; the fire is then maintained at its maximum temperature for $2\frac{1}{2}$—$3\frac{1}{2}$ hours, according to the refractory nature of the ore. Ores containing much titanium may even require 4 hours, while carbonates containing manganese may fuse well in $2\frac{1}{2}$ hours, or in less time. Three hours will generally be sufficient for ores that do not contain much titanium. When the fire has burned out, the bricks and crucibles are removed in one mass, cemented together by the slag of the fuel. The crucibles are detached, and the exteriors broken with a hammer; on inverting and tapping the brasque lining, the slag and the button of cast iron will fall into the hand, when, if they adhere together, a slight tap will suffice to separate them. Before separation, however, they should be carefully cleansed and weighed; if necessary, the slag may then be broken, and any particles of iron it retains mechanically may be extracted with a magnet. The weight of the iron being deducted from the weight of the slag and button, we obtain the weight of the slag. This ought to approximate closely to the weight of the fluxes introduced and the corresponding material of the ore. If a large amount of iron has combined with the slag it will be indicated by the excess in weight. Titanium and manganese enter the slag almost completely; hence if they are present, allowance must be made for them. Duplicate assays are made, and the two results should not differ more than 0·3—0·4 of one per cent. The *slag* ought to be well-fused, colourless, transparent, and vitreous, or white, light-grey, bluish-grey, opaque, and semi-vitreous, resembling porcelain or enamel.

A good button will be well-formed, and will separate completely from the slag.

If the metal be of good quality, the button, when wrapped in a piece of thin tin plate, and struck on the anvil, will flatten slightly before breaking. It ought to be grey or greyish-white, and the grain fine, or tolerably fine. A button of bad iron breaks readily without changing form, sometimes even pulverising: the metal is generally white and crystalline on the surface.

The following are some of the characters that may be observed in slags, and their indications with reference to the charge:—A perfectly transparent slag of greenish tint indicates an excess of silica. A stony rough slag, or one that is crystalline in fracture and dull in lustre, indicates an excess of bases.

If the product, instead of being melted, is only fritted, and contains the reduced iron interspersed as a fine grey powder, both silica and alumina are deficient in the flux, lime and magnesia being in excess. The latter is one of the most refractory substances found in iron ores, and, when present in quantity, requires an addition of both silica and lime. A vesicular slag, with the iron interspersed in malleable scales, indicates the presence in the ore, of iron and manganese silicates, or an excess of silica, which react on the carburetted iron as it forms, producing malleable iron and carbonic acid. This trouble is corrected by the addition of lime.

Manganese in small quantity gives an amethystine tint to the slag; in larger proportion it produces a yellow, green, or brown colour.

Titanium often produces a resinous, black, and scoriaceous slag, sometimes curiously wrinkled on the outside. It is covered on the outside with a metallic pellicle of the cyano-nitride of titanium with its characteristic copper colour; sometimes the slag is vitreous and of a bluish tint. *Chromium* gives a dark resinous slag, sometimes surrounded by a thin metallic coating.

The following are some characters of the button dependent on the substances named:—

Phosphorus.—A hard, brittle, white metal, known as cold-short.

Sulphur.—A strong, reticulated, mottled structure, and red-short iron.

Manganese.—A button smooth exteriorly, hard and nongraphitic: it breaks under the hammer and presents a white crystalline fracture.

Titanium.—The button is smooth on the outside, and breaks under the hammer with a deep grey fracture, dull or crystalline. It adheres strongly to the slag. The button is covered sometimes with titanium cyano-nitride with its characteristic copper colour. Titanium is said to increase the strength of the metal. It may be present to the extent of one per cent.

Chromium.—Sometimes the button is smooth, well-fused, with a brilliant crystalline fracture and tin-white colour; at other times it is white, only half-fused, or it may even form a spongy mass of a clear grey colour, according to the quantity of chromium contained in the iron. Many alloys of iron and chromium will scratch glass.

Berthier recommends the following method for estimating the other, chiefly slag-forming, components of iron-ores. The operations of this method are comprised in roasting or calcining, to drive off any volatile or combustible matters, and in treating the ore with certain acids, the object of which is to ascertain the amount of insoluble matter, by difference of weight, before and after the action has taken place.

The hydrated ores are calcined to estimate water; and those containing manganese, to reduce it to a fixed and known state of oxidation (sesquioxide). The carbonates are roasted to expel carbonic acid, and the ores from the coal-formations to burn the combustible matter with which they are mixed.

Slags and dross are also roasted to free them from charcoal. A simple calcination sometimes is sufficient, as in the case of carbonates; but where mixtures of ferric and ferrous oxides are to be assayed, they must be subjected to a long roasting, in order to convert all the contained ferrous oxide into ferric oxide.

Diluted and cold nitric or acetic acids are employed for minerals whose matrix is purely calcareous or magnesian, as these acids dissolve the earthy carbonates, without attacking either stones, clay, or the iron oxides. The residue is to be well washed, dried, and weighed, and the amount of carbonates calculated by the difference. It is now to be treated with boiling hydrochloric acid, or, what is preferable, *aqua regia*. The ores which contain substances insoluble in these acids are generally of a clayey or flinty nature. These are to be weighed, and according to their weight that of the flux to be added in the assay is determined, as will be shown hereafter.

It must be borne in mind, however, that the clays are not absolutely insoluble in hydrochloric acid, for a certain quantity of alumina is always dissolved, which is generally greater in proportion to the amount present in the iron ore.

The ores containing titanium are boiled with concentrated sulphuric acid, after they have been reduced to the finest possible state of division. All the iron, titanium, and manganese oxides are dissolved, and the stony gangues which resist the action of this acid can be estimated. The utility of this estimation will be pointed out as we proceed.

When all the operations necessary for each particular case have been completed, we know the proportion of volatile substances, of substances soluble in acetic acid, and those insoluble in hydrochloric and sulphuric acids, contained in the substance under assay.

Let A be the weight of the rough or non-calcined ore; B the weight of the same calcined; C the weight of the fluxes in a rough state; D the weight of the same calcined; P the weight of matter insoluble in hydrochloric or sulphuric acids; R the weight of the fixed substances soluble in acetic or nitric acids,—a weight which can be readily calculated when we know the loss which the ore, not treated by acids, suffers by calcination, and the residue of the treatment of this substance by acetic or nitric acid; M the weight of the button of metal and scattered globules; S the weight of the slag; and O the loss of weight in the assay, which represents the quantity of oxygen disengaged during the reduction.

The following is the disposition of the data from which, at one view, all the useful results of the assay can be determined.

In the assay has been employed:—

A, rough ore = calcined ore	B
B, of rough fluxes added = fixed flux	D
Total of fixed matter	B + D

The result has been:—

Metal—M Slag—S	Total	M + S
Loss		O
Fluxes		D
Vitrifiable matters		S—D
Substances insoluble in hydrochloric acid, &c.		T
Substances soluble in hydrochloric acid, &c.		S—D—T
Substances soluble in acetic acid		R
Substances insoluble in acetic acid, and soluble in hydrochloric acid		S—D—T—R

When the iron in the substance assayed is in a known degree of oxidation, and when but little manganese is present, the quantity of oxygen O ought to correspond very nearly with the quantity of metal M produced; if it does, the assay must be correct.

A rigorous correspondence between the two numbers, however, cannot always be obtained, because the iron is not pure, but always contains carbon, so that in ordinary assays the ferric oxide loses but from twenty-eight to twenty-nine per cent. of oxygen.

On the other hand, the quantity of iron remaining in the slag makes up in part for the carbon combined with the metal reduced; but when the assay has been made with a suitable flux, the quantity of oxide remaining is very small, and never exceeds one per cent. of the weight of the slag. When the iron is in an unknown degree of oxidation, the loss O produced in the assay gives the degree, if it has been made without accident; but if there is any doubt, and the result is of importance, the assay must be recommenced for verification. If the ferruginous matter contain manganese, and if that metal be in the state of protoxide, the verification just described can be made without modification, because the manganese dissolved in the slag is always at the *minimum* of oxidation; and when a sufficient quantity of flux is employed, the amount reduced is of no consequence. But when the manganese is in the state of red oxide, it parts with a certain quantity of oxygen on being reduced to the *minimum* of oxidation, and which quantity is estimated in the loss O, so that a perfectly accurate verification cannot be made. Nevertheless, the difference between the loss O, and the quantity of oxygen calculated from the metal M, cannot be very great, because the red oxide of manganese loses but ·068 of oxygen in its transformation to protoxide.

If the assay has been made with care, the loss of oxygen indicates the amount of iron in a very approximate manner, and nearly always with an exactitude which is surprising to those not accustomed to this kind of operation.

Titanic acid behaves in iron assays exactly as the oxides of manganese; it disengages at most but ·06 of oxygen when dissolved in the earthy glasses in contact with charcoal.

B. THE ASSAY OF IRON AND ITS ORES IN THE WET WAY.

This will be subdivided into the following sections :—

α. Assay of iron ores, pig-iron, and steel, for the metallic iron they contain.

β. Complete assay of iron ores.

γ. Estimation of carbon, sulphur, phosphorus, silicon, &c., or metallic iron and steel.

Dr. Penny's Process.—The following method of determining the amount of iron in a sample by means of a normal solution, has been contrived by Dr. F. Penny, who was led to substitute potassium bichromate for potassium permanganate, as recommended by Marguerite. The reason of employing the bichromate is, that it is an unchangeable salt, whilst the permanganate sometimes undergoes decomposition, so that its strength is variable, and each series of experiments made with it requires a separate verification by means of a weighed quantity of pure iron. This inconvenience is avoided in Dr. Penny's method, which is described in his own words as under :—

'In the first series of experiments, pure harpsichord wire was dissolved with every care in hydrochloric acid, and potassium bichromate added to the solution until the conversion of the iron protochloride into the perchloride was complete. I obtained the following results :—

	Iron.		Bichromate.
'Exp. I.	50	grs. required	44·4 grs.
" II.	39·7	" "	35·2 "
" III.	48·3	" "	42·8 "
" IV.	55·3	" "	49·2 "

'The mean of these results is, 100 parts of iron to 88·75 of bichromate.

'In the second series of experiments ferrous sulphate was employed. This salt was made from ferrous sulphide, and purified most carefully by repeated crystallisation. A known quantity of it was dissolved in water, acidulated with either pure hydrochloric or sulphuric acid, and the solution treated with bichromate :—

	Sulphate of iron.		Bichromate.
‘Exp. I.	100	grs. required	17·90 grs.
„ II.	180	„ „	32·10 „
„ III.	150	„ „	26·82 „
„ IV.	120	„ „	21·40 „

‘These experiments give the ratio of 100 parts of ferrous sulphate to 17·867 of bichromate, or 100 of iron to 88·71, which corresponds very closely to the mean result obtained with the metallic iron. Moreover, I performed a series of similar experiments with the neutral potassium chromate, and obtained results completely confirmatory of the general accuracy of the foregoing experiments. We may therefore, I think, safely conclude that 100 parts of metallic iron correspond to 88·75 of the potassium bichromate, and that 100 of the latter are equal to 112·67 of the former.

‘I shall now proceed to describe the method of employing the potassium bichromate for the determination of the amount of iron in clay-band and black-band ironstone. I shall be purposely minute, as I particularly desire that the process may be serviceable to those who, from their pursuits in life, are interested in the value and quality of ironstone, and who may be imperfectly acquainted with analytical operations.

‘A convenient quantity of the specimen is reduced to coarse powder, and one-half at least of this still further pulverised, until it is no longer gritty between the fingers. The test solution of potassium bichromate is next prepared. 44·4 grs. of the salt in fine powder are weighed out, and put into an alkalimeter (graduated into 100 equal divisions), and tepid distilled water afterwards poured in until the instrument is filled to 0. The palm of the hand is then securely placed on the top, and the contents agitated by repeatedly inverting the instrument, until the salt is dissolved and the solution rendered of uniform density throughout. It is obvious that each division of the solution thus prepared contains 0·444 gr. of bichromate, which corresponds to $\frac{1}{2}$ a gr. of metallic iron. The potassium bichromate used for this process must of course be purchased pure, or made so by repeated crystallisation, and it should be thoroughly dried by being heated to incipient fusion.

'100 grs. of the pulverised ironstone are now introduced into a Florence flask, with 1½ oz. by measure of strong hydrochloric acid, and ½ an ounce of distilled water. Heat is cautiously applied, and the mixture occasionally agitated, until the effervescence caused by the escape of the carbonic acid ceases; the heat is then increased, and the mixture made to boil, and kept at moderate ebullition for ten minutes or a quarter of an hour. During these operations it will be advisable to incline the flask, in order to avoid the projection, and consequent loss, of any portion of the liquid by spirting. About 6 oz. of water are next added, and mixed with the contents of the flask, and the whole rapidly transferred to an evaporating basin. The flask is rinsed several times with water, to remove all adhering solution.

'Several small portions of a weak solution of pure red potassium prussiate (containing one part of the salt to 40 of water) are now dropped upon a white porcelain slab, which is conveniently placed for testing the solution in the basin during the next operation.

'The prepared solution of potassium bichromate in the alkalimeter is then added very cautiously to the solution of iron, which must be repeatedly stirred, and as soon as it assumes a dark greenish shade, it should be occasionally tested with the red potassium prussiate. This may be easily done by taking out a small quantity on the top of a glass rod, and mixing it with a drop of the solution on a porcelain slab. When it is noticed that the last drop communicates a distinct red tinge, the operation is terminated. The alkalimeter is allowed to drain for a few minutes, and the number of divisions in the test-liquor consumed read off. This number multiplied by two gives the amount of iron per cent. in the specimen of ironstone, assuming that, as directed, 100 grs. have been used for the experiment. The necessary calculation for ascertaining the corresponding quantity of protoxide is obvious.

'When black-band ironstone is the subject of analysis, or when the ore affords indications, by its appearance or during the treatment with hydrochloric acid, that it contains an appreciable quantity of carbonaceous matter, then the hydrochloric acid solution must be filtered before being transferred to the basin, and the filter, with the insoluble ingredients, must be washed in the usual way with warm distilled water, slightly acidulated with hydrochloric acid until the filtrate ceases to give a blue colour with the red potassium prussiate. In those cases, also, where the presence of iron pyrites in the ironstone is suspected, it will be necessary to remove the insoluble matter by filtering before applying the bichromate solution; but with ironstones in which the insoluble ingredients are merely clay and silica, filtration is not essential.

'Now it is evident that the foregoing process, so far as I have described it, serves for the determination of that portion of iron only which exists in the ore in the state of protoxide. But many specimens of the common ironstone of this country contain appreciable quantities of ferric oxide, which, being unacted upon by the potassium bichromate, would escape estimation by the present method. By an additional and easy operation, however, the amount of metallic iron in the ingredient may be likewise determined. It is only necessary to reduce it to the minimum state of oxidation and then to add the bichromate as previously directed.

'The best and most convenient agent for effecting the reduction of the ferric oxide is sodium sulphite. The only precaution to be observed is to use it in sufficient quantity, and at the same time to take care that the iron solution contains excess of acid. When the reduction is complete, a few minutes' ebullition suffices to decompose the excess of sodium sulphite, and effectually to expel every trace of sulphurous acid.

'In order to test the exactness of this mode of estimating the iron of the peroxide, I made several experiments with peroxide prepared from known quantities of pure iron wire. The peroxide was thoroughly washed, dissolved in hydrochloric acid, reduced with sulphite of soda, and after complete expulsion of the excess of sulphurous acid, the solution was diluted with water and treated with potassium bichromate. I select three of the experiments :—

'Exp. I.	10 grs. of iron	consumed		8·87 of bichromate.	
" II.	18 "	"	"	15·94	"
" III.	25 "	"	"	22·15	"

'The mean of all my experiments on this point gives the ratio of 100 of iron to 88·6 of bichromate, which is in close accordance with the former results.

'Whenever, therefore, the ore of iron contains ferric oxide it will be necessary to add sodium sulphite to the hydrochloric acid solution before the addition of the test-liquor from the alkalimeter. The sulphite should be dissolved in distilled water, and added to the solution of iron in small successive portions, until a drop of the liquor gives merely a rose-pink colour with potassium sulphocyanide, which indicates that the reduction of the ferric salt is sufficiently perfect. The liquor is now heated till the odour of sulphurous acid is no longer perceptible. These operations should be performed while the solution is in the flask, and before it is filtered or transmitted to the basin.

'I will here mention for the guidance of those who may not be fully aware of the reactions of the oxides of iron, that the existence of an appreciable quantity of peroxide in the ironstone may be readily discovered by dissolving (as directed in the process) 39 or 40 grs. of the ore in hydrochloric acid, diluting with about 8 oz. of water, filtering, and testing a portion of the solution with potassium sulphocyanide. If a decided dark blood-red colour is produced, the quantity of ferric oxide in the stone must be determined ; but if the colour is only light red or rose-pink, the proportion is exceedingly small, and for practical purposes not worth estimating. Of course, when the specimen of ironstone has an ochrey or a reddish appearance on the surface or in the fracture the presence of a large proportion of ferric oxide is indicated, and its exact quantity must be determined.

'In conclusion, I must not omit to notice one or two circumstances which appear at first to militate against the accuracy of this process. It may be questioned whether solutions of the ferrous salts do not absorb oxygen so rapidly from the air as to influence the results obtained by this method. Marguerite has shown, and my own observations completely confirm his statement, that ferrous salts in an acid solution become peroxidised very slowly; and, in a particular experiment, I found that contact with the air during several hours caused no diminution in the quantity of potassium bichromate required. As the process may be completed in a few minutes, it is certain that no inaccuracy can arise from this cause.

'It is also important to inquire whether the chromic acid in the potassium chromate may not be partially deoxidised by hydrochloric acid alone without the presence of a ferrous salt. Such a reaction would obviously give rise to a serious error. It is well known that concentrated hydrochloric acid rapidly decomposes the chromic acid of the chromates when aided by the application of heat. But I have satisfied myself, by numerous experiments, that this acid exerts very little appreciable action upon dilute solutions of the potassium chromates, either cold or warm, and that the action is only partial even after continued ebullition; so that the present method is free from inaccuracy on this account.'

4. *Titration of Iron by Tin Protochloride.*—Mr. Sutton, in his excellent 'Volumetric Analysis' before quoted, gives the following directions for the direct titration of iron by tin protochloride.

The principle involved in this reaction is, in fact, simply a reversion of the ordinary process by permanganate and bichromate. In the case of these two reagents, the amount of oxygen *given up* by them is the measure of the quantity of iron, whereas with tin protochloride it is the amount *taken up* by it that answers the same purpose.

Fresenius (in his 'Zeitschrift für analytische Chemie,' part 1, page 26) has recorded a series of experiments made on the weak points of this process, and gives it as his opinion that it is most accurate and reliable, with proper care. The summary of his paper is as follows:—

a. A solution of ferric oxide of known strength is first prepared, by dissolving 10·03 grm. fine pianoforte wire (=10 grm. pure iron) in pure hydrochloric acid, adding chlorate of potash to complete oxidation; boiling till the excess of chlorine is removed, and diluting the solution to 1 litre.

b. A clear solution of tin protochloride, of such strength that about equal volumes of it and the iron solution are required for the complete reaction.

c. A solution of iodine in potassium iodide, containing about 0·005 grm. iodine in 1 c.c. (If the operator has the ordinary decinormal iodine solution at hand, it is equally applicable.) The operations are as follows:—

1. 1 or 2 c.c. of the tin solution are put into a beaker with a little starch liquor, and the iodine solution added from a burette till the blue colour occurs; the quantity is recorded.

2. 10 c.c. of the iron solution = 0·1 grm. iron are put into a small flask with a little hydrochloric acid, and heated to gentle boiling (preferably on a hot plate); the tin solution is then allowed to flow in from a burette until the yellow colour of the solution is nearly destroyed; it is then added drop by drop, waiting after each addition until the colour is completely gone and the reduction ended. If this is carefully managed there need be no more tin solution added than is actually required; however, to guard against any error in this respect, the solution is cooled, a little starch liquor added, and the iodine solution added by drops until a permanent blue colour is obtained. As the strength of the iodine solution compared with the tin has been found in 1, the excess of tin solution corresponding to the quantity used is deducted from the original quantity, so that by this means the volume of tin solution corresponding to 0·1 grm. iron is found.

The operator is, therefore, now in a position to estimate any unknown quantity of iron which may exist in a given solution, in the ferric state, by means of the solution of tin.

If the iron should exist partly or wholly in the ferrous state, it must be oxidised by the addition of potassium chlorate, and boiled to dissipate the excess of chlorine, as described in 2.

Example: 10 c.c. of iron solution, containing 0·1 grm. iron, required 15 c.c. of tin solution.

A solution, containing an unknown quantity of iron, was then taken for analysis, which required 12 c.c., consequently, a rule of three sum gave the proportion of iron as follows:—

15 : 0·1 grm. :: 12 : 0·08 grm.

It must be remembered that the solution of tin is not permanent, consequently it must be tested every day afresh. Two conditions are necessary in order to ensure accurate results.

1st. The iron solution must be tolerably concentrated, since the end of the reduction by loss of colour is more distinct; and, further, the dilution of the liquid to any extent interferes with the quantity of tin solution necessary to effect the reduction. Fresenius found that by diluting the 10 c.c. of iron solution with 30 c.c. of distilled water, $\frac{1}{10}$ of a c.c. more was required than in the concentrated state. This is, however, always the case with tin protochloride in an acid solution, and constitutes the weak point in Streng's method of analysis by its means: it would seem that dilution either predisposed it to rapid oxidation, or that water had the power within itself to communicate a certain proportion of oxygen to it.

2nd. The addition of the tin solution to the iron must be so regulated that only a very small quantity of iodine is necessary to estimate the excess—if this is not done another source of error steps in, namely, the influence which dilution, on the one hand, or the presence of great or small quantities of hydrochloric acid on the other, is known to exercise over this reaction. Practically it was found that where the addition of tin to the somewhat concentrated iron solution was cautiously made, so that the colour was just discharged, the mixture then rapidly cooled, starch added, and iodine till blue, the estimation was as reliable as by any other method.

Messrs. Stock and Jack ('Chemical News,' Feb. 12, 1875), modify this process as follows:—

1 grm. of ore is dissolved in 30 c.c. of strong HCl, or if not decomposed by HCl it is first fused with alkaline carbonate, and brought into HCl solution; in either case, the solution is made up to 500 c.c. with distilled water, and caused to boil. The stannous chloride may now be added in small portions at a time, but it *must* be in *dilute clear acid* solution, a convenient strength containing 10 grms. of tin per litre. The colour of the ferric solution is a fair guide to the addition of the tin-salt within certain limits; but when the colour becomes faint some other indicator must be used, and this we find in a dilute, recently prepared solution of potassium sulphocyanide, which is disposed in drops over the surface of a white tile. Special care must be taken to add the trial drops of iron solution quickly to those on the tile, and to have the beaker containing the solution in pretty close proximity to the tile, so as to guard against oxidation of solution on the glass rod with which the test drops are added. The reduction is carried so far that only a faint tinge of pink is produced, when the last addition of tin-salt has been made and allowed to boil for a few moments. The next step is the titration with potassium bichromate; and, as a vital part of the process, we make the preliminary addition of three drops of bichromate (standard solution 1 c.c. = 0·01 grm. iron), then test with potassium sulphocyanide. A distinct access of colour in this test, as compared with the last test made in reducing, is accepted as proof of the absence of stannous salt, and it only remains to complete the assay in the usual manner.

The tin solution is best prepared by placing fragments of pure tin at the bottom of a beaker, laying a small platinum crucible or cover upon them, and covering the whole with equal parts of pure hydrochloric acid and water: a large watch-glass or porcelain capsule should be placed on the top of the beaker, to exclude air and prevent loss by spirting.

The contact of the platinum with the tin sets up a galvanic current, which materially hastens the solution of the tin without at all affecting the platinum; when the acid is all saturated, it may be poured off and fresh added until sufficient solution has been obtained. The whole, freely acidified and diluted to a convenient strength, should be placed in a well-stoppered bottle, with a few fragments of tin; its strength, which is constantly lessening to a slight extent, must be found before using it.

β. Complete Assay of Iron Ores.—The ordinary constituents of clay ironstone (which is about the most complex, and of which the details of the analysis will be the most useful) are the ferric and ferrous oxides, manganese oxide, alumina, magnesia, lime. potash, soda, sulphur, phosphoric acid, carbonic acid, silica, and water.

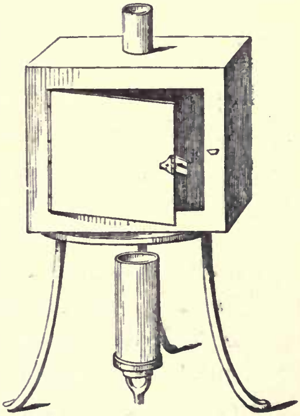
Some iron ores dissolve very readily in hydrochloric acid or in *aqua regia*; others do not, even when they are in a very fine state of division; but all do readily after fusion with an alkali, or an alkaline carbonate—as of potash or soda; hence it is advisable to fuse the finely-pulverised ore with an alkali previous to attempting its solution in an acid.

Determination of Silica, Iron Oxide, and Manganese Oxide.—The ore must be reduced to the finest possible state of division, a small quantity placed in a test-tube, and boiled for some time with hydrochloric acid. If it completely decomposes it need not be submitted to fusion with sodium carbonate, but 100 grs. may be at once weighed off, and treated in a Florence flask with about 2 ounces of hydrochloric acid, gradually heated to ebullition, and that temperature maintained until perfect decomposition has ensued. If, on the other hand, the ore does not completely decompose, 100 grs. must be carefully mixed with

500 or 600 grs. of sodium carbonate placed in a platinum crucible and fused at a bright red heat; the fusion must continue about half an hour. It may be here mentioned that the platinum crucible, previous to its introduction into the furnace, must be placed in one of clay furnished with a cover and embedded in magnesia, to protect it from the injurious effect of contact with the crucible or fuel.

When the platinum crucible and its contents are cold, it is placed in a large evaporating basin, and pure dilute hydrochloric acid poured over it: the fused mass dissolves with effervescence, and more acid must be gradually added as seems necessary, until no further action takes place. The solution being finished, the crucible is removed, washed with distilled water, and the whole, together with the washings, evaporated to dryness. The solution obtained in the first case, in which the ore was wholly decomposable by hydrochloric acid alone, is also to be evaporated to dryness. The object of this evaporation is the conversion of the silica the ore may contain, from a partially soluble to a completely insoluble state, so that the whole of it may be collected and weighed.

FIG. 90.



Towards the end of the operation, the partially-dried mass must be continually stirred, in order to prevent losses by the spirting which will otherwise take place. When cold, the contents of the basin are moistened with hydrochloric acid, and the whole left to itself for about one hour. It is then mixed with a small quantity of distilled water, gently warmed and thrown upon a filter. Every constituent of the ore, with the exception of the silica, will pass through the filter in a liquid state. The silica remaining in the filter is to be well washed with hot water, dried,* ignited in a platinum crucible, and weighed.

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* The most convenient form of apparatus for drying precipitates, filters, &c in analysis, is a little water-oven, called a 'water-bath' (see fig. 90). It con

To the liquid filtered from the silica, and with which the washings have been incorporated, add a few drops of nitric acid, and boil; when cool, add gradually pure precipitated barium carbonate until in excess, which point may be ascertained by cessation of effervescence, and by some of the carbonate remaining undissolved. The whole is now to be kept at a gentle heat for about an hour, and then poured on a filter, in which will remain the ferric oxide, alumina, and phosphoric acid, together with the excess of barium carbonate employed. The liquid which has passed through the filter is mixed with excess of ammonium sulphide, covered with a glass plate to exclude air, and left to itself for four or five hours. If any manganese were present in the ore, it will now be thrown down as a flesh-red precipitate, which must be collected on a filter, washed, dissolved in a small quantity of hydrochloric acid, the solution filtered, and excess of sodium carbonate added: manganese carbonate is precipitated, collected on a filter, washed, dried, ignited, and weighed as red oxide, every 100 parts of which correspond to 93 parts of manganous oxide, in which state it usually exists in the ore. The weight so obtained gives the percentage. The mixed precipitate of iron oxide, alumina, barium carbonate, and phosphoric acid remaining on the filter, is dissolved in a small quantity of hydrochloric acid, and the amount of iron ascertained by Dr. Penny's process, as already described. As the iron is in the state of peroxide, its reduction to protoxide must be effected by sodium sulphide, according to the method already given.

Determination of Lime and Magnesia, and part of the Phosphoric Acid.—Dissolve another 100 grs. of ore with the precautions already pointed out, only in this case the silica may be rejected, and treat the solution by the following process, which was contrived by Fresenius:—

The solution is heated to ebullition in a flask, and reduced with sodium sulphite, then precipitated with sodium

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sists of a double box of copper or tin plate about six inches square, with water between the casings, which is kept in a state of ebullition by means of a gas-flame or spirit-lamp.

carbonate, and boiled with excess of caustic soda until the precipitate appears black and granular. It is allowed to subside, the clear liquid poured off, the precipitate washed by decantation with hot water, and finally brought upon a filter of close texture and washed with hot water.

Treatment of the Precipitate.—The precipitate is again transferred, together with the filter, into the flask, and digested with hydrochloric acid. When no more black particles are perceptible it is filtered; the filter is left whole, a little water poured over it, and the flask inclined so that it remains hanging by the side while the liquid runs off: in this manner it may be quickly and completely washed. The filtered solution is reduced with sodium sulphite, heated to boiling, mixed with a few drops of chlorine water, then with an excess of sodium acetate; and when the liquid or precipitate has not a reddish tint, chlorine water is added until this is the case. The whole is boiled until the precipitate has separated, filtered hot, and the precipitate, consisting of ferric phosphate and some basic ferric acetate, washed.

To the solution just filtered from the iron phosphate, add ammonia and ammonium sulphide, and filter while hot; this removes manganese and iron, leaving lime and magnesia alone in solution. The whole is filtered while hot, and the precipitate remaining on the filter rejected. To the filtered solution is added excess of solution of ammonium oxalate: this throws down insoluble calcium oxalate, which must be collected on a filter, washed, dried, and ignited at a low red heat. The residue is now calcium carbonate, every 100 parts of which correspond to 56·29 parts of lime.

To the solution filtered from the calcium oxalate, and which contains the magnesia, add excess of sodium phosphate, agitate briskly, and set aside for twelve hours; then collect the crystalline precipitate of magnesium ammonio-phosphate on a filter, wash it with water containing a little ammonia, dry and ignite it; weigh the resulting magnesium pyro-phosphate: every 100 parts correspond to 36·67 parts of magnesia.

The precipitate containing the sodium perphosphate and basic acetate is dissolved in hydrochloric acid, reduced with sodium sulphite, boiled for some time with excess of caustic soda, and filtered. The filtered solution which contains the phosphoric acid is supersaturated with hydrochloric acid, and placed aside for future operation.

Treatment of the alkaline solution poured off from the first black precipitate. Determination of Alumina and remainder of Phosphoric Acid.—The solution is acidulated with hydrochloric acid, a little potassium chlorate added, and then boiled; it is then precipitated with ammonia (avoiding a large excess), and barium chloride added as long as a precipitate appears. After digesting for some time it is filtered. The precipitate, which contains the whole of the alumina and phosphoric acid, is collected on a filter, washed with a little water, and dissolved in as little hydrochloric acid as possible. The solution is saturated with precipitated barium carbonate, gently warming; an excess of caustic soda is added, and the heat still kept up. Any baryta contained in the solution is removed by sodium carbonate, which is added until no further precipitation takes place. The whole of the alumina is now in solution, and the whole of the phosphoric acid in the precipitate.

The solution is rendered acid with a little hydrochloric acid, boiled with a small quantity of potassium chlorate, precipitated with excess of ammonia, and allowed to stand for a few hours; after which the precipitated alumina is collected on a filter, washed, dried, ignited, and weighed: its amount represents the percentage of alumina in the ore.

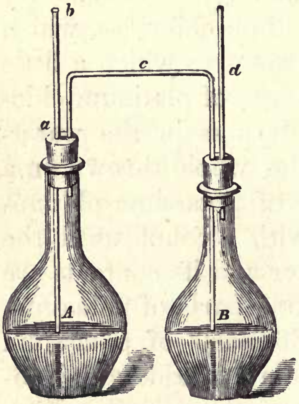
The precipitate containing the phosphoric acid is dissolved in hydrochloric acid, the baryta precipitated with dilute sulphuric acid, which is added until no further precipitate ensues; the liquid and precipitate are placed in a warm situation until the former is quite bright: it is then filtered, and to the filtered liquid is added the small portion reserved, as before directed: excess of ammonia is added to the mixture, then some ammonium chloride, and lastly magnesium sulphate. The phosphoric acid is precipitated as the magnesium ammonio-phosphate, which is washed, dried, and ignited, with the precautions already pointed out. Every 100 parts correspond to 63·33 parts of phosphoric acid.

Determination of Potash and Soda.—If the ore be completely decomposable by hydrochloric acid, dissolve at once 100 grs. in that liquid; if not, fuse the same quantity with four times its weight of barium hydrate in a platinum crucible: treat with hydrochloric acid, and separate the silica precisely as already described. To the filtered solution add an excess of baryta water; this precipitates everything but the potash and soda and part of the lime. Throw the whole on a filter, well wash the precipitate, and add the washings to the bulk of the filtered liquid; to which add excess of ammonia and ammonium carbonate: by these reagents the small quantity of lime and the excess of baryta in solution are precipitated. The solution must now be filtered, evaporated to dryness, and ignited. The dry residue consists of potassium and sodium chlorides, which must be weighed, then dissolved in water to which a little hydrochloric acid is added, then excess of platinum chloride, and the whole evaporated to dryness in the water-bath; alcohol is now added, and the whole thrown on a small filter. The yellow precipitate of potassium platino-chloride on the filter is washed with alcohol until the latter passes off colourless. The filter and its contents are then dried and weighed. Every 100 parts of potassium platino-chloride correspond to 30·56 parts of potassium chloride. The quantity of potassium chloride thus obtained is deducted from the weight of the mixed sodium and potassium chlorides as obtained above; the difference will be the amount of the sodium chloride. Every 100 parts of sodium chloride correspond to 53·28 of soda, and every 100 parts of potassium chloride to 63·25 of potash.

Determination of Sulphur.—Dissolve 100 grs. of the ore in either of the manners already described, separating the silica; in this case, however, a little nitric acid must be added to the hydrochloric acid previous to its mixture with the ore. To the filtered solution, made somewhat dilute, add excess of barium chloride, and allow to stand in a warm place for a few hours. Collect the precipitate of barium sulphate on a filter, wash, dry, ignite, and weigh. Every 100 parts correspond to 13·79 parts of sulphur.

Determination of Carbonic Acid.—The most convenient apparatus for the determination of this gas is that invented by Fresenius and Will, of which the following is a description. Fig. 91 shows its construction. *A* is a large flask of about two ounces capacity, in which the decomposition of the carbonate is effected: *B* a somewhat smaller flask, containing strong sulphuric acid: both are supplied with doubly pierced corks, for the reception of the three tubes, *a*, *c*, and *d*. The tube *a* is confined to the flask *A*, being immersed below the level of the fluid: in the same manner, *d* is only connected with the flask *B*, and only extends just below the cork. Lastly, the tube *c* enters the neck of *A* on the one side, but does not extend further, and, by a double bend, is brought into connection with *B*, which it enters, dipping into the sulphuric acid. The mouth of *a* is closed with wax during the experiment, so that no orifice is left in the whole apparatus but the mouth of the tube *d*.

FIG. 91.



The large assay balance, represented by fig. 11, is admirably suited for weighing this apparatus.

100 grs. of the ore are introduced into the flask *A*, which is then filled with water to about one-third; the apparatus is closed by the wax stopper, and brought into equilibrium on the balance by a counterpoise. The decomposition of the carbonate under examination is now induced by sucking out a small quantity of air with the mouth from the tube *d*. The air is thus drawn not only from *B*, but also from *A*, both flasks being connected by the tube *c*; bubbles of air are therefore seen passing from *A* through the sulphuric acid; and in order to restore the

equilibrium of pressure, a small quantity of sulphuric acid is forced from flask *B* into flask *A*, where coming in contact with the carbonate under examination, it decomposes it; and the carbonic acid evolved with effervescence in *A* can only escape by the tube *c* into the flask *B*, whence it must pass through the remainder of the sulphuric acid and the tube *d* into the air. This sulphuric acid condenses with great energy all the aqueous vapour, and retains everything that the current of gas might possibly carry with it. When the operation of removing a small quantity of air by the mouth, and the consequent addition of corresponding quantities of sulphuric acid to the contents of flask *A*, have been repeated until no more effervescence ensues, the decomposition is complete.

There is still, however, a portion of carbonic acid remaining in the apparatus which was previously filled with air, and some still clings to the solution in the flask *A*, which by this time has become cold. Both must be removed before the apparatus is re-weighed. For this purpose, by suction, as in the commencement, at *d*, so much sulphuric acid is caused to pass over at once as will give rise to a considerable elevation of temperature in *A*, by which means the carbonic acid in solution is evolved, and with it that portion still clinging to the other parts of the apparatus. By removing the wax stopper *b*, the mouth of *a* is opened, and air may then be drawn through the apparatus from *d* until all the carbonic acid is expelled. Here, too, all the moisture which is removed by the current of air from *A* will remain in the sulphuric acid in *B*. When the whole apparatus has cooled it is placed upon the scale, and the amount of carbonic acid is ascertained by the weights which must be added to re-establish the equilibrium.

Determination of Water.—Weigh 100 grs. of the ore and ignite for a quarter of an hour in a lightly-covered platinum crucible. When cold, weigh the ignited ore; the loss is carbonic acid and water. Deduct the amount of carbonic acid previously obtained from the total loss, and the remainder represents the quantity of water.

Reduction of Ferric to Ferrous Salts.—Sulphurous acid or metallic zinc is the reducing agent usually employed, but a much more effectual and rapid agent has been proposed in sulphuretted hydrogen by Mr. Reynolds. This answers much better than either zinc or sulphurous acid. The reduction, even in a strongly acid solution, takes place immediately; and on boiling until the sulphuretted hydrogen is expelled, the sulphur separated coagulates completely; so that, after allowing the solution to cool in the flask in which it has been boiled, a cork being placed in the neck during the cooling, filtration may be effected so rapidly that no oxidation need be feared, and the determination may then be effected with bichromate, as usual. It is better to add a considerable quantity of water to the solution before reduction to avoid the oxidation which would afterwards ensue in the filtration of a concentrated solution of protoxide of iron.

Estimation of Ferrous Oxide in the Presence of Ferric Oxide.—Messrs. Wilbur and Whittlesey have carried out a suggestion of Avery,* and applied it very successfully to the estimation of ferrous and ferric oxides in silicates and other ores of iron. Avery found that silica and many silicates can be readily and completely dissolved by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

These chemists have applied this observation to the estimation of the two oxides of iron, and have obtained such satisfactory results that their process deserves to be generally adopted for the estimation of iron in silicates. The method is as follows:—A quantity of the finely-powdered mineral to be examined is weighed in a platinum crucible; as much, or rather more than as much, powdered fluorspar (or of powdered cryolite), free from iron, is poured into the crucible; the powders are thoroughly mixed by stirring with a glass rod; the rod is wiped clean upon a fresh portion of the powdered fluoride; and the latter is thrown upon the mixture in the crucible. Strong hydrochloric acid is then poured into the crucible, until the

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* *Chemical News*, vol. xix. p. 270.

powder is thoroughly drenched and the crucible about two-thirds filled with the liquid. The crucible is set upon a water-bath, and heated until the iron has all dissolved: the proportion of iron is finally determined by titrating with a standard solution of potassium permanganate. To protect the mineral from the air during the process of solution, the crucible must be kept full of some non-oxidising gas, which can be either carbonic acid or coal-gas, as may happen to suit the convenience of the operator.

If carbonic acid be used, it is sufficient to cover the crucible with a bit of sheet lead, perforated with two holes, through one of which is thrust a glass tube communicating with a gas-bottle in which the carbonic acid is generated, while the other serves as an outlet for the escape of carbonic acid and acid vapours. The crucible is, in this case, simply set upon an ordinary water-bath.

When coal-gas is used (and this agent is to be preferred on the whole), the apparatus may be arranged as follows:—Set the charged platinum crucible upon a glass or leaden tripod, inside a wide beaker, in the bottom of which there is about an inch of water. Invert a narrower beaker within the first, so that its mouth shall be sealed by the water, and the crucible be enclosed in a transparent chamber. Coal-gas is led into this chamber through a bent glass tube, which passes down between the side of the upright and that of the inverted beaker, and delivers the gas near the top of the chamber. The surplus gas escapes through another tube similarly bent, which starts from a point below the crucible, and is burned in the outer air. To facilitate the passage of the glass tubes, the mouth of the inverted beaker may be made to rest upon three or four bits of stone or metal, or an orifice large enough to admit the tubes may be made upon the beaker. During the process of solution, the upright beaker is kept immersed in water, at or near the temperature of boiling. In case the coal-gas should contain any sulphuretted hydrogen, it would be well to purify it by means of a potash-tube. An hour and a half is ample for the solution of the iron in 0·5—1 grm. of finely-powdered trap-rock. Fifteen minutes, on the other hand, will suffice for the solution of 0·2 grm. of iron wire. Instead of hydrochloric acid, sulphuric acid may be used to act upon the mixture of fluor spar and mineral. The calcium sulphate frequently formed is objectionable, from its liability to envelope portions of the mineral, and to protect the iron from being dissolved, rather than from any tendency to interfere with the actual titration.

Experiments have shown that the presence of ferric oxide does not interfere in any way with the estimation of the ferrous oxide. It is found, also, by acting upon weighed quantities of iron wire mixed with cryolite and iron-alum, that the iron can be estimated as well in the presence of the alum as in its absence, provided only that the metallic iron be dissolved in hydrochloric acid, with the necessary precautions to prevent oxidation, before adding the other ingredients of the mixture. If the iron wire, cryolite, and ferric alum were treated all at once with acid, some of the hydrogen generated by the solution of the metallic iron would reduce a part of the ferric salt; so that in the final titration more iron would be found than was introduced into the mixture in the form of wire.

If time enough be allowed, finely-powdered sesquioxide of iron can be dissolved in this way, even after intense ignition.

To estimate ferric oxide in a silicate, a separate portion of the mineral may be treated with fluor-spar and acid, the solution reduced by zinc in a small flask in the usual way, and the total amount of iron determined with bichromate. Or, if the mineral contains only a small proportion of ferric oxide, it will be sufficient to put a bit of zinc into the crucible with the mixture of mineral, fluor-spar, and acid. The difference between the total iron and that determined as ferrous oxide is calculated as ferric oxide.

Mr. Allen effects solution of difficultly soluble ores by heating with hydrochloric acid under pressure. This method has been used very successfully in the analysis of various titanic iron ores and sands. About a gramme of the finely-powdered mineral is heated in a sealed piece of combustion tubing, half full of fuming hydrochloric acid. At first the heat of a water-bath is sufficient, but after a few hours the temperature is gradually raised to 140° or 150° C. The ore is completely decomposed in four or five hours, and after the tube has cooled the end may be broken under water, and the ferrous oxide at once estimated by bichromate. The same method will yield a solution suitable for the determination of the other constituents of the ore.

γ. *Estimation of Carbon, Sulphur, Silicon, Phosphorus, &c., in Metallic Iron and Steel.*

Carbon.—This is a problem of considerable difficulty, and to secure accurate results many special precautions are necessary, owing to the large preponderance of the iron over the carbon present. The carbon may be present in two forms—as combined carbon, and as free or graphitic carbon. The estimation may be of the total carbon present, or of either the combined or graphitic separately, and the method of analysis adopted will have to be selected accordingly. The following is a description of the most satisfactory processes which have been devised for these estimations.

A. Estimation of the Total Carbon. — Fresenius recommends that a weighed portion of the metal, in borings or chippings, be dissolved in dilute sulphuric acid by the aid of heat. The gases evolved during solution are passed over red-hot copper oxide. The gaseous hydrocarbons are burned, and the carbonic acid formed, after drying by calcium chloride, is absorbed by potash solution in a Liebig's apparatus, and thus weighed. This only gives the combined carbon, and when an estimation of the total carbon is required, the matter remaining behind, insoluble in the dilute sulphuric acid, is collected and burned in a stream of oxygen, and from the weight of the resulting carbonic acid the amount of carbon may be deduced. This quantity, added to that obtained by burning the gases over copper oxide, gives the total quantity of carbon contained in the iron. In drying the insoluble residue previous to combustion in oxygen, an elevated temperature must be carefully avoided; in fact, the safest way is to dry over sulphuric acid. The presence of hydrocarbons in the graphitic residue shows that this process cannot be safely applied for the estimation of combined carbon directly.

Weyl's very ingenious method for the estimation of the total carbon is founded upon the fact that a piece of iron, attached to the positive pole of a galvanic battery, and suspended in hydrochloric acid, is dissolved, while the hydrogen is given off at the negative pole. The formation of hydrocarbons, and a consequent loss, is in this manner prevented. One great advantage in this method is that the iron does not require to be in powder. A piece of iron 2 to 4 grammes in weight, attached to the positive pole of a Bunsen's cell, is suspended in dilute hydrochloric acid, just below the surface of the liquid. From the negative pole hydrogen passes off, while the iron dissolves quite quietly, and the strong solution of ferrous chloride formed may be seen falling in a regular stream through the lighter liquid. The iron is dissolved in about twenty-four hours, and the carbon is left behind in the same shape as the piece of metal from which it was derived. In Weyl's earlier experiments it was found that some of the liberated carbon at the positive pole was carried over to the negative pole by the mechanical working of the stream. To prevent this, a diaphragm of bladder or parchment paper is interposed between the two, which entirely obviates the possibility of loss in this way.

B. Estimation of the Graphite.—Dr. Eggertz reduces one gramme of iron to small pieces, mixes with 5 grammes of pure iodine and 5 c.c. of water in a small flask, covered with a watch-glass, and placed in ice-cold water before adding the iron. It is to be kept for twenty-four hours at 0° C., and frequently stirred meanwhile. By keeping the liquid cold, no carburetted hydrogen is produced The greater the amount of silicon in the iron the greater is the tendency to the production of carburetted hydrogen. The residue of carbon and silica left after the iron is dissolved is collected on a filter of known weight, when it is dried at from 95° to 100° C., and washed thoroughly with hot water. After twelve hours, it is to be washed with a mixture of hydrochloric acid and twice its volume of water, heated to 70° or 80° C., until the filtrate ceases to give a blue colour with ferrocyanide solution. The object of leaving the residue for twelve hours is to allow any small particles of iron, remaining undissolved by the iodine, being oxidised by atmospheric air, and prevent disengagement of hydrogen when the hydrochloric acid is added. After the hydrochloric acid is washed out of the filter, it is dried with its contents at 95° to 100° C., until constant in weight. This weighing gives the amount of the carbonaceous residue and silica (but not the whole of the silica, because some part of it would have been dissolved), and by burning the carbon away and weighing the silica the weight of the carbonaceous residue may be ascertained. The carbonaceous residue may consist either of graphite or of the compound of carbon, iodine, and water already mentioned, if the carbon was combined with the iron. To ascertain which is the case, 1 gramme of iron is dissolved in 15 c.c. of hydrochloric acid (1·12 density) in a flask covered with a watch-glass, and, when the iron is dissolved, the solution boiled for half an hour. All the carbon combined with the iron is disengaged in the form of carburetted hydrogen gas, while the graphite and silica remain. If the carbonaceous residue, left after dissolving the iron, comes in contact with atmospheric air before the liquid is boiled, it is so altered that it is not dissolved and disengaged as gas. The graphite that remains after boiling the liquid is collected on a filter of known weight, washed, dried, and weighed. It is then burnt, and the residual silica weighed to ascertain the quantity of graphite. Very satisfactory results have been obtained by this method. The differences do not amount to more than 0·1 per cent. When the quantity of carbon to be estimated is very small, more than 1 gramme of iron must be used in the analysis.

The following plan is simpler than the above, and may be used when only the graphite is required. In a beaker of 100 c.c. capacity mix 4 c.c. of sulphuric acid and 20 c.c. of water, and when the heat produced by the combination of the water and the acid has entirely disappeared, shake 2 grammes of finely powdered pig-iron into the dilute acid and boil for half an hour. (For steel and wrought-iron not less than 3 grammes should be taken, and the acid for solution increased in proportion.) The solution is then evaporated until it measures 18 c.c., allowed to cool down to the temperature of 50° C., and 4 c.c. of nitric acid, sp. gr. 1·20, added; boil for a quarter of an hour, and allow to evaporate on a water-bath, until, on holding a watch-glass over the beaker, there occurs upon it no perceptible condensation. To the dry mass add 30 c.c. of water and 5 c.c. of hydrochloric acid, sp. gr. 1·16, boil for a quarter of an hour, and add more hydrochloric acid if there appears to be anything besides silica and graphite remaining undissolved. The insoluble silica and graphite are thrown on a filter, which has been dried at 100° C. and carefully weighed, washed with cold water until the washings give no iron reaction when tested with ferrocyanide of potassium; then washed with boiling water containing 5 per cent. of nitric acid. The silica and graphite are then dried on the filter at 100° C., and weighed, ignited in a porcelain crucible, and the weight carefully taken. The difference between the weights before and after ignition gives the amount of the graphite.

Mr. Tosh gives the following process for the estimation of graphite. Two to three grammes of iron are treated with dilute hydrochloric acid, and when the solution approaches completion a considerable quantity of strong acid is added to separate the last portions of iron and manganese. The insoluble matter, consisting mostly of graphite, is collected on a carefully weighed filter, washed with hot water, dilute hydrochloric acid, solution of caustic soda, and hot water again, successively, and lastly with alcohol and ether to remove oily hydrocarbons. (By washing with dilute acid and with alkali, the iron and silica or oxide of silicon are separated.) After drying at 120° C., the filter and graphite are weighed, and burned away. The small residue (a mere trace of silica or titanic acid) is weighed, and this weight subtracted from the first gives the amount of graphite. The results obtained agree very closely.

In washing the graphite with solution of soda, there is always a brisk effervescence, due to the oxidation of oxide of silicon to silicic acid, by decomposition of water, with consequent liberation of hydrogen.

C. Estimation of Combined Carbon.—When steel, or pig-iron containing carbon in chemical combination, is dissolved in nitric acid, a soluble brown colouring matter is formed, whose colouring power is very intense, and the solution assumes a tint which is dark in proportion to the quantity of the chemically-combined carbon. Iron and graphite (or free carbon) do not influence this colouration; for the solution of nitrate of iron is only slightly greenish, unless extremely concentrated, and graphite is insoluble in nitric acid.

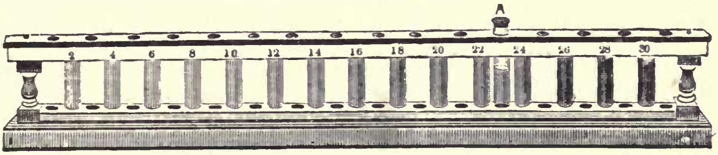
Thus, in dissolving two pieces of different steels of the same weight in nitric acid, taking care to dilute the darker solution until the two liquids present exactly the same colour, it is very evident that the more highly carburetted steel will furnish the larger quantity of liquid, and that the proportion of the volumes will indicate the relative proportion of colour in the two steels. If now the composition and content of carbon of one of the steels is known, the absolute percentage of carbon in the other steel may be immediately deduced. Dr. Eggertz has applied these reactions to a method of estimating the combined carbon. To obtain trustworthy results certain precautions must be taken.

In a cylindrical test-tube, dissolve gradually in the cold, 10 centigrammes of wrought-iron, steel, or cast-iron, reduced to a fine powder, in 1½ to 5 c.c. of nitric acid of 1·2 sp. gr. The use of nitric acid containing hydrochloric acid must be avoided, because the solution of iron would have a yellow tint. In proportion as the metal contains more carbon, more nitric acid must be used. After some time, when the chief part of the metal appears to be attacked, place the tube in a water-bath, and warm it to 80° C., in such a position that only the lower part of the tube is in contact with the warm water; a movement takes place in the acid, which favours its reaction upon the metal; a slight disengagement of carbonic acid from all the particles of carbon may be observed. The operation should always be conducted under the same circumstances as to heat and length of time. The evolution of gas having ceased (in operating upon steel, the reaction must continue two or three hours), place the tube in a large vessel filled with water, to bring the solution always to the same temperature. This precaution is indispensable, because the same liquid is darker when warm than when cold. Afterwards, pour off, as exactly as possible, the clear liquid into a graduated burette. Upon the black residue remaining in the tube pour some drops of nitric acid, and heat carefully over a lamp. If there is no further liberation of gas, the residue consists of nothing but graphite or silica. Cool the new solution, and add it to that which is already in the burette.

The liquid is then diluted with water until its colour corresponds exactly with that of the normal liquid, which latter should be of such a degree of concentration that each c.c. represents 0·0001 grm. of carbon. If, for instance, this normal liquid is prepared from cast-steel containing exactly 0·85 per cent. of carbon, 1 decigramme of that steel must be dissolved in 8·5 c.c. of nitric acid; 100 grms. of steel containing 85 centigrammes of carbon would thus be dissolved in 8500 c.c. of the normal solution, 100 c.c. of that solution would represent 1 centigramme of carbon, and, consequently, 1 c.c. of the normal solution would represent 0·0001 grm. of carbon. To compare the normal solution with the solution of iron under examination, it should be contained in a tube of the same kind, and when the two tubes are held together by daylight before a thin sheet of paper, the colour should be exactly the same in both of them. As the normal solution alters slightly in colour by keeping, and begins to become paler after twenty-four hours, it is not possible to keep such a solution for use in a tube hermetically sealed. A solution of burnt sugar* in weak alcohol gives a solution of exactly the same shade of colour as the normal solution, and maintains its colour for a considerable time when protected from the light. But the best plan is to make the solution fresh, as it is required, by dissolving 0·1 gramme of steel, containing a known amount of carbon, in 5 c.c. nitric acid, and diluting it to the requisite degree, which may be indicated by a mark upon the tube corresponding to the percentage of carbon in the steel. If an iron solution exactly the same colour as the normal solution is diluted with one-tenth its bulk of water, the colour becomes distinctly paler, so that the delicacy of the method may be judged of from this.

Several modifications of this method have been proposed. The most successful of them, affording exceedingly accurate results, was communicated to the 'Journal of the Franklin Institute,' for May, 1870, by J. Blodget Britton, and has been tested for a considerable time. Instead of a single tube, containing a standard solution for comparison, as suggested by Eggertz, a number of tubes having their solutions differently standardised, one from the other, are employed. These are arranged securely in a wooden frame, with places between for placing the tube containing the solution to be tested, and forming together a convenient portable instrument called a colorimeter—a representation of such an instrument being shown in the annexed cut. The position of the tube containing the solution to be tested is shown at A. The tubes are $\frac{5}{8}$ths of an inch in diameter,

FIG. 92.



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* Slightly burnt sugar gives a yellow solution; highly burnt sugar gives a brown solution, but by mixing these solutions the right colour may be obtained.

and $3\frac{1}{2}$ inches in length, filled with water and alcohol coloured with roasted coffee, and hermetically sealed. The solution in the tube to the left has its colour to correspond exactly with one produced by 1 grm. of iron, containing 0·02 per cent. of combined carbon, dissolved in 15 c.c. of nitric acid. The solution in the tube next to it has its colour to correspond with one produced by the same quantity of iron, but containing 0·04 per cent. of combined carbon, and so with each of the other tubes, increasing 0·02 per cent. of carbon in regular succession to the right, the last reaching 0·3 per cent., as indicated by the figures on the upper rail of the instrument. On the back of the instrument, and for the purpose of partially screening the light and allowing the different shades of colour to be distinctly discerned, there is tightly stretched between the rails some fine white parchment paper. This screen is not shown by the cut, but it serves a very important purpose. The process is conducted as follows:—1 grm. of the finely divided metal is put into a tube of about $1\frac{1}{2}$ inches in diameter and 10 inches long, and digested for fifteen or twenty minutes in 10 c.c. of nitric acid of a little more than 1·20 sp. gr., free from chlorine. The solution is then cautiously poured into a beaker, and a small portion of metal which remains undissolved and adheres to the bottom of the tube, is treated with 5 c.c. of fresh acid, exposed to a gentle heat till completely dissolved, and added to the other. The contents of the beaker, when sufficiently cool, are filtered through two thicknesses of German paper (not previously moistened, and of a diameter not exceeding $4\frac{1}{2}$ inches) into a tube about 5 inches long and of precisely the same diameter as those in the instrument. After the filtered solution has remained for some minutes at the temperature of the atmosphere, and its colour become fixed, the tube is placed in the instrument and the carbon determined by a comparison of shades: the determination may be made readily as close as 0·01 per cent. Heat should not be applied in the first instance to facilitate the solution of the metal, because a high temperature is apt to cause a slight loss of colour. Two thicknesses of paper are taken, because one alone is liable to break; and the paper should be used dry, for, if previously wetted, the water will weaken the colour of the solution; and it ought to be cut to a size not exceeding 4½ inches, to prevent undue absorption. If the metal to be examined contains more than 0·3 per cent. of carbon, 0·5 grm., or less of it, may be taken, or the solution may be diluted with an equal volume or more of water and the proper allowance made: or an instrument of higher range may be used. On the other hand, if the metal contains a very small percentage of carbon, 2 grms. of it may be taken. For preparing the standard solutions (the normal ones begin to lose colour after some hours), caramel dissolved in equal parts of water and alcohol, as suggested by Eggertz, answers well; but with roasted coffee as the colouring matter the true shades may be obtained.

Dr. Dingler has investigated this process, and gives it as his opinion that Eggertz's process is only applicable when the same quantities and qualities of raw materials are continuously applied for the production of cast-iron; but the test fails to give good results with iron and steel of different origin, since it has been found that the presence of other substances—viz., sulphur, copper, phosphorus, and silicium—affect the accuracy of the test.

Mr. E. R. Taylor has devised the following improvement upon the method of Prof. Eggertz for the determination of combined carbon ('Chemical News,' April 2, 1874).

A balance, consisting of a very fine thread of glass, with a pan in two parts, one a cup and one a cone, serves to weigh the steel. A horizontal drill, with a glass tube to form a hopper, makes and conducts the drillings of steel, as they are made, to the balance pan, which is properly supported about one-eighth of an inch above a point to which it settles, when a two-hundred-milligramme weight is placed in the pan. Being thus set, a sample of steel is placed in the drill lathe, the drillings, as before mentioned, falling into the pan below. As soon as the two-hundred-milligramme weight is in the pan, the pointer sinks to the index, when the drill is stopped. By passing a tube through a hole in the balance table, the lip of the tube offering a support for the balance cup, while the cone is pressed down with a pair of tweezers, the drillings at once fall into the tube, and are ready for treatment with acid.

A glass funnel is made with a capillary opening at the contracted lower end. This is fused to a T tube, the lateral branch of which is passed through the window of the laboratory to remove the fumes. A rubber nipple is placed on the lower end of the T tube, into which the tube containing the steel is inserted. Three c.c. are now drawn into the funnel tube, and fall in drops upon the steel below. At the expiration of this action the tube is transferred to a bath kept at the temperature of 130° C.

At the end of twenty minutes from drawing in the acid, the operation is completed ; the whole of the carbon has entered into a clear yellow solution, which has a depth of colour proportionate to the amount of combined carbon in the steel. The tubes are cooled down to a normal temperature, and compared with a series of standard colours, when it is easy to read off the amount of combined carbon in a given sample of steel.

Estimation of Sulphur in Iron and Steel.—The plan usually adopted is to dissolve a weighed quantity (about 3 grms.) of the metal in strong nitric acid, adding a little hydrochloric acid occasionally, and evaporating the solution to dryness. Dissolve the residue in very dilute warm hydrochloric acid, and precipitate the sulphuric acid in the solution by means of chloride of barium. If the precipitated barium sulphate, after washing once or twice by decantation, has a yellow or brown colour, owing to the presence of iron mechanically carried down, heat it, before filtering, with dilute hydrochloric acid.

Dr. Eggertz, to whom analytical chemistry is indebted for the colorimetric process of estimating combined carbon in iron and steel, has devised an equally expeditious plan for estimating the sulphur. He takes one decigramme of cast-iron, wrought-iron, or steel, cut up or pulverised, and passed through a sieve with holes not larger than 0·6 m.m., and introduces it, by means of a glass or glazed paper funnel, into a flask about 0·15 metre high and 5 centimetres diameter, previously containing 1 grm. of water and 0·5 grm. of concentrated sulphuric acid; or, in preference, 1·5 grm. of sulphuric acid, sp. gr. 1·25, and whose volume (1·5 c.c.) has been marked on the flask. A piece of polished silver plate (18 m.m. long, 7·5 m.m. wide, and 1 m.m. thick, with a hole at one end), composed of 75 per cent. of silver, 25 per cent. of copper, and attached to a thin platinum or silver wire, is quickly introduced into the flask, so that it may be a little below the neck; a cork is put in so as to hold the wire without completely closing it. It is allowed to stand fifteen minutes at the ordinary temperature, and the silver plate is then removed. If the iron contains sulphur, the plate is coloured by the sulphuretted hydrogen gas disengaged during the solution of the iron in the dilute sulphuric acid; and, according to the amount of sulphur present, the colouration of the plate passes to a coppery yellow, a bronze brown, a bluish brown, or a blue. These colourations are determined with the greatest accuracy—especially that of the silver plate alone, No. 1; that of coppery yellow, No. 2; that of bronze brown, No. 3; that of blue, No. 4. The intermediate degrees may be represented by decimals, thus: 2·5 if the colouration is between 2 and 3; 3·1 if the plate is one-tenth towards the blue; 3·5 if it is as much blue as brown; 3·9 if the brown colouration is feeble.

As the normal colouration No. 2, Dr. Eggertz has adopted that of the bronze called yellow metal, newly rubbed with fine sand on leather. (This metal consists of 60 parts of copper and 40 of tin.) For the colouration No. 3, a convenient alloy has not yet been found. A bronze, consisting of 85 parts of copper and 15 parts of zinc, does not quite represent the colour which should be obtained, for when freshly cleaned it is too bright, and at last takes a bluish colouration. For the colour in question it is better to use a plate of silver which remains in the flask during the solution of the iron, until it has become as brown as possible, and a slight bluish colour begins to be perceived; the plate is then removed and preserved in a well-closed tube. The colour No. 4 resembles that of a watch-spring. If the amount of sulphur is very considerable, this colouration passes to a clear bluish grey. By passing the plate of silver over a bottle of sulphide of ammonium the desired number can be easily obtained. To obtain in these assays for sulphur the proper tint on a silver plate, it is necessary to take certain precautions. The plate is to be held in pincers and cleaned as well as possible by rubbing it with a soft leather on which is placed a little fine rotten-stone. Contact with the fingers is avoided by means of a piece of paper, and the plate is to be carefully dried with a piece of filtering paper. If the plate, by cleaning or by the action of the burnisher, has been purified on its surface, this should be carefully removed by again rubbing with the leather, for pure silver is less sensitive to the action of the gas than that of the given standard. Thus it has sometimes been found that the silver employed for coinage furnishes less homogeneous plates, of which those parts richest in copper assume more quickly the blue colouration. On this account, the plates should be compared between themselves, by introducing them at the end of a wire into a flask in which iron is dissolving containing from 0·05 to 0·08 per cent. of sulphur. On introducing the plate, care must be taken not to turn the side but the edge against the strongest current of gas, which would otherwise colour one face of the plate stronger than the other. The plate should be rapidly introduced into the flask after the introduction of the iron, as then a very strong disengagement of sulphuretted hydrogen immediately takes place. After a first experiment the flask is to be filled with water several times, so as to get rid of the odour of sulphuretted hydrogen. If a steel mortar is employed to pulverise the iron, the whole of the piece selected should be reduced to a very fine powder. The mortar should be well cleaned each time, taking care to remove the disc from the bottom. Changes in temperature between 15° and 25° C. seem to have no sensible influence on the colouration of the metal; if the temperature exceeds 40° the plate becomes moist and gives false indications. Some practice is required to judge of the colouration of the plate, but it may be easily acquired. Generally the best plan is to place the standard plates of tints 1, 2, 3, &c., on a sheet of white paper by the side of the plate under experiment, exposing them to a good light near a window (but not sunlight), and to examine them with a lens. The colourations between 2 and 4 are the most difficult to recognise; but with a little experience none will vary more than 0·1, so that, for instance, the colouration may be estimated between 3·5 and 3·6.

The following is somewhat an approximation between the different colourations upon the silver plate, and the amount of sulphur in a great number of different samples of iron:—

Number of the Colouration	Percentage of Sulphur
1·0	0·00
1·2	0·01
2·0	0·02
2·5	0·03
3·0	0·04
3·1	0·05
3·2	0·06
3·3	0·07
3·5	0·08
3·6	0·09
3·7	0·10
3·8	0·12
3·9	0·15
4·0	0·20

It is evident that in this way the exact quantity of the sulphur is not determined; but several years' experience has shown that if these experiments are made with care, and the quantity of sulphur does not exceed 0·1 per cent., the results are near enough for all practical purposes. Iron which does not colour the silver plate will sometimes produce a colouration if we double the quantities of iron and acid. With half the quantities of acid and sulphurised iron, silver generally gives a little more than half the real quantity of the sulphur which is present.

Amongst experiments on the estimation of sulphur in iron, the following deserve mention:—1. The quantity of sulphur in wrought iron is often so small that it produces no colouration on the silver plate; this iron, therefore, not being red-short, may be employed for all kinds of uses. It must not, however, be forgotten that the quantity of sulphur is not equally distributed throughout a piece of iron, but that it may vary considerably in different places. On experimenting with the turnings obtained from a portion of an iron bar which was visibly red-short, a stronger tint is often obtained on the silver plate than when using other parts of the bar. The fragments obtained from red-short iron in boring a horse-shoe do not often give on the silver plate a deeper colouration than 2, and it appears to follow that ordinary wrought-iron which contains 0·02 per cent. of sulphur in certain parts cannot conveniently be employed for this purpose. If the red-short iron gives to the plate a slighter and more feeble colouration than 2, it may be supposed that the breaking is due less to sulphur than to an insufficient working of the cast-iron, the crude pieces in wrought-iron entirely free from sulphur often acting as if they were red-short. In general it appears certain that the quantity of sulphur in iron is more injurious when the iron has been badly worked. In a hard iron melted in a steel crucible we may, in spite of its containing 0·04 per cent. of sulphur, make holes like those in a horse-shoe without any trace of cracks, which may undoubtedly be attributed to the homogeneity and good working of this iron; the quantity of phosphorus being only 0·03 per cent. The lower portion of an English rolled rail, without fault, contained 0·11 per cent. of sulphur and 0·3 per cent. of phosphorus; a portion was cut off which was so red-short that it could not be made use of.

2. The richness in sulphur of steel of the best quality is such that the colourations on the silver plate vary only between 1 and 1·5. As in the case of wrought-iron, the quantity of sulphur often varies in different parts of the same piece of steel, and that also appears to be the case in a little less decided manner in cast-steel.

3. The quantity of sulphur in cast-iron is rarely so little as not to colour the plate. In the greater number of Swedish cast-irons, this quantity is such that the silver plate varies in colouration between 2 and 3. In iron for gun-castings it is between 3·3 and 3·7, and sometimes

more. In cast-iron the quantity of sulphur is often distributed unequally; there is generally more on the surface than is met with below. If the colouration of the silver plate does not exceed 3, we can assume that the cast-iron refined in the ordinary manner will not give red-short iron, especially if the refining is done carefully. But as in different methods of refining different quantities of sulphur may be removed from the iron, and in general, more if the iron is the result of a light charge of the blast furnace, it cannot be said beforehand that all cast-iron which communicates a bluish colouration to the plate will necessarily give red-short iron. This will be the case, however, with cast-iron which colours the plate as deep a blue as that of a watch-spring. In cast-iron, which gives a red-short wrought-iron, without rendering the silver plate more than brown, it is probable (the iron having been well refined) that the cause is owing to the presence of other substances than sulphur, but this occurrence is very rare. Many circumstances appear to show that the quantity of sulphur in iron diminishes with time, at least on the surface, and under favourable conditions.

The quantity of sulphur in a mineral cannot be estimated in the manner just described; all that can be done is to estimate the sulphur in the cast-iron, which is obtained by reducing the mineral in a crucible. Attention must always be paid to the following: *a.* That the powdered charcoal which fills the crucible is free from sulphur. This is ascertained by fusing iron, as free as possible from sulphur, in a crucible filled with the same powdered charcoal, and then examining the regulus obtained. If this latter gives a higher amount of sulphur than the iron originally contained the cause is attributable to the charcoal. At Fahlun, the charcoal absorbs, in a short time, much sulphur from the smoke of the burning pyrites; and the powder selected for the crucible experiments in the Mining School is obliged to be kept in closed vessels. If the charcoal employed as a combustible in the crucible furnace is exposed to the action of much sulphuretted hydrogen or sulphurous acid, the experiments show it.

b. The state of the mineral, whether unroasted, badly roasted, or well roasted. The small laboratory experiments, having for their object to ascertain how much sulphur can be removed from a mineral by roasting in bulk, are always inexact. *c.* The influence exerted on the quantity of sulphur by the minerals mixed with it. It follows, from many experiments made at the Mining School, that the more silicic acid the slag contains the more sulphur the cast-iron receives, and that the quantity of sulphur gradually diminishes in proportion as the quantity of lime is increased. In general, assays for sulphur should be made with regulus obtained from a mixture containing as little lime as possible, but giving vitreous slags. If the colouration of the silver plate does not exceed No. 3, the quantity of sulphur may be considered as insignificant, especially in experimenting on non-roasted minerals.

The lime used in blast furnaces may be assayed for sulphur in the following manner:—Mix 0·8 gramme of rich and pure iron ore with 0·2 gramme of quartz and 0·2 gramme of lime; fuse the mixture as usual in a crucible, and assay the resulting iron for sulphur. In this manner it may be ascertained if the lime contains an injurious dose of sulphur. If it were chemically pure we should obtain, by the addition of 2 or 3 per cent. of clay or talc, free from sulphuric acid, a better slag. If, on the contrary, the lime contains much silicic acid, more than 0·2 gramme should be taken for the experiment.

Dr. T. M. Brown, in a paper read before the American Institute of Mining Engineers (February 28, 1874), remarks that the method usually employed in accurate determination of sulphur in pig-iron and steel is to treat a weighed sample of borings in a flask with hydrochloric acid, and to pass the gaseous products through an alkaline solution of lead or silver, which precipitates all the sulphur of the sulphuretted hydrogen in the form of lead or silver sulphide. The sulphide thus formed is subsequently oxidised by *aqua regia*, bromine, or other oxidising agent, and the sulphuric acid formed precipitated in the usual way by barium chloride.

Mr. Brown has substituted for the alkaline metallic solution a solution of potassium permanganate of the strength of 1 gramme of permanganate to 200 c.c. of water, and finds that it gives results quite as accurate as those obtained by using an ammoniacal solution of silver. By the employment of the permanganate, it will be readily seen that there is a considerable saving of time and work. In order to test the accuracy of the method, six samples of pig-iron borings were weighed out (about six grammes each), and treated identically in the same way, with the exception that with three an ammoniacal solution of silver was used, and with the remaining three a solution of potassium permanganate. The silver sulphide formed was filtered and oxidised by bromine water. The residues, after treatment with hydrochloric acid in a flask, were invariably filtered off and washed, then evaporated twice to dryness with aqua regia, taken up with hydrochloric acid, filtered, and the filtrate added to the main solution containing the solution of permanganate. The gas then gives not the slightest blackening when passed into a lead or silver solution. After the evolution of gas has completely ceased, and air has been drawn through the apparatus for some time, the contents of the bottles are poured into a beaker, rinsed out with water, and any manganese oxide adhering to the sides or to the tubes dissolved in a little hydrochloric acid. Enough hydrochloric acid is then added to the beaker to completely decompose the permanganate and convert it into a clear, colourless solution, in which the sulphuric acid may be directly precipitated. If the solution does not become perfectly clear, owing to impurities in the permanganate used, filtration is necessary before precipitation.

Mr. C. H. Piesse places in a beaker of about 300 c.c. capacity about 3·5 to 4 grms. of the sample in drillings (weighed to within 0·01 grm. will be sufficiently accurate), and pours upon them 35 to 40 c.c. of aqua regia, consisting of 1 part HNO_3 with two parts HCl, maintaining the proportion of 10 c.c. of the mixed acids for every 1 grm. of the metal, keeping the beaker covered as well as possible with a clock-glass. After the first violence of the action has subsided boil the liquid for a few moments until the whole of the iron is dissolved, then transfer the solution, with as little washing as may be, to a porcelain basin, and evaporate as nearly as possible to dryness on a water-bath. Treat the residue with some concentrated hydrochloric acid, add about an equal bulk of water, and then filter. To the filtrate add a considerable excess of solution of barium chloride, allow to stand for about twelve hours; filter and weigh the precipitated barium sulphate with the usual precautions. Multiply the weight of barium sulphate found by 13·724, and divide the product by the weight of the iron employed; the result will be the percentage of sulphur in the sample analysed.

Mr. T. J. Morell (*Chemical News*, October 31, 1874) proposes to act on the metal with hydrochloric acid, and passes the evolved gases through an ammoniacal solution of cadmium oxide. The precipitate of cadmium sulphide obtained is collected on a small filter, dried at 212° F. and weighed.

Estimation of Sulphur in Iron Ores.—Five grammes of the mineral, ground as finely as possible in an agate mortar, are treated with potassium chlorate and hydrochloric acid. After desiccation and extraction with hydrochloric acid and water, the insoluble substances may be lead, calcium, barium, and strontium sulphates, silica, and undecomposed mineral. By stirring well and filtering the liquid whilst warm, the two former salts may generally, however, be dissolved. The filtration should be performed through a double filter, to prevent the pulverised mineral from passing through. When the clear portion of the solution has been poured upon the filter, add to the insoluble matter 5 c.c. of hydrochloric acid and 5 c.c. of water; then leave the mixture for two hours on the water-bath at a boiling temperature, when, if care be taken to stir well, the calcium sulphate will be completely dissolved. Wash the insoluble portion in warm water, and pour it on a filter, taking care to place below a flask specially to receive that portion of mineral which may have passed through the filter. The filtered liquid, whose volume is about 50 c.c., should be rapidly boiled and mixed with

2 c.c. of a saturated solution of barium chloride. (This amount is sufficient to precipitate the sulphuric acid formed from 0·1 grm. of sulphur.) After cooling add to the mixture 5 c.c. of ammonia sp. gr. 0·95, then stir well with a glass rod, and leave the whole to rest at the ordinary temperature for twenty-four hours. The clear solution should be decanted as completely as possible on to a strong filter, and the precipitate stirred up with about 20 c.c. of cold water, and then left to itself until it has quite settled. If warm water is used without having added a few drops of hydrochloric acid, a little oxide of iron will be precipitated. The clear liquid is likewise thrown on to the filter, and the operation is repeated several times with cold water, and then two or three times with boiling water, without which precaution the barium sulphate will pass through the filter. Finally collect the precipitate, and wash it with warm water. The last drops of this water, on being evaporated on a watch-glass, ought not to leave more than a scarcely visible white ring. The precipitate is then dried, heated to redness, and weighed. If it is coloured with iron oxide it must be washed with a little hydrochloric acid, dried in the water-bath, and taken up with a few drops of acid and water, and then the preceding operation repeated (washing, drying, heating, and weighing). If the precipitate has only a feeble red colour, which is often the case, this latter operation will be unnecessary.

To dissolve the lead sulphate which may occur in the insoluble portion, remove this from the filter with the end of a feather, introduce it into a flask, and pour over it 10 c.c. of concentrated ammonium acetate. The solution, after having been strongly agitated and heated in the water bath, is carefully poured on to a filter. Then wash the residue with a little ammonium acetate, and repeat the treatment until a few c.c. of solution, acidulated with a little acetic or hydrochloric acid, is not rendered turbid when warmed with barium chloride solution. The filtrate is then diluted, slightly acidified, and the sulphuric acid precipitated by means of barium chloride. After the lead sulphate has been removed, there may still occur barium and strontium sulphates in the insoluble portion. To decompose these salts the residues must be dried, heated to redness, and weighed, and then fused with five times their weight of pure dry soda. The mass is digested with water over a water-bath, the liquid filtered, and the residue washed with warm water. The silicic acid is separated from the solution, which contains the silicate, the sodium carbonate, and sulphate, by adding hydrochloric acid and drying on the water-bath. After filtering, precipitate the solution with barium chloride. To ascertain if the iron mineral contains gypsum or other soluble sulphates, take 5 grammes, place them in 20 c.c. of hydrochloric acid and 60 c.c. of distilled water, and digest them for three hours on the water-bath, with frequent agitation. The filtered solution is mixed with barium chloride and 15 c.c. of ammonia; then proceed as already described. If there are present in the mineral grains of iron- or copper-pyrites, or galena, they will only give traces of sulphuric acid in this operation.

Estimation of Silicon in Iron and Steel.—All who are occupied in the analysis of iron and steel are aware how very uncertain the determination of silicon is when the method hitherto used for its separation is followed, because cast-iron, and even bar iron and steel, are never found absolutely free from intermingled slag. This slag is decomposed by the ordinary method of dissolving the iron in acids, and its silica then augments the amount of silica formed from the silicon contained in the iron or steel. This cannot be said of every sort of cast-iron, but these sometimes contain blast-furnace slag, although pig-iron containing slag may be considered as rare. It ought also to be mentioned that crystallised silicon has been found in crystallised cast-iron from Krain, in the form of small silvery plates, which were neither acted upon by boiling aqua regia nor by ignition in oxygen gas; but they were converted into silica by fusing with potassium and sodium carbonates.

Crystallised silicon is insoluble in hot solutions of sodium carbonate, but is soluble, with development of hydrogen, in hot solutions of caustic potash, and also in hot hydrofluoric acid. The accurate determination of the silicon in iron and steel has been effected by Dr. Eggertz, who, after fruitless efforts to dissolve iron in highly diluted organic or inorganic acids, which should have no effect on the refinery slag, finally discovered such a solvent in bromine, which, when mixed with water, dissolves the iron without the slightest action on the accompanying slag. But as experimenting with bromine in large quantities is very disagreeable, trials were made to use iodine instead ; and this, like bromine, has been proved to have no effect on the slag, nor on iron oxide or proto-sesquioxide, or manganese proto-sesquioxide. At the same time, bromine dissolves iron quicker than iodine does, and is, perhaps, more easily obtainable in the requisite state of purity. Moreover, as continued experiments have shown that a solution of sodium carbonate can separate finery slag from the silica which has been formed by the use of iodine or bromine on the silicon contained in the iron, the following method for the determination of silicon and slag in bar iron or steel has been used and considered successful; the same method may be employed for cast-iron, because blast-furnace slag, when such is found, is not perceptibly changed by iodine or bromine, nor by solutions of sodium carbonate. Three grammes of bar iron or steel which has passed through a sieve of 0·2 of a line are taken for analysis. Fifteen grammes of iodine are added in small portions at a time to 15 c.c. of water in a beaker of 100 c.c. capacity. The water must be previously boiled to expel the air, which would otherwise oxidise the iron. The iodine is stirred in the water with a glass rod, in order to get rid of the air which has accompanied it, and the floating iodine particles are allowed to sink. The beaker with the iodine and water, which is kept covered with a watch-glass, is cooled in ice before the iron is put in, and during the solution it is kept at the temperature of 0° C. For the first few hours it must be well stirred every hour, or oftener, with a glass rod, but afterwards not so frequently. In consequence of the low temperature and the careful admixture of the iron (by which heat is prevented), the solution may be performed without the least development of gas, and the iron has less tendency to become oxidised by the air when at this low temperature. By pressure, and by agitating with the glass rod, the solution of the iron particles which collect at the bottom of the beaker is much facilitated; if no lumps of iron particles are visible, the beaker may be kept at the ordinary temperature, or, preferably, in ice water. If some of the solution has dried on the sides of the beaker or on the glass rod, it must be well moistened with the same solution before water is added. About 30 c.c. of water, which should be very cold in order to prevent the formation of basic salts, are added to the solution; it is then well stirred, left to settle, and the fluid with the lighter particles of graphite is poured on to a filter of 2 in. diameter; the filtration is kept up without interruption until there remains only a somewhat heavy dark powder of slag, &c. at the bottom of the beaker; about 5 c.c. of water, with a few drops of hydrochloric acid, are now poured in and stirred with the glass rod; if hydrogen is given off, it is an indication that there is still some metallic iron undissolved. The acidified water is quickly poured on the filter, in order not to act on the slag. If a development of gas is perceived, a little iodine, with sodium carbonate and water, is added for the complete solution of the iron, and the residue is thrown on the filter and washed with cold water, until a drop of the filtrate gives no reaction with a solution of 0·2 per cent. of potassium ferrocyanide contained in a small porcelain crucible. Solutions containing 0·00001 gramme of ferric oxide per c.c. show in this way very distinct reactions, particularly if a drop of dilute nitric or hydrochloric acid be added. The filtrate is evaporated to dryness, in which operation some of the iodine is sublimed away. Thirty c.c. of hydrochloric acid, 1·12 sp. gr., are then added, and it is again evaporated in order to obtain the silica which may be dissolved in it. The filter, previously dried and weighed, is again dried and weighed when containing the precipitate. It is then ignited, and the residue weighed. After ignition, the residue is boiled in a solution of soda, in order to extract the silica, and weighed. It should be observed that some part of the silica which has been formed from the silicon in the iron may possibly unite with the slag during the drying and ignition. In consequence of this, it is difficult to extract it by means of a soda solution, whence this method is not to be recommended in exact determinations of silicon.

When using bromine as a solvent 6 c.c. must be taken to 3 grammes of finely powdered iron or steel, with 60 c.c. of water, which has been previously boiled and cooled to 0° C.; and this temperature must be preserved by placing the beaker in ice water until the solution is complete, which usually takes place in two or three hours; it is cautiously stirred once or twice with a glass rod; if stirred hastily, the solution proceeds too violently. The further operations are conducted in the same manner as when using iodine. The bromine is most conveniently preserved under water, and is taken up by a pipette, which is introduced into the bottle, the upper end being kept closed by the finger.

When it is preferred to dissolve iron or steel in lumps, instead of in powder, this may be done; but it is not then necessary to place the beaker in ice water, as the metal is less violently acted upon in this form. Several days are required for the solution; the iron, and particularly the pieces of steel, must be occasionally cleaned from the graphite which adheres to their surface.

In order to determine the silica (formed from the silicon in the iron) and slag, the filter, which contains graphite (in combination with iodine or bromine and water), silica, and slag, is unfolded, whilst it is still wet, on a watch-glass. The contents are washed away from the filter (these should only occupy the lower half of the filter whilst in the funnel) with a very fine jet from a wash-bottle (so as not to obtain too much water) into a platinum or silver crucible of the capacity of 30 c.c. The loosening of the mass may be facilitated by a fine camel-hair brush. The water in the crucible is evaporated to about 6 c.c., then mixed with 3 c.c. of a saturated solution of sodium carbonate, free from silica, and the crucible put in a water-bath. It is kept in the boiling water 1 hour, during which time the liquid is stirred two or three times, and the insoluble mass crushed with a platinum spatula. The supernatant liquid is carefully poured from the insoluble mass on to a small filter, and to the mass in the crucible are added 1 c.c. of saturated solution of sodium carbonate, and 2 c.c. of water. When this has been boiled 1 hour, the whole contents of the crucible are thrown on the filter and washed. The solution of silica in soda is acidified by hydrochloric acid, and mixed with the iron solution, and the whole evaporated to dryness on a water-bath. When the solution attains the thickness of ordinary syrup, it is stirred very often with the glass rod, until the mass becomes a dry powder, and heated until the smell of hydrochloric acid has nearly gone off; the beaker is then placed in boiling water for 6 hours, 15 c.c. of hydrochloric acid of 1·12 sp. gr. are then added, and the beaker left on the water-bath 1 hour. As soon as the red powder is entirely dissolved 50 c.c. of water are added; and when no crystals of iron chloride are visible, the solution is thrown on a filter and washed with cold water, warm water forming basic iron salts which make the silica appear red. The filter containing the silica is dried and ignited in a porcelain crucible, gradually increasing the temperature to a full red heat, and weighed; if the silica is coloured red by ferric oxide, a little hydrochloric acid, 1·19 sp. gr., must be poured into the crucible. One decigramme of ignited and pure silica obtained from analysis will dissolve in the above manner in 6 c.c. of a saturated soda solution, and 12 c.c. of water. If any residue is observed after the second boiling, this arises from some impurity which has united in small quantities with the silica, rendering it insoluble. When strong hydrochloric acid is boiled with this insoluble silica, it may afterwards be dissolved. When the solution of silica is diluted with water to the volume of 50 c.c. at the ordinary temperature, it has no tendency to come into the form of jelly. Quartz powder is dissolved by the preceding method, but very slightly, but ignited titanic acid and finery slag are not acted upon, and the tersilicate slag from blast-furnaces but very little.

When the silica is quickly exposed to a high temperature a considerable loss may arise from the spirting of the water combined with the silica. Silica dried at 100° C. has been proved to retain 1 equivalent of water to 3 equivalents of silica, that is, about 6 per cent. of water, which is lost by a strong ignition. The ferric oxide is easily dissolved in the heat of a water-bath. The silica is again thrown on a filter, washed, dried, ignited, and weighed.

To ascertain the purity of the silica, it may be mixed in a platinum crucible with ten times its weight of pure ammonium fluoride, diluted with water to the thickness of syrup. The water must be evaporated on a water-bath, and the crucible heated, with a cover on it, by a gradually increasing heat over a spirit-lamp to a full red. If nothing is left in the crucible, the silica was pure, and has passed off as silicon fluoride ; but, if anything remains, the operation with ammonium fluoride must be repeated until a constant weight is obtained. When iron contains tungsten, some tungstic acid is formed, and this accompanies the silica for the most part, being dissolved by the soda solution, but it is not volatilised by the use of ammonium fluoride. Vanadic acid also accompanies the silica, behaving as tungstic acid. Instead of using ammonium fluoride, it is preferable to use hydrofluoric acid, with which the silica is moistened, and the evaporation is conducted on a water-bath. The mass left on the filter from the soda solution may be composed of—besides graphite—slag, iron oxide, titanium oxide, &c. (but not copper, at least when the iron does not contain more than 1 per cent.) ; this is dried, ignited, and weighed. The method of separating iron oxide and slag, when the iron or steel contains both these, is not yet known. If the composition of slag were always alike (which it is not) it would be easy to calculate its amount from either the silica or iron oxide obtained in the analysis. In a piece of very red-short Bessemer iron which contained no sulphur, by several experiments 0·3 per cent. of iron oxide has been obtained, and only traces of silicon. After ignition, the iron oxide may possibly be found as sesquioxide. The amount of oxygen, in case the redshortness is due to this, as it probably is, amounts to less than 0·1 per cent.

When the iron or steel for analysis contains titanium, a part of this substance follows the slag in the form of titanic acid. If such is the case, this must be melted with ten times its weight of acid, potassium sulphate, by which it is dissolved; the mass is dissolved in cold water, and the solution precipitated by boiling; the weight is determined, and subtracted from that of the slag.

In respect to the determination of silicon in cast-steel where only a trace of slag is found, the method given below for cast-iron may be employed; but 3 grammes at least ought to be taken for each experiment, and the acids for solution in proportion. The amount of silicon in bar iron and steel generally varies between 0·01 per cent. and 0·1 per cent.; but in two sorts of good cast-steel from Krupp's it has amounted to about 0·3 per cent. Slag in cast-steel has been found only in traces, but in another case it amounted to 0·2 per cent.; in good iron wire, prepared from bar iron, converted in a refinery hearth, from charcoal pig-iron, 0·33 per cent.; in puddled iron (armour-plate), from 0·75 to 3 per cent.; and in an English iron rail, to 4 or 5 per cent.

For the determination of silicon in cast-iron, in which no finery slag is found, and only exceptionally blast-furnace slag, the following method has proved suitable:—2 grammes of iron, which has passed a sieve with holes of a diameter of $\frac{1}{60}$ inch at the most, is put into a beaker of 100 c.c. capacity containing 30 c.c. of hydrochloric acid, sp. gr. 1·12. The beaker is covered with a close-fitting watch-glass, heated without delay, and the liquid kept in gentle ebullition for half an hour. All the carbon chemically combined with the iron is separated from the liquid in the form of an ill-smelling volatile hydrocarbon. If the carbon separated on solution is left in contact with the air some minutes before ebullition, it undergoes such a change that it does not go off in a volatile form; if necessary some hydrochloric acid is added, and the solution evaporated to dryness on a water-bath. When the silica is red, strong hydrochloric acid is added, as previously described. If the silica is contaminated with titanic acid, vanadic acid, or tungstic acid, it is operated upon with ammonium fluoride or hydrofluoric acid, as previously mentioned, whereby the silica is volatilised and calculated by loss. By the above method of dissolving iron in hydrochloric acid, the silicon changes, without evaporation, for the most part, to insoluble silica, which may be filtered and determined. Sometimes a very unimportant part is dissolved, especially if the boiling has been insufficient. When iron is dissolved in hydrochloric acid without heating (white cast-iron is very difficult to dissolve in this way), a still less portion of silicon is dissolved, and generally so little that it may be neglected for practical purposes. The washing is performed with hot water containing nitric acid, as previously described. When the iron is dissolved in nitric acid, a great deal of silica enters into solution. The different sorts of cast-iron appear to be slightly different in this respect. In dissolving cast-iron by the aid of heat, in very dilute sulphuric acid, a great deal of silica is dissolved, but very little when the acid is strong; as the water evaporates, the silica separates and becomes insoluble.

The method given below rests upon these circumstances, and has proved very satisfactory, whilst the removal of the acid is avoided, which is both necessary and troublesome when using hydrochloric acid with heat. The amount of silicon has, according to both methods, turned out alike. Two grammes of cast-iron, which have passed a sieve of 0·2 of a line, are shaken by small portions at a time into a beaker of 100 c.c. capacity, previously containing 18 c.c. of water with 3 c.c. pure sulphuric acid of 1·83 sp. gr., with 6 c.c. of water. The beaker is covered with a watch-glass, and placed on a water-bath: if the graphite rises on the sides of the beaker, it is pushed down into the liquid by a glass rod. When the iron is dissolved, the watch-glass is changed, after being washed, for a paper cover, and the solution evaporated on a water-bath until no condensation occurs on a watch-glass held over the beaker: 30 c.c. of water are then added, and it is frequently stirred with a glass rod, whilst on the water-bath, until the white iron salt has completely dissolved. The insoluble mass is then thrown on a filter, and washed with hot water containing 5 per cent. nitric acid, 1·2 sp. gr. (in order to dissolve all compounds of iron), as long as an iron reaction is given with potassium ferrocyanide. The filter, with its contents, is placed in a carefully tarred porcelain crucible ; it is then cautiously dried, ignited, and weighed. The purity of the silica is examined by the method previously mentioned, when considered necessary. If the cast-iron contains vanadium, this is obtained for the most part as a yellow-brown vanadic acid with the silica, from which it may be extracted by warm hydrochloric acid or by ammonia.

The amount of silicon in grey charcoal pig-iron is about 2·7 per cent. and in spiegeleisen 0·8 per cent. The amount of silicon in pig from coke blast-furnaces is rarely more than 4 per cent. The least quantity of silicon in grey cast-iron is about 0·2 per cent., and in white (spiegeleisen) 0·01 per cent. The amount is usually from 1 to 2 per cent. in cast-iron suitable for the Bessemer process, and in pig-iron for puddling about 0·5 per cent. The amount of silicon in iron of different degrees of hardness from the same charge of the blast-furnace ought to be pretty well judged by the fracture, after some determinations have been made by analysis.

Estimation of Phosphorus in Iron and Steel.—The importance of ascertaining the quantity of phosphorus in iron is very great; for, although the presence of a very small quantity of phosphorus in cast-iron does not produce any sensible modification in its properties, it nevertheless loses its most essential qualities when the proportion of phosphorus amounts to some thousandths. Almost all the methods hitherto proposed consist in treating cast-iron with oxidising agents in such a manner as to cause the phosphorus to pass into the condition of phosphoric acid, which is estimated as a magnesian compound. Several sources of error are inherent to this method, to avoid which M. Tantin liberates the phosphorus as an hydrogen compound. Experiment shows that there is not the least trace of phosphorus in the residue after the complete attack of the cast-iron by hydrochloric acid, which fact is not surprising if it be considered what strong affinities phosphorus has for hydrogen. The hydrogen phosphide produced by the action of hydrochloric acid upon cast-iron is almost always accompanied by sulphuretted, arseniuretted, and carburetted hydrogen. In order to effect the separation of these gases, first pass them into a Woulff's flask containing a solution of potash, which absorbs the sulphuretted hydrogen; the other gases are then made to traverse a solution of silver nitrate, which transforms the arseniuretted hydrogen into silver arsenite, soluble in the slightly acid liquid, whilst the phosphuretted hydrogen precipitates the silver solution and forms an insoluble phosphide. The phosphorus being thus completely separated from the sulphur and arsenic, its estimation is effected in a simple manner. The phosphide of silver is treated with aqua regia, and thus transformed into silver chloride and phosphoric acid, which is precipitated in the state of ammonio-magnesian phosphate. To get accurate results by this process, the following precautions are indispensable:—

1st. The cast-iron must be attacked very slowly, or part of the phosphuretted hydrogen may traverse the solution of silver nitrate without being absorbed.

2nd. When the solution of the cast-iron is finished, a current of hydrogen, previously washed in lead acetate, must be passed through the flask.

Mr. Tosh estimates the phosphorus in the following way: 3 grammes of the iron are dissolved in aqua regia, the solution evaporated to dryness, and the insoluble matter filtered off. The ferric chloride solution is reduced to the state of ferrous chloride, by heating with sodium sulphite. Although perfectly reduced, the solution still retains a yellow colour, due to dissolved organic matter. All excess of sulphurous acid is boiled off, a little ferric chloride is added, and the solution cautiously neutralised by means of sodium or ammonium carbonate, till the precipitate formed does not dissolve again. This small portion of ferric oxide contains all the phosphoric acid. It is filtered off, washed, re-dissolved in a little hydrochloric acid, and the phosphoric acid precipitated as magnesium ammonio-phosphate, the iron being held in solution in the ammoniacal liquid by citric acid.

Dr. Noad says the following precautions are needed to ensure accuracy when dealing with iron and steel containing very small amounts of phosphorus. The solutions should not be too bulky. When estimating phosphorus in iron and steel, from 75 to 100 grains should be taken, and the solution, at the time of adding the tartaric (or citric) acid, ammonia, and magnesium sulphate, must never be allowed to exceed in volume 3 fluid ounces. The first precipitate always carries down a little iron, which is removed by re-solution and re-precipitation after the addition of a fresh small quantity of tartaric acid. The first precipitate must not be collected till after the liquid has stood for twenty-four hours; the second precipitate is quite white, and may be filtered off after half an hour; it contains the whole of the phosphoric acid.

Estimation of Manganese in Iron.—After the silicon is determined in the iron or steel by Eggertz's method (p. 357), the manganese may be estimated in the same amount of material. The filtrate from the silicate is diluted with water until it measures 400 c.c. and accurately divided into two portions of 200 c.c. each, one of which is set on one side, and in the other the manganese is estimated in the following manner:—(In the case of wrought-iron and steel, where 3 grammes are taken, the solution is diluted to 200 c.c., and the manganese estimated without dividing the solution.) A saturated solution of sodium carbonate is added to the solution until it becomes nearly neutralised, appearing of a deep brown colour; water containing 5 per cent. of sodium carbonate is then added, drop by drop, until a slight turbidity occurs in the solution; and if, on standing in the cold, this turbidity rather increases than diminishes, sufficient carbonate has been added (if too much sodium carbonate has been added, and a precipitate is thrown down, the excess must be neutralised by hydrochloric acid); to the slightly turbid solution add $1\frac{1}{2}$ c.c. of hydrochloric acid, and heat on the water-bath until the solution becomes clear; dilute with about half as much water as the volume of the solution, and add 30 c.c. of a saturated solution of sodium acetate, boil for a quarter of an hour, allow the precipitated iron to settle, and decant the clear liquid through a filter, washing the iron by decantation with boiling water containing $\frac{1}{2}$ per cent. of sodium acetate; finally, throw the iron on the filter, and continue the washing until bromine water gives no reaction, showing that all the manganese has passed through the filter; evaporate the filtrate down to 400 or 500 c.c.; and at the temperature of 50° C. add a few drops of bromine to precipitate the manganese, and keep it near to that temperature for twelve hours, stirring occasionally with a glass rod; the solution after the addition of the bromine becomes of a yellow or brownish colour, but should be perfectly colourless before filtering. The manganese is now thrown on a filter which has been dried at 100° C., and accurately weighed, washed with cold water containing 1 per cent. of hydrochloric acid, dried at 100° C., and weighed. The precipitate is a hydrated manganese oxide, containing 59·21 per cent. of manganese. The precipitate may also be ignited in a porcelain crucible at a white heat, and is then an anhydrous manganese oxide, containing 72·05 per cent. of manganese. If copper is present it must be removed previous to the precipitation of the manganese; or the amount of copper found in the ignited oxide, and then an equivalent amount of copper oxide, subtracted from the total weight of the precipitate.

In using the first method, 20 grains of the finely-divided spiegeleisen are completely dissolved in hydrochloric acid, diluted, and a current of sulphuretted hydrogen passed through the liquid. After standing for twelve hours, the solution is filtered and washed with water containing sulphuretted hydrogen; the filtrate is boiled, 10 grs. of potassium chlorate added, the iron separated, and the manganese estimated in the usual manner. If the method used be that of determining the copper in the precipitate, the estimation must be made with the greatest care, on account of the small quantity of copper present; the solution must be decanted immediately the zinc is completely dissolved, and excess of acid must be carefully avoided, otherwise the film of copper will partially re-dissolve. It is evident that, if the precipitation be effected by ammonium sulphide or sodium carbonate, separation or estimation of the copper is likewise necessary.

Mr. E. Riley (*Chemical News*, April 27, 1877) gives the following instructions on the determination of manganese in spiegeleisen, and in many auriferous iron ores:—

There are two methods now in use—(*a*) *The Direct Method.*—The pulverised spiegeleisen (about 1 grm.) is dissolved in dilute nitric acid, sp. gr. 1·2, a little potassium chlorate and hydrochloric acid added to destroy the soluble organic matter from the combined carbon; the solution, diluted to about a litre, is neutralised with sodium or ammonium carbonate, sodium or ammonium acetate added, the solution boiled, the basic iron peracetate allowed to settle and filtered off. This precipitate is re dissolved in hydrochloric acid, and the process repeated to ensure complete separation of the manganese. The filtrates are evaporated to $1\frac{1}{2}$ litres, allowed to cool, 2 to 4 c.c. bromine added, the solution well shaken, 0·880 ammonia added in excess, the solution heated gradually for an hour, boiled for a few minutes, the precipitate allowed to settle, filtered (the filtrate should be evaporated and tested for manganese), dried, and ignited in a muffle, or over a gas blowpipe for half an hour.

(*b*) *The Indirect Method.*—The finely-powdered spiegeleisen (about 1 grm.) is dissolved in dilute sulphuric or in hydrochloric acid, the liquid diluted with recently-boiled and cooled distilled water, and the iron estimated volumetrically; to the percentage of iron thus obtained 5 per cent. is added for carbon and impurities; the difference is assumed to be manganese.

The results obtained by this method are usually too low, from the formation of soluble organic matter during the process of solution. This error can be obviated by using nitric acid for a solvent, evaporating to dryness and heating; the iron and manganese oxides are then dissolved in hydrochloric acid, the solution largely diluted, and reduced with sodium sulphite. The results thus obtained agree very closely with the direct method. Thus, for all practical purposes, the indirect method is sufficiently accurate, and can be accomplished in one hour, the direct method requiring five or six hours. The author strongly recommends the use of ammonium acetate and carbonate, instead of the corresponding soda salts in the direct method, and proves by check experiments with pure manganese sulphate, &c., the statements of Fresenius and others, that the presence of ammoniacal salts prevents the complete precipitation of manganese by bromine and ammonia, to be erroneous. On the other hand, if soda salts be used, the ignited precipitate will contain soda. The author considers that sulphur cannot exist in spiegeleisen. He determines the carbon by dissolving the iron in neutral copper chloride, and after complete solution of the iron and precipitated copper, the carbon is filtered on asbestos, and burnt with copper oxide in a current of oxygen. The carbon determinations by the colour test are unsatisfactory for high percentages of carbon. According to the author the percentage of carbon varies with the percentage of manganese.

Estimation of Manganese in Manganiferous Iron Ores. These ores contain baryta, many contain zinc oxide, and some potash or soda in appreciable quantities. The use of ammoniacal salts as mentioned in the previous part of the paper prevents any large error from the presence of the zinc oxide, but it is difficult to get rid of the baryta; even in the presence of sulphuric acid it remains in combination with the manganese, and is precipitated with it unless special precautions be taken. Lime, if present, may also be precipitated with the manganese. 1 grm. of the ore dried at 100° C. is dissolved in hydrochloric acid, the siliceous matter separated by filtration, and the larger portion of the free acid driven off. The liquid is made up to about $\frac{1}{3}$ of a litre, and allowed to stand for four hours, after adding a few drops of sulphuric acid to separate any baryta. The solution is now diluted to about 1 litre, neutralised with ammonia after the addition of ammonium acetate, boiled, allowed to settle, and filtered; the unwashed precipitate is re-dissolved in hydrochloric acid, and again precipitated with ammonia and ammonium acetate. The basic iron peracetate, after settling, is filtered off and washed three or four times with boiling distilled water, containing a few drops of ammonium acetate. The filtrate is evaporated to $1\frac{1}{2}$ litres, when cold 2 to 4 c.c. of bromine added, and the process completed as described above. After ignition the precipitate should be dissolved in a small quantity of hydrochloric acid, the residue, if any, filtered off, a drop of sulphuric acid added, and the precipitate, if any occurs, separated. It is most important to test the ignited Mn_3O_4 for impurities, baryta, zinc, lime, &c. Chlorine can be substituted for bromine, but without advantage. The ammonium sulphide process is considered to be most objectionable.

Estimation of Iron.—A standard solution of potassium bichromate is recommended, the results being usually a little high. As a reducing agent, sodium sulphite prepared in the laboratory is used, the purchased samples being always impure; sodium bisulphite should not be used. The percentages of iron in sixty samples of steel rails are given, determined by weighing as Fe_2O_3, and by standard solution of potassium bichromate; the mean difference between the two methods is 0·073 per cent.

The accurate determination of manganese in spiegeleisen is of importance commercially; as, being the most important constituent the value of the material is frequently judged by the percentage of that element alone, while the error introduced by the presence of copper is aggravated by the fact that, not only is copper worthless, but absolutely injurious.

The following method for the assay of manganese in iron and steel by Mr. Samuel Peters, Bay State Iron Works, South Boston, is not new in principle, but has given very satisfactory results :—

Dissolve 0·1 grm. pig iron or steel in 3 or 4 c.c. nitric acid, about 1·2 sp. gr., and boil gently in a long test-tube (about 8 inches long and ¾-inch diameter) for five or ten minutes, or until solution is complete; then add an excess of plumbic oxide, say 0·2 or 0·3 grm., and boil again two or three minutes.* Cool the tube and its contents in water. Filter through asbestos, washing out the test-tube and the residue on the filter with distilled water until all the colour has been washed through. Transfer to a graduated tube (¾-inch in diameter), holding 50 or 60 c.c., graduated in 0·2 c.c., and compare with a standard solution of permanganate held in a tube for that purpose. The comparison is made in the same manner as that in the Eggertz method when estimating combined carbon in steel, &c. The solution under comparison is then diluted and well mixed with distilled water (by pouring the contents of the graduated tube into a small dish, and then transferring to the tube again), until its colour is exactly of the same intensity as the standard solution. Having attained to this point, the number of c.c. is noted, and the result is obtained by multiplying each c.c. by 0·0001. Each c.c. is equivalent to 0·01 per cent. manganese when 0·1 grm. of iron is taken for analysis.

For irons containing 0·10 to 0·35 per cent. manganese, 0·1 grm. is the proper quantity; but if there be say 0·8 to 1·00 per cent., it is best to take 0·1 grm. and divide the solution (before adding the lead peroxide) in four equal parts, and use 0·25 for the estimation, taking another 0·25 for a second estimation. In case of a high percentage, as 1·00 per cent., if 0·1 grm. is taken the results are too low on account of some of the manganese escaping oxidation.

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* It is unnecessary to filter off graphite in pig-iron before boiling with plumbic oxide.

This agrees with the observations of others. With an unknown iron, one or two trials with 0·1 grm. or half that quantity will point out the probable amount, and so be a guide for the next trial. If the amount of iron taken does not yield more colour than corresponds to 25 to 35 c.c. of standard hue, it may be safely said that all the manganese is oxidised. It is as well to take this volume as the guide to the quantity of iron to be taken. The quantity of manganese in the liquor to be tested should not exceed 0·4 of a milligrm., and certainly not over half a milligrm. By taking 0·1 grm. of a spiegeleisen containing nearly 12 per cent. manganese, and diluting to 50 c.c., and taking 2 c.c. or 0·04 for the estimation of the manganese, very nearly the proper amount of manganese is obtained. This seems to show that if the division of the solution can be accurately made, and the bulk of the coloured liquid can be kept down well, the amount of manganese in spiegeleisen can be estimated very fairly.

Combined carbon in large quantity does not interfere with the accuracy of the method, for a steel containing 2·00 per cent. combined carbon and only 0·80 per cent. manganese was found to give good results by this method.

The standard is made by diluting a permanganate of potash solution of known strength until each c.c. = 0·00001 grm. manganese.

For example a $\frac{n}{10}$ solution will contain 3·16 grm. permanganate in 1000 c.c. or 0·0011 grm. manganese per c.c.; if this be diluted 110 times it will give the required strength. The standard is contained in a tube of the same bore as the one used for the analysis, or else the standard is put in the latter one, and a solution of permanganate put into a tube of nearly the same bore, and diluted until it exactly corresponds with the standard solution, when it will serve as a standard.

Permanganic acid of the proper hue keeps better than permanganate of potash of the same hue, and is of course easily made by adding nitric acid to the latter. The time occupied in obtaining a result by this method is very short (about half an hour), and it is a method that will prove of advantage in analysing steel made by the Bessemer and Siemens-Martin processes.

Mr. Galbraith ('Chemical News,' February 4, 1876) has given the following simple and accurate process for the assay of manganese in spiegeleisen:—1 grm. of the spiegeleisen is dissolved in nitric acid (sp. gr. 1·20) in a small round-bottomed flask, and evaporated to dryness. When dry, the flame, which may be either a spirit lamp or a Bunsen burner, is turned so that the bottom of the flask is cherry-red for ten minutes. It is then allowed to cool very gradually.

At this point a weighed quantity of ammonio-ferrous sulphate, or ferrous sulphate of a known strength, is put into the flask, and then heated with rather dilute hydrochloric acid. The contents of the flask very soon dissolve, but it is well to keep shaking the solution while it is being heated to prevent loss of chlorine. It only remains now to determine the iron left unoxidised, in order to arrive at the quantity of manganese, which can be done with potassium bichromate solution. It is feared that the ferrous solution may get oxidised by exposure to the air; a small piece of marble put into the flask, which can also be fitted with a cork and tube, will readily prevent that.

In four successive experiments the following results were obtained.

No.	Fe Oxidised	Equal to Manganese p. c.
1	0·2018	19·82
2	0·2103	20·65
3	0·2396	23·53
4	0·2435	23·88

No. 2 gave by ammonium acetate method 20·55 per cent., which was done with great care. No. 4 is a repetition of No. 3.

It is evident of course that there is nothing original or new in the above method; but it contrasts very favourably with the usual methods of separating the iron with sodium or ammonium acetate, and precipitating the manganese from the filtrate with bromine. It is not at all troublesome, does not take long, and has the advantage that the only chemicals and apparatus required are those which are necessary for the assay of iron ores.

Estimation of Titanium in Iron.—The detection of titanium in iron is easy, although its estimation is difficult. The best results have been obtained by following Riley's plan.* This is essentially as follows :—A weighed portion of the iron borings are treated with fuming nitric acid in a flask, a few drops of hydrochloric acid added from time to time, the whole being well boiled. The contents of the flask are then transferred to a porcelain dish, evaporated to dryness, and heated strongly. On cooling, it will be found that the iron oxide readily detaches itself from the dish, and can be easily transferred to a beaker, the portions left on the dish being dissolved in hydrochloric acid, and poured on the contents of the beaker; the dish may be rinsed out, if necessary, with strong hydrochloric acid. The contents of the beaker are boiled for from two to three hours until complete solution of the iron is effected; and as some quantity of hydrochloric acid is required for this, the best plan is to allow a large portion of the excess of acid to evaporate in the beaker, retaining only as much as is requisite to keep the iron in solution. The silica is filtered off in the usual way, after diluting with water and adding a few drops of hydrochloric acid on the filter, to dissolve the basic salt formed by the water. By this means the silica can be obtained nearly white after burning off the graphite, and very little iron will be found with it unless much phosphorus be present, as the silica invariably contains more or less iron phosphate from the insoluble iron phosphide, which cannot be completely dissolved out by hydrochloric acid. Before determining the titanium the residue from the silica should be fused with potassium bisulphate, dissolved in water and added to the solution of iron in which the titanium is to be determined. The solution is reduced with sodium sulphite, and the excess of sulphurous acid is driven off by boiling. The solution is then nearly neutralised with ammonia, and ammonium or

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* *Chemical News,* viii. 226, 233.

sodium acetate added; if there is only a small quantity of phosphoric acid, there will always be sufficient peroxide of iron to precipitate it, but if not, a few drops of nitric acid must be added so that the precipitate produced is distinctly red, and the solution boiled and filtered as quickly as possible. The residue is fused with potassium bisulphate, or where nitric acid is used, this is driven off with sulphuric acid. The result of the fusion with potassium bisulphate is dissolved in cold water (when a little iron phosphate, which remains insoluble, is separated), boiled for some hours, and allowed to stand a night in a warm place, when the titanic acid is filtered off and washed with dilute sulphuric acid, dried, ignited, and weighed.

The above process is not very satisfactory for the quantitative determination of titanic acid. The iron phosphate (insoluble in the potassium bisulphate) cannot be washed without its passing through the filter, and very frequently, also, the small amount of iron keeps up the titanic acid, as iron even in small quantities has a very great effect in preventing the precipitation of titanic acid, so that it is always advisable to add a little sodium sulphite, which reduces the iron oxide and facilitates the precipitation of the titanic acid.

Titanium may, however, be found more satisfactorily and more readily, during the process usually adopted to determine the amount of graphite in pig-iron, provided a large quantity of the pig be operated on. About 200 grains of the pig are to be dissolved in dilute hydrochloric acid; when the pig is nearly all dissolved, and the action of the acid has ceased, more hydrochloric acid is added, and the solution well boiled, so as to thoroughly extract all the iron. The solution is then thrown on dried counterpoised filters encircling each other, and the filter well washed to remove all the iron. It is then treated with dilute potash, and washed once; then re-treated with it so as to entirely remove the silica. The potash is thoroughly washed out, and the filter treated with hydrochloric acid, thoroughly washed and dried at 250° F. until the weight is constant.

This gives the graphite, on burning which a residue of a dirty light brown colour is left, which, fused with potassium bisulphate and subsequent treatment as above explained, is seen to be nearly pure titanic acid.

Mr. Tosh advises the approximate estimation of titanium in iron to be effected in the following way:—About 6 grammes of iron are dissolved in hydrochloric acid, and the whole evaporated to dryness. The dried mass is moistened with hydrochloric acid, water added, and the solution filtered. Part of the titanium exists in the solution (*a*) and part in the insoluble residue (*b*). The solution, if containing much iron perchloride, is reduced by sodium sulphite, the excess of sulphurous acid boiled off, a little iron perchloride added, and the titanic acid precipitated in combination with the ferric oxide thus introduced, by means of sodium carbonate, as in the estimation of phosphorus. The small precipitate is quickly filtered off, washed, dried, ignited, and carefully set aside. From the insoluble matter (*b*) graphite is burned off, and the silica is removed by hydrofluoric acid in the presence of sulphuric acid. To the residue after this treatment the small ferruginous precipitate from (*a*) is added, and the whole fused with potassium bisulphate. When cool the fused mass is extracted with cold water, and from the clear filtered solution titanic acid and iron are precipitated by ammonia; the precipitate is slightly washed, and ammonium sulphide added. The iron sulphide thus formed is dissolved by sulphurous acid, while the titanic acid mixed with sulphur is undissolved, and may be collected, ignited, and weighed, after which it should be tested as to its purity.

In testing a siliceous residue for titanic acid with hydrofluoric acid it must be remembered that a titanium fluoride is formed at the same time, which cannot be heated without the larger portion going off.

Mr. W. Bettell ('Chem. News,' Aug. 22, 1873) proposes the following modification of Mr. D. Forbes' process ('Select Methods in Chemical Analysis,' pp. 110, 111) for the estimation of titanic acid, which may not be unacceptable to those engaged in the analysis of titanic ores :—

Fuse about 0·5 grm. of the *finely* powdered ore with 6 grms. of pure potassium bisulphate (which has been recently fused and powdered) in a platinum crucible at a gentle heat, carefully increased to redness, and continued till the mass is in a state of tranquil fusion.

Remove from the source of heat, *allow to cool*, digest for some hours in 5 or 6 oz. of cold distilled water (not *more* than 10 oz. is to be used, as it generally causes a precipitation of some titanic acid) filter off from a little pure white silica, dilute to 45 or 50 oz., add sulphurous acid till all the iron is reduced, then boil for six hours, replacing the water as it evaporates.

The titanic acid is precipitated as a white powder, which is now to be filtered off, washed by decantation, a little sulphuric acid being added to the wash-water, to prevent it carrying titanic acid away in suspension. Dry, ignite, allow to cool, moisten with solution of ammonium carbonate, re-ignite, and weigh. The titanic acid is invariably obtained as a white powder, with a faint yellow tinge, if the process has been properly carried out.

This method of fusing with potassium bisulphate (‘Select Methods,’ p. 125) is preferable to all others for decomposing difficultly soluble iron ores.

The sample, very finely powdered, is decomposed with hydrochloric acid, and the silica is separated in the ordinary manner.

In order to oxidise the iron the solution is heated with a little potassium chloride, and is precipitated whilst warm with ammonia in slight excess.

Ferric oxide and alumina are thus precipitated along with a part of the magnesia and a little of the lime.

The precipitate, washed, dried, and ignited, is, after weighing, ground up in agate mortar, and as much of it as can be poured out again is ignited anew and weighed. (This is not the entire original quantity, some traces being lost, a circumstance which must be remembered in the calculation.) After this re-ignition and re-weighing, it is rubbed up in a silver crucible with a small quantity of sodium carbonate, a sufficiency of caustic potash is added, and the covered crucible is heated very cautiously over the lamp. At last the temperature of the fused mass is raised to redness, and kept so for about a quarter of an hour. When cold the crucible is steeped in water, to which a little alcohol is added in order to reduce manganic acid; the whole is heated to a boil, filtered, and washed with hot water. The residual ferric oxide, together with the filter, is digested in hydrochloric acid, the diluted solution is filtered and precipitated with ammonia. The filtrate from the ferric oxide is mixed with that from the first ammoniacal precipitate. The solution of alumina in potash is faintly acidified with hydrochloric acid, care being taken that nothing is lost by the effervescence of the liquid, and the alumina is precipitated with ammonium hydro-sulphide or ammonium carbonate, washed with hot water, dried, ignited, and weighed.

The filtrate from the ammoniacal precipitate is mixed in a stoppered flask with ammonium hydro-sulphide.

The precipitate of manganese sulphide is allowed to settle, filtered rapidly with exclusion of air, redissolved in hydrochloric acid, and precipitated hot with sodium carbonate. The manganous carbonate is converted by ignition into mangano-manganic oxide, and weighed as such.

The filtrate from the manganese sulphide is faintly acidulated with hydrochloric acid, heated to expel sulphuretted hydrogen and filtered. The lime is then determined by means of oxalic acid and ammonia, and the magnesia by sodium phosphate.

If the proportion of manganese is large, larger perhaps than that of the iron, as is the case in some blast-furnace slags, the following process is adopted. After the silica has been removed, ammonium chloride and a little sodium acetate are added to the liquid, which is then heated, saturated with chlorine gas, precipitated with ammonia, and boiled till the free ammonia has escaped. The precipitate which contains ferric and manganic oxides and alumina, is filtered off and washed with hot water. It is then redissolved in hydrochloric acid, with the addition of some alcohol, diluted, without filtration, and barium carbonate finely ground up in water is added in such quantity that a portion of it remains in excess. The whole is then allowed to stand for an hour with frequent stirring. The ferric oxide and alumina, together with the excess of barium carbonate, are then filtered off, washed in cold water, the baryta removed by means of sulphuric acid, filtered, and ferric oxide and alumina are precipitated with ammonia. After ignition and weighing they are separated as above mentioned. The manganic liquid is also freed from dissolved baryta by sulphuric acid supersaturated with sodium carbonate and boiled, thus determining the manganese.

From the filtrate of the three bases the lime and the magnesia are precipitated by well-known methods.

A volumetric determination of the iron in a separate portion of the sample is very valuable as a check. If the slag contains both ferrous and ferric oxides this determination is necessary. For this purpose the powdered slag, with the addition of a fragment of marble, is heated with hydrochloric acid in a small flask, and with constant shaking, till it is completely decomposed. Unless the ferric oxide is to be reduced by zinc, the whole is poured into an excess of water, and determined with the standard solution of potassium bichromate.

If the slag contains small proportions of lead or copper they are precipitated with sulphuric acid after the removal of the silica, filtered, and the liquid concentrated by evaporation before the iron is oxidised. The precipitated sulphides, which are usually small in quantity, are treated according to methods already laid down.

Small quantities of sulphur exist in many slags as sulphides, and are determined in a separate portion of the sample.

CHAPTER X.

THE ASSAY OF COPPER.

In the assay of copper by the dry way, all minerals and substances containing that metal may be divided into three classes.

Class I. *Comprises Sulphuretted Ores or Products, with or without Selenium, Antimony, or Arsenic.*

Copper glance,	Cu_2S,	containing	79·7	p. c.	of copper
Chalcopyrite,	Cu_2S, Fe_2S_3,	„	34·4	„	„
Erubesoite,	$3Cu_2S,Fe_2S_3$,	„	55·7	„	„
Bournonite,	$3Cu_2S,SbS_3+2(3PbS,SbS_3)$	„	12·7	„	„
Fahlerz,	$4(Cu_2S,FeS,ZnS,AgS,HgS).(SbS_3,AsS_3,Bi_2S_3)$	„	30—48	„	„
Covelline,	CuS,	„	66·7	„	„
Wolfsbergite,	Cu_2S,SbS_3,	„	24·9	„	„
Domeykite,	Cu_6As,	„	71·6	„	„
Copper regulus, Copper speiss, &c.					

Class II. *Oxidised Ores and Products.*

Red copper,	Cu_2O,	containing	88·7	per cent.	of copper
Malachite,	$2CuO,+H_2O$,	„	57·3	„	„
Azurite,	$2CuO,CO_2+CuO.H_2O$	„	55·1	„	„
Cyanosite,	CuO,SO_3+5H_2O,	„	25·3	„	„
Phosphate of copper,		„	30—56	„	„
Arseniate of copper,		„	25—50	„	„
Chromate, Vanadate, and Silicate of Copper; Slags, &c.					

Class III. *Copper and its Alloys.*

The different methods of assaying copper are more numerous than those for any other metal. They are, in some cases, very similar to each other, and in others based upon very different principles.

These methods may be classified in the following manner :—

A. ASSAY IN THE DRY WAY.

a. For rich Ores and Products of Class I.

1. English Copper Assay.
2. German Copper Assay.

b. For poor Ores and Products of Class I.

1. Fusion of the ore, &c., to a crude regulus, and further treatment of the same according to *a* 2.
2. Fusion of the roasted ore with reagents to collect the copper (lead, antimony, or arsenic), and refining the crude copper.

c. For Ores and Products of Class II.

1. *Reducing and solvent fusion*, with or without collecting reagents (antimony, arsenic, lead), for the copper, after the ore has been roasted, if necessary (in the case of cyanosite and arseniate of copper) with coal-dust, graphite, or ammonium carbonate.
2. *Concentration smelting* with pyrites to a regulus, which is then roasted and smelted to crude copper with or without collecting reagents for the copper.

d. Copper and its Alloys. (Class III.)

Refining with lead on the cupel, or with borax on the refining dish, with or without the addition of lead, antimony, or arsenic.

B. ASSAY IN THE WET WAY.

A. ASSAY IN THE DRY WAY.

a. For rich Ores and Products of Class I.

I. ENGLISH COPPER ASSAY.

M. L. Moissenet has given, in the 'Annales des Mines,'* a very complete description of the Cornish method of assaying copper by the dry way. The following is from a translation by Mr. W. W. Procter.

Each of the large Swansea copper-works keeps an assayer at Cornwall, whose duty it is to determine the richness in copper of all the lots of minerals in the county sold every Thursday at the *Ticketing*, and of all the

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* Vol. xiii. p. 183.

samples of foreign minerals and copper products which may be useful to the smelter.

The copper being obtained in the state of a prill or metallic button, the impurities (generally tin, antimony, &c.) are thus made evident, and the hammer soon proves the quality of the metal which we ought to expect to obtain by metallurgic treatment. As for the accuracy of the method, as far as regards the whole of the metal obtained, we shall revert to this later on. We would, however, observe that, within certain limits, the method would not be less practical on account of being inexact; for we must not forget that it has chiefly for its object to teach the smelter the *value* of the mineral, even more than its true richness.

For example, if we get too low an assay from a sample of 2 or 3 per cent., we should only from this assent to the opinion of the metallurgist, whose interest it is not to work upon very poor minerals. The same remark will apply to the case of minerals very antimonial, &c. Besides, in the description of the method we shall discover the principal phases of the Welsh process; so that it is more just to consider the Cornish assay as a metallurgy on a small scale than as a scientific laboratory method. From thence result also the necessity of long practice and the almost uselessness of theoretical knowledge for those who purpose employing this method alone.

Sir Henry de la Beche ('Report on the Geology of Cornwall,' &c. p. 595), in giving a sketch of the method, declares it to be rather rough and uncertain, and fails not to add at the conclusion a translation of a passage relative to the assay of copper pyrites from M. Berthier's treatise on assays by the dry way.

These drawbacks upon the scientific value of the Cornish method cannot injure the power of facts; they constitute but another reason which we may have for giving an account of the manner in which the first basis of the valuation of the greater part of the copper minerals has been fixed since so long a period.

Division Adopted.—The rather complex operations through which we have to pass will be better apprehended by explaining in succession—

1. The order of the operations, the nature and influence of the fluxes employed, the kind of products obtained (reactions).

2. The manipulations to which each operation gives rise, the furnaces and apparatus used, the characters of the principal products during the chief phases and at the end of each (manipulations).

We shall add to these—

3. Some information upon the influence of the principal foreign metals (tin, antimony, zinc, lead), and upon the treatment of some special coppery matters.

4. Summary considerations on the result of the English method compared with those of the analysis by the wet way.

SECTION I.—REACTIONS.

At the very outset we distinguish two kinds of assays.

1. The roasted sample.
2. The raw sample.

The first only applies to cupreous pyrites or to samples essentially formed of it—that is to say, which contain sulphur in excess; the process begins by a roasting.

In the raw assay we dispense with the roasting; we have recourse to the addition of reagents, either oxidising or sulphurising, according to the minerals; we endeavour to place them by these mixtures in the condition of a properly roasted pyritic mineral.

From this point, at least in general, the operations become identical. They consist in—

1. Fusion for regulus (regulus).
2. Calcining the regulus (calcining).
3. Fusing for coarse copper (coarse copper).
4. One or two fusions with fluxes (washings).
5. Trial by striking with a hammer, last refining (testing, refining).
6. Treatment of slags for prill.

All the slags except those of the fusion for regulus have been preserved. The fusion No. 6 gives a small supplementary button of copper, which again undergoes, if necessary, one or two washings.

As we have said, the roasting is used only for pyrites. We shall return later on to the duration and the circumstances of this operation. Its evident aim is to drive off the excess of sulphur, so as to cause the whole of the copper, with a part only of the iron which abounds in the pyrites, to pass into the state of sulphide at the time of the fusion for regulus.

I. *Regulus.*

1. *Pyrites.*—The fusion for regulus of a properly roasted pyrites is made by mixing with it equal volumes of the three fluxes—borax, fluor-spar in powder, lime slaked in powder—of each one ladle, and covering the mixture with a layer of moist common salt. The matters composing the gangue of the roasted mineral consist principally of quartz, silica, and in general of more alumina and magnesia than lime; oxide of iron, resulting from the roasting of the pyrites, is also present.

The borax only serves to give fusibility, the fluor-spar contributes to the same end by forming a fluosilicate. Otherwise it does not play an important part in the decomposition—that is to say, there is probably no production of fluoride of silicon and calcium; for this last base is added here in considerable proportion, so as to form immediately a silicate which may combine with the fluoride of calcium.

The ferric oxide being so reduced as to pass into the slag, and the different metallic oxides to pass into the regulus, yield oxygen, which reacts on the remaining sulphur. The disengagement of sulphurous acid which results from this, joined to the water contained in the fluxes, justifies, to a certain extent, the use of a layer of common salt, designed to prevent the boiling over. Besides this, the common salt being without action on the metallic sulphides, does not here produce those important effects which it exerts in the later fusions.

If the pyrites appear insufficiently roasted, we must add a little nitre, the oxidising action of which again gives off sulphur; the opposite case, that of a roasting too much prolonged, is rare; we remedy it by the addition of sulphur and tartar.

2. *Very poor Pyrites.*—In a very poor pyrites—that of Bear Haven, in Ireland, for example—the proportion of sulphur does not require us to have recourse to the roasting; we employ the three fluxes and one ladle of nitre.

3. *Variegated Copper Ore.*—Peacock ore contains less sulphur in proportion to the copper than pyrites; we also fuse with a little nitre.

4. *Sulphide of Copper.*—The sulphur is here insufficient. We add together sulphur $\frac{1}{2}$ to 1 ladle, according to the valuation; tartar $\frac{1}{4}$ to $\frac{1}{2}$ ladle—that is to say, half the volume of the sulphur. The tartar is a powerful reducing agent, and is supposed in small quantities to favour the action of the sulphur by preventing its disengagement as sulphurous acid by the oxidising matters in the mineral; but if used in excess, it acts as a desulphuriser, as well by its carbon as by its alkali.

5. *Carbonated Minerals.*—The addition of sulphur and carbon is evidently still more necessary here.

6. *Native Mixture*: $\frac{2}{3}$ sulphide copper, $\frac{1}{3}$ pyrites.—We add, in this case, nitre for the pyrites, and sulphur and tartar for the sulphide of copper; although these reagents appear sure to neutralise each other, it is possible that their simultaneous employment may be logical. The nitre probably decomposes the pyrites, which would, without it, fuse and give a very ferrous regulus, whilst the free sulphur would be of little use, on account of the sulphide of copper. Be this as it may, this is the plan adopted.

During the progress of the fusion for regulus we have still to introduce other matters, some incidentally, and others in all cases.

If a blue flame persists in escaping from the crucible, an index of the formation of sulphurous acid, we project into it sulphur 1 ladle, tartar ½ a ladle. When the fusion appears almost finished, in order to render the bath more liquid, and to facilitate the collection of the button, we throw in a little dried salt, and a flux composed beforehand of lime, a little fluor-spar, and a very little borax—that is to say, of the elements in different proportions of the mixture introduced originally.

The regulus obtained is composed principally of copper, iron, and sulphur. We shall return to the aspect and the richness which it ought to have according to the minerals treated.

II. *Calcining.*

The calcination of the regulus is one of the most important operations; it ought to be quite complete.

III. *Coarse Copper.*

To the calcined regulus is added—nitre ¼ ladle, borax ½ ladle, charcoal ⅛ ladle, dry salt 1 ladle (these quantities remain the same, whatever mineral may be assayed); tartar 2 ladles for a regulus of medium richness. Covering of moist salt, 2 ladles.

The nitre is designed to burn the sulphur which may have escaped the calcining, and to ensure the passage of the easily oxidisable metals, especially of iron, into the slag in the state of oxides. It is besides in too small proportion to act upon the copper, especially in presence of reducers whose effect is certainly later than the deflagration of the nitre.

The borax plays simply the part of a flux.

The dry salt has for its object to give fluidity to the slag. Unfortunately, if the addition of the salt attains this object, it also determines from this operation a sensible loss of copper by carrying it away with the saline vapours. We shall insist upon this point in describing the washing.

The charcoal and the tartar are especially the important reagents in the fusion. The tartar, at the same time that it is one of the most energetic reducers, is also a flux and a desulphuriser. Its use is, then, perfectly justified here, only the proportion of tartar added ought to be regulated according to the quantity of copper, which the *weight* and *aspect* of the regulus permit the experienced assayer to estimate sufficiently closely; an excess of tartar would reduce the foreign metals, and produce in consequence a very impure coarse copper.

When the fusion appears complete, we throw in some white flux,* which gives fluidity to the slag, and determines by its partial decomposition, from which a disengagement of carbonic oxide results, a stirring up of the materials. These two effects facilitate the collection of the metallic button. The potassium carbonate begins also without doubt from this operation to refine the metal a little by attacking the iron, zinc, and tin already reduced. M. Berthier ('Essai par la Voie Sèche,' vol. i. p. 393) points out this reaction:—'A part of the carbonic acid which it contains being decomposed and changed into carbonic oxide, a compound is formed consisting of alkali, carbonic acid, and metallic oxide, &c.'

Lead, copper, and antimony are not attacked.

IV. *Washings.*

In the operation of washing we put into the crucible, at the same time as the coarse copper, the following fluxes:—White flux, 1 ladle; dry salt, 2 ladles.

It is evident that the white flux is here employed as an oxidiser of the foreign metals, and with a view to the application of the above-mentioned reaction.

As for the salt, it is both useful and injurious. If it were only used with the view of augmenting the fluid mass so as to preserve the metal from contact of air, &c., it would be advantageously replaced by an excess of white flux; but it can form volatile chlorides with the arsenic and antimony

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* This white flux is prepared in the laboratory by mixing in a mortar, tartar 3 volumes, nitre 2 volumes, salt a little, then determining the combustion by the introduction of a red-hot iron rod, which is turned round until the matter ceases to deflagrate.

which the copper has retained in the form of arsenide and antimonide. Common salt is, then, to be regarded as one of the principal agents of purification put in operation by the Cornish method. On the other hand, the loss of copper which arises from the carrying off of this metal by the vapours of common salt cannot be doubted. M. Berthier has found that by heating equal weights of copper and salt until the complete volatilisation of the latter, 3 per cent. of the metal is carried off.

In the event of the coarse copper appearing too impure, we take care to add a little nitre. According to the appearance of the button we recommend the washing or not.

V. *Testing, Refining.*

The button of metal is flattened on an anvil. We thus recognise tin by the hardness, and antimony by the brittleness of the alloy. The button is then put alone in the crucible. When it presents a proper appearance—that is, when the edges assume a bright colour, the centre, which the assayer calls the eye, being dark—we hasten to put into the crucible the fluxes, which are the same as for washing, only taken in rather smaller quantity.

In general, when we have operated well, the button obtained is of a fine colour, and is regarded as pure; if we have passed the eye, it is covered with a layer of red oxide; if, on the contrary, we have put in the fluxes too soon, the button is dull.

It is easy to give an account of the reactions which take place during the refining, and which differ a little from those of the washing.

In heating the button alone in the air in the crucible, it is intended to submit it to an oxidation which ought to act sufficiently on all the foreign metals more oxidisable than copper without acting too much on the latter. The proper point is indicated by the appearance of the eye; the projection of the fluxes puts an end to the atmospheric oxidation, and determines the scorification of the oxides which expel part of the carbonic acid of the potassium carbonate, for which they substitute themselves, and give rise to triple compounds of metallic oxides, alkali, and carbonic acid.

The lead, tin, iron, and zinc oxides behave thus. When we have passed the eye, there has been a considerable formation of oxide, which leaves the button reddened, as I have indicated. At the same time the slag is strongly coloured red or green. If, on the contrary, the fluxes have been thrown in too soon, the oxidation has been insufficient, and then the refiner just falls back upon the preceding operation of washing—an operation less efficacious and even without result in the case of lead and antimony.

As for the physical phenomenon of the eye, perhaps it corresponds to the very short instant when the oxides, less dense than the copper, are concentrated at the top of the button, and there make a dark spot before attaining a temperature sufficiently elevated to acquire the brightness of the metal itself.

We may add that the minerals of Cornwall, generally more impure than foreign minerals, require a notably longer time for the appearance of the eye.

Extra Accidental Washing.—More often the refining gives a definite product, put aside to be weighed with the prill extracted from the slag ; let the button be clear, burnt, or dull. Even if the metal appeared too impure we would not recommence the refining, but would have recourse to an extra washing by putting at once into the usual crucible besides the button and the usual fluxes, the slag from the refining.

VI. *Slags for Prill.*

All the slag from the fusion for coarse copper inclusively having been preserved, we fuse them all together with :—

Tartar . . .	1 ladle	Simple reducing mixture
Charcoal . . .	traces	

We obtain a small globule variable with the circumstances of the different operations which have allowed more or less copper to pass into the slag. If the prill is not very small, and its appearance indicates a metal not sufficiently pure, we submit it to one or two washings, as above.

SECT. II.—MANIPULATIONS.

The sample, which has been taken with the utmost care, arrives at the laboratory rather coarsely powdered, still wet, and wrapped in strong packing paper: the paper is opened and placed near a furnace on the cast-iron plate which covers it; the drying is rapidly done there.

The first question is to discover the kind or kinds of minerals, so as to employ the warm or raw sample.

For this purpose we throw one or two large pinches of the mineral into a flat-bottomed copper dish, and we wash it very easily by putting in water several times and giving a rotatory motion to the matters, at the same time that we incline the dish so as to cause the muddy parts to run from the gangue. The small metallic fragment remains distinctly visible, and we can often discern by simple inspection the presence of foreign metals.

We weigh 400 grs. of the dried mineral, a quantity upon which the assay is made.

The crucibles used in Cornwall are of three sizes:—

1. Large.
2. Large second.
3. Small second.

The small seconds have externally the internal dimensions of the large, into which they fit as into a nest; the first and third are sold the one in the other, and called nested. They are the most used.

The large serve for the roasting and the fusion for regulus, the small second for calcining the regulus and all the fusions which follow.

The large seconds are only employed in place of the former when we have to treat a very large regulus.

The crucibles are of a kind rather wrinkled, and as if fused superficially; they present the appearance of coarse stoneware pottery. Their form, moderately wide, permits us to make use of them successively for the roasting and the fusion for regulus, and gives them sufficiently great stability in the fire of a wind-furnace. They are besides very resisting. They are made at Truro and Redruth.

The wind-furnace has for its principal dimensions—

		Inches
Length from front to flue		10
Breadth		8
Depth to the bars		14
Opening of the flue	length	8
	height	2

A sufficiently large space is reserved underneath the fire, where the ashes accumulate without inconvenience, but opening only by a framework contracted so as not to allow too free an access of cold air.

The furnace serves either for roastings or for fusions; in the latter case we cover it with two mounted bricks, very easy to manage, and allowing to only half open it when we wish to inspect the contents of the crucibles. We can conduct ten roastings at once; the crucibles are marked by a brush with colcothar mixed with water. The furnace having been recharged with coke, we put the crucibles on the top, and after a few minutes, the substances beginning to get warm, we stir them by means of iron rods. Each crucible receives a rod, which we leave standing there (leaning against the chimney) during the whole period of the roasting, so as to avoid the loss which would take place if we withdrew the rod. From time to time we renew the surfaces by lightly taking hold of the rod with the left hand by the upper end, whilst the right forefinger and thumb make it turn at once upon itself and round the crucible.

The duration of the roasting varies essentially with the nature and the richness of the mineral; it is never less than six or seven minutes, and may reach half an hour. When from the *sandy appearance* of the matters we consider the operation finished, we withdraw the crucible, raise the iron rod with care, and expose the crucible to the air, allowing its contents to cool slowly. The roasting has succeeded when the surface has the brown-red colour of iron oxide and the bottom only is black. In this case we proceed to the fusion for regulus by simply adding the three fluxes (borax, fluor-spar, and lime); if the bottom of the crucible appear too black, we ought to complete the oxidising action by the addition of a little nitre.

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Fusion for Regulus.

The different substances above indicated are taken from the box with a slightly concave ladle of $1\frac{3}{8}$ diameter, then mixed in the crucible with a stirring-knife. We ought to allow the heat of the wind-furnace to fall and then to recharge, so as to have a gentle fire at the commencement of the fusion for regulus. The crucibles are placed upon the coke, and supported against the walls of the furnace, which we then close with the two bricks. After about a quarter of an hour, we open the front brick, so as to observe the progress of the operation; it is at this stage that we throw the sulphur and tartar into those crucibles from which a blue flame is disengaged. Some minutes later—that is to say, nearly seventeen minutes from the commencement—we add the salt and the flux destined to collect the regulus; then (twenty minutes from the beginning) we run into a metal mould, not greased.

We make, in general, several fusions at once—four, for example; we have in consequence two moulds into which we pour the contents of the crucibles in an adopted order, so as to avoid all confusion. The matters, very rapidly solidified, are detached simply by a blow, and fall in order on a metal plate fixed in front of the laboratory window. We immediately seize them with the copper tongs, put them into a basin of the same metal, and immerse them for a moment in cold water, where it is important not to leave them too long. This immersion allows us then to separate very easily the slag from the button of regulus, itself very brittle. For this purpose the mass is put on the metal plate, and by means of a hammer we strike with care all round the slag, which breaks off pretty cleanly. We hasten to detach from the surface of the regulus the slag which may remain adherent, using a small hand chisel, without the hammer. The slags are broken, and if we find any prills of regulus they are added to the principal button. Sometimes in these breakings, and especially in those analogous for the last fusions, we surround the substances by an iron ring, placed on the metal plate, so as to avoid loss of splinters. In a general way, the slags of the fusion for regulus are rejected. We shall see further on how it may become necessary to flux them again when the mineral contains blende.

The aspect of the regulus is characteristic, and it is easy to arrive at a pretty close estimation of its richness, and consequently of the degree of success of the operation, by simple inspection of the regulus.

No. 1. A very poor regulus (coarse), that is to say, too much charged with iron, is bronzed and dull; the operation following would not be able to carry off the excess of iron at least without a corresponding loss of copper. A like regulus evidently results from an imperfect warming, or from an excess of sulphur, or from an insufficiency of nitre, as the case may be.

It contains less than 40 per cent. of copper. There is nothing for it but to reject it.

No. 2. A regulus of good appearance is in general bronzed but rather shining; it appears finer. Its richness varies from 40 to 60 per cent.

No. 3. From oxides, carbonates, and from some minerals charged with impurities (Sn, Sb) we desire to obtain a fine bluish button of a greater richness—65 to 75 per cent. We perceive, indeed, that from oxides and carbonates, to which we have only to add sulphur, and which also by their nature do not, like pyrites, contain combined iron, it is easy to obtain a richer regulus without fearing any loss of copper. As for the stanniferous and antimonial minerals, we shall return to them further on.

No. 4. In every case a regulus, the richness of which rises to 80 per cent., and of a very shining grey-blue appearance, ought to be rejected, its richness indicating the loss of a certain quantity of copper left in the slag.

Here is, in the preceding order, the result of the analyses of four buttons whose description agrees with that which we have just given, excepting, perhaps, No. 2, whose fracture is rather reddish:—

No.		Copper	Iron	Balance; sulphur and traces of foreign metals
1	Coarse, to be rejected	36·00	32·90	31·10
2	Good in general (rather too fine) .	60·00	14·70	25·30
3	Good for a carbonate, &c. . . .	65·60	10·50	13·90
4	Too fine, to be rejected . . .	80·16	2·10	17·74

If we compare these products with those obtained in the metallurgy of copper by the Welsh method, we find (Le Play, 'Annales des Mines'):—

	Matts of the operations. II. V. IV. VIII.	Copper	Iron	Different metals	Sulphur	Total of Diff. M. & S.
II.	Coarse matt (fusion of poor minerals, raw or calcined) $3Cu_2S + Fe_2S_3 + 4(Fe\ dif.\ met)S$	34·6	34·1	1·5	29·8	31·3
V.	Blue matt (fusion of the calcined coarse matt with minerals of mean richness) $0{\cdot}8Cu + 3Cu_2S + 2(Fe.\ d.m.)S$	57·2	18·5	1·0	23·3	24·3
	Reddish variety, *matte mince* $1{\cdot}3Cu + 3Cu_2S + 2(Fe.\ d.m.)S$	61·6	15·8	0·6	22·0	22·6
IV.	White matt (fusion of the calcined coarse matt with rich minerals, carbonates, and oxides) Metal—very pure type . .	77·4	0·7	0·9	21·0	21·9
	very blue variety . .	64·8	9·0	3·6	22·6	26·2
	mean . . . . . $8Cu_2S + FeS$	73·2	6·3	—	20·5	—
VIII.	Matt (roasting of extra white matt VII.) $0{\cdot}2Cu + Cu_2S$	81·1	0·2	—	18·5	—

These numbers show the evident analogy, the identity almost, of the products of the laboratory and those of the works; we may sum up by saying that the regulus ought to be richer than coarse metal, and in the case of ordinary minerals to approach if not to attain (as in the case of sample No. 2) to the composition of blue metal.

For carbonated and oxidised minerals we arrive directly at the very bluish variety of white metal.

Finally, in no case must we have a button as rich as regulus matt.

Calcining the Matt.

The matt is pounded fine in a bronze mortar; we avoid loss of fragments by means of a perforated cover and a cloth which surrounds the pestle. To facilitate the pulverisation, and avoid the sulphide greasing, we add in the mortar a small piece of coke. The pounded matt is carefully turned upon a sheet of paper, the mortar wiped out with a hare's foot, and the substance put into a small second or large-second crucible. The calcining is conducted as the roasting of a mineral; it generally lasts longer, for the expulsion of the sulphur is to be as complete as possible. It is necessary to regulate the fire with the greatest care, so as to avoid all agglomeration, and to stir almost continually. When the matter adheres to the rod, we withdraw the crucible for a moment; this inconvenience is chiefly produced, if we have not detached the slags sufficiently from the matt; the calcining is then much longer, the flames remain blue a long time, and the fumes which are disengaged have an odour which is not purely that of sulphurous acid. When the fumes and the odour cease, and the matter has taken a sandy appearance, we raise the heat; then withdraw the crucible, and allow it to cool slowly in the air as when roasting.

The mean duration of calcining is half an hour.

Coarse Copper.

The fluxes above indicated are taken from a box No. 1, except the dry salt called the refining flux, which forms part of a second box. The ladle for this box No. 2 is a little larger than for the first: it has a diameter of 1½ inch. At the beginning of the operation the furnace is well filled and lighted; the same fire ought to suffice for all the following fusions, which it is very important to conduct with great rapidity. After a moment, and if there is any frothing, we throw in some dry salt, which calms the ebullition. At the end of ten minutes, the fusion appearing complete, we throw in a pinch of white flux. A little after we withdraw successively each of the crucibles, pouring them carefully and by a single turn into each of the principal cavities of the metal mould. These moulds ought, this time only, to be greased with a cloth impregnated with suet. The crucibles are immediately put back again into the fire.

We detach the slag as previously, seize each one successively with the copper tongs, and plunge it for an instant into a basin full of water. The rest is effected as for the regulus, only the slags are preserved on the metal plate, and in the order in which we have detached them. The button of copper obtained appears more or less black; I have already indicated the influence of the tartar in excess.

Washings.

We place the button and the fluxes in a large copper shovel, lengthened and narrowed at the end, called a scoop, and we pour them into the crucible, which is already at a red heat. As the fusion is made in five or six minutes, it would be inconvenient to prolong it on account of the loss occasioned by the carrying off of copper with the vapours of common salt. The pouring is made with care by pouring first into one of the large cavities, then as soon as the metal has fallen there we finish by pouring the slag into one of the small lateral cavities. This last slag, probably rich in copper, is less fluid, and would adhere to the button, which would be difficult to cleanse. The two buttons being detached from the mould, we immerse the small one first, then finish as in the preceding operation.

Testing and Refining.

The crucible has again been put back into the furnace, after the pouring; the button tried by the hammer is put into the crucible by means of the tongs. At the end of about three or four minutes it attains the colour of the vessel, the eye manifests itself, and we rapidly throw in the fluxes put into the scoop beforehand.

The pouring is done as for the washing, with the small button of slag kept apart.

In general we get a button regarded as pure, clean copper; if not, as I have said, we proceed to an extra washing by adding exceptionally in the scoop the last slag obtained.

Prill.

The crucible this time has been left out of the furnace; put into it all the slags, collected for this purpose from the metal plate into the scoop, and upon which we have put reducing reagents. The fusion lasts a quarter of an hour; pour all at once into the large cavity; before the cooling, by means of a transverse blow, get rid of the upper beds which are still liquid, and composed principally of common salt. Then operate as above. Collect the prill, which again undergoes, if necessary, a washing.

SECT. III.—SOME MINERALS AND SUBSTANCES OF A SPECIAL NATURE—INFLUENCE OF FOREIGN METALS.

STANNIFEROUS MINERALS.—Most often we only perceive the presence of tin in a copper mineral when testing with the hammer, which reveals the nature of the bronze;

when we proceed to the refining of such a stanniferous button, it is impossible to obtain the characteristic eye; that is to say, the surface of the metal becomes quite clear, and we scarcely open the furnace when it again becomes obscure. We free it from tin by two or three extra washings. If we suspect tin from the known produce of the mineral, or the inspection of the sample in the basin, we endeavour to obtain a fine regulus, which is accomplished in the case of a warm sample by prolonging the calcining, and for the raw sample by putting in more nitre or less sulphur. It is clear that tin can only enter the regulus by virtue of the excess of sulphur necessary to the formation of the coppery matt, and that by restraining this excess of sulphur we diminish the chance of tin entering the button. The fine regulus ought to contain 70 to 75 per cent. of copper, as for the carbonated copper minerals.

Antimonial Minerals.—Antimony is also detected in the testing; the metal being rendered very brittle. We then add one or two grammes (15 to 30 grains) of lead in the refining operation. There forms an alloy of lead and antimony heavier than copper, which is poured into the small cavity of the mould. When we suspect antimony, we act as for tin—that is to say, we produce a fine regulus, a most careful roasting expelling the antimony; then we have to make two washings, and in the second to add the metallic lead.

We cause, then, three influences to act with a view of expelling the antimony:—

1. Slow oxidation at a low temperature, disengaging antimony.

2. Repeated chloridations, from whence a formation of volatile chlorides.

3. Affinity of the lead and mechanical separation of the alloy.

Zinciferous Minerals.—One of the metals which is most troublesome is zinc. We recognise it by the appearance of the regulus and by its colour, which is that of blende. Once out of ten the regulus collects sufficiently to be able to detach it; in this case we pound it, add to it the slags, and borax 1 ladle, nitre ½ ladle. We fuse anew, and obtain a good regulus, for the nitre has caused the zinc to pass into the slag in the state of oxide.

Most often the zinciferous regulus does not collect, and there is nothing for it but to begin anew by making a very prolonged roasting of at least half an hour.

Plumbiferous Minerals.—Lead is not injurious, for it does not alloy with copper. The warming is also prolonged. Lead passes into the regulus, which facilitates the collection of the matter. In the last operation the lead easily passes into the slag; it also, in case of need, carries off antimony. Thus the copper obtained from lead minerals is most malleable.

Special Cupriferous Products.

Regulus of Chili.—These are treated as those which we obtain by the fusion for regulus. Their richness, which rises to nearly 60 per cent., requires us to add much tartar in the fusion for coarse copper.

Slags of Copper.—To obtain regulus we add to the slag sulphur, tartar, and nitre: this last maintaining metals other than copper in the state of oxide in the slag.

Old Copper.—For turnings, waste of workshops, &c., yielding 97 to 98 per cent. by the assay, and containing, in fact, not much foreign matter except a little mixed dust or dirt, we take care first to glaze the crucible by fusing in it a little borax and nitre; then we treat the matters by a simple washing, the slags of which we work for prill. This last is often very considerable.

SECT. IV.—SUMMARY CONSIDERATIONS—COMPARISON OF THE RESULTS WITH THE ANALYSIS BY THE WET WAY.

After this detailed account of the numerous operations which the metal undergoes before attaining the state of button and prill, it would be superfluous to insist upon the practical difficulty of the Cornish method.

Nevertheless, in experienced hands, and in the case of daily practice, it is still a rapid method, allowing us to treat almost uniformly the different varieties of copper mineral, and at the least to remedy during the operation itself the impurities which show themselves.

As to the metallurgic accuracy, here is a small table showing comparatively the produce by the dry way (determined by a Cornish assayer) and that which we have obtained by the most precise methods of the wet way. It comprehends six samples, whose richness varies within sufficiently great limits.

Nature of the sample and produce	Dry way D.	Wet way W.	Difference W—D.
Regulus of Chili	$56\frac{1}{4} = 56{\cdot}250$	58·40	2·150
Green copper carbonate of Castile	$9\frac{3}{4} = 9{\cdot}750$	11·52	1·770
Variegated copper, Huel Damsel	$10\frac{1}{5} = 10\ 500$	11·30	0·800
Pyrites, West Wheal Seton	$8\frac{3}{8} = 8{\cdot}375$	8·40	0·025
„ United Mines	$8 = 8{\cdot}000$	10·38	2·380
„ Devon Great Consols	$4\frac{5}{8} = 4{\cdot}625$	5·60	0·975
			8·100
Mean difference	$\frac{\Sigma\,(W-D)}{6}$		1·350%

By adding the result given by the last five minerals we find

$$\Sigma D = 41{\cdot}25,\ \Sigma(W-D) = 5{\cdot}95,\ \Sigma W = 47{\cdot}20, \text{ and}$$

$$\frac{\Sigma W}{5} = 9{\cdot}44$$

By taking the ratio

$$\frac{\Sigma(W-D)}{\Sigma D} = 14{\cdot}42,$$

we see that we must add to the richness indicated by the Cornish assay about $\frac{1}{7}$ of that result, and by taking the ratio

$$\frac{\Sigma(W-D)}{\Sigma W} = 12{\cdot}60,$$

that the loss is $\frac{1}{8}$ of the copper, if we consider a mineral of 9 or 10 per cent.

Without wishing to draw a conclusion altogether general from so small a number of analyses, we nevertheless think they suffice to show that the Cornish method occasions losses always sensible and sometimes considerable. We think we may assert that upon the whole of the Cornish minerals whose mean richness varies from 6 to 7 per cent., the loss by the assay is not less than 20 per cent. of the contained copper, and that for certain pyrites of 3 to 4 per cent. it attains 30 and 40 per cent. of the metal.

The principal causes of these losses are—(1st) The quantity more or less great of copper left in the slag of the regulus; (2nd) and especially the carrying away of copper by the vapours of common salt in the fusion for coarse copper, the washing or washings, the refining and the treatment of the slag for prill.

In consequence we think they ought to bear principally on the oxidised minerals for which we make a rich regulus, and still more on the impure minerals, which besides a rich regulus have undergone several washings. Thus the minerals of Algeria, grey copper, assayed some years ago at the School of Mines, have given a produce *much* higher than that indicated by the Cornish assayers.

It may be said therefore that the results of the Cornish assay do not fall short of the truth by a fixed quantity, but become more and more inaccurate the poorer the ore. The smelter gets out of the ore more metal than the assay indicates.

The most frequent alloys of copper, *i.e. brass*, *German silver*, *gun-metal*, &c., cannot be assayed in a reliable manner in the dry way. German silver, because the nickel could not be removed at all, or only with great difficulty, and the rest because zinc and tin give such difficultly fusible oxides, that they could not be properly removed in the refining.

In the *alloys of copper with silver*, *gold* and *platinum*, the copper may be determined from the loss arising from cupellation with lead.

In all assays of copper in the dry way, the *silver* or *auriferous silver* contained in the assay sample cannot be removed, and it is generally pretty completely collected in the copper obtained. These copper assays give nowhere any indications whether gold or silver is present or not; and the amount of these metals which may be present must therefore be both sought for and determined by a special assay for them. If they are found, and in sufficiently large quantity, they are deducted from the weight of the copper.

The dry assay is mostly found in practice in smelting works, where, even in the hands of less scientifically educated than skilful assayers, with the character of the assay substance once known, and suitable practice in following out the separate manipulations, it gives results which suffice for the business of working copper in the large way.

B. ASSAYS IN THE WET WAY.

a. Colorimetric Copper Assays.

These are based upon the fact that ammonia, added in excess to the solutions of salts of copper, produces a beautiful azure blue colour, whose intensity depends upon the quantity of copper dissolved. By comparing the shades of blue colour in equally thick layers of the dissolved ammoniacal assay substance (assay fluid) with a normal or standard ammoniacal fluid whose copper contents are known, the quantity of copper in the former can be calculated when its volume is measured.

To Heine, the superintendent of the smelting works in Mansfeld, belongs the merit of having first successfully employed this reaction for the determination of small percentages of copper; and later it has been also extended by Jacquelain, Von Hubert, and Müller, to the determination of larger quantities of copper.

1. Heine's Colorimetric Method.

For the determination of the quantity of copper in bodies poor in this metal, *e.g.* in slags, lead matt, litharge, crude lead, and other plumbiferous metallurgical products, tin, cupelled silver, &c. ; in short, in all substances which contain from a trace to about 1 per cent. or a little more of copper, this method is the most advantageous to be used.

After the assay sample has been reduced to as fine a state of mechanical subdivision as possible, which with slags is best attained by sifting or washing them, one centner (3–4 grammes) of it is weighed out and dissolved, or so completely decomposed by a suitable acid that in the residue, which is to be filtered and well washed, no more copper remains behind. For this purpose nitric acid or aqua regia is employed, according to the character and particular behaviour of the substance, and the nitric acid is concentrated or somewhat diluted, as may be required. The solution is either immediately, or after the copper has been first precipitated by sulphuretted hydrogen gas and again dissolved, strongly supersaturated with caustic ammonia, and the precipitate, if any, thereby produced, digested in caustic ammonia for a considerable time, with frequent stirring at a very gentle heat (30°–40° C.), then filtered off and thoroughly washed. According to the quantity of copper present, and according to the degree of dilution, the solution obtained will appear more or less strongly coloured blue. The volume of the solution is measured in graduated vessels, and the intensity of the colour compared with and determined from fluids, which have been previously prepared as standard fluids, and which for a definite volume contain a definite, accurately weighed quantity of copper, that has been dissolved in nitric acid, precipitated by caustic ammonia, and redissolved in excess of the same. From the measured volume, and the intensity found by comparison, the quantity of copper is then determined by calculation.

Heine proposes standard fluids with one, two, three, and four assay loth of copper in one ounce (two loth, commercial weight) of the ammoniacal fluid. These four standard fluids are all-sufficient.

If the French weights and measures are used, standard fluids are taken with ·001, ·002, ·003, ·004 grammes of copper to every twenty-five cubic centimètres of the fluid.

The graduated vessels (cylinders) required for the preparation of the standard fluids, as well as for the measuring of the assay fluid, can be easily prepared by the assayer himself. One quarter of an ounce of water is weighed out a number of times in succession and poured into the cylinder, and each time the height of the fluid is marked in a durable manner on the glass with a diamond, or by etching it with hydrofluoric acid vapour, &c. Also earthen or porcelain measures, that are prepared and marked for the volumes that hold one, two, three, four, &c., ounces of water, may be used.

It is not practicable to replace the volumetric measurement by weighing, for the quality and quantity of those substances which are soluble in acids and not precipitated by ammonia, or are again dissolved by it, may vary greatly in the assay.

In the formation of the normal fluids, two assay pounds of chemically pure (galvanic) copper are weighed out on a good balance, dissolved in nitric acid, the solution supersaturated with caustic ammonia, and placed in a graduated cylinder, which is divided to whole, half, and quarter ounce volumes of water, and then water enough is added to bring the fluid to the sixteen-ounce mark. The fluid then contains $\frac{64}{16}=4$ loth of copper per ounce. Six ounces of this four-loth solution are then taken, two ounces of water added to it, and eight ounces of fluid obtained, with $\frac{24}{8}=3$ loth of copper to one ounce of water. The two-loth solution is formed in a similar way by diluting four ounces of the four-loth solution to eight ounces; the one loth, by diluting four ounces of the four-loth normal fluid to sixteen ounces. In the measuring of the assay fluid it is estimated within one-eighth of an ounce, which is sufficiently close. If in the dilutions a mistake is actually made of one-sixteenth of an ounce, the maximum of possibility, the error amounts to about two cubic centimetres, which in a whole mass of fluid of 200–500 cubic centimètres has no influence upon the solution that can be detected with the eye.

The preservation of the standard fluids, as well as the comparison of the blue assay fluids with them, must take place in glass vessels closed with ground-glass stoppers. These vessels must have the same form and size, consist of the same colourless glass, and have an equal thickness of glass in the smooth side walls. The last condition is obtained the surest by grinding. This grinding, however, which notably increases the cost of the glasses, is not indispensably necessary if the vessels are carefully formed and blown in a good glass-house. An oblong form is most advantageous for the vessels. They hold about an ounce and a half of fluid, and are about two inches long, two and a half inches high, and one inch wide, with walls about one-eighth of an inch thick.

The glasses are very advantageously formed from an unblemished sheet of plate glass of equal thickness throughout, by cementing the sides together and the insertion of a glass neck. The assayer has in the form of vessel indicated a triple control in the comparison of the assay fluid with the normal solution according as he looks through the fluid in three different directions.

The digestion of the assay sample with acid may take place in any suitable vessel whatever, a glass flask, a beaker covered with a watch-glass, &c., only no thumping and spirting of the fluid should be possible in the process. The nitric acid, &c., must be added little by little. The time required for this may vary greatly. The solution of *cupelled silver*,* *skimmings*, &c., with nitric acid is finished in a short time; on the other hand, in the examination of difficultly decomposable *slags*, with which concentrated

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* With cupelled silver, after dissolving in nitric acid, the silver may be precipitated with sodium chloride, the silver chloride filtered, washed, and the solution then mixed with caustic ammonia.

nitric acid or aqua regia will always be used, the digestion often requires to be continued at a warm temperature for two to three times in twenty-four hours. The mass must be frequently stirred with a glass rod, because many slags decompose rapidly with evolution of heat, form a thick jelly, and deposit a crust on the bottom of the glass—sub-, mono-, and bi-silicate slags mostly decompose readily, higher silicates resist complete decomposition by aqua regia—and then a preliminary solvent ignition or fusion with potassium carbonate or calcined sodium carbonate, or better, a mixture of both, is necessary, precisely in the manner given in the wet assay of copper. Here also it does no harm if some of the substance of the crucible remains adhering to it.

The decomposition of the slags by acid is complete when in the stirring with a glass rod no more grating can be perceived.

After hot water has been added to the decomposed assay, the residue is collected on a filter, well washed out, without diluting the filtrate too largely, and the copper precipitated from the solution, if necessary, with sulphuretted hydrogen gas, especially when a notable quantity of alumina and iron is present, whose slimy precipitates from the immediate precipitation with ammonia always retain copper. This precipitation of the copper has also the advantage that, as cobalt and nickel do not precipitate with it, the colouring effects which they would produce, if present, are removed. Since the copper sulphide requires for its solution but a few drops of nitric acid, in the succeeding treatment of the solution with ammonia, but a small quantity of ammoniacal salt is formed, and the specific gravity of the coloured fluid varies but very little from that of water and the normal solution. With the increase of the specific gravity of the assay solution, its volume is considerably increased, and therefore it gives too large a measure in the direct precipitation with ammonia. If the precipitation with sulphuretted hydrogen gas is completed in four to six hours, the copper sulphide is filtered out, thoroughly washed with cold water containing sulphuretted hydrogen, the filter dried, ignited in a porcelain crucible, the copper oxide formed warmed with a few drops of nitric acid or aqua regia, supersaturated with ammonia, filtered, and well washed, till the washings are no longer tinged bluish.

A precipitation of the copper with iron wire, from a solution evaporated with sulphuric acid, and a re-solution of the copper in nitric acid, consumes less time. If the copper is not precisely precipitated, errors of some 30 per cent. and more, of the whole amount of copper may occur. By repeated solution of the iron precipitate and precipitation with ammonia, all the copper cannot, however, be extracted.

In the examination of *litharge*, the solution in nitric acid may be dispensed with. The copper oxide can be at once extracted from it with caustic ammonia; however, the litharge and ammonia must then be allowed to work at least twenty-four hours on each other, with very diligent stirring, and, moreover, the litharge must be ground very fine.

The ammoniacal solution obtained from the assay is now well stirred, so that it may mix with perfect uniformity with the last washings; then, either the whole, or a part of it, is placed in a clean assay glass, and compared with the standard fluids in similarly formed glass vessels standing on a sheet of white paper. Should it correspond with none of them in the intensity of its colour, the whole of the fluid is diluted somewhat with water, until this is the case. Its volume is thereupon measured in the glass vessel graduated to ounces, &c., and noted. For a check, the dilution may be carried still farther till the colour of the assay corresponds to the next more faintly coloured standard fluid, and then the increased volume be measured anew. This might perhaps be still again repeated, but it becomes more and more uncertain. The calculation of the percentage of copper, from the intensity and the volume found, then presents no further difficulty.

Suppose that the assay fluid agrees with the normal solution of four loth of copper to the ounce of water, and its quantity amounts to five ounces, then the quantity of copper in the centner of the assay substance is 5 × 4 = 20 loth. This fluid further diluted till it equals the normal solution with three loth of copper, must measure six and two-third ounces if the obtained value of twenty loth is to be confirmed.

According to Heine's experiments, the possible error of observations in the comparisons and measurement described amounts as a maximum with the stronger normal solutions (with sixteen loth and over) to from three-quarters to one loth, with the weaker ones to scarcely half a loth of copper. In a centner of the assay substance, one loth of copper ·03 per cent. can still be determined with certainty.

Le Play determined in finely pulverised and carefully washed copper slags, the copper in one gramme of the poorest slags to within half a milligramme, and of the richest slags to within one milligramme, by using twenty-six standard fluids with various percentages of copper in cylindrical vessels. The comparison of colours in round vessels is more uncertain than in oblong ones, since in the former the light is dissipated and shadows are produced.

According to Mr. T. O. Cloud, the copper cannot be completely extracted from the finest ground slags, even after three days' digestion with aqua regia, and subsequent treatment with sulphuric acid. He recommends to fuse the slag with four parts of mixed potassium and sodium carbonates and $\frac{1}{4}$ part potassium nitrate. The fused mass is extracted with dilute sulphuric acid, the liquid evaporated down, and the copper determined galvanically or colorimetically.

As a delicate test for small quantities of copper, Dr. Endemann ('Annalen der Chemie') adds to the dilute solution concentrated hydrobromic acid, when a dark brownish-red or violet colour is at once produced.

This reaction is so delicate that $\frac{1}{100}$ milligramme of copper can be detected with certainty. One drop of a solution containing this small quantity of copper is brought on a watch-glass, then one drop of hydrobromic acid is added, and the solution is then allowed to evaporate slowly by standing the glass on a warm place. When the whole has been concentrated to about one drop, this will distinctly show a rose-red colour. The colour thus produced is about three or four times as distinct as the one which is obtained by the addition of potassium ferrocyanide. Of other metals which are examined in this direction, we find only iron to be apt to interfere with this reaction, and then only when it is present in considerable quantity.

We think that this reaction may also be utilised as a colorimetric test for the quantitative determination of small quantities of copper.

If a substance contains so little copper that the fluid does not equal the most faintly coloured standard fluid in intensity of colour, the assayer must endeavour to remedy the matter by *evaporating* till this is the case. An evaporation is, however, avoided, if possible, first because of the loss of time, and also because other precipitations, carbonate of lime, &c., are apt to be caused by it, and because, when it has to be continued too long, so much ammonia is apt to be volatilised, that a new addition of it becomes necessary.

This method of assaying soon finds the limits of its accuracy in an increasing percentage of copper in the assay sample, since with fluids rich in copper and therefore strongly coloured blue, the errors of observation soon amount to several loth. And to seek then to better oneself by diluting largely, yields no more accurate results, since a small error of observation in determining the intensity of the colour, is so much the more multiplied in the calculation of the value by the greater number of the ounces.

If *nickel* is contained in the assay substance, the assay cannot be conducted in the way prescribed, since the nickel is extracted by the acids, and dissolves also in caustic ammonia with a blue colour. The assay may also become uncertain from the presence of much *manganese*, *cobalt*, or *chromium*, since they render the hue of the blue colour dingy. *Chromium* may be completely removed by a slight boiling of the ammoniacal fluid; not so cobalt. The presence of *vanadium* or *molybdenum* does no harm.

If *nickel*, or much *cobalt* and *manganese*, is contained in the assay substance, the solution obtained by acids and filtered, though not further diluted, must first be decomposed by metallic iron. What is thrown down by the iron is collected on a small filter, washed thoroughly, and then, together with the filter, treated with dilute nitric acid. When the copper is all dissolved, this solution is supersaturated with caustic ammonia and then managed as above. With higher percentages of copper the process of the Swedish copper assay is used for determining the value. The precipitation of the copper may also be performed with sulphuretted hydrogen gas.

Le Play removes the injurious influence of manganese, nickel, and cobalt, by allowing the green or violet-coloured ammoniacal solution to stand open to the air for several weeks in a moderately warmed drying furnace, whereby a few variously coloured gelatinous flocks are gradually deposited, and the fluid, after the addition of a few drops of ammonia, then becomes pure blue.

According to Jacquelain and Von Hubert, nickel and cobalt are in a simple way rendered perfectly harmless by gradually adding white pulverised marble to the solution of the assay substance, until the effervescence ceases, and then warming the whole on the sand-bath, whereby all the copper is perfectly precipitated as carbonate, while nickel and cobalt remain dissolved. It is now filtered, washed, the residue dissolved in nitric acid, and the solution treated, as already explained, with ammonia. By the addition of potassium carbonate to the ammoniacal fluid, and heating, all the manganese precipitates, while the copper remains dissolved in the excess of ammonia, and can be separated from the manganese precipitate by filtration. The manganese must have been present as oxide in the original solution in order that the precipitation by potassium carbonate may be perfect.

The assayer may convince himself whether *nickel* or *cobalt* is present, by slightly supersaturating a blue ammoniacal solution, obtained by the ordinary process of assaying, with hydrochloric or sulphuric acid, then precipitating the copper *completely* with iron, filtering the residual solution, concentrating somewhat, if necessary, and then supersaturating with ammonia. If the fluid remains colourless, neither of the two metals is present: a blue colour indicates nickel, a red one cobalt.

Sometimes the normal solutions which when freshly prepared appear azure blue, assume a greenish hue, which renders the comparison difficult, if not impossible. Copper nitrate produces with ammonia a pure azure blue, copper sulphate a lilac colour, and copper chloride greenish hues. Sulphuric and hydrochloric acid are therefore to be avoided as much as possible in the solution. But, nevertheless, an assay fluid may sometimes—*e.g.* by standing some time in the air, or by slow filtration—become green, in which case the colour is destroyed by a few drops of nitric acid, and ammonia added anew. But sometimes also the greenish colour disappears, if the solution stands in a covered vessel in the air, or by the addition of a few drops of red cobalt ammonio-oxide.

According to Müller, also, the colour stands in the closest connection with the quantity of ammonia employed, and it therefore leads to greater accuracy in the assay if a titrated solution of ammonia is used, and the volume of the ammoniacal fluid noted, which, after neutralisation of the residual free acid, is used for the solution of copper. The solution appears more intense when viewed with a grey background than with a white one. A greenish blue colouring becomes the more noticeable the greater is the excess of ammonia, or the more ammoniacal salts are in the solution.

Dr. T. Carnelly (Manchester Philosophical Society), gives the following colorimetric method for determining small quantities of copper :—

The method of analysis consists in the comparison of the purple-brown colours produced by adding to a solution of potassium ferrocyanide—first, a solution of copper of known strength, and secondly, the solution in which the copper is to be determined.

The solution and materials required are as follows:—

(1) *Standard Copper Solution.*—Prepared by dissolving 0·393 grm. of pure $CuSO_4,5H_2O$ in one litre of water, 1 c.c. is then equivalent to 0·1mgrm. Cu.

(2) *Solution of Ammonium Nitrate.*—Made by dissolving 100 grms. of the salt in one litre of water.

(3) *Potassium Ferrocyanide Solution.* — Containing one part of the salt in 25 parts of water.

(4) *Two glass cylinders*, holding rather more than 150 c.c. each, the point equivalent to that volume being marked on the glass. They must, of course, both be of the same tint and as nearly colourless as possible.

(5) *A burette*, marked $\frac{1}{10}$ c.c., for the copper solution, a 5 c.c. pipette for the ammonium nitrate, and a small tube to deliver the potassium ferrocyanide in drops.

The following is the method of analysis:—Five drops of the potassium ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined into one of them (A), and both filled up to the mark with distilled water, 5 c.c. of the ammonium nitrate solution added to each, and then the standard copper solution runs gradually into (B), till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of cubic centimètres used are then read off. Each cubic centimètre corresponds to 0·1 mgrm. of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be estimated must be neutral, for if it contains free acid the latter lessens the depth of colour, and changes it from a purple-brown to an earthy brown. If it should be acid it is rendered slightly alkaline with ammonia, and the excess got rid of by boiling. The solution must not be alkaline, as the brown coloration is soluble in ammonia and decomposed by potash; if it is alkaline from ammonia this is remedied as before by boiling it off, while free potash, should it be present, is neutralised by an acid and the latter by ammonia.

Lead when present in not too large quantity has little or no effect on the accuracy of the method. The precipitate obtained on adding potassium ferrocyanide to a lead salt is white, and this, except when present in comparatively large quantity with respect to the copper, does not interfere with the comparison of the colours.

When copper is to be estimated in a solution containing iron the following is the method of procedure to be adopted. To the solution a few drops of nitric acid are added in order to oxidise the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present this can be done easily and completely if there is only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid, and reprecipitated by ammonia, filtered, and washed. The iron precipitate is now free from copper, and in it the iron can be estimated by dissolving in nitric acid, making the solution nearly neutral with ammonia, and determining the iron by the method given in the paper before referred to. The filtrate from the iron precipitate is boiled till all the ammonia is completely driven off, and the copper estimated in the solution so obtained as already described.

2. Jacquelain's and Von Hubert's Colorimetric Assays.

Heine's method, for the reasons stated, is suitable only for the determination of small quantities of copper. Jacquelain has extended it to the examination of all cupriferous substances, and this process has been further perfected by Von Hubert. According to the latter, a solution of any cupriferous accurately weighed substance is prepared, mixed with ammonia in excess, the ammoniacal solution (assay solution) measured at a definite volume, and a small, likewise measured portion of the measured solution diluted with water, until its blue colour shows an equal intensity with the blue colour of another solution (normal solution), also cupriferous and ammoniacal, whose copper contents are known once for all. Then, from the quantity of water added, in order to make the two fluids equal to each other in the intensity of their blue colours, the amount of copper in the substance under examination can be determined by calculation.

The normal solution is prepared by dissolving ·5 of a gramme of chemically pure copper in dilute nitric acid, adding ammonia in excess, and diluting with distilled water until the whole at 12° C. amounts to one litre=1000 cubic centimètres. The solution is filtered, and preserved in a flask provided with a glass stopper ground in to fit it.

For the preparation of the assay fluid, with substances whose percentage of copper ranges from 1·5 to the highest per cent., two grammes, and with the poorer substances five grammes, are brought into ammoniacal solution with the precautions specified in Heine's assay. This solution, with over 5 per cent. of copper, is measured at two hundred cubic centimètres, with 2 to 5 per cent. of copper at one hundred and fifty cubic centimètres, and with 2 per cent. and under, at one hundred; and also, as may be required, at 90, 80, 60, 50 c.c., according to the intensity of the fluid. Only with an extremely small quantity of copper is the assay fluid evaporated to a smaller volume, in order to be able to conduct the colorimetric test with accuracy.

The comparison of the intensity of colour of the assay fluid with the normal fluid is accomplished in two different ways, according as the former, when measured at a definite volume, is darker or lighter than the latter. This can be seen if a small arbitrary portion of each is poured into a glass tube of nine millimètres interior diameter, twelve centimètres in length, and uniform thickness, and the two tubes are held in parallel positions over a piece of white paper so that they rest firmly on it, and are inclined to it at an angle of about 45°, and direct light falls upon them. Shadow should not fall upon the tubes.

(*a*). *The Assay Fluid is Darker than the Normal*

Solution.—By means of a pipette, five cubic centimètres of the normal solution are placed in a glass tube closed at the bottom and not graduated, and seven millimètres in interior diameter and twelve centimètres long. Since 1000 c.c. of the normal solution contain ·5 of a gramme of copper, five cubic centimètres contain exactly ·0025 and the ratio 5 : ·0025 expresses once for all the known proportion of copper in the normal solution.

Five cubic centimètres of the definitely measured assay fluid are now also placed in a beaker and gradually diluted with water till they show the same intensity of colour as the normal solution. In the comparison the assay fluid must be in a similar tube to that containing the normal solution. With richer proportions a greater accuracy is attained in this comparison if the assay fluid is so far diluted that its intensity still appears as little as possible darker than that of the normal solution, and then water added carefully, and drop by drop, till its intensity is judged as little as possible lighter than that of the normal solution, whereupon the mean of the two volumes noted is taken as the correct value. The measuring of the diluted assay fluid is performed in glass tubes of nine millimètres interior diameter and fifty centimètres in length, which from their lower closed end to the circular mark designated by 0, hold exactly five cubic centimètres, and from 0 upwards are divided into cubic centimètres and tenths.

If, for example, two grammes of the assay substance have been weighed out, the assay fluid measured at 200 cubic centimètres, and five cubic centimètres of it diluted to 8·2 cubic centimètres, in order to obtain an equal intensity of colour between the normal and assay fluid, then the percentage of copper, x, follows from this according to the following chain of ratios :—

x	100 per cent.
2	200 c.c. assay fluid.
5	8·2 c.c. diluted assay = normal solution.
5	·0025 gramme of copper in normal solution.

x = 8·2 per cent. of copper.

(*b*). *The Assay Fluid is Lighter than the Normal Solution.* In this case five cubic centimètres of the normal solution are diluted till their intensity is equal to that of the assay solution that has been measured at a definite volume, and for the comparison larger tubes of nine millimètres' interior diameter are used.

If, for example, two grammes of the assay substance have been weighed out, 150 cubic centimètres of assay fluid obtained from it, and to get the same intensity of colour, five cubic centimètres of the normal solution diluted to 8·4 cubic centimètres, the quantity of copper x amounts, according to the following chain of ratios, to 2·205 per cent.:—

x	100 per cent.
2	150 c.c. assay solution.
8·4	5 c.c. normal solution.
5	·0025 gramme of copper.
x = 16·8	37·5 = 2·205 per cent.

This assay is adapted for all cupriferous substances, since nickel, cobalt, and manganese, which would influence the result unfavourably, can be removed without particular difficulty. It is also easy to be learned by those less practised in analytical operations, can be completed in a few hours, and is far less expensive than the dry assay. From two to one-tenth per cent. of copper can also be determined by it with accuracy.

Heine, however, prefers his method when a small percentage of copper is to be determined, since by it even one loth of copper in the centner = ·03 per cent., can be determined, and there is less liability to error. While in slag assays with nine to eighteen loth of copper in the centner, by Heine's method, errors of half a loth are not to be avoided, variations of more than one loth occur by Von Hubert's process. The latter works with a too deeply coloured normal fluid, corresponding to a solution of over fourteen loth of copper to one ounce of water, while Heine does not exceed four loth. The process is surer if the fluids are diluted and thicker layers of them compared, and thus the hue made artificially deeper, than if small quantities of stronger fluids are compared and the hue made artificially lighter by comparing them in thinner layers, or especially in tubes, where the light is dispersed and shade produced. The comparison in oblong glasses is therefore to be preferred to that in tubes.

By a comparison of Von Hubert's assay with that of the Oberhartz, it appears that, as Von Hubert's experiments themselves have shown, both give equally accurate results for substances not too poor in copper (*i.e.* containing not less than 5 per cent.). The Oberhartz assay allows a direct determination of the copper, requires less apparatus, is also very simple, and can be completed in a shorter time. Since different individuals are differently susceptible to colours, and the blue colour of the copper ammonio-oxide, in consequence of causes yet unknown, sometimes inclines more or less to greenish, and thereby renders observation difficult, therefore, for the sake of greater certainty, though not of greater accuracy, those assays by which a determination of the copper is possible by weight should in general be preferred to the colorimetric methods, and this is the case with the Oberhartz assay down to two per cent. With smaller percentages the colorimetric assay must be called to our aid. It is not yet settled that with higher percentages of copper the principle of colorimetry is a correct one; that is, that the intensity of the colour is directly proportional to the quantity of the colouring agent.

Since ammoniacal solutions poor in copper often show a dash of green colour, Von Hubert prepares a normal solution for such by dissolving one decigramme of copper and diluting to one litre of fluid.

b. Volumetric Copper Assays.

FLECK'S MODIFICATION OF MOHR'S METHOD.*

The proposal to take the action of solution of potassium cyanide on ammoniacal solution of copper, as the

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* This process is given by Fresenius, condensed from the 'Polytechn. Centralbl.' 1856, 1313.

foundation of a method for estimating copper, is due to Carl Mohr.[*]

The azure blue colour disappears, Cu_2Cy,NH_4Cy and KO are formed, while 1 eq. of cyanogen is separated, which, acting on the free ammonia, gives urea, urea oxalate, ammonium cyanide, and ammonium formiate (Liebig).[†]

The decomposition is not always the same: the quantity and degree of concentration of the ammonia have a marked influence on it, from which it appears that neutral ammonium salts also affect the results.

In carrying out this estimation according to the directions of Mr. Parkes, a solution of potassium cyanide is slowly added to a blue ammoniacal solution of copper, when the latter gradually loses its colour, and finally becomes quite colourless; upon this chemical reaction the estimation of copper by cyanide of potassium depends. By ascertaining by direct experiment the amount of potassium cyanide solution required to discharge the colour in an ammoniacal solution containing a given weight of copper, it is easy by a comparative experiment to determine the amount of copper in a given weight of ore.

For the preparation of the standard solution 2,000 grains of fused potassium cyanide are to be dissolved in two quarts of water, to produce a solution of which 1,000 grains measure will be equal to about ten grains of metallic copper. The solution should be preserved in green glass stoppered bottles, and kept as much as possible away from the light: it is liable to a slow decomposition, which will necessitate the standard being checked at intervals of one or two weeks. In order to standardise the solution, a burette, holding 1,000 grains measure, is filled to the zero mark, and a piece of pure electrotype copper, previously cleaned by means of dilute nitric acid, washed and dried, is accurately weighed. About eight grains may be conveniently taken; this is dissolved in a pint flask by dilute nitric acid, and, after the energy of the first action has sub-

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[*] Annal. d. Chem. u. Pharm. 94, 198; Fr. Mohr's Lehrbuch der Titriermethode, 2, 91.

[†] Annal. d. Chem. u. Pharm. 95, 118.

sided, the solution is warmed and ultimately boiled to expel all the nitrous acid fumes. It is diluted with cold water to the bulk of nearly half-a-pint, treated with ammonia in excess, and to the deep blue solution the cyanide is added from the burette until the colour is so nearly discharged that a faint lilac tint only remains. This will generally become quite bleached on standing at rest for a short time, so that the cyanide must not be added too hastily towards the end of the operation. It will be advisable to control the standard by a second experiment upon another weighed portion of copper, and to stop short of bleaching entirely the faint lilac tint of the solution. A piece of white paper folded and placed under and behind the flask during the decolorisation, will aid in recognising the proper tint of the solution.

In applying this process to the examination of copper ores, a known weight of the finely-powdered sample is introduced into a beaker provided with a glass cover, and moistened with strong sulphuric acid; strong nitric acid is then added, and the whole digested on a sand-bath until nitrous fumes are no longer given off. Should a small quantity of sulphur be separated in the treatment of pyritic ores, the small globules may be taken out, burnt, and the residual copper dissolved in a few drops of nitric acid and mixed with the remainder. Water is now to be added and left in contact for a short time to extract all the metallic salt from the insoluble residue, which need not be filtered off; and so, likewise, when ammonia is added in the next place, any ferric oxide which may thus be precipitated is left in the solution, for it is apt to contain a small proportion of copper when first thrown down; but this is entirely removed by the potassium cyanide later in the experiment.

When the ore contains much iron it is considered desirable to remove the hydrated peroxide by filtration, in order to be enabled to determine with greater precision the last effects of the potassium cyanide; and in the event of requiring to know the amount of iron present in the ore, the precipitated ferric oxide on the filter is redissolved in dilute sulphuric acid, reduced to the state of ferrous oxide by metallic zinc, and then tested in the usual way with a standard solution of potassium bichromate.

The metals which interfere with this mode of valuing copper ores, are silver, nickel, cobalt, and zinc. The first may readily be separated by adding a few drops of hydrochloric acid to the original solution: the other metals may be excluded by following one of the methods pointed out by the author for that purpose.

Fleck proposes the following modification in this process:—

Instead of caustic ammonia, use a solution of ammonium sesquicarbonate (1 in 10), warm the mixture to about 60°, and in order to render the end reaction plainer, add 2 drops of solution of potassium ferrocyanide (1 in 20): the blue colour of the solution is not altered by this addition, nor is its clearness affected. The value of the potassium cyanide solution is first determined by means of copper solution of known strength, and it is then employed on the copper solution to be examined. On dropping the potassium cyanide into the blue solution warmed to 60°, the odour of cyanogen is plainly perceptible, and the colour gradually disappears. As soon as the ammoniacal double salt of copper is destroyed, the solution becomes red from the formation of copper ferrocyanide, without any precipitate appearing, and with the addition of a final drop of potassium cyanide this red colour in its turn vanishes, so that the fluid now appears quite colourless.

The method thus modified yields, it is true, better, but still only approximate results.* Where such are good enough, the method is certainly convenient.

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* In six experiments, in which he had purposely added different quantities of carbonate of ammonia, Fleck used for 100 c.c. copper solution, in the minimum 15·2, in the maximum 15·75, in the mean 15·46 c.c. potassium cyanide solution.

E. O. Brown's Method by Sodium Hyposulphite.

The process described by Mr. E. O. Brown is particularly applicable to the determination of copper in gun-metal, brass, and other alloys which contain no large amounts of iron and lead. It is founded on the reactions between salts of copper and the neutral iodides, and on the conversion of the liberated iodine into hydriodic and tetrathionic acids by a standard solution of sodium hyposulphite.

These reactions may be thus expressed:—

$$2(CuO,\bar{A}) + 2KI = Cu_2I + I + 2(KO,\bar{A})$$
$$I + 2(NaO,S_2O_2) = NaI + NaO,S_4O_5$$

The completion of the second reaction is manifested by the bleaching effect produced upon the blue iodide of starch by the addition of the hyposulphite. A convenient strength of solution for this purpose may be made by dissolving 1,300 grains of the crystallised salt in two quarts of water. The potassium iodide must be free from iodate; and a clear solution of starch employed.

From eight to ten grains of the copper or alloy are dissolved in dilute nitric acid, and the red nitrous fumes expelled by boiling. The copper nitrate is converted into acetate by adding sodium carbonate until a portion of copper remains precipitated, and then re-dissolving in acetic acid. The solution is diluted with water, and about 60 grains of potassium iodide in the form of crystals dropped into the flask, and allowed to dissolve. The standard solution of sodium hyposulphite is now poured in from a burette, until the greater part of the dark-coloured free iodine disappears. A little of the starch solution is now added to make its presence more apparent, and the addition of the hyposulphite continued until the bleaching is completed, when the pale yellow colour of the copper subiodide will alone be visible. The amount of copper in the ore or alloy is calculated from the number of divisions indicated upon the burette.

Copper ores containing much iron (which interferes by reason of the dark red colour of the acetate) may be dissolved in nitric acid, and treated with sulphuretted hydrogen to precipitate the copper, the sulphide being collected on a filter, washed, and re-dissolved in nitric acid to produce a solution suitable for testing by this process. Or the hyposulphite may itself be employed to furnish a precipitate of copper disulphide.

Dr. Wolcott Gibbs recommends the electrolytic precipitation of copper and nickel as a method of analysis. He says :

The precipitation of copper by zinc, in a platinum vessel, with the precautions recommended by Fresenius, leaves nothing to be desired, so far as accuracy, ease, and rapidity of execution are concerned. The method labours, however, under a single disadvantage—the introduction of zinc renders it difficult, or at least inconvenient, to determine with accuracy other elements which may be present with the copper. It has occurred to me that this difficulty might be overcome, the principle of the method being still retained, by precipitating the copper by electrolysis with a separate rheomotor. The following numerical results, which are due to Mr. E. V. M'Candless, will satisfactorily show the advantages of the method for the particular cases in which it is desirable to employ it. The copper was in each case in the form of sulphate : the deposition took place in a small platinum capsule, which was made to form the negative electrode of a Bunsen's battery of one or two cells, in rather feeble action. The positive electrode consisted of a stout platinum wire, plunged into the surface of the solution of copper at its centre. The following table gives the results obtained in the analysis of pure copper sulphate :—

Number	Salt taken	Copper found	Percentage
1	1·2375	0·3145	25·41
2	0·4235	0·1075	25·38
3	1·0640	0·2705	25·42
4	1·3580	0·3440	25·33
5	0·5665	0·1450	25·59
6	0·4735	0·1205	25·48

In seven determinations of copper in the alloy of copper and nickel employed by the Government for small coins the following results were obtained :—

Number	Weight of Alloy	Copper	Percentage
1	0·4160	0·3640	87·50
2	0·6180	0·5410	87·54
3	0·4600	0·4090	88·91
4	0·5120	0·4481	87·51
5	0·4220	0·3693	87·51
6	0·2525	0·2225	88·11
7	0·3705	0·3255	87·85

The percentage of copper required by the formula $CuO,SO_3\ 5H_2O$ is 25·42, while the Government standard alloy of nickel and copper contains 87·50 per cent. of copper. The time required for precipitation varied from one to three hours, the separation of the last traces of copper being in each case determined by testing a drop of the liquid upon a porcelain plate with sulphuretted hydrogen water. The copper after precipitation was washed with distilled water, dried *in vacuo* over sulphuric acid, and weighed with the platinum vessel. The only precaution necessary is to regulate the strength of the current so that the copper may be precipitated as a compact and bright metallic coating, and to dry as quickly as possible. When the copper is thrown down in a spongy condition, it not only oxidises rapidly, but it is impossible to wash out the last traces of foreign matter contained in the solution. This is well shown by No. 3 and No. 4 of the second series, in both of which cases the copper was precipitated too rapidly. The solution from which the copper has been deposited contains the other elements present in the original substance. It may be easily poured off without loss, and the washings added.

Mr. J. M. Merrick has communicated to the 'Chemical News' a simple and accurate process of assaying copper in pyrites based on this method. Treat the pyrites with nitric acid to complete oxidation of the sulphur, evaporate to dryness, and ignite gently; then treat with a small amount of boiling water, and sufficient ammonia to precipitate and re-dissolve the copper. Filter the blue solution from the silica, iron oxide, &c., wash the filter, concentrate the washings if need be, make the filtrate sharply acid with sulphuric acid, and plate out the copper on the inside of a platinum dish which is made the cathode of a battery of the two small Grove's cells, the anode being a stout platinum wire hung in the solution. For a tolerably close result—generally sufficient in technical work—the solution in ammonia may be omitted, and the copper directly plated over from the solution filtered from the silica, &c. For the exact determination of very minute quantities of copper no method can approach it.

The nickel may be determined by electrolysis in the same manner as copper, the solution employed being the sulphate rendered ammoniacal with excess of free ammonia. Mr. M'Candless obtained in two determinations in a commercial sample 91·36 and 91·60 per cent. of nickel. In both cases the nickel was thrown down completely as a bright, coherent, metallic coating upon the platinum.

Assay of Copper Pyrites.—The following method of treating copper pyrites has been found more advantageous than the ordinary process of oxidising the mineral with aqua regia, and subsequently evaporating the solution repeatedly with hydrochloric acid, or with sulphuric acid, to expel the last traces of nitric acid. It is thus described by Mr. F. P. Pearson in the 'Chemical News':—

Place a weighed quantity of the powdered mineral, together with some potassium chlorate, in a porcelain dish. (Five grammes of a variety of a pyrites containing about 18 per cent. of copper was found to be enough for one analysis; and a quantity of potassium chlorate equal to a small teaspoonful was added to the ore.) Invert a small glass funnel with bent stem in the dish above the pyrites, and pour upon the latter rather more ordinary strong nitric acid than would be sufficient to completely cover the powder. Place the dish upon a water-bath, and, from time to time, throw into it small quantities of potassium chlorate. The doses of the chlorate must be repeated at frequent intervals, until free sulphur can no longer be seen in the dish. If need be, add nitric acid, also, from time to time, to replace that lost by evaporation.

As a general rule, it is safer and more convenient to heat the mixture on a water-bath than upon sand, though the oxidation of sulphur can be effected more easily and quickly when the mixture of nitric acid and chlorate is heated to actual boiling than at the temperature obtainable by means of a water-bath. When the last particles of sulphur have been destroyed, remove the inverted funnel from the dish, rinse it with water, and collect the rinsings in a beaker by themselves. Allow the liquid in the evaporating-dish to become cold, pour upon it a quantity of ordinary strong hydrochloric acid rather larger than the quantity of nitric acid taken at first, evaporate the mixed solution to dryness, and heat the dry residue to render silica insoluble, in case any silica be present.

Pour water upon the cold residue, and, without filtering the liquor, wash the contents of the dish into the beaker which contains the rinsings of the funnel. Heat the liquid in the beaker nearly to boiling, add to it about 25 c.c. of a strong aqueous solution of ferrous sulphate slightly acidulated with sulphuric acid, and keep the mixture at a temperature near boiling during four or five minutes, in order to destroy the small quantity of nitric acid which may have escaped decomposition in spite of the dry evaporation with hydrochloric acid.

The ferrous salt seldom acts instantaneously, but the reducing action proceeds rapidly and satisfactorily when once begun. If need be, add more of the ferrous solution, little by little, until the entire contents of the beaker become dark-coloured or black, and no more gas is disengaged.

In order to be sure that all the nitric acid has been reduced, it is as well, after the mixture of liquid and solution of ferrous sulphate has been duly heated, to place a drop of the mixture upon porcelain, and test it with potassium ferrocyanide. In general, however, the coloration of the liquid in the beaker, due to the formation of nitrous or hyponitric acid, will be a sufficient indication that the sulphate of iron has done its work. The nitrous fumes quickly disappear from the liquid at a subsequent stage of operations when metallic iron is immersed in the solution.

When enough of the ferrous sulphate has been added, filter the mixed solution into a wide beaker, precipitate the copper in the metallic state upon a sheet of iron in the usual way, and ignite the copper in a porcelain crucible, in a current of hydrogen, before weighing it.

By means of the ferrous salt, the last traces of nitric acid may be got rid of far more quickly, conveniently, and certainly than by the old system of evaporating the pyrites solution with several successive portions of hydrochloric acid. By treating the pyrites with potassium chlorate and nitric acid, it is easy to oxidise and dissolve every particle of the sulphur in the mineral, so that no portion of the latter can escape decomposition by becoming enveloped in free sulphur. When aqua regia is used, on the other hand, or a mixture of potassium chlorate and hydrochloric acid, a certain proportion of sulphur almost invariably remains undissolved, and might easily enclose portions of the mineral, so as to protect them from the solvent action of the acids.

For the Determination of Copper and Sulphur in Copper Pyrites, R. Fresenius (‘Zeitschrift für Anal. Chemie,’ 1877, p. 355), proceeds as follows :—

‘After drying at 100° C., and carefully preparing the sample, he takes for the determination of the copper 5 grm. pyrites, heats with 6 to 7 c.c. hydrochloric acid (sp. gr. 1·17), adding gradually nitric acid of sp. gr. 1·37, till no more action ensues, and digests then for some hours at a gentle heat. The contents of the flask are poured into a porcelain capsule, the flask is twice rinsed out with 10 c.c. hydrochloric acid (sp. gr. 1·12) into the capsule, and is then set aside. The contents of the capsule are then evaporated almost to dryness on the water-bath, 20 c.c. hydrochloric acid of sp. gr. 1·12 are added, heated, mixed with water, and filtered into a boiling-flask holding 500 c.c. The solution-flask is also rinsed upon the filter with water. The filter is dried, incinerated in a porcelain crucible, and the residue (in part lead sulphate) is treated with 1 c.c. aqua regia, evaporated to dryness, the residue treated with 5 c.c. hydrochloric acid (1·12 sp. gr.) slightly diluted, and the solution, which may contain a little copper, is filtered into the main solution. The solution is then precipitated with sulphuretted hydrogen at 70° C., the precipitate is filtered, washed, dried, mixed with the thoroughly burnt ash of the filter, heated with 5 c.c. nitric acid (of sp. gr. 1·2), filtered and washed. The filter is incinerated, the small residue is again heated with 2 c.c. of the same nitric acid, diluted, filtered to the main solution and washed. The solution is mixed with 12 c.c. dilute sulphuric acid (1 part acid to 5 water) evaporated to expel nitric acid, filtered to remove lead sulphate, washing with water acidulated with sulphuric acid. The copper is then precipitated with sulphuretted hydrogen at 70° C., the precipitate washed, dried, ignited along with the ash of the filter in a current of hydrogen, and weighed as copper sulphide.

'For the determination of sulphur the author fuses ½ grm. of the sample with 10 parts of a mixture of 2 parts sodium carbonate and 1 part potassium nitrate, and determines the sulphuric acid formed. For burnt ores he uses 4 parts sodium carbonate to 1 part of potassium nitrate.'

Estimation of Copper in the Mansfeld Ores by Dr. Steinbeck's Process.—This method embraces three distinct operations, viz. :—1. The extraction of the copper from the ore; 2. The separation; 3. The quantitative estimation of that metal.

1. *The Extraction of the Copper from the Ore.*—A proof centner, equal to 5 grammes of pulverised ore, is put into a flask, and there is poured over it a quantity of from 40 to 50 c.c. of crude hydrochloric acid, of a specific gravity of 1·16, whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After awhile, there is added

to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a well-arranged sand-bath for half an hour, and the contents only boiled for about fifteen minutes, after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or at the most only 0·01 to 0·03 per cent. has been left undissolved.

The extraction of the copper from the ore, according to this method, is complete even in the case of the best quality of ore, which contains about 14 per cent. of metal; while, at the same time, the very essential condition for the proper and complete separation of the metal, viz., the entire absence of nitric acid, or any of the lower degrees of oxidation of nitrogen, is fully complied with.

2. *Separation of the Copper.*—The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker of about 400 c.c. capacity; in this beaker has been previously placed a rod of metallic zinc, weighing about 50 grammes, and fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is—owing chiefly to the complete absence of nitric acid—completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace even of copper will be detected; the

spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must be always employed) has been removed, the spongy metal is repeatedly and carefully washed by decantation with fresh water, which need not be distilled, and care is taken to collect together every particle of the spongy mass.

3. *Quantitative Estimation of the Precipitated Copper.*— To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper is dissolved, by the aid of moderate heat, as copper nitrate; in the event of any small quantity of lead being present, it will of course be contaminated with lead nitrate.

When copper ores are dealt with which contain above 6 per cent. of copper, which may be sufficiently judged from the larger bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are employed for dissolving the spongy metallic mass. The solution thus obtained is left to cool, and next, immediately before titration with potassium cyanide, mixed with 10 c.c. of normal solution of ammonia, prepared by diluting 1 volume of liquid ammonia, sp. gr. 0·93, with 2 volumes of distilled water.

In the case of ores which yield over 6 per cent. of copper, and when a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then divided exactly into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue-coloured solution of oxide of copper in ammonia only contains, besides ammonium nitrate, any lead which might have been dissolved having been precipitated as hydrated lead oxide, which does not interfere with the titration with potassium cyanide. The solution of the last-named salt is so arranged that 1 c.c. thereof exactly indicates 0·005 grm. of copper. Since, for every assay, 5 grms. of ore have been taken, 1 c.c. of the titration fluid is, according to the following proportion —5 : 0·005 :: 100 : 0·1—equal to 0·1 per cent. of copper; it hence follows that, by multiplying the number of the c.c. of potassium cyanide solution used to make the blue colour of the copper solution disappear, by 0·1, the percentage of copper contained in the ore is immediately indicated.

As may be imagined, at the laboratory of the mine-owners at Eisleben, such a large number of assays are daily executed that, in this case, there can be no reason to fear a deterioration of the cyanide solution, of which large quantities are used and often fresh made; but for security's sake the solutions are purposely tested for control at least once every week. According to the described plan, six assays can be made within 4 hours; and during a working day of from 7½ to 8 hours, twenty assays have been often quite satisfactorily made by the umpires, as well as by the workmen at Eisleben.

Special Observations on this Method.—Dr. Steinbeck considered it necessary to test this method specially, in order to see what influence is exercised thereupon by (1) ammonium nitrate, (2) caustic ammonia, (3) the presence of lead oxide. The copper used to perform the experiments for this purpose was pure metal, obtained by galvano-plastic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. Five grammes of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of normal nitric acid, the flask and contents gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1,000 c.c. exactly. Thirty c.c. of this solution were always applied to test and titrate one and the same solution of potassium cyanide under all circumstances. When 5 grammes of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·15 gramme of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 grammes of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of normal nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

As regards No. 1 and No. 2 (see above), the influence of double quantities of ammonium nitrate and free caustic ammonia (the quantity of copper remaining the same), and the action of dilute solution of potassium cyanide thereupon, will become elucidated by the following facts :—

a. Thirty c.c. of the normal solution of copper, containing exactly 0·15 gramme of copper, were rendered alkaline with 10 c.c. of normal ammonia, and are found to require, for entire decoloration, 29·8 c.c. of potassium cyanide solution ; a second experiment, again with 30 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average of the two experiments is 29·85 c.c.

b. When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia solution, instead of only 8, whereby the quantity of free ammonia and of ammonium nitrate is made double what it was in the case of the experiments spoken of under *a*, there is required of the same cyanide solution 30·3 c.c. to produce decoloration. A repetition of the experiment, under exactly the same conditions, gave 30·4 c.c. of the cyanide solution employed ; the average of both experiments is, therefore, 30·35 c.c.

The difference between 30·35 and 29·85 is equal to 0·5 c.c., and that figure is therefore the coefficient of the influence of double quantities ; and supposing this to happen with the ores in question, it would only be equivalent to 0·05 per cent. of metallic copper. It is hence clear that slight aberrations of from 0·1 to 0·5 c.c. in the measuring out of 8 c.c. of normal nitric acid, used to dissolve the spongy copper, and of 10 c.c. of normal ammonia, in order to render the nitric acid copper solution alkaline, are of no consequence whatever for the technical results to be deduced from the assay; it should, moreover, be borne in mind that the quantities of free ammonia and of ammonium nitrate in the actual assay of ores, for which always a quantity of 5 grammes of ore is taken, vary according to the richness or poverty of the ores in copper; and the quotation of the following results of experiments proves that the influence of these substances is only very slightly felt in the accuracy of the results:—

Eight c.c. of the normal nitric acid have been found to contain, by means of a series of experiments, 1·353 gramme of anhydrous nitric acid; and this quantity of acid is exactly neutralised by 7·7 c.c. of normal ammonia solution, which contains 0·6515 gramme of ammonium oxide; and 10 c.c. of the said normal solution contain 0·846 gramme of ammonium oxide.

One gramme of metallic copper requires, for complete oxidation, 0·2523 gramme of oxygen, and this quantity of oxygen is given off by 0·5676 gramme of anhydrous nitric acid; while, at the same time, binoxide of nitrogen is disengaged. From these data can be calculated (1) the quantity of nitric acid which becomes decomposed when variable quantities of metallic copper are dissolved therein; (2) what quantity of nitric acid is left to form neutral nitrate of ammonium; and (3) what quantity of free ammonia will be left after a portion of that alkali has been combined with, and therefore neutralised by, copper oxide; and any remaining free nitric acid.

It is found that the quantitative variations between ores containing 1 per cent. or 6 per cent. of metal vary very little from the normal quantities exhibited by ores containing 3 per cent. of metal. The relation is as 1 : 2; and, for technical purposes, this has been proved not to be a disturbing quantity.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of a titrated solution of potassium cyanide, and especially when ammonium carbonate, sulphate, and, worse still, chloride, are simultaneously present, these salts exert a very disturbing influence.

The presence of lead oxide in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia a milkiness along with the blue tint; but the presence of this oxide does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Dr. Steinbeck, however, purposely made some experiments to test this point, and his results show that neither 50 nor 100 per cent. of addition of lead exerts any perceptible influence upon the estimation of copper, from its ores or otherwise, by means of potassium cyanide. A small quantity of accidentally occurring lead will not, therefore, affect the results, and this the less so as, generally, no ores of both metals occur together wherein both are met in sufficient quantity to make it worth while working the ore for both metals at the same time.

Since it is well known that the presence of zinc very perceptibly influences the action of a solution of potassium cyanide, when applied to the volumetrical estimation of copper, Dr. Steinbeck considered it necessary to institute some experiments in order precisely to ascertain with what quantity of zinc present along with copper this influence commences to become perceptible. The solution of zinc applied was made by dissolving the metal in the smallest possible quantity of nitric acid; and 1 c.c. of that solution contained 0·001 gramme of zinc. The results of the experiments show that the presence of zinc does not interfere with the visibility of the end of the reaction, viz., the decoloration of the copper solution. They also prove that a small quantity of zinc, less than 5 per cent. of the quantity of copper present, or 0·0075 gramme by weight of zinc, does not at all affect the action of the solution of potassium cyanide; but when the quantity of zinc increases, a very perceptible effect is seen upon the solution of cyanide; it is therefore necessary to bestow due care while washing the spongy copper, after it has been precipitated by means of zinc from its solution.

Since it has been ascertained that the action of the solution of potassium cyanide in researches of this kind is also affected by an increased temperature of the solution of copper which is to be titrated, it is strictly necessary never to operate with warm ammoniacal solutions of copper, but to suffer the same to cool down to the ordinary temperature of the air of the laboratory.

While 30 c.c. of copper solution, containing 0·15 gramme of copper, and 10 c.c. of normal ammonia solution, required at the ordinary temperature 30 c.c. of cyanide solution, the same quantities required, at between 40° to 45° C., 28·8 c.c. of solution of cyanide; and at 45° C., 28·9 c.c. of the same solution, thus proving the injurious effect of warm solutions.

Estimation of Copper in the Mansfeld Ores by M. C Luckow's Process.—This gentleman has applied to the quantitative estimation of copper a new method, based upon the precipitation of the metal in the metallic state from solutions containing either free sulphuric or nitric acids, by means of a galvanic current.

It is a great advantage of this method, that, while the copper is precipitated, it is simultaneously separated from metals with which it is often found alloyed; some of these, such as tin and antimony, are separated by treatment with nitric acid in an insoluble form, while others, like silver, can easily be removed in the form of chloride. It is, at the same time, another advantage that the state in which the copper is obtained admits of its being accurately weighed and estimated, while a great number of operations, which require much time and various apparatus, are at the same time got rid of.

Although M. Luckow had previously discovered a method of electro-metallic analysis from fluids containing free sulphuric acid, his researches on the same subject, in the case of free nitric acid, belong to a recent period. These researches brought very unexpectedly to light the curious fact that even a weak galvanic current had the power of completely precipitating copper in a pure metallic state from nitric solutions, provided they did not contain more than 0·1 grm. of anhydrous nitric acid to the c.c. (nitric acid of 1·2 sp. gr. contains 0·32 grm. of anhydrous nitric acid to the c.c.); while it was found that the action was, at the same time, more regular, and less dependent upon the power of the current than when free sulphuric acid was present. The following more commonly occurring metals are *not* precipitated by galvanic action from acid solutions:—Zinc, iron, nickel, cobalt, chromium, the metals of the earths and alkalies. The following are precipitated (*a*) in the shape of peroxides, at the positive electrode: completely, lead and manganese; incompletely, silver. When the solution contains traces of manganese, it becomes, in consequence of the formation of a salt of manganese peroxide, or of permanganic acid, deeply violet-coloured. This very sensitive reaction for manganese also takes place when small quantities of chlorine are present. The presence in the fluid of oxalic, lactic, and tartaric acids, and other readily oxidisable organic substances, and such protoxides as are readily peroxidised —for instance, iron protoxide—retards the formation of peroxides, as well as the occurrence of the reaction of manganese.

(*b*) Mercury, silver, copper, and bismuth are precipitated at the negative electrode in a metallic state. When mercury is present in the solution simultaneously with copper, the former metal is separated before the latter, in the fluid metallic state. As soon, however, as the precipitation of copper commences, an amalgam of the two metals is formed, when mercury is also present. Silver is precipitated almost simultaneously with copper, bismuth only begins to be precipitated after the greater portion of the copper has been separated. A complete separation of silver only ensues when some such substance as tartaric or other similar acid is simultaneously present in the solution. The separation of the three last-named metals, by means of galvanic action, is, therefore, unsuccessful; but, fortunately, there are many other means to accomplish this end completely.

(*c*) Metallic arsenic is only precipitated slowly, and long after the complete separation of copper, if arsenic acid happen to be present. The same remark applies to antimony, since it is well known that small quantities of antimonic acid are soluble in nitric acid.

The operations, according to Luckow's plan, are—1. Roasting the ore; 2. Solution of the roasted product; 3. Precipitation of the copper; 4. Weighing the copper.

1. *Roasting the Ore.*—Care should be taken to obtain a finely-ground average sample of the ore. Then weigh off in small porcelain capsules, previously counterpoised, quantities of from 1 to 3 grms.; these quantities are then placed on the inverted lid of an iron crucible, on the inner surface of which the powdered ore is heated over the flame of a Bunsen gas-burner. The powder may be carefully stirred up with a platinum wire, to promote the access of air during the roasting; the ignition of bituminous matter and sulphur will be ended in about seven minutes. Ores which do not contain bitumen at all need not be roasted.

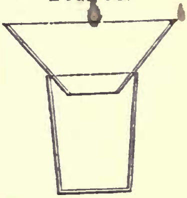
It has been already stated that in the case of poor copper ores (and those of the Mansfeld district are generally so), the quantities to be weighed off for assay should not vary according to a presumed percentage of copper. Two grms. are therefore taken, and, instead of roasting the ore on the lid of an iron crucible, small porcelain crucibles are used for that purpose.

2. *Solution of the Roasted Product.*—The iron lid is suffered to cool, the roasted powder placed on a piece of glazed paper, and any powder adhering to the lid is removed by means of a camel's-hair brush on to the paper. The powder is next transferred to small beaker glasses, and about 2 or 3 c.c. of nitric acid, of 1·2 specific gravity, are added, along with about 10 to 15 drops of concentrated sulphuric acid. The beakers are then placed on a sand-bath and moderately heated, at first; but when the contents have become nearly dry, the heat is increased, so as to evaporate and expel all sulphuric acid. The beakers

should be covered with perforated watch-glasses. This operation requires from about three-quarters of an hour to one hour. The addition of sulphuric acid is made in order to increase the oxidising action of the nitric acid, and also to convert any lime which may happen to be present in the ore into a difficultly soluble salt. It is very useful, also, to add from 10 to 20 drops of hydrochloric acid to the mixture of the two acids just alluded to, since the rapidity of the evaporation is thereby increased, and the occasional spirting about of the fluid is lessened.

The process just described may be modified, first, by the use of porcelain capsules, the contents of which are easily transferred to beakers with flat bottoms, and not higher than about 2 inches altogether. It is better, also, to use sulphuric acid, prepared with equal bulks of concentrated acid and water, and to measure off 4 c.c. for each assay; while for each assay, moreover, 6 c.c. of nitric acid and about 25 drops of hydrochloric acid are taken. Instead of covering the beaker with a perforated watch-glass, the upper part of a funnel is used, as represented in Fig. 93; with this arrangement the sulphuric acid evaporates far more readily, and loss by spirting is prevented. The beaker is heated on a well-arranged sand-bath.

FIG. 93.



3. *Precipitation of the Copper.*—As soon as the beaker after removal from the sand-bath has become quite cool, the funnel which has been used as a cover is washed on both sides, inner and outer, with nitric acid of 1·2 sp. gr., diluted with six times its bulk of pure water; the sides of the beaker are next likewise washed, and it is then filled to about half its height with the same acid. A few drops of a concentrated solution of tartaric acid are added (this acid is best kept in solution in open vessels, only slightly covered with a piece of paper); this having been done, the wire spiral, represented in Fig. 94, is carefully placed in the beaker. This spiral consists of a piece of platinum wire, about 1-12th of an inch thick, and 7½ inches long,

two-thirds of its length being so wound that the straight end of the wire projects as if it were the axis of the centre of the spiral. The convolutions of the spiral are so large that they touch the sides of the beaker, while the straight portion just touches the centre of the bottom of the vessel.

When the heating has been carefully attended to, the acid fluid added to the contents of the beaker, after evaporation to dryness, will generally be quite clear; if it happens to be turbid, 1 or 2 c.c. of a concentrated solution of barium nitrate may be added, and the thorough mixing of this saline solution with the acid contents of the beaker promoted by gently moving up and down the platinum spiral just alluded to, and allowing the fluid to rest for a few minutes after. The copper present in the mass left at the bottom of the beaker gradually dissolves, and it is not actually requisite to wait before applying the galvanic current until it is all dissolved.

FIG. 94.

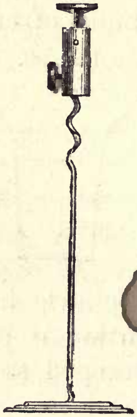


FIG. 95.

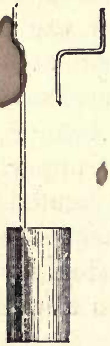
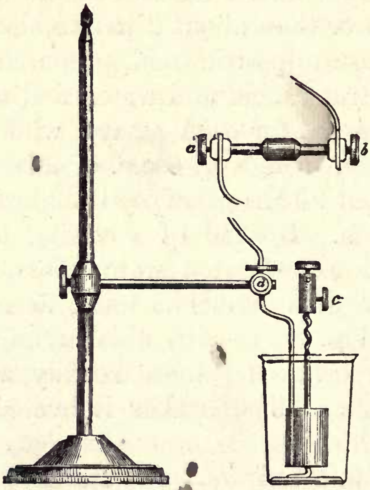


FIG. 96.



The next point is to place in the beaker the platinum foil, represented at Fig. 95, of which the dimensions are—length, $2\frac{1}{2}$ inches; width, $1\frac{1}{4}$ inch. The lower end of this platinum foil should be kept about 1-16th of an inch apart from the convolutions of the spiral. When the beaker is only half filled with liquid, the platinum foil is immersed in the same for more than three-fourths of its height. The wire fastened to this foil is fixed, by means of a screw, *a*, to the arm, *a*, *b*, of the stand, represented in Fig. 96; the other screw, *b*, serves to fasten a copper wire, proceeding from the zinc end of the galvanic battery. When the small screw clamp, *c* (Fig. 96), has been fastened to the platinum wire placed in the beaker, another wire is fastened in the top opening of the clamp, and this wire connected with the copper end of the battery, and the galvanic circuit thus closed. In a few moments after this has been done, the platinum foil, bent in the shape of the cylinder and placed inside the beaker, as before described, will be observed to become covered with a coating of metallic copper, while from the platinum wire spiral bubbles of gas escape, which facilitate, to some extent, the solution of the copper oxide in the dilute acid.

In order to ascertain whether the whole quantity of the copper has been precipitated, some more dilute nitric acid is added to the fluid in the beaker glass. If, in ten minutes after this, no more metallic copper is separated on the clean portions of the platinum foil, the operation is finished.

It must be here observed that continued practice has proved that the addition of a concentrated solution of barium nitrate acts injuriously on the process, as the metallic copper, which becomes separated, gets mixed with some insoluble barium sulphate, which increases the weight of the substance to be weighed.

The time occupied by the complete precipitation of the metal varies according to the force of the galvanic current. It takes from three to even eight hours. In order to make this point certain, all test assays are left, for eight hours consecutively, to the action of the galvanic current, experience having proved that, after that lapse of time, even with a weak current, the precipitation was so complete that all chemical reagents for detecting the presence of copper failed to discover the most minute trace of that metal.

4. *Weighing the Copper.*—The platinum cylinder to which the copper adheres, and the platinum wire spiral, are disconnected from the galvanic apparatus, the platinum cylinder carefully removed from the beaker and immediately plunged into a beaker filled with fresh cold water, and rinsed therein; next washed with alcohol, by means of a washing bottle, and then dried in a drying apparatus, and weighed after cooling. Since the platinum cylinder has been very accurately weighed *before* the experiment, its increase in weight will, of course, be that of the copper obtained.

The process here described has been somewhat modified and greatly improved upon at Eisleben, where it is in constant use, by the employment of a series of galvanic elements. It is, in the first place, found better not to disconnect the galvanic current while the copper is yet in contact with acid, so that, instead thereof, the acid fluid in the beaker is replaced by turning in a stream of water, and suffering the same to run over the sides of the beaker, and to be received into a proper vessel to hold it. In this manner all the acid is displaced, without risk of any very small quantity of copper becoming acted upon by the acid during the brief period elapsing between the disconnecting of the galvanic current and the removal from the beaker of the platinum cylinder and spiral wire. These parts, on being removed, are carefully washed, first with boiling water, next with alcohol, and then dried at a temperature of about the boiling point of water. The cylinder is then weighed, the copper coating is removed by means of nitric acid; the platinum is next washed in water, dried, and again weighed.

There are in use at Eisleben nine galvanic batteries (lead and zinc elements); these yield eighteen assays ready for weighing in twenty-four hours; and it would not be difficult for the person there employed to work with twelve batteries each of three elements. In place of the Meidinger elements, which do not remain constant for months, a thermo-electric apparatus has been introduced, with the best results. The results obtained are highly satisfactory.

The following observations may be made in reference to this method :—

(*a*) The quantity of ore taken for trial is 2 grammes ; this is found sufficient, while it consumes less acid.

(*b*) The evaporation of the acid is carried on to complete dryness on the sand-bath. Spirting of the fluid is easily prevented.

When the copper has been precipitated properly it will show its peculiar colour on the surface, and the good success of the operation may also be judged from the fact that no saline matter adheres to the platinum ; the complete absence of this saline matter has been found to be evidence of perfect removal of the copper from the fluid.

The process just described is especially applicable for rather poor ores, such as do not contain above 7 or 8 per cent. of copper. Each assay, from beginning to end, takes ten hours for complete analysis; but it is evident that the greater portion of this period does not give active employment to the assayer. The expense of working this process, after the apparatus has been once purchased, is very small. The process may also be applied to analyse richer ores, and also alloys of copper, with some slight modifications which will readily suggest themselves.

Professor Chapman, of Toronto, gives the following directions for the detection of minute traces of copper in iron pyrites and other bodies :—

Although an exceedingly small percentage of copper may be detected in blowpipe experiments by the reducing process as well as by the azure blue colouration of the flame, when the test matter is moistened with hydrochloric acid, these methods fail in certain extreme cases to give satisfactory results. It often happens that veins of iron pyrites lead at greater depths to copper pyrites. In this case, according to the experience of the writer, the iron pyrites will almost invariably hold minute traces of copper. Hence the desirability, on exploring expeditions more especially, of some ready test by which, without the necessity of employing acids or other bulky and difficultly portable reagents, these traces of copper may be detected.* The following simple method will be found to answer the purpose:—The test substance, in powder, must first be roasted on charcoal, or, better, on a fragment of porcelain,† in order to drive off the sulphur. A small portion of the roasted ore is then to be fused on platinum wire with phosphor-salt; and some potassium bisulphate is to be added to the glass (without this being removed from the wire) in two or three successive portions, or until the glass becomes more or less saturated. This effected, the bead is to be shaken off the platinum loop into a small capsule, and treated with boiling water, by which either the whole or the greater part will be dissolved; and the solution is finally to be tested with a small fragment of potassium ferrocyanide. If copper be present in more than traces, this reagent, it is well known, will produce a deep red precipitate. If the copper be present in smaller quantity—that is, in exceedingly minute traces—the precipitate will be brown or brownish-black; and if copper be entirely absent, the precipitate will be blue or green—assuming, of course, that iron pyrites or some other ferruginous substance is operated upon. In this experiment the preliminary fusion with phosphor-salt greatly facilitates the after solution of the substance in potassium bisulphate. In some instances, indeed, no solution takes place if this preliminary treatment with phosphor-salt be omitted.

Mr. J. M. Merrick has published in the 'Chemical News' a gravimetric method which has led to trustworthy results, even when the amount of copper present was very much less than half a milligramme.

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* In blowpipe practice—as far, at least, as this is possible—the operator should make it an essential aim to render himself independent of the use of mineral acids and other liquid and inconvenient reagents of a similar character. If these reagents cannot be dispensed with altogether, their use, by improved processes, may be greatly limited.

† In the roasting of metallic sulphides, &c., the writer has employed, for some years, small fragments of Berlin or Meissen porcelain, such as result from the breakage of crucibles and other vessels of that material. The test substance is crushed to powder, moistened slightly, and spread over the surface of the porcelain; and when the operation is finished, the powder is easily scraped off by the point of a knife-blade or small steel spatula. In roasting operations, rarely more than a dull red heat is required; but these porcelain fragments may be rendered white-hot, if such be necessary, without risk of fracture.

It consists simply in concentrating to a very small bulk the solution suspected to contain copper, and then depositing the copper, if present, upon platinum, by the battery. He uses for a depositing cell a very small test-tube, on a foot, cut off so as to give a vessel about 1½ inches deep. Into this is introduced the solution acidified with sulphuric acid, and a platinum anode and cathode—each about 1 inch long, and ⅛th of an inch or less wide—are hung face to face, and very close together, and the circuit being completed, very satisfactory depositions of copper are obtained with incredibly minute quantities of the metal. The amounts are determined by the increased weight of the cathode (which is provided with a platinum wire soldered on with gold, by which it is conveniently hooked on to the balance), and by the loss in weight of the same on washing it with nitric acid. The platinum must be polished and heated red-hot before the first weighing, and then gently heated before hanging in the solution. The contrast in colour between the deposited copper and bright platinum is, of course, striking and characteristic. In this way the weight of a milligramme of copper may be safely determined, while for mere qualitative analysis this method may be employed where the amount is even smaller.

CHAPTER XI.

THE ASSAY OF LEAD.

All minerals and substances containing lead may, for the purposes of the assayer by the dry way, be divided into four classes :—

Class I. comprises sulphides, antimonial or otherwise (galena, &c.).

Class II. includes all plumbiferous substances containing neither sulphur nor arsenic, or mere traces only of these elements (litharge, minium, lead carbonate, native and artificial, lead fume, cupel bottoms, furnace hearths, lead slag, &c.).

Class III. comprises all substances into whose composition either sulphuric, arsenic, chromic, or phosphoric acid, or a mixture of either, enters (pyromorphite, wolframite, &c.).

Class IV. Alloys of lead.

CLASS I.

Before describing the different modes of assaying substances of this class, it will be as well to pass in review the action of various reagents on sulphides of lead, in order that the *rationale* of the assay of those ores may be better appreciated.

Action of Oxygen.—If galena be roasted at a very gentle temperature, care being taken to avoid fusion, it will be converted into a mixture of lead oxide and lead sulphate, with evolution of sulphurous acid, thus :—

$$2(PbS)+7O=PbO+PbO,SO_3+SO_2.$$

Action of Metallic Iron.—This metal completely and readily decomposes lead sulphide, giving metallic lead in a pure state, thus:—

$$PbS + Fe = Pb + FeS.$$

On the one side we have lead sulphide and metallic iron, on the other metallic lead and iron sulphide.

The Alkalies and Alkaline Carbonates decompose lead sulphide, but only partially; pure lead is separated, and at the same time a very fusible grey slag is formed, which contains an alkaline sulphate and a compound of lead sulphide and an alkaline sulphide. A certain proportion of the alkali is reduced by the sulphur, which is converted into sulphuric acid, so that no lead oxide is produced. This reaction may be thus expressed:—

$$7(PbS) + 4(K_2O) = 4Pb + K_2O,SO_3 + 3(PbS,K_2S).$$

Potassium Nitrate completely decomposes lead sulphide, with the reduction of metallic lead and formation of potassium sulphate and sulphurous acid, thus:—

$$2(PbS) + K_2O,NO_5 = 2Pb + K_2O,SO_3 + SO_2 + N.$$

If the nitre be in excess, the lead will be oxidised in proportion to the excess present, and if there be a sufficiency added, no metallic lead at all will be produced.

Argol.—The presence of carbonaceous matter much favours the decomposition of galena, by determining the reduction of a larger quantity of potassium to the metallic state, and thereby the formation of a larger quantity of alkaline sulphide. With 4 parts of argol to 1 part of sulphide, 80 parts of lead are reduced. If the reaction were complete, the decomposition would be as follows:—

$$PbS + K_2O + C = Pb + K_2S + CO.$$

For the reactions of lead oxide (litharge) and lead sulphate on sulphide of lead, see pages 186 and 188.

From the reactions above given, it will be seen that there are many substances capable of completely reducing the lead from its sulphide, and yet few can be used safely with any advantage, as so to use them would imply a knowledge of how much sulphur and lead were in the ore to be assayed, in order to tell the precise quantity of either of the reagents required; for it is evident that if either more or less of some were added, a faulty result would be the consequence: so that some systematic mode of assay, which may be suitable for all classes of galena, whether mixed with other sulphides or with gangue, must be contrived. To facilitate this we now proceed to give an outline of the processes generally adopted in the assay of lead ores by various persons.

1. FUSION WITH POTASSIUM CARBONATE.

This plan is used at the Oberhartz, and described by Kerl as follows:—

One centner of the very finely pulverised assay substance is weighed out, mixed with three to four times its weight of pure, dry, and finely pulverised potassium carbonate, and covered over, in a small clay crucible (fig. 61), with a layer of decrepitated sodium chloride about one-fourth of an inch thick. The assays thus prepared are placed in the thoroughly heated muffle of a large assay furnace (figs. 23, 24) having a strong draught. They remain in the highest temperature of the furnace, with the mouth of the muffle closed with glowing coals, till they have come into perfect fusion (about twenty to thirty minutes). The draught opening is then closed, and at the same time the muffle opened, until the temperature has fallen so far that the crucibles appear brownish-red, and the vapours above them have greatly diminished, or have disappeared. At this heat the crucibles—whose contents must, however, always remain in perfect fusion—are maintained, according to the fusibility and composition of the assay sample, and the draught of the furnace for a longer or shorter time (ten to twenty-five, generally ten minutes). This period during which the heat is allowed to remain low, is called the *cooling* of the assay.

The furnace is now again brought back to its first temperature, by completely opening the draught and closing the muffle. Ten to fifteen minutes of this last heating are in most cases sufficient. Only poor ores, &c., which contain also a pretty large quantity of arsenic, or of iron, zinc, and copper sulphides, are allowed to continue hot five to ten minutes longer.

If many assays are to be made, it will be found advantageous to mix those which contain larger quantities of foreign sulphides, or, by reason of their earthy contents, are difficultly fusible, with more or less *borax*; or, instead of this, to place them in the back and hotter part of the muffle, while those that are very rich in lead and easily fusible are placed in front, since the latter will be hot enough here, and more easily reached by the air than those deeper in the muffle.

The crucibles, when cold, are broken, the lead buttons obtained are freed from all adhering slag or substance of the crucible, and if the assay were otherwise successful, their weight determined. The assays should not be too rapidly cooled, because the slag is thus easily cracked, and the still half-fluid button lying below is apt to be broken into several pieces.

In a successful assay, the lead melted together to a button deports itself under the hammer and knife like pure lead, and possesses also its colour. If the slag shows, upon its surface of separation from the metallic button, lead grey spots with metallic lustre, it will generally also be found that a thin layer of not completely decomposed glistening lead sulphide or subsulphide has at the same time deposited itself upon the button. This layer, if the above appearance presents itself in a high degree, can be rubbed off or removed in fine scales. The lead button itself then shows upon its surface a high metallic lustre, which does not have the colour of pure lead, but a darker and blackish hue. Assays of this kind are to be rejected; they have not been allowed to remain *cool* long enough, or they have in the process become *too* cold; they give the amount of lead too low, and often very considerably so. In assays which have stood too long in the furnace in the last fusing heat, a very bright button of lead is also found; but here the layer of undecomposed lead sulphide is wanting, as also the glistening spots on the surface of the slag surrounding the button. If the influence of the heat and air continues too long, then, besides a loss through volatilisation of the lead, a slagging of the lead oxide may take place. A button that is brittle, laminated, and brilliantly white in the fracture, indicates an insufficiency of flux, or the presence of antimony and arsenic. In successful assays the lead button generally has a bluish appearance which, although not dull, is at the same time not strongly brilliant. The slag must be completely homogeneous, and must have settled down uniformly towards the bottom of the crucible, so that it does not stick in a thick layer to the upper part of the sides of the crucible. It shows by this that it has been in proper fusion. It must have covered over the button in a thick layer (about one-fourth of an inch thick). The sodium chloride covering, or a more or less colourless slag that is formed containing sodium chloride and potassium carbonate, overlies in a still thicker layer the true dark-coloured slag containing the foreign metallic oxides. A porous slag containing metallic globules indicates a small quantity of flux or too low a temperature; a brilliant vitreous slag, too high a temperature and a slagging of lead. An assay and its duplicate must, moreover, give equal results.

Lead matt and *lead fume* are smelted, with the addition of borax and coal-dust, with potassium carbonate, and with the first the heat is allowed to last somewhat longer (perhaps to three-quarters of an hour) than with ores. The potassium carbonate assay gives for lead matt, with its not inconsiderable lead contents (30 per cent. and over), pretty satisfactory results.

The theory of this lead assay appears from the following.

If perfectly pure galena is intimately mixed with three or four times its weight of good dry potassium carbonate, placed in a clay retort, and this so arranged in the muffle of the assay furnace that its neck projects from the mouth of the muffle, while in the opening of the neck a glass tube is closely fitted, which goes into a receiver, from which it is further prolonged in a second tube, it will be observed that at first only a little water collects in the receiver, proceeding from the small quantity of moisture always present in the potassium carbonate. Later, with an incipient red heat in the retort, a gas is disengaged, which upon closer investigation proves to be pure carbonic acid gas, *i.e.* free from sulphurous acid. The disengagement of gas becomes more active with a stronger red heat, without yielding gases of different composition, but ceases again after a while. In order to obtain assurance of a complete decomposition, the retort may be kept for an hour at a very strong red heat. After the cooling and breaking of the retort, some pure lead oxide and carbonate is found deposited in the neck of it, then a pure lead button upon the bottom, and over this a brown slag, free from little globules of lead. It consists in by far the greatest part of potassium sulphide and still undecomposed potassium carbonate, but also in small part of potassium silicate derived from the silica of the retort. If this slag is treated with water till nothing further will dissolve, the substances named can be easily shown to exist in the solution. The solution is colourless, and when supersaturated with acids disengages sulphuretted hydrogen, but throws down no sulphur. In the treatment of the slag with water, lead sulphide remains behind in black flocks, even the exterior character of which shows that it is not undecomposed galena, but lead sulphide separated from a chemical combination.

If the brown slag from the retort is placed in a small uncovered crucible and brought back into the hot muffle of the assay furnace and melted, then after some time, whether the slag was covered with sodium chloride or not, a button of lead again separates at the bottom of the crucible, and the brown slag now shows itself decolorised. If the crucible is removed from the furnace too soon, only the upper layer of slag is decolorised, and that lying below is still completely unchanged. The decolorised slag consists of potassium carbonate and sulphate, and no longer contains any trace of potassium sulphide.

In the above-described lead assay, the process in the strong preliminary heat proceeds as in the retort, *i.e.* the potash of the potassium carbonate is reduced to potassium, while it yields its oxygen to the sulphur of the galena and with it forms sulphuric acid; the liberated potassium takes up sulphur from another portion of galena, forming potassium sulphide. The galena would now in this double way soon lose all its sulphur, if a combination—a sulphur salt—of potassium sulphide with lead sulphide did not form, which resists all further action of the potassium carbonate [$4\ (K_2O,CO_2) + 7PbS = 4Pb + 3\ (K_2S,PbS) + K_2O,SO_3 + 4CO_2$]. The carbonic acid of the thus decomposed potassium carbonate escapes together with that set free by the sulphuric acid formed, and causes a puffing up of the mass, by which globules of lead already separated are raised up with it, and may perhaps remain with some of the slag sticking to the upper crucible walls. They would here oxidise and produce yellow spots. The covering of sodium chloride is designed to guard against loss of lead in this and similar ways. It serves in a certain manner to rinse down the sides of the crucible.

The atmospheric oxygen, in the open crucible, is not entirely excluded by the covering of sodium chloride. In the *cooling* of the assay, it oxidises the sulphur salt contained in the upper part of the slag, forming potassium sulphate and a portion of lead sulphate. The latter, during the last high heat, decomposes the lead sulphide still remaining in the slag, in such a way as to produce metallic lead. ($PbS + PbO,SO_3 = 2Pb + 2SO_2$.) The reduced particles of lead separate well from the slag thus rendered thinly fluid. Matts must be allowed to *cool* longer than ores.

The potassium carbonate assay presupposes in general great practice and close attention on the part of the assayer; and moreover, if one wishes to find the correct value at once, without fruitless preliminary examinations, and without the necessity of repeating the assay, a general knowledge of the constituents of the assay sample, so far, for example, as this can be obtained by the aid of mineralogy, is necessary. The assay after this method, which requires but little preparation, can only be conducted in the muffle furnace, but then in pretty large number (as many as fifty at once). For its success it is indispensably necessary that the *cooling* of the assay be allowed and stopped again at the right time and in the proper degree. If it is allowed to *cool* too long, too much sulphate of lead is formed in proportion to the lead sulphide still present in the slag, and in the last heating up, by the action of the two upon each other, easily scorifiable oxide of lead is produced. ($PbS + 3PbO,SO_3 = 4PbO + 4SO_2$.) If the *cooling* is too soon interrupted, only a small part of the lead sulphide in the sulphur salt is oxidised, and by the action of the oxidised portion upon the lead sulphide, lead subsulphide is produced, which either remains in the slag or settles upon the lead button. ($2PbS + PbO,SO_3 = Pb_2S + 2Pb + 2SO_2$.) Experience gives the only means at hand to guide us here, but leaves us easily in the lurch, so that the result of the assay becomes more doubtful than in some of the methods hereafter described.

With substances containing *antimony* this assay deserves the preference over the others, since most of the antimony remains in the slag in the state of sulphide and oxide. An addition of saltpetre works advantageously. *Arsenic* and *arsenic sulphide* mostly go off in fumes during the smelting, but nevertheless always cause the formation of a brittle metallic button. *Copper sulphide* remains in great part in the slag, but a part of the copper is desulphurised and goes into the lead. If the quantity of copper present is very considerable, the button of metal may be considered as black copper, and refined, and the loss thereby occurring, reckoned as lead.

Iron protosulphide, which occurs, for example, in lead matt, is decomposed by potassium carbonate, forming metallic iron, which desulphurises the galena. *Iron pyrites*, on the other hand, occasions the forming of a large quantity of potassium sulphide and, in consequence of this, of a sulphur salt.

It follows, therefore, from the above, that ores which contain much foreign sulphides are not suited to this method of assaying, since they cause the production of a large amount of potassium sulphide, which always retains lead sulphide. By an addition of saltpetre to the potassium carbonate, these sulphides may, indeed, be partially decomposed: only an oxidation of the lead is apt to be produced, as well as a mechanical loss by the violent action of the saltpetre.

From pure galena, by the potassium carbonate assay, 80 per cent. of lead at most can be obtained. Calcined *sodium carbonate* is inferior to potassium carbonate as a desulphurising agent, and always yields a few per cent. less lead than the latter. According to Phillips, 75 to 77 per cent. of lead is obtained from galena with sodium carbonate. With *potassium cyanide*, under certain circumstances, the same result can be obtained as with potassium carbonate, and it does not require so high nor so long continued a temperature; still it offers no real advantage over potassium carbonate. An addition of 30 to 35 per cent. of saltpetre to an assay, with which ten parts of sodium carbonate are used, promotes, indeed, the desulphurising of the lead, but also increases the loss of lead.

At the Oberhartz smelting-house, the lead button is weighed out to pounds, and a difference of five pounds is allowed between different assayers. It is also a custom, though not a correct one, to allow as many pounds difference as there are tens of pounds in the weight of the lead button obtained. Thus, with a lead contents of thirty and seventy pounds, the difference in the separate assays might amount to three and seven pounds respectively.

2. FUSION WITH BLACK FLUX.

A modification of the preceding method of assaying, which is sometimes employed, consists in using, instead of the potassium carbonate, an equal quantity of black flux, or indeed of argol, or in mixing a few per cent. of powdered charcoal or flour with the potassium carbonate, or in replacing it in part by argol. Too great an addition of carbon diminishes the fusibility of the mass, and hinders the flowing together of the separated particles of lead. By using argol the operation lasts longer, because the mass remains pasty until most of the tartaric acid has been decomposed; but a greater product of lead is obtained. The chemical reaction during the operation is thereby modified so that the carbon of the black flux exerts an influence upon the potash, and partially reduces it to potassium; the potassium, thus set free, works now, as before, upon the galena. The latter is thus, without the influence of the air, more completely decomposed than by potassium carbonate alone, and the smelting is, therefore, conducted in covered crucibles (fig. 61) in the wind furnace. But since there is also potassium sulphide formed, and this dissolves lead sulphide, it is more advisable, for the completest possible separation of the lead, to perform the smelting in open crucibles in the muffle, in order to allow the atmospheric oxygen to work at the same time on the assay. The product of lead from pure galena does not generally exceed 76 to 79 per cent.

At the Victor-Frederick smelting works in the Hartz, one centner (= one hundred and fourteen pounds) of galena is mixed with three or four times as much black flux, and with pyritic ores ten pounds of borax-glass are added. The mixture is covered with sodium chloride, heated for about twenty-five minutes in the muffle furnace with a charcoal fire, and then, after the mouth of the muffle has been opened for about five minutes, taken out of the furnace.

3. FUSION WITH METALLIC IRON.

Schlutter and many of the older assayers were aware that iron would desulphurise galena, and ever after advised the addition of a certain quantity of that metal to the different fluxes which they used in lead assays; but it was at the practical School of Mines, at Montiers, that iron was first employed alone.

The process is extremely convenient and easy of execution; it always succeeds, and requires no troublesome attention. The fusion takes place quietly, without frothing or bubbling; and as the whole substance employed requires but little space, very small pots may be employed, or a very large quantity assayed. But this process can only be employed for pure galenas, or those which contain at most a few per cent. of gangue.

When galena is heated with iron, the metal is transformed into protosulphide, whence it follows, that to desulphurise galena 22·6 per cent. is required; but experience has shown that it is better to employ a little more, and 30 per cent. can be used without inconvenience. The iron employed ought to be in the state of filings, or wire cut very small. The mixture is placed in a crucible, which is three-fourths filled; the whole is covered with a layer of salt, sodium carbonate, or black flux, and exposed to a full red heat. After the flux is perfectly fused, the pot may be cooled and broken, and a button is obtained, which at first sight has a homogeneous aspect, but on being struck with the hammer separates into two distinct parts. The lower part is ductile lead: the upper a very brittle matt, of a deep bronze colour, and slightly magnetic. Pure galena yields, by this process, 72 to 79 per cent. of lead, so that there is a considerable loss, which loss is entirely due to volatilisation. Berthier says that it does not appear possible to avoid this loss, which amounts from 6 to 13 per cent., giving as a reason that it is probable galena begins to sublime before it arrives at the proper heat for decomposition.

Antimonial galenas, or galenas mixed with iron pyrites, may be assayed in the same manner; but then a sufficiency of iron must be added to reduce the antimony to the metallic state, as well as to reduce the iron pyrites to the minimum of sulphurisation. If the galena be mixed with blende, the greater portion remains in the slag, because it is only decomposed by iron at a very high temperature.

Blende being infusible by itself, much diminishes the fusibility of the matts produced ; and if it exists in very large quantity, it can even hinder their complete fusion ; in which case, some iron protosulphide and metallic iron must be added to the assay, to make the slag more fusible.

All minerals are at a minimum of sulphurisation when existing in matts from metallurgical works ; therefore, much less iron may be used in their assay than if they were pure ores. In very rich lead matts, in which the lead exists as subsulphide, from 10 to 12 per cent. is sufficient. A small excess of iron may be employed without inconvenience ; but if a larger proportion be added than is necessary to execute the desulphurisation, the matt contains some iron in the metallic state, and loses its liquidity, and in consequence retains some globules of lead.

The usual mode of assaying lead ores (galena) in the lead mills is by a modification of this process : in lieu of placing the ore in an earthen crucible, and adding nails or filings, a given weight of the ore is projected into a red-hot wrought-iron crucible, which is kept in the fire for about a quarter of an hour, or until all the galena seems decomposed. The lead thus reduced is poured into a mould ; and if the scoriaceous matter be not well fused, the iron crucible is returned to the fire and heated still more strongly, and any lead that may be separated is poured into the mould and weighed with the rest. This is a very rude and imperfect process, and gives only tolerable results with pure galenas, but is quite unsatisfactory with those containing much earthy matter, as not above half the lead is obtained, owing to volatilisation and exposure to the air, and the loss of globules in the slag. This process succeeds much better when a flux is added ; this may be argol, or sodium carbonate, or a mixture of both (see next process).

4. FUSION WITH SODIUM CARBONATE OR BLACK FLUX, AND METALLIC IRON.

When galena is heated with an alkaline flux, out of contact of air, the slag contains a double sulphide of lead and the alkaline metal employed: if iron be thrown into this fused mixture, metallic lead separates, and the iron combines with the sulphur formerly combined with the lead, and the slag will contain a double alkaline sulphide, containing iron sulphide instead of lead sulphide, thus:

$$PbS + K_2S + Fe = Pb_2 + FeSK_2S.$$

Any earthy substances the ore may contain will be dissolved by the alkaline flux, without very much impairing its fluidity. All these facts being considered, it may be readily seen that the assay of all earthy bodies containing lead sulphide may be made in this manner, with as much accuracy as this method of assay can be capable of. Either sodium carbonate or black flux may be employed as the alkaline reagent, and more of either of those substances must be employed, in proportion to the increased quantity of earthy matters the ore contains. Two parts are nearly always more than sufficient for poor ores, and are best for all cases, because an excess of flux does not diminish the yield of lead; nevertheless, it is sometimes convenient to employ, for the latter class, but half a part. As to the iron, it is employed only to separate that part of the lead which has been dissolved in the state of sulphide by the alkali, but not decomposed; so that much less may be employed than is necessary for the decomposition of the whole amount.

Experiment has shown that the maximum amount of lead from pure galena may be obtained by the use of the following mixtures:—

2 parts of black flux, or sodium carbonate, and 10 to 12 per cent. of iron.

1 part of black flux, or sodium carbonate, and 20 per cent. of iron.

½ a part of black flux, or sodium carbonate, and from 25 to 30 per cent. of iron.

When black flux is employed, and the iron is in the state of filings, it would be inconvenient to employ too much of the latter, especially if the assay were heated very strongly, because the button of lead might be contaminated with iron; but when sodium carbonate is used with small iron nails instead of filings, the excess of iron is not inconvenient, but rather useful, because the desulphurisation is certain to be complete.*

The following changes take place in both cases. That portion of iron filings mixed with the sodium carbonate which has not been sulphurised, is reduced to the state of oxide by the carbonic acid of the alkaline carbonate, and remains combined or neglected in the slag; so that the proportion of iron is never too great, and never becomes mixed with the lead. When black flux is employed, the same oxidation does not take place, on account of the presence of carbonaceous matter, so that the portion of filings not combined with sulphur, and which is merely held in suspension in the flux, passes through it with the globules of lead to the bottom of the crucible: but if, instead of filings, small nails are employed, they only suffer corrosion at their surface, without change of form or softening, and after the assay are found fixed in the surface of the button of lead, so that they can be detached very readily, and, according to Berthier, without loss of lead. This, however, we have found no easy task, and have always sustained a notable loss.

5. ROASTING AND REDUCING ASSAY.

This mode is preferable for ores and substances which contain a considerable quantity of foreign sulphides, or arsenides and antimonides, and a greater or less amount of

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* The French assayers use a piece of plate iron in the shape of a horse-shoe, which is moved about in the melted mass until no more globules of lead attach themselves to it.

In Germany a piece of iron-wire is used. What iron is not consumed by the assay is found still hanging together in a single mass.

earthy matter. It is used in many parts of Germany (at the Unterhartz), and is described by Kerl thus:—

Two assay centners of ore, matt, &c., are heated at first at a low red heat in the muffle, on a roasting dish that has been previously rubbed with chalk. After ten or fifteen minutes, they are taken out of the furnace, then again roasted at a moderate temperature for ten or fifteen minutes with frequent turning of the dish. The assay is then once more taken from the furnace, allowed to cool, rubbed up in an agate mortar, and again roasted for half an hour, whereupon it is taken out of the furnace; tallow is added while it yet glows, and it is again brought to a strong red heat. The rubbing up and calcining with tallow are repeated several times more, and when afterwards the assays have been exposed for two hours continuously to a strong red heat, with the mouth of the muffle almost entirely closed, if no more sulphurous acid vapours escape, the roasting is considered as finished. This lasts from six to twelve hours. The roasted sample is then portioned out with the balance, each portion mixed with three or four parts of black flux and an equal quantity of borax and glass, placed in a small crucible covered with sodium chloride, furnished with a little piece of coal as a cover, and smelted in the wind furnace for about a quarter of an hour after the fire is well ignited. Assays that have worked well, give nearly equal malleable buttons that do not contain matt, and a black uniformly fused slag.

The purpose of the roasting is to convert the metallic sulphides, arsenides, and antimonides into oxides. But since in the process, sulphates, antimoniates, and arseniates are produced, we seek to destroy these by repeated calcining with tallow (see above), instead of an intermixture of coal-dust or flour. By melting the roasted assay with its charge at not too high a temperature, the lead oxide is reduced, and the foreign oxides and earths contained in the sample are, by the aid of the potash in the black flux, as well as of the borax and glass, slagged off. If sulphates or sulphides have remained behind in the roasted ore, they will in the smelting be partially desulphurised by the action of the oxides, especially of the iron oxide. An addition of metallic iron would in this respect be advantageous.

The roasting is a lengthy process, and one which causes a not unimportant loss of lead. If it is not done thoroughly, then in the reduction smelting, sulphur salts are formed, which always retain lead, as also a plumbiferous matt, which surrounds the lead button. By the use of too high a temperature in the smelting, a great part of the foreign oxides is reduced, and the lead becomes contaminated. The reduction, however, cannot be entirely avoided, even with a rightly conducted temperature.

Galena melts less easily than metallic lead if the air is excluded; but is much more volatile than the latter, and is decomposed by fusion into a higher sulphide which is volatile, and a lower one (Pb_2S) which remains as a residue. Galena by roasting gives a mixture of lead oxide and sulphate, from which last the sulphuric acid cannot be separated, even at a fusing temperature. Lead sulphate becomes soft by heat, fuses at a bright white heat, and is converted by carbon, with a considerable loss of lead through volatilisation, into lead oxide, metallic lead, or lead subsulphide, according to the quantity of carbon used, and the temperature employed. With lead oxide, the sulphate easily fuses together.

6. ASSAY WITH SULPHURIC ACID.

The assay sample is rubbed as fine as possible. A suitable quantity of it is then weighed out for an assay, and boiled with four to eight times its weight of oil of vitriol until all is decomposed. All excess of sulphuric acid is then evaporated in a porcelain capsule, under a flue with a good draught, and the mass carried to dryness. Boiling sulphuric acid decomposes the sulphides, changing iron, copper, nickel, zinc, &c., into salts which dissolve readily in water, and also at the same time changing the lead sulphide into sulphate, which in water, especially when cold, and containing free sulphuric acid, is practically insoluble. The composition of the ore is in general ascertained by first heating it with nitric acid or aqua regia, and then with the addition of sulphuric acid, evaporating to dryness. The dry mass, when cold, is moistened with a small quantity of sulphuric acid, then cold water; it is afterwards, by the aid of a small brush, brought without loss upon a small filter, and washed with cold water until the filtrate is colourless. Unnecessary prolonging of the washing is to be avoided, for lead sulphate is not absolutely insoluble. The filter, with its contents, is dried in the funnel, until it can be easily taken out of it without tearing. It is now put immediately into the clay crucible, in which the lead sulphate is afterwards to be reduced, and this is placed in a very gentle stove warmth. (Some potassium carbonate may be first poured into the bottom of the crucible.) When completely dry, the crucible with the cover laid over it is very gently heated, so that the filter carbonises, which very soon happens, as the free sulphuric acid is not completely soaked out. The filter is now stirred up with a little rod, black flux or potassium carbonate with coal-dust and iron are introduced into the crucible, and intimately mixed with the lead sulphate and the rest of the insoluble residue. About four or five times the volume of the whole residue is taken of black flux, and the assay is further treated as prescribed in the portion which follows upon the assaying of lead sulphate.

In this way the lead is concentrated, and the foreign sulphides, which were specified above as the cause of the failure of the assay in such cases, completely removed. The result obtained in this way is satisfactory, and deserves the same confidence as one obtained in favourable circumstances by the ordinary lead assay from an ore with a medium or high percentage of lead.

7. ASSAY OF GALENA IN THE WET WAY.

When in contact with metallic zinc, galena is readily decomposed by acids. Even oxalic, acetic, and dilute sulphuric acids are capable, when hot, of decomposing galena,—metallic lead being deposited and sulphuretted hydrogen gas set free,—while with hydrochloric acid the decomposition is peculiarly rapid and complete.

Galena is easily decomposed, also, even in the cold by dilute nitric acid in presence of zinc; but the reaction differs in this case from that just described—not metallic lead but free sulphur is deposited, while lead nitrate goes into solution.

The reaction with zinc and hydrochloric acid has been employed with advantage by Mr. F. H. Storer, Professor of Chemistry in the Massachusetts Institute of Technology, for assaying galena, particularly the common American variety, which contains no other heavy metal besides lead. The details of the process are as follows:—Weigh out 2 or 3 grms. or more of the finely powdered galena. Place the powder in a tall beaker, together with a smooth lump of pure metallic zinc. Pour upon the mixed mineral and metal 100 or 150 c.c. of dilute hydrochloric acid which has been previously warmed to 40° or 50° C.; cover the beaker with a watch-glass or broad funnel, and put it in a moderately warm place.

Hydrochloric acid fit for the purpose may be prepared by diluting 1 volume of the ordinary commercial acid with 4 volumes of water. For the quantity of galena above indicated, the lumps of zinc should be about an inch in diameter by a quarter of an inch thick; they may be readily obtained by dropping melted zinc upon a smooth surface of wood or metal.

The zinc and acid should be allowed to act upon the mineral during fifteen or twenty minutes in order to ensure complete decomposition. Any particles of galena which may be thrown up against the cover or sides of the beaker should of course be washed back into the liquid. It is well, moreover, to stir the mixture from time to time with a glass rod.

When all the galena has been decomposed, as may be determined by the facts that the liquid has become clear, and that no more sulphuretted hydrogen is evolved, decant the liquid from the beaker into a tolerably large filter of smooth paper, in which a small piece of metallic zinc has been placed. Wash the lead and zinc in the beaker as quickly as possible with hot water, by decantation, until the liquid from the filter ceases to give an acid reaction with litmus paper; then transfer the lead from the beaker to a weighed porcelain crucible. In order to remove any portions of lead which adhere to the lump of zinc, the latter may be rubbed gently with a glass rod, and afterwards with the finger or a piece of caoutchouc, if need be. Wash out the filter into an evaporating dish, remove the fragment of zinc, and add the particles of lead thus collected to the contents of the crucible. Finally, dry the lead at a moderate heat in a current of ordinary illuminating gas, and weigh.

The lead may be conveniently dried by placing the crucible which contains it in a small cylindrical air-bath of Rammelsberg's pattern, provided with inlet and outlet tubes of glass, reaching almost to the bottom of the bath.

When the process is conducted as above described, the lead undergoes no oxidation; hence there is no occasion for igniting the precipitate in a reducing gas. The precipitate needs only to be dried out of contact with the air.

If desirable, the sulphur in the galena could be determined at the same time as the lead, by arresting the sulphuretted hydrogen in the ordinary way.

If the mineral to be analysed is contaminated with a siliceous or other insoluble gangue, the metallic lead may be dissolved in dilute nitric acid after weighing, and the insoluble impurity collected and weighed by itself. In the case of galenas which contain silver, antimony, copper, or other metals, precipitable by zinc, the proportion of each metal must be determined by assay or analysis in the usual way, after the total weight of the precipitated metals has been taken.

Besides galena, almost any of the ordinary lead compounds may evidently be assayed by the method above described. For example, metallic lead may be precipitated quickly and completely from the sulphate, chromate, nitrate, oxide, and carbonate—and with peculiar ease from the chloride—by means of zinc and hydrochloric acid. The method would also furnish an easy qualitative test for the detection of baryta in white-lead. When applied to the analysis of lead nitrate, it would probably be best to decompose the nitrate by means of a solution of sodium chloride before adding the zinc and hydrochloric acid.

In all these cases the decomposition of the lead salt by the zinc is so complete that no trace of coloration is produced when sulphuretted hydrogen is added to the liquid decanted from the metallic lead.

Attempts to determine sulphur and lead in the same portion of galena, by means of the reaction of zinc and dilute nitric acid above described, have not given satisfactory results. The free sulphur obtained by treating galena with zinc and ordinary nitric acid, diluted with three, four, and five volumes of water, always retains a small quantity of lead, while a certain amount of sulphuric acid is found in the clear liquid. It is, in short, well-nigh, or quite impossible to avoid the secondary reactions between zinc and lead nitrate, and between sulphuric and nitric acid, which set in as soon as, or just before, the last traces of the galena have been decomposed.

CLASS II.

Assay of Substances of the Second Class.—The assay of these substances is very simple indeed. Litharge, minium, lead carbonate, &c., may be assayed by simple fusion with carbonaceous matter; but when the operation is thus conducted, loss of lead is sustained: it is therefore better to add some flux which will readily fuse, and allow the globules of reduced lead to collect into one button. No flux fulfils this condition better than a mixture of sodium carbonate and argol, which is to be intimately mixed with the assay. The following is the best mode of procedure:—To 200 grains of the finely-pulverised substance add 100 grains of argol, and 300 of sodium carbonate, and intimately mix; place the mixture in a crucible which it about half fills, and cover with a layer of common salt about $\frac{1}{4}$ inch thick; submit the crucible to a very gradually increasing temperature, keeping the heat at low redness for about a quarter of an hour; then urging it to bright red until the contents of the crucible flow freely; take it from the fire and shake, tap it as directed in the copper assay, and either pour the contents into the mould or allow to cool in the crucible. If the operator be pressed for time, the mould may be used, but it is recommended to allow the assay to cool in the crucible, for unless the operator be very careful, and have had some considerable practice, he is very liable to lose a small quantity of metal in the pouring. After the contents of the mould or crucible, as the case may be, are cold, the lead may be separated from the slag by repeated gentle blows from the hammer: if any of the slag or crucible adhere to the button, the latter may be readily freed from it by placing the button between the finger and thumb with its edge on the anvil, and then gently hammering it. The lead will be so altered in shape under the hammer that the slag or crucible readily falls off; and by continuing the process, the whole may be removed. The cleaned button may then be hammered into a cubical form, and is ready for weighing.

In the assay of lead great care must be taken in the management of the temperature, as lead is sensibly volatile above a bright red heat, even when covered with flux, and still more so if any portion be uncovered from want of sufficient quantity of flux; neither must the assay remain in after the flux flows freely, for a loss may thereby occur from oxidation, by decomposition of sodium carbonate, as explained in the reduction of copper ores and the copper-refining process.

For the *rationale* of this mode of assay, refer to page 199, which explains the decomposition of lead oxide, with the production of metallic lead, carbonic acid, and water, by the agency of a substance, like argol, containing both carbon and hydrogen.

Cupel bottoms, some lead fumes, and siliceous slags, require a modified treatment in the assay, as the substances mixed with the oxide of lead (more particularly bone-ash in the cupel bottoms) are very infusible; and if the flux already mentioned as applicable to the other matters belonging to this class were employed, a very high temperature would be necessary; and as lead, as already stated, is sensibly volatile above a bright red heat, an evident loss of that metal would be the result.

Cupel bottoms may be thus assayed: 400 grains of the finely-pulverised bottoms to be mixed with 200 grains of argol, 400 grains of sodium carbonate, and 400 grains of pulverised fused borax; the mixture is placed in a crucible as already directed, covered with salt, and the fusion conducted as just described.

Lead fumes and siliceous slags require only half their weight of fused borax, with 200 argol, 400 sodium carbonate, and 400 substance (fume or slag), covered with salt.

The addition of the borax, which is a most powerful flux, causes the fusion of the assay to take place almost as readily with the last-named refractory substances as with the former easily fusible and reducible matters. The assay, however, is rather more subject to ebullition or boiling over the sides of the crucible; hence it must be carefully watched, and the instant it appears likely to do so the crucible must be removed from the fire, gently tapped on the furnace-top, and when the effervescence has subsided returned to the furnace, and this operation repeated until the fusion proceeds tranquilly.

The lead obtained in these assays, if the ore or substance contained any foreign metal, is never pure; if silver, copper, tin, or antimony be present, the whole of either of these metals will be found alloyed with the lead produced; but if the ore contains zinc, and it be heated sufficiently, only a trace remains; nevertheless the zinc carries off with it a considerable quantity of lead.

The following experiments will show what an influence the presence of zinc has upon the return of lead:—

100 parts of litharge,
100 parts of zinc oxide,
300 parts of black flux,

were fused together, and 84 parts of lead were the result.

100 parts of litharge,
100 parts of zinc oxide,
600 parts of black flux,

were fused together, and but 70 parts of lead were produced instead of 90, which the pure litharge ought to have given. Hence it will be seen that, the more zinc is reduced, the more lead is volatilised.

If iron oxide be present in the assay, it is reduced, but it remains in suspension in the slag, and the lead does not contain a trace when it has not been too strongly heated. If the assay be made at a very high temperature, the iron may be fused, and then the lead will be ferruginous ; this may be ascertained by means of the magnet. A similar result was obtained by many assayers, who thought for a long time that lead and iron could thus combine together; but by careful examination it is easily ascertained that the ferruginous buttons are but mechanical mixtures of lead and iron in grains. Indeed, by careful hammering, nearly all the iron may be removed from the lead, so that it loses its magnetic properties.

The manganese oxides, when mixed with the ore, are changed into protoxide, which remains in the flux, and is not reduced.

Wet Assay of Ores of the Second Class.—Pulverise the substance very finely, and to 100 grains placed in a flask add one ounce of nitric acid diluted with two ounces of water (if minium be the substance to be analysed, it must be first heated to redness, so as to reduce the whole of the lead it contains to the state of protoxide), and gently heat, gradually raising the temperature to the boiling-point: when all action seems to have ceased, pour the contents of the flask into an evaporating basin, and evaporate to dryness with the precautions directed in the analysis of iron ore. Allow the dry mass to cool, add a little dilute nitric acid, gently warm for an hour, then add water, boil and filter. The whole of the lead now exists in the solution as nitrate: thus, say lead carbonate had been the substance under analysis, then—

$$PbO,CO_2+NO_5=PbO,NO_5+CO_2.$$

To the filtered solution containing the nitrate as above, add solution of sodium sulphate, or dilute sulphuric acid, until no further precipitation takes place; insoluble sulphate of lead will now be thrown down; this must be allowed to completely subside by standing in a warm place; and when the supernatant liquid is quite bright, the sulphate may be collected on a filter, washed, dried in the water-bath, and weighed. It contains 68·28 per cent. of metallic lead.

The decomposition of the lead nitrate by sodium sulphate may be thus expressed—

$$PbO,NO_5+Na_2O,SO_3=PbO,SO_3+Na_2O,NO_5.$$

Determination of lead by standard solution will be described at the end of this chapter.

CLASS III.

Assay of Substances of the Third Class.—In the assay of bodies belonging to this class, a reducing agent must be employed; but if that alone be used, the sulphates and arseniates produce sulphides and arsenides, and not pure lead. The action of another reagent is therefore necessary, in order to deprive the lead of the sulphur and arsenic with which it is combined.

There are two reagents employed for the sulphates—the alkaline carbonates and metallic iron; but for the arseniates and arsenites iron must be employed, because the alkaline carbonates have no action on the arsenides.

In all cases black flux is employed; this furnishes a reducing agent for the oxides, and a flux for the earthy matters. Iron is added when the arsenites or arseniates are assayed; but that metal may either be employed or not, when the sulphates are operated upon. It is, however, always better to use it.

When a mixture of black flux and iron is employed, the assay is made in exactly the same manner as that of the sulphides (large nails are preferable whenever the use of iron is indicated in a lead assay). With the sulphate, the iron sulphide formed combines in the slag with the alkaline sulphide; but it is not so with the arseniates and arsenites. The arsenide produced mixes neither with the lead nor the slag, but gives rise to the formation of a brittle matter which adheres slightly to the button of lead.

When only black flux is employed, either of the two following processes may be adopted:—First, the ore can be fused with four parts of common black flux; then, as in the case of sulphides, the excess of carbon determines the formation of a large quantity of an alkaline sulphide; and consequently produces a desulphurisation of the lead. Secondly, it may be fused with such a proportion of black flux, containing only the requisite proportion of carbon to reduce the lead oxide, or with an equivalent mixture of sodium carbonate and charcoal. Pure lead sulphate fused with one part of sodium carbonate and 4 per cent. of charcoal gives 66 of lead; but in order to employ this method the richness of the ore must be known, and the dry way is then useless, excepting for the estimation of the silver these substances always contain.

Wet Assay of Substances of the Third Class.—These are treated in precisely the same manner as those of the preceding class.

In treating lead ores with nitric acid a loss generally results from the formation of insoluble lead sulphate. The solubility of these salts in sodium hyposulphite renders it possible to avoid this inconvenience. After treatment with nitric acid, J. Grœme (*Bulletin de la Soc. Chimique de Paris*, November 5, 1873) proposes to exhaust the residue with boiling water, until the soluble salts and the acid are completely eliminated. It is then digested in the cold with a concentrated solution of sodium hyposulphite. After this treatment has been twice or thrice repeated, the residue is exhausted again with water; the lead is then precipitated from the filtrate by sulphuretted hydrogen or ammonium sulphide; to facilitate the agglomeration of the precipitate and its washing, it is heated in the water-bath. The sulphide is then converted into sulphate, and its weight added to that of the sulphate obtained directly.

F. Maxwell Lyte thinks the following process for the management of the assay of lead in ores will be found convenient, particularly where, as is often the case, the lead to be estimated is mixed as sulphate with the matrix insoluble in acid.

He dissolves the sulphate or chloride, as the case may be, in ammonium acetate, makes the solution as neutral as possible, and estimates the lead by a standard solution of bichromate (a half decinormal solution answers well) with a silver nitrate indicator.

A. Mascazzini, previous to reducing the galena or other lead ore to the metallic state, converts the lead present in the ore into sulphate by igniting it in a porcelain crucible with ammonium sulphate, after which the ore is treated in the usual manner. The flux preferred by the author is that recommended by Plattner, consisting of 13 parts of potassium carbonate, 10 of dry sodium carbonate, 5 of previously fused borax, and 5 of well-dried starch.

To detect galena in mixtures, M. E. Jannesay throws upon coarsely powdered galena a fragment of potassium bisulphate, which gives a distinct evolution of sulphuretted hydrogen. If the two bodies are ground together the odour becomes almost insupportable. Potassium bisulphate kept in fusion for half an hour produces the same effect, perhaps with less intensity. Sulphuric acid, mixed or even heated with galena, does not give rise to a sensible disengagement of sulphuretted hydrogen. Blende gives a sulphydric odour, but less intense. Antimony, iron, mercury, and silver sulphides give off no sensible odour. Boulangerite, zinbrenite, and in general the sulphides in which lead and sulphur do not form an isolated combination, do not yield their sulphur to the potassium bisulphite.

CLASS IV.

ALLOYS OF LEAD.

ASSAY WITH SULPHURIC ACID.

No docimastic assay is known for exhibiting the lead isolated from its alloys. In individual cases a serviceable result may be attained, if the metal with which the lead is combined be determined, and its quantity then deducted. This method is, however, in general, the more unreliable the smaller is the quantity of lead, or when the lead is alloyed with several metals; so that then the quantity of lead can often only be determined by the partial or complete aid of the wet way.

For many products (*e.g.*, crude lead, hard lead—containing antimony or arsenic—plumbiferous copper, &c.), the assay with sulphuric acid described on page 459 is suitable. One assay centner of the substance is decomposed by nitric acid or aqua regia, then, with the addition of sulphuric acid, evaporated to dryness, and the dry mass treated as above directed. If the residue consists only of lead sulphate, it can be brought upon a weighed filter, and from the weight of the residue after drying, the amount of lead may be calculated. 100 parts lead sulphate contain 68·33 parts lead.

ADDITIONAL REMARKS ON THE LEAD ASSAY.

Comparison of the Different Methods for the Docimastic Determination of Lead in their application to various Products.

Markus has made the following comparative experiments with the methods of assaying lead ores most in use at the Austrian smelting works at Joachimsthal.

a. Assay with Black Flux and Iron.—One assay centner (5·7 grammes) of the finely rubbed, sifted and dried assay substance was mixed with two assay centners of black flux, made of sixteen saltpetre and forty argol, and sixty pounds of borax-glass in a mixing capsule, and put into a clay crucible, on the bottom of which a piece of thick iron wire one inch long and forty centners in weight, had been placed in a vertical position. The crucible charge, covered over with two centners of decrepitated sodium chloride, was smelted in a mineral coal muffle furnace, with the mouth of the muffle closed, and the draught half open, at a moderate temperature, the temperature then lowered for six to seven minutes by opening the mouth of the muffle, then the muffle closed again for an equal period, and the final heat then given. The cessation of the low crackling of the assay was now carefully attended to, and this, ceasing after seven to eight minutes, indicated the completion of the assay. The duration of the assay was twenty minutes.

b. Roasting and Reduction Assay with Iron.—One assay centner of galena was roasted, at first at a low temperature, for about thirty minutes on a roasting dish, and the dish then pushed into the back part of the muffle for six to eight minutes to destroy the sulphates formed. The roasted ore was rubbed fine, intimately mixed with three hundred centners of black flux, and fifty centners of borax-glass, placed in a crucible with a piece of iron weighing twenty centners at the bottom, covered with salt, and smelted as above.

c. Roasting and Fusing with Black Flux.—One centner of the roasted ore was smelted as before with three hundred centners of black flux and fifty centners of borax, but without iron.

The results obtained proved—

1. That with all those products which contain tolerably pure lead sulphide, especially with high percentages, the iron assay, *a*, gives in a remarkably predominant degree the most lead (as high as 96 per cent. of all the lead present).

2. With impure lead ores, which contain more foreign sulphides, the assay *a* gives likewise the highest percentage, though the assays *b* and *c* give only a few per cent. less.

3. If foreign sulphides are present in predominant quantity, the methods of *b* and *c* give a slightly higher percentage than that of *a*.

Levol's Fusion Assay with Potassium Ferrocyanide and Cyanide.

According to Levol, the method of assaying galena for its lead by smelting it with black flux and iron is defective in two respects. First, it is difficult to choose precisely the quantity of iron required for the reduction of the lead, and a lack or excess of it either gives too little lead or a button containing iron; and second, in order that the reaction may be complete and the lead unite to a button, we are compelled to use a very high temperature, at which lead volatilises. The first defect can indeed be removed by the use of iron crucibles, but these are easily rendered unserviceable, and require a pouring out of the fused mass, and then globules of lead are apt to remain in the slag.

By the use of a mixture of fifty parts of potassium cyanide and one hundred of anhydrous potassium ferrocyanide to one hundred of galena, the loss of lead diminishes to from 2 to 2½ per cent., probably in consequence of the easy fusibility of the mixture, and the extremely fine division of the iron in the potassium ferrocyanide. With antimonial galena this process is not applicable, as the antimony is reduced and goes into the lead. Potassium cyanide alone, gives, by reason of the greater quantity of metallic sulphide which it retains, a smaller product of lead.

DETERMINATION OF LEAD BY MEANS OF STANDARD SOLUTIONS.

1. Flores Dumonté's Method.

Determination of Lead by means of Standard Solutions. This process is due to M. Flores Dumonté, and may be thus described:—This mode of analysis is analogous to that proposed by Pelouze for the determination of copper; advantage is taken of the fact that oxide of lead is soluble in caustic potash in the same manner that copper oxide is soluble in ammonia; and from either solution the respective metal is precipitated by means of a standard solution of sodium sulphide.

The solution of sodium sulphide may be conveniently made by dissolving one ounce of sodium sulphide in one quart of water, and determining how much of it is necessary to precipitate twenty grains of lead. To this end weigh off twenty grains of lead, dissolve them in nitric acid, dilute with water, and add excess of caustic potash until the oxide of lead first thrown down is completely dissolved. The solution must now be heated to ebullition, and the sodium sulphide gradually added from the burette; at each addition a black precipitate of lead sulphide falls. The liquid is then boiled for a short time, by which means it brightens; more sodium sulphide is then added, and the whole again boiled, and these operations alternately continued until no further coloration or blackening is produced by the last drop of sulphide. The number of divisions used is then read off, and the calculation made as in Pelouze's copper assay, substituting lead for copper.

Having thus standardised the solution of sodium sulphide, the assay of a sample of ore may be thus made:—If the ore belong to the first class, dissolve it in dilute nitric acid and evaporate to dryness; to the dry mass add excess of caustic potash solution, and boil; after about a quarter of an hour's ebullition, filter and throw down the lead as directed, with the standard solution; from the amount used calculate the quantity of lead present; if the ore be of the second or third class, treat with strong nitric acid and sodium carbonate, as already directed. The lead carbonate so produced may be dissolved in either nitric or acetic acid, and to the solution thus obtained add caustic potash, &c.

2. Schwartz's Method.

Dissolve 14·730 grammes of pure potassium bichromate in sufficient water to form one litre. One cubic centimètre of this solution precipitates 0·0207 gramme of lead.

In the estimation of pure lead a certain quantity of it should be dissolved in a minimum of nitric acid, the solution diluted with water, carefully neutralised with ammonia or sodium carbonate, and excess of sodium acetate added, and the solution precipitated by the potassium bichromate solution. When the precipitation approaches its end, or when the precipitate commences readily to subside, some drops of a neutral solution of silver nitrate are deposited on a porcelain plate, and the potassium chromate solution only added by two or three drops at a time to the liquid under examination; after each addition the whole is well stirred, allowed to subside, and a drop of the clear supernatant liquor added to one of the drops of the silver solution. As soon as the potassium bichromate is in excess, the two drops form a red colour, while the precipitated lead chromate has no effect on the silver test, but simply floats on the top as a yellow precipitate. Should the solution assume a yellow colour before the silver reaction has commenced, it would indicate that not sufficient sodium acetate had been added in the first instance, and it would be necessary to add this now, and also a cubic centimètre of a normal lead solution, containing 0·0207 of lead as nitrate. The slight turbidity which first takes place soon goes off, and the operation may be proceeded with as before. One cubic centimètre must naturally, in such instance, be deducted from the amount of chrome solution, on account of the extra addition of lead.

Bismuth alone seems to interfere with the reaction, and behaves very like lead with chromic acid, and if present it requires a different mode of proceeding.

The higher oxide of mercury is not precipitated by potassium bichromate, not even in an acetic solution, while the lower oxide is; and, as it is difficult to peroxidise all the mercury when united with lead, even by long-continued boiling in nitric acid, it becomes necessary to evaporate and calcine the residue till all the mercury is volatilised. To obviate the formation of red lead, the calcined residue has to be moistened with a few drops of oxalic acid, and again dried and carefully calcined and dissolved in acetic acid; after this, the lead may be estimated as usual. To avoid the above calcinations, the mercury may be precipitated from the nitric acid solution by means of hydrochloric acid, and the liquid boiled till the calomel is converted into the higher chloride.

Copper, cadmium, zinc, iron, and cobalt do not in the least interfere with the reaction, provided the iron is peroxidised. Of the different acids, hydrochloric acid somewhat disturbs the last silver reaction, but by using larger drops, and allowing the reaction of silver chloride to go off, we obtain the usual silver chromate reaction.

Lead sulphate has first to be converted into the state of carbonate, by boiling with sodium carbonate, when it may be dissolved in acetic acid. Lead phosphate and arsenite, or other lead salts insoluble in acetic acid, may be dissolved in nitric acid, and estimated according to my older method.

3. BUISSON'S VOLUMETRIC PROCESS FOR ESTIMATING LEAD.

This process is based on the precipitation of lead by potassium bichromate and the decomposition of the excess of the reagent used by potassium iodide in a liquid acidulated with sulphuric acid. 0·5 to 1 gramme of the pulverised mineral to be tested is dissolved in dilute nitric acid. The solution is saturated with potash, and the precipitate redissolved in acetic acid. The iron is removed by boiling. To the solution separated from the iron 25 c.c. of potassium bichromate is added, and water to bring the volume up to 250 c.c. After standing for some time, the solution is filtered through a dry filter paper. To 100 c.c. of the clear liquid an excess of dilute sulphuric acid and potassium iodide are added in such a way as to redissolve the iodine set free, and then a few centimètres of starch. By means of a graduated burette, sodium hyposulphite is added until decolorisation of the starch iodide takes place. The difference of standard obtained by treating the bichromate alone, and after precipitation with a known weight of lead, gives a basis for calculating the amount of metal contained in the substance tested.

Silver, bismuth, copper, and baryta should be separated from the lead before applying this process.

4. W. Diehl proposes the following process for the volumetrical determination of lead ('Zeitschrift für Analytische Chemie'). He employs a $\frac{1}{20}$th normal solution of potassium bichromate, containing 7·38 grms. per litre, each c.c. representing 0·01035 grm. of lead, and a solution of sodium hyposulphite, containing 4 to 5 grms. per litre. To determine the relations between these two solutions, 20 to 30 c.c. water, and mixed with 20 to 25 dilute sulphuric acid (1 vol. monohydrated acid, and 2 vols. of water) a certain excess of sulphuric acid is indispensable, hydrochloric acid being less convenient. The liquid is brought to a boil, and the solution of hyposulphite is added drop by drop. The solution becomes gradually paler in colour. Towards the end, after the addition of a few drops, it is let boil up again. The end of the reaction may generally be distinguished by the liquid turning perfectly colourless, a result occasioned by a single drop. In order to judge of the colour, the flask towards the end of the operation may be set in a porcelain capsule. When very large quantities of bichromate are used the liquid does not become perfectly colourless, but slightly greenish.

In determining ores in this manner they are dissolved in aqua regia and dilute sulphuric acid, the solution concentrated till the sulphuric acid begins to evaporate, diluted with water, boiled to dissolve ferric sulphate, let cool, and filtered through a smooth filter, washing with water containing sulphuric acid. To the residue in the flask—as little as possible of which is thrown upon the filter—is added about 15 c.c. of a solution of neutral ammonium acetate, and about 50 c.c. of water. The whole is then boiled, and filtered through the same filter, into which a drop of ammonia has been put, into a flask. The same operation is then repeated with 5 c.c. ammonium acetate, and the residue is finally well washed with boiling water, to which a little of the same salt has been added. Thorough washing is necessary, since filters have been found to retain ammonium and lead acetate and tartrate with considerable obstinacy. It is then advisable further to wash the filter from its margin downwards with a little boiling dilute hydrochloric acid (1 part hydrochloric acid at sp. gr. 1·12 with 10 parts of water), and then to wash again with hot water. In this manner every trace of lead is removed from the filter. A thin filter paper should be used, and should be washed previously. The solution of lead sulphate in ammonium tartrate thus obtained is then titrated in the cold with potassium bichromate; with the aid of heat, ammonium acetate dissolves a little lead chromate. The precipitate settles readily if the flask is shaken, and the end of the reaction can be observed to within 0·2 to 0·4 c.c.

An excess of at least 2 c.c. of the chromate solution should be added, in order to obviate the solubility of the lead salt. It is advisable in every experiment to take as closely as possible an equal quantity. After thoroughly shaking, it is allowed to stand for half an hour and filtered. If the liquid passes through turbid, a few drops of a solution of sodium acetate, acidulated with acetic acid, are added. If, after all, a little lead chromate passes through the filter, the filtration is repeated. The precipitate is washed four times with cold water, and the solution is acidulated with sulphuric acid and titrated as above.

Ammonium acetate is preferable to all other ammonium salts as a solvent for lead sulphate. It is applied in a neutral or faintly acid state. Free ammonia renders the solution turbid. 1 grm. lead sulphate requires 15 c.c. of the liquid acetate for solution. Ammonium tartrate cannot be used.

For the detection of minute quantities of lead and copper (*e.g.* in the drainage of mines, &c.), Mr. Pattison Muir ('Chemical News,' January 14, 1876) proposes to use the method of Wanklyn, slightly modified (see 'Water Analysis,' Trübner and Co.).

CHAPTER XII.

THE ASSAY OF TIN.

THIS metal is always found by the assayer in the state of oxide.

Tin Oxide (SnO_2).—The appearance of this mineral gives no indication, excepting to an experienced eye, that metallic matter enters largely into its composition; yet its great density would lead one to suppose such to be the case. Its colour varies from limpid yellowish white to brownish black and opaque, passing from one to the other by all intermediate shades. It usually possesses a peculiar kind of lustre which cannot be readily described, but once seen can scarcely be mistaken. It occurs crystallised in square prisms, terminated by more or less complicated pyramids. These crystals, derived from the octahedron, are often macled or hemitropic, so that they often possess re-entering angles, which is to a certain extent characteristic. The principal varieties are the following:—

1. *Crystallised Tin Oxide* is found in more or less voluminous crystals of the colour and form as above.

2. *Disseminated Tin Oxide.*—This variety occurs in grains of various sizes, sometimes so small as not to be visible to the naked eye. It is found in the primitive rocks.

3. *Sandy Tin Oxide* forms pulverulent masses often of great extent; in appearance it is merely a brown sand.

4. *Concretionary Tin Oxide*, *Wood Tin.*—This variety occurs in small mamellated masses, the fibrous texture of which resembles that of wood; hence the name.

The following is an analysis of a sample of tin oxide from Cornwall:—

Tin	77·50
Oxygen	21·40
Iron	·25
Silica	·75

The following remarks on tin ore and the minerals which may be mistaken for it, are from the pen of Dr. A. Leibius, Senior Assayer of the Sydney branch of the Royal Mint.

The colour of native tin ore varies from white to pink, ruby-red, grey, greyish-black to black; it therefore is certainly no very reliable criterion for distinguishing tin ore.

A safer characteristic is the weight, or specific gravity, that of tin ore being 6·8 to 7·0. Unfortunately, however, the specific gravity of iron tungstate is nearly the same as that of tin oxide, in fact, a little higher, being 7·19 to 7·55.

Titaniferous iron has a specific gravity of from 4·5 to 5·0, and magnetic iron 4·9 to 5·2.

Basaltic hornblende and iron silicate have also been mistaken for tin ore; but the specific gravity of the former being only 3·1 to 3·4, and that of the latter 3·8 to 4·2, ought to have prevented such mistakes. The colour of the powdered ore forms a much better criterion than that of the unpowdered ore. The powder of good tin ore varies only from whitish-grey to dark drab, while iron tungstate powders reddish-brown, and titaniferous iron-black.

Most of the minerals appear to be mistaken for tin ore on account of their dark granular pieces having been taken for such; but Mr. Leibius has seen a sample, which consists of blackish pieces with about 50 per cent. of small indistinct crystals of a pink and dark ruby colour, with a few small white crystals. The whole mixture being pretty heavy, has certainly at first sight all the appearance of good tin ore. Even on closer inspection, when the darker portion just referred to might have been recognised as an iron compound, the ruby-coloured portion might readily pass muster for tin ore unless chemically examined. On further examination the whole sample was found to be *free* from tin. It was found to consist—1. Black portion, about 50 per cent. of the sample, having a specific gravity of 4·47, was found to be titaniferous iron. 2. Ruby-coloured and dark red pieces, about 50 per cent. of sample, with a specific gravity of 4·57, found to be zircons or hyacinths, showing the characteristic property, mentioned in Professor Thompson's excellent 'Guide to Mineral Explorers' (see *ante*, p. 288), of becoming completely and lastingly colourless when exposed to heat before the blowpipe. 3. Besides these zircons were found a few small topazes and garnets, and also a small sapphire. The specific gravity of the mixed sample as received was 4·55.

As already mentioned, there was actually no tin in the sample, and it forcibly illustrates the necessity of the precaution, in dealing with tin ore, to have it carefully assayed.

Assay of Pure Tin Oxide.—Pure tin oxide may be very readily assayed in the following manner:—Weigh off 400 grains, place them in either a black-lead or charcoal-lined crucible, cement on a cover by means of Stourbridge clay, and place in the fire. The heat should for the first quarter of an hour be a dull red, after which it may be raised to a full bright red for ten minutes, and the crucible removed with care so as not to agitate or disturb the contents; tapping in this case must not be resorted to. When the crucible is cold, remove the cover, and a button of pure tin will result; this weighed and divided by four gives the percentage. If the operation has not been carefully conducted it sometimes happens the tin is not in one button, but disseminated in globules either on the charcoal lining or on the sides of the black-lead pot; in this case the charcoal on the one hand, or the black-lead crucible on the other, must be pulverised in the mortar and passed through a sieve; the flattened particles of tin will be retained by the sieve, and can be collected and weighed. If any small particles escape the sieve, they may be separated from the lining or crucible by vanning.

If a charcoal or black-lead crucible be not at hand, an ordinary clay pot may be used, but not so successfully, excepting under certain circumstances to be hereafter described. Indeed, in Cornwall the ordinary mode of conducting this assay is in a naked crucible, thus: About 2 ounces of the ore are mixed with a small quantity of culm, and projected into a red-hot crucible. If the ore seems to fuse or work sluggishly, a little fluor-spar is added, and after about a quarter of an hour's fusing at a good high temperature, the reduced and fused tin is poured into a small ingot mould, and the slag examined for metal by pounding and vanning. This method never gives the whole of the metal. To effect this, without fear of mischance in the assay sometimes occurring, as already described with both blacklead and charcoal-lined crucibles, it may be thus conducted; always supposing the oxide to be pure, or nearly so, or at least containing little or no siliceous matter.

To 400 grains of ore add 100 grains of argol, 300 grains of sodium carbonate, and 50 grains of lime; mix well together, place in a crucible which the mixture half-fills, cover with a small quantity of sodium carbonate and 200 grains of borax. Place the whole in the furnace with the necessary precautions, raise the heat very gently, and keep it at or below a dull red heat for at least twenty minutes; then gradually increase until the whole flows freely. Remove the crucible, tap it as for copper assay, and allow to cool. When cold, break it, and a button of pure metallic tin will be found at the bottom, and a flux perfectly free from globules and containing no tin.

There is yet another process, which is more easy of execution; but the reagent employed is more expensive, not so readily obtainable, and more difficult to keep without decomposing than any of the substances above employed. The reagent now to be discussed has been introduced to the notice of the student, in another part of this volume, as a blowpipe flux, and in the assay of copper ores by standard solutions, as potassium cyanide. This is the most effective reducing flux for tin ores yet known. It acts by absorbing oxygen to form a compound known as potassium cyanate: thus—

$$SnO_2 + KCy = Sn + KO,CyO.$$

The assay, by means of this substance, may be made in ten minutes.

This method of estimating the value of tin-stone has been frequently practised by the writer, and has uniformly furnished correct results with but little expenditure of time and labour. The method of operating is as follows:—The sample having been carefully selected, is first crushed by the hammer in a steel mortar, and then further reduced to powder in an agate mortar. 100 grains is a convenient quantity to be taken for analysis, and it is always advisable to make two independent experiments upon the same sample of ore, with the view of having a control, and the highest result obtained is that upon which to place reliance, since the error must always be on the side of loss rather than excess. A couple of small Hessian crucibles, of about 3 oz. capacity, are prepared in the first instance by ramming into the bottom of them a small charge of powdered potassium cyanide sufficient to form a layer of about half an inch in depth; the weighed quantities of tin ore are then intimately mixed with from four to five times their weight of the powdered cyanide, and the mortar rinsed with a small quantity of the pure flux, which is laid upon the top of the mixture. The crucibles are then heated in a moderate fire, or over a gas-blowpipe, and kept for the space of ten minutes at a steady fusion; they are then removed, gently tapped to facilitate the formation of a single button, and allowed to cool. Upon breaking the crucibles, the reduced metal should present an almost silvery lustre, with a clean upper layer of melted flux. It is advisable to dissolve the latter in water, in order to be certain as to the absence of any trace of reduced metal or heavy particles of the original ore. There is always contained in the commercial cyanide a sufficient quantity of alkaline carbonate to secure the perfect fusion of the siliceous gangue, and other like impurities in the tin ore, but the operator should assure himself of the absence of copper and lead in the ore, either by preliminary treatment with hydrochloric acid, in which tin-stone is absolutely insoluble, or by testing the button of reduced tin after hammering or rolling for such metallic admixture. We have usually found a minute trace of iron, and sometimes gold in the melted buttons, but not so much as to add appreciably to their weight.

When worked with ordinary care, this process may be relied upon as giving numbers true to within ½ per cent., and we do not know any other method which exceeds this in accuracy and rapidity of execution. The following are a few analytical results taken at random from a number of ores assayed in this manner :—

	Tin per cent.	
	I.	II.
Sample No. 1	45·6	45·8
„ No. 2	57·2	57·6
„ No. 3	68·4	68·7

Assay of Tin Oxide mixed with Silica.—Although tin oxide is completely reducible by charcoal or other carbonaceous matter, yet it has such an affinity for silica, that whenever that substance is present the metal cannot be wholly reduced, excepting at the highest temperature of a wind furnace. The following experiments will show the influence of silica on the return of tin in an assay of oxide of that metal with black flux :—

Ore	100	100	100	100	100
Quartz	25	66	100	150	300

The first gave 52 per cent. of tin ; the second 43 per cent. ; the third, 28 per cent. ; the fourth, 10 per cent. ; and the last nothing.

The slags also produced in the treatment of tin ores in the large way give no return with black flux. This mode of assay, however, has been recommended by some, but from the foregone experiments is proved to be perfectly fallacious : that is, unless the quantity of silica present be very small in comparison to the amount of tin oxide ; and even when the latter is present in four times the quantity of the silica, as in experiment No. 1, a loss of 20 per cent of tin is sustained.

Assay of Tin Ores containing Silica and Tin Slags.—It having just been shown how injuriously the presence of silica influences the produce of tin, both in ores and slags, other methods of assay than those just described must be adopted for such substances. These will now be detailed.

Tin ores containing silica may be treated by two methods: in the first the silica must be carefully separated by vanning; if the ore be well pulverised this is the best and most expeditious method. In conducting this assay take 400 or more grains of the pulverised ore, according to its richness (if poor, as much as 2,000 grains may be taken), van it carefully, dry the enriched product, which will, if the operation has been properly conducted, be nearly pure oxide of tin, and assay it as already described for ores containing no silica. The other process of assay may be thus conducted, and is dependent upon the fact that iron displaces tin from its combination with silica: thus, if a compound of tin oxide and silica be heated to whiteness with metallic iron, a portion of the iron oxidises and replaces the tin oxide, which was previously in combination with the silica as a tin silicate, and metallic tin and iron silicate result, the tin so reduced combining with any metallic iron that may be in excess, and the button thus obtained is an alloy of tin and iron, whilst the slag is entirely deprived of tin.

In this kind of assay mix 400 grains of the siliceous tin oxide with 200 grains of iron oxide (either pulverised hæmatite or forge-scales will answer this purpose), 100 grains of pounded fluor-spar, and 100 grains of charcoal powder: place the mixture in a crucible and cover with a lid, gradually heat to dull redness, and keep at that temperature for half an hour, then heat to whiteness for another half-hour, and remove the crucible from the furnace, allow to cool, and break. The button so obtained is to be treated in the wet way, as hereafter described.

The assay of tin slags is conducted in the same manner, or simply by mixing the pulverised slag with 20 per cent. of iron filings, and fusing.

Assay of Tin Ores containing Arsenic, Sulphur, and Tungsten (*Wolfram*).—In the assay of such ores it is necessary to remove arsenic, sulphur, and tungsten, before attempting to obtain the tin in a pure state by the dry assay. Ores of tin which contain either one or all of these substances are most common: hence this mode of treatment will be generally required.

Most assayers usually submit the ore to the same mode of treatment which it undergoes on the large scale by calcination, or rather roasting, by which the greater part of the arsenical and pyritic matter is removed; this process fails, however, to remove the whole of these substances, and does not at all affect the tungsten. The following process is therefore preferable, and is founded on the fact that arsenical and other pyrites, as well as iron tungstate (wolfram usually accompanying tin ores), are completely decomposed by nitro-hydrochloric acid (*aqua regia*) at the boiling temperature, the oxide of tin alone not being affected:—Take 400 grains or more of the impure tin sample, place them in a flask, and add 1½ ounce of hydrochloric acid, and ½ an ounce of nitric acid, heat gently for about half an hour, and then boil until the greater part of the mixed acids have evaporated; the sulphur and arsenic will by this time be converted into sulphuric and arsenic acid, and the wolfram completely decomposed, its iron and manganese having become soluble, and its tungstic acid remaining in the insoluble state with the oxide of tin and any silica that may be present. Allow the flasks and contents to cool, add water, allow to settle, and decant, and so on until the water passes off tasteless. The insoluble matter in the flask is now tin oxide, silica, and tungstic acid; to remove the latter, digest for an hour at a very gentle heat with one ounce of solution of caustic ammonia, with occasional agitation; add water, and van the remainder to separate silica; nothing remains now but tin oxide, with perhaps a little silica: this is now to be dried and assayed as directed for ores containing little or no silica.

If only an approximative assay be needed, it may be accomplished after this treatment by taking the specific gravity of the remaining oxide, so that all ores of tin may be thus roughly assayed, it being premised that the above operation has been so carefully performed that nothing but tin oxide and silica remain. The specific gravity of the thus purified ore is to be taken. All now that is necessary to be known is the specific gravity of tin oxide, its percentage of pure tin, and the specific gravity of silica, and a simple calculation gives the result. The following is the formula:—

Let a represent the specific gravity of tin oxide.
" b " " " silica.
" c " " " the mixture left after treatment with acid, &c.
" w " weight of rough tin oxide or mixture left after treatment with acid, &c.
" x " " " tin oxide.
" y " " " silica.

$$\text{Then } x = \frac{a\,(c-b)}{c\,(a-b)}w;$$

$$\text{And } y = \frac{b\,(a-c)}{c\,(a-b)}w.$$

Or in arithmetical form thus—

1. From the specific gravity of the rough tin oxide (mixture of tin oxide and silica) deduct the specific gravity of the silica.
2. Multiply the remainder by the specific gravity of the tin oxide.
3. Multiply the weight of the rough tin oxide by the last product, which will make a second product, which may be called P.
4. From the specific gravity of tin oxide deduct the specific gravity of silica.
5. Multiply the difference by the specific gravity of the rough tin oxide.
6. Take this product for a divisor to divide the above product P: the quotient will be the weight of pure tin oxide in the rough oxide, and the quantity of metal can now be readily calculated.

The following is an assay worked out in this manner:—

400 grains of the ore are treated with nitro-hydrochloric acid and ammonia as above described, washed, and dried. Suppose the dried matter weighed 250 grains. The 250 grains thus obtained are placed in the specific gravity bottle, and the specific gravity is found to be 5·4.

Specific gravity of tin oxide (approximate) . . . 6·9
" silica " . . . 2·6

Sp. Gr. Rough Oxide 5·4	−	Sp. Gr. Silica 2·6	=	2·8
2·8	×	Sp. Gr. Pure oxide 6·9	=	19·32
Weight of Rough Oxide 250	×	19·32	=	P 4830
Sp. Gr. Pure oxide 6·9	−	Sp. Gr. Silica 2·6	=	4·3
4·3	×	Sp. Gr. Rough Oxide 5·4	=	23·22

$$\frac{4830}{23{\cdot}22} = 208{\cdot}4$$

208·4 grains is therefore the weight of pure oxide in the 400 grains of ore.

Now tin oxide contains 78·61 parts of pure tin, and a

$$\frac{208{\cdot}4 \times 78{\cdot}61}{100} = 163{\cdot}72$$

So that 400 grains of rough tin ore contain 163·72 grains of pure tin, and

$$\frac{163{\cdot}72}{4} = 40{\cdot}93.$$

The rough sample first operated on contains, therefore, 40·93 per cent. of metallic tin.

Another satisfactory method of assaying tin in the presence of tungsten has been described by Mr. J. H. Talbott.

The method is based on the fact already mentioned that tin oxide is reduced by potassium cyanide with great facility; while tungstic acid undergoes no reduction, even when heated with the cyanide at a high temperature. The tin and tungsten oxides are to be heated in a porcelain crucible with three or four times their weight of commercial potassium cyanide previously fused, pulverised, and thoroughly mixed with the two oxides. The mass is kept fused for a short time, when the tin separates in the form of metallic globules, while the tungstic acid unites with the alkali of the potassium cyanate and carbonate present. After cooling, the mass is to be treated with hot water, which dissolves the alkaline tungstate and other salts, and leaves the tin as metal; this is to be separated by filtration, washed, dried, and weighed as tin oxide, after oxidation in the crucible with nitric acid. The tungstic acid may be estimated by difference, or be precipitated by mercury protonitrate, after boiling the solution with nitric acid to decompose the excess of potassium cyanide present, and then re-dissolving the precipitated tungstic acid by means of an alkali.

Estimation of Tin by the Wet Method. — There are several methods of effecting this analysis, the chief difficulty being found in the intractable nature of the tin oxide, it resisting the action of all acids. This, however, may be overcome as first shown by Klaproth, who found that very finely levigated tin oxide was soluble in hydrochloric acid after a prolonged fusion with caustic potash: the following is his process:—

Fifty grains of the tin ore, reduced to the most minute state of division by levigation or otherwise, is mixed with four times its weight of caustic potash. The best mode of mixing is to place the caustic potash in a silver crucible, add its own weight of water, and apply a gentle heat until the potash is dissolved ; then stir in tin ore, and gradually evaporate to dryness, stirring all the time to prevent loss by spirting, as in the analysis of iron-stone : when thoroughly dry, enclose the silver crucible in one of clay, and submit the whole to a dull red heat for at least half an hour : rather more than less renders the perfect solution of the tin oxide more certain. When cold, act on the contents of the crucible with dilute hydrochloric acid, transfer the liquid and any undissolved matter to a flask, add some strong hydrochloric acid, and boil for half an hour. If at the end of this time any of the tin ore remains unacted on, it must be separated by decantation or otherwise from the solution, dried, again fused with potash, and then treated with hydrochloric acid, in which it will now be found totally soluble. This second operation will not be needed if care has been taken to reduce the ore to the finest possible state of division at first. The solution, however obtained, is to be evaporated to dryness, and when cold treated with a small quantity of hydrochloric acid, allowed to stand for half an hour, then water added, boiled and filtered : the whole of the tin will pass through in solution as tin chloride, and any silica or tungstic acid that may be present will remain in the filter. If the ore contained copper, lead, and iron, these metals will also be in solution —at all events, the lead partially so ; but if the ore had, previously to its fusion with caustic potash, been treated with *aqua regia*, as already described, then it will contain tin alone. It is always better thus to separate foreign matters before attempting the solution of the tin, as the after process is thereby simplified. Supposing, however, that the rough ore had been submitted to fusion with potash and then dissolved, the solution must be treated thus :—A bar of zinc must be placed in the solution, which will in course of time precipitate tin, copper, and lead; when all the metals are thus thrown down the zinc is washed and removed, the precipitated metals well washed and dried. To the dried metals strong nitric acid is now to be added, the mass gently heated, and then evaporated to dryness: when cold, it is moistened with dilute nitric acid, water added, and the whole filtered. Lead and copper will pass through the filter as soluble nitrates, and the tin will be found in the filter as insoluble peroxide; this is to be well washed, dried, ignited, and weighed. It contains 78·61 parts of metallic tin. The amount of tin thus obtained, when multiplied by two, will represent the percentage of the ore.

If, before the action of caustic potash, the ore had been submitted to the action of *aqua regia*, sulphuretted hydrogen may be passed through the solution of tin chloride, when tin sulphide will be precipitated; this is to be washed, dried, gently calcined in a platinum crucible until all smell of sulphurous acid has ceased, allowed to cool, reheated with a fragment of ammonium carbonate, as in the case of roasting copper sulphide, and when cold weighed as pure oxide of tin. The calculation for metal is made as above.

Mr. J. W. B. Hallet has found that tin-stone is very easily resolved by fusion with three or four times its weight of potassium fluoride. The mineral must be finely pulverised. The fused mass is treated directly in the crucible with sulphuric acid to expel fluorine, after which, by adding water, filtering, and boiling the filtrate, the whole of the tin is thrown down as stannic acid, which is to be separated from traces of iron in the usual manner. This method of resolving the ore of tin is much more convenient than fusion with caustic alkalies, or with sulphur and carbonate of sodium.

M. Moissenet precipitates the metal from a solution of the chloride by means of zinc, and then melts the precipitated metal in stearic acid. His process comprises five operations:—

1. Purification of the ore by treatment with *aqua regia*.
2. Reduction of the residue in the presence of charcoal.

3. Solution of the tin and iron in hydrochloric acid.
4. Precipitation of the tin by means of zinc.
5. Fusion of the precipitate into a button in stearic acid.

The precipitation of tin by zinc is very rapid, and takes place in strongly acid solutions : but the amount of acid and the dilution of the chloride influence the condition of the precipitate. In some solutions it appears in brilliant needles, but in very dilute solutions, and always towards the end of an operation, it is only a muddy deposit. The author recommends that a button of zinc be suspended in the liquid by means of a copper wire. When the precipitation is finished, the metal is collected and pressed into a porcelain capsule. The lump so formed is melted in a few minutes if a piece of stearine is added to it.

Assay of Tin in Gun- and Bell-Metal.—The following process has been employed for some years in H. Sainte-Claire Deville's laboratory :—Dissolve about 5 grms. of the alloy in strong nitric acid contained in a flask provided with a funnel in the neck to prevent loss by spirting. When quite dissolved boil the strong solution for about twenty minutes ; dilute with two or three times its bulk of water and boil again for the same time. Separate the insoluble tin oxide by decantation, or filtration, and weigh after calcining it. (The tin oxide is sometimes rose-coloured, owing to the presence of minute traces of gold ; this may be disregarded.) The nitric acid solution freed from the tin is evaporated on a small platinum or porcelain dish, and the residue is calcined at a dull red heat. In this manner a mixture of oxides is obtained in a sufficient quantity to suffice for at least two analyses.

About 2 grms. of the finely pulverised oxides are placed in a small platinum or porcelain boat, and thence introduced into a small glass tube closed with a good cork suitable for weighing. The boat, the tube, and the cork having been previously weighed, the weight of the oxides is obtained after they have been heated to dull redness in the apparatus, through which a current of dry air circulates. After having weighed the whole, the current of air is replaced by dry hydrogen, and the tube is heated over a lamp until the contents cease to lose weight. It then contains unreduced zinc oxide together with copper, lead, and iron in the metallic state; the colour of the product shows the operator when the experiment is concluded. On weighing again the loss of weight indicates with great accuracy the amount of oxygen contained in the oxides of these three metals.

If the iron and lead are present in inappreciable quantities, by multiplying this loss by 5 will be given very nearly the weight of copper present, and, in consequence, the composition of the alloy itself.

For bronze, bell-metal, gun-metal, etc., E. Burse ('Zeitschrift für Analytische Chemie,' 1878, p. 58) proceeds as follows: 1 grm. of the alloy, cut in pieces, is placed in a beaker, covered with 6 c.c. nitric acid, of sp. gr. 1·5: 3 c.c. water are then slowly poured in and the beaker quickly covered. When the whole is dissolved it is heated to a boil and diluted with 500 c.c. boiling water. The tin oxide, after it is completely settled, is washed with boiling water, and weighed. The filtrate, for the expulsion of nitric acid is evaporated with two grms. sulphuric acid, and the copper, with the addition of sulphurous acid, is precipitated with a solution of 2 grm. ammonium sulphocyanide. The copper sulphocyanide, after settling, washing, and drying, is weighed as such, or is converted into sulphide. The filtrate is concentrated with the addition of nitric acid, and mixed with ammonia in excess. If iron oxide is deposited it is filtered off and weighed. The ammoniacal solution of zinc is mixed with ammonium sulphide, avoiding excess, the sulphide when deposited is filtered off, dried, and, after ignition with sulphur in a current of hydrogen, weighed.

Estimation of Tin by means of a Standard Solution.—The first process to be described is due to M. Gaultier de Claubry, and may be thus performed: The standard solution is made by dissolving 100 grains of iodine in 1 quart of proof spirit (spirit of wine having a specific gravity of ·920), and is thus standardised. Ten grains of pure tin are dissolved in excess of hydrochloric acid, the solution boiled, and allowed to cool: the burette is now filled with the solution of iodine, which is gradually added to that of the tin until the former ceases to be decolorised; as soon, therefore, as the tin solution assumes a faint yellow tinge, sufficient iodine has been added; the quantity thus found sufficient is then noted, and the amount of tin each division of iodine solution is equivalent to, is calculated as for iron, copper, and the other standard solutions.

In the actual assay of tin ore by means of this solution it is necessary that the whole of the tin present be reduced to the state of protochloride: this may be readily effected by boiling the solution of tin for a quarter of an hour with excess of metallic iron, and filtering. To the solution so obtained the iodine is added as above. The tin ore is dissolved by any of the methods already described.

M. Lenssen * estimates tin by means of the iodine solution, but he operates in a liquid containing double potassium and sodium tartrate, and sodium bicarbonate in excess. The results M. Lenssen obtained by this method are satisfactory, by using the atomic weight of tin generally adopted (59). We shall see farther on why M. Lenssen's results agree.

M. Stromeyer † having recently occupied himself with the same subject, has succeeded in solving the difficulty. The solution of stannous chloride is carefully introduced into an excess of ferric chloride. The salt of iron becomes reduced to a minimum, according to the following equation:—

$$2Sn + 2(Fe_2Cl_6) = 2SnCl_2 + 4FeCl_2.$$

It is then estimated by permanganate, as if it were a salt of iron protoxide. The results M. Stromeyer obtains in this way are very exact. The author adds that such a method of estimating is applicable only in the absence of copper or iron, as these two metals decompose potassium permanganate as well as the tin; but it may be of great use in the estimation of commercial salts of tin.

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* 'Annalen der Chemie und Pharmacie,' vol. cxiv. p. 114.

† *Ibid.* vol. cxvii. p. 261.

A method for the analysis of tin ore consists in reducing the finely-powdered ore, in a hand porcelain vessel, in a current of hydrogen gas. A bright red heat must be applied and maintained for a considerable time. The sample is allowed to cool in a current of hydrogen and weighed, the operation being preferably repeated to make sure that the reduction is complete. The loss of weight gives the quantity of stannic acid, tin peroxide (1 part by weight of oxygen representing 4·673 parts tin peroxide), if no other oxide is present which may be reduced at the same time. But as tin-stone contains almost always iron oxide, part of the loss is due to this compound, so that the crucible, with its contents, should be digested in a beaker with hydrochloric acid. When dissolved, it is diluted, filtered into a large flask, the quantity of the residue (silica, etc.) determined, the liquid supersaturated with ammonia, a sufficient quantity of ammonium sulphide added with flowers of sulphur, so as to convert the stannous sulphide into stannic sulphide, which then dissolves in the ammonium sulphide. The whole is digested in the flask, loosely stoppered, till the black iron sulphide is separated from the yellow liquid, filtered under cover, washed with the addition of a little ammonium sulphide, dissolved in hydrochloric acid, oxidised with potassium chlorate, and the ferric oxide (iron peroxide) precipitated with ammonia. The tin may be directly determined by precipitating the solution of sulphide with dilute sulphuric acid, using a slight excess. The vessel is loosely covered with paper, and very gently heated, till it no longer smells of sulphuretted hydrogen. The yellow tin sulphide is washed upon the filter, dried enough to enable it to be taken out of the funnel along with the paper, and heated very gently, for a considerable time, in a porcelain crucible, at first covered and then open. When the odour of sulphurous acid is no longer perceptible, the contents of the funnel are moistened with a few drops of nitric acid, and are then gradually heated, with excess of air, ultimately to full redness. The tin sulphide is thus converted into stannic acid, which is heated for a short time with a little ammonium carbonate to remove every trace of sulphuric acid.

In another method for the assay of tin-stone, the finely-ground sample is mixed in a porcelain crucible with 3 parts sodium carbonate, and 3 parts of sulphur, and the mixture is melted—covered—over the lamp. When cold, the crucible is laid in water, and heat is applied till the mass dissolves, iron or other electro-positive metals remaining as a black sulphide, which is filtered off, washed, and when dry ignited in the air, in order to convert it into iron oxide. From the dilute alkaline solution the tin sulphide is precipitated by dilute sulphuric acid, as directed above.

In case of impure tin ores, the insoluble sulphide may consist of iron, zinc, copper, and bismuth; whilst the soluble, along with the tin, may contain arsenic, tungsten, and molybdenum. A process for the separation of tin from tungsten has been given at p. 487.

Tin slags are decomposed by means of *aqua regia*, and the tin, etc., precipitated by a current of sulphuretted hydrogen.

Tin furnace products may be in part alloys of tin and iron, lead, tungsten, cobalt, and arsenic. They are finely powdered, digested with *aqua regia*, the tin thrown down with sulphuretted hydrogen, and the tin sulphide treated as already directed. If the proportion of tungstic acid is considerable, after digestion in *aqua regia* and diluting, the tungstic acid separates along with some stannic acid. This deposit is filtered off, washed, dried, and repeatedly ignited with sal-ammoniac, in a covered porcelain crucible, till the weight of the residual tungstic acid is constant. The stannic acid is found as difference. Sulphuretted hydrogen is then passed into the acid solution (from which the tungstic acid has been deposited); the remaining tin is thus precipitated as sulphide, and is filtered off. Iron and manganese are determined in the filtrate. (*F. Rammelsberg's Quant. Chem. Analyses.*)

We have seen that M. Stromeyer, by a happy modification, has reduced the estimation of tin to that of iron. Applying the same principle, a salt of copper may be substituted for a salt of iron. An equivalent quantity of copper can thus be estimated in place of tin; and M. Mohr's as well as M. Terreil's * experiments show that copper can be very exactly estimated by permanganate of potash.

A double decomposition takes place on protochloride of tin being added to nitrate or chloride of copper in excess; a salt of suboxide of copper forms, and the tin passes to the maximum state of oxidation, according to the following equation:—

$$4CuO + 2SnCl_2 = 2Cu_2O + SnCl_4 + SnO_2.$$

To estimate tin it is, then, sufficient to transform it into protochloride, to add to it a solution of nitrate of copper slightly in excess, before diluting it with water, and to titrate the liquid obtained by permanganate of potash.

There are then three different processes for estimating tin by potassium permanganate:—1. To operate with water freed from air by boiling, protecting it from access of air while cooling. 2. To oxidise protoxide of tin in an alkaline medium. 3. To decompose stannous chloride either by a salt of iron, as proposed by M. Stromeyer, or by a salt of copper.

Alloys of tin and lead, such as solder, inferior tinfoil, and the coating of terne plates, may be treated thus, according to Rammelsberg:—

Oxidise with nitric acid; evaporate to dryness in the water-bath; heat the residue rather more strongly; moisten with nitric acid when cold; dilute and separate the stannic acid (tin peroxide) by filtration, washing till the filtrate has no longer an acid reaction. When dry the precipitate is detached from the filter, and placed in a porcelain crucible; the paper is burnt on the lid, the

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* *Comptes-Rendus*, vol. xlvi. p. 230.

ash added to the contents of the crucible, moistened with a few drops of nitric acid, heated, and finally ignited. The tin is calculated from the stannic acid.

In the filtrate the lead is determined as sulphate by the addition of sulphuric acid. (See ‘Separation of Lead from Copper and Zinc.’)

CHAPTER XIII.

THE ASSAY OF ANTIMONY.

ANTIMONIAL substances susceptible of being assayed by the dry way are divisible into two classes.

CLASS I. In this class are comprised native antimony and all antimonial substances containing oxygen or chlorine, and but little or no sulphur.

These substances are the following:—

Native antimony, Sb,
Antimony oxide, Sb_2O_3,
Antimonious acid, Sb_2O_4,
Antimonic acid, Sb_2O_5.

CLASS II. includes antimony sulphide and all antimonial ores containing much sulphur.

Antimony sulphide, Sb_2S_3,
Antimony oxysulphide, $Sb_2O_3 + 2Sb_2S_3$,
Haidingerite, $2Sb_2S_3 + 3FeS$.

ASSAY OF ORES OF THE FIRST CLASS.

All antimony oxides are very readily reduced by charcoal; so that their assay presents no difficulty. The assay is conducted in precisely the same manner as that of lead oxide; only, as antimony is much more volatile than lead, the heat must be managed with care, and the assay taken from the fire as soon as finished. When all suitable precautions are taken, the loss of antimony is not very considerable; but Berthier says it is never less than from 5 to 6 per cent. This, we think, is too high. Thus the pure protoxide gives 77 per cent. of metal, and antimonious acid 75. The reduction is readily made, without addition, in a charcoal crucible; but when the substance to be assayed is mixed with impurities, some flux must be added. It succeeds equally well with 3 parts of black flux, with 1 part of tartar, with 1 part of sodium carbonate, and 15 per cent. of charcoal, or any other equivalent reducing flux.

When the substance under assay contains iron oxide, the latter oxide is more or less reduced, and the metallic iron alloys with the antimony.

Oxidised minerals which contain but a small quantity of sulphur can also be assayed in this manner; because the sulphide gives up to black flux the small quantity of antimony which it contains, so that but little remains in the slag. The common glass of antimony produces by this method of assay 70 per cent. of antimony, and occasionally even more than that.

The ores of this class occur very seldom, and are only in rare cases subject to assaying.

ASSAY OF ORES OF THE SECOND CLASS.

As pure antimony sulphide (antimonium crudum) as well as metallic antimony (regulus of antimony) are mercantile substances, the assays of the ores of this class have for their object the determination of both these bodies.

1. ASSAY OF PURE ANTIMONY SULPHIDE (ANTIMONIUM CRUDUM).

Antimony sulphide is almost the only mineral from which antimonium crudum is produced. This mineral generally occurs intermixed with very refractory gangue (gneiss, quartz, limestone, etc.). Antimony sulphide fuses readily at a low red heat, and is not changed during fusion, if atmospheric air is precluded. At a white heat it volatilises without change of composition.

The assay of antimony sulphide is now effected by a liquation process, *i.e.* by heating the mineral sufficiently in order to melt the antimony sulphide, and, by this means, to separate it from the refractory gangue. The production of antimony sulphide on a large scale is done in the same way.

For the purpose of assaying, two pots or crucibles are used, one standing in the other, and leaving sufficient space between the two to receive the fused antimony sulphide. The bottom of the inside crucible is furnished with holes. The mineral to be assayed is put into the inside crucible, the latter is then closed with a cover, and hermetically luted; the joints of the two crucibles are also luted. The under crucible is then put on the hearth of a furnace, enclosed with ashes or sand, in order to keep it cool, and the upper crucible, as far as it is outside of the under crucible, is covered with coal, and heated to a moderate red heat. The antimony sulphide will then melt and collect in the under crucible, from which it may be taken out, after cooling, and weighed.

2. ASSAY OF REGULUS OF ANTIMONY.

This assay may be made in two ways: first, by roasting and fusing the oxidised matter with black flux; secondly, by fusing the crude ore with iron, or iron scales, with or without the addition of black flux.

The roasting of antimony sulphide requires much care, for it is very fusible and volatile, as is also the oxide its decomposition gives rise to. The heat ought to be very low during the operation, and the substance continually stirred. When no more sulphurous acid is given off, we may feel assured that it is perfectly roasted, because no sulphate is ever formed in this operation.

The roasted sulphide is then fused with three parts of black flux, or its equivalent.

Metallic iron very readily separates all the sulphur from antimony sulphide; but as iron sulphide has a specific gravity near that of antimony, the separation is very difficult to manage: a strong fire must be employed when the desulphurisation is complete, to keep the whole body in full fusion, for a considerable time. With these precautions, two buttons are obtained, which separate very well: the one white, and in large plates, which is antimony; and the other a bronze yellow, a little brighter than the ordinary iron sulphide, because it is mixed with a little metallic antimony. During the operation a considerable portion of antimony is always volatilised, which, by this process, is an inconvenience impossible to avoid.

It is, nevertheless, practised in the large way in some factories; but a good result is not generally obtained. It, however, appears that when all the necessary precautions are taken, it can be employed with advantage.

The first precaution which is indispensable is, mixing with the sulphide only the precise proportion of iron necessary to effect its decomposition, which quantity amounts to about 42 per cent. of its weight. If more be used, the antimony, having a great tendency to play the part of an electro-negative element, will combine with the surplus, and an iron antimonide results, part of which will remain in the antimony and part in the slag.

Further, the iron ought to be in the finest possible state of division. If the masses be large, a portion of antimony sulphide is volatilised before they can be fully attacked. In general, 63 per cent. of antimony can be extracted from sulphide by the aid of iron in the small way, but on the large scale it seems that 55 per cent. is the maximum.

Cast iron cannot be employed instead of wrought, because sulphur has very little action on it. The desulphurisation is imperfect, and the slag adheres to the reduced metal.

One of the greatest inconveniences in separating sulphur from antimony by means of iron is the strong heat necessary to separate the slag from the metal. This might be remedied by making the slag more fusible and less heavy, by the addition of some flux, as an alkaline carbonate or sulphate.

If antimony sulphide be fused with an alkaline carbonate and charcoal, a regulus is obtained, and a slag composed of an alkaline sulphide and antimony sulphide. If metallic iron be thrown into this slag whilst in fusion, all the antimony separates immediately, and a new slag is formed as fluid as the former, containing iron sulphide and a sulphide of the alkaline base employed. If, instead of the above process, the iron be mixed intimately with the antimony sulphide and carbonated alkali, the result is the same—100 parts of sulphide, 42 of metallic iron, 50 of sodium carbonate mixed with one-tenth of its weight of charcoal, or 50 of black flux, give 65 to 66 of regulus; with the same proportion of iron, and only 10 of flux, only 62 per cent. can be obtained. In these two cases the fusion takes place very rapidly and without bubbling, and the slag, which is very liquid, separates readily from the metal. By employing 1 part of alkaline flux, the proportion of iron can be reduced from 25 to 30 per cent., and the product of metal is always from 65 to 66 per cent.

Hence, in making an assay of antimony sulphide, it is always better to employ a smaller quantity of iron than is necessary to complete the desulphurisation, and make up for it by increasing the quantity of flux: then it may be ensured that no excess of iron will be present.

The alkaline sulphates are decomposed into alkaline sulphides by the agency of charcoal at a slightly elevated temperature. The sulphides of the alkaline metals, by combining with the other metallic sulphides, augment their fusibility very considerably. Thus when sodium sulphate, mixed with about one-fifth of its weight of charcoal, is added to a mixture of antimony sulphide and metallic iron, the metallic antimony separates very rapidly, and the slag almost instantly becomes perfectly fluid.

But it must be noted that the presence of an alkaline sulphide diminishes the product of regulus, unless the proportion of iron be augmented at the same time.

For instance, with

100 parts of antimony sulphide,
42 parts of iron,
100 parts of sodium sulphate,
20 parts of charcoal,

but 22 parts of regulus were furnished; but with

100 parts of antimony sulphide,
42 parts of iron,
10 parts of sodium sulphate,
2 parts of charcoal,

62 parts of antimony were easily obtained.

Instead of metallic iron, pure iron oxide may be used, or any ferruginous matter whatever, provided it is rich; but it is necessary to add, at the same time, an alkaline flux and charcoal to reduce the iron oxide.

Not less than 40 parts of iron scales can be employed for 100 of antimony sulphide, and then, on the addition of 50 to 100 parts of sodium carbonate and 8 to 10 of charcoal, about 56 of regulus are obtained; but if with 100 parts of sodium carbonate from 14 to 15 parts of charcoal be employed, 65 parts of antimony are the result. By augmenting the proportion of scales, that of soda may be diminished. Thus, if from 56 to 60 parts of scales, 10 of soda, and 10 of charcoal be employed, 50 parts of regulus are the result; and if the proportion of soda be 50, and that of carbon 10, from 65 to 66, and even 67, parts of regulus are obtainable.

The fusion always takes place quickly, and the slags are very fluid.

When antimony sulphide is fused with forge slag (ferrous silicate), sodium carbonate, and charcoal, a very white crystalline regulus, in large plates, is obtained; together with a bronze-yellow matt, and a black, opaque, vitreous slag, shining like jet, in which the greatest portion of the alkali employed appeared to be concentrated.

These three substances separate very readily from each other.

100 parts of antimony sulphide,
80 parts of forge slag,
50 parts of sodium carbonate,
10 parts of charcoal,

produced very readily 60 parts of regulus.

Antimony sulphide may also be analysed by boiling with aqua regia. The residue consists of sulphur and gangue. It is to be washed and dried, then weighed and ignited. The loss will be sulphur, and the remainder is pure gangue.

Water is then added to the filtered solution, which will cause the precipitation of some of its contained antimony as oxychloride: this must be separated by filtration. The solution is then to be saturated with potassium carbonate, and a new precipitate will be formed. The solution is to be filtered, and made slightly acid; then barium nitrate must be added to it to separate its sulphur as barium sulphate, which is to be washed, dried, and weighed: its weight indicates the amount of sulphur: 116 parts are equal to 16 parts of sulphur.

The precipitate by water of oxychloride which remains on the filter is redissolved by hydrochloric acid, and its antimony separated in the metallic state by means of zinc. The precipitate formed by potassium carbonate may contain lead, copper, iron, and antimony. It must be treated with nitric acid; this dissolves everything but the antimony, which may then be estimated as antimonic acid.

It is always best, before conducting the analysis of antimony sulphide, to affuse it with very dilute hydrochloric acid, in order to dissolve a portion of the calcium carbonate, which may form part of the gangue. As the composition of the antimony sulphide is constant, the following process is sufficient in the assay of an antimonial ore:—

Boil the ore, after treatment with dilute hydrochloric acid, with concentrated hydrochloric acid, which dissolves only antimony sulphide, and precipitate the metal as oxychloride by means of water.

Or, after all gangue soluble in dilute hydrochloric acid has been removed, the residue may be weighed, and then acted on by boiling hydrochloric acid, until all action ceases. The residue must be well washed with weak hydrochloric acid, dried, ignited, and weighed; the loss of weight corresponds to the percentage of pure antimony sulphide, which contains 72·7 per cent. of metal.

Franz Becker (‘Zeitschrift für Analyt. Chemie,’ 1878, p. 185) mixes 1 part of the ore with 3 parts sodium carbonate, and 3 parts sulphur; melts in a porcelain crucible, extracts with hot water, decomposes the filtrate with hydrochloric acid, and converts the antimony sulphide into oxide in the usual manner.

The following method of determining antimony is given by Mr. Sutton:—

The oxide of the metal, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralised by neutral sodium carbonate, then a cold saturated solution of sodium bicarbonate added in the proportion of 20 c.c. to about 0·1 grm. of Sb_2O_3; to the clear solution starch liquor and $\frac{N}{10}$ iodine are added until the blue colour appears; the colour disappears after a little time, therefore the first appearance of a permanent blue is accepted as the true measure of iodine required.

$$1 \text{ c.c. } \tfrac{N}{10} \text{ iodine} = 0{\cdot}0061 \text{ grm. Sb.}$$

Detection of Antimony in Sublimates.—In the examination of mineral bodies for antimony, the test substance is often roasted in an open tube for the production of a white sublimate. Dr. E. Chapman, Professor of Mineralogy at Toronto, recommends for the detection of antimony in this substance the following process—a method more especially available when the operator has only a portable blowpipe-case at his command:—The portion of the tube to which the chief part of the sublimate is attached is to be cut off by a triangular file, and dropped into a test-tube containing some tartaric acid dissolved in water. This being warmed, or gently boiled, a part at least of the sublimate will be dissolved. Some potassium bisulphate—either alone, or mixed with some sodium carbonate and a little borax, the latter to prevent absorption—is then to be fused on charcoal in a reducing flame; and the alkaline sulphide thus produced is to be removed by the point of the knife-blade, and placed in a small porcelain capsule. The hepatic mass is most easily separated from the charcoal by removing it before it has time to solidify. Some of the tartaric acid solution is then to be dropped upon it, when the well-known orange-coloured precipitate of antimony sulphide will at once result.

In performing this test, it is as well to employ a somewhat large fragment of the test substance, so as to obtain a thick deposit in the tube. It is advisable also to hold the tube in not too inclined a position, in order to let but a moderate current of air pass through it; and care must be taken not to expose the sublimate to the action of the flame, otherwise it might be converted almost wholly into a compound of antimonious and antimonic acids, the greater part of which would remain undissolved in the tartaric acid. A sublimate of arsenious acid, treated in this manner, would of course yield a yellow precipitate, easily distinguishable by its colour, however, from the deep orange antimonial sulphide. The crystalline character, &c., of this sublimate would also effectually prevent any chance of misconception.

To distinguish Arseniuretted Hydrogen from Antimoniuretted Hydrogen.—On passing a mixture of these two gases through a tube containing solid pieces of caustic potash, these become covered with a brilliant metallic coating of antimony, whilst the arseniuretted compound escapes undecomposed. A lye of potash, density 1·250, only acts very slightly in a similar case. The fragments of potash which have become metallised by the deposit of antimony are altered in the air; they soon become white in water, the metallic coating falling to the bottom; but when they are attempted to be collected on a filter they dissolve before the liquid has even passed through. In the clear filtrate, antimony is found in solution.

For the *Separation of Tin from Antimony and Arsenic*, Dr. Clemens Winckler (‘Zeitschrift für Analyt. Chemie,’ 1875, p. 163) proceeds as follows:—If the object is an alloy it is dissolved in a mixture of 4 parts hydrochloric acid, and 5 parts water, with the addition of a sufficient quantity of tartaric acid. If the mixed metals exist as sulphides they are collected on a filter, washed, and dissolved upon it in dilute potash lye. The filtrate is mixed with tartaric acid, treated with a current of chlorine, or with bromine in slight excess neutralised with hydrochloric acid. In either case the solution is introduced into a beaker, diluted to 300 or 400 c.c., and so much solution of calcium chloride of a known strength is added that the subsequently precipitated calcium carbonate may exceed the tin present by about 15 times in weight. The liquid is then neutralised with potassium carbonate, potassium cyanide is added, and afterwards a slight excess of potassium carbonate, so that the lime may be totally precipitated. The liquid is then heated till it begins to boil; it is allowed to settle, the liquid poured upon a filter without disturbing the sediment, which is then treated with fresh water, boiled up, allowed to settle, and the clear liquid poured upon the filter. In this manner the bulk of the antimony is removed.

The precipitate in the beaker is removed in a little concentrated hydrochloric acid, tartaric acid is added, the liquid again neutralised with potassium carbonate, and precipitated with potassium cyanide.

After boiling, the liquid is poured as above through the same filter, three successive portions of water are added, heating each time to a boil, and the precipitate is finally brought upon the filter and completely washed. All the arsenic and antimony are now found in the filtrate, and all the tin, with an excess of calcium carbonate, in the precipitate.

For the assay of alloys of lead and antimony such as type-metal, the comminuted alloy is digested in a flask with concentrated nitric acid till the antimony is oxidised. It is then slightly diluted with water, supersaturated with ammonia, and mixed with an excess of ammonium bi-hydrosulphide, which must be concentrated and yellow. If recently prepared a small quantity of flowers of sulphur is added. The whole is digested in the flask for some time, heating at last almost to a boil. The flask is then corked up and let stand till the deposit, which must be of a pure black, has subsided, while the supernatant liquid is yellow. If this is not the case more ammonium bi-hydrosulphide is needed. When cold the undissolved lead sulphide is separated by filtration from the solution of the antimony sulphide, washed with cold water, dried, placed in a tared porcelain crucible, the filter burnt separately to ashes, which are added to the precipitate along with some sulphur, and the whole is ignited in a current of hydrogen. After the crucible with its contents has been weighed the addition of sulphur and the ignition are repeated, in order to find if the weight is constant. The lead is calculated from the weight of the lead sulphide.

The solution of antimony sulphide is mixed, drop by drop, with hydrochloric acid, stirring all the time till the reaction becomes slightly acid. The beaker is covered with a glass plate and allowed to stand till the antimony sulphide is deposited. It is digested at a very gentle heat till the odour of sulphuretted hydrogen has ceased; when cold it is filtered upon a filter, dried at 120° C., and washed with cold water to which a few drops of hydrochloric acid have been added. When air-dry it is kept at the heat of 120°–130° C. in the hot air oven till its weight is constant. A weighed portion of this substance is placed in a bulb-tube and heated in a current of dry carbonic acid, at first very gently, and afterwards at 200°–300°. The black-grey tin sulphide remains, which is allowed to cool in a current of carbonic acid and weighed.

CHAPTER XIV.

THE ASSAY OF ZINC.

All bodies containing zinc, usually found in the assay office, may be divided into four classes :—

Class I.—Zinc ores, in which the metal exists as oxide not combined with silica :—

Earthy zinc oxide, ZnO.
Manganiferous zinc oxide, $ZnO + (MnO)$.
Zinc aluminate, Gahnite, $ZnO,6Al_2O_3$.
Franklinite, $3(FeO,ZnO) + (Fe_2O_3,Mn_2O_3)$.
Anhydrous zinc carbonate, ZnO,CO_2.
Hydrated zinc carbonate, $ZnO,3H_2O + 3ZnO,CO_2$.

Class II.—Zinc ores, in which the metal exists, as in the former class, as oxide, but partly or wholly combined with silica :—

Anhydrous zinc silicate.
Hydrated zinc silicate, electric calamine, $ZnO_2,SiO_3 + ZnO,H_2O$.

Class III.—Zinc ores, in which the metal is partly or wholly combined with sulphur.

Zinc sulphide (blende, *Black Jack*), ZnS.
Zinc oxysulphide. (This is rare.)
Zinc sulphate, $ZnO, SO_3,7H_2O$.
Zinc selenide, $ZnSe$. (Very rare.)

Class IV.—Alloys.

ASSAY OF ORES OF THE FIRST CLASS.

In order to reduce the zinc oxide contained in substances of this class, it is sufficient to mix them with charcoal and expose them to a white heat.

At the moment of reduction the zinc is in a vaporised state. Its vapours, however, are readily condensable, so that the operation may be conducted in an ordinary retort, and all the metal is deposited in the neck without the slightest loss. It seems from this that nothing is so easy, at first sight, as the assay of zinc oxide; but it is not so. It is very easy to reduce all the oxide, but it is not so easy to collect all the zinc; nor is it easy to condense it all in the metallic state, and in consequence to determine the precise proportion in the ore submitted to assay.

This difficulty consists, firstly, in the deposit being extended over a large surface, and it often adheres very strongly to the sides of the retort, so that it is nearly impossible to detach it; and secondly, as the neck of the retort is open, the air having access to it, brings to the state of oxide all the vapour nearest the end of the neck. The proportion of zinc oxidised is larger in proportion to the smallness of the quantity submitted to assay, and is always very considerable where no more than 200 to 400 grains are operated upon.

It is not, therefore, in the extraction of the zinc from its oxide that the assay is rendered partially uncertain, but in its collection.

The distillation of zinc requires a very high temperature, and cannot be performed in retorts of glass; those of earthenware must be employed. It is not necessary to lute these retorts when they are of good quality; and they are better thin, because they heat more rapidly, and are not so likely to crack.

After the mixture of oxide and charcoal has been introduced into the retort, it is placed in the fire. The neck ought to have a long tube of glass, with a narrow bore adapted to it, so as to collect all the zinc which may escape from the wide part of the neck of the retort. This disposition is also convenient, as it does not allow such a free access of air.

It is heated gradually until it is white inside; the zinc is reduced and volatilised, and condensed in the neck: the greater the heat, the nearer the orifice. The metal can be detached readily from the neck, if it be well blackleaded inside. It is necessary, from time to time, to observe the state of the neck, because when very narrow it is often obstructed, and, if not cleaned out with an iron rod, an explosion might be caused.

When the operation is finished the apparatus is allowed to cool, the retort taken out, placed carefully on its side, and broken, in order that any particles of zinc which have condensed in its dome may be removed.

If the approximate proportion of metallic zinc alone be required, all is collected and fused at a very gentle heat in a crucible with some black flux; but if the true quantity of zinc is to be estimated it must be done in a more exact manner. The deposit must be collected with all possible care; the neck must then be broken to pieces, and every piece having adhering to it either zinc or oxide must be placed on one side, and digested in hot nitric acid, which takes up those substances. If any be in the glass tube, it must be carefully cleansed by means of acid, and the solution added to that produced by the digestion of the broken neck, and the deposit mechanically collected, in nitric acid. The solution is then evaporated gradually to dryness, and heated to redness. The nitrate, by these means, is decomposed and transformed into oxide, four-fifths of the weight of which is equal to the quantity of metallic zinc produced in the assay.

The foregoing is the method of estimation by distillation; the following is the method of estimation by difference. Two plans of assay in this manner may be adopted: firstly, at an ordinary assay temperature; secondly, at a very high temperature, as that of an iron assay. In all cases it is necessary to commence with the expulsion of all volatile bodies the ore may contain. If water or carbonic acid alone be present, simple calcination will do; but if carbonaceous matter, roasting must be had recourse to.

When the assay is made at an ordinary assay temperature, the sample is finely pulverised and mixed with from 15 to 20 per cent. of equally finely pulverised charcoal, and pressed into a crucible, on which a cover is placed, but not luted, and rapidly heated to whiteness. When no more zinc vapour is disengaged it is cooled, and the mixture in the pot collected. The residue ought to be pulverulent; but as it is mixed with some charcoal, it is roasted, and then weighed. It is evident that the loss represents the zinc oxide; the charcoal added, it is true, leaves a small quantity of ash, but it is too small to be worth accounting for.

In making the assay in the manner described, it is to be feared that a small quantity of the oxide might remain undecomposed, and that a part of the residue might adhere to the crucible, and could not be detached; and lastly, there is always a degree of uncertainty as to the state of oxidation in which the iron will exist after roasting. No inconvenience of this nature presents itself when the assay is made at a very high temperature. This mode is the most exact of all, and leaves nothing to be desired.

The assays of zinc at a high temperature are made exactly as those of iron. They are made in a charcoal crucible, with the addition of fixed fluxes, suitable to effect the fusion of the gangues mixed with the zinc oxide, if they be not fusible by themselves. The button is weighed; it is a compound of slag and grains of iron, which are collected and their weight ascertained, and, by the difference, that of the slag. The weight of oxygen which the iron has lost during its reduction is then added to it, and by deducting from the substance the weight of the button and the oxygen so obtained, we have the proportion of zinc oxide reduced in the assay. On the other hand, by deducting from the weight of the slag the weight of flux added, the weight of earthy substances and irreducible oxides which were mixed with the zinc oxide is ascertained.

These results can be shown in a tabular form, in the following manner:—

Let m be the weight of the crude ore, n the weight of the calcined ore, r the weight of the flux added, f the weight of the cast iron, s the weight of the slag, o the weight of oxygen combined with the iron, calculated from the weight of metal produced, z the weight of the zinc oxide, then :—

$$\begin{array}{lr}
m \text{ crude ore} = \text{calcined ore} & n \\
r \text{ fixed fluxes} & r \\ \hline
 & n+r
\end{array}$$

$$\begin{array}{l}
\left.\begin{array}{lr}\text{Gives metal} & f \\ \text{Gives slag} & s\end{array}\right\} \left.\begin{array}{l}\text{Total } f+s \\ \text{Oxygen } \quad o\end{array}\right\} f+s+o \\
\qquad\qquad\qquad\qquad \text{Zinc oxide } n+r-f-s-o \\
\begin{array}{lr}
 & \\ \hline
\text{Flux added} & r \\ \hline
\text{Earthy matter} & s-r
\end{array}
\end{array}$$

The following is an actual experiment by Berthier :—

$$\begin{array}{lr}
100 \text{ crude ore} = \text{calcined ore} & 83{\cdot}3 \\
10 \text{ kaolin (china clay) acted on by acids} & 10{\cdot}0 \\
7 \text{ marble} = \text{lime} & 4{\cdot}0 \\ \hline
 & 97{\cdot}3
\end{array}$$

$$\begin{array}{l}
\left.\begin{array}{lr}\text{Gave metal} & 45{\cdot}3 \\ \text{Gave slag} & 16{\cdot}3\end{array}\right\} \left.\begin{array}{lr}\text{Total} & 61{\cdot}3 \\ \text{Oxygen} & 19{\cdot}4\end{array}\right\} \text{Total} \quad 80{\cdot}7 \\
\qquad\qquad\qquad\qquad\qquad\qquad \text{Zinc oxide} \quad 16{\cdot}6 \\
\begin{array}{lr}
\text{Fluxes added} & 14{\cdot}0 \\
\text{Earthy matters} & 2{\cdot}0
\end{array}
\end{array}$$

The above result was confirmed by wet analysis, showing at once the exactitude of the process.

Determination of Amount of Zinc by the Wet Process in Ores of the First Class.—Dissolve 50 grains of the finely-pulverised ore in nitric acid, evaporate to dryness, allow to cool. Digest the cold mass with a little dilute nitric acid, gently warming during the digestion, add water, and then filter. To the filtered solution add excess of caustic ammonia, gently warm, and filter. The excess of caustic ammonia dissolves the zinc oxide which it at first threw down, as well as any manganese oxide that may be present. This solution containing the zinc, and probably manganese, must be separated from the precipitate produced by the ammonia by filtration, the insoluble matter in the filter washed with water containing a little ammonia, and the washings so obtained added to the first strong filtrate. If no manganese be present, ammonium sulphide may now be added to the filtered liquid until it produces no further white precipitate of zinc oxide. The liquid and precipitate must now be allowed to stand in a warm place for about an hour, then filtered, and the zinc sulphide on the filter washed with water containing a little ammonium sulphide. After a few washings it is to be dissolved in dilute hydrochloric acid, and, if necessary, the solution filtered. To the filtered solution is added excess of sodium carbonate; zinc carbonate is thrown down, which in its turn is collected on a filter, washed, dried, separated from the filter, ignited, and weighed. Four-fifths of its weight is metallic zinc. If, by previous experiments by blowpipe or otherwise, manganese were found to be present, the ammoniacal solution containing the mixed oxides must be thus treated: Excess of acetic acid is to be added to it, and a stream of sulphuretted hydrogen gas passed through it until no further precipitation takes place; by this means the whole of the zinc is deposited as sulphide, whilst the manganese remains untouched in the liquid. The zinc sulphide is to be collected on a filter and treated with hydrochloric acid, &c., as just described.

ASSAY OF ORES OF THE SECOND CLASS.

Zinc silicates are not reducible by charcoal alone; but when in contact with substances which have the property of combining with silica, they are reduced completely, even at a moderate temperature. All the modes of assay just described for ores of the first class apply to those of the second, with the exception that the flux, instead of being merely reducing, must have a true fluxing property also: lime or magnesia are good fluxes.

Wet Determination of Zinc in Ores of the Second Class.

Ores of this class are best decomposed by strong hydrochloric acid with a small admixture of nitric acid. When thoroughly decomposed, and the solution evaporated to dryness, it is moistened with hydrochloric acid, and treated exactly as described for Ores of the First Class.

ASSAY OF ORES OF THE THIRD CLASS.

In order to assay the substances containing sulphur which belong to this class they must be roasted, and then treated as the ores of the first and second class. Zinc sulphide may be roasted without difficulty; and when the operation is made with care, the roasted ore contains neither sulphur nor sulphuric acid. The only precaution necessary to observe is, that the heat must be carefully regulated at first, in order to avoid fusion which might take place, especially when a certain amount of iron sulphide is present. Towards the end the heat may be increased to decompose any sulphate that may be formed. Both a reducing and fusing substance must be added in this case, as in the last, in order to determine the fusion of the gangue.

Wet Determination of Zinc in Ores of the Third Class. These ores are to be finely pulverised, treated with strong nitric acid, at first with a gentle heat; and lastly, boiled until the sulphur separates in bright yellow transparent globules, as described under the Wet Assay of Copper Ores of the Second Class. The solution so obtained is to be evaporated to dryness, moistened with hydrochloric acid, and treated as described for ores of the first class.

If ores of this class, or of either of the two former, contain copper, they must be thus treated:—

The ore is to be decomposed by an appropriate acid, evaporated to dryness, moistened with hydrochloric acid, water added, and the solution filtered. A current of sulphuretted hydrogen gas is now to be passed through the solution until, even after violent agitation, it smells strongly of it. It is now to be filtered, and the black precipitate on the filter contains all the copper as copper sulphide, that substance being insoluble in dilute acid, whilst in a solution acidulated with either of the strong mineral acids —as nitric, hydrochloric, or sulphuric—zinc is not at all acted on by sulphuretted hydrogen. The solution, now freed from copper, is placed in an evaporating basin and boiled for about a quarter of an hour; nitric acid is then added to peroxidise all the iron present, and the solution allowed to cool. When cold, the zinc is separated by means of ammonia, and the ammoniacal solution treated as already described.

FOURTH CLASS. ALLOYS.

The alloys of zinc with iron, copper, and tin may be assayed by heating them to whiteness for about an hour in a charcoal crucible with an earthy flux (calcium silicate is the best), and weighing the resulting button: the loss will be nearly equivalent to the quantity of zinc present.

The Wet Determination of Zinc in Substances of the Fourth Class.—These substances are treated precisely as described under the heads Wet Determination of Zinc in First, Second, and Third Classes.

VOLUMETRIC DETERMINATION OF ZINC.

Galetti's Process.—A good method for volumetrically determining the amount of zinc in ores is given in the 'Zeitschrift für analytische Chemie,' for 1869, by Maurizio Galetti, Chief Assayer at the Royal Assay Office, Genoa. The following is a description of the process:—Supposing zinc sulphide (blende) is to be assayed, about half a gramme of the finely pulverised ore is to be treated with concentrated nitric acid, and boiled to incipient dryness, until the sulphur left undissolved does not contain any particles of undissolved ore. Then add strong hydrochloric acid, and boil again until no nitric acid is left. Calamine (zinc carbonate) should at once be acted upon with hydrochloric acid; but, in order to make sure of the complete oxidation of all the iron the ore may happen to contain, it is best to add to the acid a few decigrammes of pure potassium chlorate. After having boiled this solution for a few minutes, it is diluted with distilled water; a large excess of ammonia is added to the solution, which is then boiled and slightly acidified with acetic acid. After brisk agitation, boil again for a few minutes, and then supersaturate with ammonia. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to half a litre. This having been done the fluid is very cautiously and gradually acidified with dilute acetic acid, one part acid sp. gr. 1·07 to 10 of distilled water. Any large excess of this should be avoided, as the solution should only be very slightly acid. As soon as the basic iron acetate has subsided, the precipitation of the zinc by means of a standard solution of potassium ferrocyanide may be proceeded with.

The ferrocyanide solution is made by dissolving 41·25 grms. of the said salt in as much distilled water as will make the solution weigh exactly one kilogramme.

The presence of compounds of lead (as, for instance, lead carbonate, sulphate, or sulphide) occurring along with the ores of zinc, does not interfere with the completeness of the precipitation of zinc as zinc ferrocyanide. This even holds good up to 10 per cent. of metallic lead. Since some ores of zinc, especially calamine, often contain manganese, it is best to add to the ammoniacal solution, before any acetic acid is added, a few drops (from 2 to 4) of bromine, in order to convert the manganese protoxide into protosesquioxide, leaving the solution standing for twenty-four hours after the addition of the bromine.

The ammoniacal solution of zinc chloride being colourless, there should be added to it, previous to cautious acidification by means of dilute acetic acid, a few drops of tincture of litmus, in order to more readily hit the precise point of sufficient acidification, which is known by the blue colouration changing to a rose-red.

The zinc ferrocyanide which is mixed with iron oxide preserves its naturally white colour as long as the liquid contains free zinc, but its colour changes to a greyish-white as soon as a very slight excess of the ferrocyanide standard solution is present; the liquid also then becomes turbid, and the precipitate settles very slowly. By these characteristic signs the end of the operation may be always recognised. In order to make sure, the liquid should be touched with a glass rod which has been just previously moistened with a dilute solution of ammoniacal copper nitrate; this will have the effect of indicating any excess of the ferrocyanide solution, by producing the more or less intense colour characteristic of copper ferrocyanide. The zinc solution should be at a temperature of from 40° to 50°, whereby the rapid subsidence of the zinc ferrocyanide is promoted.

Filtration is not necessary, as the presence of the gelatinous silica (due to the decomposition of zinc silicates occurring in the ores of that metal) does not interfere with the correctness of this method of estimating zinc quantitatively.

Fresenius* gives the following methods for the volumetric determination of zinc:—

1. Method of Schaffner,† modified by C. Künzel‡ as employed in the Belgian Zinc-works; described by C. Groll.§

a. Solution of the Ore and Preparation of the Ammoniacal Solution.

Powder and dry the ore.

Take 0·5 grm. in the case of rich ores, 1 grm. in the case of poor ores, transfer to a small flask, dissolve in hydrochloric acid, with addition of some nitric acid by the aid of heat, expel the excess of acid by evaporation, add some water, and then excess of ammonia. Filter into a beaker, and wash the residue with lukewarm water and ammonia till ammonium sulphide ceases to produce a white turbidity in the washings. The zinc oxide remaining in the hydrated ferric oxide is disregarded. Its quantity, according to Groll, does not exceed 0·3—0·5 per cent. This statement probably has reference only to ores containing relatively little iron; where much iron is present the

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* 4th English edition, p. 653, published by Churchill and Sons.

† 'Journ. f. prakt. Chem.' 73, 410.

‡ *Ibid.* 88, 486.

§ 'Zeitschrift f. anal. Chem.' 1, 21.

quantity of zinc left behind in the precipitate may be not inconsiderable. The error thus arising may be greatly diminished by dissolving the slightly washed iron precipitate in hydrochloric acid, and adding excess of ammonia. But the surer mode of proceeding is to add to the original solution—after evaporating off the greater part of the free acid as above, and allowing to cool—dilute sodium carbonate nearly to neutralisation, then to precipitate the ferric oxide with boiling sodium acetate, to filter, and wash. The washings, after being concentrated by evaporation, are added to the filtrate, and the whole is then mixed with ammonia till the first formed precipitate is redissolved.

If the ore contains manganese—provided approximate results will suffice—digest the solution of the ore in acids, after the addition of excess of ammonia and water, at a gentle heat, for a long time, and then filter off, with the iron precipitate, the hydrated manganese protosesquioxide which has separated from the action of the air. The safer course—though undoubtedly less simple—is, after separating the iron with sodium acetate, to precipitate the manganese by passing chlorine, or by adding bromine and heating.

If lead is present, it is separated by evaporating the aqua regia solution with sulphuric acid, taking up the residue with water and filtering; then proceed as directed.*

b. Preparation and Standardising of the Sodium Sulphide Solution.

The solution of sodium sulphide is prepared either by dissolving crystallised sodium sulphide in water (about 100 grm. to 1,000–1,200 water) or by supersaturating a solution of soda, free from carbonic acid, with sulphuretted hydrogen, and subsequently heating the solution in a flask

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* Concerning the direct treatment of roasted zinc ores with a mixture of carbonated and caustic ammonia, comp. E. Schmidt (*Journ. f. prakt. Chem.* 51, 257). By this treatment the zinc oxide, which was combined with carbonic acid, is dissolved, whilst that combined with silicic acid is, for the most part, left undissolved.

to expel the excess of sulphuretted hydrogen. Whichever way it is prepared, the solution is afterwards diluted, so that 1 c.c. may precipitate about 0·01 grm. zinc. Prepare a solution of zinc by dissolving 10 grm. chemically pure zinc in hydrochloric acid, or 44·122 grm. dry crystallised potassium and zinc sulphate in water, or 68·133 grm. dry crystallised potassium and zinc sulphate in water, and making the solution in either case up to 1 litre with water.

Each c.c. of this solution corresponds to 0·01 grm. zinc. Now measure off 30–50 c.c. of this zinc solution into a beaker, add ammonia till the precipitate is redissolved, and then 400–500 c.c. distilled water. Run in sodium sulphide as long as a distinct precipitate continues to be formed, then stir briskly, remove a drop of the fluid on the end of a rod to a porcelain plate, spread it out so that it may cover a somewhat large surface, and place in the middle a drop of pure dilute solution of nickel chloride. If the edge of the drop of nickel solution remains blue or green proceed with the addition of sodium sulphide, testing from time to time, till at last a blackish grey colouration appears surrounding the nickel solution. The reaction is now completed, the whole of the zinc is precipitated, and a slight excess of sodium sulphide has been added. The precise depth of colour of the nickel must be observed and remembered, as it will have to serve as the stopping signal in future experiments. To make sure that the zinc is really quite precipitated, you may add a few tenths of a c.c. more of the reagent, and test again; of course the colour of the nickel drop must be darker. Note the number of c.c. used, and repeat the experiment, running in at once the necessary quantity of the reagent *less* 1 c.c., and then adding 0·2 c.c. at a time till the end-reaction is reached. The last experiment is considered the more correct one. The sodium sulphide solution must be restandardised before each new series of analyses—that is, if it is kept in bottles containing air; if, on the contrary, oxygen is excluded by passing the air through an alkaline solution of pyrogallic acid previous to its entering the bottle, the solution would without doubt keep unaltered.

c. Determination of the Zinc in the Solution of the Ore.

Proceed in the same way with the ammoniacal solution prepared in *a* as with the known zinc solution in *b*. Here also repeat the experiment, the second time running in at once the required number of c.c., less 1 of sodium sulphide, and then adding 0·2 c.c. at a time till the end-reaction makes its appearance. The second result is considered the true one. There are three different ways in which this repetition of the experiment may be made. You may either weigh out at the first two portions of the zinc ore, or you may weigh out double the quantity required for one experiment, and make the ammoniacal solution up to 1 litre, and employ ½ litre for each experiment; or, lastly, having reached the end-reaction in the first experiment, you may add 1 c.c. of the known zinc solution, which will destroy the excess of sodium sulphide, and run in sodium sulphide in portions of 0·2 c.c. till the end-reaction is again attained. Of course, in this last process to obtain the second result, you deduct from the whole quantity of sodium sulphide used the amount of the same, corresponding to 1 c.c. of the zinc solution.

If the ore contains copper, which frequently occurs in the case of blendes, determine by a preliminary experiment the number of c.c. of sodium sulphide which are necessary to precipitate the copper, and at the completion of the zinc-analysis deduct them. In this case, let the drop to be tested with nickel solution pass through a small filter on its way to the porcelain plate, in order to avoid the injurious influence of the copper sulphide on the nickel reaction. If, however, the copper amounts to more than 2 per cent., remove it from the acid solution by sulphuretted hydrogen, evaporate the filtrate with nitric acid, dilute, treat with ammonia, and determine the zinc as above.

In careful hands the error will, according to C. Künzel, never exceed ½ per cent.

d. Further Modification of the Process.

To ascertain the point when the whole of the zinc is precipitated and the sodium sulphide begins to predominate, Schaffner* employed flocks of hydrated ferric oxide, which he produced by the addition of a few drops of ferric chloride to the ammoniacal zinc solution, and which settled at the bottom; while Barreswil† used small pieces of white porcelain, which were covered with ferric chloride, and thrown into the ammoniacal zinc solution. Sodium sulphide is added till the flocks or the pieces of porcelain turn black. In neither case is the end-reaction so exact as with nickel solution.

With the help of lead-paper, however, the point may be hit with great precision. Moisten a piece of white filter-paper with solution of lead acetate, place it on a layer of blotting-paper, drop some ammonium carbonate upon it, so as to form a thin coating of lead carbonate, let the blotting-paper absorb the excess of moisture, and then spread the lead-paper on a porcelain plate. As soon as you imagine the zinc to be nearly all precipitated, lay a small piece of filter-paper on the lead-paper, and then dip the end of a blunt glass rod in the fluid, and press it somewhat gently on the small piece of filter-paper. When the sodium sulphide begins to be in excess, a brown spot forms on the lead-paper. Fr. Mohr‡ applies the lead reaction in another manner. He makes an alkaline solution of lead by warming together lead acetate, Rochelle salt and solution of soda; he first places a drop of this on filter-paper, and then close by a drop of the precipitated zinc solution, so that the circle formed by the spreading of the solution to be tested may cut the circle of the lead solution. As soon as the sodium sulphide begins to predominate, the portion of the circumference of the lead circle which lies in the other circle turns black.

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* 'Journ. f. prakt. Chem.' 73, 410.

† 'Journ. de pharm.' 1857, 431; 'Polyt. Centralbl.' 1858, 285.

‡ Mohr's 'Lehrbuch der Titrirmethode,' 2 Aufl. 377.

2. H. Schwarz's Method.*

Prepare an ammoniacal solution as in 1, *a*.

Heat gently, and mix with a moderate excess of ammonium sulphide. Allow the precipitated zinc sulphide to subside, then filter, using a tolerably large plaited filter of rapidly filtering paper, moistened with boiling water, and warming the fluid to acelerate the operation, which would otherwise require considerable time. Wash the precipitate with warm water mixed with a little ammonia, until the last drops no longer blacken a solution of lead oxide in soda.

Transfer the filter with the precipitate to a beaker, add a dilute solution of slightly acidified ferric chloride, cover with a close-fitting glass plate, and let the mixture stand for ten minutes; then heat gently. Under these circumstances the zinc sulphide decomposes completely with the ferric chloride to zinc chloride, ferrous chloride, and sulphur: $Fe_2Cl_6 + ZnS = Zn\,Cl_2 + S + 2FeCl_2$.

Now add sulphuric acid, and heat gently until the sulphur has agglutinated. Filter, and wash the filter, and determine the iron in the fluid as protochloride by permanganate,† 2 eq. iron correspond to 1 eq. zinc. If the quantity of zinc sulphide is not very great, the filter may be broken, and the zinc sulphide washed into a flask which already contains the solution of ferric chloride. The great objection to this method lies in the washing of the zinc sulphide, which, as is well known, is a long and troublesome operation. A possible loss of sulphuretted hydrogen on mixing the zinc sulphide with ferric chloride may be prevented by conducting the decomposition in a flask, connected with a U-tube containing ferric chloride.

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* See his 'Anleitung zu Maassanalysen,' Nachträge, p. 29 (Brunswick). Compare also v. Gellhorn ('Chem. Centralbl.' 1853, 291), who has made many analyses by Schwarz's method.

† Without doubt the ferric chloride might be replaced by the ferric sulphate, by which means the presence of hydrochloric acid would be avoided.

3. Carl Mohr's Method.*

This method is based upon the following considerations:—

I. If a solution of zinc acetate, acidified with acetic acid, is mixed with an excess of potassium ferrocyanide, the whole of the zinc is thrown down in the form of a reddish-yellow precipitate of zinc ferrocyanide, $Zn_3\,(Cy_6Fe_2)$.

II. If solution of potassium iodide is now added in excess, we have this decomposition:—$2[Zn_3\,(Cy_6Fe_2)] + 2KI + 2(\bar{A},HO) = 3[Zn_3\,(Cy_3Fe)] + 2(KO,\bar{A}) + H_2(Cy_3Fe) + 2I$.

III. 1 eq. liberated iodine corresponds, accordingly, to 3 eq. zinc.

IV. If potassium iodide is made to act upon zinc ferrocyanide in a neutral fluid, the liberated iodine acts upon the potassium ferrocyanide present in that case, which leads to the formation of a little potassium ferrocyanide; the remaining free iodine, therefore, will not indicate, with accuracy, the quantity of zinc present. But whereas the reaction actually takes place in acid solution of zinc acetate, as above directed, it may be assumed that potassium acetate and free hydroferrocyanic acid are formed; and as iodine exercises no appreciable action upon the latter substance, the iodine liberated in the process indicates, with tolerable accuracy, the amount of zinc present.

The process is as follows:—

Treat the ore with aqua regia, as in 1, *a*, and drive off the greater part of the free acid; nearly neutralise with sodium carbonate, add sodium acetate in excess, boil, filter, and wash with boiling water mixed with a little sodium acetate. The solution is free from iron: it contains the whole of the zinc, but, in presence of manganese, also the whole of the latter metal. Hence the process is not applicable in the presence of manganese.

Mix the solution of zinc, prepared as directed, with potassium ferrocyanide in slight excess, *i.e.* until a sample of the clear supernatant fluid gives a blue precipitate with a ferrous salt. Then add a sufficient quantity

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* Dingler's 'Polyt. Journ.' 148, 115.

of potassium iodide. The fluid acquires a brown colour, in consequence of the liberation of iodine; the white precipitate of zinc ferrocyanide is suspended in the brown fluid.

Determine now the free iodine by means of sodium hyposulphite, and calculate 3 eq. zinc for each eq. iodine. The results obtained by C. Mohr are very satisfactory. The method can be employed only if the acetic acid solution contains no other heavy metal besides zinc, and, more particularly, no manganese.

For determining the value of zinc powder, J. Drewson proposes the following method:—

He prepares two solutions, the one of pure fused potassium dichromate—say 40 grms. per 1,000 c.c.—and the other of crystalline ferrous sulphate, about 200 grms. in 1,000 c.c. The iron solution must be strongly acidulated with sulphuric acid to prevent oxidation. In order to find the respective value of the two liquids, 10 c.c. of the iron solution are measured into a beaker, a little sulphuric acid is added, and the other solution is dropped in from a burette until a drop of the mixture is no longer turned blue by potassium ferrocyanide. About 1 grm. of the zinc powder is then weighed, placed in a beaker with 100 c.c. of the chromic solution; 10 c.c. of dilute sulphuric acid are added, the whole is well stirred, 10 c.c. more of the sulphuric acid are added, and allowed to act for about a quarter of an hour, with diligent stirring. When everything is dissolved except a small insoluble residue, an excess of sulphuric acid is added, and 50 c.c. of the iron solution, in order to reduce the greater part of the excess of chromate; more of the iron solution is then added from a burette, till a drop displays a distinct blue reaction with ferrocyanide, and the mixture is then titrated back with chromate till this reaction disappears. From the total number of c.c. of the iron solution consumed, the quantity is deducted which corresponds to the ferrous solution employed. The chromate contained in the remainder, if multiplied by 0·66113, shows the metallic zinc contained in the powder.

In order to separate copper from zinc by a single precipitation with sulphuretted hydrogen, G. Larsen ('Zeitschrift für analyt. Chemie,' 1878, p. 312) passes sulphuretted hydrogen into the solution, filters, washes the precipitate first with hydrochloric acid of sp. gr. 1·05, through which sulphuretted hydrogen has been passed, and then with pure sulphuretted hydrogen water. Both the precipitation and the washing are effected in heat.

Brass, pinchbeck, false gold-leaf, bronze not containing tin, etc., are dissolved in nitric acid as directed for alloys of silver and copper.

The acid liquid is diluted with water and a current of sulphuretted hydrogen is introduced, the vessel being kept covered with a glass plate. This is continued till the precipitate has subsided and the liquid becomes clear and colourless. The precipitate—copper sulphide—is poured upon a filter, and the filtrate collected in an evaporation-basin. To prevent oxidation the filtration must be performed rapidly, and the air excluded as far as possible by keeping the funnel and the beaker covered with a glass plate. The filter should be kept constantly full, till it has received all the precipitate.

All particles adhering to the sides of the beaker and to the gas delivery tube, are washed into the filter by means of a feather and the washing-bottle. The precipitate is then washed on the filter moderately with cold water, a few drops of sulphuretted hydrogen water being added each time. The precipitate is dried, transferred to a tared porcelain crucible, upon the lid of which the filter is reduced to ashes, which are added to the precipitate. The whole is mixed with a few centigrms. of flowers of sulphur, and the crucible is covered with a peculiar lid, in which a bent porcelain tube opens, through which dried hydrogen is introduced into the crucible, which is then placed over a lamp, and as soon as the common air is expelled from the apparatus it is heated to redness. The contents are then let cool in the current of hydrogen. Thus is obtained pure cuprous sulphide, Cu_2S, which is weighed, and from its weight that of the copper is calculated.

The filtrate containing the zinc is concentrated by evaporation to expel excess of sulphuretted hydrogen. Crystallised sodium carbonate is then gradually added, with stirring till the effervescence ceases, the precipitation is effected, and the liquid has an alterative reaction. In order to lose nothing by spirting, the beaker is kept covered with a glass plate, which is afterwards rinsed into the beaker by means of the washing-bottle. The liquid is brought to a boil, filtered, and the precipitate well washed with boiling water. It is dried and strongly ignited, when it becomes converted into zinc oxide. The filter is burnt on the lid of the crucible. The zinc oxide is weighed, and from it the zinc is calculated.

If lead is also present, the solution of the metals is placed in an evaporating-dish, and mixed with so much moderately concentrated sulphuric acid as to convert the lead into sulphate and leave an excess, which is afterwards chiefly expelled by evaporation. When cold, water and a little alcohol are added; the precipitate is poured upon a filter, dried at 120°, washed with cold alcoholic water, dried, and weighed.

The filtrate is treated with sulphuretted hydrogen, as for the determination of copper, etc. (*Rammelsberg*).

CHAPTER XV.

THE ASSAY OF MERCURY.

MERCURY is found in the native or metallic state, and as sulphide or cinnabar :—

Native mercury, Hg.
Mercury sulphide, cinnabar, Hg_2S.
Bituminous mercury sulphide.

There are other minerals of mercury met with, but hitherto not in sufficient quantity to be worked for the metal. They are :—

Zinciferous mercury subsulphide.
Zinciferous mercury sulphide.
Mercury selenide.
Mercury subchloride.
Mercury iodide.
Silver amalgam (*see* Silver).

Assay of Mercurial Ores.—The determination of mercury is always made by distillation. In case the mercury is present in the form of native mercury, or mercury oxide, it is distilled without any addition. The ore (say from 500 to 1,000 grains) is placed in an iron or earthenware retort, which is set over a suitable fire, and the heat raised gradually, and kept up, until the whole of the mercury has passed over. The mercury which passes over is collected either in the neck of the retort, or in a receiver fitted for that purpose—such as a glass flask kept cool by affusion with water. When but a small quantity is operated upon (say 150 to 200 grains), it is most convenient to use a glass retort, or bent tube retort, heating it gradually over a charcoal fire, taking care to keep the upper part so hot that no metallic mercury may adhere to it. It must be heated nearly to the melting point of the glass, and until all the mercury has come over.

When the operation is finished, the neck is cut off, weighed, the mercury detached, and weighed again: the loss of weight is the amount of mercury. Or the metal may be detached by means of a feather, and allowed to fall into a basin of water, which, if heated for a few seconds, will cause the mercury to collect into one globule: the water may be decanted, and the mercury dried at the ordinary temperature, and weighed.

The mercury wholly condenses in the neck of the retort, under the form of a metallic dew. Some may by chance pass off: but in order to prevent such an occurrence, the beak of the retort is plunged into water, or a loose plug of linen, moistened with water, is introduced into the neck, the end of which is plunged into water, by which means the neck of the retort is kept constantly cool, and the mercury is found deposited on the linen, from which it may be detached by shaking in water.

When large quantities of substances containing mercury are operated upon, it is necessary to heat very strongly towards the end, in order that the centre of the mass may receive a sufficient amount of heat to effect its decomposition. Naked glass retorts cannot be used; and either coated glass or porcelain retorts must be employed. In the large way, as in the distillation of amalgams, &c., cast-iron retorts are used.

As before stated, all substances containing mercury, either in its metallic state or as oxide, are distilled without addition, but with the others it is necessary to employ some reagent which will separate and retain the sulphur, selenium, &c.; which reagent may be a metal, as iron, copper, or tin; or black flux, or a mixture of quick lime and charcoal: iron filings are most often used. For cinnabar about 50 per cent. of iron filings is required, in order to prevent any of it being sublimed; the true quantity required is only about 24 per cent., but an excess is necessary, in order, as before stated, to prevent loss: 50

per cent. of iron filings may be employed for the selenides, &c. When black flux is used, from about 50 to 70 per cent. is employed. Caustic lime may be employed in the proportion of 30 per cent. mixed with 30 per cent. of its weight of charcoal. After the ore to be assayed is carefully mixed with any of the above fluxes, it is always advisable to cover it, when in the retort, with a thin layer of the flux employed, in order to avoid all chance of any loss.

In estimating mercury by distillation it is necessary, especially if the metal is in the state of chloride or sulphide, to take certain precautions, without which a portion of the sulphide or chloride would volatilise without decomposition. H. Rose gives the following directions for carrying out the operation:—Introduce into a glass tube capable of resisting fusion, closed at one end, and measuring from 35 to 50 centimètres in length, a column of sodium bicarbonate, then one of quick-lime, and then a well-blended mixture of the mercurial compound and quick-lime, and, finally, a column of quick-lime. The open end of the tube is drawn out and bent round so as to enter a small flask containing water. The tube is heated as if for an organic analysis, commencing at the open end and finishing with the sodium bicarbonate. The operation ended, cut the bent end of the tube. Collect all the mercury in the flask, dry with paper, and afterwards over sulphuric acid, and then weigh it.

The quick-lime should not be replaced by hydrate of lime. That would occasion all the inconvenience of an analysis of a sulphuretted combination of mercury. The water, acting on the calcium sulphide, would form sulphuretted hydrogen, which, by dissolving in the water of the receiver, would, in time, transform a portion of the reduced mercury into sulphide. It is advisable in some cases to replace the sodium bicarbonate by magnesium carbonate.

Combinations containing mercury iodide are not entirely decomposed when treated as above. Biniodide and protoiodide are condensed in the extremity of the tube simultaneously with the metallic mercury.

To analyse these combinations recourse must be had to metallic copper, the operation being similar to that with quick-lime.

Berthier, who experimented with an ore containing arsenic, realgar, &c., and cinnabar from Huanca-Vélica, in Peru, found, after very many fruitless experiments, the following method best adapted to its examination for mercury:—

The ore was heated in a retort with four to five times its weight of litharge. From the litharge, the arsenic sulphide, &c., a fusible slaggy mass was formed, while the cinnabar was decomposed into sulphurous acid and metallic mercury. The mercury volatilised completely at a moderate heat, and collected in the fore part of the neck of the retort and in the receiver. The single precaution which must be observed for the success of the assay, consists in only gradually and moderately heating the clay or glass retort, in order to prevent its being perforated by the corroding effect of the litharge before the operation is ended.

If the assay sample is extremely poor in mercury, the ordinary assay method becomes somewhat inconvenient and uncertain, on account of the large quantity which must then be subjected to distillation in the assay. For this case Berthier found it more appropriate to digest the assay sample with aqua regia, wash it thoroughly, evaporate the whole mass of fluid to dryness, and then treat the dry mass, which contains all the mercury as chloride, further in the dry way He found that if mercury chloride (corrosive sublimate) is heated with litharge, it volatilises without undergoing any change. If, besides the litharge, coal-dust is also added, or if instead of it metallic lead is used in great excess, the chloride is reduced to subchloride, which volatilises, but not the smallest drop of mercury is thus produced. The best reducing agent for the mercury chloride contained in the dry mass, is black flux, of which three parts by weight are used. Since the mass to be subjected to distillation has been greatly diminished by the treatment of aqua regia, and the subsequent evaporation, and no high heat is now required for the decomposition, the distillation may be performed in a glass retort. When the gangue in the poor ore is calcium carbonate, all the lime is dissolved out, *before* the treatment with aqua regia, by moderately strong acetic acid.

By this method the smallest trace of mercury in an ore or amalgamation product can be shown and determined by its weight.

Eschka's process for assaying mercury ores is given as follows in the 'Chemical News' for July 1872. The method may be used for cinnabar, mercuriferous fahlerz, &c. The ore should be weighed in a balance turning with one milligramme. The quantity of ore for the assay varies according to its richness, as follows :—

Ore containing	up to	1	per cent.	. . .	10	grammes
,,	1 ,,	10	,,	. . .	5	,,
,,	10 ,,	30	,,	. . .	2	,,
,,	over	30	,,	. . .	1	,,

The ore is introduced into a porcelain crucible, the edge of which has been ground flat, and mixed with about half its weight of clean iron filings by means of a glass rod, and is then evenly covered with a layer of iron filings about $\frac{1}{4}$ to $\frac{3}{8}$ inch thick. A concave cover, made of fine gold, about two inches in diameter and 12 to 15 grammes in weight, is now placed on the crucible after having been carefully weighed ; the concavity is filled with distilled water and the crucible placed on a triangle and heated for ten minutes by a Bunsen burner or Argand spirit-lamp, during which time the mercury is volatilised and deposits itself on the gold. The gold cover is then removed, the water poured off, and the mirror of mercury on the convex side washed with alcohol from a wash bottle. After being dried in the water-bath, the cover is allowed to cool thoroughly, and is then weighed in a balance turning with $\frac{1}{2}$ milligramme with 50 grammes in the pan. The increase of weight gives the quantity of quicksilver in the ore. During the weighing the cover is placed on an empty porcelain crucible. The quicksilver is then driven off by heating the cover gently in the flame of a Bunsen burner or a spirit-lamp, in a place where there is a good draught, and the empty crucible and cover are subjected to a second weighing as a check. In order that the assay should succeed the following conditions must be fulfilled:—The cover must fit closely, so as to avoid loss of quicksilver, and must be deep enough to hold a sufficient quantity of water to keep it cool. The iron filings must be free from grease, which would prevent the proper formation of the mirror; the washing with alcohol must not be omitted, as it removes all the bituminous substances which spoil the mirror, and assists the drying; it must be dried in a water-bath for two or three minutes, cooled in the desiccator, and weighed when fully cool. When assaying rich ores the alcohol used in washing the cover must be collected, as it may contain a little amalgam; it must be poured into the concavity of the cover, which will take up any little globules of quicksilver. The most exact results are obtained in the case of poor ores containing less than ten per cent.

Assay for the Amount of Cinnabar in an Ore.—The ore to be assayed is distilled, without addition, in a glass retort, and the sublimed cinnabar collected and weighed. The ores containing mercury combined with sulphur are often mixed with bituminous matters and calcium carbonate: then, when an assay is to be made for cinnabar, it often happens that a portion of it is decomposed, either by the carbon present or by the aid of the bituminous matter and lime, and a little metallic mercury is driven off with the cinnabar. In this case, having weighed the mixture of cinnabar and mercury, the mixture is treated with nitric acid, which dissolves only the latter, and pure cinnabar remains, whose weight is taken, and the quantity of mercury dissolved ascertained by the difference; and from that the quantity of cinnabar calculated which that quantity of mercury would yield. Every 86 parts of mercury furnish about 100 of cinnabar.

If the gangue of the ore be fixed, in the fire, the assay may be made by mere calcination, and the loss of weight will correspond either to the metallic mercury, oxide, or sulphide it may contain.

For the determination of mercury in the wet way in its usual ores, which are mixtures of cinnabar with limestone, clay, iron oxide, and bituminous matters, the sample is first treated with hydrochloric acid, which dissolves the lime, etc. The liquid is then poured off and the residue digested with aqua regia, when the mercury is dissolved as chloride. The solution is filtered off from the insoluble residue, the greater part of the free acid removed by evaporation, diluted and heated with a solution of sulphurous acid, to reduce the ferric oxide to the ferrous condition. Without previous filtration it is then treated with sulphuretted hydrogen, the precipitate of mercury sulphide is brought upon a weighed filter, and dried at 100–110° C. Any free sulphur present may be removed by digestion with a solution of sodium hyposulphite. The mercury sulphide may be afterwards tested for the presence of other metals of volatilisation.

If it is intended to weigh mercury as mercurous chloride (calomel) after reduction with stannous chloride, the ore should be dissolved not in aqua regia, but in a mixture of hydrochloric acid and potassium chlorate. Free chlorine is expelled by heat, and the liquid is placed in a flask and mixed with a clear solution of stannous chloride, to which hydrochloric acid has been added, and the whole is boiled for a few moments. When cold, the liquid is decanted off, the mercury rinsed in a crucible, washed with acid water, and dried in the exsiccator.

In amalgams mercury is generally determined by placing the sample in a porcelain crucible and heating in a current of hydrogen gas, when the mercury is volatilised. *Rammelsberg.*

(This method, however, is not applicable to the amalgams of the alkaline metals.)

VOLUMETRIC ESTIMATION OF MERCURY.

The process we have found most trustworthy is that of M. J. Personne, described in the 'Comptes Rendus,' lvi. 63, as follows. The author says:—

'The process at which I have arrived, after many fruitless attempts, is founded on a well-known fact—that a combination of mercury iodide with potassium iodide forming the double iodide, HgI,KI, gives a colourless solution. Thus, two solutions in equal quantities, one containing one equivalent of mercury bichloride, the other two equivalents of potassium iodide, being mixed, by pouring the mercurial solution into that of the potassium iodide, mercury iodide will be produced by the contact of the two solutions, which dissolves in proportion to its formation, until the mercurial solution added is equal in volume to that of the alkaline iodide used, according to the following equation:—

$$\mathrm{HgCl} + 2\mathrm{KI} = \mathrm{HgI,KI} + \mathrm{KCl}.$$

The slightest excess of bichloride causes the formation of a persistent red precipitate, giving the liquid a very perceptible red tint even by artificial light. This colouration, which indicates that the saturation is complete, gives to this mode of estimation a precision and nicety quite as great as that of litmus, used to ascertain the saturation of an acid by a base. The mercurial solution must always be poured into the alkaline iodide—not the alkaline iodide into the mercurial solution; otherwise, though the last reaction may be the same, it is impossible to obtain exact results, because the mercury iodide produced, not being brought simultaneously with its formation (in a nascent state) into contact with the alkaline iodide with which it is to combine, becomes sufficiently cohesive to dissolve but slowly in the potassium iodide. Thus, in operating with the same liquids, the quantity of alkaline iodide which must be added to dissolve the mercury iodide precipitated varies according to the time employed in effecting the estimation, and that in considerable proportions I have no doubt that it is through operating in this way that potassium iodide has hitherto been rejected as a medium for the exact estimation of mercury.

'Two normal liquids are necessary to effect this estimation.

'1. *Normal Standard Solution of Potassium Iodide.*—Obtained by dissolving 33·20 grammes of pure potassium iodide in water enough to make 1 litre of solution. 10 cubic centimètres of this solution represent 0·1 grm. of metallic mercury.

'2. *Normal Standard Solution of Mercury Bichloride.* Prepared by dissolving 13·55 grammes of mercury bichloride in water, so as to make 1 litre of solution. The solution of mercurial salt is facilitated by the addition of 5 equivalents, or 30 grammes, of sodium chloride, which has no influence on the reaction, like all neutral alkaline salts; 10 cubic centimètres of this solution also represent 0·1 grm. of mercury. Of these 10 centimètres, divided into 100 parts, each division represents 0·001 grm. of mercury. This mercurial solution serves to test the purity of the alkaline iodide solution or to give the standard of an unknown solution.

'Liquids ten times more diluted may be prepared without injuring the nicety of the reaction or the exactness of the results; fractions of a milligramme may thus be estimated.

'The estimation is effected in the following manner:—10 cubic centimètres of a normal solution of iodide being measured into a small saturating vessel, pour into it, constantly shaking the vessel, the solution of bichloride, measured in Gay-Lussac's burette. If the two liquids are pure, it will require exactly 100 divisions of the burette before the light red tint appears in the saturated liquid to indicate the close of the operation. When the mercurial solution is weak a proportionally larger quantity must be added. If, on the other hand, it is too strong, less must be added. As will be perceived, this is very similar to the chlorometric process.

'This new method of estimating mercury being applicable only to bichloride, it became desirable to extend its application to a greater number of mercurial compounds, if not to all. This side of the question presented difficulties not easily resolved in a satisfactory manner. It was, in fact, necessary to transform all the mercurial compounds into a perfectly neutral solution of bichloride. I was obliged to set aside successively the use of aqua regia, and even of hypochlorous acid. The great volatility of mercury bichloride, even in a boiling solution, caused too great a loss. M. Rivot's process—that is to say, the action of chlorine in a solution of hydrate of potash or soda—is perfectly successful. Take, for instance, the estimation of mercury in cinnabar. Reduce one gramme of cinnabar to a fine powder. Weigh it on paper, and introduce it into a matrass. Pour into the matrass 20 cubic centimètres of a caustic soda solution, with which mix the paper and its contents by quickly shaking; then send a current of chlorine, which need not be washed, into the liquid. The action of the chlorine produces a slight heat, which is gradually brought to boiling-point, by which time all the matter will have disappeared. To ensure success, the temperature must be carefully managed at the commencement. If it is raised too quickly, part of the matter remains undissolved. The solution being complete and saturated with chlorine, it is kept boiling long enough to expel all the excess of chlorine. The boiling may be prolonged without incurring any loss of bichloride, which is not volatile in presence of alkaline chloride. The solution when cooled is poured into a graduated tube. The matrass as well as the tube for conducting the chlorine are washed two or three times with water, and the washing added to the original liquid, so as to form 100 cubic centimètres of solution. I effected the estimation with the standard solution of iodide, of which 10 centimètres represent 1·0 grm. of mercury. To saturate these 10 centimètres it required 115 divisions of the chloromercurial solution. These 115 divisions contain then 0·10 grm. of mercury. Now, as all the mercury contained in the analysed cinnabar is spread through the 10,000 divisions of solution, we have the quantity of mercury found by the experiment by means of a simple proportion.'

Mr. G. Attwood gives the following process for the quantitative blowpipe assay of mercury. The compounds to be assayed may be divided into three classes. Class A, containing metallic mercury, cinnabar, tiemanite, suboxide, protoxide, and mixed sulphides. Class B, calomel, corrosive sublimate, and iodide of mercury. Class C, amalgam of gold, silver, copper, lead, zinc, tin, &c.

Class A.—10 to 20 grains of the ore, finely powdered and passed through a sieve, 2,000 holes to the square inch, are mixed with 5 to 10 times their weight of powdered litharge and distilled over a spirit-lamp in a small glass retort, 1½ inch long and ¼ inch in diameter. To this retort is fitted, by means of a cork, a glass tube, slightly curved, 2½ inches long and $\frac{6}{10}$ths of an inch in diameter. The end of this tube dips under water contained in a small porcelain crucible. The operation lasts only a few minutes. The mercury is carefully collected from the glass tube and crucible. The retort is broken up and its contents carefully powdered and examined by a lens for mercury. The globules are then united by gently warming under water, and the dry mercury weighed.

Class B.—A quantity of the finely-powdered ore, equal to 10 grs., is mixed with three times its volume of potassium oxalate, and one volume of potassium cyanide. The apparatus closely resembles that used in Class A, but the retort has a small bulb.

Class C.—These amalgams are sometimes powdered with difficulty, and it is often advantageous to add a known weight of pure mercury, so as to render them semi-fluid before distilling. 10 to 30 grs. of the amalgam are usually taken for an assay. A turned steel retort is used for distillation, which is effected in a small charcoal furnace heated by a blowpipe flame; the head of the retort is accurately ground to fit over the body. The retort, including the cup and cap, is 1 inch high; the neck of the cap is 2 inches long. The paper contains full-size illustrations of the different retorts, &c., which are made by Casella. (See 'Journal of the Chemical Society,' 1879.)

CHAPTER XVI.

THE ASSAY OF SILVER.

All argentiferous substances may be divided into two classes, as follows:—

Class I.—Minerals containing silver,

Silver glance (AgS) containing 87 per cent. of Ag.
Brittle silver ore ($6AgS,SbS_3$) containing 70·4 per cent. of Ag.
Light red silver ore ($3AgS,AsS_3$) containing 65·4 per cent. of Ag.
Dark red silver ore ($3AgS,SbS_3$) containing 59 per cent. of Ag.
Light and dark fahlerz (argentiferous grey copper ore), containing from 5·7 to 18–31·8 per cent. of Ag.
Argentiferous copper sulphide (Cu_2S,AgS) containing 53 per cent. of Ag.
Polybasite $9(Cu_2S,AgS) + (SbS_3,AsS_3)$ containing 72 94 per cent. of Ag.
Slags.
Cupel bottoms.
Dross.
Litharge, etc.

Class II.—Metallic silver and alloys, either native or otherwise.

General Observations on the Assay of Ores and Substances of Class No. 1.

In order to separate silver from this class of substances, an alloy of the precious metal with lead must be formed. The different methods by which this object can be attained are the following: firstly, fusion with a reducing flux; secondly, fusion with oxidising reagents; thirdly, scorification.

All substances containing lead in the state of oxide, such as carbonates, phosphates, &c., are fused directly with a reducing flux, as also are slags, old cupels, litharge, &c. All plumbiferous sulphides, &c., containing silver, are assayed as for lead by the processes already pointed out, taking care to follow the method which gives the largest proportion of lead.

All argentiferous minerals containing copper may be assayed as copper ores; because an alloy of copper and silver can be cupelled by means of lead.

In making assays of silver with lead or copper, it is sometimes necessary to commence the operation by roasting the ore; under other circumstances, also, argentiferous matters are roasted.

There is nothing very particular to be observed in this roasting; the temperature alone requires attention by managing well at the commencement of the operation, in order to avoid softening, and especially to avoid a very rapid disengagement of arsenical vapours, because a very considerable amount of silver may be lost by that means.

All substances which contain reducible oxides are fused with a reducing flux, as also those from which charcoal separates metals which alloy with lead, or metals which do not hinder the process of cupellation; but it is necessary to add to the reducing flux a certain proportion of litharge, in order to produce metallic lead, with which the silver may alloy. A mixture of metallic lead and any suitable flux may be substituted for that of litharge and a reducing flux; but the latter is preferable, because the lead produced is uniformly diffused throughout the whole mass of flux &c., not allowing a particle of silver to escape its action.

The reducing agent employed in nearly all assays is charcoal, either in its ordinary state, or as it is found in black flux. Starch and other analogous substances may be, as before mentioned, substituted for it: crude argol is, however, the best reducing agent. The portion employed must be varied according to circumstances, so that the silver-lead produced be not too rich, or that too great a proportion of lead be reduced. If the silver-lead be too rich, much of the precious metal may be lost in the slag, and if too great a quantity of lead be produced, silver is again lost, owing to the long exposure to the fire during cupellation; and indeed this is the most fruitful cause of loss, for more is lost in this manner than by having too little lead produced. In order to know the right proportions, the following data will serve as a guide:—1 part of charcoal reduces about 30 parts of lead from litharge, and 1 part of black flux reduces about 1 part of lead.

The fluxes employed in this kind of assay are litharge, black flux, potassium or sodium carbonate, and borax. Litharge is an exceedingly convenient flux, because it occupies very little room, and fuses without bubbling, producing very liquid scoriæ with nearly every substance. Experiment has shown that nearly all argillaceous, stony, and ferruginous substances fuse very well with from 8 to 12 or more parts of litharge. If from $\frac{1}{2}$ to 1 part of black flux, or $\frac{1}{50}$th to $\frac{1}{25}$th of charcoal, be added to 1 of ore, from $\frac{1}{2}$ a part to 1 part of silver-lead will be produced.

Black flux is employed in the fusion of all substances containing a large proportion of alumina, or in which lime is the predominant substance—from 2 to 3 parts of this flux generally suffice—1 part of litharge is added to the assay, which is wholly reduced, producing nothing but lead.

Potassium or sodium carbonates produce exactly the same effects as the alkali of the black flux. A certain quantity of charcoal must, in this case, be added to the assay.

Schlutter fuses the poor refuses of goldsmiths' workshops, mixtures of fragments of crucibles, glass, &c., with 2 parts of potassium carbonate, when they are very earthy, and with 1 part only when they contain much glass, adding, at the same time, to the mixture, a little litharge and granulated lead.

Borax has, like litharge, the advantage of being an universal flux; it is useful especially for the fusion of substances containing much lime; but it is necessary to take great care in the assay, in order to avoid the loss which its boiling up might occasion. This only applies, however, to its use in its ordinary state; if previously fused, that is, used as glass of borax, no particular care need be taken.

FUSION WITH OXIDISING REAGENTS.

Litharge.—The oxidising agents employed in the assay of argentiferous substances are litharge and nitre. Litharge attacks all the sulphides, arsenio-sulphides, &c., and oxidises nearly all the elements, excepting silver, when employed in sufficient quantity; and a quantity of lead equivalent to the oxidisable matters present is reduced, so that there results from the assay a slag containing an excess of lead oxide, and an alloy of lead and silver, very little contaminated with foreign metals, if no copper be present, and which can be submitted directly to cupellation. This method of assay is exceedingly convenient and quick.

The pulverised mineral is well mixed with litharge and the mixture placed in a crucible, which may be very nearly filled, as there is scarcely any boiling up when the pot and its contents are submitted to the fire. A thin layer of pure litharge is placed above the mixture, the whole is then heated rapidly, and as soon as the litharge, &c., is completely fused, the crucible is taken from the fire. It is inconvenient to heat it for any length of time, on account of the corrosive action litharge has on the substance of the crucible, which it rapidly destroys.

The proportion of litharge which must be employed depends upon the nature and quantity of oxidisable matters present in the ore. It ought in general to be very great, because it is absolutely necessary that no sulphurous matters be present, so that the slag may not contain the least trace of silver. But it is known how much litharge is required to decompose the metallic sulphides. Pyrites requires about 50 parts; mispickel, blende, antimony sulphide, copper pyrites, grey cobalt, and grey copper require from about twenty-five to about forty times their weight. For sulphide of bismuth 10 are sufficient, and for galena or silver sulphide but 4 or 5 parts need be employed. The proportion of litharge will not be so great for a mineral containing much stony gangue as for one entirely metallic. Experiment has proved, that the assay of rough schlichs, such as those treated in the large way by amalgamation, can be made very exactly with from 10 to 12 parts of litharge.

Alloys of silver with the very oxidisable metals, such as those of iron, antimony, tin, zinc, &c., can be assayed by means of litharge; but in order to have a successful result the alloys should be reduced to a very fine state of division, so that they must be at least granulated; and it is very often necessary to repeat the operation several times on the fresh alloy of lead produced.

The method of assay just pointed out is inconvenient, on account of the large quantity of lead it produces; pyrites giving 8½ parts, copper pyrites and blende 7 parts, antimony sulphide and grey copper about 6 parts, &c. In order to avoid this inconvenience, part of the oxidation can be performed by means of nitre. Nitre alone, employed in excess, oxidises all metallic and combustible substances found with silver, and even, under certain circumstances, a portion of the silver itself; but when the proportion is insufficient to oxidise the whole, and when the mixture contains at the same time litharge, after the nitre has produced its action the litharge acts in its turn on the remainder of the oxidisable substances, and the resulting lead carries down the silver set free. So that, by employing suitable proportions of nitre and litharge, all the silver contained in oxidisable minerals may be extracted, and any quantity of lead required may be thus alloyed with it.

As to the requisite proportion of nitre, it can be come at by practice, aided by the following data. It requires about 2½ parts of nitre to completely oxidise iron pyrites, 1½ for sulphide of antimony, and ⅔ for galena.

This determination can be ascertained at once as follows: fuse 1 part of the mineral with 30 of litharge, and weigh the resulting button of lead; and having fixed upon the quantity of lead necessary to carry on the cupellation properly, deduct it from the whole weight of the button, and the difference will be the amount of lead necessary to leave the slag in the state of oxide; and as it has been proved by experiment that 1 part of lead requires ·25 to ·30 of nitre, that is, from 25 to 30 per cent., it is easy to calculate the quantity necessary to be added.

When the ore contains sulphur, the latter forms with the nitre, potassium sulphate, which swims on the slag without combining with it.

The assay of silver ores by means of nitre is advantageous and useful in a variety of cases. If we wish to determine, for example, very exactly the percentage of silver in a poor galena, a large quantity, say a quarter of a pound, must be fused with about an ounce or an ounce and a half of nitre, and a quarter of a pound of sodium carbonate, or, better still, the same quantity of litharge, one of either of which must be employed to flux the gangue and temper the deflagration. After the fusion, all the contained silver will be found alloyed with a very small quantity of lead.

Sometimes the assay is made with a larger quantity of nitre than is requisite for the oxidation, and when the mixture is perfectly fused a certain quantity of metallic lead is added, taking care to cover the whole surface of the mixture, either by using granulated lead or a convenient mixture of litharge and charcoal, or litharge and galena. The shower of metallic lead passing through the fluid mass alloys with all the silver it finds in its passage, and so concentrates it.

This process, however, cannot always be confidently employed. If an excess of nitre be employed with substances susceptible of forming peroxides capable of attacking silver, such as some cupreous substances, the lead added reduces the greater part, but not the whole of the silver in the ore, so that the assay will not be perfect.

Special Directions for the Crucible Assay of Ores and Substances of the First Class.

The ores and substances belonging to this class may, for the convenience of assay, be further subdivided on the following principle. It has already been seen that sulphur, and other substances having a great affinity for oxygen, reduce metallic lead from litharge in proportion to the amount of reducing matter present; and as it is necessary in this kind of assay that no more than a certain quantity of lead alloy should be submitted to cupellation, some kind of control must be exercised by the assayer, to keep the quantity of lead reduced in due and proper bounds. This is readily accomplished by what is called a 'preliminary assay,' by which all ores and substances of this class are divided into three sections:—1st, ores which, on fusion with excess of litharge, give no metallic lead, or less than their own weight; 2ndly, those which give their own weight, or nearly their own weight, of metallic lead; 3rdly, those which give more than their own weight of metallic lead. The preliminary or classification assay is thus conducted:—

Carefully mix 20 grains of the finely pulverised ore (all silver ores must be passed through a sieve with 80 meshes to the linear inch) with 500 grains of litharge; place the mixture in a crucible which it only half fills; set the crucible, after careful warming, in a perfectly bright fire, and get up the heat as rapidly as possible, so as to finish the operation in a short time, to prevent the action of the reducing gases of the furnace on the lead oxide, because if a great length of time were taken in the operation, a portion of the lead reduced might be traceable to the furnace gases, and the result of the experiment vitiated. After the contents of the crucible are fully fused, and the surface perfectly smooth, the crucible may be removed and allowed to cool, and when cold broken. One of three circumstances may now present itself to the assayer: 1st, no lead, or less than 20 grains, has been reduced; 2ndly, 20 or nearly 20 grains, more or less, may be reduced; and 3rdly, more than 20 grains may have been reduced.

Now, as it has been already stated, 200 grains of lead alloy is a suitable amount to cupel, and as 200 grains is the best quantity of ore to submit to assay, it will be evident that ores and substances of the second section, or those bodies which give their own weight, or nearly their own weight, of lead alloy, simply require fusion with a suitable quantity of litharge and an appropriate flux. Ores of the first section require the addition of a reducing agent, in quantity equivalent to the standard amount of lead alloy (200 grains); and ores of the third section require an equivalent quantity of an oxidising agent, or an amount of some body which will oxidise the lead in excess of 200 grains of alloy.

The reducing agent employed is argol; the oxidising agent potassium nitrate. It is necessary, before commencing an assay of a silver ore, to determine how much lead a given weight of the argol the assayer has in use will reduce; as also how much lead a given weight of potassium nitrate will oxidise. These assays are thus made:—

Assay of Reducing Power of Argol.—Carefully mix 20 grains of the argol to be tested with 500 grains of litharge and 200 grains of sodium carbonate; place the mixture in a suitable crucible, and cover with 200 grains of common salt. (It is best to mix two such quantities, and take the mean of the results.) Fuse with the precautions pointed out in assay of substances of the first class, containing lead.

Weigh the resulting buttons, and take a note of the mean weight, which will represent the amount of lead reducible by 20 grains of argol.

Assay of Oxidising Power of Potassium Nitrate.—Mix 20 grains of finely-powdered potassium nitrate, 50 grains of argol, 500 grains of litharge, and 200 grains of sodium carbonate; cover with 200 grains of common salt, and fuse as above. Weigh the resulting button. Now calculate the amount of lead which should have been reduced by 50 grains of argol, and the difference between that and the amount of lead reduced in this experiment will represent the amount of lead oxidised by 20 grains of potassium nitrate.

Thirty to 32 grains of ordinary red argol reduce about 200 grains of lead; and 23 grains of pure potassium nitrate oxidise about 100 grains of lead. The assayer must, however, adopt the numbers found by himself by experiment, as the samples of argol and nitre may be more or less impure. He must also examine every fresh supply of litharge for the amount of silver it contains, in the following manner :—

Assay of Litharge for Silver.—Mix 1,000 grains of litharge with 30 grains (or any other quantity that may, by experiment, be found requisite) of argol, 200 grains of sodium carbonate, and cover with salt, as already directed. Fuse the mixture in a suitable crucible ; allow it to cool ; break and cupel the button obtained, as hereafter to be described ; take a note of the amount of silver obtained ; and as 1,000 grains of litharge is the standard quantity for a silver assay, the amount of silver, indicated as above, is to be deducted from the amount of silver obtained in the assay of any silver ore, until that quantity of litharge is consumed.

Assay of Ores of the First Section.—Make a preliminary assay, as already described. Suppose 10 grains of lead result ; then, as 20 have furnished 10 grains, so 200 grains of ore would furnish 100 grains of lead, or 100 grains less than the quantity best adapted for cupellation ; so that, referring to the assay of argol, and finding that from 30 to 32 grains reduce 200 grains of lead, then it is clear that the reducing power of from 15 to 16 grains of argol, in addition to the reducing power of 200 grains of ore, is necessary to furnish 200 grains of lead alloy. In this case the ingredients required in the actual assay, or 'assay proper,' would stand thus :—

200 grains of ore.
200 grains of sodium carbonate.
1,000 grains of litharge.
15 to 16 grains of argol.

These materials are to be thoroughly well mixed, placed in a crucible which they about half fill, and covered first with 200 grains of common salt, and then 200 grains of borax, and submitted to the fire with the usual precaution; when the flux flows smoothly the assay is complete; it may be removed and allowed to cool, the crucible broken, and the button obtained must be hammered into a cubical form, and should approximate to 200 grains, either more or less, within 10 grains. Two crucibles must always be prepared. It will also be here convenient to mention that the argol and potassium nitrate are the only substances whose quantities vary in the assay of silver ores, the amount of these variations being determined by the preliminary or classification assay.

Assay of Ores of the Second Section.—If the preliminary assay of the sample submitted to assay furnish from 18 to 22 grains of lead, then the assay proper may be thus made:—

200 grains of the ore,
200 grains of sodium carbonate,
1,000 grains of litharge,

well mixed and covered with salt and borax as above. Fuse with due care, and reserve buttons of lead alloy for cupellation.

Assay of Ores of the Third Section.—If the sample on preliminary assay furnished 40 grains of lead, then the 200 grains employed in assay proper would give 400 grains or 200 grains of lead in excess; refer now to note-book for quantity of lead oxidised by nitre: suppose the nitre pure as just stated, 23 grains will oxidise 100, therefore 46 grains are equivalent to 200, and the assay proper will stand thus:—

200 grains of the ore.
200 grains of sodium carbonate.
1,000 grains of litharge.
46 grains of potassium nitrate.

The potassium nitrate is to be weighed first, finely pulverised, and then well mixed with the remaining substances, and covered with salt and borax. The crucible in this assay must be larger than in the two preceding cases; the mixture should not more than one-third fill it, as there is a considerable action set up between the oxygen of the nitre and the sulphur or arsenic, or any other substance that may be the reducing agent in the ore; for in fact the nitre does not directly oxidise the lead, which sulphur &c., might have reduced, but oxidises its equivalent quantity of sulphur, or whatever other reducing substance there may be in the ore, so as only to leave a sufficient amount to reduce 200 grains of lead, in lieu of the 400 as indicated by preliminary assay, or when the reducing power of the ore was allowed to come into full play. The buttons obtained in this case are also to be reserved for cupellation.

Scorification.—Scorification has, like fusion with litharge, the effect of producing an alloy of lead capable of cupellation, and a very fusible slag composed of lead oxide, and all the matters foreign to silver, converted into the state of oxide. In the crucible assay as just described the oxidation of these substances takes place by the action of the litharge, which furnishes at the same time by its reduction the lead necessary to form the alloy, whilst in scorification all the substances susceptible of oxidation are oxidised in the roasting by means of the oxygen of the air, and the litharge itself is produced by the oxidation of part of the lead mixed with the ore to be assayed.

In this operation vessels termed scorifiers (see p. 136) are employed. They are heated in the muffle of the cupelling furnace, and as many assays may be made at one time as the muffle holds scorifiers.

Before introducing the scorifiers into the muffle, a given weight of the ore reduced to powder is mixed intimately with a certain quantity of granulated lead, and placed in each. They must then be heated gradually for about a quarter of an hour, with the door of the muffle closed, in order to fuse the lead; then diminish the heat and allow access of air by opening the door. The current thus established in the muffle soon causes the commencement of the roasting; and this roasting goes on without its being necessary to continually agitate the mass, as in the case of pulverulent substances.

During the oxidation, a slag is formed on the fluid metal, which is thrown towards the edges, and which, by continually augmenting, at last entirely covers the bath. This slag, which is often solid at the commencement, becomes softer and softer, and at last becomes perfectly fluid; because, in proportion to the advance of the operation, the proportion of lead oxide continually increases. When it is judged that the scorification has been carried far enough, the melted matter is stirred with a rod of iron, in order to mix with the mass the hard or pasty parts attached to the bottom or sides of the scorifier. The fire is then urged so as to completely liquefy the slags. It may be ascertained when they are sufficiently fluid by plunging into them a red-hot iron rod, which must only be covered with a slight coating, capable of running off, and not solidifying into a drop at the end.

This condition of liquidity is indispensable, in order to enable the metallic globules to unite into a single button. When this end is not attained, it is because the scorification has not been carried sufficiently far, or because a sufficient quantity of lead has not been added to form the flux, in which case a fresh quantity must be added, or, what is preferable, the assay recommenced with larger proportions.

When the operation is finished, the scorifier must be removed, and its contents immediately poured into a circular or hemispherical ingot mould (see fig. 29, p. 67). The metallic particles fall to the bottom, and as the cooling proceeds they form a button covered by the slag, which is readily detachable by a blow of a hammer; it ought to be very homogeneous and vitreous, and its colour varying from brown to greenish.

It is always advisable to examine it, and ascertain if it contain metallic globules. The button ought to be as ductile as ordinary lead; if not, it cannot be cupelled, and must be submitted to a fresh operation. It is in general advantageous to push the scorification to its greatest extent, because experiment has proved that less silver is lost than when a large button is cupelled. Nevertheless, there is a limit, because if the silver-lead produced be too rich, the least loss in the shape of globules would cause a notable one in the silver. Besides, as litharge exercises a very corrosive action on earthy matters, if the scorification be continued for a great length of time, it sometimes happens the vessel is pierced, and the assay has to be recommenced. The button of lead remaining ought to weigh about 200 to 300 grains, when the ores treated are of ordinary richness. The length of time a scorification takes is from half an hour to an hour. The scorifier can be rendered less permeable to the litharge by being rubbed inside with chalk, or, better still, red ochre.

There may be distinguished three distinct periods in the operation, viz. the roasting, the fusion, and the scorification. At first a strong fire is employed; but the doors of the furnace are opened as soon as the mixture is fused. The mineral, being specifically lighter than the lead, is then seen floating on its surface, or forming masses in it; the roasting then commences, and from the appearance of the vapours, the nature of the combustible matter it contains may be judged. Sulphur produces clear grey vapours; zinc, blackish vapours, and a brilliant white flame; arsenic, whitish-grey vapours; antimony, fine red vapours, &c. When no more fumes are seen, the mineral has disappeared, and the fused lead is perfectly uncovered, the roasting has terminated; this generally requires from eighteen to twenty minutes. At this time the fire is urged, so as to cause all the substances in the scorifier to fuse. It can be ascertained that the fusion is complete by the following signs: at the instant the muffle is opened the button becomes whitish-red with a greyish-black band, and there arise from the melted mass clear white fumes of lead, and the slag appears like a ring encircling the metal. The third period then commences: the furnace is cooled, as in the roasting, and the lead is allowed to scorify until it is entirely covered with fused oxide; this last period generally lasts about fifteen minutes. The fire is then increased for about five minutes, and the contents of the scorifier poured into the mould.

The process of scorification is applicable to all argentiferous matters, and is at the same time the most exact method of assay, as also the most convenient, when a large number of assays are required at the same time, because they are entirely executed in the muffle, which, with most assayers, is generally hot: it, however, requires a greater number of vessels—as cupels, &c.

When the silver ores are stony, the lead oxide formed during the roasting combines with the gangue, forming a fusible compound, whilst the remaining lead alloys with the silver. When the ores are metallic, the oxidisable bodies absorb oxygen from the atmosphere; and the oxides so formed combine with the litharge produced at the same time, forming a compound which becomes very fusible in proportion as the lead oxide increases; and if the scorification has not been pushed sufficiently far, the button will contain, besides silver and lead, a little copper, which will not, however, interfere with the cupellation. There is this one peculiarity about scorification, that however small the proportion of lead may be that is used, at the end of the operation the slag does not contain any oxysulphide. For instance, even when oxysulphides are produced in the course of scorification, they are completely decomposed in the roasting, and in consequence it is very rarely that the slag retains any proportion of silver; and as to the proportion of lead employed, only just enough to render the slag liquid, and to produce sufficient lead for cupellation, is necessary.

It is different, however, when the sulphides and arseniosulphides are assayed by means of litharge; for from 30 to 50 parts of that substance must be employed to prevent the scoriæ retaining any silver, or, as already pointed out, a certain proportion of nitre must be added.

All scorifications may be conducted by the simple addition of lead; but it has been proved that the operation proceeds more quickly, and with less danger to the scorifier, when borax is employed. This salt dissolves the oxides in proportion as they are produced, as also the gangues, and forms a very liquid slag from the commencement of the operation, which does not happen when lead alone is used, because litharge, which can alone cause the fusion, is only present in the slag in sufficient proportion at a very advanced stage of the operation.

When the slag is liquid at the beginning of the operation (as occurs in the use of borax), it is continually thrown on the sides of the scorifier, and forms a ring on the surface of the bath, leaving in the centre the metallic substance, having a considerable extent of surface, which is continually diminishing.

The current of air, being thus directly in contact with the fused metals, rapidly causes their oxidation, which does not take place when the semi-fluid substances float here and there on the metallic bath. The proportion of lead and borax necessary for a scorification varies exceedingly, according to the nature of the substance under assay, and ought to be greater in proportion as the substances, or resulting oxides, are difficult of fusion. In ordinary cases 12 parts of lead, and 1 of glass of borax, are employed; but sometimes 32 of lead, and 3 of borax, are required. A large proportion of borax is useful, especially when the substances contain much lime, zinc oxide, or tin oxide.

Instead of borax, glass of lead may be employed. It acts as a flux on silica; but its action is much less effective than that of borax.

There are some substances which scorify with a small proportion of lead. Thus, for galena and copper sulphide, 2 parts of lead suffice; but 8 parts are required for ores which contain much gangue.

Silver antimonide can be scorified with 8 parts of lead, but according to experiments made in the Hartz, it appears that the slag retains about $\frac{1}{140}$th of silver; with 16 parts of lead $\frac{1}{200}$th of fine metal is still lost; but with 3 of borax and 16 of lead not the slightest trace remains in the slag.

It is very difficult to separate tin and silver by the dry way. The best method is to roast the alloy in a scorifier, adding to it 16 parts of lead and 3 of borax at least, and operating as before described.

Speiss almost always contains silver, and is one of the most difficult substances to assay. If nickel be present, the button cannot be cupelled. Generally, speiss may be scorified with 16 parts of lead; and the same operation is gone through twice or thrice, adding each time a fresh quantity of lead. The operation would probably succeed by roasting the speiss in the scorifier before adding the lead.

Special Instructions for the Scorification Assay of Ores of the First Class.—This mode of assay has an advantage over the crucible assay just described, inasmuch as if properly conducted no preliminary assay is required: but this is greatly counterbalanced by the fact that not more than 50 grains of ore can be operated on in one scorifier, and that good or trustworthy results cannot be obtained by this method unless four scorifiers are employed for each assay, so that in all 200 grains of ore may be employed. There are thus employed four scorifiers to three crucibles, and four cupels to two cupels; as in one case four buttons are to be submitted to cupellation, and in the other only two. When very rich copper ores, however, have to be assayed for silver, the plan by scorification is very useful, as in the crucible operation much copper is reduced with the lead, so as to require a very large quantity of lead for its conveyance as oxide into the cupel. This class of assay will, however, be particularly noticed under the head Assay of the Alloys of Silver.

Assay in Scorifier.—Weigh out 300 grains of granulated lead, place them in a scorifier, then add 50 grains of pulverised fused borax, and 50 grains of the ore to be assayed, well mix them in the scorifier by aid of a spatula, and cover the mixture with other 300 grains of granulated lead: prepare in this way four scorifiers, place them in the muffle with the tongs (*b*, fig. 28, page 66) and carefully watch them with all the precautions before pointed out: when the surface of the metal is quite covered with fused oxide, pour the contents of each scorifier into one of the hollows of the mould depicted at fig. 29, page 67. When the mass of slag and metal is cold, separate the latter from the former by means of the hammer and anvil, hammer the metal into the form of a cube, and reserve it for cupellation.

Assay of Substances of the First Class admixed with Native or Metallic Silver.—The same kind of calculation is necessary in the assay of ores as above, as in the case of copper ores containing metallic copper. The sample must be carefully weighed. Suppose it to weigh 2,500 grains. It must be pulverised, and as much as possible passed through the sieve with eighty meshes to the linear inch. It will be thus divided into two parts: the one passing through the sieve is mineralised silver—that is, silver ore of various kinds mixed with earthy matter, and a very small quantity of metallic silver which has been sufficiently divided to pass through a sieve of such a degree of fineness; the other, impure metallic silver, which has been unable to pass through the sieve. The weights of both portions are carefully taken, and thus noted—

Rough metallic silver	5·07 grs.
Ore through sieve	2494·93 „
Total weight of sample	2500·00 „

Assay the ore which passed through the sieve as already directed, and the rough silver as directed under the head Assay of Silver Alloys. Note the quantity of silver obtained in each experiment. Thus: suppose 200 grains of ore yielded 2 grains of fine silver, and the 5·07 grains of rough silver 4 grains of fine silver by cupellation, the number of ounces of fine silver in the ton is thus calculated.

On referring to Table III. in Appendix, it will be found that if 200 grains of ore yield 2 grains of fine silver, 1 ton will yield 326 oz. 13 dwts. 8 grs. of fine silver; so that the average produce of the ore is the above amount.

Then, if 5·07 grains of rough silver yield 4 grains of fine silver, 200 grains would yield, by calculation, 159·763 grains of fine silver.

Thus—

$$\frac{200 \times 4}{5{\cdot}07} = 159{\cdot}763$$

Now, by referring to Table III. in the Appendix, it will be found that 200 grains of ore give 159 grains of fine silver = 25,970 ounces per ton: and that 200 grains of ore give ·763 grains of fine silver = 124 ozs. 12 dwts. 11 grains; therefore, the 5·07 grains of rough silver contain after the rate of 26,094 ozs. 12 dwts. 11 grs. per ton, thus—

25,970 ozs. + 124 ozs. 12 dwts. 11 grs. = 26,094 ozs. 12 dwts. 11 grs.

Thus we have—

	ozs.	dwts.	grs.
Average produce of ore	326	13	8
Average produce of rough silver . .	26,094	12	11

per ton of 20 cwts.

Then, as in the case of the copper, multiply the weight and produce of each portion together, add the resulting total products, and divide the sum by the weight of the sample. For this purpose it is better to reduce the pennyweights and grains to their decimal values. Thus 13 dwts. 8 grs. is nearly equal to ·67 of an ounce, and 12 dwts. 11 grs. to ·62 of an ounce; therefore the quantities above will stand thus—326·67 ozs., and 260,94·62 ozs.

$$\begin{array}{ll} \text{Then} & 326{\cdot}67 \times 2494{\cdot}93 = 815018{\cdot}7831 \\ \text{and} & 26094{\cdot}62 \times 5{\cdot}07 = 132296{\cdot}7234 \\ \text{and} & \dfrac{815018{\cdot}7831 + 132299{\cdot}7234}{2500} = 378{\cdot}9 \text{ oz.} \end{array}$$

or 378 ozs. 18 dwts. (nearly) per ton of the original sample, before pulverising and sifting.

In every case of assay yet described, it may be mentioned that if the sample contained gold, the whole of that metal will be found with the silver, as obtained by cupellation, and may be separated as stated in the chapter on the Assay of Gold.

Cupellation.—Cupellation is one of the most ingenious operations that can be imagined; it has been known from time immemorial, has many characters in common with scorification, and is effected in nearly the same manner. Like that, it has for its end the separation of silver and gold from different foreign substances, by means of lead; but it differs in this, that the scoriæ produced are absorbed by the substance of the vessel named a cupel, in which the operation is made, instead of remaining on the melted metal, the latter remaining uncovered and in contact with the air, so that the extraneous metals are not only oxidised, but also all the lead; and there remains nothing but the pure metals, silver and gold, or an alloy of them, in the cupel.

Cupellation requires, as an indispensable condition, that the slag should have the property of penetrating and soaking into the body of the substance forming the cupel; it is, therefore, only applicable to a certain number of substances, and not to all, like scorification. Lead and bismuth oxides, in a state of purity, are the only oxides which possess the property of soaking into the cupel; but by the aid of one or the other, various oxides which by themselves form infusible scoriæ on the cupel, acquire the property of passing through it: therefore, on making a cupellation, it is necessary to fuse the substance with a sufficient proportion of lead or bismuth, so that the oxides they produce may combine with the oxides of all the foreign metals produced in the operation, and carry them into the body of the cupel.

This proportion varies with the nature of the substances cupelled, and other circumstances. The quantity required in ordinary cases will be mentioned hereafter.

The cupels or porous vessels in which the operation is made, ought to have a sufficiently loose texture to allow the fused oxides to penetrate them easily, and at the same time to possess sufficient solidity to enable them to bear handling without fracture; and, moreover, they ought to be of such a nature as not to enter into fusion with either lead or bismuth oxide. For a description of their mode of manufacture, see p. 133.

The following is the method in which an ordinary cupellation is conducted:—The furnace being heated, the bottom of the muffle is covered with cupels, placing the largest towards the end; and if they are required to be heated as quickly as possible, they may be placed upside down, and turned, at the instant of use, by means of the tongs. When the interior of the muffle is reddish-white, the matters to be cupelled may be introduced. When the cupels have been placed in their proper position, great care must be taken from the commencement to blow out of them all cinders, ashes, and other extraneous substances which may have fallen into them.

The substance to be cupelled is sometimes an alloy, which can pass without addition of lead, and sometimes a compound, to which lead must be added. In the first case, the alloy is laid hold of by a small pair of forceps, and deposited gently in the cupel. In the second case, the substance to be cupelled is enveloped in a sheet of lead of suitable weight, and placed, as before, in the cupel; or the necessary quantity of lead may be first placed in the cupel, and when the lead is fused, the substance to be cupelled added, taking care not to agitate the melted mass and cause loss by splashing. If the substance to be cupelled is in very small pieces, as grains or powder, it must be enveloped in a small piece of blotting-paper, or, still better, in a piece of very thin sheet lead, giving it a slightly spherical form, and dropping it gently into the mass of molten metal in the cupel. Sometimes the substance is gradually added, by means of a small iron spoon; but it is preferable to use paper, or thin lead, as just recommended.

When the cupels are filled, the furnace is closed, either by the door or by pieces of lighted fuel, so that the fused metals may become of the same temperature as the muffle. When this point has been gained, air is allowed to pass into the furnace; the metallic bath is then in the state termed *uncovered*; that is, it presents a convex surface, very smooth and without slag. When the air comes in contact with it, it becomes very lustrous, and is covered with luminous and iridescent patches, which move on the surface, and are thrown towards the sides. These spots are occasioned by the fused oxide of lead which is continually forming, and which, covering the bath with a very thin coating of variable thickness, presents the phenomenon of coloured rings.

The fused litharge, possessing the power of moistening (so to speak) the cupel, is rapidly absorbed by it when sufficiently porous, so that the metallic alloy is covered and uncovered every instant, which establishes on its surface a continual motion from the centre to the circumference. At the same time a vapour rises from the cupels which fills the muffle, and is produced by the vapour of lead burning in the atmosphere. An annular spot is soon observed on the cupel around the metal, and this spot increases incessantly until it has reached its edges.

In proportion as the operation proceeds, the metallic bath of silver-lead diminishes, becoming more and more rounded; the shining points with which it is covered become larger and move more rapidly; lastly, as the whole of the lead separates, the button seems agitated by a rapid movement, by which it is made to turn on its axis; it becomes very lustrous, and presents over its whole surface all the tints of the rainbow: suddenly the agitation ceases, the button becomes dull and immovable, and after a few instants it takes the look of pure silver. This last part in the operation of cupellation is termed the *brightening*, *fulguration*, or *coruscation*.

If the button be taken from the muffle directly after the brightening, it may throw off portions of its substance; this must be avoided, especially when the button is large. The button, when covered by mammillated and crystalline asperities, is said to have 'vegetated.' The cause of this effect seems to be, that when the fused buttons are suddenly exposed to the cold air, the silver solidifies on the surface, whilst that in the interior remains liquid. The solid crust, contracted by cooling, strongly compresses the liquid interior, which opens passages for itself, through which it passes out, and around which it solidifies when in contact with the cool air. But it sometimes happens that, when the contraction is very strong, a small portion of the silver is thrown off in the shape of grains, which are lost.

After brightening, the cupels must be left for a few minutes in the furnace, and drawn gradually to the mouth, before they are taken out, so that the cooling may be slow and gradual. These precautions are nearly superfluous when the buttons are not larger than the head of an ordinary pin.

As silver is sensibly volatile, it is essential, in order that the smallest possible quantity be lost, to make the cupellation at as low a temperature as may be. On the other hand, the heat ought to be sufficiently great, so that the litharge may be well fused and absorbed by the cupel; and, moreover, if the temperature be too low, the operation lasts a very long time, and the loss by volatilisation will be more considerable than if the assay had been made rapidly at a much higher temperature.

Experience has proved that the heat is too great when the cupels are whitish and the metallic matter they contain can scarcely be seen, and when the fume is scarcely visible and rises rapidly to the arch of the muffle. On the contrary, the heat is not strong enough when the smoke is thick and heavy, falling in the muffle, and when the litharge can be seen not liquid enough to be absorbed, forming lumps and scales about the assay. When the degree of heat is suitable the cupel is red, and the fused metal very luminous and clear.

In general, it is good to give a strong heat at the commencement, so as to well uncover the bath, then to cool down, and increase the heat at the end of the operation for a few minutes, in order to aid the brightening. There can be no inconvenience in urging the temperature at first, because the silver-lead is then poor, and much precious metal cannot be lost by volatilisation. The increase of fire given towards the end is for the purpose of separating the last traces of lead, from which it is very difficult to free the silver, but this strong fire must not be continued long, otherwise there might be a notable loss by volatilisation. When the assay of very poor argentiferous matters is made, the heat can be kept up nearly all through the cupellation. It generally succeeds better when the temperature is too high than too low.

The force of the current of air which passes through the muffle is another very important thing in the success of the operation. Too strong a current cools the cupel, oxidises too rapidly, and the assay would be spoilt. With too feeble a current the operation proceeds slowly, the assay remains a long time in the fire, and much silver is lost by volatilisation.

When the litharge is produced more rapidly than it can be absorbed by the cupel, or when it is not liquid enough, which may happen from the furnace being too cold, or when other oxides, produced at the same time, diminish its fusibility, it accumulates gradually on the fluid metal, forming at first a ring which envelopes its circumference, and which, gradually extending, covers the whole surface; at this period the assay becomes dull, and all movement ceases. When the operation is carefully attended to, it is nearly always possible to avoid this accident. If at the first moment any signs are manifested of this evil, the temperature of the muffle must be raised, either by shutting the door, or placing in it burning fuel; the assay will, in a little time, resume its ordinary course. But when the cause of the mishap is supposed to be the abundance of foreign oxides in the assay, a fresh proportion of lead must be added.

It can be ascertained whether an assay has *passed* well by the aspect of the button. It ought to be well rounded, white, and clear, to be crystalline below, and readily detached from the cupel. When it retains lead it is brilliant below and livid above, and does not adhere at all to the cupel.

In order to detach the button, seize it with a strong pair of pliers (see fig. 97), and examine with a microscope, (see fig. 98), brushing it to detach small particles of litharge which may adhere to it, and place it in the pan of a balance (fig. 13, page 24), which will indicate the $\frac{1}{1000}$th of a grain. The weight of the silver furnished by the lead or litharge employed in the operation ought to be subtracted from the amount of silver obtained; so that it is necessary to ascertain the richness of these matters beforehand, as they are never completely free from silver. The poorest of them contain from $\frac{1}{100000}$th to $\frac{1}{10000}$th.

Sometimes an equal quantity of lead is placed in another cupel, and the silver thus obtained placed in the balance-pan containing the weights.

Cupellation does not give the exact proportion of silver contained in an alloy. There is always a loss, and this loss is always greater than that which takes place in the large way, as in the latter process a greater quantity is always obtained than that determined by the assay. The loss of silver is traceable to three causes: 1st, to volatilisation; 2ndly, to oxidation; 3rdly, and lastly, to the absorption of minute globules of silver into the body of the cupel. It is certain volatilisation takes place, because a notable quantity of silver is always found deposited on the sides of the furnace and chimney in the shape of dust; and silver, which is volatile by itself, becomes much more so when alloyed with lead, and is carried away by the vapours of the latter, and found in the pulverulent deposits, termed *lead smoke* or *fume*, which proceed from the combustion of the latter

FIG. 97.

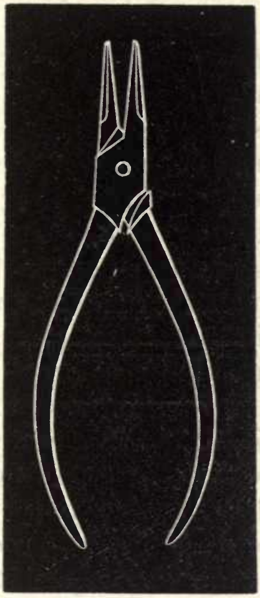
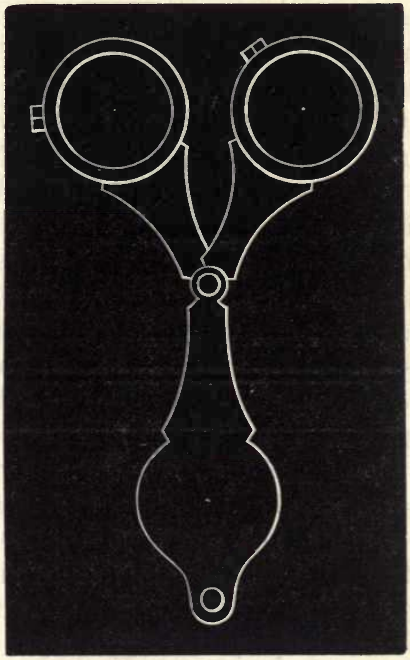


FIG. 98.



metal in the air. Nevertheless, this cause of loss is not very important, for it is rare that the fume contains more than $\frac{1}{10000}$th of silver, and accurate experiments have proved that in cupellation in the small way not more than two to three per cent. of lead is volatilised. It is certain that a portion of the silver found in cupels which have been used for assays exist in the state of oxide, for no part of their mass is free—it is found even in the bottom; besides it is known that the lead carbonate precipitated from lead acetate made from litharge contains silver, and a notable quantity of that metal is found even in the lead sulphate prepared by means of alum from the acetate (unless the sulphate is repeatedly washed with water).

It has been remarked that the centres of cupels which have been used for assays are richer in silver than the parts near the circumference, and that under the button there is a spot of bright yellow, which appears to be a compound of silver. But the most important cause of loss in an assay is the property which the alloys of silver and lead possess of introducing themselves into the pores of the cupel. The quantity thus lost is in proportion to the coarseness of the cupel. For the same quantity of silver, the loss which takes place in an assay varies according to the nature of the alloy, and the circumstances under which the assay is made; so that it is not possible to form accurate tables of correction. This loss is much augmented with the quantity of lead employed, but without its being proportionate; so that when scorification is had recourse to, it is advantageous to continue the operation for some length of time, in order that the metallic button may be reduced to the smallest suitable volume.

In the assay of rich alloys, the proportion to the total amount of silver is very small, but notable; and it has been calculated for the alloys of copper employed in the arts at $\frac{1}{3000}$th; but in the assay of poor ores, such as galena and other minerals treated in the large way, the loss is very great, for it is usually as high as $\frac{1}{500}$th.

By extracting the lead from cupels used in this class of assay, the metal furnished contains from about $\frac{1}{300000}$th to $\frac{1}{500000}$th of silver. The following experiment will give an idea of the influence of the proportion of lead on the loss of silver: 100 grains of commercial litharge were fused with 10 grains of black flux, and gave 27 grains of lead, and a slag; this was pulverised and reduced in the same crucible with 15 grains of black flux, and a second button was produced weighing 45 grains. These two buttons being cupelled separately, gave, the first ·0035 and the second ·001 only of silver. Three new quantities of 100 grains of the same litharge were fused; the first with ½ a part of starch, the second with 2½, and the third with 10 of the same reducing agent. The resulting buttons of lead weighed respectively 5, 28, and 79 grains. These buttons were cupelled, and furnished ·0035, ·0035, and ·003 respectively. From these experiments it will be seen that when the litharge is not reduced completely, there remains a notable proportion of silver in the scoriæ; but, nevertheless, in order to extract the largest possible quantity, the whole must not be reduced. Indeed, but a twentieth part only need be reduced, because more precious metal is lost in the cupellation of a large quantity of lead than remains in the portion not reduced. The loss of silver in large cupellations is less than that which takes place in an assay, because in the large way the litharge, or the greater part of it, is run off; whilst in an assay the cupel totally absorbs it, so that the latter presents, relatively to the same mass of lead, a very much smaller surface in the large than in the small way; now it can be readily seen that the quantity of silver lost by absorption into the pores of the cupel must be proportioned to its surface, all things being equal.

It has been ascertained by experiment that a cupel absorbs about its own weight of litharge; so that from this fact a cupel of the proper size may be chosen, when the weight of lead to be cupelled is ascertained. It is always better to have the cupel about ⅓ or ¼ as heavy again as the lead to be cupelled.

The various metals found in an alloy, which can be submitted to cupellation, scorify in proportion to their oxidisability. Those most oxidisable scorify with the greatest rapidity, and *vice versâ*; so that those which have the greatest affinity for oxygen accumulate in the first portions of litharge formed, which, by that means becoming less fusible, sometimes lose the property of penetrating the cupel; hence the reason why cupellations always present more difficulties at the commencement of the operation than towards the end, when the litharge formed is nearly pure lead oxide, and can contain only copper oxide.

The appearance of the cupel used in an assay will give indications of the metals the alloy contained. Pure lead colours the cupel straw-yellow, verging on lemon-yellow. Bismuth, straw-yellow passing into orange-yellow. Copper gives a grey, dirty red, or brown, according to its proportion. Iron gives black scoriæ, which form at the commencement of the operation, and are generally found at the circumference of the cupel. Tin gives a grey slag. Zinc leaves a yellowish ring on the cupel, producing a very luminous flame, and occasioning losses by carrying silver in its vapour, and by projecting it from the cupel in its ebullition. Antimony and lead sulphate in excess give litharge-yellow scoriæ, which crack the cupel; but, when not produced in too great a proportion, are gradually absorbed by the litharge. If the lead alloy submitted to cupellation is found to produce this effect, a fresh portion must be mixed with its own weight of lead and scorified: the button so obtained can now be cupelled.

Amalgamation.—There are a certain number of argentiferous matters which can be assayed by amalgamation, as they are treated in the large way by that method. Amongst these are native silver, chlorides, sulphides, and arsenio-sulphides, which contain neither lead nor copper.

But this process is seldom had recourse to, because it is long, troublesome, and less exact than those just described.

Substances of the Second Class.

- Native silver.
- Alloys of copper and silver.
- Alloys of other metals and silver (artificial).
- Silver antimonide.
- Silver arsenide.
- Silver telluride ($AgTe$)
- Auriferous silver telluride (see gold).
- Silver hydrargyride (amalgam), (Hg^2Ag).
- Silver auride (see gold).

The following method of separating silver from galena is given in the 'Chemical News,' vol. ii. p. 239.

'Galena consists, as is well known, of lead sulphide, mixed with a variable proportion of silver sulphide, and both these substances fuse together, or melt at a bright red heat. Now, it so happens that, when silver sulphide is fused with lead chloride, what is called a double decomposition takes place; that is to say, silver chloride and sulphide of lead are formed. Consequently, if we fuse together a quantity of argentiferous galena and lead chloride, we shall remove the whole of the silver from the galena, and replace it by lead sulphide. This, then, is the process: mix together the galena and lead chloride in the proportion of 100 lbs. of galena, 1 lb. of lead chloride, and 10 lbs. of sodium chloride or common salt; or, if the galena be very argentiferous, add a larger amount of lead chloride. The whole is then fused together, when the silver chloride and common salt rise to the surface, and may be skimmed off, and the desilverised galena falls and may be run out from the bottom. The mixture of silver chloride and salt may then be decomposed by lime and charcoal, or in any other manner, so as to reduce the silver and a portion of the surplus lead chloride, by which a metallic mass will result, suitable for the operation of the cupel.'

General Remarks on the Assay of the Alloys of Silver and Copper.—The assay of these alloys is nearly always accomplished (at least in England) by cupellation. This assay is most important, as it is by the results obtained in the manner hereafter described that the price or value of all kinds of silver bullion is determined.

This class of cupellation is effected without difficulty, because the copper oxide forms so slowly, that the litharge is always enabled to pass it into the body of the cupel. After having weighed the lead and placed it in the cupel, as soon as it is perfectly fused place in it the alloy to be assayed, wrapped either in blotting-paper or thin leaf-lead. It is essential, in this class of assay, to employ a sufficient quantity of lead to carry away all the copper. We may always be sure of succeeding, whatever the alloy may be, by employing the maximum proportion of lead, that is to say, the quantity necessary to pass pure copper; but as the loss which the silver undergoes increases with the length of the operation and with the mass of the oxidised matters, it is indispensable to reduce this loss as much as possible by reducing the proportion of lead to that which is strictly necessary. Long experience has proved that silver opposes the oxidation of copper by its affinity, so that it is necessary to add a larger amount of lead in proportion to the quantity of silver present.

M. D'Arcet has obtained the following results by the most accurate experiments:—

Standard of silver	Quantity of copper alloyed	Quantity of lead necessary	Relation of lead to copper
1000	0	$\frac{3}{10}$ths	
950	50	3	60 to 1
900	100	7	70 — 1
800	200	10	50 — 1
700	300	12	40 — 1
600	400	14	35 — 1
500	500	16 to 17	32 — 1
400	600	16 — 17	27 — 1
300	700	16 — 17	23 — 1
200	800	16 — 17	20 — 1
100	900	16 — 17	18 — 1
pure copper	1000	16 — 17	16 — 1

It is remarkable that below the standard of 500, the same proportion of lead must be employed, whatever that of copper. This fact is repeatedly verified by experiment. Whenever fine silver is fused in a cupel, it is always necessary to add lead, in order to cause the button to unite and form well. If less than $\frac{3}{10}$ths of lead be employed, the button will be badly formed; the litharge cannot separate but by the action of a very strong heat, and a considerable loss of silver ensues. If, on the contrary, $\frac{3}{10}$ths of lead is exceeded, the cupellation goes on well, but the loss is greater on account of the duration of the process. These proportions also ought to vary with the temperature. M. Chaudet has found that, to cupel an alloy containing $\frac{900}{1000}$ths of silver, 5 parts of lead are required in the middle of the muffle, 10 in the front, and only 3 at the back.

The proportion of copper carried off by litharge varies not only with the temperature, but even for the same temperature in relation to the amount of copper and lead the alloy contains. By cupelling 100 parts of copper with different proportions of lead in the same furnace, M. Karsten obtained the following results :—

Lead added	Copper remaining after cupellation	Quantity of lead consumed in carrying off 1 of copper
100	78·75	3·
200	70·12	7·1
300	60·12	7·7
400	49·40	7·9
500	38·75	8·1
600	26·25	8·15
700	19·75	8·00
800	8·75	8·70
900	5·62	9·50
1000	1·25	10·10
1050	0·00	10·50

From which we see that the lead carried away from $\frac{1}{15}$th to $\frac{1}{10}$th of its weight of copper. Much less lead can be employed in a cupellation by making the alloy maintain its richness of copper throughout the operation. This can be accomplished by adding to the alloy in the cupel small doses of lead, in proportion as that first added disappears by oxidation. If, for example, an alloy composed of 4 parts of copper and one of silver be fused with 10 of lead, by adding successive small doses of the latter, as already pointed out, but 7 parts will be consumed, although in the regular way from 16 to 17 would be employed.

The proportion of copper oxide contained in the litharge increases each instant, and goes on incessantly increasing when an alloy of copper and lead is cupelled which contains an excess of copper. According to M. Karsten, this proportion is always about 13 per cent. at the commencement, and 36, or more than a third, at the end of the operation.

In the assay of the coined alloys of copper and silver, the loss of silver may even amount to five thousandths; but the loss is variable, and is proportionally greater as the standard of the alloy is lower.

The following Table contains the results of many experiments made on this subject :—

Exact standard	Standard found by cupellation	Loss, or the quantity of fine metal to be added to the standard as obtained by cupellation
1000	998·97	1·03
975	973·24	1·76
950	947·50	2·50
925	921·75	3·25
900	896·00	4·00
875	870·93	4·07
850	845·85	4·13
825	820·78	4·22
800	795·70	4·30
775	770·59	4·41
750	745·38	4·52
725	720·36	4·64
700	695·25	4·75
675	670·27	4·73
650	645·29	4·71
625	620·30	4·70
600	595·32	4·68
575	570·32	4·68
550	545·32	4 68
525	520·32	4·68
500	495·32	4·68
475	470·50	4·50
450	445·69	4·31
425	420·87	4·13
400	396·05	3·95
375	371·39	3·61
350	346·73	3·27
325	322·06	2·94
300	297·40	2·60
275	272·42	2·58
250	247·44	2·56
225	222·45	2·55
200	197·47	2·55
175	173·88	2·12
150	148·30	1·70
125	123·71	1·29
100	99·12	0·88
75	74·34	0·66
50	49·56	0·44
25	24 78	0·22

These numbers, however, are not constant, and vary with the circumstances under which the assays are made: two assays made from the same ingot, by the same assayer, may differ as much as four or five thousandths. Tillet has remarked that the cupels can retain double as much silver as is lost; which proves, as has already been mentioned, that the silver obtained by cupellation is not perfectly pure, but may retain as much as 1 per cent. of lead.

Special Instructions for the Assay of the Alloys of Silver and Copper.

As before stated, peculiar weights are employed in the assay of silver bullion; and the silver assay pound, with its divisions, will be found described at pages 31–32.

In the 'General Remarks on the Assay of the Alloys of Silver and Copper,' it will be seen that the alloy must be cupelled with a quantity of lead, varying with the amount of copper present in the alloy. Standard silver cupels very well with five times its weight of lead; but when the approximative quantity of alloy present is not known, it must be determined by a preliminary assay.

Assay for Approximative Quantity of Alloy.—Weigh off 50 grains of pure or test lead; place them in a cupel previously made red-hot; when the lead is fused, and its surface covered with oxide, place in it by means of the light tongs (*a*, fig. 28, page 66) 2 grains of the alloy under assay, wrapped in a small piece of thin paper. Allow the cupellation to go on according to the instructions, and with all the precautions already given, and when complete, weigh the resulting button, and, according to its weight, add lead in the actual assay in the quantity that is sufficient, as exhibited in the Table at page 566.

Assay Proper of Silver Bullion.—In this assay the operator requires silver known to be standard, and pure lead. With the possession of the above substances the assay is thus proceeded with:—Place the 12 grains weight = 1 lb., in the scale pan, and exactly counterbalance it with standard silver. This is to serve as a check. Remove the weight, and in its place add so much of the alloy to be assayed that the balance is again equal. In one cupel, that destined to receive the check sample, place 60 grains of lead; and in another cupel place such a number of grains of lead as may be found necessary by the preliminary assay. When the lead in both cupels is fused, add the silver alloy, and cupel with the necessary precautions. When the buttons in the cupels are cold, seize them with the pliers, and if necessary cleanse them with a hard brush, and place one in each balance-pan. If they exactly balance each other, the alloy operated on is standard silver; if, however, it weighs less than the button produced from the check sample by the weight equivalent to 2 pennyweights, then it is 2 pennyweights worse than standard: on the other hand, if it be heavier by the same weight, it is 2 pennyweights better than standard. Silver is also reported as so much fine: thus standard silver may be reported as 11 ounces 2 pennyweights fine, and so on. In case extreme accuracy be required, correction must be made according to the standard as shown by the Table at page 568. The standard silver in England is $\frac{975}{1000}$ fine.

Assay of Alloys of Copper and Silver.—In the treatment on the large scale of copper ores containing silver, the contained silver is found alloyed with the copper, and it often falls under the assayer's province to determine the quantity of precious metal. An assay of this kind is most conveniently accomplished by scorification before cupellation, thus:—Prepare four scorifiers; weigh into each of them 50 grains of the alloy, 50 grains of fused borax, and 600 grains of lead, and proceed as already described under the head 'Assay of Ores of the First Class by Scorification.' When the four buttons of lead are obtained, place them together in another scorifier, and submit to the furnace until the contents of the scorifier are completely covered with oxide; pour as usual, and cupel the resulting mass of lead.

Alloys of Platinum and Silver.—If any substance containing platinum as well as silver were assayed as already described, the button resulting from the cupellation would, in addition to the silver, contain the whole of the platinum.

In such a case the button so obtained must be thus treated:—

If the alloy contain much platinum, it must be fused with twice its weight of silver; then treated with hot nitric acid; evaporate the solution nearly to dryness; add water and hydrochloric acid, until no further precipitation of silver as a white curdy precipitate (silver chloride) takes place. The silver chloride may be collected either on a filter or by decantation. The solution containing the platinum is treated with excess of sal-ammoniac solution until no further precipitation takes place; the solution evaporated to dryness. When cold, dilute alcohol is added; and the insoluble yellow matter (platinum ammonio-chloride) collected on a filter, washed with alcohol, dried, and ignited. The ignited residue is metallic platinum, which is weighed. The loss of weight which the alloy from cupel has sustained represents the amount of silver previously alloyed with it.

Alloy of Platinum, Silver, and Copper.—Treat such an alloy as above; and the liquid, filtered from the platinum ammonio-chloride, will contain the copper. Acidulate it with hydrochloric acid, add metallic zinc, and proceed as directed under the head 'Wet Copper Assay.'

Native Silver, Rough Silver left on Sieve during Pulverisation of Silver Ores of First Class, and Native Alloys of Silver—as Antimonides, &c.—are treated by scorification and cupellation in precisely the same manner as just described for alloys of copper and silver.

Dr. W. Dyce proposed, in 'Tilloch's Philosophical Magazine' for 1805, the following process for separating gold and silver from the baser metals:—

'Hitherto the process has always been, as far as I have understood it, attended with considerable difficulty in the execution; but, by that which I am about to describe, it is done with exact certainty. It was discovered and communicated to me by a gentleman in the neighbourhood. The process consists in mixing not less than two parts of powdered manganese with the impure or compound metal, which should be previously flattened or spread out so as to expose as large a surface as possible, and broken or cut into small pieces for the convenience of putting the whole into a crucible, which is then to be kept in a sufficient heat for a short time. On removing the whole from the fire, and allowing it to cool, the mixture is found to be converted into a brownish powder, which powder or oxide is then to be mixed with an equal proportion of powdered glass, and then submitted in a crucible to a sufficient heat, so as to fuse the whole, when the perfect metals are found at the bottom in a state of extreme purity, a circumstance of no small importance to the artist and the chemist, the latter of whom will find no difficulty in separating the one from the other with so little trouble compared with the usual processes, that I have no doubt it will always be practised in preference to the cupel.'

Assay of Silver Bullion by the Wet Method.—From that which has been stated under the head of 'Cupellation,' it will be observed that there are many sources of error; such as volatilisation of the precious metal, its oxidation in the presence of excess of lead oxide and atmospheric oxygen, and lastly, its absorption into the body of the cupel either as oxide or metal, or in both states. These losses, as before stated, vary with the temperature, the amount of lead employed, and the texture of the cupel; and, as may be seen from the table of corrections as drawn up by D'Arcet, give a very erroneous assay, unless the addition necessary for each standard be made.

Considerable attention was called to this matter in France some years since, and a Special Commission was appointed to examine the subject thoroughly, and, if possible, to devise some means of assay which might be both easy and accurate. The result of this examination was the invention of a process of assay at once elegant and trustworthy: and as a full account of this method has not, to the author's knowledge, been translated and published in this country,* he has prepared the present from M. Gay-Lussac's Report, which formed a part of a com-

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* Some portion of this report has been published in Dr. Ure's 'Dictionary of Arts, Mines, and Manufactures.'

munication from M. Thiers to Earl Granville, and which appeared in the original language in the year 1837, in a Report on the Royal Mint.

The process of assay about to be described consists in determining the fineness of silver bullion by the quantity of a standard solution of common salt necessary to fully and exactly precipitate the silver contained in a known weight of alloy. This process is based on the following principles:—

The alloy, previously dissolved in nitric acid, is mixed with a standard solution of common salt, which precipitates the silver as chloride, a compound perfectly insoluble in water, and even in acids.

The quantity of silver chloride precipitated is determined not by its weight, which would be less exact and occupy too much time, but by the weight or volume of the standard solution of common salt necessary to exactly precipitate the silver previously dissolved in nitric acid.

The term of complete precipitation of the silver can be readily recognised by the cessation of all cloudiness when the salt solution is gradually poured into that of the nitrate of silver. One milligramme of that metal is readily detected in 150 grammes of liquid; and even a half or a quarter of a milligramme may be detected, if the liquid be perfectly bright before the addition of the salt solution.

By violent agitation during a minute or two, the liquid, rendered milky by the precipitation of silver chloride, becomes sufficiently bright after a few moments' repose to allow of the effect of the addition of half a milligramme of silver to be perceptible. Filtration of the liquid is more efficacious than agitation; but the latter, which is much more rapid, generally suffices. The presence of copper, lead, or any other metal, with the exception of mercury (the presence of the latter metal requires a slight modification of the process, which will be hereafter pointed out), in the silver solution, has no sensible influence on the quantity of salt required for precipitation: in other words, the same quantity of silver, pure or alloyed, requires for its precipitation a constant quantity of the standard salt solution.

Supposing that 1 gramme of pure silver be the quantity operated on, the solution of salt required to exactly precipitate the whole of the silver ought to be of such strength that, if it be measured by weight, it shall weigh exactly 100 grammes, or if by volume 100 cubic centimètres. This quantity of salt solution is divided into 1000 parts, called thousandths.

The standard of an alloy of silver is generally the number of thousandths of solution of salt necessary to precipitate the silver contained in a gramme of the alloy.

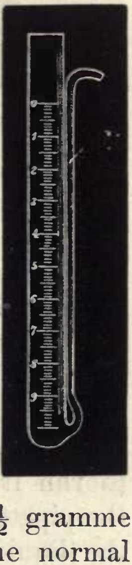
Measurement of the Solution of Common Salt.—The solution of common salt will hereafter be termed the normal solution of common salt. It can be measured by weight or volume. The measure by weight gives greater precision, and it has the special advantage of being independent of temperature; but it requires too much time in numerous assays. The measure by volume gives a sufficient exactitude, and requires much less time than the measure by weight; it is, indeed, liable to the influence of temperature, but tables for correction will be appended.

Fig. 99.

Measure of the Normal Solution of Salt by Weight.—This solution should be so made that 100 grammes will exactly precipitate 1 gramme of pure silver dissolved in nitric acid. In order to point out the method of taking the weight it must be supposed to have been previously prepared. After the process of taking the weight is described, the mode of preparing the solution will be given.

The solution is weighed in a burette (fig. 99) whose capacity is from 115 to 120 grammes of the solution, and divided into grammes. These divisions are for the purpose of approximatively determining the weight of solution, so as to shorten the operation of weighing. The burette is represented as closed by a cork, *B*, in order to prevent evaporation of the solution when the instrument is not in use. It is also easy to remedy the inconvenience of evaporation, by rinsing the burette with a small quantity of the fresh solution. On pouring the solution from the orifice, *O*, of the burette, each division will furnish from 8 to 10 drops; and consequently the weight of a drop is about a decigramme. The burette is filled with solution to the division *o*; it is then tared in a balance capable of turning with a centigramme. The burette is then removed, and its place supplied with a weight equivalent to the amount of solution required—100 grammes, for instance. The solution is then gradually poured from the burette into a bottle appointed for its reception, until the equilibrium is nearly established. It is not easy to attain the point exactly, as no smaller quantity than a drop can be poured from the burette. This, however, is a matter of indifference; it suffices to know the exact weight of the solution poured out: suppose it to be 99 gr. 85 c. The mode of more nearly approximating the required weight of 100 grammes will now be pointed out.

FIG. 100.



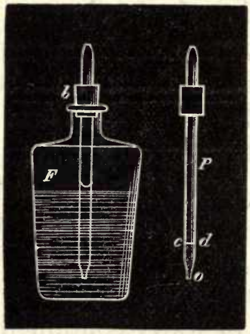
It must be remarked that it is not the amount of water contained in the 100 grammes that is of consequence, but only the quantity of salt found in solution; this should exactly represent 1000 thousandths of pure silver. If now 100 grammes of the normal solution be mixed with 900 grammes of water, it is evident that 1 gramme of this new solution is equivalent to a decigramme of the first, and consequently it will be easy to obtain 100 grammes of the normal solution, or rather the 1000 thousandths of salt it ought to contain; it will now be sufficient to add to the 99 grammes already poured from the burette, $1\frac{1}{2}$ gramme of the new solution. It can be weighed, like the normal solution, to a drop nearly, in the burette (fig. 100), of such a diameter that each small division represents a decigramme of liquid, and consequently a centigramme of the normal solution; but it is more readily measured by volume, preparing it in the manner to be hereafter pointed out. To avoid all confusion, a solution to be termed a *decime* solution of common salt is one containing the same quantity of salt as the normal solution, in a weight or volume ten times greater.

A *decime* solution of silver is a solution of silver equivalent to the latter, both mutually suffering complete decomposition.

Preparation of the Decime Solution of Common Salt.—One hundred grammes of the normal solution of common salt are weighed in a flask (fig. 101) containing a kilogramme of pure water, when filled up to the mark *a b*, or 1000 cubic centimètres; this quantity is made up with pure water, taking care to agitate the whole well, to render the mixture homogeneous. A cubic centimètre of this solution represents 1 thousandth of silver. This quantity is readily obtained by means of a pipette (fig. 102), gauged so that when filled up with water to the mark *c d*, it shall allow 1 gramme, or 1 cubic centimètre, to run freely, the small quantity of liquid remaining in the pipette not forming part of the gramme. In pouring the liquid by drops, a little more or a little less than

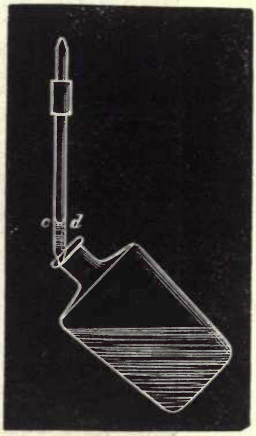
FIG. 101.

FIG. 102.



twenty may be counted, according to the size of the orifice, *o*. This number will not vary more than one drop. Half a cubic centimètre will consequently be represented by 10 drops, and a quarter by 5. The precision arrived at by this method of measurement suffices, since the possible error on the cubic centimètre will be but one-twentieth of that quantity, or one-twentieth of a thousandth; if, however, many measures be required, then compensation must be made.

FIG. 103.

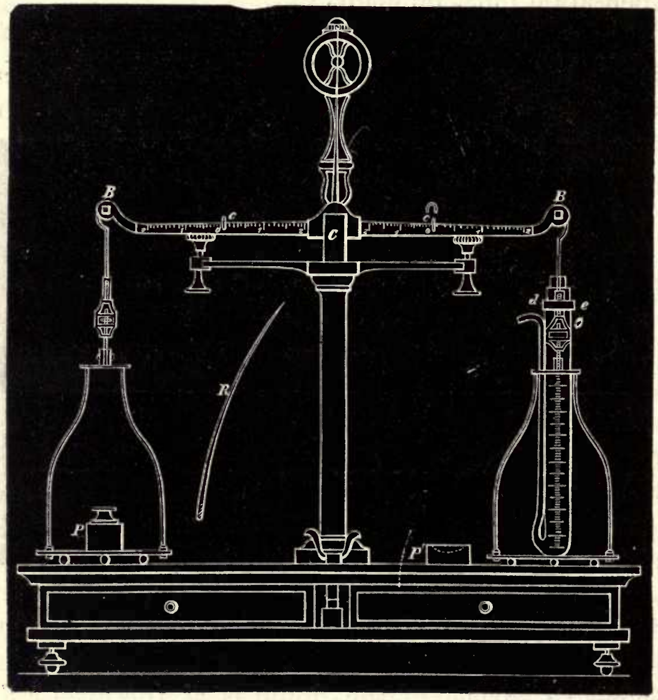


The decime solution of common salt requisite for assays must be kept in a bottle (Fig. 102) closed by a cork, traversed by the pipette, firmly fixed in a hole bored for that purpose. To measure a thousandth with the pipette, the bottle is held with one hand, and the pipette with the other (Fig. 103). The pipette is taken from the solution after its upper orifice has been closed by the forefinger; the lower orifice is then inclined against the edge of the flask to remove the liquid, which without this precaution would remain there: the mark *c d* is then raised to the level of the eye, and by a suitable pressure of the forefinger on the upper orifice, which may be obtained by giving the pipette a slight alternating circular movement between the fingers, the solution is allowed to run out gradually. The instant the concave surface of the liquid is at the level *c d*, the pipette is firmly closed by pressure of the forefinger on its orifice, which is held above the bottle into which the solution is to be poured, and the forefinger removed so that it can be emptied. It is here necessary to remark, that in order to regulate the slow and regular runnings of the liquid from the pipette, by the pressure of the forefinger, the latter ought to be neither too moist nor too dry: if too dry it will not perfectly close the orifice, even by strong pressure; if too moist, it prevents the entrance of air, and the liquid will not run, or if it do, it will be irregularly.

This observation should not be lost sight of in the use of the large burettes mentioned hereafter.

Preparation of the Decime Solution of Silver.—The decime solution of silver is prepared by dissolving 1 gramme of pure silver in nitric acid, in a flask holding 1 litre (see Fig. 101), and then diluting the solution with distilled water, so that, cooled at the ordinary temperature of the air, it shall occupy exactly the volume of one litre. It is measured in precisely the same manner as the decime salt solution.

FIG. 104.



Weighing the Normal Solution of Common Salt.—To execute this operation with rapidity, a balance similar to that represented at Fig. 104 is employed. The arms are divided as in the assay balance described at p. 25; each of the arms, C B and C B, are furnished with a rider, *c*, of such a weight (about 5 decigrammes) that moved from the right or the left of the centre, C, of each arm, it indicates two decigrammes. The space traversed by the rider is divided into twenty equal parts, representing an equal number of centigrammes.

We will take for example the weighing of 100 grammes of normal solution of common salt, which is that most frequently made in the determination of the standard of all varieties of argentiferous matter.

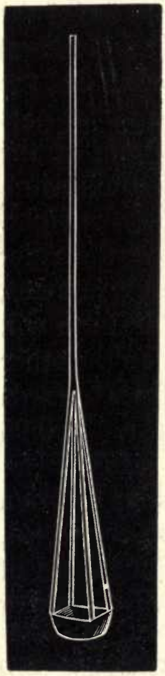
There are two weights, one, *P*, equal to the tare of the burette when full of solution to the mark *o*, the other, *P′*, equals 100 grammes. The burette is filled with solution, and placed on the right-hand pan of the balance, on which it is kept in position by the collar *d e*, and through which it is passed before placing it on the pan. The tare, *P*, of the burette is supposed to be on the opposite side. If the equilibrium be not perfect, it is effected by the rider on the left; the burette is then removed, and 100 grammes of the solution (either more or less to one or two decigrammes) poured out. The burette is then again placed in the balance, with the 100-gramme weight *P′*, the upper part of which is slightly concave to receive the bottom of the burette, in order to prevent it sliding off. The equilibrium is again established by the aid of the rider on the right. If, for instance, it is found necessary to remove the rider 15 divisions towards *B*, which represents 15 centigrammes, the weight of the solution poured out of the burette will be equal to 100 gr. − 0·15 gr. = 99·85 gr. If, on the other hand, it is necessary to move the rider six divisions towards c, the weight of the solution will be 100 gr. + 0·06 gr. = 100·06 gr.

The above method of weighing the salt solution appears to be the most convenient that can be employed, although it is not very expeditious. Other methods of weighing and measuring will be given in an appendix to this article.

Preparation of the Normal Solution of Common Salt when measured by weight.—After having pointed out the method of weighing the normal solution of salt, and of taking very small quantities, its preparation will be described.

Supposing the salt as well as the water to be employed are pure, the two substances have only to be taken in the following proportions:—0·5427 kilogramme of salt and 99·4573 kilogrammes of water, to form 100 kilogrammes of solution, of which 100 grammes will exactly precipitate 1 gramme of silver. But instead of pure salt, which is difficult to procure, and which besides rapidly alters by the absorption of atmospheric moisture, it is preferable to employ a concentrated solution of commercial salt, which can be prepared in large quantities, and kept for use as needed. The quantity of salt it contains can be ascertained by evaporating a portion to dryness, and by a few experiments it is easy to determine in what proportion it shall be mixed with water to produce a solution, 100 grammes of which shall exactly precipitate 1 gramme of silver.

FIG. 105.



Suppose, for example, that the salt solution contains 250 grammes of salt per kilogramme, and that it is necessary to prepare 100 kilogrammes of the normal solution. Now, since for the preparation of this quantity 0·5427 kilogramme of pure salt is required, we have the following proportion:—

$$0{\cdot}250 : 1 :: 0{\cdot}5427 : x = 2{\cdot}1708 \text{ kilogs.}$$

To this last weight enough water is added to make up 100 kilogrammes, that is to say, 97·8292 kilogrammes, which quantity can be readily measured by means of a flask containing 5 or 6 kilogrammes previously gauged.

The mixture must be well agitated by means of the agitator (Fig. 107), which is made of an osier twig, split into four branches, to the extremities of which is attached a small square piece of silk. This substance is employed to avoid the separation of filaments which would ensue from the use of any other material. This agitator can be introduced into very small openings, and is exceedingly serviceable in agitating large masses of liquid.

When well mixed, the solution must be assayed. To effect this, dissolve 1 gramme of silver in nitric acid, sp. gr. 1·290, in a stoppered bottle (Fig. 106) holding about 200 grammes of water, tare the burette (Fig. 99) filled with the solution, and pour rather more than less into the bottle; in proportion as the salt employed is impure, more than 100 grammes will be required to precipitate 1 gramme of silver. The mixture is at first milky, but, by vigorously shaking the bottle, having its stopper firmly fixed, for about a minute, and then allowing it to remain at rest for a short time, the liquid will become perfectly bright: two drops of the solution must then be poured into it from the burette: if a cloudiness is produced, it is agitated again to brighten it, and two drops more added. This must be continued until the last two drops added give no precipitate. The operation is then terminated, and nothing remains to state but the result.

FIG. 106.

Supposing the total weight of solution poured from the burette is 101·880 grammes, the last two drops must not be reckoned, because they produce no effect; the two preceding drops were necessary, but in part only; that is to say, the number of drops to be deducted is less than four, and more than two, or rather it is the mean term, three. Or the weight of a drop can be known exactly by taking that of a dozen: suppose it is equal to 0·082 gramme, three times that number must be deducted, or 0·255 grammes from 101·880 grammes: there will remain 101·625 grammes, representing the quantity of normal solution necessary to precipitate 1 gramme of silver.

The solution is thus found to be too weak; to bring it to its proper standard it is necessary to remove 1·625 gramme of water from the 101·625 grammes of solution, or, what is the same thing, to add to the normal solution a certain quantity of the concentrated solution of common salt, which quantity may be found by the following proportion :—

Salt Sol.

100 : 1·625 :: 2·1708 kilogrs. of silver solution : $x = 0·0353$.

After the addition of this quantity of salt to the normal solution, a fresh assay is made, proceeding in precisely the same manner as before; taking care, however, to pour from the burette a weight of solution slightly under 100 grammes, or 1000 decigrammes; for instance, 998·4 decigrammes, because it is not possible, in pouring the solution by drops, to arrive at the exact weight, 1000 decigrammes. To ascertain the true standard in the most exact manner possible, a decime solution must be prepared by weighing 100 grammes of the normal solution, and diluting it with pure water, so that it shall occupy one litre: a cubic centimètre of this solution will represent a decigramme of the normal solution. This decime solution will not be rigorously exact, since the normal solution has not been truly standardised; but it is easily perceived that the error thus committed is very small, and that it may be neglected. Nevertheless, as soon as the normal solution is perfectly standardised, it is better to prepare another decime solution.

A decime solution may be immediately obtained by dissolving 0·5427 gramme of pure sea-salt in such a quantity of water that the whole will occupy one litre; yet the first process is preferable.

With the decime solution the assay may be thus continued, remembering that the pipette described at Fig. 102 is a cubic centimètre containing 20 drops; that the half, therefore, is represented by 10 drops, and the fourth by 5.

To the 998·4 decigrammes of normal solution already added, pour one pipette and 12 drops of the decime solution, which will exactly complete the weight of 1000 decigrammes of normal solution. The mixture is agitated to brighten it, and one-thousandth of common salt or one pipette of the decime solution added. If this causes a cloudiness, it is agitated and a second thousandth added. This last should produce no opalescence. The weight of normal solution necessary to exactly precipitate one gramme of silver will be between 1000 and 1001 decigrammes; that is to say, the mean will be equal to 1000·5. The standard of the normal solution is then too weak by half a thousandth; to correct this a quantity of concentrated salt solution must be added equal to half a thousandth of that already added (2·1708 + 0·0353 = 2·2061 kilogrammes); that is to say, 1·1 gramme.

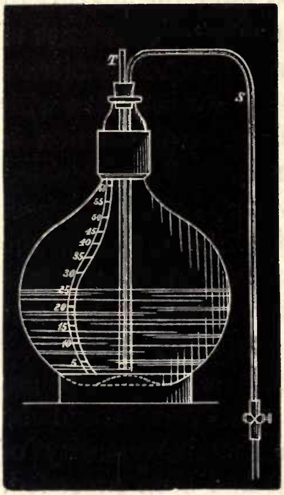
A new assay is then made for verification.

When the standard of a solution is very nearly arrived at, it is well to employ filtration to detect the slightest opalescence, at least when sufficient time is not allowed for the liquid to become perfectly bright. The surest method when the standard is nearly attained, is to place some of the liquid in two test-glasses, and pour into one a few drops of the decime solution of common salt, and into the other a corresponding number of drops of the decime solution of silver nitrate. It may then be determined on which side the opalescence is manifested, and the assay of the normal solution may be continued after the mixture of the liquid in the two glasses, since the two quantities of the decime solutions of common salt and silver nitrate mutually decompose each other, and do not interfere with the assay. Once the standard of the normal solution is definitely fixed, the sum of the quantities of the concentrated solution of common salt which have been employed, as well as those of the water, must be noted, and in the preparation of a new normal solution the proportions found as above would only have to be mixed to obtain at once a solution having very nearly its true standard.

In determining the standard of the normal solution, supposing that it were always too weak, it would be necessary to add to the solution a certain quantity of common salt; but if the true amount had been exceeded, and it had been found too strong, the solution would have to be precipitated with the decime solution of silver; and knowing the number of cubic centimètres or thousandths of silver which had been necessary to precipitate the excess of common salt, it could be determined what amount of water must be added to reduce the normal solution to standard. For instance, if 2 thousandths of the decime solution of silver had been consumed, 2 thousandths of its weight of water would have to be added to the total amount of solution; that is to say, 0·2 kilogramme or 200 grammes.

Preservation of the Normal Solution of Common Salt.—The most suitable vessel for containing the normal solution of common salt is one of glass, because that cannot affect the standard. Large glass bottles, termed *carboys*, are found in commerce. These bottles contain from 50 to 60 litres, and are very applicable for this purpose. Fig. 107 represents one of these bottles fixed in a stand formed of a sieve hoop. It is graduated into litres or kilogrammes of water, and a paper scale fixed on its side shows at any time the quantity of contained liquid. It is closed by an hydraulic valve, made of sheet iron, but the bell or cover is of glass. The detail of this valve is shown at Fig. 108. The air can only enter the bottle by the narrow tube *T*, and cannot pass out by it; consequently evaporation is not to be feared. The neck of the valve should be about a decimètre deep, into which mercury should be poured, but only to about one-third of its height.

FIG. 107.



The solution is drawn from the bottle by the syphon *S*. This is furnished with a stopcock; but this syphon being brittle, at least when not of metal, is not convenient in use, since it is incorporated with the bell of the valve: it is, therefore, preferable to pierce the bottom of the bottle (Fig. 109), and fix a metal tube (*T*) by means of a plate moulded on the bottom and cemented to it. This tube is raised a little above the bottom of the bottle, and covered by a small cup, the object of which is to protect it from any of the mercury which might fall into it. It is terminated at its other extremity by a very narrow tube, so that the flow of the solution may not be too rapid.

FIG. 108.

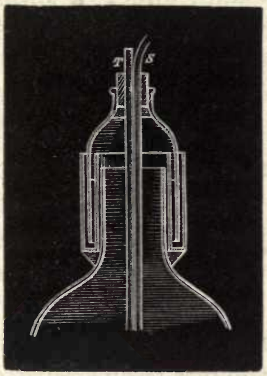
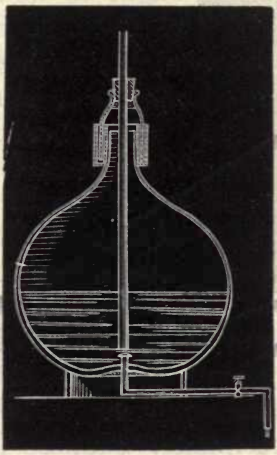


FIG. 109.



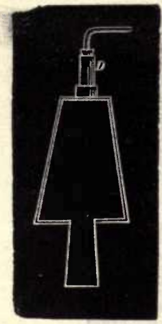
Hereafter a metal reservoir will be described which has all the advantages of a glass vessel without its inconveniences.

Application of the Process described in the Determination of the Standard of a Silver Alloy.—The alloy is supposed to be that made into coin, the mean standard of which is fixed at 900 thousandths, but which may vary from 897 to 903 thousandths without ceasing to be legal (French standard for coin). One gramme is dissolved in the bottle (fig. 106) by about 10 grammes of nitric acid, sp. gr. 1·290. This quantity of nitric acid can be readily taken by means of the pipette *P* (fig. 110), which contains 7·7 grammes of water to the mark *a b*. The solution may be accelerated by placing the bottle in a small pan of hot water, the bottom of which must be covered with a piece of cloth, so as to prevent contact of the glass and metal. The solution finished, and the flask slightly cooled, the

FIG. 110.

nitrous vapour must be removed by a blower (see fig. 111), the nozzle of which is formed of a piece of bent glass tube, connected by a cork with a copper socket *D*, having a screw inside. This operation ought to be effected, as well as the solution of the alloy in nitric acid, under a chimney with a strong current of air, to carry off the nitrous vapour.

FIG. 111.



The burette (fig. 99), being filled with the normal solution of common salt, and tared, about 90 grammes are poured into the solution of the alloy; say 89·85 grammes. After agitating the liquor, a cubic centimètre of the decime solution of common salt is added representing one-thousandth of silver. If a cloudiness be observed, agitate again, and add a second thousandth of common salt, and so on, until the last thousandth gives no precipitate. Suppose it to be the fourth: that must not be counted, because it has produced no effect; and only a half of the third must be taken, because only a portion of that was necessary. The standard of the alloy would be consequently equal to $898{\cdot}5 + 2{\cdot}5 = 901$.

If it be desirable to approach still nearer to the true standard of the alloy, half-thousandths must be added until the last half-thousandth gives no precipitate; and in order to avoid all confusion, it is better to write with chalk on a blackboard the thousandths of common salt, preceding them by the plus sign +, and on the other side the thousandths of silver nitrate, preceding them by the sign − minus.

In the above example, after the addition of the 4 thousandths of common salt, the last of which has produced no cloudiness, $1\frac{1}{2}$ thousandth of nitrate of silver is added, which destroys $1\frac{1}{2}$ thousandth of common salt, and brightens the liquid. If another half-thousandth of nitrate of silver produce no precipitate, it is not taken into account, and is struck off from the table. From whence it is concluded that the quantity of nitrate of silver necessary to destroy the excess of common salt is more than 1 and less than $1\frac{1}{2}$; that is to say, nearly the $\frac{1}{4}$ of a thousandth, and is equal to $1\frac{1}{4}$. Thus the number of thousandths of salt really used is $4-1·25=2·75$. The standard of the alloy, therefore, is $898·50+2·75=901·25$.

Another example, everything else remaining as above: Suppose the first thousandth of salt did not precipitate. This is a proof that too much normal solution of common salt has been employed, and that there is an excess of salt in the liquid. Add one-thousandth of silver, and agitate: things are now as at first, but it is nevertheless known that it is with nitrate of silver the process must be continued. One-thousandth has been added, which produced a precipitate; the second does not. The standard of the alloy is consequently $898·5-0·5=898$. To approach still nearer to the real standard, destroy the last 2 thousandths of silver by 2 thousandths of common salt, and add half a thousandth of silver—a cloudiness is produced, as already known; but another half-thousandth does not precipitate. The standard of the alloy is therefore $898·50-0·25=898·25$.

This process, on which it would be useless to enlarge further at present, because many other parts of the process to be presently described apply to it, is general, and gives exactly the standard of an alloy when it is known approximatively, which can always be ascertained by a previous rough assay.

Correction of the Standard of the Normal Solution of Salt when the Temperature Varies.—It has been admitted that, in the determination of the standard of the normal solution of salt, the temperature has remained constant. Assays made under these circumstances need no correction; but if the temperature changes, the same measure of solution will not contain the same amount of salt. Supposing the solution of salt has been standardised at 15°. If, at the time an experiment is made, the temperature is 18°, for instance, the solution will be found too weak, since it has become expanded, and the pipette holds less than its weight. If, on the other hand, the temperature falls to 12°, the solution becomes concentrated, and is found too strong. It is therefore necessary to determine the correction to be made for any variation of temperature that may occur.

To this end the temperature of a solution of common salt has been gradually raised from 0....5....10....15....20.... 25....30 degrees, and three pipettefuls of the solution exactly weighed at each of the above temperatures. One-third of the total weight gives the mean weight of the contents of a pipette. The corresponding weights of a pipetteful of solution are then entered, and form the second column of the following table, called 'Table of Correction for the Variations of Temperature in the Normal Solution of Salt.' By this table correction may be made for any temperature between 0 and 30 degrees, when the solution of salt has been standardised within the same limits. Suppose, for example, the solution had been standardised at 15°, and that at the time it was used its temperature was 18°. On referring to the second column of the table, it will be seen that the weight of a measure of solution at 15° is 100·099 gr.; and at 18° 100·065 gr.; the difference 0·034 gr. is the quantity of solution taken too little, and consequently it must be added to the normal measure, so that it may be equal to one thousand thousandths. If the temperature of the solution had fallen to 10°, the difference of weight between a measure at 10° and a measure at 15° will be 0·019 gr., which must, on the contrary, be deducted from the measure, as it has been taken in excess. These differences of weight of a measure of solution at 15°, and that of a measure for any other temperature, form the column 15° in the table, where they are expressed in thousandths. They are written on the same horizontal line as the temperatures to which each corresponds, with the sign + when they are to be added, and the sign – when to be subtracted. The columns 5°, 10°, 20°, 25°, 30° have been calculated in the same manner, to meet cases in which the normal solution had been graduated at each of the above-named temperatures. Thus, to calculate the column 10°, take the number 100·118 from the column of weights as a point of departure, and find the difference for all the other numbers in the same column.

An application of this Table will be given hereafter.

TABLE OF CORRECTIONS FOR VARIATIONS IN TEMPERATURE OF THE NORMAL SALT SOLUTION.

Temperature	Weight	5°	10°	15°	20°	25°	30°
Degrees	Grammes	Mill.	Mill.	Mill.	Mill.	Mill.	Mill.
4	100·109	0·0	−0·1	+0·1	+0·7	+1·7	+2·7
5	100·113	0·0	−0·1	+0·1	+0·7	+1·7	+2·8
6	100·115	0·0	0·0	+0·2	+0·8	+1·7	+2·8
7	100·118	+0·1	0·0	+0·2	+0·8	+1·7	+2·8
8	100·120	+0·1	0·0	+0·2	+0·8	+1·8	+2·8
9	100·120	+0·1	0·0	+0·2	+0·8	+1·8	+2·8
10	100·118	+0·1	0·0	+0·2	+0·8	+1·7	+2·8
11	100·116	0·0	0·0	+0·2	+0·8	+1·7	+2·8
12	100·114	0·0	0·0	+0·2	+0·8	+1·7	+2·8
13	100·110	0·0	−0·1	+0·1	+0·7	+1·7	+2·7
14	100·106	−0·1	−0·1	+0·1	+0·7	+1·6	+2·7
15	100·099	−0·1	−0·2	0·0	+0·6	+1·6	+2·6
16	100·090	−0·2	−0·3	−0·1	+0·5	+1·5	+2·5
17	100·078	−0·4	−0·4	−0·2	+0·4	+1·3	+2·4
18	100·065	−0·5	−0·5	−0·3	+0·3	+1·2	+2·3
19	100·053	−0·6	−0·7	−0·5	+0·1	+1·1	+2·2
20	100·039	−0·7	−0·8	−0·6	0·0	+1·0	+2·0
21	100·021	−0·9	−1·0	−0·8	−0·2	+0·8	+1·9
22	100·001	−1·1	−1·2	−1·0	−0·4	+0·6	+1·7
23	99·983	−1·3	−1·4	−1·2	−0·6	+0·4	+1·5
24	99·964	−1·5	−1·5	−1·4	−0·8	+0·2	+1·3
25	99·944	−1·7	−1·7	−1·6	−1·0	0·0	+1·1
26	99·924	−1·9	−1·9	−1·8	−1·2	−0·2	+0·9
27	99·902	−2·1	−2·2	−2·0	−1·4	−0·4	+0·7
28	99·879	−2·3	−2·4	−2·2	−1·6	−0·7	+0·4
29	99·858	−2·6	−2·6	−2·4	−1·8	−0·9	+0·2
30	99·836	−2·8	−2·8	−2·6	−2·0	−1·1	0·0

TABLE FOR THE ASSAY, BY THE WET METHOD, OF AN ALLOY CONTAINING ANY PROPORTIONS WHATEVER OF SILVER, BY THE EMPLOYMENT OF A CONSTANT MEASURE OF THE NORMAL SOLUTION OF COMMON SALT.

The process by which the normal solution of salt is measured by weight is applicable to the assay of every kind of alloy, since it suffices to take a weight of the solution corresponding to the presumed standard of the silver, and complete the assay by means of the decime solution; the process by volume, however, has not the same advantage, because the volume of normal solution cannot be varied in the same manner as the weight. This inconvenience, however, is of no very great consequence, for, by keeping the volume of normal solution constant, it suffices to vary the weight of the alloy, taking in each particular case a weight which contains approximatively one gramme of pure silver. Suppose the alloy has a standard of about 900 thousandths, we have the following proportion:—

$$900 \text{ thousandths} : 1000 \text{ of alloy} :: 1000 \text{ thousandths} : x = 1111{\cdot}1.$$

If that weight be now taken to ascertain the standard of the alloy, it may be found, for instance, that to the measure of 1000 thousandths of salt it is yet necessary to add 4 thousandths of salt to precipitate the whole of the silver; that is to say, that 1111·1 of alloy really contain 1004 of silver. From this result the real standard of the alloy may be found to be 903·6, by the following equation:—

$$1111{\cdot}1 : 1004 :: 1000 : x = 903{\cdot}6.$$

But such calculations, however simple, should be avoided where numerous daily assays are made, not only on account of the time consumed, but still more from the errors to which such operations are necessarily exposed. Fortunately, all these inconveniences may be avoided by the use of tables, which entirely free the assayer from calculation.

Wishing in weighing the alloy to avoid fractions of thousandths, and only making use of tenths and half-tenths of thousandths, the weight of alloy increases, starting from a gramme, from 5 to 5 thousandths, and the corresponding standard for each of these weights has been sought, all containing one gramme of pure silver. Thus the weight 1020 of alloy, in which there are 1000 of silver and 20 of copper, corresponds to the standard 980·39, obtained by the proportion—

$$1020 : 1000 :: 1000 : x = 980{\cdot}39.$$

On this principle are formed the first and second columns of the table marked Salt. The first contains the weight of each alloy, and the second its corresponding standard. The following columns, 1, 2, 3, to 10, give the standard of the alloy, when, instead of the 1000 milligrammes of silver it was supposed to contain, it really contained 1, 2, 3, &c. more, and consequently 1, 2, 3, &c. milligrammes of copper less.

Another table, constructed in the same manner as the preceding, and marked Silver Nitrate, gives the standard of the alloy when, under the weight given in the first column, it contains 1, 2, 3, &c. milligrammes less silver, and as much more copper. Thus, for example, an alloy of the weight of 1020 (1000 silver and 20 copper) has for its standard 980·4 in both tables. If it always contains in the same weight 4 more silver and consequently 4 less copper, its standard would be 984·3, and would be found in the 'Salt' table at the intersection of the column 4, and the horizontal line 1020. If, on the contrary, it contains 4 less of silver and 4 more of copper, its standard will be 976·5, and will be found in the 'Silver Nitrate' table, at the intersection of the column 4, and the horizontal line 1020.

Tables for Determining the Standard of any Silver approximatively containing

	SILVER				
Weight of Assay in Milligrs.	0	1	2	3	4
1000	1000·0	999·0	998·0	997·0	996·0
1005	995·0	994·0	993·0	992·0	991·0
1010	990·1	989·1	988·1	987·1	986·1
1015	985·2	984·2	983·2	982·3	981·3
1020	980·4	979·4	978·4	977·4	976·5
1025	975·6	974·6	973·7	972·7	971·7
1030	970·9	969·9	968·9	968·0	967·0
1035	966·2	965·2	964·2	963·3	962·3
1040	961·5	960·6	959·6	958·6	957·7
1045	956·9	956·0	955·0	954·1	953·1
1050	952·4	951·4	950·5	949·5	948·6
1055	947·9	946·9	946·0	945·0	944·1
1060	943·4	942·4	941·5	940·6	939·6
1065	939·0	938·0	937·1	936·1	935·2
1070	934·6	933·6	932·7	931·8	930·8
1075	930·2	929·3	928·4	927·4	926·5
1080	925·9	925·0	924·1	923·1	922·2
1085	921·7	920·7	919·8	918·9	918·0
1090	917·4	916·5	915·6	914·7	913·8
1095	913·2	912·3	911·4	910·5	909·6
1100	909·1	908·2	907·3	906·4	905·4
1105	905·0	904·1	903·2	902·3	901·4
1110	900·9	900·0	899·1	898·2	897·3
1115	896·9	896·0	895·1	894·2	893·3
1120	892·9	892·0	891·1	890·2	889·3
1125	888·9	888·0	887·1	886·2	885·3
1130	885·0	884·1	883·2	882·3	881·4
1135	881·1	880·2	879·3	878·4	877·5
1140	877·2	876·3	875·4	874·6	873·7
1145	873·4	872·5	871·6	870·7	869·9
1150	869·6	868·7	867·8	867·0	866·1
1155	865·8	864·9	864·1	863·2	862·3
1160	862·1	861·2	860·3	859·5	858·6
1165	858·4	857·5	856·6	855·8	854·9
1170	854·7	853·8	853·0	852·1	851·3
1175	851·1	850·2	849·4	848·5	847·7
1180	847·5	846·6	845·8	844·9	844·1
1185	843·9	843·0	842·2	841·3	840·5

Alloy by employing an Amount of Alloy always the same Amount of Silver.

NITRATE.					
5	6	7	8	9	10
995·0	994·0	993·0	992·0	991·0	990·0
990·0	989·0	988·1	987·1	986·1	985·1
985·1	984·2	983·2	982·2	981·2	980·2
980·3	979·3	978·3	977·3	976·4	975·4
975·5	974·5	973·5	972·5	971·6	970·6
970·7	969·8	968·8	967·8	966·8	965·8
966·0	965·0	964·1	963·1	962·1	961·2
961·3	960·4	959·4	958·4	957·5	956·5
956·7	955·8	954·8	953·8	952·9	951·9
952·1	951·2	950·2	949·3	948·3	947·4
947·6	946·7	945·7	944·8	943·8	942·9
943·1	942·2	941·2	940·3	939·3	938·4
938·7	937·7	936·8	935·8	934·9	934·0
934·3	933·3	932·4	931·4	930·5	929·6
929·9	929·0	928·0	927·1	926·2	925·2
925·6	924·7	923·7	922·8	921·9	920·9
921·3	920·4	919·4	918·5	917·6	916·7
917·0	916·1	915·2	914·3	913·4	912·4
912·8	911·9	911·0	910·1	909·2	908·3
908·7	907·8	906·8	905·9	905·0	904·1
904·5	903·6	902·7	901·8	900·9	900·0
900·4	899·5	898·6	897·7	896·8	895·9
896·4	895·5	894·6	893·7	892·8	891·9
892·4	891·5	890·6	889·7	888·8	887·9
888·4	887·5	886·6	885·7	884·8	883·9
884·4	883·6	882·7	881·8	880·9	880·0
880·5	879·6	878·8	877·9	877·0	876·1
876·7	875·8	874·9	874·0	873·1	872·3
872·8	871·9	871·0	870·2	869·3	868·4
869·0	868·1	867·2	866·4	865·5	864·6
865·2	864·3	863·5	862·6	861·7	860·9
861·5	860·6	859·7	858·9	858·0	857·1
857·8	856·9	856·0	855·2	854·3	853·4
854·1	853·2	852·4	851·5	850·6	849·8
850·4	849·6	848·7	847·9	847·0	846·1
846·8	846·0	845·1	844·3	843·4	842·5
843·2	842·4	841·5	840·7	839·8	839·0
839·7	838·8	838·0	837·1	836·3	835·4

	SILVER				
Weight of Assay in Milligrs.	0	1	2	3	4
1190	840·3	849·5	838·7	837·8	837·0
1195	836·8	836·0	835·1	834·3	833·5
1200	833·3	832·5	831·7	830·8	830·0
1205	829·9	829·0	828·2	827·4	826·6
1210	826·4	825·6	824·8	824·0	823·1
1215	823·0	822·2	821·4	820·6	819·7
1220	819·7	818·8	818·0	817·2	816·4
1225	816·3	815·5	814·7	813·9	813·1
1230	813·0	812·2	811·4	810·6	809·8
1235	809·7	808·9	808·1	807·3	806·5
1240	806·5	805·6	804·8	804·0	803·2
1245	803·2	802·4	801·6	800·8	800·0
1250	800·0	799·2	798·4	797·6	796·8
1255	796·8	796·0	795·2	794·4	793·6
1260	793·6	792·9	792·1	791·3	790·5
1265	790·5	789·7	788·9	788·1	787·3
1270	787·4	786·6	785·8	785·0	784·2
1275	784·3	783·5	782·7	782·0	781·2
1280	781·2	780·5	779·7	778·9	778·1
1285	778·2	777·4	776·6	775·9	775·1
1290	775·2	774·4	773·6	772·9	772·1
1295	772·2	771·4	770·7	769·9	769·1
1300	769·2	768·5	767·7	766·9	766·1
1305	766·3	765·5	764·7	764·0	763·2
1310	763·4	762·6	761·8	761·1	760·3
1315	760·5	759·7	758·9	758·2	757·4
1320	757·6	756·8	756·1	755·3	754·5
1325	754·7	754·0	753·2	752·4	751·7
1330	751·9	751·1	750·4	749·6	748·9
1335	749·1	748·3	747·6	746·8	746·1
1340	746·3	745·5	744·8	744·0	743·3
1345	743·5	742·7	742·0	741·3	740·5
1350	740·7	740·0	739·3	738·5	737·8
1355	738·0	737·3	736·5	735·8	735·1
1360	735·3	734·6	733·8	733·1	732·4
1365	732·6	731·9	731·1	730·4	729·7
1370	729·9	729·2	728·5	727·7	727·0
1375	727·3	726·5	725·8	725·1	724·4
1380	724·6	723·9	723·2	722·5	721·7
1385	722·0	721·3	720·6	719·9	719·1
1390	719·4	718·7	718·0	717·3	716·5
1395	716·8	716·1	715·4	714·7	714·0
1400	714·3	713·6	712·9	712·1	711·4

NITRATE—*continued.*

5	6	7	8	9	10
836·1	835·3	834·5	833·6	832·8	831·9
832·6	831·8	831·0	830·1	829·3	828·4
829·2	828·3	827·5	826·7	825·8	825·0
825·7	824·9	824·1	823·2	822·4	821·6
822·3	821·5	820·7	819·8	819·0	818·2
818·9	818·1	817·3	816·5	815·6	814·8
815·6	814·7	813·9	813·1	812·3	811·5
812·2	811·4	810·6	809·8	809·0	808·2
808·9	808·1	807·3	806·5	805·7	804·9
805·7	804·9	804·0	803·2	802·4	801·6
802·4	801·6	800·8	800·0	799·2	798·4
799·2	798·4	797·6	796·8	796·0	795·2
796·0	795·2	794·4	793·6	792·8	792·0
792·8	792·0	791·2	790·4	789·6	788·8
789·7	788·9	788·1	787·3	786·5	785·7
786·6	785·8	785·0	784·2	783·4	782·6
783·5	782·7	781·9	781·1	780·3	779·5
780·4	779·6	778·8	778·0	777·3	776·5
777·3	776·6	775·8	775·0	774·2	773·4
774·3	773·5	772·8	772·0	771·2	770·4
771·3	770 5	769·8	769·0	768·2	767·4
768·3	767·6	766·8	766·0	765·2	764·5
765·4	764·6	763·8	763·1	762·3	761·5
762·4	761·7	760·9	760·1	759·4	758·6
759·5	758·8	758·0	757·2	756·5	755·7
756·6	755·9	755·1	754·4	753·6	752·8
753·8	753·0	752·3	751·5	750·8	750·0
750·9	750·2	749·4	748·7	747·9	747·2
748·1	747·4	746·6	745·9	745·1	744·4
745·3	744·6	743·8	743·1	742·3	741·6
742·5	741·8	741·0	740·3	739·5	738·8
736·8	739·0	738·3	737·5	736·8	736·1
737·0	736·3	735·6	734·8	734·1	733·3
734·3	733·6	732·8	732·1	731·4	730·6
731·6	730·9	730·1	729·4	728·7	727·9
728·9	728·2	727·5	726·7	726·0	725·3
726·3	725·5	724·8	724·1	723·4	722·6
723·6	722·9	722·2	721·4	720·7	720·0
721·0	720·3	719·6	718·8	718·1	717·4
718·4	717·7	717·0	716·2	715·5	714·8
715·8	715·1	714·4	713·7	712·9	712·2
713·3	712·5	711·8	711·1	710·4	709·7
710·7	710·0	709·3	708·6	707·9	707·1

SILVER

Weight of Assay in Milligrs.	0	1	2	3	4
1405	711·7	711·0	710·3	709·6	708·9
1410	709·2	708·5	707·8	707·1	706·4
1415	706·7	706·0	705·3	704·6	703·9
1420	704·2	703·5	702·8	702·1	701·4
1425	701·8	701·0	700·3	699·6	698·9
1430	699·3	698·6	697·9	697·2	696·5
1435	696·9	696·2	695·5	694·8	694·1
1440	694·4	693·7	693·1	692·4	691·7
1445	692·0	691·3	690·7	690·0	689·3
1450	689·7	689·0	688·3	687·6	686·9
1455	687·3	686·6	685·9	685·2	684·5
1460	684·9	684·2	683·6	682·9	682·2
1465	682·6	681·9	681·2	680·6	679·9
1470	680·3	679·6	678·9	678·2	677·5
1475	678·0	677·3	676·6	675·9	675·2
1480	675·7	675·0	674·3	673·6	673·0
1485	673·4	672·7	672·0	671·4	670·7
1490	671·1	670·5	669·8	669·1	668·5
1495	668·9	668·2	667·6	666·9	666·2
1500	666·7	666·0	665·3	664·7	664·0
1505	664·5	663·8	663·1	662·5	661·8
1510	662·3	661·6	660·9	660·3	659·6
1515	660·1	659·4	658·7	658·1	657·4
1520	657·9	657·2	656·6	655·9	655·3
1525	655·7	655·1	654·4	653·8	653·1
1530	653·6	652·9	652·3	651·6	651·0
1535	651·5	650·8	650·2	649·5	648·9
1540	649·4	648·7	648·0	647·4	646·7
1545	647·2	646·6	645·9	645·3	644·7
1550	645·2	644·5	643·9	643·2	642·6
1555	643·1	642·4	641·8	641·2	640·5
1560	641·0	640·4	639·7	639·1	638·5
1565	639·0	638·3	637·7	637·1	636·4
1570	636·9	636·3	635·7	635·0	634·4
1575	634·9	634·3	633·6	633·0	632·4
1580	632·9	632·3	631·6	631·0	630·4
1585	630·9	630·3	629·6	629·0	628·4
1590	628·9	628·3	627·7	627·0	626·4
1595	627·0	626·3	625·7	625·1	624·4
1600	625·0	624·4	623·7	623·1	622·5
1605	623·1	622·4	621·8	621·2	620·6
1610	621·1	620·5	619·9	619·2	618·6
1615	619·2	618·6	618·0	617·3	616·7

NITRATE—*continued.*

5	6	7	8	9	10
708·2	707·5	706·8	706·0	705·3	704·6
705·7	705·0	704·3	703·5	702·8	702·1
703·2	702·5	701·8	701·1	700·3	699·6
700·7	700·0	699·3	698·6	697·9	697·2
698·2	697·5	696·8	696·1	695·4	694·7
695·8	695·1	694·4	693·7	693·0	692·3
693·4	692·7	692·0	691·3	690·6	689·9
691·0	690·3	689·6	688·9	688·2	687·5
688·6	687·9	687·2	686·5	685·8	685·1
686·2	685·5	684·8	684·1	683·4	682·8
683·8	683·2	682·5	681·8	681·1	680·4
681·5	680·8	680·1	679·4	678·8	678·1
679·2	678·5	677·8	677·1	676·4	675·8
676·9	676·2	675·5	674·8	674·1	673·5
674·6	673·9	673·2	672·5	671·9	671·2
672·3	671·6	670·9	670·3	669·6	668·9
670·0	669·4	668·7	668·0	667·3	666·7
667·8	667·1	666·4	665·8	665·1	664·4
665·5	664·9	664·2	663·5	662·9	662·2
663·3	662·7	662·0	661·3	660·7	660·0
661·1	660·5	659·8	659·1	658·5	657·8
658·9	658·3	657·6	656·9	656·3	655·6
656·8	656·1	655·4	654·8	654·1	653·5
654·6	653·9	653·3	652·6	652·0	651·3
652·5	651·8	651·1	650·5	649·8	649·2
650·3	649·7	649·0	648·4	647·7	647·1
648·2	647·6	646·9	646·2	645·6	644·9
646·1	645·4	644·8	644·2	643·5	642·9
644·0	643·4	642·7	642·1	641·4	640·8
641·9	641·3	640·6	640·0	639·3	638·7
639·9	639·3	638·6	637·9	637·3	636·7
637·8	637·2	636·5	635·9	635·3	634·6
635·8	635·1	634·5	633·9	633·2	632·6
633·8	633·1	632·5	631·8	631·2	630·6
631·7	631·1	630·5	629·8	629·2	628·6
629·7	629·1	628·5	627·8	627·2	626·6
627·8	627·1	626·5	625·9	625·2	624·6
625·8	625·2	624·5	623·9	623·3	622·6
623·8	623·2	622·6	621·9	621·3	620·7
621·9	621·2	620·6	620·0	619·4	618·7
619·9	619·3	618·7	618·1	617·4	616·1
618·0	617·4	616·8	616·1	615·5	614·9
616·1	615·5	614·9	614·2	613·6	613·0

SILVER

Weight of Assay in Milligrs.	0	1	2	3	4
1620	617·3	616·7	616·0	615·4	614·8
1625	615·4	614·8	614·1	613·5	612·9
1630	613·5	612·9	612·3	611·7	611·0
1635	611·6	611·0	610·4	609·8	609·2
1640	609·8	609·1	608·5	607·9	607·3
1645	607·9	607·3	606·7	606·1	605·5
1650	606·1	605·4	604·8	604·2	603·6
1655	604·2	603·6	603·0	602·4	601·8
1660	602·4	601·8	601·2	600·6	600·0
1665	600·6	600·0	599·4	598·8	598·2
1670	598·8	598·2	597·6	597·0	596·4
1675	597·0	596·4	595·8	595·2	594·6
1680	595·2	594·6	594·0	593·4	592·9
1685	593·5	592·9	592·3	591·7	591·1
1690	591·7	591·1	590·5	589·9	589·3
1695	590·0	589·4	588·8	588·2	587·6
1700	588·2	587·6	587·1	586·5	585·9
1705	586·5	585·9	585·3	584·7	584·2
1710	584·8	584·2	583·6	583·0	582·5
1715	583·1	582·5	581·9	581·3	580·8
1720	581·4	580·8	580·2	579·6	579·1
1725	579·7	579·1	578·5	578·0	577·4
1730	578·0	577·5	576·9	576·3	575·7
1735	576·4	575·8	575·2	574·6	574·1
1740	574·7	574·1	573·6	573·0	572·4
1745	573·1	572·5	571·9	571·3	570·8
1750	571·4	570·9	570·3	569·7	569·1
1755	569·8	569·2	568·7	568·1	567·5
1760	568·2	567·6	567·0	566·5	565·9
1765	566·6	566·0	565·4	564·9	564·3
1770	565·0	564·4	563·8	563·3	562·7
1775	563·4	562·8	562·2	561·7	561·1
1780	561·8	561·2	560·7	560·1	559·5
1785	560·2	559·7	559·1	558·5	558·0
1790	558·7	558·1	557·5	557·0	556·4
1795	557·1	556·5	556·0	555·4	554·9
1800	555·6	555·0	554·4	553·9	553·3
1805	554·0	553·5	552·9	552·3	551·8
1810	552·5	551·9	551·4	550·8	550·3
1815	551·0	550·4	549·9	549·3	548·8
1820	549·4	548·9	548·3	547·8	547·2
1825	547·9	547·4	546·8	546·3	545·7
1830	546·4	545·9	545·4	544·8	544·3

NITRATE—*continued.*

5	6	7	8	9	10
614·2	613·6	613·0	612·3	611·7	611·1
612·3	611·7	611·1	610·5	609·8	609·2
610·4	609·8	609·2	608·6	608·0	607·4
608·6	607·9	607·3	606·7	606·1	605·5
606·7	606·1	605·5	604·9	604·3	603·7
604·9	604·3	603·6	603·0	602·4	601·8
603·0	602·4	601·8	601·2	600·6	600·0
601·2	600·6	600·0	599·4	598·8	598·2
599·4	598·8	598·2	597·6	597·0	596·4
597·6	597·0	596·4	595·8	595·2	594·6
595·8	595·2	594·6	594·0	593·4	592·8
594·0	593·4	592·8	592·2	591·6	591·0
592·3	591·7	591·1	590·5	589·9	589·3
590·5	589·9	589·3	588·7	588·1	587·5
588·8	588·2	587·6	587·0	586·4	585·8
587·0	586·4	585·8	585·2	584·7	584·1
585·3	584·7	584·1	583·5	582·9	582·3
583·6	583·0	582·4	581·8	581·2	580·6
581·9	581·3	580·7	580·1	579·5	578·9
580·2	579·6	579·0	578·4	577·8	577·3
578·5	577·9	577·3	576·7	576·2	575·6
576·8	576·2	575·6	575·1	574·5	573·9
575·1	574·6	574·0	573·4	572·8	572·2
573·5	572·9	572·3	571·8	571·2	570·6
571·8	571·3	570·7	570·1	569·5	569·0
570·2	569·6	569·0	568·5	567·9	567·3
568·6	568·0	567·4	566·9	566·3	565·7
566·9	566·4	565·8	565·2	564·7	564·1
565·3	564·8	564·2	563·6	563·1	562·5
563·7	563·2	562·6	562·0	561·5	560·9
562·1	561·6	561·0	560·4	559·9	559·3
560·6	560·0	559·4	558·9	558·3	557·7
559·0	558·4	557·9	557·3	556·7	556·2
557·4	556·9	556·3	555·7	555·2	554·6
555·9	555·3	554·7	554·2	553·6	553·1
554·3	553·8	553·2	552·6	552·1	551·5
552·8	552·2	551·7	551·1	550·6	550·0
551·2	550·7	550·1	549·6	549·0	548·5
549·7	549·2	548·6	548·1	547·5	547·0
548·2	547·7	547·1	546·6	546·0	545·5
546·7	546·2	545·6	545·1	544·5	544·0
545·2	544·7	544·1	543·6	543·0	542·5
542·7	543·2	542·6	542·1	541·5	541·0

SILVER

Weight of Assay in Milligrs.	0	1	2	3	4
1835	545·0	544·4	543·9	543·3	542·8
1840	543·5	542·9	542·4	541·8	541·3
1845	542·0	541·5	540·9	540·4	539·8
1850	540·5	540·0	539·5	538·9	538·4
1855	539·1	538·5	538·0	537·5	536·9
1860	537·6	537·1	536·6	536·0	535·5
1865	536·2	535·7	535·1	534·6	534·0
1870	534·8	534·2	533·7	533·2	532·6
1875	533·3	532·8	532·3	531·7	531·2
1880	531·9	531·4	530·8	530·3	529·8
1885	530·5	530·0	529·4	528·9	528·4
1890	529·1	528·6	528·0	527·5	527·0
1895	527·7	527·2	526·6	526·1	525·6
1900	526·3	525·8	525·3	524·7	524·2
1905	524·9	524·4	523·2	523·4	522·8
1910	523·6	523·0	522·5	522·0	521·5
1915	522·2	521·7	521·1	520·6	520·1
1920	520·8	520·3	519·8	519·3	518·7
1925	519·5	519·0	518·4	517·9	517·4
1930	518·1	517·6	517·1	516·6	516·1
1935	516·8	516·3	515·8	515·2	514·7
1940	515·5	514·9	514·4	513·9	513·4
1945	514·1	513·6	513·1	512·6	512·1
1950	512·8	512·3	511·8	511·3	510·8
1955	511·5	511·0	510·5	510·0	509·5
1960	510·2	509·7	509·2	508·7	508·2
1965	508·9	508·4	507·9	507·4	506·9
1970	507·6	507·1	506·6	506·1	505·7
1975	506·3	505·8	505·3	504·8	504·3
1980	505·0	504·5	504·0	503·5	503·0
1985	503·8	503·3	502·8	502·3	501·8
1990	502·5	502·0	501·5	501·0	500·5
1995	501·3	500·7	500·2	499·7	499·2
2000	500·0	499·5	499·0	498·5	498·0

NITRATE—*continued.*

5	6	7	8	9	10
542·2	541·7	541·1	540·6	540·0	539·5
540·8	540·2	539·7	539·1	538·6	538·0
539·3	538·7	538·2	537·7	537·1	536·6
537·8	537·3	536·8	536·2	535·7	535·1
536·4	535·8	535·3	534·8	534·2	533·7
534·9	534·4	533·9	533·3	532·8	532·3
533·5	533·0	532·4	531·9	531·4	530·8
532·1	531·5	531·0	530·5	529·9	529·4
530·7	530·1	529·6	529·1	528·5	528·0
529·3	528·7	528·2	527·7	527·1	526·6
527·8	527·3	526·8	526·3	525·7	525·2
526·5	525·9	525·4	524·9	524·3	523·8
525·1	524·5	524·0	523·5	523·0	522·4
523·7	523·2	522·6	522·1	521·6	521·0
522·3	521·8	521·3	520·7	520·2	519·7
520·9	520·4	519·9	519·4	518·8	518·3
519·6	519·1	518·5	518·0	517·5	517·0
518·2	517·7	517·2	516·7	516·1	515·6
516·9	516·4	515·8	515·3	514·8	514·3
515·5	515·0	514·5	514·0	513·5	512·9
514·2	513·7	513·2	512·7	512·1	511·6
512·9	512·4	511·9	511·3	510·8	510·3
511·6	511·0	510·5	510·0	509·5	509·0
510·3	509·7	509·2	508·7	508·2	507·7
508·9	508·4	507·9	507·4	506·9	506·4
507·6	507·1	506·6	506·1	505·6	505·1
506·4	505·8	505·3	504·8	504·3	503·8
505·1	504·6	504·1	503·5	503·0	502·5
503·8	503·3	502·8	502·3	501·8	501·3
502·5	509·0	501·5	501·0	500·5	500·0
501·3	500·8	500·2	499·7	499·2	498·7
500·0	499·5	499·0	498·5	498·0	497·5
498·7	498·2	497·7	497·2	496·7	496·2
497·5	497·0	496·5	496·0	495·5	495·0

Tables for Determining the Standard of any Silver approximately containing

					COMMON
Weight of Assay in Milligrs.	0	1	2	3	4
1000	1000·0				
1005	995·0	996·0	997·0	998·0	999·0
1010	990·1	991·1	992·1	993·1	994·1
1015	985·2	986·2	987·2	988·2	989·2
1020	980·4	981·4	982·4	983·3	984·3
1025	975·6	976·6	977·6	978·5	979·5
1030	970·9	971·8	972·8	973·8	974·8
1035	966·2	967·1	968·1	969·1	970·0
1040	961·5	962·5	963·5	964·4	965·4
1045	956·9	957·9	958·8	959·8	960·8
1050	952·4	953·3	954·3	955·2	956·2
1055	947·9	948·8	949·8	950·7	951·7
1060	943·4	944·3	945·3	946·2	947·2
1065	939·0	939·9	940·8	941·8	942·7
1070	934·6	935·5	936·4	937·4	938·3
1075	930·2	931·2	932·1	933·0	933·9
1080	925·9	926·8	927·8	928·7	929·6
1085	921·7	922·6	923·5	924·4	925·3
1090	917·4	918·3	919·3	920·2	921·1
1095	913·2	914·2	915·1	916·0	917·0
1100	909·1	910·0	910·9	911·8	912·7
1105	905·0	905·9	906·8	907·7	908·6
1110	900·9	901·8	902·7	903·6	904·5
1115	896·9	897·8	898·6	899·5	900·4
1120	892·9	893·7	894·6	895·5	896·4
1125	888·9	889·8	890·7	891·6	892·4
1130	885·0	885·8	886·7	887·6	888·5
1135	881·1	881·9	882·8	883·7	884·6
1140	877·2	878·1	878·9	879·8	880·7
1145	873·4	874·2	875·1	876·0	876·9
1150	869·6	870·4	871·3	872·2	873·0
1155	865·8	866·7	867·5	868·4	869·3
1160	862·1	862·9	863·8	864·7	865·5
1165	858·4	859·2	860·1	860·9	861·8
1170	854·7	855·6	856·4	857·3	858·1
1175	851·1	851·9	852·8	853·6	854·5
1180	847·5	848·3	849·2	850·0	850·8
1185	843·9	844·7	845·6	846·4	847·3

Alloy by employing an Amount of Alloy always the same Amount of Silver.

SALT					
5	6	7	8	9	10
1000·0					
995·0	996·0	997·0	998·0	999·0	1000·0
990·1	991·1	992·1	993·1	994·1	995·1
985·3	986·3	987·2	988·2	989·2	990·2
980·5	981·5	982·4	983·4	984·4	985·4
975·7	976·7	977·7	978·6	979·6	980·6
971·0	972·0	972·9	973·9	974·9	975·8
966·3	967·3	968·3	969·2	970·2	971·1
961·7	962·7	963·6	964·6	965·5	966·5
957·1	958·1	959·0	960·0	960·9	961·9
952·6	953·5	954·5	955·4	956·4	957·3
948·1	949·1	950·0	950·9	951·9	952·8
943·7	944·6	945·5	946·5	947·4	948·4
939·3	940·2	941·1	942·1	943·0	943·9
934·9	935·8	936·7	937·7	938·6	939·5
930·6	931·5	932·4	933·3	934·3	935·2
926·3	927·2	928·1	929·0	930·0	930·9
922·0	922·9	923·8	924·8	925·7	926·6
917·8	918·7	919·6	920·5	921·5	922·4
913·6	914·5	915·4	916·4	917·3	918·2
909·5	910·4	911·3	912·2	913·1	914·0
905·4	906·3	907·2	908·1	909·0	909·9
901·3	902·2	903·1	904·0	904·9	905·8
897·3	898·2	899·1	900·0	900·9	901·8
893·3	894·2	895·1	896·0	896·9	897·8
889·4	890·3	891·1	892·0	892·9	893·8
885·5	886·3	887·2	888·1	889·0	889·9
881·6	882·5	883·3	884·2	885·1	886·0
877·7	878·6	879·5	880·3	881·2	882·1
873·9	874·8	875·7	876·5	877·4	878·3
870·1	871·0	871·9	872·7	873·6	874·5
866·4	867·2	868·1	869·0	869·8	870·7
862·7	863·5	864·4	865·2	866·1	866·9
859·0	859·8	860·7	861·5	862·4	863·2
855·3	856·2	857·0	857·9	858·7	859·6
851·7	852·5	853·4	854·2	855·1	855·9
848·1	848·9	849·8	850·6	851·5	852·3

					COMMON
Weight of Assay in Milligrs.	0	1	2	3	4
1190	840·3	841·2	842·0	842·9	843·7
1195	836·8	837·7	838·5	839·3	840·2
1200	833·3	834·2	835·0	835·8	836·7
1205	829·9	830·7	831·5	832·4	833·2
1210	826·4	827·3	828·1	828·9	829·7
1215	823·0	823·9	824·7	825·5	826·3
1220	819·7	820·5	821·3	822·1	822·9
1225	816·3	817·1	818·0	818·8	819·6
1230	813·0	813·8	814·6	815·4	816·3
1235	809·7	810·5	811·3	812·1	813·0
1240	806·5	807·3	808·1	808·9	809·7
1245	803·2	804·0	804·8	805·6	806·4
1250	800·0	800·8	801·6	802·4	803·2
1255	796·8	797·6	798·4	799·2	800·0
1260	793·6	794·4	795·2	796·0	796·8
1265	790·5	791·3	792·1	792·9	793·7
1270	787·4	788·2	789·0	789·8	790·5
1275	784·3	785·1	785·9	786·7	787·4
1280	781·2	782·0	782·8	783·6	784·4
1285	778·2	779·0	779·8	780·5	781·3
1290	775·2	776·0	776·7	777·5	778·3
1295	772·2	773·0	773·7	774·5	775·3
1300	769·2	770·0	770·8	771·5	772·3
1305	766·3	767·0	767·8	768·6	769·3
1310	763·4	764·1	764·9	765·6	766·4
1315	760·5	761·2	762·0	762·7	763·5
1320	757·6	758·3	759·1	759·8	760·6
1325	754·7	755·5	756·2	757·0	757·7
1330	751·9	752·6	753·4	754·1	754·9
1335	749·1	749·8	750·6	751·3	752·1
1340	746·3	747·0	747·8	748·5	749·2
1345	743·5	744·2	745·0	745·7	746·5
1350	740·7	741·5	742·2	743·0	743·7
1355	738·0	738·7	739·5	740·2	741·0
1360	735·3	736·0	736·8	737·5	738·2
1365	732·6	733·3	734·1	734·8	735·5
1370	729·9	730·7	731·4	732·1	732·8
1375	727·3	728·0	728·7	729·4	730·2
1380	724·6	725·4	726·1	726·8	727·5
1385	722·0	722·7	723·5	724·2	724·9
1390	719·4	720·1	720·9	721·6	722·3
1395	716·8	717·6	718·3	719·0	719·7
1400	714·3	715·0	715·7	716·4	717·1

SALT—*continued.*

5	6	7	8	9	10
844·5	845·4	846·2	847·1	847·9	848·7
841·0	841·8	842·7	843·5	844·3	845·2
837·5	838·3	839·2	840·0	840·8	841·7
834·0	834·8	835·7	836·5	837·3	838·2
830·6	831·4	832·2	833·1	833·9	834·7
827·2	828·0	828·8	829·6	830·4	831·3
823·8	824·6	825·4	826·2	827·0	827·9
820·4	821·2	822·0	822·9	823·7	824·5
817·1	817·9	818·7	819·5	820·3	821·1
813·8	814·6	815·4	816·2	817·0	817·8
810·5	811·3	812·1	812·9	813·7	814·5
807·2	808·0	808·8	809·6	810·4	811·2
804·0	804·8	805·6	806·4	807·2	808·0
800·8	801·6	802·4	803·2	804·0	804·8
797·6	798·4	799·2	800·0	800·8	801·6
794·5	795·3	796·0	796·8	797·6	798·4
791·3	792·1	792·9	793·7	794·5	795·3
788·2	789·0	789·8	790·6	791·4	792·2
785·2	786·0	786·7	787·5	788·3	789·1
782·1	782·9	783·7	784·4	785·2	786·0
779·1	779·8	780·6	781·4	782·2	782·9
776·1	776·8	777·6	778·4	779·1	779·9
773·1	773·8	774·6	775·4	776·1	776·9
770·1	770·9	771·6	772·4	773·2	773·9
767·2	767·9	768·7	769·5	770·2	771·0
764·3	765·0	765·8	766·5	767·3	768·1
761·4	762·1	762·9	763·6	764·4	765·2
758·5	759·2	760·0	760·7	761·5	762·3
755·6	756·4	757·1	757·9	758·6	759·4
752·8	753·6	754·3	755·1	755·8	756·6
750·0	750·7	751·5	752·2	753·0	753·7
747·2	748·0	748·7	749·4	750·2	750·9
744·4	745·2	745·9	746·7	747·4	748·1
741·7	742·4	743·2	743·9	744·6	745·4
739·0	739·7	740·4	741·2	741·9	742·6
736·3	737·0	737·7	738·5	739·2	739·9
733·6	734·3	735·0	735·8	736·5	737·2
730·9	731·6	732·4	733·2	733·8	734·5
728·3	729·0	729·7	730·4	731·2	731·9
725·6	726·3	727·1	727·8	728·5	729·2
723·0	723·7	724·5	725·2	725·9	726·6
720·4	721·1	721·9	722·6	723·3	724·0
717·9	718·6	719·3	720·0	720·7	721·4

					COMMON
Weight of Assay in Milligrs.	0	1	2	3	4
1405	711·7	712·5	713·2	713·9	714·6
1410	709·2	709·9	710·6	711·3	712·1
1415	706·7	707·4	708·1	708·8	709·5
1420	704·2	704·9	705·6	706·3	707·0
1425	701·8	702·5	703·2	703·9	704·6
1430	699·3	700·0	700·7	701·4	702·1
1435	696·9	697·6	698·3	698·9	699·6
1440	694·4	695·1	695·8	696·5	697·2
1445	692·0	692·7	693·4	694·1	694·8
1450	689·7	690·3	691·0	691·7	692·4
1455	687·3	688·0	688·7	689·3	690·0
1460	684·9	685·6	686·3	687·0	687·7
1465	682·6	683·3	684·0	684·6	685·3
1470	680·3	680·9	681·6	682·3	683·0
1475	678·0	678·6	679·3	680·0	680·7
1480	675·7	676·3	677·0	677·7	678·4
1485	673·4	674·1	674·7	675·4	676·1
1490	671·1	671·8	672·5	673·1	673·8
1495	668·9	669·6	670·2	670·9	671·6
1500	666·7	667·3	668·0	668·7	669·3
1505	664·5	665·1	665·8	666·4	667·1
1510	662·3	662·9	663·6	664·2	664·9
1515	660·1	660·7	661·4	662·0	662·7
1520	657·9	658·5	659·2	659·9	660·5
1525	655·7	656·4	657·0	657·7	658·4
1530	653·6	654·2	654·9	655·6	656·2
1535	651·5	652·1	652·8	653·4	654·1
1540	649·4	650·0	650·6	651·3	651·9
1545	647·2	647·9	648·5	649·2	649·8
1550	645·2	645·8	646·4	647·1	647·7
1555	643·1	643·7	644·4	645·0	645·7
1560	641·0	641·7	642·3	642·9	643·6
1565	639·0	639·6	640·3	640·9	641·5
1570	636·9	637·6	638·2	638·8	639·5
1575	634·9	635·6	636·2	636·8	637·5
1580	632·9	633·5	634·2	634·8	635·4
1585	630·9	631·5	632·2	632·8	633·4
1590	628·9	629·6	630·2	630·8	631·4
1595	627·0	627·6	628·2	628·8	629·5
1600	625·0	625·6	626·2	626·9	627·5
1605	623·1	623·7	624·3	624·9	625·5
1610	621·1	621·7	622·4	623·0	623·6
1615	619·2	619·8	620·4	621·0	621·7

SALT—*continued.*

5	6	7	8	9	10
715·3	716·0	716·7	717·4	718·1	718·9
712·8	713·5	714·2	714·9	715·6	716·3
710·2	710·9	711·7	712·4	713·1	713·8
707·7	708·4	709·2	709·9	710·6	711·3
705·3	706·0	706·7	707·4	708·1	708·8
702·8	703·5	704·2	704·9	705·6	706·3
700·3	701·0	701·7	702·4	703·1	703·8
697·9	698·6	699·3	700·0	700·7	701·4
695·5	696·2	696·9	697·6	698·3	699·0
693·1	693·8	694·5	695·2	695·9	696·6
690·7	691·4	692·1	692·8	693·5	694·2
688·4	689·0	689·7	690·4	691·1	691·8
686·0	686·7	687·4	688·0	688·7	689·4
683·7	684·3	685·0	685·7	686·4	687·1
681·4	682·0	682·7	683·4	684·1	684·7
679·1	679·7	680·4	681·1	681·8	682·4
676·8	677·4	678·1	678·8	679·5	680·1
674·5	675·2	675·8	676·5	677·2	677·8
672·2	672·9	673·6	674·2	674·9	675·6
670·0	670·7	671·3	672·0	672·7	673·3
667·8	668·4	669·1	669·8	670·4	671·1
665·6	666·2	666·9	667·5	668·2	668·7
663·4	664·0	664·7	665·3	666·0	656·7
661·2	661·8	662·5	663·2	663·8	664·5
659·0	659·7	660·3	661·0	661·6	662·3
656·9	657·5	658·2	658·8	659·5	660·1
654·7	655·4	656·0	656·7	657·3	658·0
652·6	653·2	653·9	654·5	655·2	655·8
650·5	651·1	651·8	652·4	653·1	653·7
648·4	649·0	649·7	650·3	651·0	651·6
646·3	646·9	647·6	648·2	648·9	649·5
644·2	644·9	645·5	646·1	646·8	647·4
642·2	642·8	643·4	644·1	644·7	645·4
640·1	640·8	641·4	642·0	642·7	643·3
638·1	638·7	639·4	640·0	640·6	641·3
636·1	636·7	637·3	638·0	638·6	639·2
634·1	634·7	635·3	636·0	636·6	637·2
632·1	632·7	633·3	634·0	634·6	635·2
630·1	630·7	631·3	632·0	632·6	633·2
628·1	628·7	629·4	630·0	630·6	631·2
626·2	626·8	627·4	628·0	628·7	629·3
624·2	624·8	625·5	626·1	626·7	627·3
622·3	622·9	623 5	624·1	624·8	625·4

					COMMON
Weight of Assay in Milligrs.	0	1	2	3	4
1620	617·3	617·9	618·5	619·1	619·7
1625	615·4	616·0	616·6	617·2	617·8
1630	613·5	614·1	614·7	615·3	615·9
1635	611·6	612·2	612·8	613·5	614·1
1640	609·8	610·4	611·0	611·6	612·2
1645	607·9	608·5	609·1	609·7	610·3
1650	606·1	606·7	607·3	607·9	608·5
1655	604·2	604·8	605·4	606·0	606·6
1660	602·4	603·0	603·6	604·2	604·8
1665	600·6	601·2	601·8	602·4	603·0
1670	598·8	599·4	600·0	600·6	601·2
1675	597·0	597·6	598·2	598·8	599·4
1680	595·2	595·8	596·4	597·0	597·6
1685	593·5	594·1	594·7	595·2	595·8
1690	591·7	592·3	592·9	593·5	594·1
1695	590·0	590·6	591·1	591·7	592·3
1700	588·2	588·8	589·4	590·0	590·6
1705	586·5	587·1	587·7	588·3	588·9
1710	584·8	585·4	586·0	586·5	587·1
1715	583·1	583·7	584·3	584·8	585·4
1720	581·4	582·0	582·6	583·1	583·7
1725	579·7	580·3	580·9	581·4	582·0
1730	578·0	578·6	579·2	579·8	580·3
1735	576·4	576·9	577·5	578·1	578·7
1740	574·7	575·3	575·9	576·4	577·0
1745	573·1	573·6	574·2	574·8	575·4
1750	571·4	572·0	572·6	573·1	573·7
1755	569·8	570·4	570·9	571·5	572·1
1760	568·2	568·7	569·3	569·9	570·4
1765	566·6	567·1	567·7	568·3	568·8
1770	565·0	565·5	566·1	566·7	567·2
1775	563·4	563·9	564·5	565·1	565·6
1780	561·8	562·4	562·9	563·5	564·0
1785	560·2	560·8	561·3	561·9	562·5
1790	558·7	559·2	559·8	560·3	560·9
1795	557·1	557·7	558·2	558·8	559·3
1800	555·6	556·1	556·7	557·2	557·8
1805	554·0	554·6	555·1	555·7	556·2
1810	552·5	553·0	553·6	554·1	554·7
1815	551·0	551·5	552·1	552·6	553·2
1820	549·4	550·0	550·5	551·1	551·6
1825	547·9	548·5	549·0	549·6	550·1
1830	546·4	547·0	547·5	548·1	548·6

SALT—*continued.*

5	6	7	8	9	10
620·4	621·0	621·6	622·2	622·8	623·5
618·5	619·1	619·7	620·3	620·9	621·5
616·6	617·2	617·8	618·4	619·0	619·6
614·7	615·3	615·9	616·5	617·1	617·7
612·8	613·4	614·0	614·6	615·2	615·8
610·9	611·5	612·2	612·8	613·4	614·0
609·1	609·7	610·3	610·9	611·5	612·1
607·2	607·8	608·5	609·1	609·7	610·3
605·4	606·0	606·6	607·2	607·8	608·4
603·6	604·2	604·8	605·4	606·0	606·6
601·8	602·4	603·0	603·6	604·2	604·8
600·0	600·6	601·2	601·8	602·4	603·0
598·2	598·8	599·4	600·0	600·6	601·2
596·4	597·0	597·6	598·2	598·9	599·4
594·7	595·3	595·9	596·4	597·0	597·6
592·9	593·5	594·1	594·7	595·3	595·9
591·2	591·8	592·3	592·9	593·5	594·1
589·4	590·0	590·6	591·2	591·8	592·4
587·7	588·3	588·9	589·5	590·1	590·6
586·0	586·6	587·2	587·8	588·3	588·9
584·3	584·9	585·5	586·0	586·6	587·2
582·6	583·2	583·8	584·3	584·9	585·5
580·9	581·5	582·1	582·7	583·2	583·8
579·2	579·8	580·4	581·0	581·6	582·1
577·6	578·2	578·7	579·3	579·9	580·5
575·9	576·5	577·1	577·6	578·2	578·8
574·3	574·9	575·4	576·0	576·6	577·1
572·6	573·2	573·8	574·4	574·9	575·5
571·0	571·6	572·2	572·7	573·3	573·9
569·4	570·0	570·5	571·1	571·7	572·2
567·8	568·4	568·9	569·5	570·1	570·6
566·2	566·8	567·3	567·9	568·4	569·0
564·6	565·2	565·7	566·3	566·8	567·4
563·0	563·6	564·1	564·7	565·3	565·8
561·4	562·0	562·6	563·1	563·7	564·2
559·9	560·4	561·0	561·6	562·1	562·7
558·3	558·9	559·4	560·0	560·6	561·1
556·8	557·3	557·9	558·4	559·0	559·6
555·2	555·8	556·3	556·9	557·5	558·0
553·7	554·3	554·8	555·4	555·9	556·5
552·2	552·7	553·3	553·8	554·4	554·9
550·7	551·2	551·8	552·3	552·9	553·4
549·2	549·7	550·3	550·8	551·4	551·9

COMMON

Weight of Assay in Milligrs.	0	1	2	3	4
1835	545·0	545·5	546·0	546·6	547·1
1840	543·5	544·0	544·6	545·1	545·6
1845	542·0	542·5	543·1	543·6	544·2
1850	540·5	541·1	541·6	542·2	542·7
1855	539·1	539·6	540·2	540·7	541·2
1860	537·6	538·2	538·7	539·2	539·8
1865	536·2	536·7	537·3	537·8	538·3
1870	534·8	535·3	535·8	536·4	536·9
1875	533·3	533·9	534·4	534·9	535·5
1880	531·9	532·4	533·0	533·5	534·0
1885	530·5	531·0	531·6	532·1	532·6
1890	529·1	529·6	530·2	530·7	531·2
1895	527·7	528·2	528·8	529·3	529·8
1900	526·3	526·8	527·4	527·9	528·4
1905	524·9	525·4	526·0	526·5	527·0
1910	523·6	524·1	524·6	525·1	525·6
1915	522·2	522·7	523·2	523·8	524·3
1920	520·8	521·3	521·9	522·4	522·9
1925	519·5	520·0	520·5	521·0	521·6
1930	518·1	518·6	519·2	519·7	520·2
1935	516·8	517·3	517·8	518·3	518·9
1940	515·5	516·0	516·5	517·0	517·5
1945	514·1	514·6	515·2	515·7	516·2
1950	512·8	513·3	513·8	514·4	514·9
1955	511·5	512·0	512·5	513·0	513·5
1960	510·2	510·7	511·2	511·7	512·2
1965	508·9	509·4	509·9	510·4	510·9
1970	507·6	508·1	508·6	509·1	509·6
1975	506·3	506·8	507·3	507·8	508·3
1980	505·0	505·6	506·1	506·6	507·1
1985	503·8	504·3	504·8	505·3	505·8
1990	502·5	503·0	503·5	504·0	504·5
1995	501·3	501·8	502·3	502·8	503·3
2000	500·0	500·5	501·0	501·5	502·0

SALT—*continued.*

5	6	7	8	9	10
547·7	548·2	548·8	549·3	549·9	550·4
546·2	546·7	547·3	547·8	548·4	548·9
544·7	545·3	545·8	546·3	546·9	547·4
543·2	543·8	544·3	544·9	545·4	545·9
541·8	542·3	542·9	543·4	543·9	544·5
540·3	540·9	541·4	541·9	542·5	543·0
538·9	539·4	539·9	540·5	541·0	541·5
537·4	538·0	538·5	539·0	539·6	540·1
536·0	536·5	537·1	537·6	538·1	538·7
534·6	535·1	535·6	536·2	536·7	537·2
533·2	533·7	534·2	534·7	535·3	535·8
531·7	532·3	532·8	533·3	533·9	534·4
530·3	530·9	531·4	531·9	532·4	533·0
528·9	529·5	530·0	530·5	531·0	531·6
527·6	528·1	528·6	529·1	529·7	530·2
526·2	526·7	527·2	527·7	528·3	528·8
524·8	525·3	525·8	526·4	526·9	527·4
523·4	524·0	524·5	525·0	525·5	526·0
522·1	522·6	523·1	523·6	524·2	524·7
520·7	521·2	521·8	522·3	522·8	523·3
519·4	519·9	520·4	520·9	521·4	522·0
518·0	518·6	519·1	519·6	520·1	520·6
516·7	517·2	517·7	518·2	518·8	519·3
515·4	515·9	516·4	516·9	517·4	517·9
514·1	514·6	515·1	515·6	516·1	516·6
512·8	513·3	513·8	514·3	514·8	515·3
511·4	512·0	512·5	513·0	513·5	514·0
510·1	510·7	511·2	511·7	512·2	512·7
508·9	509·4	509·9	510·4	510·9	511·4
507·6	508·1	508·6	509·1	509·6	510·1
506·3	506·8	507·3	507·8	508·3	508·8
505·0	505·5	506·0	506·5	507·0	507·5
503·8	504·3	504·8	505·3	505·8	506·3
502·5	503·0	503·5	504·0	504·5	505·0

APPLICATION.

Assay of Pure, or nearly Pure, Silver, the Temperature of the Normal Solution of Salt being that at which it was standardised.

First Example.—Let the ingot of silver have an approximative standard of from 995 to 1000 thousandths. Take one gramme; dissolve it in ten grammes of nitric acid, in the bottle, fig. 106. Then pour into the bottle an exact measure of the normal solution of salt, and brighten by agitation. The silver not being supposed to be quite pure, the standard is not further sought for by the decime solution of salt, but that of silver nitrate is employed.

One thousandth of this latter solution is poured into the bottle; it becomes cloudy, and is well agitated. A second and a third thousandth also give a precipitate, but not so a fourth. From these data the following is the method of ascertaining the standard of the alloy :—

The last thousandth of the decime solution of silver, having produced no cloudiness, is not to be counted. The third was necessary, but only partially so; consequently the number of thousandths of silver necessary to decompose the excess of salt is more than 2 and less than 3 ; in other words, it is equal to the mean, $2\frac{1}{2}$; but since $2\frac{1}{2}$ thousandths of silver have been required to complete the precipitation of salt representing 1000 thousandths of silver, it is evident that the silver submitted to assay contained $2\frac{1}{2}$ thousandths of alloy, and that its standard, to within nearly half a thousandth, is but $997\frac{1}{2}$.

If it be considered necessary to arrive nearer the true standard, the following proofs must be employed :—Pour into the solution $1\frac{1}{2}$ thousandths of salt, which will decompose a like number of thousandths of silver.* After due

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* It has already been stated how a thousandth of the decime solution may be subdivided by the number of drops furnished by the pipette. If, for instance, it contains 20 drops, 10 will give the half, 5 the quarter, &c. Half a thousandth may also be obtained by diluting the solution with its volume of water, and using a whole pipetteful. This latter plan has been found the best in practice.

agitation, add half a thousandth of silver nitrate. Supposing a cloudiness is produced, no further addition must be made; for it is already known that above the third thousandth no precipitate is formed in the liquid by silver nitrate, and consequently only half of the last half-thousandth must be calculated, as only a portion of it was necessary. From which, the entire number of thousandths of silver nitrate being $4\frac{1}{4}$, and those of salt $1\frac{1}{2}$, there remains $2\frac{3}{4}$ for the number of thousandths of nitrate of silver added to the normal solution; and consequently the standard of the alloy is $1000-2\frac{3}{4}=997\frac{1}{4}$. If, on the other hand, the last half-thousandth of the silver nitrate had produced no cloudiness, it would not have to be reckoned, and only half of the preceding half-thousandth would have been taken. Thus from the 4 thousandths of silver nitrate employed a quarter of a thousandth is deducted; and from the difference, $3\frac{3}{4}$, is yet deducted $1\frac{1}{2}$ of salt, the final remainder being $2\frac{1}{4}$ thousandths of silver nitrate which have been added to the normal solution: the standard of the alloy would be $1000-2\frac{1}{4}=997\frac{3}{4}$.

Although the above-described operation is very simple, yet it is desirable, in order to avoid all confusion, to note in writing such thousandths of salt or silver nitrate as are added. The thousandths of salt indicating an increase of standard should be preceded by the sign +; and the thousandths of silver nitrate announcing a diminution of standard, by the sign −.

Second Example.—Suppose the ingot has a presumed standard of 895 thousandths, and the temperature of the normal solution supposed invariable.

Find in the table of standards (Salt Table), first column, that which approaches the nearest to 895; it will be found to be 896·9, corresponding to the weight of 1115 milligrammes. This weight of the alloy is taken and dissolved in nitric acid, a measure of normal solution of salt added, and the whole well agitated. The operator is, however, doubtful whether the assay must be proceeded with by the decime salt solution, or the silver nitrate decime solution. If the former produces a precipitate, it is gone on with; but if it does not precipitate, that already added is decomposed by a similar addition of the second, and the solution rendered bright by agitation. A starting point has now been arrived at for the continuance of the assay, for it is known that the silver nitrate solution must be employed.

Suppose, then, that the alloy, after the addition of the measure of normal solution, yet gives a precipitate with the decime solution of salt. The first 5 thousandths produce a precipitate, but not the sixth, which consequently is not counted. The fifth has only been partially required, so that it is more than 4 thousandths, and less than 5, or the mean, 4½, is the quantity required to entirely precipitate the excess of silver in the alloy submitted to assay. But by neglecting at first the fraction 0·5, seek in the Salt Table of Standards the number found on the longitudinal line of the weight 1115, under column 4; it is 900·4, and on adding 0·5 to this number, we have 900·9, or 901, for the required standard.

Supposing, however, that the same alloy, after the addition of the normal measure of salt, gives a precipitate with silver nitrate, and that the 3 first thousandths produce a cloudiness, but not the fourth. The number of thousandths of silver nitrate really necessary for complete precipitation will be very nearly 2½. To ascertain the real standard of the alloy of which 1115 thousandths were supposed to contain about 1000 thousandths of silver, take the number found in the horizontal line 1115, and in the column 2 of the Silver Nitrate Table. This number, which is 895·1, diminished by the fraction 0·5, gives 894·6 for the standard of the alloy to within half a thousandth.

Third Example.—The actual temperature of the normal solution of salt being 18° when it was standardised at 15°.

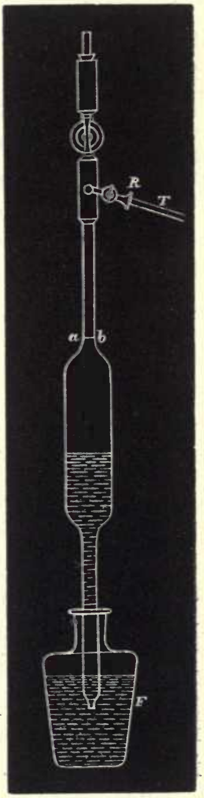
The ingot of silver submitted to assay has an approximative standard of 795 thousandths. Find in the Salt Table of Standards, first column, that which is nearest to it; it is 793·7, corresponding to the weight 1260. This weight of the alloy is taken, and the operation proceeded with as already described. Supposing it had required 6·5 thousandths of salt to precipitate the whole of the silver contained in the alloy to within half a thousandth, the required standard, without correction for temperature, will be $798{\cdot}4+0{\cdot}4=798{\cdot}8$. But, making this correction, recourse must be had to the table, page 589, column 15: the number 0·3, which will be found in the horizontal line 18 and the column 15, possesses the – sign; consequently it must be deducted from 798·8, and the remainder, 798·5, will be the standard weight. If the temperature of the solution, instead of being 3° higher than at the time it was standardised, was 3° lower, or 12°, the correction must be added, and would be equal to +0·2. The standard of the alloy would consequently be $798{\cdot}8+0{\cdot}2=799$.

Graduation of the Normal Solution of Salt, the Temperature being different to that at which it was wished to be graduated.

Two equally ready processes can be employed. The one consists in reducing the temperature of the solution to the desired degree before standardising; the other, in determining its standard without regard to the temperature of the solution, and then correcting its influence by the aid of the tables of correction already given.

First Process.—Place the liquid to be graduated in a bottle, *F*, fig. 112. Introduce a thermometer, and heat to a determinate degree, say 20° for instance. This done, place the jet of the pipette in the bottle; raise the liquid by aspiration by means of the conical tube, *T*, fig. 112, which is adapted to the opening of the air-cock, *R*. As soon as the liquid is raised a little above the mark *a b*, which determines the capacity of the pipette, close the stopcock, and complete

FIG. 112.



the measurement as usual. This same means of filling the pipette by aspiration may be employed to fill it either with caustic alkali or nitric acid, as the case may be, to cleanse it instead of taking it to pieces.

Second Method.—The solution of salt being supposed at a temperature of 16°, and it is desired to graduate it at that of 20°. Proceed with the standardising without regard to temperature; but when it is obtained in each trial assay, it is necessary to make the correction required by the temperature.

If, for example, in an approximative assay the standard of the solution was expressed by 1001·5 this standard would not only be too weak by 1·5 thousandth, but, according to the table of temperatures, by yet another 0·5, for the solution is weakened by this quantity, by passing from 16° to 20°. The standard, if taken at this last temperature, would be too low by 2 thousandths, and must consequently be corrected.

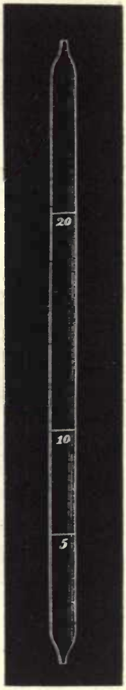
If, on the other hand, the standard of the solution were too high instead of too low, and expressed by 998·5 at the temperature of 16°; at that of 20°, the solution being weakened by 0·5, the standard would only be but one thousandth too high, and it must be corrected by that quantity.

Approximative Determination of the Standard of an Unknown Alloy.

It has always been supposed in the experiments already detailed, that the approximative standard of the alloy submitted to assay was known: and this, indeed, is nearly always the case. If, however, this be unknown, two means are available for obtaining the necessary knowledge. A decigramme of the alloy is cupelled with one gramme of lead; or if it be desirable not to use the cupel, it may be ascertained by the wet method, in the following manner:—

The assayer supposes the standard of the alloy known to be about a twentieth, and it can always be found nearer than that by touch, density, &c. A weight relative to its supposed standard is taken, and its standard sought by adding the decime liquid by 10 thousandths at a time, by means of pipettes of this capacity (see fig. 113). The term of complete precipitation is soon passed, and the standard of the alloy to about 5 thousandths is thus ascertained. The approximate standard to $2\frac{1}{2}$ thousandths may be obtained by adding only 5 thousandths of solution at a time.

FIG. 131.



Suppose the alloy 840 thousandths. Take the weight 1190, corresponding to this standard, and proceed as in an ordinary assay, adding each time, for example, a pipette of 10 thousandths of salt solution. It is found the fifth pipette gives no precipitate, and consequently the number of thousandths of salt for the precipitate of the silver to within 5 thousandths is 35. The 1199 of alloy will therefore contain $1000 + 35 = 1035$ of silver; and the approximative standard will be obtained by the proportion—

$$1120 : 1035 :: 1000 : x = 869{\cdot}7.$$

Modes of Abridging Manipulation.

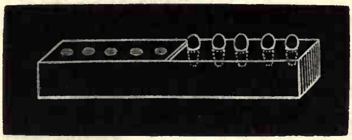
In the statement already given of the mode of conducting the assay by the wet method, only such instructions have been given as were necessary for its full comprehension, and everything that might call away or fatigue the attention has been omitted. Nevertheless, here it will be convenient to describe some methods of abridging the necessary manipulations, supposing that ten, or at least five, assays are made at once.

FIG. 114.

Bottles.—It is necessary to have these all, as nearly as possible, of the same height and diameter. They are marked progressively on the shoulder, as are also their stoppers (fig. 114), thus—1, 2, 3, 4, &c. They are taken successively by tens, in the natural order.

The stoppers are placed on a support, numbered in the same manner (fig. 115). The support is pierced with ten holes, distinguished in precedence by a mark between the fifth and sixth.

Fig. 115.



Stand. — Each ten flasks are in turn placed in a case or stand of japanned tin-plate (fig. 116), having ten compartments numbered from 1 to 10. Each of these compartments is cut anteriorly to about half their length, so as to allow the numbers of the bottles to be seen. The same stand serves for all the series, by making the same units correspond : thus, No. 23 of the third series is placed in stand No. 3, &c. When each flask is charged with the alloy, about 10 grammes of nitric acid, 40° C., are measured by a pipette (fig. 113) introduced into the bottles by means of a funnel with a large neck (fig. 117). The whole are then exposed to the heat of a water-bath, to facilitate the solution of the alloy.

Fig. 116.

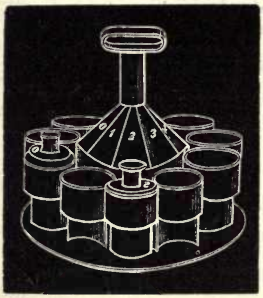


Fig. 117.

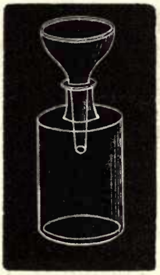
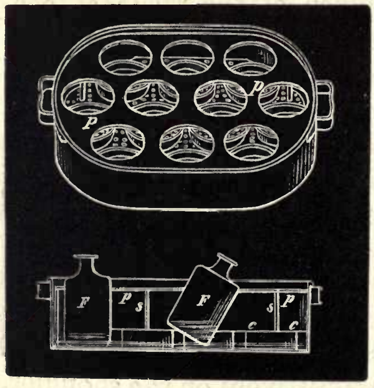


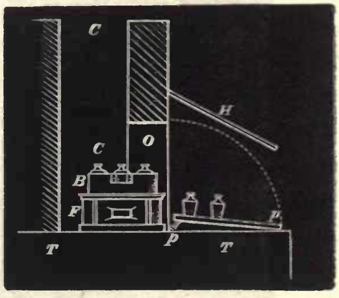
Fig. 118.



Water-bath.—This is an oblong tin-plate vessel, calculated to receive 10 bottles (fig. 118). It has a movable double bottom, pierced with small holes, the principal object of which is to prevent the fracture of the bottles by isolating them from the bottom of the vessel, which is immediately exposed to the heat. On the movable bottom are soldered the cylinders *c c*, three or four centimètres in height, and above which, at the distance of eight centimètres, is a sheet of tin plate, *p p*, pierced with ten holes, corresponding to the cylinders, and connected with the movable bottom by the supports, *s s*. These cylinders, and the sheet of tin plate, are destined to isolate the bottles, *F F*, one from the other in the bath, and to keep them some time suspended over it, when the water is boiling, before complete immersion. The water-bath may be replaced by a steam-bath ; the bottles will then be supported by a grating above the surface of the water. The solution of the alloy in the nitric acid takes place rapidly, and as it gives rise to an abundant evolution of nitrous vapour, it must be made under a flue having a good draught.

Flue.—This is represented at fig. 119. *C C* is a flue resting on a table or support, *T T*, about 90 centimètres high. The anterior side in the figure is removed to show the water-bath *B*, and the furnace *F*. The opening *O* of the flue is closed by the wooden door, *p*, movable on two eccentric pivots, which keep it up during the solution, and allow it to fall so that the flask may be placed upon it. The nitrous vapour is removed from the bottles with the blower (fig. 111). The hood, *H*, prevents the diffusion of the nitrous vapour in the laboratory.

FIG. 119.



Agitator.—Figure 120 gives a sufficiently exact idea of this apparatus, and dispenses with a long description. It has ten cylindrical compartments, numbering from 1 to 10. The bottles, after solution of the alloy, are placed in it in the order of their numbers. The agitator is then placed by the side of the pipette, by which is measured the normal solution of salt, and into each flask is poured a pipetteful of the solution. The bottles are fitted with their stoppers, previously moistened with distilled water (fig. 121); they are then fixed in order with wooden wedges (fig. 122). The agitator is suspended to a spring, *R*, and a rapid alternating movement given to it with both hands, by which the solution is agitated, and in less than a minute rendered as clear as water. The movement is assisted by a spiral spring, *B*, fixed to the agitator and its stand. The agitation finished, the wedges are removed, and placed in the vacant spaces between the compartments. The agitator is taken from the spring, and the bottles placed in order on a table prepared to receive them.

FIG. 120.

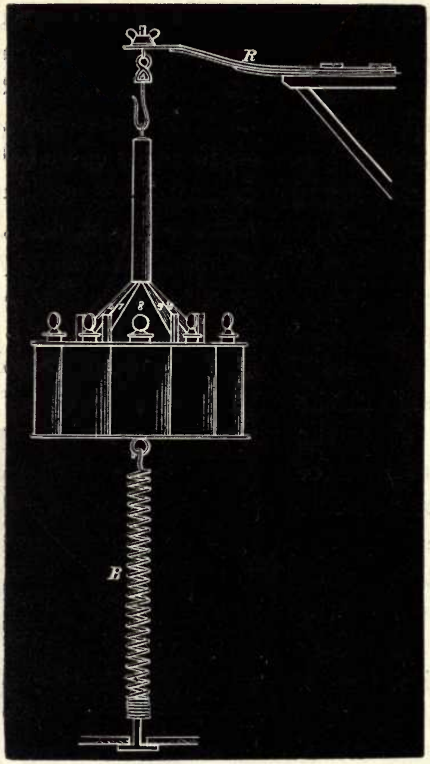


FIG. 121.

FIG. 122.

Table.—This table (fig. 123) has a double bottom; the upper is pierced with ten holes, a little larger than the diameter of the bottles, and of such a distance from the lower portion, or false bottom, that the flasks do not rise above its edge, or at least but little. This deposition is to protect the silver chloride from the light, for it decomposes in contact with water, and a little hydrochloric acid is produced, which requires for its precipitation a certain quantity of silver nitrate, and so lowers the standard of the alloy. This cause of error is, however, not very great, at least when the light does not fall directly on the chloride; but it is easy to avoid, and should not be neglected. The disposition already pointed out does not at all complicate the process, and is moreover useful, as it prevents the fracture or upsetting of the bottles. When but one bottle is operated on, it is placed for agitation in a japanned tin-plate cylinder, which is held as shown at fig. 124. On placing the bottles in their respective places on the table, a brisk circular movement is given to them, so as to remove any silver chloride adhering to the sides; their stoppers are removed and suspended by spring pincers, *a a*. These are formed of sheet-iron wire (see fig. 125). A thousandth of the decime solution is then poured into each bottle, and before this has been completed there will have

FIG. 123.

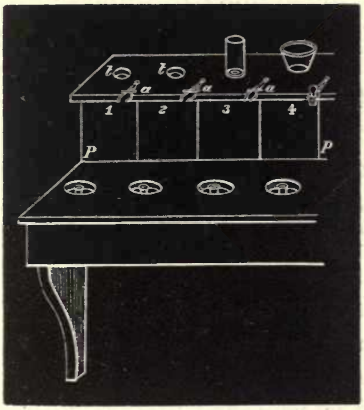
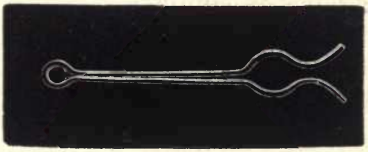


FIG. 124.

FIG. 125.

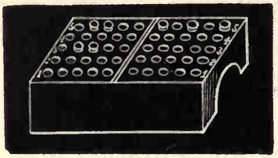


formed in the first bottles where there is any precipitate, a well-marked nebular layer about a centimètre in thickness. At the back of the table is a black board, *P P*, divided into compartments numbered from 1 to 10, on each of which is marked with chalk the number of thousandths of decime liquid added to the contents of the corresponding bottle. The thousandths of salt announcing augmentation of standard are preceded by the sign +, those of silver nitrate by the sign −.

Lastly, the black board carries a small shelf pierced with holes, *t t*, and these receive the funnels or drain the bottles; on this shelf also are fastened the pincers for sustaining the stoppers.

Cleaning the Bottles.—The assays terminated, the liquid from each flask is poured into a large vessel in which there is always a slight excess of common salt; and when it is full, the clear supernatant fluid is removed by means of a syphon. Immediately will be given the means of reducing the silver chloride so collected to the metallic state. The bottles, to the number of ten, are first rinsed with the same water passed from one to the other, then a second, and then a third time with fresh water. They are then placed to drain on the board just mentioned, and the stoppers are placed in a stand by series of tens (see figs. 126 and 115). It is important to remark, that when a glass has been rinsed with distilled water, care must be taken not to rub it with the fingers, for water poured in such a vessel would always be clouded on the addition of silver nitrate. This effect is due to the chlorides contained in the perspiration, and is of course more to be guarded against in summer.

Fig. 126.



Reduction of Silver Chloride, obtained in the Assay of Alloys by the Wet Method.

Silver chloride can be reduced without sensible loss, after having been well washed, by plunging it into scraps of iron or zinc, and adding dilute sulphuric acid in sufficient quantity to set up a slight disengagement of hydrogen gas. The whole can be left to itself, and in the course of a few days the silver is completely reduced. This point can be easily determined by the colour and nature of the product, but better still by treating a small quantity with ammonia, which, if the chloride is perfectly reduced, will give no precipitate or cloudiness on treatment with an acid. The chlorine remains in solution in the water combined with zinc or iron. The residue must now be washed; the first washings are made with acidulated water, to dissolve iron oxide which might have formed, and the following with ordinary water: after having completed the washing as much water as may be left is decanted, the mass dried, and a little powdered borax added. Nothing now remains but to fuse it. The powdered silver being voluminous, it is placed by separate portions in the crucible, in proportion as it sinks. The heat should be at first moderate, but towards the end of the operation should be sufficiently high to reduce the silver and slag to a state of complete liquidity. If it be found that not quite all the chloride was reduced by the iron or zinc, a little potassium or sodium carbonate may be added to the powdered silver. The standard of silver thus obtained is from 999 to 1000 thousandths.

Preparation of Pure Silver.

Take the silver prepared as above, dissolve it in nitric acid, and leave the solution some time in perfect rest in water, to deposit any gold it might contain. Decant the solution, and precipitate with common salt, well wash the precipitate, and reduce it, when the resulting silver will be pure.

M. Gay Lussac here gives a description of a process for the precipitation of chlorine from nitric acid for use in the mode of assay already described; but as that acid in a state of ordinary purity forms an article of commerce, and can be obtained at most operative chemists, the process will not be here reproduced.

Modifications required in the Assay of Silver Alloys containing Mercury.

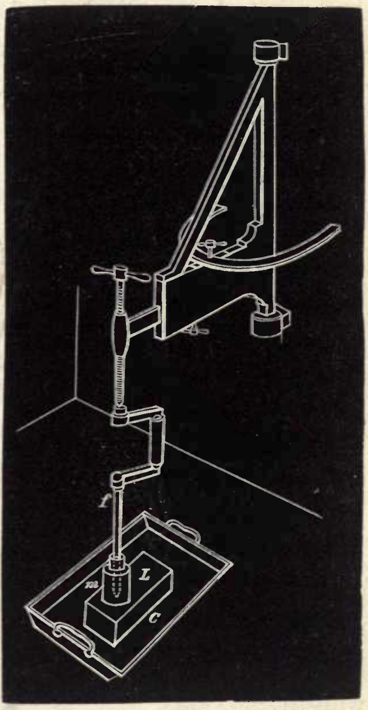
Whenever mercury is present in solution with silver, it is thrown down as insoluble chloride, and the assay rendered inaccurate. The presence of mercury in silver can be readily detected by the remarkable change which occurs in silver chloride on exposure to light (viz. blackening) when free from mercury; but if the smallest quantity of the latter metal be present, no blackening will ensue. This source of error was removed by M. Levol in the following manner:—The sample being dissolved, as usual, in nitric acid, it was supersaturated with 25 cubic centimètres of caustic ammonia; the pipetteful of normal solution was then added, and the excess of ammonia supersaturated with 20 cubic centimètres of acetic acid, and the operation continued in the usual way.

Some little time after the publication of this, M. Gay Lussac examined the above process himself, and very considerably simplified it. He says:—'After having confirmed by several experiments the accuracy of M. Levol's process, I thought it might be simplified by adding to the nitric solution of silver the ammonia and acetic acid at one and the same time, but in sufficient quantity to saturate the whole of the nitric acid, both that in combination with the silver and that in the free state. Ten grammes of ammonium acetate were added, with a little water, to the silver dissolved in nitric acid, and the assay finished in the ordinary manner. The quantity indicated by synthesis was found very accurately, although 100 thousandths of mercury had been added.' Finally, M. Gay Lussac found that 10 grammes of sodium acetate, in crystals, also fully answered the purpose; and as that is a very cheap commercial salt, it is the best adapted for overcoming the difficulty in this class of assay, as regards the presence of mercury.

Method of Taking the Assay from the Ingot.

The ingots are so rarely perfectly homogeneous, even taking as a starting-point the standard 950 thousandths, that the differences remarked between the assays of samples made in different places should rather be attributed to the above cause than to the assay itself. It is important, therefore, to take a sample in a uniform manner, and from the same depth, on the upper surface of the ingot as on the lower. This condition is perfectly fulfilled by boring the ingots with a kind of drill, similar to that employed by the smith, and which is represented at Fig. 127. The ingot, *L*, is placed in a copper tray, *C*; and in order to retain the borings, which might otherwise be thrown out, the drill, *f*, is surrounded by a casing, *m*, which does not impede its motion, and stands freely on the ingot. After a few turns of the drill, the first borings, which are not pure, are removed by means of a feather, and only those following are collected and reserved for assay. If it be desirable to try the lateral faces, it is necessary to employ a pressure screw, to keep the ingot in the position that may be deemed necessary.

FIG. 127.



Method of Assaying Silver Bars adopted in the Assay Offices of H.M. Indian Mints.

According to the report of H. E. Busteed, M.D., H.M. Madras Army, refining assay master, Calcutta Mint, the silver bars are assayed by determining the silver as chloride. The cupellation assay is not correct enough to satisfy the sellers and purchasers: the Gay Lussac assay is not used because most of the bullion contains mercury, lead, and other base metals; because a previous cupellation assay is required; because the high temperature of the climate causes an evaporation of the salt solution; and because a large number of persons would be necessary on account of the large daily number of assays.

The credit is due to Mr. J. Dodd, a former assay master of the Calcutta Mint (and a surgeon in the Madras army), of having encountered those difficulties of manipulation, and of having overcome them, inasmuch as he modified and simplified them, and in short so systematised the whole practical working of the process as to render its application to the assaying of silver, to any amount, easy, accurate, and economical.

The process is technically known as the 'chloride process.' It is thus described by Dr. Busteed in the 'Chemical News' for November 1871:—

The samples (or 'musters') for assay are, to save time, first approximately weighed by an assistant; they are then placed (each sample in duplicate) in small shallow saucers of polished copper, and so brought in batches of 40 on a board, containing in numerical order receptacles for the little saucer, to the assay master, who, in the delicate assay balance, exactly brings each sample to the one required weight.*

As each sample is weighed, it is transferred from the platinum skiff of the balance to a bottle on the left hand of the assayer, by means of a small copper funnel. The bottles† for this purpose are held in readiness for the musters by an assistant, and, on receiving them, are removed into the laboratory in batches of six.

On being taken to the laboratory, they are ranged on a circular platform or turn-table, and there one of the

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* The amount of this weight will be more particularly referred to farther on.

† The chief appliances will be described more fully at the conclusion of the description of the process.

(European) assistants adds by means of a pipette 1½ drms. of nitric acid to each bottle, which are then (without their stoppers) transferred to a sand-bath and exposed to a considerable degree of heat, till solution of the contents is effected.

The specific gravity of the nitric acid used is generally 1·200, *i.e.*, in the case of known alloys of only copper and silver, such as the standard meltings, coins, &c.; but when the nature of the alloy is uncertain, such as bazaar silver, or some sycee (where the presence of mercury may be suspected), a stronger acid of sp. gr. 1·320 is used. It has been found, too, by experience, that the chlorides from fine bar silver agglomerate better when the solution has been effected in the stronger acid.

When the samples have been completely dissolved,* the bottles are brought back to the platform, and there each receives through a glass funnel† about six ounces of cold distilled water.

There is then added to each bottle, through a glass pipette as before, 1½ drms. of hydrochloric acid, sp. gr. 1·060, which immediately converts the silver present into the characteristic white precipitate of silver chloride, which forms in slow-falling curdy volumes.

The stoppers (previously dipped in distilled water) are then carefully replaced, and the bottles are allowed to stand for five minutes.

The bottles are next well shaken two and two by the laboratory workmen for three or four minutes, till the chloride aggregates and rapidly falls down; any particles which may remain attached to the neck or upper part of the bottles are washed down by a quick circular motion, and more distilled water being added to within about two inches of the neck (great caution being observed in removing and returning the stoppers), the bottles are then allowed to rest each in its assigned place on the platform for four hours.

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* A slight residuum of gold, as a black powder, is very generally seen.

† The portion of this which enters the neck of the bottle is protected or sheathed, with an inch of india-rubber tubing, to prevent chipping, if struck against the neck of the bottle.

At the expiration of that period, the clear supernatant liquid (blue-coloured when copper is present) is removed by a glass syphon, which is lowered to within an inch of the deposited chloride, the greatest care being taken that none of it is drawn up into the syphon. As each platform is made to revolve on its centre, according as each bottle is syphoned, the operator sitting in one place brings the platform round till the next bottle in order gets under the syphon, which is thus in rotation lowered into each. The fluid escapes from the long leg of the syphon through a funnel fitted in the table to a jar placed underneath.

After the first syphoning, the bottles are immediately filled again with distilled water, and each gets a quiet circular motion for a few moments, and the precipitate is again allowed to settle as evenly as possible; this time it will be sufficient to allow them to rest for two hours, when they are again syphoned as before and the stoppers returned.

Under ordinary circumstances these two washings are sufficient; but if the silver is evidently 'coarse,' a third or fourth washing is similarly given.

When it is considered that the chlorides have been sufficiently washed, the bottles are placed for half an hour in a reclining position on their platforms; this causes the chloride to fall and settle to one spot, and renders its removal from the bottles more easy.

Meantime a pneumatic trough has been got ready, capable of containing a batch of twenty inverted bottles; the trough is filled with distilled water; for each bottle there is placed on the floor of the trough a small porcelain saucer holding a little Wedgwood crucible or cup, each numbered to correspond to the bottles. A laboratory workman then removes the stoppers from the bottles, and hands them one by one to an assistant at the trough, who, placing his forefinger over the mouth of each bottle, inverts it over its corresponding cup, and does not remove his finger till the neck of the bottle has passed down through the water and well into the cup; then the finger being taken away, the bulk of the chloride falls by its own weight to the bottom of the cup.

The bottle is held in the position by two rings, one (the larger) above the other, which are fixed to the sides of the trough; this arrangement retains each bottle *in situ*, at the proper slant, and admits of the operator gently revolving or slightly raising the bottle with his left hand, while with the right he patiently taps the bottom and sides till the whole of the chloride has been dexterously got out; the finger is then again placed over the mouth, and the bottle raised up through the rings and handed (mouth upwards) to the assayer, or to the supervising assistant standing by, who carefully examines it to see that every particle of chloride has been dropped into the cup. When this part of the manipulation has been neatly done, none of the chloride falls over into the saucer which is placed as a precautionary measure under each cup.

When the chloride falls into the cup, it is in an uneven lumpy state, and not in a favourable condition for being uniformly dried; it has, therefore, next to be broken up. For this purpose the cups (containing the chlorides, and water to the brim) on removal from the trough are taken in batches on a tray to an assistant seated at a steady table, who first carefully decants off about half the water, and then with a finely-polished glass rod (four inches long and one-third of an inch thick) gently stirs and beats the lumpy precipitate, while revolving the cup on the table; this causes it to lie evenly and loosely at the bottom of the cup as a purplish grey powder, not too fine.

He next washes the rod over the cup with distilled water from a drop bottle, lest any of the chloride may be adhering to it, and sprinkles a drop or two from it on to the surface of the water in each cup, so as to cause to sink any minute particles that may happen to remain floating. He then, after an interval of ten minutes, drains off about three-fourths of the supernatant water, which he lets run down the rod into a vessel near him, and with a tap or two of the rod on the outside of the cup to still further loosen the deposit, this part of the manipulation is concluded.

The crucibles are next taken to the drying furnace, where a steam bath is ready to receive them; on the perforated upper plate of this they are ranged, and allowed to remain for about an hour. This gradually, and without spurting, frees the chlorides from moisture, which may be known by their caking, *i.e.* leaving the sides of the cups round the edges and forming at the bottom of each a loose cake, resembling somewhat a gun-wad. The crucibles are then arranged on a hot-air plate and there exposed to a temperature of between 300° and 350° (F.) for about two hours, till thoroughly dried, when they are ready for weighing.* When the above manipulations have been carefully and satisfactorily gone through, each little cup contains an unbroken, tolerably firm, cake of chloride of silver, lying unattached, which admits of being easily grasped with a pair of forceps, and cleanly lifted out of the cup and conveyed to the skiff of the assay balance in which it is weighed. The cups are generally brought from the laboratory to the assayer at the balance in batches of eight or ten. A 'standard,' synthetically prepared of pure silver and copper, and an assay pound of pure silver, are introduced with each day's set of assays, and their chlorides dried with the others, and the analysis of them verified before weighing the rest. Occasionally these 'checks' are also fused and weighed in a porcelain capsule, but the weight found never differs from that of the chloride merely dried as above.

Once or twice a month, the silver is recovered from the accumulated chlorides, which are well pounded in a mortar and brought to a powder and then mixed with a proper proportion of chalk and charcoal, and put into a wrought-iron crucible and reduced with heat. The metallic silver so recovered is transferred to the mint.

Under the circumstances of the solution and of the precipitation as detailed above, should any gold happen to be present in the sample operated on, it is not dissolved, and therefore becomes entangled with the precipitated

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* The chlorides are weighed warm, to obviate the risk of their absorbing moisture; a precaution especially necessary in the heavy monsoon weather in this country.

silver chloride and dried and weighed with it, and accordingly comes to be regarded and valued as silver. In this the chloride process resembles that by cupellation, which likewise takes no distinguishing cognisance of gold; and both these processes contrast in this respect with the volumetric one, which is a rigid analysis for silver alone; so that, strictly speaking, an assay conducted by either of the first-named methods ascertains the proportion present of 'the precious metals,' *i.e.* silver and gold.*

Should mercury be present it does not interfere with the result, when the solution has been effected in excess of nitric acid with strong heat. Thus the mercury becomes peroxidised, and hydrochloric acid forms no precipitate in solutions of mercuric salts; any mercuric chloride resulting from the combination would remain in solution, and be washed away in the course of the process.

Should lead happen to be present, hydrochloric acid gives no precipitate in a dilute solution, the lead chloride being soluble in a certain proportion of distilled water; but even were the proportion of lead to silver tolerably large, and the lead chloride happened to be thrown down, the repeated washings would dissolve and get rid of it.

With regard to the weight of the small portion taken to represent the mass, the system prevails in the Indian mints of taking samples for assay by granulating a small portion of the contents of each melting-pot: when the metal is in a thorough state of fusion and has just been well stirred, a small ladleful of the molten metal is quickly poured from a tolerable height into a vessel of water, and the granules so formed received on a strainer, lifted out, and perfectly dried.† The weight of this specimen repre-

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* Much of the silver which finds its way to the Indian mints is rich in gold; for instance, sycee contains on an average somewhat about 12 grs. in the troy pound. This in minting operations is considered as silver, and as such it enters into the coinage. There being as yet no refineries established here, through which such silver could pass to the mechanical departments of the mints, the silver coins made during a period when a heavy importation of sycee had been worked up, contain as much as 4 or 6 grains of gold in every 32 tolas or 1 pound troy.

† The introduction into the Calcutta Mint of this system of taking musters is attributable to Dr. Boycott, late Assay Master, and to Dr. Shekelton, who,

senting each pot was first fixed at 24 grs., technically called the 'assay pound:' this, in the case of pure silver, yielded 31·87 grs. of silver chloride, while the same quantity of Indian standard silver (which is $\frac{11}{12}$ths silver plus $\frac{1}{12}$th copper = 916·66 in 1000) yielded $\frac{1}{12}$th less, or 29·21 grs.: on the weight of chloride being ascertained in each case, a table which was calculated and prepared for the purpose was referred to, and the equivalent fineness assigned to the $\frac{1}{2}$ dwt., plus the odd grs., when any. But when it became desirable to prepare for the decimal form of notation, a number more convenient than 31·97 was looked for to represent purity or 1000, and 25 was fixed on as a desirable starting-point, particularly as the quantity of pure silver yielding that amount of chloride, viz., 18·825 grs., was quite large enough to represent each pot.*

The weight, therefore, of the 'assay pound' in use at present is 18·825 grs. This produces (with chlorine) in the case of pure silver 25 grs. of silver chloride.†

But to obviate the necessity of constant reference to a calculated table to find the equivalent in pure silver of the amount of silver chloride found in each case, it was ingeniously arranged to stamp each of the assay weights not with its actual weight, but with the figures representing the proportion per mille of pure metal which such a weight of chloride so found corresponds to: thus, sup-

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by a number of interesting experiments, satisfied themselves that samples so taken represent the mass of mixed metal to be valued much more fairly than samples of the same mass cut or gouged from it after it has been poured and allowed to cool in the ingot moulds, where a partial separation of the copper from the silver seems to take place; the result being, according to the above experiments, that in the case of ingots cast in upright moulds all the outside is much below the average fineness of the mass on assay, and the centre much above it. This refers to alloys of silver and copper mixed in or about the proportion of 'standard.' According to M. Levol, however, it would appear that when an alloy of silver and copper in which the proportion of the latter is very high (viz., over 28 per cent.) has been melted, poured, and allowed to cool, an opposite result to the above is found, viz., the outside of the ingots is above the average fineness. An assay, therefore, from a granulated sample must give a much nearer approximation to truth than one from a cut sample.

* The average weight of the contents of each melting-pot is 12,500 tolas, or about 390 pounds troy, so that the specimen taken to represent this is but about the 119,000th part; each sample is assayed in duplicate.

† The basis for these numbers was founded on the proportion in which, according to Turner, silver combines with chlorine, viz., 100 parts with 32·80.

posing a melting of five-franc pieces was being assayed, and the chloride resulting from the assay pound operated on weighed 22·5 grs. (showing the actual pure contents in the sample to be 16·94 grs.), instead of referring to a table to see the equivalent per mille-age of silver, that weight which is actually 22·5 grs. has 900 marked on it, and the assayer simply reads the 'touch' from it.

Accordingly, the assay weights are as follows:—

Actual weight in grs.		Figures marked on the weights
25·000		1000·00
22·910	(Std.)	916·66
22·500		900·00
20·000		800·00
17·500		700·00
15·000		600·00
12·500		500·00
10·000		400·00
7·500		300·00
5·000		200·00
2·500		100·00
1·250		50·00
1·000		40·00
0·750		30·00
0·500		20·00
0·250		10·00
0·125		5·00
0·100		4·00
0·075		3·00
0·050		2·00
0 025		1·00

Assay lb., weight=18·825 grs.

An ordinary day's work consists of eighty assays,* estimating imported bullion to the value of four lacs of rupees, and standard meltings and coins to the value of five lacs. But on emergencies, in time of heavy pressure, by working extra hours, as many as 164 assays have been daily conducted, estimating to the value of eight lacs of rupees, and standard coins and meltings to the value of fourteen lacs.

Such is an outline of the method of assay worked on a large scale; of course successful results from it cannot be expected unless each step in the manipulation be conducted with great care and accuracy, and only then after much practice and experience.

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* Exclusive of any gold assays which may be going on.

The natives of this country possess great aptitude in acquiring the skill and consequent lightness of touch so essential for delicate manipulation; this, added to their characteristic patience, makes them admirable subordinates in an assay laboratory, under judicious supervision; moreover, their labour is cheap; so that, on the whole, the process seems to be especially suitable for an Indian mint.

When bar silver is imported from the Continent, the assays of it, made here, almost invariably correspond most closely with those previously made of it in Paris by the volumetric method. But were further proof needed of the practical accuracy of this system, it is to be found in the very close proximity to the legal standard at which the large Indian coinage has been maintained for many years, as annually reported by the assayers to the Royal Mint of Great Britain, who test the fineness of the Indian pyx coins by the French wet process.

Without this method (improved and made more perfect, as it has been, in the hands of successive assay officers), it would have been very difficult for the assay establishments of the Indian mints to have dealt with, in the same time and with the same accuracy, the immense importation of silver to India during the last fifteen years. In the single year 1865–66 there was poured into the Indian mints, and manufactured into coin, silver alone reaching in value to the prodigious amount of over fourteen millions sterling.

The system which enabled the assay officers to value such a rapid and heavy influx with accuracy, and with satisfaction to the importer on the one hand, and to the mint (the buyer) on the other, and to faithfully maintain the immense resulting coinage close to legal standard, has been put to a severe test. If success be the criterion of merit, the twenty years' large experience of this method gained in the Indian mints goes to show that it is worthy of a yet wider field of utility.

Apparatus and Appliances required.

(1.) The bottles used in this process are of thin (but strong) white glass, and contain about 12 fluid oz.; about 6 inches in height and 2½ inches in diameter at the bottom, which should present a perfectly even, level floor; they are without any (abrupt) shoulder, but become gradually pyramidal from about half-way up to the neck; this shape favours the easy dropping out of the chloride. The neck is about one inch in length, polished on its inner surface; the stoppers are of ground glass, polished, with globular heads, and are made to fit with the utmost accuracy and smoothness. The bottles and stoppers are numbered, to correspond with the number on the muster board and also on the cups.

(2.) The 'cups' are Wedgwood crucibles, smooth and thin, about 1½ inches in height, 1½ inches in diameter above, and a little less than 1 inch in outside diameter at the bottom. The floor should be perfectly level, and neither it nor the sides should present any roughness likely to retain the chloride. The cups are all numbered.

(3.) The porcelain saucers are shallow, ¾ of an inch in depth; the upper diameter is about 4 inches, the lower 2½ inches.

(4.) The turn-table is a circular board of about 3 feet in diameter, fenced by a brass railing (or by a simple ledge); its centre is occupied by a raised platform about 2 feet in diameter, between which and the rail the bottles (26 on each) stand, the round outer edge of the platform having semi-lunar niches cut in it, into which the bottles fit; opposite to each niche on the platform is a little concavity in which the stoppers rest when not in the bottles. Each turn-table is made to revolve on its centre in either direction, and is raised about 6 inches above the long general table on which all are supported; close to each a funnel is fitted into the lower (supporting) table for conducting away the fluid syphoned from each set of bottles.

(5.) The trough is a basin of cast-iron (painted); it may be oblong or round, raised to about the height of 3 feet from the ground; when round and large enough for twenty bottles, space and distilled water may be economised by having a platform insulated in the centre. This is convenient for resting the bottles on after the chlorides have been got out. A trough of this kind may be about 2½ feet in diameter, having a space 7 inches broad and 4 deep all round between the circumference of the basin itself and the outer edge of the island platform. Into this space is poured distilled water to the depth of 3 inches. From the rim of the trough hang as many brass supports as there are bottles to be inverted; there are two circular clasps connected at the back to a bar common to both; one, the larger, is 1½ inches above the smaller and lower one, which is under water; they are open in front (or towards the centre of the basin) to about ¼ of an inch in width. The openings of both are in the same line, owing to the lower (smaller) segment being projected towards the centre by an abrupt curve in the connecting bar, by which they hang from the brim. This arrangement receives and fixes the inverted bottles in the required position. The distilled water is removed from the trough by the withdrawal of a plug. These troughs are sometimes made to revolve on the centre.

(6.) The drop bottle used for washing down the glass rod when breaking up the chlorides, and for sprinkling the surface of the cups, is small-sized, round, so as to be easily grasped; it holds about 6 ozs. The stopper is hollow, with two small tubes leading from its head, one opposite to the other. Glass is so liable to break or chip, that a hollow silver stopper is now generally substituted.

(7.) The steam-bath is simply a square vessel made of sheet copper, between 3 and 4 inches deep, the top or upper plate of which has a number of circular openings about two-thirds of the diameter of a Wedgwood crucible. There is also a steam escape pipe leading from the centre below to about a foot in height. They are of various sizes, to contain from 10 to 150 pots: they are raised or moved by two lateral handles.

(8.) Hot-air plate of thin sheet iron bored with holes for the reception of the crucibles, raised by iron feet about $1\frac{1}{2}$ inch above the furnace plate. It is furnished with a square tin cover, which fits over it. This is provided with lateral apertures for the escape of heated air, and with a tube from its roof for the reception of a thermometer.

The drying furnace on which the above rest is surmounted by a hood, the door of which (glazed) slides up and down by weights and pulleys; the plate is heated by means of gas jets; it has a good draught to carry off the nitrous fumes, as on it the musters are dissolved in the first instance on a sand bath.

(9.) The forceps for removing the cake of chloride from each cup to the skiff of the balance should not be too sharp in its grasp; it is much improved by having the blades tipped for about an inch from the points with platinum about $\frac{1}{8}$ inch in width.

(10.) It is a convenience to have the assay weights arranged in a set of ivory compartments in the weight box; on the floor of each compartment are engraved the figures corresponding to those engraved on the weight which occupies it; by this means the assayer has merely to glance at his weight box to see what weights are in the pan of the balance, and to read off the 'touch' when each chloride is counterpoised.

Mr. J. Volhard gives ('Liebig's Annalen') the following process for the volumetric assay of silver by means of a solution of ammonium sulphocyanide.

In a nitric solution of silver to which a soluble ferric salt has been added, a permanent redness does not appear on the gradual addition of a dilute solution of ammonium or potassium sulphocyanide, until all the silver has been thrown down as a sulphocyanide. If we know how much of the sulphocyanide solution is required to precipitate a known weight of silver we can determine volumetrically the quantity of silver present in any acid argentic solution, the ferric salt serving as an indicator. For the preparation of the standard solution the author uses ammonium sulphocyanide, though Lindermann prefers the potassium salt; both in dilute solution are permanent. But the ammonium salt is less frequently contaminated with chlorides, which interfere greatly if present in more than mere traces. The solution may be conveniently made of such a strength that 1 c.c. indicates 1 centigramme of silver. The weighed quantity of the salt is dissolved in water, and diluted in a graduated flask so far that 7·5 grms. (or 8 grms. if the salt appears very damp) may be contained in each litre. For the precipitation of 1 grm. of silver 0·704 grm. of pure ammonium sulphocyanide is requisite; 0·5 grm. of chemically pure silver is then weighed out, dissolved in 8 to 10 c.c. of pure nitric acid of sp. gr 1·20, and after the complete solution of the metal, the nitrous acid is expelled by boiling or prolonged heating on the sand-bath, and the solution is allowed to cool. It is then diluted with 200 c.c. of water, and 5 c.c. of a cold saturated solution of ammonia-iron alum are added. If the colour of the ferric salt is perceptible, a little pure colourless nitric acid is added till it disappears. The sulphocyanide solution is then added from a burette. At first a white precipitate is produced, which remains suspended in the liquid like silver chloride, rendering it milky. On the further addition of sulphocyanide each drop produces a blood-red cloud, which quickly disappears on agitation. As the point of saturation is reached, the silver sulphocyanide collects in flocks, and the liquid grows clearer, without becoming perfectly limpid, as long as a trace of silver remains in solution. As soon as all the silver is precipitated the flocculent precipitate quickly deposits, and the supernatant liquid becomes quite clear. The sulphocyanide solution is added by drops till this point is attained, and till a very faint light brown colour appears in the liquid, which does not vanish on repeated agitation. The colour is most easily perceived if the liquid is held, not up to the light, but against a white wall turned away from the window.

For a repetition of the experiment it is convenient to use a silver solution of a known strength. For this purpose 10 grms. of pure silver are dissolved in nitric acid in a litre flask, the nitrous acid is expelled, the liquid is allowed to cool, and diluted up to the volume. For use 50 c.c. are taken with a pipette. If the above-mentioned proportions are preserved for 0·5 grm. silver, or 50 c.c. of the silver solution, somewhat less than 50 c.c. of the sulphocyanide solution will be required, whence the needful dilution can be calculated. If 48·5 c.c. sulphocyanide have been used, then to every 48·5 c.c. of the solution 15 c.c. of water must be added.

The solution is perfectly permanent, even on being kept for two years. The silver solution must have a decidedly acid reaction from free nitric acid, which it is quite unnecessary to neutralise, for it is important that the proportion of acid in different experiments should be approximately equal. It is, however, essential for the constancy of the results that the ferric salt should be in large excess, and should be used approximately in one and the same proportion to the total volume of the fluid. It must also be remembered that the colour of ferric sulphocyanide is destroyed by nitrous acid at common temperatures, and by nitric acid on the application of heat. Hence follows the necessity of completely expelling all nitrous acid, and of allowing the liquid to become cold before the operation is begun. The nitric acid used in this process should be kept in the dark.

Titration of Silver in Presence of other Metals.

Copper.—The proportion of copper in an alloy may reach 70 per cent. without in the least affecting the accuracy of the process. Beyond this limit the recognition of the final reaction is somewhat doubtful, since after the precipitation of the silver the liquid is rendered opaque and discoloured by the formation of black copper sulphocyanide. The only remedy in such cases is to add a known weight of pure silver to the alloy, so as to reduce the proportion of copper below 70 per cent., as is done in Gay-Lussac's process.

Mercury.—In presence of this metal silver cannot be titrated with sulphocyanide solution. This defect is of little consequence, as mercury is readily expelled.

Palladium renders the titration of silver with sulphocyanide inaccurate, this metal appearing in the result as silver. This is an important circumstance from a technical point of view, since palladium; though frequently present in silver, occurs in very small quantities.

As regards other metals soluble in nitric acid and found along with silver in alloys and ores, lead, cadmium, thallium, bismuth, zinc, iron, and manganese are without influence. The recognition of the final reaction in solutions strongly coloured by salts of cobalt or nickel, requires some practice. At first a few drops of sulphocyanide will always be added in excess. It is then recommended to titrate back with a solution of silver, when the pure colour of the cobalt or nickel will appear so suddenly and distinctly, that it will conversely be easy to seize the exact point, when the colour of the solution is modified to a yellowish brown by the addition of the colour of ferric sulphocyanide. When the change of shade has been observed four or five times by titrating backwards and forwards with exactly corresponding solutions of silver and of sulphocyanide, such a certainty in the recognition of the final reaction will be attained that there can be no doubt as to the addition of a half drop more or less.

The presence of tin, antimony, and arsenic does not interfere with the accuracy of the process.

Mr. C. A. M. Balling gives the following instructions for the direct determination of silver in galena by Volhard's process :—From 2 to 5 grms. of the galena, according to its supposed richness in silver, are very finely ground and intimately mixed in a porcelain mortar with from three to four times its weight of a flux composed of equal parts of soda and saltpetre, placed in a porcelain crucible, covered, and heated over a burner to thorough fusion, when the mixture is well stirred with a glass rod. It is then let cool and placed in an evaporating dish partly filled with water, in which the melted matter is softened, dissolved out of the crucible into the dish, which is then heated, and the watery solution is filtered into a flask. The residue on the filter, after being well washed, is rinsed back into the dish, very dilute nitric acid is added, and the whole evaporated to dryness. The dry residue is taken up in water acidulated with nitric acid, heated, and filtered into the same flask in which is the aqueous solution. The residue is washed with hot water, the filtrate is allowed to cool in the flask, ferric sulphate or iron alum is added, and the liquid is titrated.—*Oest. Zeitschrift Bergu. Hütten.*

BLOWPIPE ASSAY OF SILVER.

The following very complete method for the blowpipe assay of silver and its ores is given by David Forbes, F.R.S., in the 'Chemical News,' Nos. 380, 384, 392, 396, 398, and 412.

The blowpipe assay of silver ores was first described in 1827 by Harkort,* and subsequently considerably improved by Plattner. This assay process is in all cases based upon the reduction to a metallic state of all the silver contained in the compound in question along with more or less metallic lead, which latter metal, when not already present in sufficient quantity in the substance itself under examination, is added in the state of granulated lead to the assay previous to its reduction. The globule of silver-lead thus obtained, if soft and free from such elements as would interfere with its treatment upon the cupel, may then be at once cupelled before the blowpipe until the pure silver alone remains upon the bone-ash surface of the cupel; but if not, it is previously submitted to a scorifying or oxidising treatment upon charcoal until all such substances are either slagged off or volatilised, and the resulting silver-lead globule cupelled as before.

As, therefore, the final operation in all silver assays is invariably that of cupelling the silver-lead alloy obtained from the previous reduction of the substance, effected by methods differing according to the nature of the argen-

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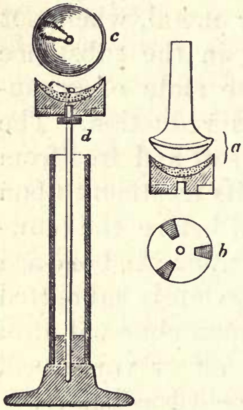
* 'Die Probirkunst mit dem Löthrohre.' Freiberg, 1827, I. Heft (all published).

tiferous ore or compound under examination, it is here considered advisable to introduce the description of the silver assay by an explanation of this process.

In the ordinary process of cupellation in the muffle, bone-ash or other cupels are employed of a size large enough to absorb the whole of the litharge produced from the oxidation of the lead in the assay.

This, however, should not be the case when using the blowpipe; for as the heating powers of that instrument are limited, it is found in practice much better to accomplish this result by two distinct operations—the first being a concentration of the silver-lead in which the greater part of the lead is converted by oxidation into litharge remaining upon, but not, or only very slightly, absorbed by, the bone-ash cupel: and the second in cupelling the small concentrated metallic bead so obtained upon a fresh cupel until the remaining lead is totally absorbed by the cupel and the silver left behind in a pure state. By this means a much larger weight of the silver-lead alloy can be submitted to assay, and, for reasons hereafter to be explained, much more exact results are obtained than would be the case when the cupellation is conducted at one operation in the ordinary manner.

FIG. 128.



The apparatus used by the author for these operations are shown to a scale of one-half their real size in the woodcuts Fig. 128 (*a* to *d*).

In Fig. 128, *a* represents in section a small cylindrical mould of iron, seven-tenths of an inch in diameter, and about four-tenths high, in which is turned a cup-shaped nearly hemispherical depression two-tenths of an inch deep in centre, the inner surface of which is left rough, or marked with minute ridges and furrows for the purpose of enabling it to retain more firmly the bone-ash lining which is stamped into it by means of the polished bolt, also shown in the figure. This mould rests upon the stand *d*, having for this purpose a small central socket in its base, into which the central pivot of the stand enters. This socket is seen in the ground plan, *b*, of the base of the mould, which shows likewise three small grooves or slots made to enable a steady hold to be taken of it, when hot, by the forceps. The stand itself is composed of a small turned ivory or wood base, fixed into a short piece of strong glass tubing, which, from its non-conducting powers, serves as an excellent handle. In the centre of the base a slight iron rod rising above the level of the glass outer tube serves as a support for the cupel mould, into the socket in the base of which it enters.

Bone-ash is best prepared by burning bones which have previously been boiled several times, so as to extract all animal matter. The best bone-ash is made from the core-bone of the horns of cattle well boiled out and burned. The ash from this is more uniform than from the other bones, which have in general a very compact enamel-like exterior surface, whilst the interior is of a much softer nature.

Concentration of the Silver-lead.—A cupel is prepared by filling the above described cupel mould with bone-ash powder not finer than will pass through a sieve containing from forty to fifty holes in the linear inch, and should be well dried and kept in an air-tight bottle, and the whole pressed down with the bolt, using a few taps of the hammer. It is then heated strongly in the oxidising blowpipe flame, in order to drive off any hygroscopic moisture. The bone-ash surface of the cupel, after heating, should be smooth, and present no cracks; if the reverse, these may be removed by using the bolt again and reheating.* The silver-lead, beaten on the anvil into the form of a cube, is placed gently upon the surface of the bone-ash, and, directing a pretty strong oxidising flame on to its surface, it is fused, and quickly attains a bright metallic appearance, and commences to oxidise with a rapid rotatory movement.

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* These precautions are very important, as the slightest trace of moisture in the substance of the bone-ash would inevitably cause a spurting of the metal during the operation.

(Occasionally, when the assay is large, and much copper or nickel present, the globule may, under this operation, cover itself with a crust of lead oxide or solidify; in such cases direct the blue point of a strong flame steadily on to one spot on the surface of the lead globule, until it commences oxidising and rotating. In some cases where much nickel is present, an infusible scale, impeding or even preventing this action, may form, but will disappear on adding more lead—say from three to six grains, according to the thickness of this scale or crust.) When this occurs the cupel is slightly inclined from the lamp, and a fine blue point obtained by placing the blowpipe nozzle deeper into the flame, and the lamp is directed at about an angle of 30° on to the globule—not, however, so near as to touch it with the blue point, but only with the outer flame, so moderating it as to keep the assay at a gentle red heat, and not allowing the rotation to become too violent.

This oxidising fusion should be carried on at the lowest temperature sufficient to keep up the rotatory movement, and to prevent a crust of litharge accumulating upon the surface of the globule, but still sufficiently high to hinder the metallic globule from solidifying. Should this, however, happen, a stronger flame must be employed for a moment until the metal is again in rotation; such interruptions should, however, be avoided. The proper temperature can only be learned by practice. A too high temperature is still more injurious, causing the lead to volatilise, and, if rich in silver, carry some of that metal mechanically along with it. The litharge, also, instead of remaining on the cupel, would be absorbed by the bone-ash, and as the surface of the metallic globule is covered by a too thin coating of fused litharge, some silver may be absorbed along with the litharge. In this operation, in order to avoid loss of silver, the fused globule should be always kept in contact with the melted litharge.

By the above treatment, the air has free access to the assay, and the oxidation of the lead and associated foreign metals goes on rapidly. The surface of the melted globule, when poor in silver, shows a brilliant play of iridescent colours, which does not take place when very rich in silver. The litharge is driven to the edge of the globule, heating itself up and solidifying behind and around it. When the globule becomes so hemmed in by the litharge as to present too small a surface for oxidation, the cupel is moved so as to be more horizontal (having been previously kept in an inclined position), thus causing the lead globule to slide by its own weight on one side, and expose a fresh surface to the oxidising action. When the lead is pure, the litharge formed has a reddish-yellow colour, but if copper is present it is nearly black.

In concentrating silver-lead, it must be remembered that an alloy of lead and silver, if in the proportion of about 86 per cent. silver along with 14 per cent. lead, when cooled slowly in the litharge behaves in a manner analogous to the spitting of pure silver, throwing out a whitish-grey pulverulent excrescence rich in silver. For this reason, therefore, the concentration above described should be stopped when the globule is supposed to contain about six parts silver along with one part in weight of lead. In case, however, this limit should have been exceeded, it is advisable at once to push the concentration still further until the silver globule contains but very little lead. In practice with poor ores it is usual to concentrate the lead until the globule is reduced to the size of a small mustard-seed, or in rich ores to some two or three times that size. Upon arriving at this point, the cupel is withdrawn very gradually from the flame, so that the cooling shall take place as slowly as possible until the globule has solidified in its envelope of litharge. If cooled too quickly, the litharge, contracting suddenly, would throw out the globule, or even cause it to spirt; in such case it should be touched by the point of the blue flame so as to fuse it to a round globule, which is cooled slowly, as before described. The globule is now reserved for the next operation, for which purpose it is, when quite cold, extracted from the litharge surrounding it.

Cupellation.—The bone-ash required for this process should be of the best quality and in the most impalpable powder, prepared by elutriating finely-ground bone-ash, and drying the product before use.

The cupel, still hot from the last operation, is placed upon the anvil, and the crust of litharge, with its enclosed metallic bead, gently removed, leaving the hot coarse bone-ash beneath it in the mould; upon this a small quantity of the elutriated bone-ash is placed, so as to fill up the cavity, and the whole, whilst hot, stamped down by the bolt, previously slightly warmed, with a few taps of the hammer. The cupel thus formed is heated strongly in the oxidising flame, which should leave the surface perfectly smooth, and free from any fissures or scales; if such appear, the bolt must again be used, and the cupel reheated. In this process it is very important that the cupel should possess as smooth a surface as possible, whilst at the same time the substance of the cupel beneath should not be too compact, so as thereby to permit the litharge to filter through and be readily absorbed, leaving the silver bead upon the smooth upper surface.

The bead of silver-lead obtained from the last operation is taken out of the litharge in which it is embedded, and, after removing any trace of adherent bone-ash or litharge, is slightly flattened to prevent its rolling about upon the surface of the cupel.

It is now put into the cupel prepared as before described, placing it on the side furthest from the lamp and a little above the centre of the cupel, which is now inclined slightly towards the lamp, and is heated by the oxidising flame directed downwards upon it, this causing the globule, when fused and oxidising, to move of itself into the centre of the cupel. The cupel is now brought into a horizontal position, and the flame, directed on to it at an angle of about forty-five degrees, is made to play upon the bone-ash surface immediately surrounding the globule, without, however, touching it, so as to keep this part of the cupel at a red heat sufficiently strong to insure the globule being in constant oxidising fusion, and at the same time to cause the perfect absorption of the litharge, so as to prevent any scales of litharge forming upon the surface of the cupel under the globule, which would impede the oxidation, as well as prevent the silver bead being easily detached at the conclusion of the operation. Should the heat at any time be too low and the globule solidify, it must be touched for an instant with the point of the flame and proceeded with as before. Should (in consequence of the bone-ash not having been sufficiently heated to absorb the litharge perfectly) a little litharge adhere pertinaciously to the globule, or a particle of the bone-ash cupel attach itself, the cupel should be slightly inclined, so as to allow the globule to move by its own weight on to another and clean part of the cupel, leaving the litharge or bone-ash behind it; but, if not sufficiently heavy to do so, a small piece of pure lead may be fused to it in order to increase its weight, and so allow of the same proceeding being adopted.

By slightly inclining the cupel-stand, and moving it so as to present in turn all parts of the surface surrounding the globule to the action of the flame, the cupellation proceeds rapidly. If, however, the assay contains very little silver, it will be found necessary to move the globule from one spot to another on the cupel, in order to present a fresh surface for absorbing the litharge formed; this is done by simply inclining the cupel-stand, remembering that the bone-ash surrounding the globule must always be kept at a red heat, without ever touching the globule itself by the flame.

In assays rich in silver a play of iridescent colours appears some seconds before the 'brightening,' which disappears the moment the silver becomes pure; as soon as this is observed the cupel should be moved in a circular manner, so that the globule is nearly touched all round by the point of the blue flame, and this is continued until the surface of the melted silver is seen to be quite free from any litharge, upon which it is very gradually withdrawn from the flame so as to cool the assay by degrees very slowly, in order to prevent 'spitting.'

When the silver-lead is very poor, this play of colours is not apparent, and as soon as the rotatory movement of the globule ceases, the heat must be increased for an instant, in order to remove the last thin but pertinacious film or scale of litharge, and subsequently the assay is cooled gradually; when cold it should, whilst still upon the cupel, be examined by a lens, to see whether the bead possesses a pure silver colour, as, if not, it must be reheated.

Frequently, when the 'brightening' takes place, the silver globule is found to spread out, and, after cooling, although of a white colour, is found to appear somewhat less spherical or more flattened in shape than a corresponding globule of pure silver would be. This arises from the presence of copper still remaining in the silver, and in such cases a small piece of pure lead (about from one-half to one and a half grain in weight, according to size of assay) should be fused on the cupel along with the silver, and the cupellation of the whole conducted as before on another part of the cupel, when the silver globule will be obtained pure, and nearly spherical in shape. Sometimes the silver globule in 'brightening' may still remain covered with a thin film of litharge, although otherwise pure; this arises from too little heat having been employed in the last stage of the operation, and consequently the bead should be re-heated in a strong oxidising flame until this litharge is absorbed, and the globule, after slow cooling, appears pure.

If the instructions here given be strictly attended to, it will be found after some practice that very accurate results may be obtained in the blowpipe assay for silver, and that no difficulty will be found in detecting the presence and determining the amount of silver present, even when in as small a quantity as half an ounce to the ton. When substances containing very little silver or less than that amount are examined, several assays should be made, and the silver-lead obtained concentrated separately, after which the various globules should be united and cupelled together in one operation.

It is hardly necessary to remark that the lead employed in assaying should be free from silver, or if not, its actual contents in silver should be determined, and subtracted from the amount found in the assay.

Assay lead containing less than one quarter of an ounce to the ton of lead can readily be obtained, or can be made by precipitating a solution of acetate of lead by metallic zinc, rejecting the first portion of lead thrown down. In all cases the lead should be fused and granulated finely—the granulated lead for use in these assays being previously passed through a sieve containing forty holes to the linear inch. It is also useful to have some lead in the form of wire, as being very convenient for adding in small portions to assays when on the cupel.

Determination of the Weight of the Silver Globule obtained on Cupellation.—As the amount of lead which can, by the method before described, be conveniently cupelled before the blowpipe is necessarily limited, the silver globule which remains upon the bone-ash surface of the cupel at the end of the operation is, when substances poor in silver have been examined, frequently so very minute that its weight could not be determined with correctness by the most delicate balances in general use.

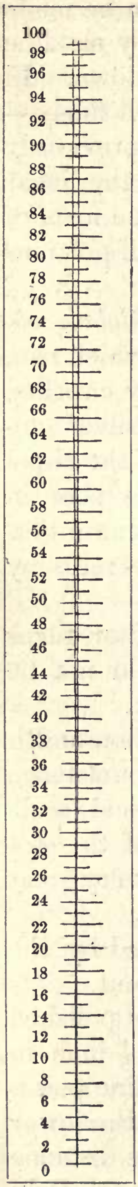
The blowpipe balance employed by the author turns readily with one-thousandth of a grain, but could not be used for determining weights below that amount.

Globules of silver of far less weight than one-thousandth are distinctly visible to the naked eye—a circumstance which induced Harkort to invent a volumetrical scale based upon the measurement of the diameters of the globules, which scale in practice has been found of very great utility in the blowpipe assay of silver.

The scale for this purpose which is employed by the author is shown in full size in the annexed woodcut.

This figure represents a small strip of highly polished ivory about $6\frac{1}{2}$ inches long, $\frac{2}{3}$ inch broad, and $\frac{1}{8}$ inch in thickness, on which are drawn, by an extremely fine point, two very fine and distinct lines emanating from the lower or zero point, and diverging upwards until, at the distance of exactly six English standard inches, they are precisely four-hundredth parts of an inch apart. This distance (six inches) is, as shown in woodcut, divided into 100 equal parts by cross lines numbered in accordance from zero upwards. It is now evident if a small globule of silver be placed in the space between these two lines, using a magnifying glass to assist the eye in moving it up or down until the diameter of the globule is exactly contained within the lines themselves, that we have at once a means of estimating the diameter of the globule itself, and therefrom are enabled to calculate its weight.

Fig. 129.



As the silver globules which cool upon the surface of the bone-ash cupel are not true spheres, but are considerably flattened on the lower surface, where they touch and rest upon the cupel, it follows that the weight of globules corresponding in diameter to the extent of divergence at the different degrees of the scale cannot be calculated directly from their diameters as spheres, but require to have their actual weight experimentally determined in the same manner as employed by Plattner.

The table here appended has been calculated by the author, and in one column shows the diameter in English inches corresponding to each number or degree of the scale itself, and in the two next columns the respective weights of the flattened spheres which correspond to each degree or diameter; for convenience these weights are given in the different columns in decimals, both of English grains and of French grammes.

These weights are calculated from the following data, found as the average result of several very careful and closely approximating assays, which showed that globules of silver exactly corresponding to No. 95 on this scale, or 0·038 inch in diameter, possessed a weight of 0·0475573 grains or 0·003079 grammes. From this the

No. on scale	Greatest diameter in inches	Weight of globule in grains	Weight of globule in grammes
1	0·0004	0·00000005	0·000000003
2	0·0008	0·00000044	0·000000028
3	0·0012	0·00000149	0·000000096
4	0·0016	0·00000355	0·000000229
5	0·0020	0·0000069	0·00000044
6	0·0024	0·0000119	0·00000077
7	0·0028	0·0000190	0·00000120
8	0·0032	0·0000284	0·00000184
9	0·0036	0·0000403	0·00000262
10	0·0040	0·0000554	0·00000359
11	0·0044	0·0000736	0·00000478
12	0·0048	0·0000958	0·00000620
13	0·0052	0·0001218	0·00000789
14	0·0056	0·0001522	0·00000985
15	0·0060	0·0001872	0·00001203
16	0·0064	0·0002272	0·00001471
17	0·0068	0·0002725	0·00001764
18	0·0072	0·0003234	0·00002094
19	0·0076	0·0003804	0·00002463
20	0·0080	0·0004437	0·00002872
21	0·0084	0·0005137	0·00003327
22	0·0088	0·0005906	0·00003823
23	0·0092	0·0006748	0·00004367
24	0·0096	0·0007668	0·00004964
25	0·0100	0·0008667	0·00005611
26	0·0104	0·0009749	0·00006311
27	0·0108	0·0010918	0·00007068
28	0·0112	0·0012176	0·00007883
29	0·0116	0·0013528	0·00008758
30	0·0120	0·0014976	0·00009696
31	0·0124	0·0016524	0·00010698
32	0·0128	0·0018176	0·00011677
33	0·0132	0·0019934	0·00012817
34	0·0136	0·0021801	0·00014114
35	0·0140	0·0023786	0·00015397
36	0·0144	0·0025879	0·00016755
37	0·0148	0·0028097	0·00018190
38	0·0152	0·0030437	0·00019705
39	0·0156	0·0032903	0·00021302
40	0·0160	0·0035550	0·00022983
41	0·0164	0·0038230	0·00024751
42	0·0168	0·0041096	0·00026606
43	0·0172	0·0044111	0·00028553
44	0·0176	0·0047250	0·00030589
45	0·0180	0·0050546	0·00032725
46	0·0184	0·0053991	0·00034955
47	0·0188	0·0057590	0·00037285
48	0·0192	0·0061344	0·00039716
49	0·0196	0·0065258	0·00042250
50	0·0200	0·0069335	0·00044890
51	0·0204	0·0073581	0·00047638
52	0·0208	0·0077799	0·00050495
53	0·0212	0·0082580	0·00053464
54	0·0216	0·00873438	0·00056549
55	0·0220	0·00922854	0·00059748
56	0·0224	0·0097412	0·00063067

No. on scale	Greatest diameter in inches	Weight of globule in grains	Weight of globule in grammes
57	0·0228	0·0102725	0·00066506
58	0·0232	0·0108228	0·00070021
59	0·0236	0·0113922	0·00073753
60	0·0240	0·0119815	0·00077570
61	0·0244	0·0125901	0·00081513
62	0·0248	0·0132119	0·00085588
63	0·0252	0·0138901	0·00089797
64	0·0256	0·0145440	0·00094141
65	0·0260	0·0152311	0·00098623
66	0·0264	0·0159472	0·00103245
67	0·0268	0·0166828	0·00108010
68	0·0272	0·0174414	0·00112918
69	0·0276	0·0182220	0·00117974
70	0·0280	0·0190256	0·00123177
71	0·0284	0·0198529	0·00128535
72	0·0288	0·0207035	0·00134041
73	0·0292	0·0215782	0·00139704
74	0·0296	0·0224469	0·00145525
75	0·0300	0·0234010	0·00151504
76	0·0304	0·0243496	0·00157645
77	0·0308	0·0253224	0·00163950
78	0·0312	0·0263228	0·00170422
79	0·0316	0·0273484	0·00177060
80	0·0320	0·0284000	0·00183869
81	0·0324	0·0294789	0·00190852
82	0·0328	0·0305838	0·00198008
83	0·0332	0·0317162	0·00205340
84	0·0336	0·0328768	0·00212851
85	0·0340	0·0340649	0·00220549
86	0·0344	0·0349739	0·00228400
87	0·0348	0·0364422	0·00235938
88	0·0352	0·0378008	0·00244730
89	0·0356	0·0390138	0·00253168
90	0·0360	0·0404368	0·00261797
91	0·0364	0·0417943	0·00270790
92	0·0368	0·0431930	0·00279642
93	0·0372	0·0446162	0·00288860
94	0·0376	0·0460718	0·00298279
95	0·0380	0·0475573	0·00307900
96	0·0384	0·0465239	0·00317728
97	0·0388	0·0506249	0·00327759
98	0·0392	0·0522069	0·00338020
99	0·0396	0·0538215	0·00348452
100	0·0400	0·0554688	0·00359138

respective weights of all the other numbers or degrees on this scale were calculated, on the principle that solids were to one another in the ratio of the cubes of their diameters. This mode of calculation is not, however, absolutely correct in principle, for the amount of flattening of the under surface of the globule diminishes in reality with the decreasing volume of the globule. In actual practice, however, this difference may be assumed to be so small that it may be neglected without injury to the correctness of the results.

The smaller the diameter of the globule, the less will be the difference or variation in weight in descending the degrees of this scale, since the globules themselves vary in weight with the cubes of their diameters; for this reason, also, all such globules as come within the scope of the balance employed should be weighed in preference to being measured, and this scale should be regarded as more specially applicable to the smaller globules beyond the reach of the balance.

Cupellation Loss.—This term is applied to indicate a minute loss of silver, unavoidably sustained in the process of cupellation, which arises from a small portion of that metal being mechanically carried along with the litharge into the body of the cupel. The amount of this loss increases with the quantity of lead present in the assay (whether contained originally in the assay or added subsequently for the purpose of slagging off the copper, &c.); it is relatively greater as the silver globule is larger, but represents a larger percentage of the silver actually contained in the assay, in proportion as the silver globule obtained diminishes in size. It has, however, been experimentally proved that, in assays of like richness in silver, this loss remains constant when the same temperature has been employed, and similar weights of lead have been oxidised in the operation.

In the blowpipe assay this loss is not confined to the ultimate operation of cupellation, but occurs, though in a less degree, in the concentration of the silver-lead, and in the previous scorification of the assay, had such operation preceded the concentration. The total loss in the blowpipe assay is found, however, to be less than in the ordinary muffle assay, since in the latter case the whole of the oxidised lead is directly absorbed by the cupel.

In mercantile assays of ore it is not customary to pay attention to the cupellation loss, and the results are usually stated in the weight of silver actually obtained. Where, however, great accuracy is required, especially when the substances are very rich in silver, the cupellation loss is added to the weight of the silver globule obtained, in order to arrive at the true percentage.

The amount to be added for this purpose is shown in the annexed table, which is slightly modified from Plattner's:—

Actual percentage of silver found by assay	Cupellation loss, or percentage of silver to be added to the actual percentage found by assay in order to show the true percentage of silver contained in same. The entire amount of lead in or added to the assay being the following multiples of the original weight of assay:—									
	1	2	3	4	5	6	8	11	13	16
99·75 99·5	0·25	0·32	0·39	0·45	0·50					
90 . .	0·22	0·29	0·36	0·42	0·47	0·69	0·83			
80 . .	0·20	0·26	0·33	0·39	0·44	0·64	0·75			
70 . .	0·18	0·23	0·29	0·35	0·40	0·58	0·68	0·82		
60 . .	0·16	0·20	0·26	0·30	0·36	0·52	0·61	0·74		
50 . .	0·14	0·17	0·23	0·26	0·32	0·46	0·54	0·65		
40 . .	0·12	0·15	0·20	0·22	0·27	0·39	0·46	0·55	0·62	
35 . .	0·11	0·13	0·18	0·18	0·25	0·36	0·42	0·50	0·57	
30 . .	0·10	0·12	0·16	0·16	0·22	0·32	0·38	0·45	0·51	
25 . .	0·09	0·10	0·14	0·14	0·20	0·29	0·34	0·40	0·45	
20 . .	0·08	0·09	0·12	0·12	0·17	0·25	0·29	0·35	0·39	0·45
15 . .	0·07	0·08	0·10	0·11	0·15	0·20	0·23	0·28	0·32	0·37
12 . .	0·06	0·07	0·09	0·10	0·13	0·17	0·19	0·23	0·26	0·22
10 . .	0·05	0·06	0·08	0·09	0·11	0·15	0·17	0·20	0·23	0·27
9 . .	0·04	0·05	0·07	0·08	0·10	0·14	0·16	0·18	0·21	0·25
8 . .	0·03	0·04	0·06	0·07	0·09	0·13	0·15	0·16	0·18	0·22
7 . .	0·02	0·03	0·05	0·06	0·08	0·12	0·13	0·14	0·16	0·20
6 . .	0·01	0·02	0·04	0·05	0·07	0·10	0·11	0·12	0·14	0·17
5 . .		0·01	0·03	0·04	0·06	0·09	0·10	0·11	0·12	0·14
4 . .			0·02	0·03	0·05	0·07	0·08	0·09	0·10	0·11
3 . .			0·01	0·02	0·04	0·05	0·06	0·07	0·08	0·09
2 . .				0·01	0·03	0·04	0·04	0·05	0·06	0·07
1 . .					0·01	0·03	0·03	0·04	0·04	0·05

The use of this table is best explained by an example, as the following:—An assay to which there had been added, in all, five times its weight of assay lead, gave a globule of silver equivalent to six per cent. Upon referring to the table it will be seen that the cupellation loss for this would be 0·07; consequently the true percentage of silver contained in the assay would be 6·07. This table is only extended to whole numbers, but fractional parts can easily be calculated from the same.

When the globules of silver are so minute that they cannot be weighed, but must be measured upon the scale, the cupellation loss should not be added, since, as a rule, it would be less than the difference which might arise from errors of observation likely to occur when measuring their diameters upon the scale.

In the case of beginners, it will be found that the cupellation is usually carried on at too high a temperature, and that thereby a greater loss is occasioned than would be accounted for by the above table. After some trials the necessary experience will be acquired in keeping up the proper temperature at which this operation should be effected.

It now becomes necessary to consider in detail the processes requisite for extracting the silver contents (in combination with lead) from the various metallic alloys of silver which are met with in nature or produced in the arts.

In considering these, the following classification of the substances will be found convenient:—

METALLIC ALLOYS.

A. Capable of direct Cupellation.

- *a.* Consisting chiefly of lead or bismuth; silver-lead and argentiferous bismuth, native bismuthic silver.
- *b.* Consisting chiefly of silver: native silver, bar silver, test silver, precipitated silver, retorted silver amalgam, standard silver, alloys of silver with gold and copper.
- *c.* Consisting chiefly of copper: native copper, copper ingot, sheet or wire, cement copper, copper coins, copper-nickel alloys.

B. Incapable of direct Cupellation.

- *a.* Containing much copper or nickel, with more or less sulphur, arsenic, zinc, &c.; unrefined or black copper, brass, German silver.
- *b.* Containing tin; argentiferous tin, bronze, bell-metal, gun-metal, bronze coinage.
- *c.* Containing antimony, tellurium, or zinc.
- *d.* Containing mercury: amalgams.
- *e.* Containing much iron: argentiferous steel, bears from smelting furnaces.

A. Metallic Alloys capable of direct Cupellation.

a. Consisting chiefly of Lead or Bismuth.—In determining the silver contained in these alloys, it is only requisite to place a clean piece of the same, weighing about from one to ten grains according to its probable richness in silver, upon a cupel of coarse bone-ash, and proceed by concentration and cupellation exactly as has been already described under these heads.

Should the substance be not altogether metallic, or not free from adherent slag, earthy matter, or other extraneous matter, it should previously be fused on charcoal with a little borax in the reducing blowpipe flame, and the clean metallic globule then removed from the charcoal, and treated as before. In order to remove the globule from the adherent borax-glass, it may be allowed to cool, and then detached; or, after a little practice, it will be found easy, by a quick movement of the charcoal, to cause the globule, still melted, to detach itself completely, and drop on the anvil in the form of a single somewhat flattened globule, without suffering any loss of lead adhering to the charcoal.

In the case of argentiferous bismuth alloys the process is carried on in all respects the same as if silver-lead were being treated. As, however, the bismuth globule is very brittle, care must be taken when separating the concentrated globule from the litharge, as, if not carefully done, a loss may easily be sustained from a portion of the globule remaining behind adherent to the litharge. It is better, therefore, to remove the litharge by degrees from the globule with the aid of the forceps.

Argentiferous bismuth, free from lead, when cupelled alone, invariably leaves a globule of silver, having a dull frosted surface. If, however, at the end of the operation a small quantity of lead ($\frac{1}{4}$ to $\frac{1}{2}$ a grain) be added, and fused along with it, the silver globule then obtained will be perfectly bright and free from all bismuth.

In the case of native bismuthic silver it is advisable to fuse the previously weighed mineral with a little lead and borax-glass on charcoal in the reducing flame, so as to free it from any adherent earthy matter, and then proceed by concentration and cupellation, as before described.

b. Consisting chiefly of Silver: native silver, bar, test, and precipitated silver, retorted silver amalgam, standard silver, silver coin and other alloys of silver with gold and copper.—These alloys may be at once fused with lead on the cupel itself, and the operation finished as before described. In general, however, it is better to fuse the weighed assay previously with the requisite amount of pure lead and a little borax-glass, say from a quarter to half the weight of assay, in the reducing flame at a low heat on charcoal until the globule commences to rotate. This ensures having a perfectly clean button of silver-lead, which is then cupelled in the ordinary manner.

In most cases the quantity of lead to be added need not exceed that of the weight of the alloy, but when several percentages of copper are present in the assay, as in the case of many coins, &c., the lead should be increased to some three, or even five, times the weight of the assay in proportion to the amount of copper actually contained in the substance under examination, and which will be treated of more at length under the head of copper-silver alloys.

When no more lead has been added to the assay than its own weight, the cupellation may be concluded in one operation by inclining the stand, and so moving the globule to a clean part of the cupel; but when more copper is present, it is preferable to concentrate first and cupel subsequently, in order thereby to reduce the cupellation loss to its minimum.

In the concentration as much copper as possible should be slagged off with the lead, which is effected by inclining the cupel somewhat more than usual, so that its surface may be less covered up with the litharge and exposed as much as possible to oxidation, by which means the litharge, as it forms, is enabled to carry off more of the copper contained in the silver-lead.

Should the silver globule after cupellation show indications of still containing copper, as before noticed, when treating of cupellation, a small quantity of lead must be fused along with it, and the cupellation finished as usual.

As at the present time no means are known by which silver can be separated from gold by the use of the blowpipe in all cases of alloys containing gold, this metal remains to the last along with the silver, and the result in such cases always indicates the combined weight of both these metals contained in the alloy under examination. The wet assay must be resorted to for effecting their separation.

c. Containing chiefly Copper: native copper, ingot, wire or sheet copper, cement copper, copper coins, copper-nickel alloys.—Under the most favourable conditions in cupellation, the amount of lead requisite, when converted into litharge, to slag off one part of copper along with it as oxide, amounts to between seventeen and eighteen times its weight. In the blowpipe assay it is usual to add to any cupriferous alloy an amount of pure lead equal to twenty times the amount of copper contained in the alloy, in order to ensure the whole of the copper being separated in the litharge. In the case of nickel the amount of lead required is somewhat less than with copper, but in practice the same amount of lead may be employed.

When the copper is quite clean the requisite amount of lead may be added to it in a single piece on the cupel, fused and cupelled as usual, after previous concentration of the silver-lead to a small-sized globule.

It is generally found, however, that traces of iron, slag, gangue, or other foreign matter, are present; and, consequently, it is usually advisable to fuse the assay along with the requisite amount of lead, and about one-half its own weight of borax-glass in the reducing flame, until the whole of the substance is seen to have perfectly combined or alloyed with the lead, and the globule has entered into brisk rotation, whilst at the same time no detached metallic globules are seen in the borax-glass.

The concentration of the silver-lead and cupellation are then conducted as usual, taking care when concentrating to incline the cupel-stand so as to expose as much as possible of the metallic surface of the melted globule to the oxidising action of the air, with a view of enabling the litharge whilst forming to carry off as much copper along with it as possible.

Should the silver globule obtained after cupellation spread out, or appear to the eye more flattened than usual with globules of pure silver, it indicates that some copper still remains, and a small piece of assay lead (½ to 1 grain weight) should be placed alongside it whilst still on the cupel, fused together, and the cupellation finished on a clean part of the same cupel as usual.

Precipitated or cement copper, especially that which is in the crude state, and has not been melted and run into ingots, is often very impure, containing so much iron, lead, arsenic, earthy matter, &c., as not to admit of direct cupellation, and in such case should be treated as pertaining to class B. *a.*

B. METALLIC ALLOYS INCAPABLE OF DIRECT CUPELLATION.

a. Containing much Copper or Nickel, with frequently some little sulphur, arsenic, zinc, iron, cobalt, &c., as unrefined or black copper, brass, German silver, &c.—As the presence of these extraneous matters would interfere with the cupellation, either by causing a loss of silver-lead projected from the cupel upon the evolution of the volatile substances present, or by forming oxides which could not be absorbed by the cupel, it is necessary to eliminate such substances by a scorification with borax on charcoal, previous to concentration or cupellation.

In the case of unrefined and black copper, the portion used in the examination is placed in the scoop with twenty times its weight of assay lead, and its own weight of powdered borax-glass, mixed with the spatula, and transferred to a soda-paper cornet. It is then fused on charcoal in the reducing flame, which should be constant and uninterrupted, until all particles have completely united, and a brisk rotation sets in, which is kept up for a short time, when the silver-lead globule, which should appear bright on the surface after cooling, is concentrated and cupelled precisely as is directed under A. *c.* By this preliminary scorification the sulphur, arsenic, and zinc are volatilised, and any lead, cobalt, or iron slagged off into the borax-glass.

In the assay of brass and German silver, the quantity employed is fluxed with its own weight of borax-glass, but only requires ten times its weight of assay-lead. The operation is commenced as before, but the globule is kept somewhat longer in rotation (always keeping the flame directed only on to the borax glass), so as to allow the zinc present to be completely volatilised, which is evident when the surface of the silver-lead becomes bright, on which the heat is increased for a few moments to expel the last traces of that metal, and the silver lead thus obtained is concentrated and cupelled as before.

The silver globule obtained from the cupellation of substances rich in copper generally requires the addition of a small quantity of lead and re-cupellation (as before described), in order to insure its freedom from copper.

b. Containing Tin: argentiferous tin, bronze, bell and gun metal, bronze coinage, &c.—Alloys of silver with other metals containing tin do not admit of being cupelled, since the oxide of tin formed by the oxidation of that metal is not absorbed by the bone ash of the cupel along with the litharge; it consequently remains upon the surface of the cupel, and if present in any quantity interferes with the operation. As tin is not volatile when heated on charcoal either in the oxidising or reducing blowpipe flame, it cannot be so dissipated, and, in consequence, the entire amount of tin contained in any alloy under examination must be removed by oxidation or scorification from the silver-lead, previous to its being submitted to cupellation.

For this purpose, 1 part of the stanniferous alloy is fluxed with from 5 to 15 parts of granulated assay lead (according to the amount of copper suspected to be present in the alloy), 0·5 part anhydrous sodium carbonate, and 0·5 part pulverised borax-glass, made up as usual in a soda-paper cornet, and the whole at first gently heated in the reducing flame until the soda-paper is charred and the alloy has afterwards united with the lead to form a single globule, whilst the borax and soda have combined as a glass or slag in which the soda prevents the easily oxidisable tin becoming oxidised to any extent before a perfect alloy has been formed with the lead, which then contains the whole of the silver.

As soon as this is effected, the blowpipe flame is altered to an oxidising one, and the metallic globule is kept at the point of the blue flame, which should touch it so as to cause the tin to become oxidised and be at once taken up by the glass surrounding it.

Should, however, it be seen that minute globules of metallic tin made their appearance on the outer edge of the slag or glass,* the operation must be at once discontinued, and the assay allowed to cool; after cooling the metallic globule is detached from the slag surrounding it, and being placed in a cavity on charcoal, is fused in the reducing flame along with a small piece of borax-glass and afterwards treated with the oxidising flame exactly as before (and if necessary, which is seldom the case, unless when treating argentiferous block-tin, this operation may again require to be repeated), until it is seen that the surface of the metallic silver-lead globule does not any longer become covered with a crust or scales of tin oxide, but presents a pure and bright metallic surface.

The silver-lead globule is now quite free from tin, and can be cupelled and the amount of silver determined as usual.

c. Metallic alloys containing much antimony, tellurium, or zinc: antimonial silver and argentiferous antimony, telluric silver, and argentiferous zinc.—Alloys of antimony with silver when treated on charcoal in the oxidising flame give off all their antimony, leaving the silver behind as a metallic globule having a frosted external appearance;

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* This occurs when the flux has become so saturated with tin oxide that it cannot take up any more.

telluric silver, on the contrary, however, when treated in a similar manner, only evolves a part of its tellurium, and even after cupellation with lead a small amount of tellurium generally remains behind alloyed with the silver.

All these compounds may be assayed as follows :—

One part of the alloy is placed in a soda-paper cornet along with 5 parts of granulated assay lead, and 0·5 part of pulverised borax-glass, and fused in the reducing flame until the globule and slag are well developed; the oxidising flame is now directed on to the globule, causing the whole of the zinc, along with most of the antimony and part of the tellurium, to volatilise before the lead commences oxidising. The last traces of antimony are removed with some difficulty, during which operation some portion of the lead becomes oxidised. On cooling, the globule is separated from the slag and concentrated upon a coarse bone-ash cupel as usual, and if no tellurium were present in the concentrated silver-lead, this may now be cupelled as usual.

If tellurium is present—as is seen by the concentrated globule of silver-lead possessing a dark-coloured exterior—it must be remelted with 5 parts of assay lead and again concentrated; and these operations, if necessary, must be repeated until the surface of the concentrated globule is found to be clean and bright, as is usual with pure silver-lead, when it may be cupelled fine and the silver globule weighed.

It sometimes happens, even after all these precautions have been taken, that the silver globule after cupellation shows a crystalline, greyish-white, frosted appearance, from its still containing tellurium; in such cases its own weight of assay lead (in one piece) should be placed beside it on the cupel, melted together, and the globule again cupelled fine on another part of the surface of the same cupel. In assaying substances very rich in tellurium the results obtained are, however, not very satisfactory, and may be as much as one or two per cent. too low, even after employing all precautions.

d. Compounds of Silver with Mercury: arquerite, native and artificial amalgams and argentiferous mercury.—The assay of these compounds is very simple. A weighed quantity of the liquid or solid amalgam is placed in a small bulb-tube, and heated over the lamp very gradually in order to avoid spirting and to allow the mercury to volatilise quietly;* the heat is increased by degrees as long as any mercury is driven off, and the residue is heated for some time at a red heat in order to drive off as much mercury as possible without fusing the glass or causing the residual silver to adhere to it. The mercury expelled condenses itself above the bulb on to the upper part of the tube, and by gently tapping will collect in globules, which by carefully turning the tube, unite and can be poured out of the tube; after which the silver, left behind as a porous mass, may be removed from the tube, and after being fluxed with an equal weight of granulated assay lead and half its weight of borax-glass, must be fused on charcoal in the reducing flame, and the button, on cooling, cupelled as usual. Should, however, much copper have been present in the amalgam, a proportionately larger amount of assay lead is required to be added.

When the argentiferous residue is extremely small, as is often the case when assaying argentiferous mercury, this may adhere firmly to the glass of the tube. On such occasions this part of the tube must be cut off with the adherent residue, and the whole fused in a strong reducing flame along with its own weight of granulated assay lead, and with half its weight of anhydrous sodium carbonate. Upon cooling, the globule of silver-lead thus obtained is cupelled as usual.

e. Compounds chiefly consisting of Iron: argentiferous-steel; cast-iron; bears from smelting furnaces.—Compounds consisting principally of iron with a small percentage of silver, although occasionally produced in the arts intentionally, as, for example, the so-called silver-steel, are com-

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* In the case of solid amalgams, which often spirt very violently, this may be obviated by wrapping the assay in a small piece of tissue paper, and heating it in a blowpipe crucible, when all the mercury is given off quietly, leaving the silver behind.

monly found on the blowing-out of furnaces used in the smelting of silver and copper ores, and are frequently rich in silver, as is the case with the bears from the silver furnaces at Kongsberg in Norway. An alloy of iron with silver is occasionally also found appearing in small quantities on the surface of melted silver in the process of casting, and in some cases at least this may be due to the action of the melted silver on the iron rods used for stirring up the molten metal.

As iron cannot be made to alloy itself with lead before the blowpipe, it becomes necessary to extract the silver by a more indirect process than is used in the case of other alloys containing that metal. In order to remove the iron the alloy must first be converted into iron and silver sulphide, and to effect this the iron or steel must be reduced to powder, or fragments none greater than about a quarter of a grain in weight; for which purpose steel when hardened may require to be softened previously.

One part of the finely-divided iron or steel is now mixed with 0·75 part sulphur, eight parts granulated assay lead, and one part pulverised borax-glass: the mixture after being placed in a soda-paper cornet is carefully fused in a cavity on charcoal in the reducing flame, until the whole appears as a fluid globule containing both the lead and iron in combination with the sulphur. Without removing either this globule or the glass surrounding it from the charcoal, an amount of borax-glass in one or more fragments (in all about equal in weight to the original amount of iron employed), is now added (in order to combine with and slag off the whole of the iron), and fused along with the former globule, after which the whole is submitted to a strong oxidising flame until the impure lead globule shows itself protruding from the slag.

The charcoal is then inclined, so that the lead is alone subjected to the action of the outer flame, in order to volatilise the sulphur, and at the same time oxidise the iron which goes into the slag; this operation is continued until the globule of lead appears with a bright metallic surface; should it on cooling, however, be found to possess a black colour, and to be brittle, it must be still further oxidised as before described.

The silver-lead thus obtained will now be found to contain all the silver, and at the same time to be free from both iron and sulphur, and can be cupelled as usual.

No notice is here taken of alloys of silver and gold, since these metals cannot be separated before the blowpipe by any process yet known; and in all cases where gold may be present in an alloy, treated as here directed for obtaining its contents in silver, the gold also will be found to follow along with the silver, and must be parted from that metal by the wet method, in order to enable the true amount of silver present in the substance to be ascertained.

Alloys of Silver and Copper.—A quantity of from 1 to 2 grms. is placed in a small flask or beaker, treated with a sufficient quantity of pure nitric acid of a moderate strength, covered with a watch-glass and digested at a gentle heat till totally dissolved. The solution is then diluted with water, and the silver precipitated with hydrochloric acid, which is added drop by drop as long as anything is thrown down. It is then allowed to digest at a very gentle heat till the supernatant liquid is clear. The liquid is then poured upon a dried and counterpoised filter; the silver chloride is stirred up with a little water, and brought upon the filter, the glass being perfectly rinsed out by aid of the washing-bottle. A few drops of nitric acid may be usefully added to the rinsing-water. The washing is afterwards continued with pure water till the droppings have no longer an acid reaction. The filter with its contents is dried, and from its weight that of the silver is calculated.

CHAPTER XVII.

THE ASSAY OF GOLD.

FOR the purposes of assay, all substances containing gold may be divided into two classes, as in the case of silver.

The *First Class* comprises ores containing gold in a mineralised form.

The *Second Class* comprises all alloys of gold, native or artificial.

CLASS I.—*Minerals.*

Graphic Tellurium, $(AuAg)Te_3$, containing 30 per cent. of gold, and 10 per cent. of silver.

Folliated Tellurium, $(Pb,Au,Ag)_2(Te,Sb,S)_3$ containing about 9 per cent. of gold.

CLASS II.—*Alloys of Gold.*

Native Gold, AuAg, containing 65-99 per cent. of gold.

Palladium Gold, AuPd, containing about 86 per cent. of gold.

Rhodium Gold, AuRh, containing 59-66 per cent. of gold.

Gold Amalgam, $(Au,Ag)_2Hg_5$, containing 38 per cent. of gold.

Artificial Alloys, Gold coin, jewellery, &c.

Of the foregoing list, native gold alone occurs in nature in sufficient abundance to acquire any great commercial value. It is commonly found in a quartzose gangue, and nearly always associated with one, or more, of the following minerals: iron and copper pyrites, mispickel or arsenical pyrites, blende, galena, many antimonial minerals, and nearly all the primitive rocks. All auriferous slags, amalgamation residues and tailings, belong to this class.

If silver or platinum are associated with the gold in the mineral subjected to assay, it will be found combined with the gold obtained by cupellation; and all gold so obtained must be submitted to the 'parting process,' which see further on.

When gold is associated in quantity with quartz, its percentage can be approximatively ascertained in the same manner as that of pure tin-stone when mixed with quartz (see page 486). If possible, a fragment of the gold must be detached from the quartz, and its specific gravity taken: if this be not possible, and the gold is nearly fine, the number 19 may be adopted. It is better, however, to determine experimentally the specific gravity of both quartz and gold.

Native Gold and Aurides of Silver (*Native*) are found in variously contorted and branched filaments, in scales, in plates, in small irregular masses, in the crevices or on the surface of common ferruginous and other quartz.

The author has received two specimens of gold, one from Wales, and the other from the Britannia Mine, Devon; and found both to be absolutely fine gold.

Artificial Alloys of Gold.—The only one of these alloys which will be specially noticed here, is the standard gold of this realm. It is composed of 22 parts of fine gold and 2 parts of alloy, constituting 22-carat or standard gold.

ASSAY OF GOLD ORES.*

The assay of gold ores embrace the following steps:—

1. Preparation of the sample. 2. Collection of the gold in a button of metallic lead. 3. Cupellation of the

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* For some portions of the following method of assaying gold ores, the Editor is indebted to Mr. T. M. Blossom, who has had great experience in the laboratory of the School of Mines, Columbia College, U.S.A. (See 'Chemical News,' Nos. 607, 609, 628, 635, 636.)

lead button, by which the lead is oxidised and absorbed by the cupel, leaving behind a bead of the gold and silver. 4. Weighing the bead. 5. Inquartation, parting, and cupellation of the gold residue. 6. Weighing the gold bead.

1. *Preparation of the Sample.*—It is essential, in the first place, to obtain a fair average sample of the ore, otherwise the results of the assay may be commercially worthless. Selection must be left to the judgment of the assayer. The sample must be dried, if necessary, care being taken not to roast it. It must then be pounded in an iron mortar and passed through a sieve of eighty meshes to the linear inch. If any native metal, in the form of scales or filaments, remain upon the sieve, take the weights, separately, of what has passed through and of what is left upon the sieve. The latter must be assayed according to 'Assay of Alloys,' and the result referred to the whole amount of ore. It is essential that the whole of the sample, except the malleable portion, be passed through the sieve Mix thoroughly the sifted ore.

2. *The Collection of the Gold and Silver* in a button of metallic lead is effected in a crucible, or in a scorifier, whence two methods of assay :—

(*a*) Crucible assay. (*b*) Scorification assay.

The former is applicable to all ores; the latter is limited, practically, by the small size of scorifiers, to the richer ores.

(*a*) *Crucible Assay.*—An ore of gold and silver is composed of precious metal, gangue, and oxides, sulphides, &c., of foreign metals. To collect the precious metals in a button of lead, the ore is mixed with litharge, suitable fluxes, an oxidising or a reducing agent, and fused in the crucible. Litharge is reduced to metallic lead; the latter seizes upon the precious metals and collects in a button at the bottom of the crucible, while the foreign materials form, with the fluxes, a fusible slag above the lead button. The crucible is broken when cold, and the malleable button detached from the slag by hammering on an anvil.

The Charge.—The weight of ore taken for an assay depends upon its supposed richness or poverty, since it is required to obtain finally a bead of precious metal of convenient size for weighing, and, at the same time, neither too large for cupellation (*vide* cupellation) nor so small as seriously to affect the calculated results, through losses sustained in the assay. As a rule, it is usual to take one, two, or four assay tons for gold ores.

The ores require the following reagents:—Litharge, sodium carbonate, and one of the reducing agents, argol and charcoal, or an oxidising agent, as nitre, with invariably a cover of salt one-quarter to half an inch in depth. Borax, silica, and other reagents are very useful at times, but no general rule can be given for their employment. This matter must be left to the judgment of the assayer, guided by the known properties of the reagents and by the composition of the ore. It is well, in this connection, to bear in mind the principle that for basic impurities, an acid flux is needed, and for an acid gangue a basic flux. As a rule, employ a weight of litharge twice that of the ore, and of sodium carbonate, the same as of ore. These proportions also may be modified to advantage, according to the composition of the ore. The proportion of nitre, or of reducing agent, depends upon the reducing power of the ore, hence it is variable in every case. These reagents are added to control the size of the lead button.

Size of the Lead Button.—There are two limits to the size of the button: (1) it must be large enough, or, in other words, enough litharge must be reduced throughout the mass to collect all the precious metal, and, at the same time (2) there should not be a useless excess of lead, which would occasion loss of silver in the subsequent cupellation.

These two conditions cannot always be fulfilled, but in this case the latter must be sacrificed. It has been found that a button of 15 to 20 grammes is the best size for a weight of ore from one-third to four assay tons. This is also a convenient size for a cupellation. A button that is too large for cupellation can, however, always be reduced in size by scorifying.

These requirements necessitate, in many instances, a preliminary assay of the ore to determine its reducing power. The reducing power of an ore is due to the presence of sulphur, arsenic, antimony, zinc, &c., but generally to sulphur contained in pyrites, &c.

Preliminary Assay of Ore.

Charge.	Ore	2 grms.
	Litharge	25 ,,
	Sodium Carbonate . .	10 ,,
	Salt	Cover.

A duplicate assay need not be made.

Warm the crucible before placing it in the fire, which should be perfectly bright, and should be urged to effect complete fusion in the shortest possible time. When the contents of the crucible are in quiet fusion, it must be withdrawn, to prevent further reducing action of the furnace gases. Tap the crucible gently, and when cold break it open.

Three cases may arise here. Two grammes of ore may yield—

1. No lead, or less than three grammes.
2. Three grammes lead.
3. More than three grammes.

The reducing power is stated thus: 2 grms. ore $=x$ grms. lead. Let us suppose that we shall take for the regular assay $\frac{1}{3}$ assay ton of ore, and that the reducing power is found to be 2 grms. ore $=1{\cdot}5$ grms. lead: $\frac{1}{3}$ assay ton or 10 grms. (about) ore will in this case reduce 7·5 grms. lead, and as the required button is 15 grms., we must add enough argol, or charcoal, to reduce 7·5 grms. in addition; taking argol as 8·5, we shall require $7{\cdot}5 \div 8{\cdot}5$ grms. or 0·882 grms., say 1 grm., or charcoal $7{\cdot}5 \div 28 = 0{\cdot}268$, say 0·3 grm.

If the reducing power correspond to the third case, a similar calculation will indicate how much nitre is needed to oxidise part of the sulphur, arsenic, or other reducing agent, and thus prevent the reduction of a button larger than 15 grammes. In the second case, ten grammes of ore would reduce a button of 15 grms., and neither argol nor nitre would be required.

The character of slag obtained in the preliminary assay may also suggest some modification of the regular charge. If it be earthy, for instance, we would add borax-glass or silica. Experience will often enable the assayer to judge of the reducing power with sufficient exactness, without an extra assay. Cases will arise, however, in which he must make a preliminary assay, or roast the ore, and it is always best to roast when there is a large amount of sulphur in the ore. He will then have an ore of no reducing power.—(Case I.)

Ores to be Roasted.—Ores containing a large amount of sulphur, or arsenic, antimony or zinc, should always be roasted. In the former case if the ore be not roasted, there will be danger of the formation of oxysulphides, which are very fusible, but are not decomposed even at a white heat, and enter the slag carrying silver with them. A large quantity of nitre also subjects the contents of the crucible to the liability of boiling over: even should this mishap not occur, the great evolution of nitrous and sulphurous vapours puffs up the mass throughout the crucible, and the globules of lead afterward reduced may be left adhering to the sides, not being washed down by the retreating charge. Arsenic and antimony produce arseniates and antimoniates, which carry silver into the slag. Zinc increases the loss of silver by volatilisation and also in the slag.

Roasting the Ore.—The ore may be roasted conveniently in a cast-iron pan over the crucible furnace. There ought to be a hood over the furnace, to carry off the fumes of sulphurous, arsenious, and other acids. The pan should be covered with a coating of red ochre, or, still better, of chalk. The former is put on wet with a brush. An excellent even coating of the latter may be obtained by making a chalk paste, of proper consistence, in the pan, and turning with the hand so as to spread the paste while the pan is being held over the fire to dry. The coating prevents a loss of ore and injury to the pan through the sulphides attacking the iron.

The weighed sample must be spread over the pan and stirred with a bent wire until all danger of fusion is past. The pan must be heated gradually at first, not above a dull red heat for some time, and may be brought, finally, to a full red, or higher heat. Too high a heat at the outset might cause the fusion of sulphides and the formation of matter troublesome to roast. A rapid disengagement of arsenic, antimony, or zinc, would cause, also, a mechanical loss of silver, by carrying if off in their vapours. Should fusion take place, it is better to weigh out a fresh portion of ore and roast again with more care. If this be not done the fused portions must be pulverised in a mortar and re-roasted. Generally, in roasting sulphides, the operation may be considered finished when, after keeping the pan at a full red heat for some time, no more fumes of sulphurous acid can be perceived. As there is danger, however, of the formation of sulphates, especially if copper pyrites be present, it is best always to mix some ammonium carbonate with the ore, after the fumes have ceased, and to cover the pan. The ore is thus confined in an atmosphere of ammonium carbonate, which decomposes the sulphates with formation of volatile sulphate of ammonia.

Arsenic and antimony require the addition of fine charcoal, to reduce any arseniates and antimoniates that may have been formed during the roasting. Care must be taken to burn out all the charcoal.

If the ore contain a very fusible sulphide, as antimony-glance or galena, it may be mixed with some fine sand previous to roasting.

The roasting of ores may also be done in the muffle in an earthen saucer.

Fusion.

The charge prepared according to the foregoing directions is thoroughly mixed and placed in a crucible, which it should not more than two-thirds fill. A hot fire should be employed, and the crucible removed when complete fusion has taken place. This ought to require from twenty to twenty-five minutes. The crucible is tapped, as usual, and broken when cold.

(*b*) *Scorification Assay.* The reagents necessary for a scorification assay are test-lead and borax-glass. The ore is mixed with these in suitable proportions, the mixture put in a scorifier and fused in a muffle. The operation affords an alloy of lead with the precious metals, and a slag composed of litharge with the impurities and gangue of the ore. The assay might be made with lead only, but it is advantageous to add some borax. There will be required of lead only enough to render the slag liquid and to furnish lead for the button. The proportions of both lead and borax will vary, and should be greater in proportion as the gangue and metallic oxides are more difficult of fusion. The following table exhibits the proportions found by experience to be best adapted to the different gangues. The proportions are referred to one part of ore.

Character of Gangue	Parts Test-Lead	Parts Borax
Quartzose	8	
Basic (Fe_2O_3, Al_2O_3, CaO), &c.	8	0·25–1·00
Galena	5–6	0·15
Arsenical	16	0·10–0·50
Antimonial	16	0·10–1·00
Fahlerz	12–16	0·10–0·15
Iron pyrites	10–15	0·10–0·20
Blende	10–15	0·10–0·20

No preliminary roasting is required. As in the crucible assay, the weight of ore taken depends very much upon its richness, but is generally a third, sixth, or tenth of an assay ton. If one scorifier will not contain the charge, it is best to weigh equal fractional parts for the number required, rather than to weigh the whole charge and roughly divide it between the scorifiers. In case of an accident to one of the scorifiers, the known loss can easily be restored, if the former course be followed. The exact parts that lead and borax perform in scorification can be understood best from a description of the operation in detail.

Three distinct periods may be noted in the working:—1. Roasting; 2. Fusion; 3. Scorification. A strong heat is maintained, at first, in order to melt the lead. This is effected by closing the muffle and regulating the draught. As soon as the lead is fused the muffle is opened, and the ore is seen floating upon the surface of the lead.

1. The roasting now commences, and is continued at a moderate heat until no more fumes are seen, and the ore has disappeared.

2. The heat should now be raised in order to fuse thoroughly all the material in the scorifier. When the fusion is complete, clear white fumes of lead may be seen arising from the scorifier, there is an intermittent play of colours across the bright surface of the lead, and the slag produced encircles the metallic bath like a ring. The borax plays an important part just here, by giving liquidity to the slag, thus permitting it to be thrown to the side as fast as formed, exposing a clear surface of lead for oxidation. If borax be not added and the ore contain a difficultly fusible gangue, the scoriæ will float in detached masses over the lead, impeding the oxidation, until sufficient litharge has been formed to give it liquidity.

3. When the fusion is complete, the heat may be lowered and the third period of scorification continued until the ring of slag, which is continually growing smaller, closes over the residue of metallic lead. The heat should again be raised, to liquefy the slag and allow the metallic lead to settle, after which the scorifier is removed from the furnace. If the button is wanted immediately for cupellation, the contents of the scorifier may be poured into an iron or copper mould coated with red ochre. It is thus soon cooled. Otherwise allow the contents to

solidify in the scorifier, and break this for the button when cold. Hammer the button as usual.

The whole assay occupies about thirty-five minutes.

In making the charge, it is customary to mix the ore with a part of the test-lead and with borax, and to cover this in the scorifier with the rest of the lead. This will prevent loss of ore prior to fusion. Too much borax should not be added at first. If a large amount is needed, it is better to mix only a portion with the ore—one gramme, for instance—and to introduce the rest wrapped up in paper, as needed during the operation. Some of it may be reserved for the final heating after the lead is slagged over. If too much were added at first, the lead would be slagged over before the necessary reactions had taken place.

The Lead Button.—The lead button submitted to cupellation must be malleable and of the proper size for the cupel. A good cupel will absorb its own weight of litharge, but it is better to use a cupel one-quarter to a third as heavy again as the lead button. The cupels in ordinary use weigh about 18 grammes, hence a button of 12 to 15 grammes is the proper size for them. If the button be too large it may be reduced in size by scorification. In case of doubt it is better to scorify, since there is less loss in this operation than in cupellation. A brittle button may be due to the presence of sulphur, arsenic, antimony, zinc, or litharge. In either case it must be scorified before cupellation, and with test-lead if necessary. If the button contain copper it must be scorified until no more copper can be seen on hammering out the button. If nickel be present the button cannot be cupelled. This, however, will occur but rarely.

3. *Cupellation.*—The lead button obtained by the foregoing operations is next cupelled. This operation is similar in many respects to scorification, but differs from it in that the scoriæ formed are absorbed entirely by the cupel, leaving a pure bead of the precious metals. This property of the absorption of scoriæ is an indispensable condition in cupellation, so that, unlike scorification, it is

limited to a few substances capable of being absorbed by the cupel. The oxides of lead and bismuth alone can be absorbed in a state of purity, but they can carry along with them certain proportions of other substances which, by themselves, would form infusible scoriæ. It is thus that we are enabled to get rid of small amounts of copper, iron, arsenic, &c., remaining in the lead button. Bismuth is seldom, if ever, used for this purpose. The proportion of lead required to carry off the different impurities varies according to circumstances. In the case of lead buttons from an assay, there is always an excess of lead, if they have been properly purified. Other cases will be treated under the head of Assay of Alloys, where the necessary tables will be given.

The operation of cupelling a lead button is conducted as follows :—

The cupels must be carefully dried before use, and must be free from cracks, which would cause a loss of precious metal. The bottom of the muffle should be covered with sand to prevent injury to it in case of the upsetting of a cupel. A cupel having been selected, it should be wiped carefully with the finger, and all extraneous matter blown out. It may then be placed in the muffle. Before the introduction of the lead button, the muffle should have attained a reddish-white heat, and the cupel should be of the same temperature. This being attained, the button is placed in the cupel with a pair of forceps, gently, so as not to injure it. The muffle should now be closed, either by a door or by a piece of lighted charcoal, to bring the fused button to the same temperature. This done, the muffle is opened and air allowed to enter ; the button, which at first appears bright and uncovered, is soon covered with a film of oxide moving in luminous patches over the surface, and being continually thrown toward the edge, where it is absorbed by the cupel. White fumes of lead arise, and the button is surrounded by a ring of the absorbed litharge, which continually widens until it reaches the edge of the cupel. The button thus gradually diminishes in size by oxidation and absorption, and becomes more convex; the luminous patches become larger and move more quickly; and when, finally, the last of the lead is absorbed, the button appears to revolve rapidly on its axis, becomes very brilliant, and is suffused with all the tints of the rainbow; the movement is suddenly checked, the button becomes dull for a few instants, and then presents the appearance of the pure precious metals. The latter part of the operation is called the 'brightening' of the button. Should the bead be large, and composed, in great part at least, of silver, it must be removed slowly and gradually from the furnace, to prevent loss by 'spitting,' which might happen if the cupel were removed at once from the muffle. When a cupel is withdrawn directly after brightening, the button is liable to be covered by mammillated and crystalline protuberances, and is then said to have 'vegetated' or 'spit.' Portions of the metal are sometimes thrown off and lost. Whatever the cause may be, this does not occur if the button be withdrawn gradually, so as to permit a slow and gradual cooling. In case the bead be very large, say 100–300 milligrammes, it is well to cover it with a hot cupel, which will retard the cooling and prevent the loss of small particles that may be thrown off despite all care. If the bead is not larger than the head of an ordinary pin, the danger of vegetation is slight, and no great precautions need be taken in its removal.

It is well to raise the heat of the furnace just before the brightening, or to push the cupel into a hotter part of the muffle, in order to aid the brightening and get rid of the last traces of lead, which are somewhat difficult to remove. The button should also, for the latter purpose, be heated strongly a few seconds after brightening.

Silver is sensibly volatile at a high heat; the loss of gold is slight, and may be disregarded. In the assay of ores this loss need not be considered, but in bullion assay a correction is necessary, for which a table will be given under Assays of Alloys. The loss of silver increases with the temperature, but we must avoid, in cupellation, the two extremes of a high heat and quick work and a low heat with prolonged work. Of the two extremes the latter is worse. The following are indices of favourable working:—The muffle is reddish-white, the cupel is red, the fused metal very luminous and clear, the lead fumes rise slowly to the top of the muffle, and the litharge is completely absorbed by the cupel.

The heat is too great when the cupels are whitish, when the fused metal is seen with difficulty, and the scarcely-visible fumes rise rapidly in the muffle.

The heat is too low when the fumes are thick and fall in the muffle, and when the unabsorbed litharge is seen forming lumps and scales about the button.

The degree of heat should bear some relation to the richness of the alloy, and may be greater according as the lead is poorer in silver. By bearing this in mind the assayer may often hasten the operation without detriment to the assay. The draught of air through the muffle must also be regulated. Too strong a current cools the cupel and oxidises the lead faster than it can be absorbed, thus endangering the assay. Too slow a current prolongs the operation and increases the loss by volatilisation. In ordinary work this matter, however, occasions very little trouble.

It happens sometimes that the material in the cupel becomes solidified in the midst of an operation, stopping all further action. This disaster is called the 'freezing' of the button, and is occasioned by the following conditions; a production of litharge more rapidly than it can be absorbed by the cupel, and infusible scoriæ, due to a cold furnace, or to an excess of foreign oxides. In either case the scoriæ gradually extend over the surface of the button until it is entirely covered, when further movement ceases. This disaster may sometimes be prevented or remedied by raising the heat of the muffle; if this fails, or if the accident be due to foreign oxides, an addition of pure lead must be made to the assay; in either case, the results are unreliable.

An assay that has *passed* well, furnishes a bead well-rounded and clear, crystalline below, and readily to be detached from the cupel. If the bead contain lead, it is brilliant below, and does not adhere at all to the cupel. If the bead exhibits rootlets passing down into the substance of the cupel, the results are inaccurate.

GENERAL OBSERVATIONS ON THE ASSAY OF GOLD ORES.

Gold and Copper, Proportion of Lead.—The alloys of gold and copper are cupelled like the alloys of gold and silver; but as copper has a very great affinity for gold, it is necessary to use a larger proportion of lead to ensure its oxidation when combined with gold than when united with silver. This proportion varies according to the standard and the temperature. It is admitted that for the same standard there must, under similar circumstances, be twice as much lead used in the cupellation of gold as for that of silver. Thus, 14 parts, at least, ought to be employed in common furnaces for an assay of gold coin which contains 0·1 of copper. There is no inconvenience in employing a little more, as it does not increase the loss of gold. However great the proportion of lead may be that is added to the cupreous gold for the purpose of cupellation, the button retains always a very small quantity of copper, which a fresh cupellation does not free it from, and which occasions what is termed the surcharge. This surcharge, being very slight, can be neglected in assays of minerals; but it is necessary to take notice of it in the assay of alloys. But it is known that the presence of silver much facilitates the separation of copper from gold, and it is rare that an alloy of cupreous gold does not contain a little silver, which must be separated: and when that is not the case, a small quantity of that metal can be introduced into the alloy, so as to be in about the proportion of 3 parts to 1 of gold. When an assay is to be made of an alloy of gold and copper, a sufficient quantity of silver is to be added to fulfil this condition according to the presumed standard, which is determined approximatively by a preliminary assay, and then cupelled with lead.

Examination on the Touchstone.—This method is based upon the fact, that the richer an alloy is in gold the more clearly does a streak drawn with it on a black ground present a pure gold-yellow colour, and the less is it attacked by pure nitric acid or by a test acid. This *test acid* consists of ninety-eight parts pure nitric acid of 1·34 spec. grav. (37° Beaumé), two parts pure hydrochloric acid of 1·173 spec. grav. (21° B.), and twenty-five parts distilled water. To judge of the richness of the alloy to be examined, its streak is compared with marks drawn with alloys (*the touch-needles*) whose richness is accurately known. In order to get correctly the streak of the alloy to be tested, the surface of the metal must first be somewhat filed away, since this may be impure, or, as with coins and jewellery, it may have been made somewhat richer by boiling with acid, and the so-called colouring of the goldsmith, and a clean fracture is rarely to be obtained. Five series of prepared touch-needles are required. The first series consists of copper and gold, and is called the *red series*, and the proportion of gold increases by half-carats in the successive needles. The second series, the *white series*, contains needles of gold and silver, in which the proportion of gold likewise increases by half-carats. The third series, a *mixed one*, contains needles in which the quantities of silver and copper are equal, and the proportion of gold also increases by half-carats. The fourth consists also of needles for a mixed series, in which the silver is to the copper as 2 : 1, and the gold increases by half-carats; and the fifth is also formed of needles for a mixed series, in which the quantity of silver is to that of the copper as 1 : 2. Moreover, in mints and stamping bureaux, alloys are used which correspond precisely to the legal standards. The testing upon the touchstone begins by determining to which series the alloy to be examined belongs. Then those touch-needles are rubbed against the stone whose marks most nearly approximate in colour to that of the alloy. The marks must form a thin continuous layer. A drop of pure nitric acid is now placed upon them with a glass rod, and its comparative effect observed.

The acid is allowed to work a short time, and then wiped off, in order to see whether the streak appears unchanged, or whether it has more or less disappeared. The test acid above is also used. This is so composed that it does not work at all upon an alloy containing eighteen carats and more of gold, and with such an alloy the streak, after using the acid, will not be wiped off with a fine linen rag, provided that stone and acid had a temperature of 10 to 12° C. Pure nitric acid produces almost no effect upon an alloy of fifteen or sixteen carats fine, and over. The testing on the touchstone can indeed make no pretension to accuracy, especially where the amount of gold is small, but it yields sufficiently useful results for a preliminary test. It requires, however, a sharp and very practised eye. Moreover, the preparation of the touch-needles is wearisome, as the required proportion is not always quickly reached, nor are good malleable alloys always obtained. The touchstone, therefore, is in general only used where frequent gold assays are to be made of alloys varying in richness, or where (as frequently with gold plate) an examination on the touchstone will suffice.

TABLE FOR PROPORTION OF LEAD TO BE EMPLOYED IN THE CUPELLATION OF GOLD AND COPPER.

Gold in alloy	Lead required	Ratio of lead in the assay to the copper, &c.
1000 thousandths	1 part	———
900 „	10 parts	100,000 : 1
800 „	16 „	80,000 : 1
700 „	22 „	73,333 : 1
600 „	24 „	60,000 : 1
500 „	26 „	52,600 : 1
400 „	34 „	56,666 : 1
300		48,571 : 1
200		42,500 : 1
100		37,377 : 1
50		

Kandelhardt gives the ratio in the following table :—

Gold in 1000 parts	Quantity of lead required
1000 fine gold	8 times the weight of the alloy
980 — 920	12 „ „ „
920 — 875	16 „ „ „
875 — 750	20 „ „ „
750 — 600	24 „ „ „
600 — 350	28 „ „ „
350 — 0	32 „ „ „

Gold, Silver, Platinum, and Copper.—The presence of platinum in an alloy renders the separation of the oxidisable metals, more especially copper, very difficult by cupellation. It appears, indeed, that it would be almost impossible to arrive at it, if the alloy of copper contained nothing but gold and platinum. It is necessary that silver be present at the same time. When this metal is absent, it is requisite to add a quantity of it, which ought to be equivalent to double the weight of the gold and platinum united, and cupel at the strongest heat which can be obtained in a good muffle with a suitable proportion of lead. This proportion varies much according to the composition of the alloy, and the temperature at which the operation is carried on.

Experience has shown that the copper can be more completely separated and less silver lost by cupelling at a high temperature, with the least possible quantity of lead, than by employing more lead, and working at a lower temperature. M. Chaudet has made several assays, in order to determine the proportion of lead required for the cupellation of the three following alloys:—

	1.	2.	3.
Gold	0·100	0·020	0·005
Platinum	0·100	0·200	0·300
Silver	0·250	0·580	0·595
Copper	0·550	0·200	0·100

and has found, for the first, that by employing 20 parts of lead the separation is very nearly complete; but that at a high temperature there is a loss of silver, and in order to render the assay correct, it must be cupelled at the latter temperature, with only 14 of lead; for the second, 8 of lead, at a high temperature; and for the third, 30 parts of lead are necessary, at the same high temperature of the muffle; but it is almost impossible to separate all the copper, and no advantage can be obtained by increasing the quantity of lead. When almost the last traces of the copper are separated, the button must be cupelled afresh, with a small quantity of lead; but a small quantity of silver is nearly always lost. In all cases, in order that no lead shall remain, it is necessary to leave the assay button some few minutes in the muffle after cupellation is finished.

The alloys of gold and silver which contain platinum show, either by cupellation or parting, certain characters which prove the presence of the metal. If the assay be not heated very strongly, it does not pass, and the button becomes flat; this effect becomes very sensible when the platinum is to the gold in the proportion of 2 to 100. Under the same circumstances, the nitric acid solution proceeding from the parting is coloured straw-yellow. At the moment an assay of an alloy containing platinum terminates, the motion is slower, and the coloured bands are less numerous, more obscure, and remain a much longer time than when there is no platinum; the button does not uncover, and the surface does not become as brilliant as that of an alloy of gold or silver, but it remains dull and tarnished. When the assay is well made, it is to be remarked that the edges of the button are thicker and more rounded than in ordinary assays, and it is of a dull white, approaching a little to yellow; and lastly, its surface is wholly or in part crystalline. These effects are sensible even when the gold does not contain more than 0·01 of platinum. When the alloy contains more than 10 parts of platinum to 90 of gold, the annealed cornet produced in the parting process is of a pale yellow, or tarnished silver colour.

Gold alloyed with Silver.—The separation of gold from silver is termed *parting.* Parting is not only used to separate silver from gold, but for the separation of other metals, such as copper, when cupellation does not separate it entirely. Parting by the wet process is carried on by the means of nitric acid, *aqua regia*, or sulphuric acid.

When an alloy of gold and silver has been reduced by a flatting mill to very thin plates, it is sufficient that it contains 2½ of silver to 1 of gold in order that the parting may be effected completely by nitric acid, and takes place much less easily when the silver in the alloy is in larger proportion; but when this proportion exceeds 3 parts of silver for 1 of gold, then the latter is obtained in leaves so fine, that there is risk incurred of losing some in the subsequent manipulation, and even by the act of boiling the acid liquid.

We must always, therefore, when a very exact assay is required, contrive that the alloy shall contain a little less than 3 parts of silver to 1 of gold, a proportion which long experience has demonstrated to be the best. If the alloy contain less than $2\frac{1}{2}$ of silver to 1 of gold, the silver does not wholly dissolve, because there is a part of it so enveloped in the gold that the strongest acid does not act on it.*

Inquartation.—The operation by which the alloy is brought to this standard is termed *quartation*, or *inquartation.* It consists in fusing the alloy in a cupel, with 2 parts of lead and the quantity of fine silver, or fine gold, necessary to bring it to the desired composition. This quantity is estimated according to the approximative determination of the standard of the alloy, which ought to be made either by means of a preliminary assay, as hereafter described, or by means of the touchstone. If we do not employ the whole of the alloy the assay will not be exact, because the gold and silver are not always found distributed in an uniform manner; at least every time it is not poured into a cold ingot mould.

Operation.—The cupelled and quartated button is flattened on an anvil and annealed, in order to soften it. It is laminated to give it a certain thickness, and is then annealed afresh, and rolled into a cornet or spiral around the quill of a pen. It is necessary that the alloy should be reduced to a suitable thickness, on the one hand, in order that the silver may be dissolved completely; and, on the other, that the plate of gold may remain whole after the operation. The following is that which experience has proved best. The quantity of matter operated upon, or taken for the assay, should be about 12 grains, and the alloys resulting from these 12 grains, and the silver em-

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* Pettenkoffer and others have shown that less than two parts of silver will suffice, and be even advantageous.

ployed in the inquartation, should be made into a plate of from 18 to 20 lines in length and 4 or 5 in breadth.

The cornet for assay is placed in a glass matrass, capable of containing about three ounces of water; pure nitric acid is added at different times, and heat applied. When all the silver is dissolved, it is washed by decantation with water; the matrass is reversed into a small crucible, the cornet falls out and is dried. In this state the cornet is very fragile, and of a dull red colour; it is annealed in a muffle, and heated gradually without fusion. It becomes thereby much contracted, and acquires a metallic lustre, and so much solidity that it can be weighed without fear of breaking it. Its weight can be ascertained in the assay balance.

There are many ways of employing nitric acid. Formerly 2½ ounces (thirty-five times the weight of the alloy) of nitric acid (1·15 sp. gr.) was poured upon the inquartated cornet, and boiled gently for fifteen or twenty minutes, the liquid decanted and replaced by 1½ of acid (1·24 or 1·26), twenty-four times the weight of the alloy, boiling for twelve minutes, then decanting and washing, &c. Vauquelain advised, in his 'Manuel de l'Essayeur,' to pour on the quartated cornet—the weight of the assay being 7·7 grains—554 to 770 grains of nitric acid (1·16 sp. gr.), which ought to fill the matrass half or two-thirds, and boil gently for twenty, or twenty-two minutes at most, to decant and replace the liquid by 500 to 800 grains of acid (1·26 sp. gr.), and to boil for eight or ten minutes. The assay is to be acted on always twice, because if we employ at once very strong acid, the action will be too brisk, and the cornet might be broken or carried out of the matrass, and, on the other side, the acid of 1·16 sp. gr. cannot dissolve the last portions of silver, which are very difficult to separate from the gold.

Surcharge.—It is remarked that by following this method the cornet always retains a small quantity of silver, so that fine gold submitted to quartation and parting always weighs more after than before the operation. The augmentation of weight which it undergoes is termed the *surcharge*; this surcharge is commonly from 0·001 to 0·002. M. Chaudet has found means to avoid it. In order to do so, pour on to the quartated cornet nitric acid of 1·16 sp. gr., and heat for three or four minutes only; replace this acid by acid of 1·26 sp. gr., and boil during ten minutes; decant and make a second boiling with acid of 1·26 sp. gr., which boil for eight or ten minutes. The assay requires but from twenty to twenty-three minutes, and, according to M. Chaudet, gives perfectly pure gold.

A source of loss occurs in parting operations and refining on the large scale, from the solution of gold in nitric acid, even when it is quite free from hydrochloric acid, in consequence of the formation of nitrous acid. To ascertain the amount of loss from this source in ordinary assay operations, Mr. Makin took four specimens of pure gold accurately weighed, added the usual proportions of fine silver and lead, and then cupelled them. The resulting buttons were rolled, coiled, and parted with nitric acid, the cornets being boiled in two acids of different strengths a different number of times. Calling the weighings before the operation 1000, the results were as follows:—

1.	Boiled in acid twice	999·6
2.	„ three times	999·2
3.	„ four „	998·7
4.	„ five „	997·9

The loss is thus seen to increase as the boilings are multiplied.

When silver is present in large quantity, Mr. Makin believes that the solvent action of nitrous acid is restrained by electrical action, the gold becoming the negative and the silver the positive pole of a circuit; but as the silver is removed, the solution of the gold goes on more rapidly. The cause of the evolution of nitrous acid is evident as long as there is any silver present, and it often results from the use of charcoal to prevent 'bumping.' When charcoal is thoroughly carbonised, it does not materially affect the acid; but if it contain woody matter, nitrous acid is sure to be set free. Mr. Makin has given up the use of charcoal on this account.

The commercial importance of this subject will be admitted, when we remember the enormous value of the metals dealt with in this country, and that the question of profit and loss in commercial transactions with them are almost entirely in the hands of the assayer. A knowledge of these facts may also serve to account for some of the discrepancies between assayers.

In the assay of auriferous ores, the button produced by cupellation commonly contains silver. When the proportion of this metal surpasses that of inquartation, the button is flattened between two pieces of paper, and treated by pure nitric acid. The gold remains under the form of a yellowish-brown powder, which is weighed immediately, or fused in the cupel enveloped in a sheet of lead. When the quantity is extremely small and imponderable, we can assure ourselves at least of its presence by treating the residue left by nitric acid with *aqua regia*; if it contain gold, it dissolves and gives a yellowish liquid, in which a drop of solution of chloride of tin or the crystallised chloride forms a deposit of purple of Cassius of a violet colour: this character proves the presence of the smallest traces of gold. When the gold predominates in the button, it is necessary to re-fuse it with three times or less its weight of silver, and recommence the assay with the addition of this preparation of silver.

Aqua Regia.—When gold is the largest portion of the alloy, and when there are reasons for not adding silver, the parting can be made by *aqua regia*. In this case, all the gold is dissolved, and the silver converted into chloride; the chloride is washed, dried perfectly, and weighed. When the gold is precipitated by ferrous sulphate, it is washed with a little hydrochloric acid, and annealed strongly before weighing, or even annealed so far as to fuse it, and then cupelled with lead.

If an alloy, containing much silver, be treated by this process, it sometimes happens that the excess of silver chloride prevents the complete solution of the gold. In this case it is necessary to reduce the alloy to an excessively thin plate, to dissolve the chloride in ammonia, and to treat afresh with *aqua regia*. This process can rarely be made use of on the large scale, because the precipitation of gold by ferrous sulphate is long and troublesome.

M. G. Rose fuses the alloy with lead, over a spirit-lamp, in a porcelain crucible, acts on it with nitric acid, which dissolves the silver and lead, precipitates the silver by a solution of lead chloride; lastly, the auriferous residue is dissolved by *aqua regia*, and the gold precipitated by ferrous chloride.

For the separation of gold and silver and their determination in alloys, H. von Jüptner ('Zeitschrift für Analytische Chemie,' 1879, 105) alloys the metal with 5 to 8 parts of zinc, and dissolves in nitric acid; zinc, silver, copper, &c., dissolve, whilst gold and the platinum metals remain, and also tin as oxide, if present. The zinc alloy is easily found, and the metals in the crucible are best covered with resin to prevent oxidation.

If it is known that neither tin nor platinum is present, it is sufficient to decant, dry, and weigh in order to find the weight of the gold.

If the platinum metals or tin are suspected the residue is dissolved in *aqua regia*, the free chlorine is expelled by boiling, the gold is reduced with ferrous ammonium sulphate of known strength, and the excess of ferrous oxide titrated with potassium permanganate. From the quantity of ferrous oxides consumed in the reduction of the gold its proportion may be calculated.

All the silver is contained in the nitric acid solution of the zinc alloy.

By another method for the separation of gold and silver the metal is alloyed with 5 to 8 parts of zinc, for which the heat of a Bunsen burner is sufficient. The alloy is dissolved in nitric acid, when gold (with platinum and tin as stannic oxide, if present) remains undissolved. To separate gold from platinum and tin they are dissolved in *aqua regia*, the platinum metals are precipitated with ammonia, the free chlorine is expelled, and the liquid is mixed with excess of ammonio-ferrous sulphate, the excess of which is determined by titrating back with permanganate (‘Zeitschrift für Anal. Chemie,’ 18, 104).

Standard of the Alloys of Gold.—The real standard of the alloys of gold is expressed in fractions of unity, as in the case of alloys of silver. We suppose 24 carats in unity, and 32–32nds in the carat; the unity contains then 768–32nds. After these data the following table has been formed, which expresses the relation of 32nds and carats to decimal fractions of the unity :—

32nds	Decimals
1	0·001302
2	0·002604
3	0·003906
4	0·005208
5	0·006510
6	0·007912
7	0·009115
8	0·010415
9	0·011718
10	0·013021
11	0·014323
12	0·015625
13	0·016927
14	0·018230
15	0·019531
16	0·020833
17	0·022135
18	0·023436
19	0·024740
20	0·026042
21	0·027343
22	0·028644
23	0·029948
24	0·031250
25	0·032552
26	0·033854
27	0·035156
28	0·036460
29	0·037760
30	0·039062
31	0·040364
32	0·041667

Carats	Decimals
1	0·041667
2	0·083334
3	0·125001
4	0·166667
5	0·208333
6	0·250000
7	0·291666
8	0·333333
9	0·374999
10	0·416667
11	0·458630
12	0·500000
13	0·541667
14	0·583333
15	0·624555
16	0·666667
17	0·707333
18	0·750000
19	0·791666
20	0·833333
21	0·874999
22	0·916666
23	0·958333
24	1·000000

Assays of Gold Coin and Bullion (Alloys of Gold and Copper, or Gold, Silver, and Copper).

Preliminary Assay.—As in the case of silver assaying the quantity of lead to be employed is of importance, a preliminary assay must be made when the standard of the alloy to be examined is not approximatively known. It is thus effected:—To 2 grains of the alloy add 6 grains of fine silver and 50 grains of pure lead. The lead must be introduced into a hot cupel, and when fused, and its surface fully uncovered, the alloy and silver may be added, wrapped either in thin paper or a small quantity of lead foil. The cupellation finished, and the cupel cold, the button of gold and silver must be removed from the cupel by aid of the pliers, and if necessary cleansed. Hammer it to a thin plate on the anvil, place it in a small evaporating basin, and treat it with half an ounce of nitric acid. (It may be here mentioned, that the nitric acid employed in the assay of gold must be chemically pure, and special care must be taken that it contains no trace of chlorine.) The evaporating basin is gently heated until all action ceases. The brownish residue is repeatedly washed with hot water, dried, ignited, and weighed; and from its weight the amount of lead and silver to be added in the actual assay may be determined. The presence of copper in the alloy is indicated by the blackness of the cupel where it is saturated with oxide.

Assay Proper.—In this case it will be supposed that standard gold is the alloy operated on, and that preliminary assay has given about 91½ per cent. of gold. On referring to the table (page 681), it will be found that between 27 and 30 parts of lead are required for such percentage of gold, and that, according to the general observations on this class of assay, three times its weight (that is, the weight of fine silver) will be required to so dilute the gold that nitric acid can attack and dissolve out the whole of the silver combined with it.

Place the weight representing 24 carats in the pan of the balance, and exactly counterpoise it with the gold to be assayed; two portions should be thus weighed. Two portions of fine silver must now be weighed; 33 grains will be required for each 24 carats of gold, as 22 carats, or 11 grains, of fine gold exist in the 24 carats, and three times the quantity of silver is necessary. 300 grains of lead must be placed in a hot cupel (two being thus prepared), and, as in the preliminary assay, when the surface is fully uncovered, the gold and silver are added, and the cupellation proceeded with, taking all the precautions already fully pointed out elsewhere.

The button so obtained is cleaned, hammered on the anvil, then annealed and passed between the rollers of a small flatting-mill; being occasionally annealed, in order to prevent the laminated button cracking at the edges. When reduced to the desired degree of thinness it is again annealed and rolled round a quill or glass rod into a spiral, termed a cornet. This cornet is placed in a parting flask with 1½ oz. of nitric acid, sp. gr. 1·16, very gently heated to the boiling point, and at that maintained for ten minutes. The acid is then to be poured off, and 2 oz. of nitric acid, sp. gr. 1·26, added, and again boiled for ten minutes. This second acid is also poured off, and a third quantity of like specific gravity added and boiled. The cornet is then well washed with distilled water, and the flask, filled with distilled water, is inverted, having its mouth closed with the thumb. The cornet will fall through the water without breaking, and can be introduced, together with some of the water, into a small crucible (cornet crucible), the water poured off, the crucible and gold gradually dried, and then heated to redness. When cold, the final operation of weighing may be performed, thus:—The weight representing 22 carats is placed in one pan of the balance, and the cornet in the other: as the gold employed was supposed to be standard, it ought to weigh exactly 22 carats. If, however, gold of greater or less fineness had been submitted to assay—say of 23 and 21 carats respectively—1 carat weight would have been required in the pan containing the 22-carat weight, to counterbalance the gold carat: in this case the gold would be 23 carats fine, or, in the usual mode of reporting, 'one carat better.' If, on the other hand, the 1 carat weight had been found necessary in the pan containing the cornet, the gold would be 21 carats fine, or 'one carat worse.'

In cases where it is known that the gold under examination contains no silver, the only alloy being copper, its fineness can be determined by cupelling 24 carats with its proper portion of lead, and weighing the resulting button, which should represent the amount of fine gold in the alloy assayed.

Parting Assays.—Parting assays are those assays by which the amount of fine gold and fine silver in any alloy is determined. When the amount of gold exceeds that of the silver, it is called 'gold parting;' when the amount of silver exceeds that of the gold, 'silver parting.'

In this assay the weights employed in the silver assay are employed, as the report is made in ounces of fine metal per pound Troy.

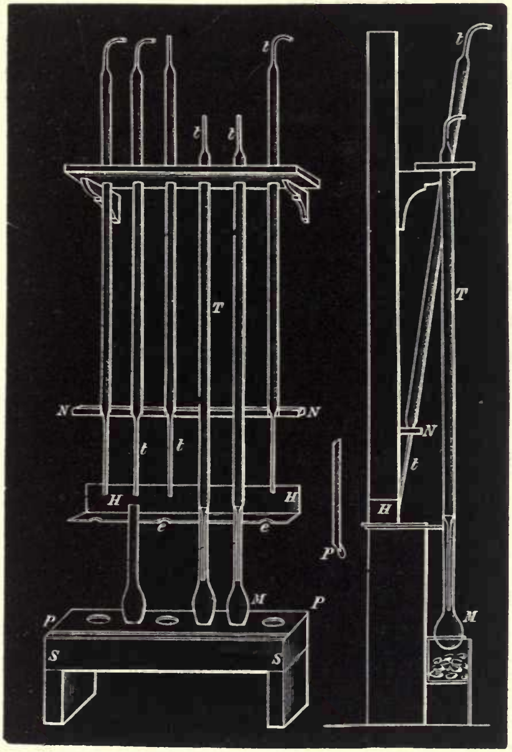
12 grains (representing 1 lb. Troy) of the alloy are weighed off, cupelled with 300 grains of lead, and the resulting button, containing only gold and silver, is weighed. Suppose it weigh 10 grains, then 2 grains, = 2 ounces in the pound of alloy, is copper or some other metal, which has been oxidised and carried into the cupel with the litharge. A preliminary assay must be made of the alloy, to ascertain the approximative quantity of silver and gold, so as to apportion the amount of silver in the assay proper: this amount being found, it is to be weighed off, added to the button of fine gold and silver obtained as above, and the whole cupelled with 200 grains of lead; the cupelled mass of gold and silver laminated and treated with nitric acid, as already described, and the resulting gold weighed. Suppose the weight to be 8 grains, = 8 ounces, the result would stand thus:—

Copper or other base metal	2 oz.
Gold	8 "
Silver	2 "
	12 oz.

The above arrangement is very convenient for accomplishing gold assays, and is the one employed in the assay office of the French Mint. The annexed cut (fig. 130) represents this apparatus.

The assay flask, *M*, being charged with the cornet, a constant amount of acid is added with a pipette. On the addition of the second acid a small piece of charcoal is placed in the flask: this serves to prevent bumping during ebullition. The flasks are supported on a plate of sheet iron, *P*, pierced with holes or by a grating, and the acid vapours, before escaping by the flue, pass into glass tubes, *TT*, about half an inch in diameter, and four feet long: at each end a narrower tube, *t*, is fused. The lower tube freely enters the neck of the flask; and as the space between is so small that a layer of acid remains suspended and obstructs the passage of the acid vapours, they are thus forced to pass into the large tube, where, for the greater part, they condense and fall into the flasks. By this means the quantity of acid employed in the assay can be diminished, as there is no loss by evaporation, and the

FIG. 130.



results are found to be more constant. In order that the passage to the large tube for the acid vapours may always remain free, the end of the narrow tube passing into the flask must be cut at an angle (see *P*). The drops of acid collect at this part, and never close the tube.

Assay of Pyrites for Gold.

Mr. J. M. Merrick gives the following method for assaying pyrites for gold :—

'One pound, or even 18 ounces (avoirdupois), of fine marble-dust is mixed with 8 ounces of finely pulverised and sifted pyrites; the whole then re-sifted and put into a Hessian crucible, which should be about one-third filled by the mixture. The crucible is set as usual on a fire-brick, and a fire of hard coal is made around it, the coals being heaped up to within an inch of the top. The crucible is covered with a piece of brick or a piece of sheet iron. During the first half-hour the contents should be stirred once or twice. As the fire grows brisker the carbonic acid evolved keeps the contents of the crucible in brisk ebullition, and the mixture should be stirred well every 5 or 10 minutes. On stirring during this time, the iron rod used seems to meet with but little resistance from the light mass, but at the end of about 1½ hours the evolution of gas suddenly ceases, the red-hot mass becomes heavy, sinks, and requires considerable force to keep it stirred. It must be stirred well and vigorously, however, for about half an hour, not leaving it unstirred for more than a minute, otherwise the mass will fuse or cake, and the assay will be almost inevitably ruined.

'When a sample taken out in an iron spoon gives off no smell of sulphur, the entire contents of the crucible must be turned into a stoneware pot or a wooden bucket half filled with water, and well stirred. When the powder —which should be uniform and free from lumps or fused pieces—has settled, the water must be poured off, the wet mass allowed to drain, and then transferred to a large earthen bowl or porcelain mortar. Here it is to be amalgamated with about 2 ounces of mercury, to which a little bit of sodium amalgam has been added. The amalgamation, as well as the stirring in the fire, is a tedious process, and one which it is as well to do by proxy. It does not consist in merely grinding with a pestle the mercury in among the particles of the roasted ore, but this ore itself must be ground in contact with the mercury, until the particles are so fine that they will float suspended in water for several seconds. At the end of—say—10 minutes' thorough grinding, the contents of the bowl are to be brought into one mass in the bottom of the vessel, the bowl then sunk in a tub of water, and the contents "washed down"—an operation not easily described, but familiar enough to every old Californian. It consists essentially in shaking the bowl half full of ore and water in such a way that the mercury, gold particles, and unground ore sink to the bottom, while the light and finely-ground ore is floated off into the tub. The ore remaining is re-ground and re-washed, and these processes are repeated till nothing but the mercury remains in the bottom of the bowl or mortar. This mercury is then dried with filter-paper, and heated in a porcelain capsule over a Bunsen flame, very gently, until it is sublimed and the gold remains behind. The film of gold may then be scraped up and melted, with a little borax and nitre, in the very smallest-sized Hessian crucible, either with the foot blowpipe or in a charcoal furnace, by which means a round, clean button of gold, suitable for weighing, will be obtained.

'This method has its disadvantages and its counterbalancing merits. On the one hand, it must be admitted to be tedious, laborious, and to a considerable degree uncertain. Some analysts fail with it altogether, while none who have tried it, so far as I know, get closely agreeing results.

'But, on the other side, it is as certain that this method will indicate the presence of gold, and will bring out the gold in a weighable form from pyritic ores, where the assay by smelting will not show a remote trace of the precious metal; and that where the fire assay shows a certain percentage this will invariably bring out a larger amount. Large returns have been obtained by this amalgamation method from iron pyritic ores, which have been repeatedly assayed in the ordinary way, by chemists of great eminence, with uniformly negative results.'

Detection of Minute Traces of Gold in Minerals.—Mr. Skey, analyst to the Geological Survey of New Zealand, has devised a plan which gives very good results, even when small quantities of mineral are operated on. He employs iodine or bromine for the purpose of dissolving out the gold. Both of these substances differ from chlorine especially in their relatively feeble affinities for hydrogen, so that there is less fear that from the generation of hydrogen acids any great preponderance of other matters would be dissolved along with the gold. Either of these substances can be safely and advantageously employed for the separation of gold from its matrix.

The following particulars of experiments made by this method will be useful in showing what is approximately the smallest quantity of gold that can be positively separated and identified when operating upon a limited quantity.

1st. 2 grms. of roasted 'buddle headings' from a quartz mine at the Thames, N.Z., known to contain gold at the rate of 1 oz. or so to the ton, was well shaken for a little while with its volume of alcoholic solution of iodine, then allowed to subside. A piece of Swedish filter-paper was then saturated with the clear supernatant liquid, and afterwards burned to an ash; the ash, in the place of being white, as it would be if pure, was coloured purple; the colouring matter was quickly removed by bromine—a clear indication of the presence of gold. The time occupied by the whole process was twenty minutes.

2nd. 1 grm. of the same 'buddle headings,' mixed with such a quantity of earth as to reduce the proportion of gold present to 2 dwt. per ton, was kept in contact with its own volume of the tincture of iodine for two hours, with occasional stirring; a piece of filter-paper was then saturated with the liquid, and dried, five times consecutively, and finally burnt off as before; in this case, also, the colour of the residual ash was purple, and it gave the reaction of gold.

3rd. 32 grms. of siliceous hematite, finely-pounded, were thoroughly mixed with precipitated gold to the amount of 2 dwts. per ton; then ignited and treated with bromine water. After two hours the solution was filtered, and evaporated to a bulk of 20 minims; this gave a good reaction of gold to the 'tin chloride' test.

4th. 100 grms. of the hematite, with precipitated gold at the rate of ½ dwt. per ton, treated as before, but this time well washed at the expiration of two hours; the washings evaporated along with the first filtrate, gave a fainter, but still decided, reaction of gold to the same test.

5th. Iodine, as tincture, substituted for bromine in Experiments 3 and 4, gave similar results; the only variation made was, that, as a precautionary measure allowing for its slower action, they were kept in contact for twelve hours.

Careful experiments have been made to compare the results of the common amalgamating process with the foregoing, and it has been found that it is not certain, with the same expenditure of labour, to get reliable indications of gold, when present in less quantity than 2 dwt. per ton, operating upon about 100 grms. of material.

In summing up the results of these experiments, it appears, then, that for qualitative examinations for gold, or for quantitative determinations in certain cases, iodine and bromine are each superior to mercury. It also appears that a proportion of gold equal to ½ dwt. per ton, upon a bulk of about 4 ozs. of ferruginous matters, can be easily and rapidly detected. Of course, by operating upon larger bulks, gold could be discovered by this process, were it present in far less quantities, but this is sufficiently near for the majority of cases.

These processes are especially adapted for the separation of gold from sulphides, as the preliminary roasting is extremely favourable to them, the loss in the substitution of oxygen for sulphur amounting to 25 per cent. by weight, while the volume remains constant (or nearly so); hence there is a corresponding porosity in the product, by which every particle of it is thrown open to contact with the solution. This mechanical accessibility obviously cannot be taken advantage of by mercury.

With sulphides these processes are practically exhaustive, while, at the same time, the simultaneous extraction of other matters is so trifling, that the proper tests for gold can be safely applied directly to the concentrated solution. In the roasting of pyrites it is necessary to raise the temperature towards the end to a full red heat, in order to decompose the ferruginous sulphates, since if these remained iron would get into the solution. In the case of an excess of calcium carbonate being present, it is proper to gently re-ignite the roasted mineral, &c., with ammonium carbonate, or much lime might get into the iodine or bromine solution. On the other hand, a very high temperature is to be avoided, for a considerable quantity of fine gold can escape detection in this way, by the partial vitrification of the more fusible of the silicates.

The identification of gold by the combustion of its salts with filter-paper seems to promise a raipd method of estimating it, comparatively, by the aid of a series of prepared test-papers, representing gold in different degrees of dilution.

It seemed at one time possible that the assay of silver alloys might be simply and rapidly effected by the aid of the spectroscope. The researches of Professor Chandler Roberts, F.R.S., Chemist to the Mint, and of Mr. A. E. Outerbridge, Assistant in the Assay Department of the United States Mint, show that for the present at least these expectations are groundless.

It has been shown by Mr. Capel that the $\frac{1}{4000}$ of a milligramme of gold will show a spectrum, if the spark be passed through a weak solution of the pure metal. But when operating on a slip of alloy formed of—

Silver	708
Copper	254
Gold	38
	1000

the spectra of copper and silver alone were visible. In an alloy of gold and copper containing from 200 to 250 parts in the thousand of the precious metal, the gold spectrum is barely visible. On the other hand, in an alloy of gold and copper containing 1 per cent. of the latter, the copper spectrum was distinctly shown. In copper alloyed with 20 per cent. of nickel, the spectrum of the latter is not visible. Hence we arrive at the interesting fact that when two or more metals are present, the spark will to some extent elect for its vehicle the one which is most rapidly volatilised.

It is also not possible to obtain alloys of gold so perfectly homogeneous that the quantity of metal volatilised and giving the spectrum may safely represent the whole melt.

CHAPTER XVIII.

THE ASSAY OF PLATINUM.

PLATINUM is found in a native or metallic state. It occurs very rarely, yet it is exceedingly probable that wherever gold is found this metal will more or less accompany it.

It is found disseminated in sand, in the form of grains varying in size from gunpowder to hempseed: this last size they rarely exceed, yet, as in the case of gold, nuggets have been found of large size and weight. Its colour is steel-grey, or rather, a tinge between silver-white and steel-grey.

The sands from which platinum is derived are remarkable, from the number and importance of their principal constituents. With the platinum may be found Au, Ag, Hg, Fe, Cu, Cr, Ti, Ir, Os, R, and Pd. Besides all these metals, precious stones have also been found associated with it.

The following plan will serve to detect platinum in admixture with gold and other heavy matters obtained by washing or vanning sands, earths, &c.

Act on a small quantity by mercury, and separate the amalgam; by this means the gold is removed. To the residue add aqua regia and boil, evaporate the solution to dryness, add a little hydrochloric acid and water, boil and filter. To the filtered solution add a strong solution of sal ammoniac (ammonium chloride). If a bright yellow, or reddish-yellow, granular precipitate falls, platinum is present in the sand.

A still more ready method is the following:—Separate as much earthy matter as possible by careful washing. If gold is present separate that by amalgamation. Dry the residue and take its specific gravity; if it be above 10, platinum is most likely present. The specific gravity of native platinum, free from earthy matter, is from 16 to 19.

Analysis of Platinum Ores.—The platinum sands often contain metallic compounds of iron and platinum, not only capable of being attracted by the magnet, but possessed even of polarity. These grains have a different composition from those not magnetic, as shown in the two following analyses by Berzelius:—

Analysis of the non-magnetic grains:—

Platinum		78·94
Iridium		4·97
Rhodium		·86
Palladium		·28
Iron		11·04
Copper		·70
Osmi-iridium	in grains	1·00
	in scales	·96
		98·75

Analysis of the magnetic grains:—

Platinum	73·58
Iridium	2·35
Rhodium	1·15
Palladium	·30
Iron	12·98
Copper	5·20
Insoluble matters	2·30
	97·86

These grains being separated, their relative proportion is estimated.

Bunsen's method of analysing platinum ores is as follows:—The ores employed contain no osmium, and were relatively rich in rhodium.

Platinum and Palladium.—It is easy to effect the almost complete separation of platinum and palladium from rhodium, iridium, and ruthenium. The original material is mixed in a Hessian crucible, with from $\frac{1}{2}$ to $\frac{1}{3}$ its weight of ammonium chloride, heated until the latter is completely volatilised, allowed to glow gently until only the vapours of ferric chloride show themselves, and then placed in a porcelain dish and evaporated to a syrupy consistency, with from two to three times its weight of raw *commercial* nitric acid. By this treatment with ammonium chloride the metals present not belonging to the platinum group will have been partially converted to lower chlorides, the rhodium, iridium, and ruthenium will have been rendered insoluble, and the silica present as gangue converted from a gelatinous mass to a finely pulverulent condition, in which state it will admit of speedy filtering.

The chlorine compounds, produced by the ammonium chloride, give, upon digestion with nitric acid, just enough hydrochloric acid to dissolve the platinum to bichloride, while the metallic copper and iron present act so far reducingly upon the palladium (in solution in nitric acid) that it remains in solution, not as bichloride, but as the protochloride, which latter is not precipitated with potassium chloride. The mass is diluted with water, filtered, and the solution saturated with potassium chloride, and the greater part of the platinum separated pure as potassium platinochloride, which is washed out first with potassium chloride, and later with absolute alcohol (the last washings must not be added to the solution).

The filtrate is poured into a large flask (which can be made airtight), which will not be more than half-filled with it. Chlorine gas is passed into this flask, and it is from time to time shaken vigorously, until no further absorption of gas takes place, when all the palladium will have separated as a cinnabar-red precipitate of potassium palladiochloride (somewhat impure, however, from traces of platinum, iridium, and rhodium). The fluid from which these precipitates were obtained is now evaporated, not quite to dryness, with hydrochloric acid; and, upon addition of just so much water as is necessary to dissolve out the potassium chloride and other soluble salts (aiding the operation by rubbing with a pestle), there remains behind a dirty, yellow-coloured precipitate. This is separated by filtration, boiled with caustic soda and a few drops of alsolute alcohol. Hydrochloric acid is added to dissolve the precipitate formed, and the liquid then saturated with potassium chloride; the result is a precipitate of chemically pure potassium platinochloride. The mother liquid contains only copper and no platinum metals.

The purification of the cinnabar-red precipitate of palladium is accomplished as follows:—Dissolve in boiling water, whereby a portion of the chloride dissolves, with evolution of chlorine, to palladium protochloride. Then evaporate with 2½ times its weight of oxalic acid, and dissolve again in a solution of potassium chloride: whereupon potassium platinochloride remains behind, chemically pure. Wash out as before.

The brown liquid is then somewhat concentrated upon the water-bath: and upon cooling, there separate bright green, well-formed crystals of potassium palladio-protochloride (with some potassium chloride), which upon testing, proves free from the other platinum metals.

The fluid poured off from these crystals is then neutralised carefully with caustic soda, and gives a slight precipitate of copper and iron, which is filtered off. Upon adding potassium iodide to the filtrate, all the palladium separates as palladium iodide. To avoid adding an excess of the reagent, it is best to take from time to time a drop from the fluid with a capillary tube, and put the same upon a watch-glass. As long as the precipitation is incomplete, the drop appears, upon a white background *brown*; when complete, it is *colourless*; when the reagent is present in excess it is *red*. This is tested for its purity by reducing it to metallic palladium, and then heating and dissolving in nitric acid; when pure, it must dissolve completely. The whole mass is now reduced in a slow stream of hydrogen gas (whereby the iodine can be obtained again, as hydriodic acid, by absorbing with water). At last the mass must be strongly heated, to decompose slight traces of the palladium subiodide which are formed.

The mother liquid from which all this platinum and palladium have been obtained may contain some iridium and rhodium; it is, therefore, evaporated to dryness with a little potassium iodide, whereby a mixture of rhodium and iridium iodides separates. This can either be dissolved in aqua regia, and the two metals separated (as will hereafter be described) by sodium bisulphate, or it can be united with the next portion from which these metals will be obtained.

Ruthenium, Rhodium, and Iridium.—The residue from the original material which remains, after treatment with ammonium chloride and nitric acid, is treated as follows, to get the metals in a form adapted to further chemical treatment.

The method depends upon the behaviour of zinc chloride to zinc. If a piece of zinc be melted, it rapidly covers itself with a stratum of oxide. If, to the melted metal, a metal like iridium be added, the oxide stratum hinders the latter from coming into contact with the zinc, even though it be pushed beneath the surface. If, however, a few grains of ammonium chloride be added to it, ammonia, hydrogen, and zinc chloride will be formed, which last dissolves the oxide stratum to basic zinc chloride. The zinc below resembles mercury in lustre and mobility. As soon as the chloride has dissolved as much of the oxide as is possible for it, the oxide stratum again forms, and is instantly removed again by the addition of more ammonium chloride. The melted zinc, strewn with ammonium chloride, also possesses, like mercury, the property of attacking other metals, if the affinity exists of forming with them alloys. By strewing ammonium chloride upon the melted zinc, a quiet surging is kept up, as the ammonia and hydrogen are given off. Many oxides and chlorides (among which are those of the platinum metals), when they come into contact with this atmosphere of reducing gases, and with the basic zinc chloride, are instantly reduced and dissolved to alloys by the zinc. In making the solution, the zinc, in a porcelain dish, should be constantly rotated: the gangue remains in the basic chloride. The regulus, immediately upon solidifying, should be taken from the capsule, out of the yet fluid basic chloride, and washed off with acetic acid until all the basic chloride is dissolved away. The gangue can be quantitatively determined by filtration and weighing

If the regulus is not immediately removed, the containing vessel will be broken, owing to the unequal expansion of the porcelain and the metal.

The best proportions for a quantitative separation are, to 1 part of the platinum metals, from 20 to 30 parts of zinc. For an ordinary separation 7 parts of zinc are sufficient.

For the extraction of the residues remaining after the treatment with nitric acid, this method is admirably adapted. By fusing only once with zinc for two or three hours, all the platinum metals are extracted. The operation is as follows :—

From 3 to 3·5 kilos. of commercial zinc are fused in a 2-litre Hessian crucible, ammonium chloride from time to time strewn upon it, 400 grms. of residue, previously heated to faint glowing with ammonium chloride, are added, and the temperature kept, for two or three hours, just above the fusing point of the alloy, by adding, whenever the mass threatens to solidify, some ammonium chloride. The mass is divided into three strata after solidification has taken place.

The outer stratum, easily broken away by a blow from a hammer, contains no platinum metals. The next contains some particles of the zinc and platinum alloy, imbedded in the basic zinc chloride ; it is porous, and not very thick. The inner stratum consists of a beautiful crystalline regulus.

To obtain the alloy from the middle stratum, it is only necessary to wash repeatedly with water ; and the alloy gained is, of course, to be added to the regulus. To obtain this regulus as pure as possible, it is again fused with 500 grms. of zinc and some ammonium chloride, then granulated in water, and the granules dissolved in fuming hydrochloric acid. The acid attacks the regulus with the greatest energy, and the solution is complete in less than an hour. The zinc chloride can be used for the next operation.

The platinum metals are found at the bottom of the vessel, in the form of a finely-divided black powder, which is contaminated with zinc, and with traces of iron, copper, &c., from the latter. It cannot be purified with nitric acid, nor with aqua regia, for part of the platinum metals will thereby be dissolved, or, at best, so suspended in the fluid that filtration is impossible. If, however, the powder is treated with hydrocholoric acid, singularly enough, all the impurities are dissolved ; not only zinc and iron, but also lead and copper, dissolve readily with the generation of hydrogen. The explanation is readily found in electrical currents produced by the contact of the metals, the stream passing from the positive zinc, iron, &c., to the negative platinum metals, hydrogen being given from the latter, and chlorine from the former, and uniting with them. The metallic powder, after thorough washing, possesses the property, upon being gently heated, of exploding weakly, and, when highly heated, with violence, the explosion being accompanied with the evolution of light, although neither hydrogen, chlorine, nitrogen, nor aqueous vapour are given off; and, as these are the only elements which it is possible that the metallic powder could have taken up, it must be assumed that these metals are, by this treatment, converted into an allotropic condition, and that, upon heating, they return, with more or less energy, to their original condition. The powder contains, mainly, rhodium and iridium ; but there are traces present of platinum, palladium, lead, copper, iron, and zinc

It is intimately mixed with about 3 or 4 times its weight of completely anhydrous barium chloride, and a stream of chlorine gas led over it at a tolerably high temperature. The operation is concluded when particles of ferric chloride show themselves on the neck of the flasks containing the powder. These are carefully brushed away with filter-paper. Some water is now added, and the mass of the platinum metals dissolved with the evolution of heat. There remains behind insoluble matter, which, upon reduction with hydrogen, alloying with zinc, and treatment with hydrochloric acid, furnishes ruthenium. From the solution all the barium chloride is removed by careful addition of sulphuric acid. The platinum metals are now completely freed from all other metals by reduction with hydrogen, the temperature being, throughout the operation, maintained at nearly 100° C., by means of a constant water-bath. Platinum and palladium chiefly separate first; then mainly rhodium; and the last portions consist almost entirely of iridium. It is best to break off the operation when the fluid has assumed a greenish-yellow colour. The last portions of iridium (obtained by evaporating the solution to dryness, fusing with sodium carbonate, and treatment with aqua regia) are added to the portion, afterwards to be again rendered workable by renewed treatment with barium chloride. The operation of reduction is hastened by concentrating the fluid; in doing which care must be taken to guard against explosion, on account of the hydrogen. The separated metals are treated with aqua regia, and the platinum and palladium thus dissolved separated from each other as already described. The traces of rhodium and iridium in the mother liquid can be removed entirely by continued boiling with potassium iodide (whereby they precipitate as iodides); they are then dissolved in aqua regia and added to the insoluble portion.

This insoluble and partly-oxidised portion is now again reduced by hydrogen gas, treated, as before described, with barium chloride, and, after the removal of the barium, the last traces of platinum and palladium removed by boiling with caustic soda. Rhodium and iridium now alone remain to be separated.

The brown-red fluid is, for this purpose, evaporated with hydrochloric acid, and, after filtration, treated with sodium bisulphite in great excess, and the whole allowed to remain quietly in the cold for several days. The double rhodium and sodium sulphide separates slowly, giving a lemon-yellow precipitate. The solution becomes lighter and lighter, and finally almost colourless. The colour of the precipitate changes with that of the fluid, becoming, with it, lighter. This precipitate, upon washing, contains the rhodium almost pure.

Upon heating the fluid gently, a yellow-white precipitate separates, which consists mainly of rhodium, but contains also some iridium. After filtering off this precipitate, the solution, upon being concentrated to a small volume, gives yet two precipitates—

1. A curdy, slowly-separating, yellowish-white precipitate containing nearly chemically pure iridium, with but the faintest traces of rhodium.

2. A heavy, crystalline powder, quickly separating, which is readily freed from the first by decantation. Upon testing, it gives all the reactions for iridium, but likewise some peculiar reactions not shown by the latter.

The complete separation of rhodium from iridium is accomplished by treating the yellow precipitates with concentrated sulphuric acid. They are added in small portions to the acid, heated in a porcelain capsule until all the sulphurous acid has escaped, and then left upon the sand-bath until the free sulphuric acid has been driven off and sodium sulphate formed. Upon boiling the mass in water, all the iridium dissolves as sulphate, with a chrome-green colour, while the rhodium remains behind as a flesh-coloured double salt of sodium and rhodium. The latter is boiled in *aqua regia*, and washed by decantation. It is insoluble in water, hydrochloric or nitric acids, and in *aqua regia*. The rhodium and iridium are now completely separated.

The first yellow precipitate obtained in the cold by the sodium bisulphite gives, by this treatment, the rhodium quite pure. The second and third precipitates, containing much iridium, give a very fine rhodium, but still slightly contaminated with iridium. The products, therefore, obtained by this treatment with sulphuric acid (which betray their contamination with iridium by their somewhat brownish colour) are collected for themselves, the rhodium separated therefrom by glowing, treated again with barium chloride, and the operation of separation repeated. The green solution, containing only iridium, is gradually heated over an ordinary burner, in a porcelain capsule, and afterwards upon the sand-bath, to remove the excess of sulphuric acid; and, finally, the capsule and its contents are highly heated in a Hessian crucible. There is formed thereby sodium sulphate and iridium sesquioxide. Upon boiling the mass with water, the last remains behind as a black, insoluble powder, which is readily washed by decantation.

C. Lea's Process for Analysing Platinum Ores.—The ores on which these analyses were performed contained chiefly iridium, together with ruthenium, osmium, rhodium, and platinum. It was a Californian osmiridium which had already undergone a preliminary fusion with nitre and caustic potash.

This material is boiled with *aqua regia* to extract all the soluble portions, the residue then ignited with nitre and caustic soda,* and the fused mass heated with water. From the resulting solution small portions of potassium osmite crystallise out. The metallic oxides are next precipitated, and this precipitate, together with the portions insoluble in water. is boiled again with *aqua regia*, ignited again, &c. These ignitions still leave a small portion of unattacked residue.

The boiling with *aqua regia* is continued for a long time, in order to get rid as thoroughly as possible of the osmic acid. Even 200 hours boiling, however, still leave osmium in the solution in easily recognisable, but in comparatively small, quantity. The greatest advantage is found throughout the whole of this part of the operation from the use of a blowing apparatus, by the aid of which all inconvenience from the fumes of osmic acid is avoided. The apparatus is constantly swept clear by a powerful air current, and the osmic acid is removed as fast as it is volatilised. As the ignition of the ore with alkaline nitrate and caustic alkali scarcely drives off any osmium, and as almost all inconvenience in manipulating the resulting

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* Attention is necessary to the order in which these substances are employed. If the caustic soda is melted first, it attacks the iron vessel strongly, and may even go through. If added last it causes sudden and violent effervescence, with danger of boiling over. Therefore, place the nitre first in the vessel, and when it is fused add the caustic soda. When a red heat is obtained add the osmiridium by degrees.

solutions can be avoided by throwing down the metals with alcohol from the hot alkaline solution, in place of using acid, it is clear that the difficulties arising from the noxious effects of osmic acid can be almost wholly removed from each of the various stages of the process.

A very prolonged treatment with *aqua regia* is found to have the great advantage of converting nearly the whole of the ruthenium into bichloride. The separation of ruthenium in this form from the other metals is so easy in comparison with the difficulties presented by the separation of the sesquichloride, that this advantage cannot be looked upon as other than a very material one.

Sal-ammoniac is next added to the mixed solution in quantity sufficient to saturate it. The sandy crystalline precipitate (A) is thoroughly washed out, first with saturated, and then with dilute sal-ammoniac solution. The saturated solution of ammonium salt carries through with it nearly the whole of the ruthenium as bichloride (B); the dilute solution is found to contain small quantities of iridium, rhodium, and ruthenium (C).

Over (A), water acidulated with hydrochloric acid is placed, and allowed to stand for some days. This is treated with ammonia and boiled. The precipitate, when treated with hydrochloric acid, furnishes green osmium chloride, with traces of ruthenium.

In these preliminary steps, Claus's process has been followed, which undoubtedly offers advantages over any other, and best brings the metals into a convenient state for separation, varying it only by prolonging the treatment with *aqua regia*, and converting the ruthenium principally into bichloride instead of sesquichloride.

We have now three portions of material:—(A), consisting of ammonium iridiochloride, containing also ruthenium, osmium, rhodium and platinum in small quantities. (The ore under examination contained no palladium, which metal, if present, has always its own peculiar mode of separation, and does not enhance the difficulties of operation.) (B), containing ruthenium bichloride, together with iron in quantity, copper, and other base metals which may be present. Finally (C), containing chiefly ruthenium bichloride, mixed with small quantities of iridium and rhodium.

The next step in the process is to introduce the ammonium iridiochloride (A) into a large flask with twenty to twenty-five times its weight of water, and apply heat until the solution is brought to the boiling-point; the whole of the ammonium iridiochloride should be brought into solution in order that the reduction to be effected may not occupy too long a time, as otherwise the platinum and ruthenium salt, if any be present, might likewise be attacked. Crystals of oxalic acid are thrown in as soon as the solution actually boils, whereupon a lively effervescence takes place, and the iridium salt is rapidly reduced. As fast as the effervescence subsides, more oxalic acid is added until further additions cease to produce any effect. When this is the case, the liquid is allowed to boil for two or three minutes longer, not more; the heat is to be removed, and the flask plunged into cold water.

By this treatment any platinum present is unaffected. Sal-ammoniac in crystals is added, about half enough to saturate the quantity of water present. The sal-ammoniac may be added immediately before the flask is removed from the fire. After cooling, the solution should be left for a few days in a shallow basin, whereby the ammonium platinochloride will separate out as a yellow, a reddish, or even (especially if the quantity of water used was insufficient) as a black crystalline powder, according to the quantity of iridium which it may contain.

The mother liquor is to be again placed in a flask, and boiled with *aqua regia*. On cooling, the ammonium iridiochloride crystallises out, and any traces of rhodium and ruthenium which may be present remain in solution. The iridium salt is to be washed with a mixture of two parts of a saturated solution of sal-ammoniac and three parts of water, and may then be regarded as pure.

The treatment by oxalic acid affords iridium free from all traces of ruthenium.

The treatment of solutions (B) and (C) presents no difficulty. With (B) the best plan is to place the solution aside in a beaker covered with filter paper for some time. Treated in this way, the bichloride gradually crystallises out, and by re-crystallisations may be obtained in a state of perfect purity.

Solution (C) is to be evaporated to dryness, and reduced to an impalpable powder. It is then to be thrown upon a filter, and thoroughly washed with a perfectly saturated solution of sal-ammoniac. The ruthenium bichloride is thus carried through, with perhaps a trace of rhodium sesquichloride, from which, however, it is easily freed by crystallisation. From the residue, the rhodium and ammonium sesquichloride is removed by a dilute solution of sal-ammoniac, perfectly free from the iridium, which is left behind.

In connection with this separation, Mr. Lea makes a remark which, though of special reference to this particular case, is also applicable to all those cases in which the double chlorides of the platinum metals are to be separated by their various solubilities in solution of sal-ammoniac. This most valuable process, for which we are indebted, as for so much else, to Claus, whose untiring labours have made him the father of this department of chemistry, requires to be applied with some attention to minutiæ.

The crystalline matter must be reduced to the finest powder, and after being thrown upon the filter it must be washed continuously until the separation is effected. Any interruption of the washing is followed by more or less crystallisation of sal-ammoniac through the material, which precludes an effectual separation. The same material which in a state of coarse powder will hardly yield up enough ruthenium bichloride to colour the sal-ammoniac solution, will, when thoroughly pulverised, give an almost opaque blood-red filtrate.

Solution (C) may be subjected to a different treatment from the foregoing, and oxalic acid may be used to effect the separation. The solution is to be brought to the boiling-point, and oxalic acid added as long as effervescence is produced. The iridium bichloride is thereby reduced, the ruthenium bichloride and the rhodium sesquichloride are not affected. Sal-ammoniac is then to be dissolved in the solution to thorough saturation. By standing and repose the double rhodium and ammonium chloride separate out. The solution is then re-oxidised by boiling with *aqua regia*; by standing for some days in a cool place, the ammonium iridiochloride crystallises out, and the supernatant solution contains the double ammonium chloride and ruthenium bichloride, which may be rendered pure by several re-crystallisations.

For purifying the double iridium and ammonium chloride the oxalic process is decidedly the best. It is simple and less trouble, and there is the further advantage that the platinum is left in the condition of double chloride, whereas when the usual method of treating with aqueous sulphuretted hydrogen is used, the platinum is apt to be converted partly into sulphide, together with any traces of rhodium and ruthenium which may be present. When oxalic acid is used, the platinum remains behind as a reddish powder, containing some iridium, from which it may be freed in the ordinary manner, if it is present in quantity sufficient to be worth working.

For treating a mixture such as that which is here designated as (C), containing no platinum, and only ruthenium present in the form of ammonium rutheniochloride, it is unnecessary to apply reducing agents, and the first method described is the best. But if it be proposed to effect the separation by the reduction of the iridium compound, the method here described is preferable to that based on the use of sulphuretted hydrogen even in this case.

The action of oxalic acid on the platinum metals is interesting; its reducing effect upon iridium bichloride at the boiling-point is immediate. On ruthenium bichloride it seems to have no effect whatever, and they may be boiled together for a length of time without sensible result. In a trial made with ruthenium and ammonium sesquichloride, the oxalic acid was boiled with the metallic salt for a considerable time without any effect becoming visible, but by long-continued boiling a gradual precipitation took place. When ammonium platinochloride was boiled with oxalic acid, no effect was produced for a considerable time, but gradually the platinum salt diminished in quantity, and the liquid acquired a stronger yellow colour, perhaps owing to formation of soluble platinic oxalate. This process will not, however, furnish an easy and convenient method of purifying commercial platinum from the iridium always found in it, as the reduction of very small quantities of double iridium and ammonium chloride in the presence of a large proportion of the corresponding platinum salt is difficult and slow, and the platinum salt itself is evidently attacked.

The following method of Analysis of Platinum Ores, by MM. Deville and H. Debray, may be useful. The ores of platinum contain the following substances:—

1. Sand. The whole of the sand is never removed by washing the ore; and the sand contains quartz, zircon, chromate of iron, and, in the Russian ores, titanate of iron.

2. Osmiridium.

3. Platinum, iridium, rhodium, and palladium, combined, no doubt in the form of an alloy.

4. Copper and iron, which exist in the ores in a metallic state, for the iron found in the sand is not soluble in acids.

5. Gold, and, oftener than is supposed, a little silver. The latter metal is generally found with the palladium, and it is very rarely that palladium is obtained quite free from silver when it is prepared by the old processes.

1. *Sand.*—To estimate the sand we take a small assay crucible, or an ordinary crucible with smooth sides, and melt in it a little borax, so as to glaze the inside. We now introduce from 7 to 10 grammes of pure granulated silver, and 2 grammes of the ore fairly taken and weighed very accurately. Over the platinum we put 10 grammes of fused borax, and one or two small pieces of wood charcoal. The silver is now melted, and care must be taken to keep

it for some time a little hotter than the melting point, so that the borax may be very liquid, and may dissolve the vitreous matters which accompany the platinum and constitute the sand. The crucible is now allowed to cool, and when it is cold, the button, which will contain the silver, osmium, platinum, and all the other metals, is detached, and if necessary digested for a time with weak fluoric acid to remove the last portions of borax. It is now heated to a faint redness, and then weighed. The weight of the button, subtracted from the sum of the weight of the ore and silver employed, will give the amount of sand contained in the ore. For example:—

	Milligr.
Californian ore	2000
Silver	7221
	9221
After fusion, the button weighed . .	9162
Consequently, the ore contained, sand .	59

It is very important to know this number, for it represents the only matter absolutely destitute of value which the ore contains; and this simple operation may be considered the most important performed in estimating the value of an ore. It is, besides, performed so quickly, that it is as well to do at the same time two or three specimens, taken from different parts of a lot of platinum powder.

2. *Osmiridium.*—Another 2 grammes of the ore weighed very accurately are treated with aqua regia at 70° (Cent.) until the platinum is entirely dissolved. The aqua regia must be renewed occasionally for 12 or 15 hours, or until it is no longer coloured. It is best to perform this operation in a large beaker, and to place a cover over it to prevent loss. The solution must be decanted with the greatest care from the metallic spangles of the osmiridium and the sand which remain at the bottom of the beaker. If necessary it may be filtered, but as little as possible of the osmide must be allowed to go on the paper. The insoluble residue must be washed by decantation, then dried and weighed, after having added what remained on the filter. By subtracting the weight of the residue from the weight

of the sand obtained in the former operation, we obtain the weight of the osmiridium. For instance, in the Californian ore we had :—

	Milligr.
Osmiridium and sand	81
Sand	59
Osmiridium	22

The button obtained in determining the sand might be employed in this operation. In that case it is necessary to dissolve out the silver with nitric acid, and then proceed with the residue, as we have just directed.

3. *Platinum and Iridium.*—The solution in aqua regia obtained in the last operation is evaporated to dryness at a low temperature, and the residue is re-dissolved in a small quantity of water (if it should not entirely dissolve in the water, some more aqua regia must be added, and the evaporation repeated), to which is added about twice as much pure alcohol; lastly, we add a great excess of sal ammoniac in crystals. The whole is now slightly warmed to complete the solution of the sal ammoniac; it is then stirred, and afterwards set aside for 24 hours. The orange-yellow, or even reddish-brown, precipitate which is formed contains the platinum and the iridium, but some remains in the solution. The precipitate must be thrown on a filter and washed with alcohol. Afterwards the filter is dried in a platinum crucible, placed, for greater safety, within a larger one, and afterwards heated by degrees to low redness. The crucibles are now uncovered, and the filter is burnt at the lowest possible temperature. Once or twice after the incineration of the filter a piece of paper saturated with turpentine should be introduced into the crucible, by which means the iridium oxide will be reduced, and the expulsion of the last traces of osmium will be effected. The crucible is now heated to whiteness until it no longer loses weight, or the reduction is finished in a current of hydrogen.

The liquid separated from the platinum-yellow by filtration is evaporated until the ammonium chloride crystallises in great quantity. It is allowed to cool, is then decanted, and on a filter is collected a small quantity of a deep violet-coloured salt, which is the iridium ammonio-chloride mixed with a little of the platinum salt. This is first washed with a solution of sal ammoniac, and then with alcohol. The salt is then ignited, and if necessary reduced by hydrogen like the platinum salt. The mixture of platinum and iridium obtained by the two reductions is then weighed. The two metals are now digested at about 40° or 50° (Cent.) in aqua regia, diluted with about 4 or 5 times its weight of water—the aqua regia being renewed until it is no longer coloured. The residue is pure iridium. To obtain the weight of the platinum the weight of the iridium is subtracted from that of the mixture of the two. This method of separating the two metals is very accurate if the aqua regia used be weak, and the contact with it prolonged.

4. *Palladium*, *Iron*, *and Copper*.—The liquid charged with sal ammoniac and alcohol, from which the platinum and iridium have been separated, is evaporated to get rid of the alcohol, and then treated with an excess of nitric acid, which transforms the ammonium chloride into nitrogen and hydrochloric acid. It is now evaporated almost to dryness. The residue is removed to a covered porcelain crucible which is weighed with great care. When the matter is dry it is moistened with concentrated ammonium sulphide and afterwards dusted over with 2 or 3 grammes of pure sulphur. When dry this crucible is placed within a larger one of clay, and surrounded with pieces of wood charcoal. The two, covered, are now set in a cold furnace which is filled up with charcoal, and the fire is lighted at the top to avoid the projection of any matter from the crucible, if it were too quickly heated. After reaching a bright red heat, the crucibles are allowed to cool. The porcelain crucible now contains palladium in a metallic state, with the sulphides of iron and copper, and also the gold and rhodium. This mixture is moistened with concentrated nitric acid, which, after prolonged digestion at 70°, dissolves the palladium, iron, and copper, forming at the same time a little sulphuric acid. The solution of the

nitrates is poured off from the residue, which is washed by decantation, and the solutions and washings are evaporated to dryness, and then calcined at a strong red heat. In this way the palladium is reduced, and the iron and copper pass to the state of oxides, which are easily separated from the palladium by means of strong hydrochloric acid. The palladium remains in the crucible, in which it is again strongly ignited and then weighed.

The iron and copper chlorides are now evaporated to dryness at a temperature but little above 100° (Cent.) and are then treated with ammonia. The ferric chloride having lost nearly all its acid, has become insoluble ; but the copper chloride is readily dissolved, and may be filtered from the iron which is washed, ignited, and weighed. The copper solution is now evaporated almost to dryness, and then mixed with excess of nitric acid, and heated to drive off the ammonium chloride. Afterwards the copper nitrate is ignited and weighed. The weight of the copper is always so small that the hygroscopic water the copper oxide may absorb may be neglected.

5. *Gold and Platinum.*—The residue insoluble in nitric acid is weighed and treated with very dilute aqua regia which takes up the gold, and sometimes, but very rarely, traces of platinum. To ascertain if platinum be present, evaporate to dryness, and re-dissolve by alcohol and ammonium chloride. If any platinum-yellow remain, it must be ignited and weighed. The difference in the weight of the porcelain crucible before and after the treatment by aqua regia, gives the weight of the gold, from which, if any be found, the weight of the platinum must be deducted.

6. *Rhodium.*—The residue left in the crucible is rhodium, which must be reduced in a current of hydrogen.

We append the results of some analyses of platinum ores, by MM. Deville and Debray. (See Table on next page.)

M. A. Guyard gives the following process for the extraction of metals from platiniferous residues :—

‘ This process comprises three different operations, which I will succinctly describe.

‘ 1. *Solution of the Residues.*—The mother liquors which

ANALYSES OF PLATINUM ORES FROM VARIOUS SOURCES.

	Columbia	California	Oregon	Spain	Australia	Russia
Platinum . .	80·00	79·85	51·45	45·70	59·80	77·50
Iridium . .	1·55	4·20	0·40	0·95	2·20	1·45
Rhodium . .	2·50	0·65	0 65	2·65	1·50	2·80
Palladium . .	1·00	1·95	0·15	0·85	1·50	0·85
Gold . . .	1·50	0·55	0·85	3·15	2·40	(*)
Copper . .	0·65	0·75	2·15	1·05	1·10	2·15
Iron . . .	7·20	4·95	4·30	6·80	4·30	9 60
Osmiridium .	1·40	4·95	37·30	2·85	25·00	2·35
Sand . . .	4·35	2 60	3 00	35·95	1·20	1·00
Osmium and loss	—	0·05	—	0·05	0·80	2·30
	100·15	100·00	100·25	100·00	100·00	100·00

remain after the precipitation of platinum by sal ammoniac come from solutions of crude or commercial platinum. They always contain iron, mostly produced from the iron sulphate used for the precipitation of gold, lead, copper, palladium, platinum, and especially rhodium. These mother liquors are acidulated by hydrochloric acid, and are then ready to be investigated. To recall their composition, I shall distinguish them here only as residues in solution. It need only be mentioned that iron, which is generally used for the precipitation, must be avoided.

'Solid residues are melted at once with three times their weight of a mixture of equal parts of soda and sodium nitrate. The fusion is effected at a bright red heat in a thick iron vessel. It is accomplished without bubbling or projection, and requires about an hour. During the last twenty minutes the mass must be constantly stirred with an iron spoon. The operation is extremely simple.

'These residues contain osmiridium, unattackable by all chemical agents, attackable osmide, some grains of triple alloy of platinum, iridium, and rhodium, which aqua regia will not dissolve, but which nitre completely oxidises and completely breaks up. They also contain the gangue characteristic of platinum ores—quartz, silicates of all bases, titanates, hyacinths, &c., &c.

'The mixture I make use of oxidises all that is oxidis-

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* Gold, if any, counted in the loss.

able, and breaks up the gangue, which it partly dissolves. The melted mass contains all the bodies above mentioned, besides a large quantity of iron oxide taken from the sides of the vessel in which the operation is performed. The fused mass is poured into cast-iron moulds. When solid it is broken into fragments and boiled with sufficient water to obtain a strong solution of soda, capable of holding all the gelatinous acids in solution. It also contains osmium in the state of osmiate.* It is filtered from insoluble matter, and then supersaturated with hydrochloric acid. The insoluble oxides are freed by washing from the excess of alkali, and are then dissolved in aqua regia.

'This solution contains iron, copper, lead, iridium, rhodium, platinum, and ruthenium. It is separated from the undissolved osmide, evaporated to expel the excess of aqua regia, and dissolved in water and hydrochloric acid.

'2. *Precipitation of Liquids by Sulphuretted Hydrogen.*—Liquids obtained as above are ready for precipitation by hydrosulphuric acid.

'The apparatus in which all the liquids are precipitated is composed of a sulphuretted hydrogen gas generator by the action of sulphuric acid on iron sulphide. This generator communicates with four or five large earthenware jars, holding about seventy litres, arranged precisely as in Wolff's apparatus. A special tube conducts to each of them the vapour destined to heat the liquid which they contain.

'The whole apparatus is enclosed in a well-fitted wood stove placed near a chimney, with which it communicates. As to the small quantities of unabsorbed gas, they are conducted into the chimney, where the fire creates a strong draught. By this means, also, all smell is avoided during the precipitation; but after the operation air is forced through the apparatus from large gasometers. It expels the hydrochloric acid which saturates the mother liquors, and these can then be manipulated free from smell.†

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* This solution is separately precipitated by hydrosulphuric acid. Osmium sulphide is thus isolated.

† A carbonic acid generator may be substituted for the gasometers and the air with no difference in the result.

'The experiment is carried on during the precipitation in the following manner: when the generator begins to disengage gas, the temperature of the liquids is raised to about 70°. This temperature is maintained for nearly fifteen hours, that being the time required for the complete precipitation of the sulphides, which collect better under the influence of heat. The operation is concluded when there remains but a very slight yellow tint in the mother liquor, arising from the presence of a little soluble iridium sulphide. This mother liquor is poured from the precipitated sulphides into a vessel with pieces of iron, which takes off a little of the iridium. The sulphides are filtered through linen filters.

'3. *Purification and Treatment of the Sulphides.*—The mass of sulphides thus separated from the iron and from all other bodies not precipitated by the sulphuretted gas, contains, in addition to the sulphides of the platinum metals, a large proportion of sulphur and the sulphides of copper and lead. To get rid of these bodies, I have thought of concentrated sulphuric acid, which changes them to sulphurous acid and sulphates, while it does not act on the sulphides of the precious metals. This refining can be effected in an iron vessel; but Mr. Matthey, who neglects nothing to ensure the certainty and exactness of the results, makes use of platinum.

'When, after prolonged boiling, no more sulphurous acid is given off, the refining is complete.

'The mass of sulphides, diluted with a quantity of water, is thrown on filters, and thoroughly washed, until ammonia no longer shows any trace of copper or iron in the filtered liquid.

'At this point the precious metals are entirely freed from iron, which is so detrimental to them, and from copper, and contain only a little lead sulphate, which separates by itself during an ulterior reaction. They are then, moreover, in a condition to be dissolved by simple nitric acid or by *aqua regia*, and this is not their least valuable condition.

'*Treatment of the Sulphides.*—The sulphides are next dissolved in *aqua regia*, which should not be previously prepared, because its action on sulphates is sudden and energetic; it heats so rapidly, and the disengagement of gas is so great that, were it previously prepared, it would certainly be thrown from the vessels.

'I add then moderately strong cold nitric acid, and add it gradually, because its action is strong. A quantity of rutilant vapours are disengaged. Hydrochloric acid is added when the effervescence ceases. It is then gradually heated to boiling, which is necessary to obtain a complete solution.

'The solution is poured from the deposited lead chloride, and the ordinary method with sal ammoniac is used to separate the different metals it contains. Experiments on large quantities of material have fully proved the advantages of this process.'

Analysis of Osmiridium.—Wöhler's method of resolving osmiridium consists in passing moist chlorine over the ore mixed with common salt and heated to low redness in a glass or porcelain tube. This method is invaluable in analysis, and gives excellent results in working the ore upon a small scale. In all cases, however, several repetitions of the process are necessary for complete resolution or reduction to a soluble form. On the other hand, it can scarcely be doubted that this method could be advantageously employed upon the large scale, if vessels of porcelain of large size and of a proper shape could be obtained. Such vessels might be constructed in the form of long and flattened ellipsoids, furnished at each extremity with wide tubes several inches in length, and would be of great utility in various chemical processes. No process of fusion with oxidising agents compares with Wöhler's method in point of elegance, as no iron or other impurities afterwards to be removed are introduced by the process itself.

Claus's method of resolving the ore consists in fusing for an hour, at a red heat, a mixture of one part of ore with one part of caustic potash and two of saltpetre. The fused mass is to be poured out upon a stone, allowed to cool, broken into small pieces or powdered, and then introduced into a flask, which is to be filled with cold water and allowed to stand for twenty-four hours. The clear deep orange-red solution of potassium osmiate and rutheniate is then to be drawn off by means of a syphon, and the black mass remaining again washed in the same manner. The finely-divided oxidised portion of the insoluble matter may now be separated from the unattacked ore by diffusion in water and pouring off, after the subsidence of the heavier ore. The unattacked ore is then to be fused a second time with potash and saltpetre and treated as before. Claus asserts that he has been able in this manner to resolve the Siberian osmiridium completely in two operations.

Dr. Wolcott Gibbs, to whom the chemistry of the platinum metals is so greatly indebted, recommends the following process for the analysis of osmiridium:—The ore, which is usually very impure, is in the first place to be fused with three times its weight of dry sodium carbonate. The fused mass after cooling is to be treated with hot water, to remove all the soluble portions, and then the lighter portions are to be separated by washing from the heavy unattacked ore. In this manner the greater part of the silica and other impurities present may be removed. A previous purification of this kind is not indispensable, and may be omitted altogether when the ore is in plates or large grains; but it is very desirable when the ore is in fine powder, and greatly facilitates the subsequent action of the oxidising mixture. By cutting off the top of a mercury bottle a wrought-iron crucible is obtained, in which 600 grms. of osmiridium may be fused at one operation with potash and saltpetre as above. There is usually little or no foaming, and if any occur it may easily be checked by stirring with an iron rod. No sensible quantity of osmic acid is given off during the process, which with a little care is entirely free from danger. In this manner 1,500 grms. of ore have been worked up in a few hours in three successive operations. The fused mass is to be broken into pieces with a hammer, and placed in a clean iron pot. Boiling water, containing about one-tenth of its volume of strong alcohol, is then to be added, and the whole is to be boiled over an open fire until the fused mass is completely disintegrated. The potassium osmiate is, in this manner, reduced to osmite, while the potassium rutheniate is completely decomposed, the ruthenium being precipitated as a black powder. It is advantageous, after boiling for some time, to pour off the supernatant liquid with the lighter portions of the oxides, and boil a second time with a fresh mixture of alcohol and water. In this manner we obtain a solution of potassium osmite, a large quantity of black oxides, and a heavy black and coarse powder. This last consists chiefly of undecomposed ore, mixed with a small quantity of the iridium oxides, &c., with scales of iron oxide from the crucible, and, if the ore has not been previously purified, with the impurities of the ore itself. The greater specific gravity of this residual mass renders it very easy to pour off from it the mixture of black oxides with the solution of osmite of potash and alkaline salts. This solution with the suspended powder is to be poured into a beaker and allowed to settle. The heavy black powder remaining in the iron pot is then to be perfectly dried over the fire, and fused a second time with potash and saltpetre as before. The fused mass is to be treated exactly as after the first fusion. The heavy portions remaining after this operation may be fused a third time with the oxidising mixture. When, however, the ore has been previously purified by fusion with sodium carbonate, or when it was originally in the form of clean scales, the heavy portion remaining after two successive oxidations will be found to consist chiefly of scales of iron oxide.

The solutions containing potassium osmite and alkaline salts are to be carefully drawn off by a syphon from the black oxides which have settled to the bottom of the containing vessels. The oxides may then be washed with hot water containing a little alcohol, and introduced into a capacious retort. By this process, when carefully executed, no trace of osmic acid escapes—an advantage not to be despised, as the deleterious effects of this body upon the lungs have not been exaggerated, and too much care cannot be taken to avoid inhaling it.

The solution of alkaline salts contains only a portion of the osmium in the ore. The other portion exists in the mixture of oxide, and must be separated by distillation. For this purpose the retort should be provided with a safety-tube, passing through the tubulure, and with a receiver kept cold, and connected by a wide bent tube with a series of two or three two-necked bottles containing a strong solution of caustic potash with a little alcohol, and also kept cold. All the tubulures and connections must be made perfectly tight. Strong hydrochloric acid is then to be cautiously poured into the retort, through the safety-tube, in small portions at a time. The reaction which ensues is often violent; great heat is evolved, and a portion of the osmic acid distils over immediately, and condenses in the receiver in the form of colourless needles. When a large excess of acid has been added, the action has entirely ceased, and the retort has become cold, heat may be applied by means of a sand-bath. The osmic acid gradually distils over, and condenses in the receiver and in the two-necked bottles. Especial care must be taken that the beak of the retort is not too small at the extremity, as it may otherwise become completely stopped up with the condensed osmic acid. The same applies to the tubes which connect the receivers and two-necked bottles. The distillation should be continued for some time after osmic acid ceases to appear in the neck of the retort; when this has once become hot, the acid condenses, and passes into the receiver in the form of oily drops.

When the distillation is finished, the retort is to be allowed to cool, and then separated from the receiver, which is to be immediately closed with a cork. By gently heating the receiver in a water-bath, the contained osmic acid may be driven over into the two-necked bottles, where it condenses in the alkaline solution, and is reduced by the alcohol to potassium osmite. The solution thus obtained may be added to that obtained directly from the fused mass of ore, and on evaporation in a water-bath and cooling, will yield crystals of potassium osmite, the salt being but slightly soluble in strong saline solutions. The mother liquor from the crystals contains only traces of osmium, and may be thrown away as worthless.

The dissolved portions drawn off from the retort have a very dark brown-red colour. The solution is to be evaporated to dryness, re-dissolved in hot water and again evaporated, after adding a little hydrochloric acid, and this process repeated till no smell of osmic acid can be perceived. A cold and saturated solution of potassium chloride is then to be added in large excess. This dissolves the iron and palladium chlorides which may be present, leaving platinum, iridium, rhodium, and ruthenium as double chlorides, insoluble in a strong solution of the alkaline chloride.

The undissolved mass is to be well washed with a saturated solution of potassium chloride, which is preferable to sal-ammoniac. In this manner nearly the whole of the iron and palladium may be removed, while any insoluble impurities contained in the ore remain with the mixed double chlorides.

For the separation of osmium from the other metals of the group, the best plan seems to be the one which is universally employed, namely, the volatilisation of the osmium in the form of osmic acid.

Mr. Nelson W. Perry (' Engineering and Mining Journal ') proposes the following method for the assay of platinum alloys containing base metal, silver, platinum, gold, and osmiridium.

Charge, platinum alloy 200 milligrammes, pure silver 150 milligrammes, or sufficient to produce perfect cupellation (exact weight).

Wrap charge in sheet lead and cupel. Weigh button. Loss = base metal.

Flatten button, anneal, roll out thin, anneal again, and make into cornet as in gold bullion assay. Introduce cornet into parting flask and part with concentrated sulphuric acid. Wash, anneal, and weigh. Loss from previous weight = silver in original alloy + silver added for cupellation.

Alloy cornet with at least twelve times the amount of silver that there is platinum present, and as before, form cornet, and part first with nitric acid, sp. gr. 1·16, and then nitric acid, sp. gr. 1·26. Wash thoroughly, anneal in annealing cup, and weigh. Loss = platinum.

Treat residue with aqua regia, obtain gold by loss, the residue is osmiridium.

Time to complete assay in duplicate, 2 hours, 45 min.

The quality of the silver added should at least be sufficient, so that after the addition of the silver the alloy will be to the gold as 3 : 1.

As platinum and osmiridium add greatly to the infusibility of the compound, silver in sufficient quantity must be added to prevent 'freezing' and give a perfect cupellation. Any large excess over these requirements is to be avoided, first, because the residue, after parting, will in that case be non-adherent, and in a more or less fine state of subdivision, which may occasion loss in washing by decantation; second, the larger the button cupelled, the more difficult it is to obtain a good cupellation, and the greater loss of silver during the process. It may, for this reason, sometimes be necessary to use only 100 milligrammes of the alloy for assay instead of 200 milligrammes as above.

The cupellation should take place at a moderate temperature, until near the 'blick,' when the assay should be thrust back into the hottest part of the furnace to prevent 'freezing.' The button must remain in the muffle until *all* the lead is gone.

In parting with sulphuric acid boil for several minutes. In other respects this operation is identical with the gold bullion assay. Any large excess of silver over twelve times the amount of platinum in alloy is to be avoided, as it causes the residue, after parting, to be too fine and float, thereby occasioning loss in washing. Insufficient silver is even worse, as the platinum will then be only incompletely dissolved.

CHAPTER XIX.

THE ASSAY OF BISMUTH.

THE following varieties of bismuth ores are met with, but are somewhat rare:—

Native Bismuth.
Bismuth Oxide.
Bismuth Sulphide.
Bismuth Persulphide.
Cupriferous Bismuth Sulphide.
Plumbo-cupriferous Bismuth Sulphide.
Plumbo-argentiferous Bismuth Sulphide.

Native Bismuth possesses a tolerably bright metallic lustre; its colour yellowish-white, often iridescent. It fuses in the candle flame. It is generally found in small amorphous lamellar masses, yet it occasionally occurs in acute rhomboidal as well as cubical and octahedral crystals.

This substance does not seem to form veins by itself, but generally accompanies other minerals, particularly those of cobalt, nickel, arsenic, and lead.

To within a recent period the chief source of the commercial product has been native bismuth. But this limited source is becoming well-nigh exhausted, whilst the demand for this metal, especially in a great state of purity, is increasing every day. It has thus become a matter of necessity to look for fresh fields of exploration, for new deposits: and as bismuth ores of every description mixed up with other ores of various kinds are now used for the extraction of bismuth, the assay of this metal has lost some of its former simplicity. Mr. Hugo Tamm has done more than any metallurgist towards perfecting the assay of bismuth, and from his papers on this subject in the 'Chemical News,' Nos. 639 and 640, the following method of assay is condensed :—

Assaying of Bismuth Ores.—Whenever the ore to be tried is of a simple nature, is free from admixture with other ores, and contains bismuth in the metallic state, or in the state of sulphide, of oxide, or of carbonate, or, as sometimes occurs, consists of a mixture of oxide, carbonate, sulphate, and oxychloride, the assaying of bismuth is reduced to the very simple operation of mixing the ore with as fusible a flux as can easily be obtained, to which a reducing substance, generally charcoal powder, is added in proper quantity.

It is of course useless to lay down particular rules concerning the nature or the quantity of the flux, and of the reducing substance to be employed in this operation; indeed, it is not advisable to do so, and it is by far the best to be guided by the nature of the materials at hand, and by the results of a few trials with varied proportions of flux and of the reducing agent; the aim of the assayer being the highest amount of metal that can be obtained in a given instance. Still, one of the best fluxes, as well as one of the most simple, consists of a mixture of two parts of potassium or sodium carbonate, and one part of sodium chloride, to which a proper amount of red argol or of potassium cyanide on the small scale, and powdered charcoal on the large scale, are added.

Assaying of Bismuth in Ores containing a large amount of Copper.—The problem of the direct separation of bismuth from ores containing large proportions of copper has hitherto been one of difficulty, and its solution, which was of considerable importance, offered great interest. The difficulty consisted chiefly in the fact that both copper and bismuth behave, in nearly every instance, in an identical manner with docimastic reagents; but Mr. Tamm has happily hit upon a most simple and practical means of effecting the direct separation of those two metals.

The chief kinds of ores containing both bismuth and copper are the bismuth-copper pyrites or sulphuretted ores, and the double bismuth and copper oxides or carbonates, or oxidised ores.

Both kinds of ores may be, and generally are, contaminated with other metals, but these foreign metals constitute only, as a rule, a small fraction of the whole, and the problem of their elimination will be given further on.

The reaction upon which the separation of bismuth from copper is founded consists in the fact that, in presence of alkaline fluxes, carbonaceous reagents, and, of course, among them carbon itself, reduce bismuth sulphide to the metallic state, while copper sulphide is not reduced.

In the treatment of sulphuretted ores, both metals being already in the state of sulphides, all that is required is to run them down with a mixture of potassium carbonate or soda, and salt, to which a little flowers of sulphur or ground sulphur, and charcoal or any other carbonaceous substance, are added.

In this operation metallic bismuth is extracted quite easily, and the metal thus obtained is tolerably free from copper. It is recommended to add a little sulphur in order to insure a complete sulphurisation of copper during the whole of the operation, and especially to prevent any desulphurisation of copper by the alkali, and, consequently, to prevent, as much as possible, this metal from being reduced.

With oxidised ores the operation is very similar in every respect to the one just described, and it differs from it only in the amount of sulphur used, which is greater in this instance, since the whole of the metals have to be sulphurised.

Three parts of the ore are mixed with from two to three parts of a flux composed of:—

Sodium carbonate	5 parts
Salt	2 „
Sulphur	2 „
Charcoal powder	1 „

Both the composition of the flux and the amount to be used may be altered with advantage to suit each particular case. A few synthetical trials, in the hands of a person accustomed to metallurgical operations, are all that are required to make the best use of this reaction.

In general, it is to be observed that the amount of flux and of reagents required for the assaying may be considerably *reduced* when the operation is carried on on a larger scale. On the other hand, it is scarcely worth while mentioning that, in the operation of assaying, potassium cyanide forms an admirable substitute for carbon.

During the process of extracting bismuth by means of sulphur and carbon there is a loss of about 8 per cent. of the bismuth contained in the ore. This loss is unavoidable, but there is a more than proportionate loss of the metals arsenic, antimony, and lead, which in this operation are reduced with bismuth, and the crude metal obtained by this process is not so impure as the corresponding metal obtained by the direct reduction of the oxidised ores; besides the whole of the copper remains in the slag.

Whenever the sulphur-carbon process is employed, the use of iron stirrers must be carefully avoided, for the reason that copper sulphide is rapidly reduced to the metallic state by this metal, especially in the presence of alkalies.

This process for the separation of bismuth from copper will be found chiefly useful and important for the separation of bismuth in minerals containing large quantities of copper. When, on the contrary, this metal exists only in smaller proportions, it is more advantageous to run down the whole of the metals, and to separate them afterwards in the special operations of refining. But it is recommended that the sulphur-carbon process be used for the treatment of the somewhat abundant ores of bismuth formed of bismuth and lead oxides, and small proportions of arsenious acid and antimonious acid, with a little copper oxide; for there is as yet no direct means of smelting pure bismuth from ores containing large proportions of lead, but it has been observed that bismuth extracted by the sulphur process contains less lead than the corresponding metal obtained direct from the oxidised ore. The same remark applies to arsenic and antimony, and this is in accordance with the behaviour of the sulphides of these metals with alkaline sulphides.

Refining Crude Bismuth.—The various ores of bismuth above described, whether sulphuretted or oxidised, are seldom formed of bismuth and iron only, or of only bismuth, copper, and iron. They nearly always are contaminated by various proportions of lead, arsenic, or antimony, metals which are reduced with bismuth, partially at least, whatever process has been used for the extraction of bismuth, and besides, the metal obtained by the sulphur process from copper bismuth ores still contains a small quantity of copper, which it is important to remove.

Bismuth extracted by any process is so generally free from iron that no notice need be taken of this metal, which remains wholly in the slags.

The fracture of good bismuth and that of its various alloys is so characteristic that it is not often necessary to have recourse to tests in order to determine what particular processes will have to be used for the refining of the crude metal.

Pure bismuth is tougher than most of its alloys. Its fracture is bright, and it possesses a fine reddish colour. Bismuth containing arsenic gives a beautiful fracture consisting of large laminæ of a whiter colour than that of pure bismuth. Copper mixes with bismuth without alloying with it, and is almost always discernible. The fracture of bismuth containing antimony is dull and is mostly composed of very small crystals. Lead does not prevent bismuth from crystallising in large crystals, but these crystals are studded all over with fine crystals. Sulphur imparts a black tinge to metallic bismuth.

To these appearances, which almost suffice to an experienced eye, may be added a few simple tests.

It is difficult to detect arsenic in the presence of a large quantity of bismuth by means of reagents, and the most simple way of detecting this substance is to heat the bismuth on charcoal, with the oxidising flame of the blowpipe. Very small quantities of arsenic may be detected by the garlic odour evolved.

To detect copper the metal is dissolved in nitric acid, the solution is supersaturated by ammonia, and filtered. The blue colour of the filtrate indicates the presence of copper.

When bismuth dissolves in strong nitric acid, with the formation of a cloudy white precipitate which does not disappear on the addition of water, it is because antimony is present.

When bismuth dissolves in strong nitric acid, with the formation of a very white granular or crystalline precipitate which dissolves freely on the addition of water, the presence of lead is indicated.

But to detect with absolute certainty the presence of even very small proportions of lead, the metal is dissolved in nitric acid. The solution is supersaturated with ammonia, and re-acidulated with the smallest amount of hydrochloric acid which will give a clear liquor. This liquor is then precipitated by a large excess of boiling water. Water must be added until no further precipitation takes place. The whole is then filtered, and the filtrate is saturated with a mixture of ammonia and ammonium carbonate; when a yellowish-white precipitate is formed it is because lead exists in the bismuth.

It may be useful to submit the metal to be refined to these various tests in order to ascertain beforehand which refining process should be used. But it is essential to apply each test to the refined metal, so as to verify its degree of purity.

PURIFICATION OF THE REDUCED BISMUTH.

Purification of Bismuth from Arsenic.—The separation of bismuth from arsenic is founded on the almost absolute want of affinity of bismuth for iron, on the readiness with which arsenic combines with iron, and on the fact that the iron arsenide thus formed does not alloy with bismuth. This operation is conducted in the following manner:—

Bismuth is melted at a relatively high temperature, at a bright red heat, under cover of borax or flux, to avoid loss of bismuth by volatilisation, and strips of iron are plunged into the molten metal. Iron is, according to the technical expression, rapidly 'eaten away,' forming iron arsenide, which rises to the surface of the metal.

When it is ascertained that fresh pieces of iron are no longer attacked, the whole is allowed to cool. The iron arsenide sets rapidly, and the bismuth, which is still fluid, is poured out of the crucible into moulds. Singularly enough, this process, which succeeds in perfection for the separation of arsenic, is valueless when applied to the separation of bismuth from antimony; although, be it noticed, the affinity of this metal for iron is very great. Some antimony is removed by this process, but part of it only, and it must be admitted that bismuth has as much, or more, affinity for antimony than iron.

Purification of Bismuth from Antimony.—The best way of separating the two metals is to melt the alloy with a quantity of bismuth oxide, equal to two and a half or three times the weight of the antimony contained in the alloy. The bismuth oxide is instantaneously reduced to the metallic state, and antimony is liberated under the form of antimony oxide, which combines with a little bismuth oxide, and floats on the surface of the pure metal, whence it can easily be removed.

This operation must be performed in clay crucibles, and both carbon and iron must be carefully excluded, to avoid any reduction of antimony oxide. The least traces of antimony may be removed by this process without any difficulty whatever.

Purification of Bismuth from Copper.—When bismuth ores contain only a small percentage of copper, and when the ores are oxidised ores, it is advantageous to reduce them at once by carbon and fluxes, without going through the sulphurising process; and, as a matter of course, all the copper is alloyed with the bismuth.

On the other hand, bismuth extracted from copper ores by the sulphur process contains, even in the best conducted operation, a certain proportion of copper which must be removed. This elimination has hitherto presented very great difficulties, and could not be effected without losing a large amount of bismuth. Mr. Tamm has, however, devised the following method, by melting the alloy with potassium sulphocyanide.

The sulphocyanide is prepared during the process of refining, by mixing together eight parts of potassium cyanide and three parts of flowers of sulphur. One part of this mixture is thrown on to sixteen parts of the metal melted at a low temperature.

A reaction soon takes place, by which the mass of the metal is brought to a bright red heat, and, at the same time, the sulphocyanide begins to burn vividly, throwing, in every direction, showers of scintillating sparks emitting a blue light.

The crucible is covered over, and great care must be taken to prevent the heat from rising above the burning point of the sulphocyanide, a temperature at which bismuth sulphide begins to volatilise.

The reaction is allowed to exhaust itself, and, when all is quiet, and after the metal has been well stirred with a clay stirrer (iron must be avoided), the flux is allowed to set, and the metal, which is still fluid, is poured out into moulds.

Purification of Bismuth from Sulphur.—The metal obtained in the above operation contains some sulphur. To remove this substance, the metal is melted with iron or carbon; the separation is thus effected easily.

The several processes here proposed are chiefly useful for the refining of bismuth alloyed with one metal.

There is no dry method of refining by one process bismuth alloyed with several metals; but the successive use of these different methods can safely be recommended.

Copper should be removed first, for the reason that some lead, antimony, and arsenic are eliminated at the same time.

Bismuth should next be freed from antimony, and, lastly, from arsenic and sulphur.

Herr Thürach ('Journal für Prakt. Chemie,' P. S. 14, 315) precipitates with sulphuretted hydrogen from a hot solution, washes with hot water, heats for a considerable time to 200–300° in a covered crucible, roasts in the open crucible, and finally ignites strongly and weighs as bismuth oxide.

VOLUMETRIC ASSAY OF BISMUTH.

Mr. R. W. Pearson has given the following process for the Volumetric Assay of Bismuth.

Preparation of Standard Solution.—·7135 grain of pure crystallised potassium bichromate is dissolved in 100 grains of water. Call this solution the bichrome test A. In a similar way, prepare a second solution, one-tenth the strength of bichrome test A; ·07135 grain of potassium bichromate dissolved in 100 grains of water, will furnish such a solution; call it the bichrome test B. Bichrome test C, one-tenth the strength of solution B, is also prepared by dissolving ·007135 grain of the potassium bichromate in 100 grains of water.

These figures can be multiplied to any convenient number. These solutions will contain potassium bichromate, in 100 grains of bichrome test A, equal to 1 grain of bismuth; in 100 grains of bichrome test B, equal to 0·1 grain of bismuth; and in 100 grains of bichrome test C, equal to ·01 grain of bismuth.

The bismuth should be in the form of nitrate, and the solution kept hot during the experiment, as the precipitated chromate collects more readily then; after complete precipitation of the bismuth the solution will exhibit a characteristic colour, produced by excess of the bichromate of potash.

By employing a standard solution of bismuth it has been ascertained that 71·35 parts of potassium bichromate are required to combine with 100 parts of bismuth.

For alloys of tin, lead, and bismuth (fusible metal) the alloy, finely divided, is oxidised in a roomy flask with nitric acid, the liquid is somewhat diluted, supersaturated with ammonia, and digested for a long time and with frequent agitation with ammonium hydrosulphide, to which a little sulphur has been added. The tin is thus dissolved as sulphide. The lead and bismuth sulphides are filtered off and washed with cold water. The liquid containing the tin sulphide is slightly supersaturated with dilute sulphuric acid and very gently warmed, the vessel being loosely covered with paper till the odour of sulphuretted hydrogen has disappeared. The yellow tin sulphide is washed on a filter with cold water, and treated as directed for the analysis of tin ore.

The lead and bismuth sulphides are dried, detached from the filter, which is incinerated with the usual precautions, the whole digested with nitric acid, and the solution concentrated at last with the addition of hydrochloric acid till it is reduced to a small bulk, and the greatest part of the lead is separated as chloride. The proportion of acid must be so large that the liquid is not rendered turbid by a slight addition of water. Sulphuric acid is added, and the whole let stand, but with frequent stirring. After the lead chloride has been converted into sulphate a little alcohol of 0·80 sp. gr. is added, and the whole brought upon a weighed filter, where it is washed, first with alcohol acidulated with hydrochloric acid, and afterwards with water.

In the filtrate all the bismuth is precipitated as basic chloride by the addition of water in large excess, and filtered off (the filtrate being tested with sulphuretted hydrogen), washed with cold water, dried, and melted at a moderate heat with four parts potassium cyanide in a covered porcelain crucible (Rammelsberg).

Mr. M. Patteson Muir (‘Chem. News,’ April 27, 1877) finds the following solution a most sensitive test for bismuth:—12 grms. crystalline tartaric acid, and 4 grms. stannous chloride are dissolved in caustic potash, producing a clear liquid of a decidedly alkaline reaction, which should remain clear at 60° to 70° C. To the liquid to be tested is added a considerable quantity of tartaric acid. It is warmed and made alkaline with caustic potash. A few c.c. of the stannous chloride solution (called from its first discoverer Schneider's reagent) are added, and the liquid warmed to 60° to 70° C. for a few minutes. If bismuth is present to the extent of one part in 210,000 parts, a brownish-black colour is produced. Mercury must be absent; copper and manganese interfere slightly.

CHAPTER XX.

THE ASSAY OF CHROMIUM.

The principal ore of this metal which occurs in commerce is known as chrome iron, or chrome iron ore. It is found in amorphous masses of a brownish-black colour, approaching an iron grey. Its fracture is uneven, sometimes lamellar; and its powder is greyish.

The two following analyses will give a general idea of its composition:—

Chromium oxide	36·0	43·7
Ferric oxide	37·0	34·7
Alumina	21·5	20·3
Silica	5·0	2·0
	99·5	100·7

Assay of Chrome Iron Ore.

Chrome iron ore, like native tin oxide, is very difficultly decomposable by ordinary reagents.

Dr. Genth, of Philadelphia, who has had much experience in the analysis of chrome-iron ore, gives the following process; it is very trustworthy, although long and somewhat tedious.

Of the chrome ore, reduced to an impalpable powder, put 0·5 gramme in a platinum crucible about 2 inches high, nearly 1¾ inch wide, and holding 52 grammes of water, and place upon it 6 grammes of pure fused potassium bisulphate, and heat with the greatest care for about 15 minutes, at a temperature scarcely above the fusing point of the bisulphate; then the heat is gradually raised, but not higher than to make the bottom of the crucible red hot, and kept at this temperature from 15 to 20 minutes. Never permit the mass to rise to half the height of the crucible. (If the fusion with potassium bisulphate is done too rapidly a portion of the analysis is very apt to be lost by spattering, from the escape of sulphurous acid, resulting from the oxidation of the ferrous oxide by the sulphuric acid.) The mass begins now to fuse quietly, and vapours of sulphuric acid go off more freely; it should then be kept at a red heat for about twenty minutes, and the heat next raised as high as necessary to drive off the second equivalent of sulphuric acid, and even to decompose a portion of the iron and chromium sulphates. To the fused mass add about three grammes of pure sodium carbonate, and fuse the mixture, and then, by degrees, keeping the temperature for about one hour at a dull red heat, about the same quantity of saltpetre; next heat for fifteen minutes at a bright red heat. The fused mass is dissolved in boiling water, filtered whilst boiling, and washed with boiling water.

The insoluble residue, containing the greater portion of the silicic acid, titanic acid, and alumina, the ferric oxide, zirconia, and—if the fusion has been conducted at a temperature sufficiently high to convert the saltpetre into caustic potash, and the above precautions have been used—all the magnesia, is re-dissolved in dilute warm hydrochloric acid, which generally dissolves it readily and completely, and rarely leaves undecomposed ore behind; but if so, this residue must invariably be fused in a small crucible as before, adding, after the separation of the insoluble portion, the solution containing the small quantity of chromic acid to the first filtrate. (The certainly less troublesome method, to deduct the insoluble portion from the original weight, is bad; such residues have never the composition of the original ore.) The filtrate contains the whole quantity of the chromium as chromic acid, sometimes a trace of manganic acid, small quantities of silicic acid, alumina, and rarely titanic acid. To this solution add an excess of ammonium nitrate, and evaporate over a water-bath nearly to dryness, and until all the liberated ammonia has been expelled. The precipitate, remaining on addition of water, contains the silicic acid, titanic acid, alumina, and manganic oxide, which had gone into solution with the chromic acid; it is filtered off, and the filtrate made strongly acid with sulphurous acid, carefully heated to boiling, precipitated with a slight excess of ammonia, boiled for a few minutes, and filtered. Dr. Genth says he formerly acidulated the chromic acid solution by hydrochloric acid and then added sulphurous acid, but he several times observed that, although an excess of sulphurous acid had been used, a small portion of the chromic acid escaped reduction, the filtrate from the ammonia precipitate being yellow. He has in vain tried to find the reason for this singular behaviour. Since using sulphurous acid only, he has never been troubled with anything similar.

It is exceedingly difficult to wash out the chromic oxide; it succeeds best in the following way:—After the precipitate has settled, the clear liquid is passed through the filter, then boiling water is added to the precipitate, and after settling, the supernatant liquid is filtered; the precipitate then is put on the filter, and washed twice or three times with boiling water; it is then washed back again into the dish and boiled with water until the little lumps which clog together are completely broken up, and it is then filtered again, and this operation repeated until the wash-waters do not show the presence of any sulphates when tested with barium chloride. The precipitate is then dried and burned. No matter how well it may have been washed, it almost invariably contains minute quantities of alkalies, in the presence of which a little chromic oxide is converted into chromic acid. The ignited precipitate is therefore put into a dish, boiled with water, a few drops of sulphurous acid added, precipitated by ammonia, filtered, washed, dried, ignited, and weighed.

n this manner the chromic oxide is obtained quite pure, and repeated analyses of the same sample of ore never vary 0·25 per cent. of chromic acid.

Mr. O'Neill uses a volumetric method to estimate the chromic acid, depending upon the capability of sulphurous acid to deoxidise chromic acid at the ordinary temperature in the presence of free sulphuric acid. Prepare a strong solution of sodium bisulphite, by passing sulphurous acid through caustic soda to saturation, and then make it alkaline with caustic soda, so as to have a neutral sulphite, which is less readily oxidised by keeping than the bisulphite. Use a dilute solution made from this concentrated sulphite, of such a strength that one grain of pure potassium bichromate requires about, and not less than, 200 grains measure of the sulphite to deoxidise it. The value of the sulphite must be determined for every operation, since it is continually absorbing oxygen. This is done twice by weighing out three grains, and four grains of pure bichromate, dissolving each of them in ten ounces of water and acidulating freely with sulphuric acid, then adding the sulphite from the burette, with continual stirring, until the chromic acid is destroyed. The stopping-point may be ascertained by the colour when one is accustomed to the reaction, but even an experienced eye will often be glad of additional evidence. A mixture of potassium iodide and boiled starch, slightly acidulated, forms a delicate test; it has usually a faint colour, which is even preferable to a colourless mixture. An exceedingly small quantity of chromic acid developes the blue colour in spots of this mixture, and a very slight excess of sulphite makes it colourless. One division of the sulphite test-liquor, or 0·05 grain of potassium bichromate in twelve ounces of water, easily and quickly influences the test mixture. The chromate from the chrome ore is tested in the same manner, and the quantity of chromium oxide or chromic acid calculated from the equivalents of potassium bichromate. The tenth of a grain more than five is taken to allow for all losses, and the results are multiplied by twenty for the percentage. 151 of potassium bichromate is reckoned equivalent to 80 of green oxide of chromium, and 104 of chromic acid. A determination can be made by this process in three or four hours, and a double determination in a little longer time.

Dr. Wolcott Gibbs has shown that chrome-iron ore may be completely resolved by fusion with fluohydrate of potassium fluoride. In this and in all similar applications of the fluohydrate it is best to evaporate the finely-pulverised mineral to dryness with a concentrated solution of the salt. On subsequently heating to low redness, the resolution of the mineral is effected with the utmost ease, a portion of the chromium being usually oxidised to chromic acid by the oxygen of the air. After expelling the fluorine by heating the fused mass with sulphuric acid, the remaining mass is dissolved in water, rendered nearly neutral by a solution of sodium carbonate, and sodium acetate is added in excess. A current of chlorine gas, or a solution of chlorine water, then readily converts the whole of the chromium present into chromic acid, especially when the solution is hot, and when it is kept nearly neutral by the occasional addition of sodium carbonate. The excess of chlorine is easily got rid of by boiling.

The iron and alumina may then be precipitated together by boiling the solution in the presence of excess of sodium acetate. It is more convenient and equally accurate to neutralise the solution with ammonia, separate the ferric oxide by filtration, and determine the chromium in the filtrate by reduction and precipitation with ammonia.

For the technical determination of chromium in chromite, Mr. Clarke fuses with cryolite and potassium bisulphate. The mass is then treated with a little strong hydrochloric acid, and allowed to digest for about ten minutes. Then upon boiling with water, the whole dissolves. The solution should then be neutralised, sodium acetate added, and the chromium oxidised to chromic acid by a current of chlorine gas, or by boiling with sodium hypochlorite solution. The chromium may then be separated from other substances, as directed by Dr. W. Gibbs. When chromite is fused with potassium bisulphate and cryolite, and saltpetre is added to the mass, as soon as clear fusion is obtained, the chromium is nearly all oxidised to chromic acid. If the mass be boiled with a solution of sodium carbonate, and the liquid filtered, a filtrate is obtained which contains nearly all, but not quite all, the chromium as alkaline chromates, free from iron or alumina;

but invariably the residue upon the filter contains traces of chromium. When chromite is fused with the acid potassium fluoride, a part of the chromium is usually oxidised to chromic acid by the oxygen of the air; and in one case that came under Mr. Clarke's observation, when he heated the resulting mass with sulphuric acid, red fumes were given off, which were probably the so-called chromium terfluoride.

When potassium bisulphate *alone* is used for the decomposition of chromite, &c., it is necessary that the mineral should be reduced to extremely fine powder; but when the mixture of bisulphate and fluoride is employed, although the mineral should be in fine powder, such an extreme state of subdivision is by no means required, and thus much labour is saved.

Determination of Chromium by means of Standard Solution.—This process is the converse of the determination of iron by means of solution of potassium chromate.

The chrome ore is treated with potassium nitrate and sodium carbonate, as above described; and the solution of potassium chromate so obtained has an excess of hydrochloric acid added to it.

It is stated at page 321, under the head of Iron Assay by Standard Solution, that 100 parts of metallic iron correspond to and are represented by 88·6 grains of potassium bichromate. Now 88·6 grains of potassium bichromate contain 32·96 grains of chromium; therefore 100 grains of iron are equal to 32·96 of chromium. From these data a standard solution can be readily made: thus—Dissolve 50 grains of harpsichord wire in excess of hydrochloric acid; place the solution in a burette, and fill up to 100 on the instrument with water, and well mix: it is now evident that every division of the burette will equal or represent ·1648 grain of chromium. The assay is now thus proceeded with:—Gradually add the standard solution of iron to the solution of potassium bichromate acidulated with hydrochloric acid, until a drop of the solution mixed with a drop of solution of potassium ferrocyanide gives a pale blue colour: a slight excess of ferrous oxide is then present, showing that all the chromic acid has been reduced to the state of chromium oxide. Now observe how many divisions of the iron solution have been required, and multiply them by ·1648: the resulting number will represent the amount of metallic chromium in the sample submitted to assay.

For the determination of chromium in iron and steel Mr. J. O. Arnold ('Chem. News,' Dec. 10, 1880, p. 285) weighs out from 1 to 5 grms. of steel (in drillings) according to the amount of chromium present (this may be ascertained by a rough colorimetric test). Place the metal in a wide, covered beaker, and add 20 c.c. of strong hydrochloric acid; heat till all action is at an end; rinse the cover and sides of the beaker from splashings, and evaporate the solution *gently* to complete dryness. If the evaporation has not been too rapid, the chlorides may be almost entirely detached from the bottom of the beaker in a brittle cake. This is broken up into small pieces by means of a platinum spatula, and as much as possible is brushed out into a clean dry porcelain dish. A small quantity of the chlorides will, however, remain adhering to the beaker; this may be removed with 2 or 3 c.c. of dilute hydrochloric acid. The solution is poured into a deep platinum crucible, the beaker rinsed with 1 or 2 c.c. of water, the washings added to the crucible, the contents of which are now evaporated to dryness on a sand-bath. When dry the main quantity of the chlorides is carefully brushed out of the porcelain into the platinum dish, and is reduced to a fine powder by means of a little pestle made from glass rod. The spatula and pestle are cleaned into the crucible. The finely-divided chlorides are now thoroughly mixed with an excess of fusion mixture (1 part dry sodium carbonate to 1 part powdered nitre), a cover is placed over the crucible, and its contents are fused over a gas blowpipe till quite liquid. By this treatment the iron is converted into insoluble oxide, the manganese, silica, and chromium respectively into alkaline manganate, silicate, and chromate. When cool the crucible is placed in a beaker containing 80 c.c. of boiling water, and is gently boiled till the fused mass is detached and dissolved out. This may be assisted by occasional stirring with a glass rod. When clear from oxide, remove the crucible and cover, washing them well with hot water. Add 3 or 4 drops of alcohol to decompose the manganate, and allow the iron and manganese oxides to settle thoroughly. When the supernatant liquid is quite clear it is decanted on a close double filter, the filtrate being received into a clean beaker. The precipitates are disturbed as little as possible. When all the clear liquid has passed through, the filter is well washed with hot water. The precipitates are now washed twice by decantation with 30 c.c. of hot water; at the second washing the contents of the beaker are allowed to drain *gently* into the filter, which is now allowed to drain thoroughly, and is removed without further washing. These precautions in washing must be strictly carried out, as the ferric oxide is in such an exceedingly fine state of division that any attempt to wash or disturb it on the filter will inevitably cause some of it to pass through into the chromium solution. The *clear* yellow filtrate contains chromium and silica, to it is added 20 c.c. of hydrochloric acid, the cover being kept on the beaker, to prevent the projection of the solution by the evolved carbonic acid. The solution is now well boiled until all the carbonic acid and nitrous fumes are driven off. Its colour will now be green, owing to reduction to chloride. Dilute ammonia is added until alkaline, and the solution heated nearly to boiling. The resulting precipitates consist of chromium silicate mixed with alkaline salts. It is collected on a filter (previously well washed with hot dilute hydrochloric acid to free it from iron), and is slightly washed. When the washings have drained through, the precipitate is dissolved off the filter with hot dilute hydrochloric acid, the filtrate being received into the beaker in which the precipitation took place. The solution is now evaporated to dryness to render the silica insoluble. The soluble is taken up with 10 c.c. hydrochloric acid and 90 c.c. of water, and is filtered through a washed filter into a clean beaker, the filter being well washed. The precipitation is now repeated as above, and the chromic hydrate comes down free from silica and alkaline salts. It is collected, washed, dried, ignited, and weighed as chromic oxide.

Precautions.—Only three or four drops of alcohol should be added, as this quantity is sufficient, not only to precipitate the manganese, but also to effect the reduction to chloride. If too much is added organic compounds are formed, which tend to prevent the complete precipitation of the hydrate. The ammonia in the last precipitation should be added in the least possible excess, and the solution should be heated gently *nearly* to boiling. If any great excess of ammonia be present, and if the solution is boiled, the glass of the beaker is attacked and the result is high. The method, if properly carried out, is accurate.

Mr. W. J. Sell has devised the following method for the volumetric estimation of chromium. The solution, containing chromium acidified with sulphuric acid, is boiled, and a dilute solution of permanganate added to the boiling liquid until a purplish tint remains after boiling for three minutes. The solution is then rendered slightly alkaline with sodium carbonate, alcohol is added, and the manganese filtered off. The chromic acid in the filtrate is estimated by titration with iodine and sodium hyposulphate. The author has successfully applied the method to the estimation of chromium in chromic iron ore. He recommends the following plan of effecting its decomposition. The chromic iron ore is placed on the top of about ten times its weight of a mixture, composed of one molecule of well-fused and powdered sodium bisulphate to two molecules of sodium fluoride, and the whole is ignited for fifteen minutes. An amount of sodium bisulphate is now added equal to that of the mixture taken, and when thoroughly fused a further addition of an equal quantity of bisulphate is made, the mass fused, and then rapidly cooled. The fused mass so obtained dissolves completely in boiling water acidified with sulphuric acid. In this way a determination can be made in an hour and a quarter.

Dr. R. Kayser ('Zeitschrift für Analytische Chemie,' 1876, p. 187) mixes one part of the finely-powdered ore, preferably elutriated with two parts pure soda-ash and three parts hydrate of lime, the latter ingredient prepared by treating calcined marble with water till it falls to powder. The mixture is heated to bright redness for an hour in an open crucible, stirring frequently.

CHAPTER XXI.

THE ASSAY OF ARSENIC.

THE minerals from which arsenic is produced are the following :—

Native arsenic.
Arsenical pyrites, $FeS_2 + FeAs$, containing 46·6 As and 19·6 S.
Arsenical pyrites, Fe_4As_3, containing 66·8 As.
Speiskobalt (Co,NiFe), As.
Glanzkobalt, $CoS_2 + CoAs$.
Coppernickel, Ni_2As.
Nickel and cobalt arsenical pyrites $(Co,Ni,Fe)S_2 + (Co,Ni,Fe),As$.
White arsenical nickel, NiAs ; Tennantite $(Cu_2S,SeS)^4,AsS_3$.
Realgar, AsS_2 and yellow arsenic AsS_3.

Assay for Arsenic.—50 grains of the finely pulverised mineral are deflagrated with 200 of potassium nitrate and 200 of sodium carbonate in a porcelain crucible. When the crucible is cold, it and its contents are to be treated with water, as in the case of chromium. The solution will contain potassium arseniate, and (if the ore had in its constitution sulphur, which is most likely) potassium sulphate. Lead nitrate must be added to the solution (made neutral with nitric acid, if requisite) : a mixture of lead arseniate and sulphate is precipitated ; this precipitate is well washed on a filter, and digested with dilute nitric acid ; this agent dissolves out the lead arseniate, and leaves the sulphate. Filter, and saturate the filtered solution with soda, which will throw down the arseniate ; this must be collected on a filter, washed, dried, and weighed. Every 100 parts correspond to 22·2 of metallic arsenic, or 29 parts of arsenious acid (the common white arsenic of commerce).

This method is only approximative : the following is the better plan :—

Digest the ore in strong nitric acid until nothing more is taken up (the action may be facilitated by the occasional addition of a crystal or two of potassium chlorate), and all action on the addition of fresh acid is at an end: dilute with water, and filter: to the filtered solution add lead nitrate, and proceed as above.

For estimating the amount of arsenic in ores, Mr. Parnell says that the neatest, simplest, and most accurate mode of procedure is to heat the finely-divided sample in a gentle stream of chlorine gas to a temperature of about 200° C., and to collect the escaping arsenic chloride in chlorine-water. If free from antimony, the liquid may be well boiled, to expel free chlorine, and the arsenic precipitated with sulphuretted hydrogen, and weighed as pentasulphide.

In cases where the arsenic is obtained in the form of arsenio-magnesian phosphate (as in separation of the metal from antimony or copper), the most accurate plan would be to dissolve the precipitate in hydrochloric acid, and precipitate the arsenic as pentasulphide. When the amount of arsenic is small, it may be weighed as the double arseniate. The sample should not, however, be dried at a higher temperature than that of an ordinary water-bath—namely, about 95° C. Perfectly accurate results could, no doubt, be obtained by drying the precipitate over sulphuric acid, when it retains its six equivalents of water. The only objection is that it would take many days for a filter containing a precipitate to be properly dried by this means.

CHAPTER XXII.

THE ASSAY OF MANGANESE.

THE following are the commercially valuable minerals containing manganese.

Pyrolusite,	MnO_2,	containing	18·0	p.c. of available	oxygen.
Braunite,	Mn_2O_3,	„	10·0	„	„
Manganite,	Mn_2O_3,	„	9·0	„	„
Varvicite,	$Mn_2O_2 + Mn_2O_3,HO$,	„	13·8	„	„
Hausmannite,	$MnO + Mn_2O_3$,	„	6·8	„	„
Psilomelane,	Mn_2O_3.				

The assay of this metal is confined to the amount of peroxide any one of its ores may contain. There are several methods of effecting this, and the best of these will be described below.

Valuation of Manganese Ores.—The best methods used for the valuation of manganese ores are not necessarily those which give in the most rapid and accurate manner the absolute amount of manganese peroxide present in the ore. The analyst must bear in mind that the commercial value of manganese ore depends on its power of liberating chlorine from hydrochloric acid; and it not unfrequently happens that an ore, which on accurate analysis would be reported to contain a high percentage of manganese peroxide, likewise contains some other mineral (iron protoxide or magnetic oxide), which will materially reduce the value of the manganese as a chlorine-yielding ore. It is on this account that some processes—excellent though they be from a purely analytical point of view—have fallen into discredit amongst manufacturers, whilst other processes which do not profess to give the amount of manganese peroxide *actually* present, but only that *available* for liberating chlorine, are now generally adopted. In the following pages are given the methods of testing manganese ore for the available peroxide which have best stood the test of practical experience.

Messrs. Sherer and Rumpf, after examining all the most approved methods in Dr. Fresenius's laboratory at Wiesbaden, have come to the conclusion that Bunsen's method is the best for rapidly giving the amount of available manganese in an ore. This process is carried out by dissolving a weighed quantity of the sample in strong hydrochloric acid in a small flask, until complete decomposition has taken place. The escaping chlorine is received in a strong solution of potassium iodide, and the liberated iodine subsequently estimated by means of a standard solution of sodium hyposulphite and a solution of starch. To prevent the solution of potassium iodide from being sucked back into the generating flask, a few small pieces of magnesite are introduced with the manganese, so that a continual slight escape of carbonic acid takes place through the solution. The solution of sodium hyposulphite is tested by means of carefully prepared pure iodine, dissolved in potassium iodide. The solution should be of such a strength that 1000 c.c. of sodium hyposulphite solution corresponds to from 2 to 3 grms. of manganese peroxide. In this estimation the iodine liberated by the chlorine should be tested as soon as possible after the decomposition; it gives higher results after standing 24 hours than before. These higher results are caused by the liberation of iodine by spontaneous decomposition of hydriodic acid, set free by the hydrochloric acid, distilled over during the process. The following experiment proves this:—A few drops of hydrochloric acid were added to a solution of potassium iodide. The solution remained for some hours colourless, but, after standing twenty-four hours, had become quite yellow, and was found to contain free iodine sufficient to indicate 8 per cent. of manganese peroxide when titrated with hyposulphite.

Messrs. Sherer and Rumpf have made the suggestion that the value of manganese ores should be measured by chlorometrical degrees rather than by the actual percentage of binoxide; thus tending in the same direction as the resolution * passed by the Association of Alkali Manufacturers in 1869, in reference to this subject—a decision which would seem also to indicate a desire on the part of manufacturers that tests of manganese ore should express the amount of peroxide *available* for liberating chlorine, and not the amount *actually* present in the ores.

For the above reasons, Dr. Paul adopts Mohr's method of using a known quantity of a standard solution of oxalic acid, together with excess of sulphuric acid, for dissolving the ore; if necessary, boiling until the ore is completely dissolved, and then, by means of a standard solution of permanganate, determining the quantity of oxalic acid remaining undecomposed. This method is very convenient for testing manganese ores, and involves only one weighing for each test. The results obtained are also very uniform.

This method has also the advantage of giving results which fairly represent the amount of available peroxide in manganese ores; for any iron that may be present as metal or protoxide would consume an equivalent quantity of permanganate solution, and thus apparently reduce the quantity of oxalic acid decomposed by the peroxide to an extent proportionate to the amount of iron existing in the ore. Thus, for instance, if the quantity of oxalic acid decomposed by 100 grains of manganese ore free from iron or ferrous oxide were 109·53 grains, the ore would contain 76·5 per cent. of peroxide, and the whole of that would be available. But, if the 100 grains of ore also contained 5·6 grains of metallic iron, or an equivalent of protoxide, the permanganate solution required for peroxidising that iron would represent 6·3 grains of oxalic acid, and the quantity of oxalic acid decomposed by the peroxide would appear so much less than it really was, or 103·23 grains instead of 109·53 grains. Accordingly, the amount of peroxide would be represented as 72·1 per cent. instead of 76·5 per cent.: and that would, in fact,

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* 'That, as the testing of manganese according to the method of Will and Fresenius, is, in the opinion of the meeting, incorrect, and yields uncertain results, it is recommended to members of this Association not to buy by that test.'

be the amount of peroxide available for generating chlorine.

This method of testing recommends itself by its simplicity, and by the fact that the standard solutions of oxalic acid and permanganate will keep for a long time without alteration of value. The oxalic acid solution contains 63 grms. in the litre, and 1 c.c. is equivalent to 5 c.c. of the permanganate solution.

Mr. John Pattinson prefers a modification of Otto's process for the valuation of manganese, which consists in boiling the ore with a known weight of a proto-salt of iron, and then estimating the excess of iron by a standard solution of potassium bichromate. This modified process, in his opinion, requires less skill and care at the hands of the operator than Bunsen's method, as described by Messrs. Scherer and Rumpf. 30 grs. of clean iron wire are placed in a 20-oz. flask, along with 3 ozs. of dilute sulphuric acid, made by adding 3 parts of water to 1 of oil of vitriol. A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 30 grs. of the finely-pounded and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 8 or 10 ozs. with distilled water. The amount of iron remaining unoxidised in the solution is then ascertained by means of a standard solution of potassium bichromate. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been peroxidised by the manganese ore, and from this can be calculated the percentage of manganese peroxide contained in the ore. Thus, supposing it were found that 4 grs. of iron remained unoxidised, then $30-4=26$ grs. of iron, which have been oxidised by the 30 grs. of ore. By a simple calculation it is found that this 26 grs. of iron are equivalent to 20·43 grs. of manganese peroxide, the amount of peroxide in the 30 grs. of ore. The percentage is, therefore, 68·10.

It must be understood that if an ore contains a mixture of one atom of manganic oxide, and two atoms of magnetic iron oxide, or 27·3 per cent. of the former, with 72·7 per cent. of the latter; in such a mixture the method of Fresenius and Will will indicate with precision the amount of manganese peroxide, but on adding hydrochloric acid to this mixture not a trace of chlorine will be given off, since the free atom of oxygen of the manganese peroxide is just sufficient for the oxidation of the 2 atoms of iron protoxide of the magnetic iron ore; in the same way a mixture of manganese binoxide with iron protosulphate or protocarbonate of that metal will be perfectly worthless as an article for chlorine-making use.

Dr. Mohr accordingly recommends that manganese ores and samples of manganese peroxide should be always tested, previous to analysis, with an astatic magnetic needle, and he further recommends Dr. Bunsen's process (given on p. 752) as the best and surest method of analysis. This process is really the same as that which the manufacturer employs for making chlorine; any magnetic iron ore present will become oxidised in both processes, and a special examination for magnetic iron oxide is rendered unnecessary, while the available manganese for the production of chlorine only is estimated.

Mr. J. Pattinson proposes the following method of precipitating manganese entirely as peroxide, and applies it to the volumetric determination of manganese. He finds that the whole of the manganese in a solution of manganous chloride can be precipitated as peroxide, if a certain amount of *ferric chloride* be present, by a sufficient excess of a solution of chloride of lime or bromine water, adding, after heating the solution to from 140° to 160° F., an excess of calcium carbonate, and then well stirring the mixture. Zinc chloride may be substituted for ferric chloride. The author recommends the following solutions, etc. The clear liquid obtained by decantation from a 1·5 per cent. solution of bleaching-powder, light granular calcium carbonate obtained by precipitating an excess of calcium chloride by sodium carbonate at 180° F., a 1 per cent. solution of ferrous sulphate in dilute (1 in 4) sulphuric acid, standard solution of potassium dichromate equivalent to 1 part of iron in 100 of solution. The application of the process to manganiferous iron ores is as follows:—10 grains of the ore, dried at 212°, are dissolved in a 20 oz. beaker in about 100 fluid grains of hydrochloric acid (sp. gr. 1·18). Calcium carbonate is then added, until the free acid is neutralised and the liquid turns slightly reddish. 6 or 7 drops of hydrochloric acid are now added, and 1000 grains of the bleaching-powder solution, or 500 grains of saturated bromine water, and boiling water run in until the temperature is raised from 140° to 160° F.; 25 grains of calcium carbonate are added, and the whole well stirred. If the supernatant solution has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated oxides of iron and manganese are filtered off and washed. 1000 grains of the acidified ferrous sulphate solution are carefully measured into the 20-oz. beaker already used; the filter, with its washed contents, added. A certain quantity of the ferrous sulphate is oxidised by the manganese binoxide, this quantity is estimated with the standard dichromate solution, when the quantity of manganese binoxide can easily be calculated. The iron present must be at least equal in weight to the manganese during the precipitation, in order to ensure the absence of lower oxides.

CHAPTER XXIII.

THE ASSAY OF NICKEL AND COBALT ORES.

ORES OF NICKEL.

Nickel oxide.
Nickel sulphide
Nickel arsenide; kupfernickel.
Nickel arsenio-sulphide; grey nickel.
Nickel antimonio-sulphide.
Nickel arseniate.
Nickel arsenite.
Nickel silicate.

ORES OF COBALT.

Cobalt oxide.
Cobalt sulphide; cobaltine.
Cobalt sulphate.
The cobalt arsenides.
Arsenio-sulphide, or grey cobalt.
Cobalt arsenite.

THE analysis of cobalt ores is the most tedious, with the exception of those of platinum, of any that fall under the assayer's notice—the greatest difficulty being in the separation of cobalt and nickel. The following is Mr. Hadow's process:—

The only examination which the ore need undergo previously to the solution of a weighed quantity is with the view of obtaining a rough idea as to the amount of arsenic and cobalt or nickel present in the sample; for this purpose a little may be roasted on charcoal, or ignited in a tube, to see whether arsenic readily sublimes; another portion, of a few grains weight, may be dissolved in *aqua regia* in a test-tube, when the depth of the blue or green colour will serve as an indication of the degree of richness of the ore in cobalt and nickel.

If the ore is rich, from 20 to 30 grains; if poor, from

50 to 100 grains, in a state of fine division, are weighed out for the analysis. If much arsenic has been found, the portion, after weighing, had better be ignited in a small porcelain capsule or crucible over a gauze burner, when it generally ignites and smoulders away, evolving abundance of arsenious acid. The powder ready for solution is transferred to a small 4-oz. flask by means of glazed letter-paper and a camel's-hair paint-brush to sweep in the last particles; the mouth of the flask is then partially closed by a small funnel placed to catch the drops projected during solution. The ore is then drenched with hydrochloric acid, nitric acid being added from time to time, until all heavy metallic-looking particles are found to have disappeared from the bottom of the flask. The solution may then be decanted from the insoluble matters into a half-pint beaker, together with the washings of the flask; and as sulphur frequently remains, entangling portions of undissolved ore, it is advisable to transfer the undissolved residue from the flask into a capsule, drying and igniting the contents of the latter, and then digesting again the ignited matters in a little more *aqua regia*; the whole of the latter, both dissolved and undissolved, may now be added to the first portion in the half-pint beaker.

To separate out iron, arsenic, phosphoric acid, and aluminium from the solution, sodium acetate may be added at once, and the liquid boiled; a far better mode, however, is to effect a *partial* separation of these ingredients by the addition of calcium carbonate in excess to the solution of the ore, and after filtering out the solution containing the greater portion of the cobalt and nickel, and partly washing the precipitate, to extract the last traces of cobalt and nickel from the latter by dissolving it in hydrochloric acid, adding excess of sodium acetate and boiling. The first filtrate from the precipitate by calcium carbonate had better be collected apart from the second filtrate from the precipitate produced by sodium acetate, and received in a beaker capable of holding at least a quart. The solution of the precipitate by calcium carbonate is best effected in a beaker, after the removal of the precipitate from the filter; this is easily effected by inclining the funnel over the beaker and sending a stream of water from the wash-bottle between the filter and the upper edge of the mass of precipitate, when the latter will soon become detached and slide off into the beaker below: it is here treated with dilute hydrochloric acid, to dissolve all but the insoluble residues of the ore which had not been previously filtered off, and then a solution of sodium acetate is added in excess (indicated by the deep red colour of liquid) and the whole, heated to boiling, may be filtered at once. Iron thus separated out, in presence of free acetic acid, has less tendency to retain cobalt than when precipitated by means of calcium carbonate, besides which the cobalt and nickel in the filtrate are left in the condition of acetates, a necessary step preparatory to their separation from manganese, &c.

This method of separating out iron, &c., though very effectual, was often at first found to be attended with difficulties, for if much arsenic were not present the basic iron acetate frequently became slimy towards the end of the filtration, only allowing the boiling washing water to pass with such extreme slowness as to render the method almost useless, until it was found that the addition of a little sodium sulphate during the washing at once and permanently effected a cure, causing filtration to proceed rapidly, and diminishing the tendency of the iron to pass the filter; another difficulty was, that when sodium acetate was added at once to the original solution of the ore, the solution, often containing much cobalt and nickel as acetates, and filtered in a concentrated state, yielded to the filter paper sufficient cobalt and nickel to occasion distinct loss; this was avoided by separating out the great bulk of the cobalt and nickel in solution as chlorides by means of calcium carbonate, as above recommended, and then the weaker solution, being comparatively strongly acid, could be filtered without loss. This second filtrate may still retain traces of iron; a little sodium acetate may be added to make sure that none remains in the condition of chloride, which would be indicated at once by a reddening of the liquid, and the whole is then boiled thoroughly once more; if rendered at all turbid passed through a filter again, then nearly neutralised with ammonia, and finally added to the bulk of the cobalt and nickel solution in the quart beaker. There will in all probability be enough of the sodium and ammonium acetates present to convert the entire quantity of cobalt and nickel into acetates without further addition, and rendering it thus ready for the next operation.

If sulphuretted hydrogen be now transmitted through the solution containing cobalt and nickel, these metals are perfectly and completely separated without a trace of manganese, magnesium, calcium, aluminium, or soluble silica, which, when present, invariably accompany the sulphides precipitated by ammonium sulphide; the sulphides, moreover, thus precipitated from an acetic solution, have much less tendency to oxidise while on the filter, so that their washing may be more perfectly accomplished than in the former case. The passage of sulphuretted hydrogen may be conveniently effected at the end of the day, and the next morning the sulphides will be found perfectly settled at the bottom of the beaker, permitting the great bulk of the liquid (tested first to make sure of the removal of cobalt and nickel) to be drawn off and thrown away, or at least rapidly run through a filter; the sulphides collected at the bottom, together with that which always adheres to the sides of the beaker, and which may be detached without loss by a caoutchouc-covered glass rod, are then well washed on the filter with boiling water until all soluble matters are perfectly removed. The sulphides, perfectly washed, are now to be dried by placing the funnel with the filter in a broken beaker on wire gauze, at a safe distance over a lamp, and when dry they may be detached from the filter into a small beaker of from 1 to 2 oz. capacity, capable of being covered with a watch-glass; the filter itself is ignited, and the well-burnt ashes added to the sulphides, which are then to be *cautiously* treated with nitric acid, the action being rather violent, and, if care be not taken, liable to occasion loss. With the aid of a little heat, the whole should pass into solution.

In addition to cobalt and nickel the solution may still contain zinc, together with copper, and other metals precipitable by sulphuretted hydrogen from hydrochloric solutions; by passing sulphuretted hydrogen now through the nitric solution, somewhat diluted, these latter are readily precipitated and removed by filtration. Zinc, however, may still remain, to detect and remove which it is necessary to expel the sulphuretted hydrogen still remaining in the solution by boiling, to add solution of ammonia until a precipitate occurs, and then to acidify pretty strongly with acetic acid; if sulphuretted hydrogen slowly transmitted, or fresh sulphuretted hydrogen water, occasions a milkiness, zinc is present, and the slow passage of the gas is to be continued until the precipitate begins to show signs of darkening. The liquid is then filtered. The zinc may be identified as such by collecting and igniting the precipitate, when a trace of cobalt carried down with it (and which may be separated out, if desired, by a repetition of the process on the precipitate) will produce the beautiful and well-known Rinman's green.

The filtrate, containing only nickel, cobalt, and salts of ammonia, is treated with some pure sulphuric acid and evaporated to dryness in a weighed capsule, and heated sufficiently to expel the excess of sulphuric acid and all the ammoniacal salts. The residual cobalt and nickel sulphates may now be weighed in a covered crucible. This form of weighing these metals is easy, exact, and may be rapidly executed. The weight of the ash of a filter of the size used for collecting the sulphides must be ascertained after treatment with sulphuric acid, and subsequent expulsion of the excess, and this weight deducted from the total sulphates, in order to obtain perfectly correct results.

Assay of Nickel Ores.—The ore of nickel usually met with is the arsenide, containing variable quantities of cobalt and iron, and frequently also copper and bismuth. It is finely powdered, mixed with 2 parts of solid caustic soda and 1½ part of sulphur, and fused in an earthen crucible, gradually increasing the heat to dull redness, at which temperature it is to be kept for some time. The mass is then digested in water, which dissolves the soluble sodium sulpho-arseniate, and leaves, when washed by decantation, crystallised nickel sulphide. Attack this with warm hydrochloric acid containing a little nitric acid.

The solution heated to about 70° C. is then submitted to a current of sulphuretted hydrogen, which must be continually passed until the liquid is cold. It is then to be covered over and left at rest for 24 hours; the arsenic, copper, and bismuth come down as sulphides. These are filtered off, and the filtrate is heated with potassium chlorate or sodium hypochlorite to bring the iron to the state of sesquioxide, which is then precipitated by ebullition with excess of sodium acetate. The filtrate from the basic iron acetate is concentrated by evaporation and mixed with a saturated solution of potassium nitrite,* which will precipitate all the cobalt.

The yellow precipitate washed with a saturated solution of potassium chloride may be treated as described below. The nickel is precipitated from the liquid either in the state of oxide by means of caustic potash, or after concentration, by a saturated and warm solution of potassium binoxalate. The precipitated oxalate upon calcination leaves pure nickel.

Assay of Commercial Metallic Nickel.—Dissolve the metal in hydrochloric acid containing a little nitric acid. Pass sulphuretted hydrogen through the solution until the metallic impurities are thrown down, and then precipitate the nickel and cobalt by a warm saturated solution of potassium binoxalate. The precipitate after being washed and calcined leaves the nickel (containing a little cobalt) in the metallic state.

Assay of Cobalt Ores.—Metallic cobalt may be prepared from its ores (arsenide or sulphide) by a similar process to that adopted in the case of nickel. When the mineral

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* Potassium nitrite is prepared by fusing, in an iron crucible, 1 part of nitre with 2 parts of granulated lead, stirring well with an iron spatula, and then heating to redness until the lead is completely oxidised. The fused mass, after cooling, is extracted with water, and the small amount of lead which is dissolved is precipitated by carefully adding a mixture of caustic ammonia and ammonium carbonate or sulphide.

contains more than 70 per cent. of arsenic, a preliminary fusion should be performed with chloride of sodium, to remove most of the arsenic. This may be continued by roasting or by fusion with a mixture of sodium carbonate and sulphur.

As nickel is almost invariably present in cobalt ores, this metal will require to be separated. Wöhler recommends for this purpose the potassium nitrite process. The yellow cobalt precipitate is dissolved in as small a quantity of hydrochloric acid as possible, and sodium acetate is then added; the addition of a warm saturated solution of oxalic acid now precipitates the cobalt as oxalate. This oxalate after being washed and dried may be packed closely in a crucible of biscuit porcelain, protected by enclosure in a Hessian crucible. The covers being well luted on, the whole is heated in a wind furnace or a forge. If a sufficient temperature has been obtained the cobalt will be in the form of a fused button.

Separation of Nickel and Cobalt.—A method of separating these metals, given some years since by Liebig, consists in boiling the mixed double nickel and potassium cyanides, cobalt and potassium cyanides, with oxide of mercury. Nickel oxide is precipitated, while an equivalent quantity of mercury is dissolved as cyanide. The method certainly gives good results, but is not free from objection. Long boiling is necessary before the precipitation is complete, and it is difficult to prevent bumping during ebullition. The excess of mercury oxide must be separated from the nickel oxide by a special operation, and the nickel afterwards again precipitated by caustic alkali.

According to Wolcott Gibbs,* these inconveniences may be completely avoided by employing, instead of the oxide alone, a solution of the oxide in the mercury cyanide. When this solution is added to a hot solution of the double cyanide of nickel and potassium, the whole of the nickel is immediately thrown down as a pale green hydrate of the protoxide. Under the same circumstances

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* 'Chemical News,' March 17, 1865.

cobalt is not precipitated from the double cobalt and potassium cyanide. Mr. W. N. Hill, who has repeatedly employed this method and carefully tested it, has found that the separation effected is complete. No cobalt can be detected in the precipitated nickel oxide by the blow pipe, nor can the nickel be detected in the cobalt (finally separated as oxide) by Plattner's process with the gold bead. The solution of mercury oxide is easily obtained by boiling the oxide with a strong solution of the cyanide, and filtering. According to Kuhn, the cyanide formed in this manner has the formula $HgCy + 3HgO$. The hydrated nickel oxide precipitated may be filtered off, washed, dried, ignited, and weighed. The cobalt is more readily and conveniently determined by difference, when, as it is always possible, the two metals have been weighed together as sulphates. We are not prepared to say that this modification of Liebig's method of separating nickel and cobalt gives better results than Stromeyer's process by means of potassium nitrite, but it is at least very much more convenient, and requires much less time. The complete precipitation of cobalt in the form of $Co_2O_3,2NO_3 + 3KO,NO_3$ usually requires at least forty-eight hours, and rarely succeeds perfectly except in experienced hands.

M. Terreil has proposed a very excellent method for separating these two metals. The author's method is founded—(1) on the insolubility of roseocobaltic hydrochlorate in acid liquids and ammoniacal salts, discovered by M. Fremy; (2) on the rapid transformation of ordinary salts of cobalt into roseocobaltic salts, under the double influence of ammonia and oxidising bodies—such as potassium permanganate and alkaline hypochlorites; (3) on the complete precipitation of manganese in ammoniacal liquids by alkaline hypochlorites, and potassium permanganate.

To separate cobalt from nickel, operate in the following manner:—

To the solution of the two metals add an excess of ammonia, which re-dissolves the two oxides; add to the hot ammoniacal liquid a solution of potassium permanganate, sufficient to cause the liquid to remain coloured violet for a few instants by the excess of permanganate. Boil the liquid for a few minutes, then add a slight excess of hydrochloric acid, to re-dissolve the manganese oxide which will have formed. Heat the liquid gently for twenty or twenty-five minutes, then let it stand for about twenty-four hours. All the cobalt will then be deposited in the form of a beautiful red-violet crystalline powder; the precipitate is roseocobaltic hydrochlorate, which collect on a weighed filter, wash it on the filter with cold water, then with diluted hydrochloric acid, or with a solution of ammoniacal salt, and then with ordinary alcohol, which frees it from ammoniacal salt. Dry it at 110°, and weigh. 100 parts of roseocobaltic hydrochlorate correspond to 22·761 of metallic cobalt, or to 28·959 of protoxide of cobalt.

It is, however, better to take a given quantity of the roseocobaltic salt, and reduce it by dry hydrogen; this leaves perfectly pure cobalt to be weighed.

Next boil the solution containing nickel to expel the alcohol which has been introduced in washing the cobaltic salt; saturate it with ammonia, add another small excess of permanganate of potash, and boil. All the manganese will be precipitated; filter the liquid, and all the nickel will be found in the filtrate, from which it may easily be separated in the state of sulphide, and then transformed into oxide.

By this process the presence of a ten-thousandth part of cobalt in a salt of nickel may be ascertained.

In this operation an alkaline hypochlorite may take the place of the potassium permanganate, but then the deposit of roseocobaltic salt takes place with extreme slowness, and several days are required to complete it. This reagent is preferable to permanganate when manganese is to be separated from nickel and cobalt.

Quantitative Assay of Small Proportions of Cobalt in Nickel.—The following method is proposed by Dr. Fleitmann. It is well known that from solutions containing both these metals the cobalt is first precipitated by hypochlorites, as a brown hydrate, and the nickel hydrate does not fall until after a further addition. The partial precipitation with sodium hypochlorite is so conducted that at least two parts of nickel may be thrown down to one of cobalt. The proportion may be judged by the colour of the solution of the precipitate. If this solution is decidedly red, more of the precipitant must be added. After a slight washing the precipitate is dissolved on the filter with warm hydrochloric acid, the excess of chlorine removed by boiling, and the mixture of cobaltous and nickelous oxides is precipitated from the warm solution with potash lye. The precipitate is filtered, slightly washed with water, dissolved in acetic or nitric acid, and the cobalt is then precipitated in the ordinary manner with potassium nitrite.

Detection of Nickel before the Blowpipe.—The following is Plattner's method for detecting nickel, when contained in large quantities of cobalt:—

Fuse in the oxidising flame a moderate quantity of borax to a bead in the loop of platinum wire, with sufficient oxide of cobalt to give an opaque glass; remove the assay, and prepare one or two similar beads, and place the whole in a charcoal cavity, with a button of pure gold weighing from fifty to eighty milligrammes. The operator must now heat in the reducing flame, until he is satisfied that the whole of the nickel is in a metallic state; the charcoal during the action must be inclined alternately backwards and forwards, so that the gold button may flow through the melted glass, and form an alloy with the reduced particles of nickel. When the golden globule solidifies, it must be extracted with a forceps, placed between paper, and struck with a hammer, so as to detach all the adhering vitreous parts. The auriferous button, which has become more or less grey, from the presence of nickel, and also more brittle than pure gold, is now to be mixed with microcosmic salt, and heated for some time in the oxidising flame. If the borax-glass has not been in the first instance oversaturated with oxide of cobalt, a bead will now be obtained, which is coloured only by oxide of nickel, and will therefore appear brownish-red while hot, and when cold reddish-yellow. Should portions of oxide of cobalt be also reduced, as the cobalt is oxidised before the nickel, either a blue glass, coloured by oxide of cobalt, or a green one—if some nickel was also oxidised—will be obtained. In either case the glass must be separated from the button, mixed with more microcosmic salt, and heated in the oxidising flame until it acquires a tinge. If the borax-glass had not been oversaturated at the commencement, the colour now obtained will proceed from nickel, although the cobalt oxide contains a trace only; but if nickel oxide be not present, the microcosmic bead remains perfectly colourless.

In the assay of substances containing cobalt, nickel, and zinc, Alex. Olassen (‘Zeitschrift für Anal. Chemie,’ 1879, p. 189) proceeds as follows:—

To the solution rendered as neutral as possible, he adds so much neutral potassium oxalate (1 part of the salt and 3 parts water) that the precipitate is redissolved. He then adds, with stirring, acetic acid about equal to the volume of the liquid. The precipitate becomes crystalline at a temperature of 50° to 60° C., and the liquid remains clear. The precipitate is washed with a mixture of equal volumes concentrated acetic acid, alcohol, and water. The dry precipitates, after the filter has been burnt on a platinum wire, are first ignited very slightly in a covered platinum crucible, so that no particles may be expelled by the escaping carbonic oxide, and finally are ignited in an open crucible.

Ores containing Sulphur, Arsenic, Nickel, Cobalt, and Iron.—(Arsenical nickel-glance, cobalt-glance, red and white nickel pyrites, cobalt speiss, commercial nickel.)

In nickel and cobalt-glance sulphur is present in great quantity, and is rarely absent in the remaining ores. Its determination is best affected in a separate portion. For the separation and estimation of the metals the finely-powdered sample is oxidised either with *aqua regia* or with hydrochloric acid and potassium chlorate, and the arsenic is determined as directed for the arsenides and sulph-arsenides of iron.

The liquid filtered from the arsenic sulphide is freed from sulphuretted hydrogen by heat, the iron is oxidised with potassium chlorate, the free chlorine expelled by heat and the addition of a little alcohol, the liquid is largely diluted, placed in a basin and mixed with sodium carbonate, till the acid reaction becomes very faint. Barium carbonate levigated in water to a fine paste is then added, till it lies at the bottom of the vessel. After repeated stirring the iron is all precipitated. It is filtered off, dissolved in dilute hydrochloric acid, sulphuric acid is added, the precipitate of barium sulphate removed, and the ferric oxide precipitated with ammonia. The liquid containing the nickel and cobalt is freed from soluble barium compounds by means of sulphuric acid, and the barium sulphate is removed by filtration.

The filtrate, containing the nickel and cobalt, is placed in a basin, supersaturated with potash, heated to a boil, filtered, washed with hot water, and the mixture of both oxides dissolved in acetic acid. To this liquid is added a concentrated solution of potassium nitrite (if it contains free potash an excess of acetic acid must be present), and the whole is let stand for 24 hours.

A yellow precipitate of potassium cobaltic nitrite is produced, which is filtered off and washed in the cold with a saturated solution of potassium chloride. More potassium nitrite is added to the filtrate to ascertain whether anything further is deposited. The yellow precipitate is digested with hydrochloric acid, in which it dissolves, diluted, filtered into a basin, and the cobalt oxide is precipitated by boiling with an excess of potash. The precipitate is washed hot, and when dry it is placed in a porcelain crucible and strongly ignited in a current of hydrogen. After being allowed to cool in the same current, it is weighed in the covered crucible as metallic cobalt. It is then well washed with water, ignited again in the stream of hydrogen, and finally weighed.

In the liquid filtered from the cobaltic precipitate the nickel is thrown down by boiling with potash. When carefully washed, dried, and ignited, it yields pure nickel oxide, from the weight of which that of the metal is calculated.

Many substances of this class contain other constituents in smaller proportion.

Commercial nickel contains silicon, which on dissolving the metal in nitric acid, etc., is separated out as silica. For its determination the whole is evaporated to dryness in the water-bath, the residue when cold is moistened with acid and treated with water. The silica is then filtered off, and the other constituents are determined in the filtrate in the usual manner.

The ores of nickel and cobalt and speiss-nickel contain antimony. It is precipitated by sulphuretted hydrogen along with arsenic. The precipitate is dissolved in *aqua regia*, and the two metals are separated in the usual manner.

The above ores and furnace products may also contain copper, bismuth, and lead. In presence of small quantities of these metals sulphuretted hydrogen should be passed through the solution of the mixture for a rather shorter time at first. These are precipitated before arsenic, but are accompanied by a part of it. The precipitate is filtered off, and the passage of the sulphuretted hydrogen through the filtrate is continued till the arsenic is completely deposited.

The precipitated sulphides whilst still moist are placed in a flask together with the filter, and are digested for a considerable time with concentrated yellow ammonium hydrosulphide. When cold the solution is diluted and filtered with exclusion of air, washed with water, to which a few drops of ammonium hydrosulphide have been added; the filtrate is slightly supersaturated with hydrochloric acid, and the precipitate of arsenic sulphide is filtered off and added to the main arsenical precipitate. The sulphides (copper, bismuth, and lead) if their quantity permits are separated by methods already given. If the quantities of these metals are considerable, as is the case in many furnace products, their assay is conducted as pointed out for lead- and copper-speiss.—*Rammelsberg*.

Alloys of Copper, Zinc, and Nickel.—The assay is conducted as has been directed for alloys of copper and zinc. The solution filtered from the copper sulphide, and containing the zinc and nickel, is concentrated by evaporation in order to remove the excess of sulphuretted hydrogen. It is then poured into a flask, supersaturated with pure potash and hydrocyanic acid, enough to dissolve the whole to a yellow liquid. From this solution the zinc is precipitated as zinc sulphide by means of potassium monosulphide (prepared by reducing potassium sulphate with charcoal), and caused to settle by digestion. It is then passed through a covered filter, the filtrate being collected in a flask, washed with cold water, to which a little potassium sulphide has been added, redissolved by digestion with hydrochloric acid in a covered beaker till the odour of sulphuretted hydrogen has entirely disappeared; the diluted solution is filtered into a capsule, and the zinc oxide is thrown down by means of sodium carbonate.

The filtrate from the zinc sulphide is boiled in the flask with *aqua regia* till the odour both of sulphuretted hydrogen and hydrochloric acid are expelled, and do not return on the addition of a little acid. The liquid is then placed in a basin, supersaturated with potash, and kept at a boil for a few minutes. The hydrated nickel-oxide is washed with hot water, dried, ignited and weighed, the proportion of the metal being calculated from the weight of the nickel-oxide.

In the electrolytic assay of copper and nickel Herpin proceeds as follows in the assay of alloys of these metals: He dissolves 1 grm. of the sample in nitric acid in a flask capable of holding 250 c.c., evaporates almost to dryness, and adds 4–5 c.c. sulphuric acid, and water enough to make up a volume of 60–70 c.c. The liquid is rinsed into a platinum capsule and submitted to electrolysis. The copper only is deposited from an acid solution.

The liquid, still containing the nickel, is poured into a flask like the one used for dissolving the alloy; the platinum capsule is rinsed first with water, then with alcohol, dried and weighed to determine the copper.

The nickeliferous liquid, *plus* the washings, is heated to a boil, partially neutralised with sodium carbonate, and supersaturated with ammonia till it takes a blue colour. It is then placed in the platinum capsule, and submitted to electrolysis. Traces of lead and iron do not interfere.

W. Ohl ('Zeitschrift für Anal. Chemie,' 1879, 523) gives the following process for the assay of a nickel speiss: 1 grm. finely-ground is placed in a beaker holding 300 c.c., and covered with nitric acid or *aqua regia.* The beaker is covered with a watch-glass and set on the sand-bath. When it is completely dissolved the watch-glass is taken off and the liquid evaporated to dryness. About 5 m.m. of pure concentrated hydrochloric acid are added, and after the mass is dissolved the beaker is half-filled with water. When the solution is hot, sulphuretted hydrogen is passed through it till cold. It is again set to warm, and again treated with the same gas till cold. The precipitate of copper and arsenic is quickly deposited, and the supernatant liquid becomes clear. As arsenic sulphide is slightly soluble in water containing sulphuretted hydrogen, the beaker is set in a warm place till the smell becomes very faint. If the precipitate is a fine uniform yellow it is washed on filtering with cold pure water; if darker, and therefore containing more water, it is washed with sulphuretted hydrogen water.

The filtrate containing cobalt and nickel is evaporated to dryness in a capsule holding ¾ litre, adding a little potassium chlorate to oxidise iron. The residue is taken up with a little hot water and hydrochloric acid, precipitated with pure solution of soda till the reaction is alkaline, redissolved in pure acetic acid, largely diluted and heated to a boil. The iron is all deposited as basic ferric acetate, which is filtered off and washed with hot water till a drop of ammonium sulphide produces no turbidity in a drop of the washings. The solution, freed from the iron, is evaporated to dryness, dissolved in water, and a few c.c. of dilute sulphuric acid, placed in a beaker holding 600 c.c., supersaturated with ammonia, and submitted to the electric current.

When the electrolysis is complete, a drop of the liquid is withdrawn with a pipette, filtered and mixed with a drop of ammonium sulphide. If no turbidity is formed the platinum cone is withdrawn, washed first in water, and then in absolute alcohol, and dried. The increase of weight gives the sum of the cobalt and nickel.

LEAD- AND COPPER-SPEISS.

These substances are very complicated products formed during the metallurgical treatment of arseniferous and antimoniferous ores of lead and copper. They may contain copper, lead, iron, nickel, cobalt, zinc, bismuth, silver, arsenic, antimony, and sulphur.

A. Speiss containing little or no Lead or Antimony.—One portion is taken for the determination of sulphur, and another is dissolved in *aqua regia*, or in a mixture of hydrochloric acid and potassium chlorate. The proportion of silver is generally so small that no silver chloride remains. If any lead chloride is separated it is dissolved by heating in water. The solution is treated with sulphuretted hydrogen, when lead, copper, bismuth, antimony, and arsenic are deposited. To ascertain that the arsenic is completely precipitated the liquid is heated and again treated with sulphuretted hydrogen. The metallic sulphides are digested with concentrated yellow ammonium hydrosulphide, in order to dissolve the arsenic and antimony sulphides.

After filtration both are precipitated by hydrochloric acid, and separated as directed under arsenical iron.

The undissolved sulphides of copper, lead, and bismuth are allowed to become air-dry, and are then detached from the filter, which is incinerated in a small porcelain crucible. Firstly, these ashes and then the total sulphides are dissolved in nitric acid. The sulphur, which is not quite pure, is filtered off and gently heated in a porcelain crucible, the slight residue being digested again with nitric acid and added to the main solution (if lead sulphate remains unattacked it must be collected on a weighed filter). The nitric solution of the three metals is concentrated by evaporation, and the lead separated as already directed. The filtrate is saturated with sodium carbonate, potassa is added, the whole heated to a boil, the oxides are filtered off, washed slightly, dissolved in the smallest quantity of hydrochloric acid, and the bismuth is precipitated by the addition of much water as basic oxychloride, which is reduced by potassium-cyanide, as already described. Copper is precipitated from the filtrate by sulphuretted hydrogen.

In the filtrate from the first sulphuretted hydrogen precipitate there are still found iron (as ferrous oxide), nickel, cobalt, and zinc. The liquid is concentrated to expel sulphuretted hydrogen and most of the free acid; the iron is peroxidised by the addition of a little potassium chlorate, diluted, the free chlorine expelled by heating with a few drops of alcohol, and the iron oxide is separated from zinc, nickel, and cobalt as directed for arsenical nickel-glance, &c.

B. Speiss containing much Lead or Antimony.—The process to be followed is tedious, and requires much care. The substance, finely powdered, is decomposed by heating in a current of chlorine gas.

The apparatus requisite consists of a capacious flask, in which the necessary chlorine gas is evolved from a mixture of 2 parts black oxide of manganese, 3 parts of common salt and dilute sulphuric acid ($1\frac{1}{2}$ to 2 parts water to 1 part of the monohydrated acid). The flask is closed with a cork, through which passes a tube bent twice at right angles. Its longer leg dips into concentrated sulphuric acid contained in a second flask, where the gas is partially dried and whence it issues to pass by another tube into a chloride of calcium apparatus, and thence into the bulb-tube in which the reaction is to take place. The tube is tared, from 1 to 2 grms. of the finely-ground sample is inserted into the bulb through its wider tube, both ends are cleaned with a feather, so that none remains except in the bulb, and the whole is weighed to find the exact quantity which has been taken for analysis. The shorter tube is then connected to the chloride of calcium apparatus, and the longer, or bent tube, is conducted through a cork into a receiver, which resembles a Liebig's bulb-tube on a larger scale, and with parallel limbs. It is filled with dilute hydrochloric acid, to which a little tartaric acid is added, if the body under analysis contains antimony. From the second limb of this receiver a bent tube passes into a Woolf's bottle, and dips into the same solution. From the other aperture passes a tube which carries away the escaping chlorine. When all parts of the apparatus are full of chlorine heat is carefully and gradually applied to the bulb, which must not reach visible redness. After the completion of the operation the bulb contains the non-volatile lead, silver, bismuth, copper, nickel, cobalt chlorides, and in part those of iron and zinc. They are dissolved out by means of water and hydrochloric acid; undecomposed portions of the sample and silver chloride may remain, and are collected upon a weighed filter, and after weighing treated with ammonia, which dissolves the silver chloride, leaving the undecomposed matter behind. The hydrochloric solution is filtered into dilute sulphuric acid, evaporated, and the lead separated as lead sulphate. The filtrate is precipitated with sulphuretted hydrogen, and copper and bismuth are separated by dissolving the sulphides in hydrochloric acid, to which a little nitric acid is added, the solution concentrated to a small bulk, the bismuth precipitated by water, the basic bismuth chloride reduced by potassium cyanide, and in the filtrate the copper precipitated by sulphuretted hydrogen in the ordinary manner. The filtrate from which the copper and bismuth sulphides were removed, contains iron, zinc, nickel, and cobalt, and is treated as already pointed out.

From the volatile chlorides contained in the liquid from the receivers the sulphuric acid is removed by barium chloride, and any excess of the latter, by the cautious addition of sulphuric acid. Antimony and arsenic are precipitated by sulphuretted hydrogen, and separated in the usual manner. The filtrate contains the volatilised portions of iron and zinc, which are also dealt with by ordinary methods.

CHAPTER XXIV.

THE ASSAY OF SULPHUR.

The only commercially valuable Sulphur-minerals are :—

I. *Sulphurous Earth* (native sulphur).

In Sicily these minerals are divided into five classes :—

1. Very rich	ores,	containing	32—34	per cent.	sulphur
2. Rich	”	”	24—26	”	”
3. Good	”	”	16—18	”	”
4. Middling	”	”	8— 9	”	”
5. Poor	”	”	3— 5	”	”

II. *Iron and Copper Pyrites* (FeS_2), and (Cu_2S, Fe_2S_3).

These ores are used to a very large extent for the manufacture of sulphuric acid.

In order to approximatively estimate the value of ores of the first class for such manufacture, the following method of assay may be used.

Assay by Distillation.—A certain quantity of the pulverised sulphurous earth is heated in a glass retort, which is furnished with a receiver. The retort is then heated, gradually raising the temperature, till no more sulphur is evolved. The latter will collect in the neck of the retort and receiver, which may be, in all cases, of glass, and must be kept cool.

The sulphur derived from sulphurous earth is generally pure, whilst that from pyrites frequently contains arsenic and selenium, and sometimes traces of thallium.

ASSAY OF IRON AND COPPER PYRITES.

A. Assay of Sulphur in the Dry Way.—Fuse the weighed ore with a weighed quantity of anhydrous sodium carbonate, twice as much potassium chlorate as ore, and from 12 to 20 times as much sodium chloride (added to moderate the action); carbonic acid is expelled, potassium chloride formed, and all the sulphur converted into sodium sulphate; by dissolving the residue in water and estimating alkalimetrically the unaltered sodium carbonate by a standard acid solution, the portion converted into sulphate, and hence the sulphur in the ore, is known. Besides the difficulty of preventing loss by deflagration, this method is open to the small errors caused by the reckoning all arsenic present to be sulphur: this, however, is usually of no moment for commercial purposes; and calcium carbonate in the ore may, if required, be previously dissolved out by dilute hydrochloric acid.

In performing fusions of sulphur compounds with nitre or potassium chlorate the operator must bear in mind a source of error, first pointed out by Dr. David S. Price, in consequence of sulphur compounds being contained in the coal-gas which frequently serves as fuel in these experiments. By exposing a small quantity of fused nitre, on the *outside* of a platinum capsule, to the flame of a Bunsen gas-burner for three-quarters of an hour, Dr. Price succeeded in detecting the presence of sulphuric acid to an amount equivalent to 12 milligrammes of sulphur. This sulphuric acid had been formed by the oxidation of the sulphur in the coal-gas, and, when dissolved in water, it gave an immediate precipitate with chloride of barium. By making a similar experiment with the use of a spirit-lamp as the source of heat, no trace of potassium sulphate was formed; nor was any appreciable amount of sulphuric acid generated in another trial made by fusing a small quantity of nitre *inside* a platinum capsule heated over gas; but whenever the fused salt crept over the edges of the capsule, some potassium sulphate was sure to be formed. This observation may become a matter of importance when the amount of sulphur in pig-iron is determined by fusion with pure nitre, for the author has remarked that samples containing much manganese are especially liable to impart to the fused salt a tendency to creep up and escape over the sides of the crucible.

B. Assay of Sulphur in the Wet Way.—Mr. C. R. A. Wright recommends the following process as being the one best adapted for commercial purposes:—A known weight of the ore reduced to fine powder is oxidised (best in a small flask with a funnel in the mouth to avoid loss by spirting, and heated on a sand-bath), either by strong nitric acid, or aqua regia, perfectly free from sulphuric acid; after the oxidation is complete, the liquid is evaporated down as far as possible to expel the majority of the remaining nitric or hydrochloric acid; the residue is boiled with a little water, and almost but not quite neutralised by ammonia; a solution of barium chloride of known strength is then added until no further precipitate is produced, the exact point being found by filtering off a little of the liquid after each addition of barium chloride, and adding to it a few more drops of the standard solution, care being always taken, in case of a further precipitate being thus produced, to add this filtrate to the original solution, and mix well before filtering a second time. In case of overstepping the mark, it is convenient to have at hand a solution of sodium sulphate of strength precisely equal to that of the barium chloride; this solution may then be cautiously added, with repeated filtration and examination of the filtrate with the sulphate solution, until the point is just reached when addition of sulphate solution produces no further precipitate; by subtracting the volume of sulphate solution thus used from the total volume of barium solution added, the exact quantity of this latter consumed is known. If 1 grm. of sulphur ore be taken, and 32·5 grms. of pure anhydrous barium chloride be dissolved in a litre of fluid, each cubic centimètre of barium solution used will represent $\frac{1}{2}$ per cent. of sulphur in the ore examined: 22·19 grms. of anhydrous sodium sulphate being dissolved to a litre for the second solution. In case of lead being contained in the ore, an error is introduced from the formation of insoluble lead sulphate; as lead, however, rarely occurs in any perceptible quantity, this error is negligible, the process only giving approximate results.

Where greater accuracy is required, it is advisable to precipitate the sulphuric acid formed from the original liquid (filtered from insoluble residue) by barium nitrate or chloride, and to weigh the barium sulphate produced. Instead of oxidising by acids, the powdered ore may be suspended in caustic potash (free from sulphate), and oxidised by passing washed chlorine into the liquid; lead, being converted into dioxide, is thus rendered non-injurious; the alkaline liquid obtained is acidified, and precipitated by chloride of barium as before. In the volumetric determination usually pursued, a curious circumstance is occasionally observable when much free acid exists in the solution, viz., that a point may be reached when the filtered liquid is clear, and remains so even on standing for a short time, but yields a cloud, or even a precipitate, on the addition either of barium solution or sulphate solution; this source of error is mostly avoidable by nearly neutralising the free acid with ammonia.

Instead of chlorine, hypochlorous acid may be used to transform the sulphur of pyrites into sulphuric acid, which is then estimated by barium chloride. Finely pulverise the mineral and suspend it in water, through which a current of gaseous hypochlorous acid, or, better still, hypochloric acid is passed; this entirely dissolves the pyrites. Hypochlorous acid is prepared by heating a milk of calcium carbonate through which a current of chlorine is passed to saturation. Hypochloric acid is obtained by heating in a water-bath a tube, supplied with a cork and delivery tube, and containing a mixture of nine equivalents of oxalic acid and one equivalent of chlorate of potash.

Mr. A. H. Pearson has given the following very accurate method of estimating sulphur in pyrites:—Weigh out 1 grm. or less of the powdered ore, place the powder in a porcelain dish, together with a small quantity of potassium chlorate, pour upon it some 50 c.c. of pure nitric acid of 39° B., and cover the mixture with an inverted glass funnel with bent stem. Set the dish upon a water-bath, and heat the water to boiling. From time to time throw crystals of potassium chlorate into the hot acid. By adding rather large crystals of the chlorate at frequent intervals, it is easy to oxidise the whole of the sulphide in half an hour; but, since the solution obtained in that case is highly charged with saline matter, it will usually be found more advantageous to use less of the potassium chlorate, and to allow a somewhat longer time for the process of oxidation.

When all the sulphur has been oxidised, rinse the funnel with water, and remove it from the dish. Evaporate the liquid to a small bulk, then add to it a little concentrated hydrochloric acid, and again evaporate to absolute dryness, in order to render silicic acid insoluble. Moisten the residue with concentrated hydrochloric acid, mix it with water, and filter to separate silicic acid and gangue.

To the filtrate from the silicic acid add a quantity of solid tartaric acid, about as much as that of the pyrites originally taken; heat the liquid almost to boiling, and add to it an excess of barium chloride, to precipitate the sulphuric acid. After the barium sulphate has been allowed to subside, wash it thoroughly by decantation, first with hot water, and afterwards with a dilute solution of ammonium acetate (the latter may be prepared at the moment of use by mixing ammonia-water and acetic acid). The purpose of the ammonium acetate is to dissolve any barium nitrate which may adhere to the sulphate; that of the tartaric acid is to prevent the precipitation of iron compounds together with the barium sulphate. In an experiment where 0·7 grm. of pyrites was oxidised with potassium chlorate and nitric acid, and the filtrate from silica was acidulated with hydrochloric acid without the addition of tartaric acid, there was thrown down, on the addition of barium chloride, a bright yellow precipitate, which became darker-coloured when the solution was boiled. It was not only found to be impossible to wash out the iron with which this precipitate was contaminated, but the consistency of the precipitate was such that it was a difficult matter even to wash away the saline liquor in which it was formed.

M. A. Houzeau, in his so-called gravi-volumetric process, attacks 1 gramme of the powdered ore with a mixture of 4 parts pure potassium nitrate, and 3 parts sodium carbonate, likewise pure. The saline mass is dissolved in hot water, and the ferric oxide filtered from the alkaline sulphate. The washing waters are added to the filtrate, and, after cooling, it is made up with distilled water to half a litre. A portion is then taken (10 c.c.) and acidulated with a few drops of pure acetic acid, and the sulphuric acid is rapidly determined, as the author has elsewhere indicated for selenitic waters, by making use of a standard solution of barium chloride, applied by the aid of the *gravi-volumeter* in place of the ordinary burette, the use of which, in such determinations, yields merely erroneous results. In the gravi-volumeter the weight of the standard solution shows the quantity of the reagent which has been used. But each drop of the barytic liquid delivered by the gravi-volumeter weighs at the temperature of 13° exactly 0·050 grm.

In the Freiberg works, 1 grm. of finely-ground ore is mixed with 3 grms. anhydrous sodium carbonate, and an equal weight of saltpetre. This mixture is placed in an iron crucible, melted in a muffle. At a red heat, the mass is dissolved in hot water, and the liquid is filtered into a beaker, in which there is a little hydrochloric acid to saturate the excess of soda. The liquid, which should have an acid reaction, is then boiled for a short time, and the sulphuric acid is determined volumetrically with a solution of barium chloride standardised, so that 1 c.c. indicates 2 per cent. of sulphur.

B. Deutecom adopts the following process:—1 grm. pyrites was mixed in a large covered crucible with 8 grms. of a mixture of equal parts potassium chlorate, sodium carbonate, and sodium chloride. The crucible is heated at first gently, so as to dry the contents, which are afterwards melted at a high temperature. The mass, when cold, is treated with boiling water, and the solution, together with the deposit, is introduced into a measuring-flask of 200 c.c., filled up, filtered, and the sulphuric acid is determined in aliquot parts, say 50 c.c. The insoluble residue does not retain any sulphuric acid. In this manner the use of nitric acid is evaded. The decomposition of the potassium chlorate is complete.

In assaying pyrites for sulphur only by fusion, Mr. P. Holland has obtained good results by the following process, which may be useful in such laboratories as do not possess large platinum crucibles. A test-tube, or piece of sealed combustion tube, about 6 inches long and half an inch in internal width, is fitted with a cork and delivery tube, the latter bent at a right angle, and long enough to reach to the bottom of the flask in which it is intended to make the titration. The fusion mixture consists of equal parts of nitre and ignited sodium bicarbonate, both free from sulphur, dry, and in fine powder. Nine to ten grammes are taken in an operation, together with one of pyrites; the latter must be in exceedingly fine powder. The two are mixed in a warm porcelain dish or agate mortar, and transferred to the tube without loss. The delivery tube is then inserted, with its extremity dipping into the flask. A channel is made on the surface of the mixture, and the tube, suitably supported, is heated by small portions at a time with a Bunsen gas flame, commencing as usual with the anterior portion. When the operation is progressing favourably, the deflagration proceeds for a few seconds after removing the flame.

There is no danger to be apprehended, and the tube does not crack or blow out with proper care. When the tube has been heated throughout, and the deflagration has ceased, it is then more strongly heated with a Herapath or powerful gas flame. It is a good plan at this stage to slip a coil of wire gauze over the tube, which helps to accumulate the heat. It is not, however, necessary that the contents should be fused a second time; at least this has not been done in experiments appended. The sulphur ores examined have yielded their sulphur readily.

The gaseous products of the combustion, which mechanically carry over with them small quantities of sulphates or sulphuric acid, being heavier than air, collect in the flask, and are washed by shaking with a little water, closing the flask with the palm of the hand. The delivery tube is also washed. That containing the fused mass is carefully broken and put in the flask, together with sufficient hydrochloric acid to dissolve nearly the whole of the iron oxide; then ammonia is added, until a precipitate of oxide reappears; and lastly, as much hydrochloric acid and water as is necessary to bring the fluid to the conditions which were obtained when the barium solution was standardised. The author has used 2 c.c. of free acid, and the total volume of solution was 200 c.c.

CHAPTER XXV.

DISCRIMINATION OF GEMS AND PRECIOUS STONES.

SIMPLE characteristics of and means of recognising many gems and precious stones have been given at page 287, in the section on the discrimination of minerals.

The present chapter contains much information which could not appropriately be introduced in the previous chapter, which was intended chiefly for the use of travellers and explorers. Some trifling repetitions occur purposely to save the inconvenience of referring back.

The principal sources of recognition are colour, crystalline form, specific gravity, and hardness. In the present chapter will be introduced all the most constantly occurring natural forms of the gems and precious stones mentioned.

The specific gravity or density of a substance is the proportion of its weight to its volume, and it forms a characteristic property of substances. A full description of the method of taking specific gravities has been given at pages 236, 237.

COLOURLESS STONES.

THE DIAMOND.

(See also p. 252.)

Specific gravity, 3·48 to 3·52; hardness, 10. The diamond is the hardest of all known substances. The diamond is the only substance which is capable of cutting glass, although most gems will scratch glass; hence it is the utmost term of hardness. When cut and polished, it is the most brilliant gem. It frequently becomes phosphorescent on exposure to light. The greater number of diamonds are limpid and colourless, but many coloured specimens are found; as rose, yellow, orange, blue, green, brown, or even black. It sometimes occurs in regular crystals, octahedrons, dodecahedrons, and more complex forms; see figs. 131, 132, 133, 134.

The crystalline faces are often curved. The cleavage is octahedral and highly perfect; hence, although diamonds are so exceedingly hard, they are very brittle, owing to their tendency to facile cleavage. Like most gems, they become electrical by friction; but it has been remarked that other gems do not, unless they have been previously polished.

FIG. 131.

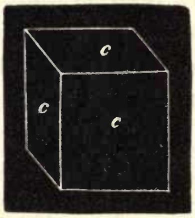


FIG. 132.

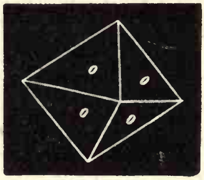


FIG. 133.

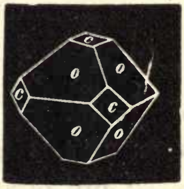
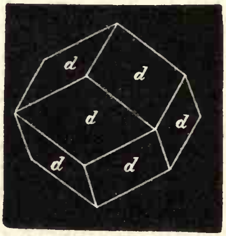


FIG. 134.



Composition (C): Pure carbon.

Speaking of diamonds, Professor Orton says that few things are so unpromising and unattractive as these gems in their native state. Hence their slow discovery. There is little doubt that diamonds exist in many places as yet unknown, or where their presence is unsuspected. It is very difficult for the unpractised eye to distinguish them from crystals of quartz or topaz. The colour constitutes the main difficulty in detecting their presence. They are of various shades of yellowish-brown, green, blue, and rose-red, and thus closely resemble the common gravel by which they are surrounded. Often they are not unlike a lump of gum arabic, neither brilliant nor transparent. The finest, however, are colourless, and appear like rock crystals.

In Brazil, where great numbers of diamonds, chiefly of small size, have been discovered, the method of searching for them is to wash the sand of certain rivers in a manner precisely similar to that employed in the gold fields, namely, by prospecting pans. A shovelful of earth is thrown into the pan, which is then immersed in water, and gently moved about. As the washing goes on, the pebbles, dirt, and sand are removed, and the pan then contains about a pint of thin mud. Great caution is now observed, and ultimately there remains only a small quantity of sand. The diamonds and particles of gold, if present, sink to the bottom, being heavier, and are selected and removed by the practised fingers of the operator. But how shall the gems be detected by one who in a jeweller's shop could not separate them from quartz or French paste? The difficulty can only be overcome by testing such stones as may be suspected to be precious. Let these be tried by the very sure operation of attempting to cut with their sharp corners glass, crystal, or quartz. When too minute to be held between the finger and thumb, the specimens may be pressed into the end of a stick of hard wood and run along the surface of window glass. A diamond will make its mark, and cause, too, a ready fracture in the line over which it has travelled. It will also easily scratch rock crystal, as few crystals will.

But a more certain and peculiar characteristic of the diamond lies in the form of its crystals. The ruby and topaz will scratch quartz, but no mineral which will scratch quartz has the *curved edges* of the diamond. In small crystals this peculiarity can be seen only by means of a magnifying glass; but it is invariably present. Interrupted, convex, or rounded angles are sure indications of genuineness Quartz crystal is surrounded by six faces, the diamond by four. The diamond breaks with difficulty; and hence a test sometimes used is to place the specimen between two hard bodies, as a couple of coins, and force them together with the hands. Such a pressure will crush a particle of quartz, but the diamond will only indent the metal.

The imperfections of the diamond, and, in fact, of all cut gems, are made visible by putting them into oil of cassia, when the slightest flaw will be seen.

If a rough diamond resemble a drop of clear spring water, in the middle of which you perceive a strong light; or if it has a rough coat, so that you can hardly see through it, but white, and as if made rough by art, yet clear of flaws or veins; or if the coat be smooth and bright, with a tincture of green in it,—it is a good stone. If it has a milky cast or a yellowish-green coat, beware of it. Rough diamonds with a greenish crust are the most limpid when cut.

Diamonds are found in loose pebbly earth, along with gold, a little way below the surface, towards the lower outlet of broad valleys, rather than upon the ridges of the adjoining hills.

Prof. Silliman, on examining with the microscope a small parcel of the sand resulting from the hydraulic treatment of ores, found that they abounded in fine colourless zircons, along with crystals of topaz, fragments of quartz, grains of chrome iron, and titanic acid, and globular bodies of a very high refractive power, which he believes to be diamonds.

Mr. J. Torry, in a single sample of the sands washed from the gold ores of Nicaragua, found twenty mineral species, some of them very rare.

For determining the specific gravity of certain minerals, and separating diamond dust or small diamonds and other gems from quartz, sand, &c., Mr. E. Sonstardt* uses a solution in water of pure potassium iodide and pure mercuric iodide in cold water. It should be diluted to such a strength that quartz will just float in it. (See *ante*, page 237.)

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* 'Chemical News,' March 20, 1874.

QUARTZ

Specific gravity, 2·55 to 2·7; hardness, 7. Quartz occurs in many forms, and has often by inexperienced persons been mistaken for the diamond, owing to the lustre of its crystals and its considerable hardness. It, however, can always be distinguished from the diamond by its crystalline faces, hardness, and specific gravity (see example in Table I.).

FIG. 135.

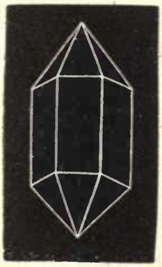


FIG. 136.

FIG. 137.

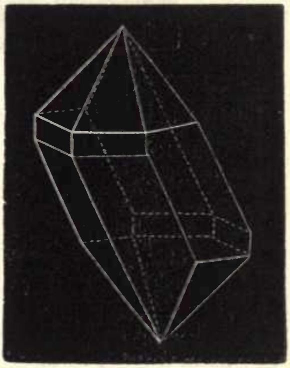


FIG. 138.

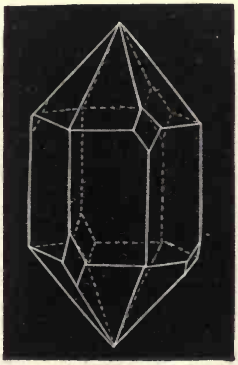
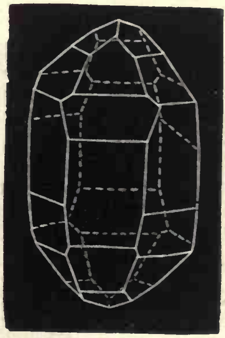


FIG. 139.



It usually occurs in six-sided prisms, more or less modified, terminated with six-sided pyramids. Traces of cleavage are seldom or ever apparent. Some of its salient forms are shown in figs. 135, 136, 137, 138, 139, 140, 141.

FIG. 140.

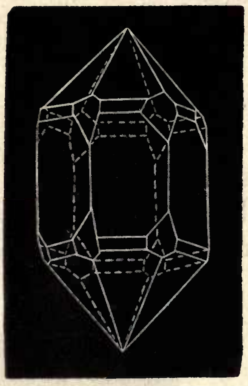
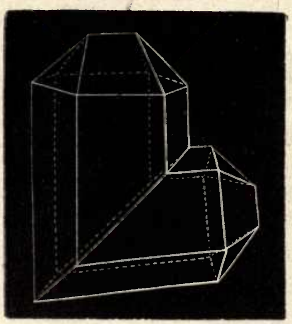


FIG. 141.



Some crystals are as pellucid as glass; others, however, assume all the shades of colour mentioned in the case of the diamond.

Composition (SiO_2): Pure silica or silicic acid.

WHITE ZIRCON.

Specific gravity, 4·44 to 4·8; hardness, 7·5. This stone is often found crystallised in nature in four-sided prisms, terminated by four-sided or rhomboidal or triangular pyramids, and other forms. See figs. 142, 143, 144, 145, 146, 147.

FIG. 142.

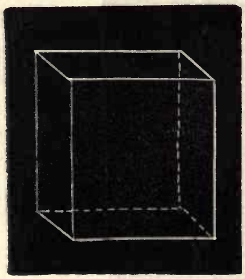


FIG. 143.

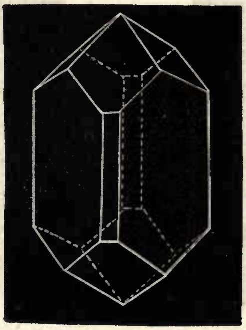
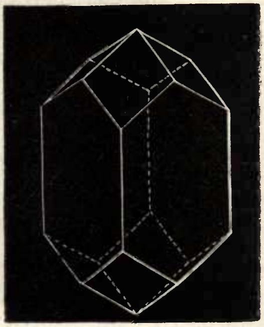


FIG. 144.



These stones are often employed in jewellery under the name of 'rough diamonds.' They often occur brownish-red and brown, red, yellow, and grey; these varieties will be treated under their appropriate heads. It can be readily distinguished from the diamond and quartz by hardness and specific gravity; also by the action of strong hydrochloric acid, which, if dropped on the diamond or quartz, and allowed to remain for a little time, produces no change, but if a zircon be so treated, the spot on which the acid was placed remains dull.

FIG. 145.

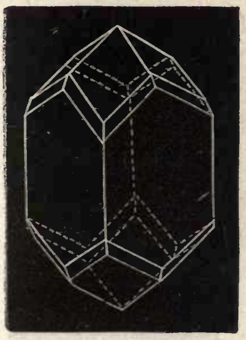


FIG. 146.

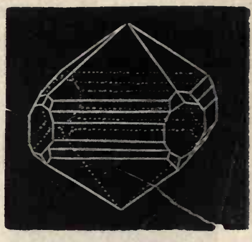
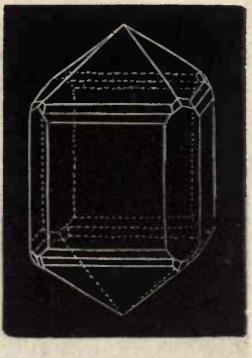


FIG. 147.



Composition (Zr_2O_3,SiO_2) :—

Zirconia	67·2
Silicic acid	33·5
	100·7

WHITE SAPPHIRE.

Specific gravity, 3·97 to 4·27; hardness, 9. This stone, in hardness, is next to the diamond. It occurs variously coloured; other colours will be discussed under their appropriate heads. It crystallises in the rhombohedric system, usually in six-sided prisms, but often so very rough as not to be readily distinguishable. May be distinguished by gravity and hardness from all the preceding.

Composition (Al_2O_3) :—Pure alumina.

WHITE TOPAZ.

Specific gravity, 3·54; hardness, 9. This variety of topaz, known for its limpidity by the term 'gouttes d'eau,' when polished has nearly the same lustre as the diamond;

the topaz, however, occurs of many colours—see hereafter. It crystallises in the right rectangular prismatic system. Some of its natural forms are shown in figs. 148, 149, 150, 151, 152, 153.

It is readily rendered electric, and retains its electricity for a very considerable time; it is also pyro-electric, or becomes electric when heated,—a property by which it is distinguished from the diamond, its specific gravity being so similar that it cannot be made available as a means of discriminating between the two stones. From the other stones in this group, with the exception of the sapphire, it is readily distinguished by its hardness and gravity, and from the latter by its gravity and pyro-electricity.

Fig. 148.

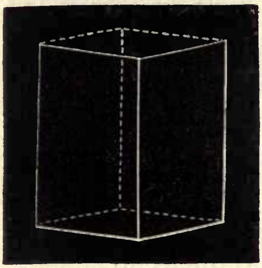


Fig. 149.

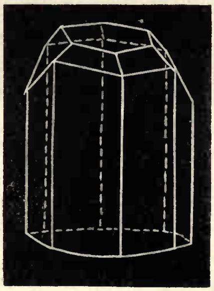


Fig. 150.

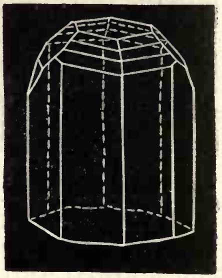


Fig. 151.

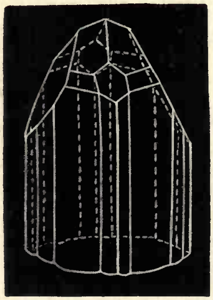


Fig. 152.

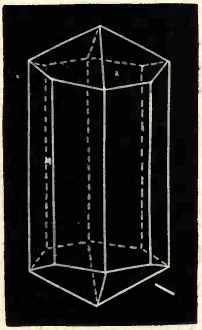
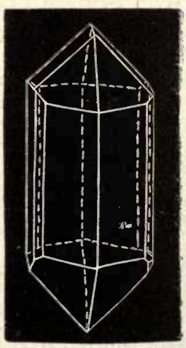


Fig. 153.



Composition:—

Silica	34·2
Alumina	57·5
Fluorine	7·8
	99·5

TABLE I.

COMPARATIVE TABLE OF THE WEIGHTS OF COLOURLESS STONES WEIGHED IN AIR AND WATER.

Weight in Air	Weight in Water				
Grains	White Zircon	White Sapphire	White Topaz	White Diamond	White Quartz
1	0·775	0·766	0·716	0·715	0·611
4	3·10	3·06	2·86	2·86	2·42
8	6·20	6·12	5·72	5·72	4·86
12	9·30	9·18	8·58	8·58	7·31
16	12·40	12·25	11·55	11·45	9·75
20	15·50	15·31	14·42	14·31	12·19
24	18·60	18·37	17·28	17·17	14·64
28	21·70	21·44	20·16	20·13	17·08
32	24·80	24·51	23·01	22·90	19·53
36	27·90	27·57	25·88	25·76	11·98
40	31·00	30·64	28·75	28·63	24·43
44	34·10	33·71	31·61	31·49	26·88
48	37·20	36·76	34·47	34·35	29·32
52	40·30	39·82	37·34	37·21	31·77
56	43·40	42·89	40·20	40·17	34·21
60	46·50	45·95	43·06	42·94	36·66
64	49·60	49·01	45·93	45·80	39·11
68	52·70	52·07	48·90	48·66	41·56
72	55·80	55·14	51·77	51·52	44·00
76	58·90	58·21	54·63	54·38	46·44
80	62·00	61·28	57·49	57·24	48·88
84	65·10	64·34	60·35	60·12	51·32
88	68·20	67·41	63·22	62·97	53·76
92	71·30	70·47	66·08	65·30	56·21
96	74·40	73·54	68·94	68·69	58·65
100	77·50	76·60	71·80	71·55	61·09
Specific Gravity	4·44	4·27	3·54	3·52	2·55

*Example of the use of Table I.**—A colourless stone, weighing 40 grains in air, is reduced to 24·43 in water. Look in the first column to 40, and then trace along its horizontal line until a number very nearly approaching 24·43 is found; refer then to the heading of the table, above the number found, and the name there expressed will be that of the stone examined. Supposing, however, the weight of the stone be 41 grains, still the number 24·43 will be the nearest in the table, and ·611 must be added to it, as that sum would be the weight of 41 grains

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* The Tables of Comparative Weights were calculated by Brard.

of quartz or water. From the numbers obtained by calculation also can the specific gravity be determined. If this course be pursued, refer to the bottom line of the table for a corresponding number, and to the heading of the table for the name of the stone. When the weight is any even number of grains (that is, without fractions), the readiest way is to refer to the table (first column) for the number of grains, and then to the horizontal line to corresponding number obtained, which is the weight in water.

Diamond and topaz, however, have very nearly equal densities, and a second characteristic must be had recourse to in order to determine the nature of two stones which have an equal weight in water. This auxiliary character is the development of electricity by heat, a phenomenon exhibited by the topaz but not by the diamond. The test of hardness may be also resorted to.

YELLOW STONES.

YELLOW ZIRCON (JARGON).

The crystalline form, characteristics, and composition of this stone have been described under the head 'White Zircon.'

YELLOW SAPPHIRE.

Characteristics, &c., described under 'White Sapphire.'

CYMOPHANE (CHRYSOBERYL).

Specific gravity, 3·65 to 3·89; hardness, 8·5. The cymophane is nearly as hard as the sapphire, harder than the topaz and the emerald; it readily scratches quartz. Its colour is greenish-yellow, and has been placed in the list of yellow stones rather than green, because usually the yellowish tint is the most decided. This tint, which is very agreeable in itself, is often relieved by a small spot of light of a bluish-white tinge, which moves from point to point of the stone as the position of the latter is varied. It is rarely found in regular crystals, but more generally occurs in rolled and rounded masses. For some of its forms, however, see figs. 154, 155, 156, 157.

FIG. 154.

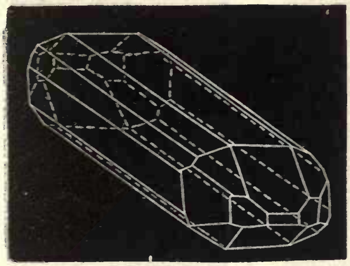


FIG. 155.

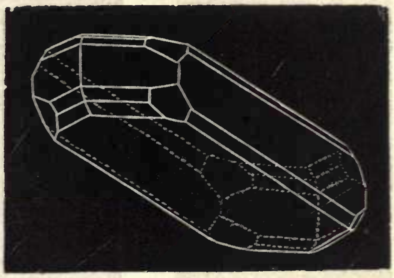


FIG. 156.

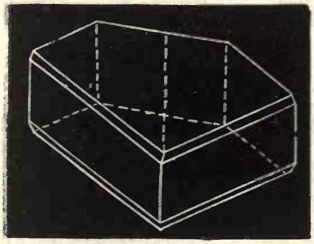
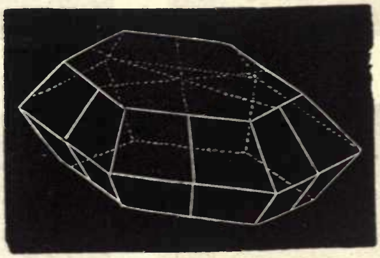


FIG. 157.



Composition:—No. 1 is a sample from the Brazils; No. 2, from Siberia.

	1.	2.
Alumina	78·10	78·92
Glucina	17·94	18·02
Iron oxide	4·46	3·12
Chromium oxide	—	0·36
Copper and lead oxides	—	0·29
	100·50	100·71

YELLOW TOPAZ.

The general characteristics of this stone are described under 'White Topaz.'

YELLOW TOURMALINE.

Specific gravity, 3·00 to 3·22; hardness, 7 to 7·5. The tourmaline becomes electrical by heat; one portion of a crystal attracts light bodies, the other repels them. Its colour is very varied. The tourmaline has a vitreous fracture. It occurs in semicrystalline prisms of irregular form, generally deeply striated, and in prisms of six or more sides, variously terminated, one end usually differing from the other.

Fig. 158.

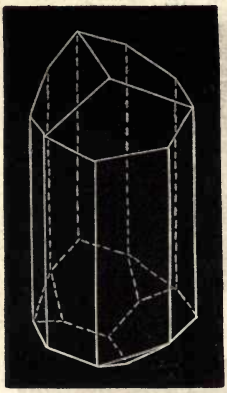


Fig. 159.

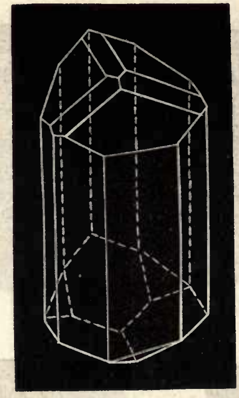


Fig. 160.

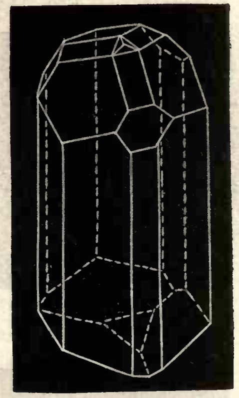


Fig. 161.

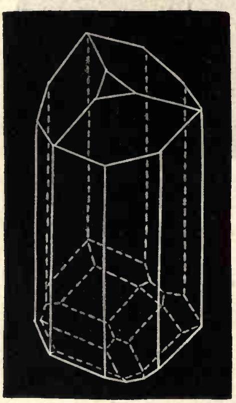


Fig. 162.

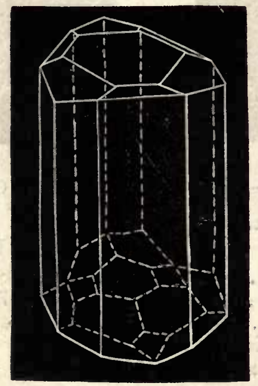
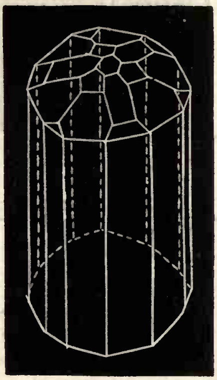


Fig. 163.



Figs. 158, 159, 160, 161, 162, and 163 represent some of the forms of this mineral.

YELLOW EMERALD.

Specific gravity, 2·73 to 2·76; hardness, 7·5 to 8. The emerald occurs of many colours; its tint *par excellence* is green; but there are many varieties tinged more or less yellow or blue, and they even occur white. Its fracture

FIG. 164.

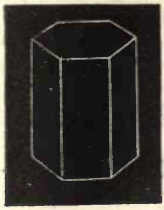


FIG. 165.

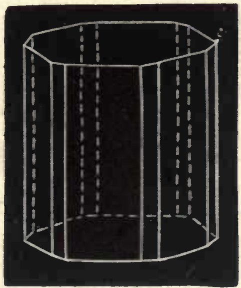


FIG. 166.

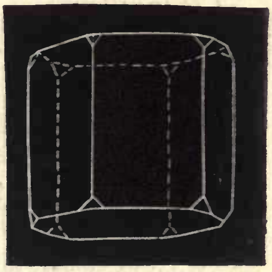


FIG. 167.

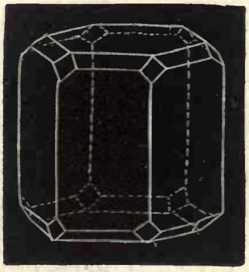


FIG. 168.

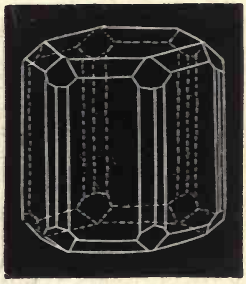


FIG. 169.

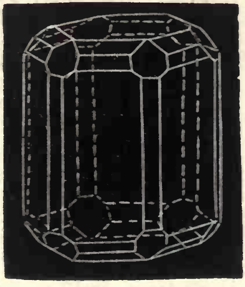
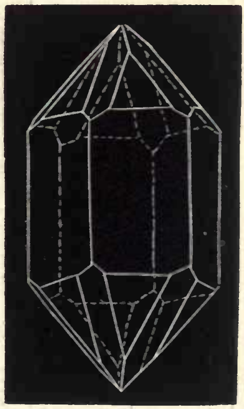


FIG. 170



is vitreous, brilliant, and undulating. Its common form is the hexahedral prism, sometimes deeply striated longitudinally. It readily cleaves parallel to all the planes of its primary form—the hexahedral prism.

The above are some of the forms it assumes: figs. 164, 165, 166, 167, 168, 169, and 170.

Composition:—

Glucina	15·50
Silica	66·45
Alumina	16·75
Iron oxide	·60
	99·30

The green varieties contain a small quantity of chromium oxide.

Table II.

Comparative Table of the Weights of Yellow Stones weighed in Air and Water.

Weight in air	Weight in Water						
Grains	Yellow Zircon	Yellow Sapphire	Yellow Cymophane	Yellow Topaz	Yellow Tourmaline	Yellow Emerald	Yellow Quartz
1	0·775	0·766	9·738	0·716	0·690	0·633	0·611
4	3·10	3·06	2·95	2·86	2·76	2·53	2·42
8	6·20	6·12	5·90	5·72	5·52	5·06	4·86
12	9·30	9·18	8·85	8·58	8·28	7·59	7·31
16	12·40	12·25	11·80	11·55	11·04	10·12	9·75
20	15·50	15·31	14·75	14·42	13·80	12·65	12·19
24	18·60	18·07	17·70	17·28	16·56	15·19	14·04
28	21·70	21 44	20·65	20·15	19·32	17·72	17·08
32	24·80	24·51	23·60	23·01	20·08	20·25	19·53
36	27 90	27·57	26·55	25·88	24·84	22·77	21·98
40	31·00	30·64	29·50	29·75	27·60	25·30	24·43
44	34·10	33·71	32·45	31·61	30·36	27·83	26·88
48	37·20	36·76	35·40	34·47	33·12	30·36	29·32
52	40·30	39·82	38·35	37·34	35·88	32·89	31·77
56	43·40	42·89	41·30	40·20	38 64	35·43	34·21
60	46·50	45·95	44·25	43·06	41·40	37·94	36·66
64	49·60	49·01	47·20	45·93	44·16	40·47	39·11
68	52·70	52·08	50·15	48·90	46·92	43·00	41·56
72	55·80	55·14	53·10	51·77	49 68	45·53	44·00
76	58·90	58·21	56·05	54·63	52·44	48·07	46·44
80	62·00	61·28	59·00	57·49	55·20	50·60	48·88
84	65·10	64·34	61·95	60·35	57·96	53·13	51·32
88	68·20	67·41	64·90	63·22	60 72	55·66	53·76
92	71·30	70·47	67·85	66·08	63·48	58·19	56·21
96	74·40	73·54	70·80	68·94	66·24	60·72	58·65
100	77·50	76·60	73·75	71·80	69·00	63·25	61·09
Specific Gravity	4·44	4·27	3·89	3·53	3·22	2·72	2·55

YELLOW QUARTZ.

For the characteristics, hardness, &c., of this mineral, see 'White Quartz.'

BROWN AND FLAME-COLOURED STONES.

ZIRCON (HYACINTH).

For characteristics, &c., see 'White Zircon.'

VERMEIL GARNET, NOBLE GARNET, ALMANDINE.

Specific gravity, 4 to 4·2; hardness, 6·5 to 7·5. There are very many varieties of garnet, variously coloured; but their crystalline form—a rhombic dodecahedron, more or less modified—is a distinguishing characteristic. The colouring matter of the garnet is iron. Figs. 171, 172, 173, 174 and 175 represent some of its crystalline forms.

FIG. 171.

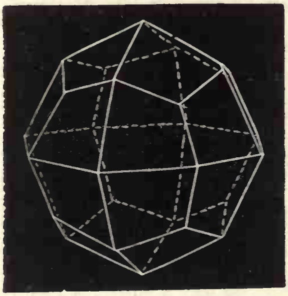


FIG. 172.

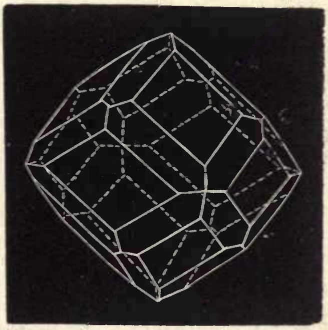


FIG. 173.

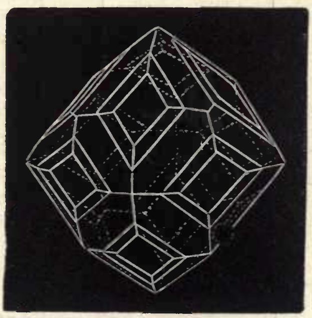


FIG. 174.

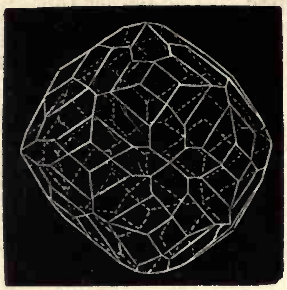
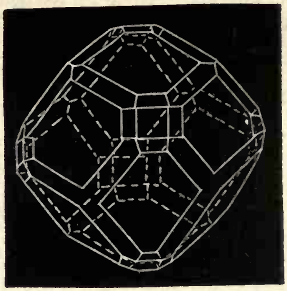


FIG. 175.



Composition :—

Silica	33·75
Alumina	27·25
Iron oxide	36·00
Manganese oxide	·25
	97·25

TABLE III.

COMPARATIVE TABLE OF THE WEIGHTS OF BROWNISH AND FLAME-COLOURED STONES WEIGHED IN AIR AND WATER.

Weight in Air	Weight in water			
Grains	Hyacinthine Zircon	Vermeil Garnet	Essonite	Tourmaline
1	0·775	0·750	0·710	0·690
4	3·10	3·00	2·87	2·76
8	6·20	6·00	5·74	5·52
12	9·30	9·00	8·61	8·28
16	12·40	12·00	11·48	11·04
20	15·50	15·00	14·35	13·80
24	18·60	18·00	17·22	16·56
28	21·70	21·00	20·09	19·32
32	24·80	24·00	22·96	22·08
36	27·90	27·00	25·83	24·84
40	31·30	30·00	28·70	27·60
44	34·10	33·00	31·57	30·36
48	37·20	36·00	34·44	33·12
52	40·30	39·00	37·31	35·88
56	43·40	42·00	40·18	38·64
60	46·50	45·00	43·05	41·40
64	49·60	48·00	45·92	44·16
68	52·70	51·00	48·79	46·92
72	55·80	54·00	51·66	49·68
76	58·90	57·00	54·53	52·44
80	61·00	60·00	57·40	55·20
84	65·10	63·00	60·27	57·96
88	68·20	66·00	63·14	60·72
92	71·30	69·00	66·01	63·48
96	74·40	72·00	68·88	66·24
100	77·50	75·00	71·75	69·00
Specific Gravity	4·44	4·00	3·54	3·22

ESSONITE, CINNAMON STONE.

Specific gravity, 3·5 to 3·6. This stone has an agreeable orange-yellow tinge, which becomes a warm and brilliant tint when the mass is large. This stone is not usually found crystalline, but in irregular forms and masses, which are characterised by fissures in all directions.

Composition :—

Silica	38·80
Alumina	21·20
Lime	31·25
Iron oxide with small quantities of Potash and Magnesia	6 50
	97·75

TOURMALINE.

For the characteristics of this mineral see ‘Yellow Tourmaline.’

RED AND ROSE-COLOURED STONES.

RED SAPPHIRE (ORIENTAL RUBY).

For characteristics, crystalline form, &c., see ‘White Sapphire.’

DEEP RED GARNET, NOBLE GARNET.

For characteristics, &c., see ‘Vermeil Garnet.’

SPINEL RUBY.

Specific gravity 3·5 to 3·6 : hardness, 8. The spinel readily scratches quartz, but is scratched by the sapphire. Its special colour is red, approaching a rose tint: this tinge, however, undergoes various modifications, such as scarlet, red, rose, yellowish-red, and reddish-purple: it is also found blue and black. Its fracture is flattish-conchoidal, with a splendent vitreous lustre. It occurs crystallised in regular octahedrons, sometimes having their edges replaced as in macles: sometimes it assumes the globular form. The spinel may be distinguished from the red sapphire and the garnet by hardness and specific gravity; and from reddish topaz, which possesses nearly the same specific gravity, by its electric properties.

Composition of spinel ruby:—

Silica	·02
Alumina	69·01
Magnesia	26·21
Iron protoxide	0·71
Chromium oxide	1·11
	99·06

REDDISH TOPAZ.

For characteristics, &c., see 'White Topaz.'

RED TOURMALINE.

For characteristics, &c., see 'Yellow Tourmaline.'

TABLE IV.

COMPARATIVE TABLE OF THE WEIGHTS OF RED OR ROSE-COLOURED STONES WEIGHED IN AIR AND WATER.

Weight in Air	Weight in Water				
Grains	Red Sapphire	Deep Garnets	Spinel	Smoke or Red Topaz	Red Tourmaline
1	0·766	0·750	0·722	0·716	0·690
4	3·060	3·700	2·880	2·860	2·760
8	6·120	6·000	5·770	5·720	5·520
12	9·180	9·000	8·660	8·585	8·280
16	12·250	12·000	11·550	11·550	11·040
20	15·310	15·000	14·440	14·420	13·800
24	18·370	18·000	17·330	17·280	16·560
28	21·440	21·000	20·220	20·150	19·320
32	24·510	24·000	23·110	23·610	22·080
36	27·570	27·000	26·000	25·880	24·840
40	30·640	30·000	28·880	28·750	27·600
44	33·710	33·000	31·770	31·610	30·360
48	36·760	36·000	34·660	34·470	33·120
52	39·820	39·000	37·550	37·340	35·880
56	42·890	42·000	40·440	40·200	38·640
60	44·950	45·000	43·300	43·060	41·400
64	49·010	48·000	46·220	45·930	44·160
68	52·080	51·000	49·110	48·900	46·920
72	55·140	54·000	51·990	51·770	49·680
76	58·210	57·000	54·880	54·630	52·440
80	61·280	60·000	57·770	57·490	52·200
84	64·340	63·000	60·660	60·350	57·960
88	67·410	66·000	63·550	63·220	60·720
92	70·470	69·000	66·440	66·080	63·480
96	73·540	72·000	69·330	68·940	66·240
100	76·600	75·000	72·220	71·800	69·000
Specific Gravity	4·270	4·000	3·600	3·530	3·220

BLUE STONES.

BLUE SAPPHIRE.

For characteristics, &c., see ‘White Sapphire.’

DISTHENE, CYANITE.

Specific gravity, 3·5 to 3·7; hardness, 5 to 7. Fine specimens of disthene possess a bright blue colour, which passes insensibly into a deep sky blue. Its transparency is nearly perfect, and it presents small pearly reflections, which add to the beauty of its colour. The primary form of its crystals is a doubly oblique prism, and they cleave very readily in the direction of their length. It can be readily distinguished from the sapphire by its being less hard, as also by its specific gravity. Figs. 176, 177, and 178 represent some of its crystalline forms.

FIG. 176.

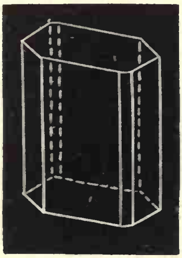


FIG. 177.

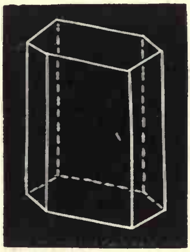
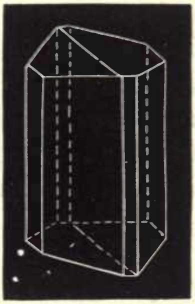


FIG. 178.



Composition of a specimen from St. Gothard:—

Silica	43·0
Alumina	55·0
Iron oxide	·5
	98·5

BLUE TOPAZ.

For characteristics, &c., see ‘White Topaz.’ Blue topaz and disthene having the same specific gravity, may by that test alone be confounded with each other; but the appearance of each is so different that they can rarely be confounded. If, however, the electrical test be applied, no fear of mistaking one for the other need be entertained, as only the topaz becomes electrical.

BLUE TOURMALINE.

For characteristics, &c., see 'Yellow Tourmaline.'

BLUE BERYL.

For characteristics, &c., see 'Emerald.' The tint and appearance of this stone and that of the blue topaz are so similar that they cannot be distinguished by that test; their specific gravities, however, are so different that they may, by this simple means, be readily discriminated.

DICHROITE, WATER SAPPHIRE.

Specific gravity, 2·56 to 2·65; hardness, 7 to 7·5. The chief characteristic of this stone, is that it possesses a double colour; that is, it is a fine blue or a normal yellow, as it is viewed in the direction of its base, or the planes of a hexahedral prism, which is its crystalline form. It can be thus readily distinguished, as also by its having nearly the same specific gravity as quartz, and thus being the lightest of the blue stones. Composition:—

Silica	48·35
Alumina	31·71
Magnesia	10·16
Iron protoxide	8·12
Manganese protoxide	·33
Loss in fire (water?)	·60
	99·27

TURQUOISE.

Specific gravity, 2·8 to 3; hardness, 5 to 6. This stone has not been placed in the list of specific gravities, as it can be so readily detected by its appearance. It is bright or greenish-blue in colour; its aspect is earthy or compact. It scratches apatite, and even glass; but is scratched by quartz. It occurs filling fissures, or forming concretions in siliceous and argillo-ferruginous rocks. Composition:—

Phosphoric acid	17·86
Alumina	10·01
Silica	8·90
Iron peroxide	36·82
Lime	0·15
Water and fluoric acid	25·95
	99·69

TABLE V.

COMPARATIVE TABLE OF THE WEIGHTS OF BLUE STONES WEIGHED IN AIR AND WATER.

Weight in Air Grains	Weight in Water					
	Blue Sapphire	Disthene, Cyanite	Blue Topaz	Tourmaline	Blue Beryl	Dichroite, Water Sapphire
1	0·766	0·717	0·716	0·690	0·633	0·622
4	3·06	2·87	2·86	2·16	2·53	2·49
8	6·12	5·74	5·72	5·52	5·06	4·98
12	9·18	8·61	8·58	8·28	7·59	7·47
16	12·25	11·48	11·45	11·04	10·12	9·96
20	15·31	14·35	14·42	13·80	12·65	12·45
24	18·37	17·22	17·18	16·56	15·19	14·94
28	21·44	20·09	20·05	19·32	17·72	17·43
32	24·51	22·96	22·91	20·08	20·25	19·92
36	27·57	25·83	25·78	24·84	22·77	22·41
40	30·64	28·70	28·65	27·60	25·30	24·90
44	33·71	31·57	31·51	30·66	27·83	27·39
48	36·76	34·44	34·37	33·12	30·36	29·88
52	39·82	37·31	37·24	35·88	32·89	32·37
56	42·89	40·18	40·10	38·64	35·43	34·86
60	45·95	43·05	42·96	41·40	37·94	37·35
64	49·01	45·92	45·83	44·16	40·47	39·84
68	52·08	48·79	48·80	46·92	43·00	42·33
72	55·14	51·66	51·67	49·68	45·53	44·82
76	58·21	54·53	54·53	52·44	48·07	47·31
80	61·28	57·40	57·49	55·20	50·60	49·80
84	64·34	60·27	60·25	57·96	53·13	52·29
88	67·41	63·14	63·12	60·72	55·66	54·78
92	70·47	66·01	65·98	63·48	58·19	57·27
96	73·54	68·88	63·84	66·24	60·72	59·76
100	76·60	71·75	71·70	69·00	63·25	62·25
Specific Gravity	4·27	3·54	3·53	3·22	2·72	2·65

VIOLET STONES.

VIOLET SAPPHIRE.

For characteristics, &c., see 'White Sapphire.'

VIOLET TOURMALINE

For characteristics, &c., see 'Yellow Tourmaline.'

VIOLET QUARTZ, AMETHYST.

For characteristics, &c., see 'White Quartz.'

TABLE VI.

COMPARATIVE TABLE OF THE WEIGHTS OF VIOLET STONES WEIGHED IN AIR AND WATER.

Weight in Air Grains	Weight in Water		
	Violet Sapphire	Violet Tourmaline	Amethystine Quartz (Amethyst)
1	0·766	0·690	0·611
4	3·06	2·76	2·42
8	6·12	5·52	4·86
12	9·18	8·28	7·31
16	12·25	11·04	9·75
20	15·31	13·80	12·19
24	18·37	16·56	14·64
28	21·44	19·32	17 08
32	24·51	20·08	19·53
36	27·57	24·84	21·98
40	30·64	27·60	24·43
44	33·71	30·36	26·88
48	36·76	33·12	29·32
52	39·82	35·88	31·77
56	42·89	38·64	34·21
60	45·95	41·40	36·66
64	49·01	44·16	39·11
68	52·02	46·92	41·56
72	55·14	49·68	44·00
76	58·21	52·44	46·44
80	61·28	55·20	48·88
84	64·34	57·96	51·32
88	67·41	60·72	53·76
92	70·47	63·48	56·21
96	73·54	66·24	58·65
100	76·60	69·00	61·09
Specific Gravity	4·27	3·22	2·55

GREEN STONES.

GREEN SAPPHIRE.

For characteristics, &c., see 'Yellow Emerald.'

PERIDOT, CRYSOLITE.

Specific gravity, 3·3 to 3·5; hardness, 6·5 to 7. This stone has a more or less deep olive or yellowish-green colour. It is more generally found in rolled grains than in regular prismatic crystals. It is possessed in a very high degree of double refraction. Figs. 179, 180, 181, and 182 represent some of its crystalline forms.

GREEN TOURMALINE.

For characteristics, see 'Yellow Tourmaline.'

EMERALD.

For characteristics, see 'Yellow Emerald.'

FIG. 179.

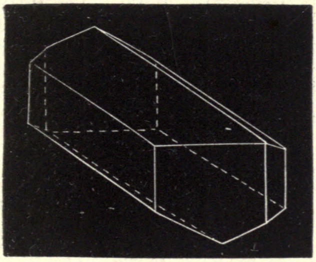


FIG. 180.

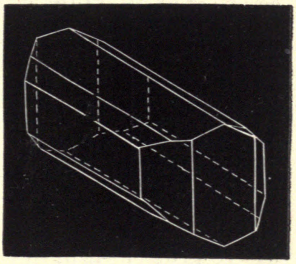


FIG. 181.

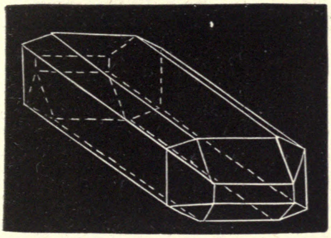
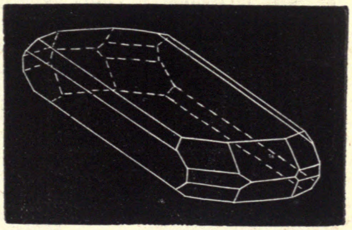


FIG. 182.



AQUA-MARINE.

This stone possesses a very pale green tinge. For other characteristics, see 'Yellow Emerald.'

CHRYSOPRASE.

This mineral is a green-coloured quartz, and can be readily recognised by referring to the characteristics of quartz.

TABLE VII.

COMPARATIVE TABLE OF THE WEIGHTS OF GREEN STONES WEIGHED IN AIR AND WATER.

Weight in Air	Weight in Water					
Grains	Green Sapphire	Peridot	Green Tourmaline	Emerald	Aqua-marine	Chrysoprase
1	0·766	0·708	0·690	0·633	0·633	0·611
4	3·06	2·83	2·76	2·53	2·53	2·42
8	6·12	5·66	5·52	5·06	5·06	4·86
12	9·18	8·49	8·28	7·59	7·59	7·31
16	12·25	11·32	11·04	10·12	10·12	9·75
20	15·31	14·16	13·80	12·65	12·65	12·19
24	18·37	16·99	16·56	15·19	15·19	14·64
28	21·44	19·82	19·32	17·72	17·72	17·08
32	24·51	22·65	22·08	20·25	20·25	19·53
36	27·57	25·48	24·84	22·77	27·77	21·98
40	30·64	28·32	27·60	25·30	25·30	24·43
44	33·71	31·15	30·36	27·83	27·83	36·88
48	36·76	33·98	33·12	30·36	30·36	29·32
52	39·82	36·81	35·88	32·89	32·89	31·77
56	42·89	39·64	38·64	35·43	35·43	34·21
60	45·95	42·48	41·40	37·94	37·94	36·66
64	49·01	45·31	44·16	40·47	40·47	39·11
68	52·08	48·14	46·92	43·00	43·00	41·56
72	55·14	50 97	49·68	45·53	45·53	44·00
76	58·21	53·80	52·44	48·07	48·07	46·44
80	61·28	56·64	55·20	50·60	50·60	48·88
84	64·34	59·47	57·96	53·13	53·13	51·32
88	67·41	62·30	60·72	55·66	55·66	53·76
92	70·47	65·13	63·48	58·19	58·19	56·21
96	73·54	67·96	66·24	60·72	60·72	58·65
100	76·60	70·80	69·00	63·25	63·25	61·09
Specific Gravity	4·27	3·42	3·22	2·72	2·72	2·56

STONES POSSESSING A PLAY OF COLOURS (*CHATOYANT*).

In the following list of stones no regard has been paid to absolute colours, but only to the play of colours the stones exhibit. This play or reflection is of two kinds: in some, as the sapphires, it appears as a white star with six rays, on a blue, red, or yellow ground; or on a purple ground in the garnet. In others it is but a point or mass of pearly light, which sometimes appears to occupy the whole of the stone, and varies according to the inclination given to the stone. The cymophane, crysolite quartz, Egyptian emerald, felspar, and cat's eye belong to this class.

The specific gravities of such stones as the opal, &c., have not been given, as their appearance sufficiently characterises them.

SAPPHIRE.

For characteristies, &c., see ‘White Saphhire.’

GARNET.

For characteristics, &c., see ‘Vermeil Garnet.’

CYMOPHANE.

See ‘Cymophane.’

ANTIQUE EMERALD.

For characteristics, &c., see ‘Yellow Emerald.’

QUARTZ.

See ‘White Quartz.’

FIG. 183.

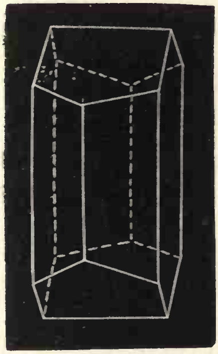


FIG. 184.

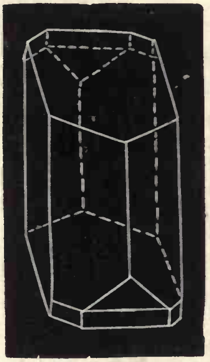


FIG. 185.

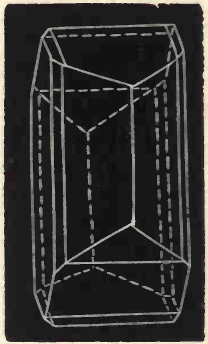


FIG. 186.

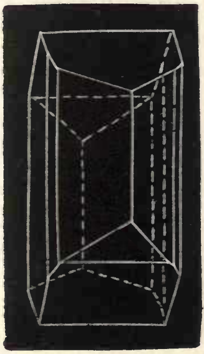


FIG. 187.

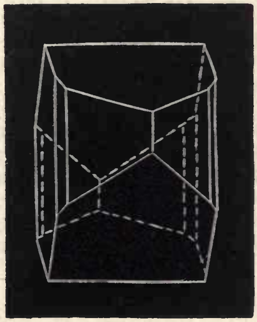
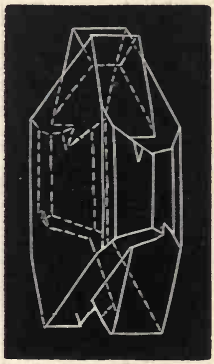


FIG. 188.



FELSPAR, NACREOUS FELSPAR, FISH-EYE, &c.

Specific gravity, 2·3 to 2·5; hardness 4·5 to 5. This species of felspar has a lamellar texture. It will be seen by the lowness of its specific gravity that it cannot be readily confounded with other stones. In appearance its transparency is nebulous, and it presents pearly white reflections, which float about and vacillate in proportion as its position changes. The foregoing are some of the forms of felspar; see Figs. 183, 184, 185, 186, 187, and 188.

Composition:—

Potash	5·26
Silica	52·90
Lime	25·20
Water	16·00
Fluoric acid	0 82
	100·18

TABLE VIII.

COMPARATIVE TABLE OF THE WEIGHTS OF STONES POSSESSING A PLAY OF COLOURS (CHATOYANT).

Weight in Air	Weight in Water					
Grains	Sapphires	Garnets	Cymophane	Antique Emerald	Quartz	Felspar
1	0·766	0·750	0·738	0·633	0·611	0·592
4	3·06	3·00	2·95	2·53	2·42	2·37
8	6·12	6·00	5·90	5·06	4·86	4·74
12	9·18	9·00	8·85	7·59	7·31	7·11
16	12·25	12·00	11·80	10·12	9·75	9·47
20	15·31	15·00	14·75	12·65	12·19	11·84
24	18·37	18·00	17·70	15·19	14·64	14·20
28	21·44	21·00	20·65	17·72	17·08	16·57
32	24·51	24·00	23·60	20·25	19·53	18·94
36	27·57	27·00	26·55	22·77	21·98	21·31
40	30·64	30·00	29·50	25·30	24·43	23·68
44	33·71	33·00	32·46	27·83	26·88	26·05
48	36·76	36·00	35·40	30·36	29·32	28·42
52	39·84	39·00	38·35	32·89	31·77	30·79
56	42·89	42·00	41·30	35·43	34·21	33·15
60	45·95	45·00	44·25	37·94	36·66	35·52
64	49·01	48·00	47·20	40·47	39·11	37·88
68	52·07	51·00	50·15	43·00	41·56	40·25
72	55·14	54·00	53·10	45·53	44·00	42·62
76	58·21	57·00	56·05	48·07	46·44	44·99
80	61·28	60·00	59·00	50·60	48·88	47·36
84	64·34	63·00	61·95	53·13	51·32	49·73
88	67·47	66·00	64·90	55·66	53·76	52·10
92	70·47	69·00	67·85	58·19	56·21	54·47
96	73·54	72·00	70·80	60·72	58·65	56·84
100	76·60	75·00	73·75	63·25	61·09	59·21
Specific Gravity	4·27	4·00	3·89	2·72	2·55	2·45

GLASS AND ARTIFICIAL GEMS.

Glass is often used to imitate gems, but can be easily distinguished by the following characters:—

1. *Inferior brilliancy.*—Though in many cases artificial gems have a fine lustre, they are invariably soft. The materials which communicate brilliancy to glass impair its hardness; and the result is that glass gems, when examined by a lens, are generally found to have blunt or jagged corners and edges, and surfaces covered with minute, irregular scratches. This is invariably the case after the glass gem has been a little in use, and thus the brilliancy soon becomes impaired.

2. *Inferior hardness.*—Artificial gems can be scratched with a knife, using a slight pressure. Faint scratches are made visible by breathing upon them, whereas true gems retain the original brilliancy which they possessed on leaving the lapidary's wheel. The polished faces of true gems cannot be scratched with a knife; moreover, after long wear, they show no signs of scratches.

3. Polished gems become readily electric by friction, particularly the topaz and diamond; but glass imitations require much longer friction to produce the same effect, and also retain the electric power for a shorter time.

4. Glass is fusible in the blowpipe flame.

APPENDIX.

TABLE I

Showing the Quantity of Fine Gold in 1 oz. of any Alloy to ⅛ of a Carat Grain and the Mint Value of 1 oz. of each Alloy.

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
1	0	0·000	24	0	0	4	4	11·4545
0	19	23·375	23	3	7	4	4	10·1271
0	19	22·750	23	3	6	4	4	8·7997
0	19	22·125	23	3	5	4	4	7·4723
0	19	21·500	23	3	4	4	4	6·1448
0	19	20·875	23	3	3	4	4	4·8174
0	19	20·250	23	3	2	4	4	3·4900
0	19	19·625	23	3	1	4	4	2·1626
0	19	19·000	23	3	0	4	4	0·8352
0	19	18·375	23	2	7	4	3	11·5078
0	19	17·750	23	2	6	4	3	10·1804
0	19	17·125	23	2	5	4	3	8·8529
0	19	16·500	23	2	4	4	3	7·5255
0	19	15·875	23	2	3	4	3	6·1981
0	19	15·250	23	2	2	4	3	4·8707
0	19	14·625	23	2	1	4	3	3·5433
0	19	14·000	23	2	0	4	3	2·2159
0	19	13·375	23	1	7	4	3	0·8885
0	19	12·750	23	1	6	4	2	11·5610
0	19	12·125	23	1	5	4	2	10·2336
0	19	11·500	23	1	4	4	2	8·9062
0	19	10·875	23	1	3	4	2	7·5788
0	19	10·250	23	1	2	4	2	6·2514
0	19	9·625	23	1	1	4	2	4·9240
0	19	9·000	23	1	0	4	2	3·5965
0	19	8·375	23	0	7	4	2	2·2691
0	19	7·750	23	0	6	4	2	0·9417
0	19	7·125	23	0	5	4	1	11·6143
0	19	6·500	23	0	4	4	1	10·2869
0	19	5·875	23	0	3	4	1	8·9595
0	19	5·250	23	0	2	4	1	7·6321
0	19	4·625	23	0	1	4	1	6·3047
0	19	4·000	23	0	0	4	1	4·9772
0	19	3·375	22	3	7	4	1	3·6498
0	19	2·750	22	3	6	4	1	2·3224

FINE GOLD, Per Ounce			CARAT GOLD, Per Ounce			STERLING VALUE, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	19	2·125	22	3	5	4	1	0·9950
0	19	1·500	22	3	4	4	0	11·6676
0	19	0·875	22	3	3	4	0	10·3402
0	19	0·250	22	3	2	4	0	8·0127
0	18	23·625	22	3	1	4	0	7·6854
0	18	23·000	22	3	0	4	0	6·3579
0	18	22·375	22	2	7	4	0	4·0305
0	18	21·750	22	2	6	4	0	3·7031
0	18	21·125	22	2	5	4	0	2·3757
0	18	20·500	22	2	4	4	0	0·0482
0	18	19·875	22	2	3	3	19	11·7208
0	18	19·250	22	2	2	3	19	10·3934
0	18	18·625	22	2	1	3	19	8·0660
0	18	18·000	22	2	0	3	19	7·7386
0	18	17·375	22	1	7	3	19	6·4112
0	18	16·750	22	1	6	3	19	4·0838
0	18	16·125	22	1	5	3	19	3·7563
0	18	15·500	22	1	4	3	19	2·4289
0	18	14·875	22	1	3	3	19	0·1015
0	18	14·250	22	1	2	3	18	11·7741
0	18	13·625	22	1	1	3	18	10·4467
0	18	13·000	22	1	0	3	18	8·1193
0	18	12·375	22	0	7	3	18	7·7919
0	18	11·750	22	0	6	3	18	6·4644
0	18	11·125	22	0	5	3	18	4·1370
0	18	10·500	22	0	4	3	18	3·8096
0	18	9·875	22	0	3	3	18	2·4822
0	18	9·250	22	0	2	3	18	0·1548
0	18	8·625	22	0	1	3	17	11·8274
0	18	8·000	22	0	0	3	17	10·5000
0	18	7·375	21	3	7	3	17	8·1725
0	18	6·750	21	3	6	3	17	7·8451
0	18	6·125	21	3	5	3	17	6·5177
0	18	5·500	21	3	4	3	17	4·1903
0	18	4·875	21	3	3	3	17	3·8629
0	18	4·250	21	3	2	3	17	2·5355
0	18	3·625	21	3	1	3	17	0·2081
0	18	3·000	21	3	0	3	16	11·8806
0	18	2·375	21	2	7	3	16	10·5532
0	18	1·750	21	2	6	3	16	8·2258
0	18	1·125	21	2	5	3	16	7·8984
0	18	0·500	21	2	4	3	16	6·5710
0	17	23·875	21	2	3	3	16	4·2436
0	17	23·250	21	2	2	3	16	3·9162

FINE GOLD, Per Ounce			CARAT GOLD, Per Ounce			STERLING VALUE, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	17	22·625	21	2	1	3	16	2·5887
0	17	22·000	21	2	0	3	16	1·2613
0	17	21·375	21	1	7	3	15	11·9339
0	17	20·750	21	1	6	3	15	10·6065
0	17	20·125	21	1	5	3	15	9·2791
0	17	19·500	21	1	4	3	15	7·9517
0	17	18·875	21	1	3	3	15	6·6243
0	17	18·250	21	1	2	3	15	5·2968
0	17	17·625	21	1	1	3	15	3·9694
0	17	17·000	21	1	0	3	15	2·6420
0	17	16·375	21	0	7	3	15	1·3146
0	17	15·750	21	0	6	3	14	11·9872
0	17	15·125	21	0	5	3	14	10·6598
0	17	14·500	21	0	4	3	14	9·3324
0	17	13·875	21	0	3	3	14	8·0049
0	17	13·250	21	0	2	3	14	6·6775
0	17	12·625	21	0	1	3	14	5·3501
0	17	12·000	21	0	0	3	14	4·0227
0	17	11·375	20	3	7	3	14	2·6953
0	17	10·750	20	3	6	3	14	1·3678
0	17	10·125	20	3	5	3	14	0·0404
0	17	9·500	20	3	4	3	13	10·7130
0	17	8·875	20	3	3	3	13	9·3856
0	17	8·250	20	3	2	3	13	8·0582
0	17	7·625	20	3	1	3	13	6·7308
0	17	7·000	20	3	0	3	13	5·4034
0	17	6·375	20	2	7	3	13	4·0759
0	17	5·750	20	2	6	3	13	2·7485
0	17	5·125	20	2	5	3	13	1·4211
0	17	4·500	20	2	4	3	13	0·0937
0	17	3·875	20	2	3	3	12	10·7663
0	17	3·250	20	2	2	3	12	9·4389
0	17	2·625	20	2	1	3	12	8·1115
0	17	2·000	20	2	0	3	12	6·7840
0	17	1·375	20	1	7	3	12	5·4566
0	17	0·750	20	1	6	3	12	4·1292
0	17	0·125	20	1	5	3	12	2·8018
0	16	23·500	20	1	4	3	12	1·4744
0	16	22·875	20	1	3	3	12	0·1470
0	16	22·250	20	1	2	3	11	10·8196
0	16	21·625	20	1	1	3	11	9·4921
0	16	21·000	20	1	0	3	11	8·1647
0	16	20·375	20	0	7	3	11	6·8373
0	16	19·750	20	0	6	3	11	5·5099

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	16	19·125	20	0	5	3	11	4·1825
0	16	18·500	20	0	4	3	11	2·8551
0	16	17·875	20	0	3	3	11	1·5277
0	16	17·250	20	0	2	3	11	0·2002
0	16	16·625	20	0	1	3	10	10·8728
0	16	16·000	20	0	0	3	10	9·5454
0	16	15·375	19	3	7	3	10	8·2180
0	16	14·750	19	3	6	3	10	6·8906
0	16	14·125	19	3	5	3	10	5·5632
0	16	13·500	19	3	4	3	10	4·2357
0	16	12·875	19	3	3	3	10	2·9083
0	16	12·250	19	3	2	3	10	1·5809
0	16	11·625	19	3	1	3	10	0·2534
0	16	11·000	19	3	0	3	9	10·9260
0	16	10·375	19	2	7	3	9	9·5986
0	16	9·750	19	2	6	3	9	8·2712
0	16	9·125	19	2	5	3	9	6·9437
0	16	8·500	19	2	4	3	9	5·6163
0	16	7·875	19	2	3	3	9	4·2889
0	16	7·250	19	2	2	3	9	2·9615
0	16	6·625	19	2	1	3	9	1·6341
0	16	6·000	19	2	0	3	9	0·3067
0	16	5·375	19	1	7	3	8	10·9793
0	16	4·750	19	1	6	3	8	9·6518
0	16	4·125	19	1	5	3	8	8·3244
0	16	3·500	19	1	4	3	8	6·9970
0	16	2·875	19	1	3	3	8	5·6696
0	16	2·250	19	1	2	3	8	4·3422
0	16	1·625	19	1	1	3	8	3·0148
0	16	1·000	19	1	0	3	8	1·6874
0	16	0·375	19	0	7	3	8	0·3599
0	15	23·750	19	0	6	3	7	11·0325
0	15	23·125	19	0	5	3	7	9·7051
0	15	22·500	19	0	4	3	7	8·3777
0	15	21·875	19	0	3	3	7	7·0503
0	15	21·250	19	0	2	3	7	5·7229
0	15	20·625	19	0	1	3	7	4·3955
0	15	20·000	19	0	0	3	7	3·0681
0	15	19·375	18	3	7	3	7	1·7407
0	15	18·750	18	3	6	3	7	0·4133
0	15	18·125	18	3	5	3	6	11·0859
0	15	17·500	18	3	4	3	6	9·7585
0	15	16·875	18	3	3	3	6	8·4311
0	15	16·250	18	3	2	3	6	7·1036

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	15	15·625	18	3	1	3	6	5·7762
0	15	15·000	18	3	0	3	6	4·4488
0	15	14·375	18	2	7	3	6	3·1214
0	15	13·750	18	2	6	3	6	1·7940
0	15	13·125	18	2	5	3	6	0·4666
0	15	12·500	18	2	4	3	5	11·1392
0	15	11·875	18	2	3	3	5	9·8117
0	15	11·250	18	2	2	3	5	8·4843
0	15	10·625	18	2	1	3	5	7·1569
0	15	10·000	18	2	0	3	5	5·8295
0	15	9·375	18	1	7	3	5	4·5021
0	15	8·750	18	1	6	3	5	3·1747
0	15	8·125	18	1	5	3	5	1·8473
0	15	7·500	18	1	4	3	5	0·5198
0	15	6·875	18	1	3	3	4	11·1924
0	15	6·250	18	1	2	3	4	9·8650
0	15	5·625	18	1	1	3	4	8·5376
0	15	5·000	18	1	0	3	4	7·2102
0	15	4·375	18	0	7	3	4	5·8828
0	15	3·750	18	0	6	3	4	4·5554
0	15	3·125	18	0	5	3	4	3·2279
0	15	2·500	18	0	4	3	4	1·9005
0	15	1·875	18	0	3	3	4	0·5731
0	15	1·250	18	0	2	3	3	11·2457
0	15	0·625	18	0	1	3	3	9·9183
0	15	0·000	18	0	0	3	3	8·5909
0	14	23·375	17	3	7	3	3	7·2634
0	14	22·750	17	3	6	3	3	5·9360
0	14	22·125	17	3	5	3	3	4·6086
0	14	21·500	17	3	4	3	3	3·2812
0	14	20·875	17	3	3	3	3	1·9538
0	14	20·250	17	3	2	3	3	0·6264
0	14	19·625	17	3	1	3	2	11·2990
0	14	19·000	17	3	0	3	2	9·9715
0	14	18·375	17	2	7	3	2	8·6441
0	14	17·750	17	2	6	3	2	7·3167
0	14	17·125	17	2	5	3	2	5·9893
0	14	16·500	17	2	4	3	2	4·6619
0	14	15·875	17	2	3	3	2	3·3345
0	14	15·250	17	2	2	3	2	2·0071
0	14	14·625	17	2	1	3	2	0·6796
0	14	14·000	17	2	0	3	1	11·3522
0	14	13·375	17	1	7	3	1	10·0248
0	14	12·750	17	1	6	3	1	8·6974

FINE GOLD, Per Ounce			CARAT GOLD, Per Ounce			STERLING VALUE, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	14	12·125	17	1	5	3	1	7·3700
0	14	11·500	17	1	4	3	1	6·0426
0	14	10·875	17	1	3	3	1	4·7152
0	14	10·250	17	1	2	3	1	3·3877
0	14	9·625	17	1	1	3	1	2·0603
0	14	9·000	17	1	0	3	1	0·7329
0	14	8·375	17	0	7	3	0	11·4055
0	14	7·750	17	0	6	3	0	10·0781
0	14	7·125	17	0	5	3	0	8·7507
0	14	6·500	17	0	4	3	0	7·4233
0	14	5·875	17	0	3	3	0	6·0958
0	14	5·250	17	0	2	3	0	4·7684
0	14	4·625	17	0	1	3	0	3·4410
0	14	4·000	17	0	0	3	0	2·1136
0	14	3·375	16	3	7	3	0	0·7862
0	14	2·750	16	3	6	2	19	11·4588
0	14	2·125	16	3	5	2	19	10·1313
0	14	1·500	16	3	4	2	19	8·8039
0	14	0·875	16	3	3	2	19	7·4765
0	14	0·250	16	3	2	2	19	6·1491
0	13	23·625	16	3	1	2	19	4·8217
0	13	23·000	16	3	0	2	19	3·4943
0	13	22·375	16	2	7	2	19	2·1669
0	13	21·750	16	2	6	2	19	0·8394
0	13	21·125	16	2	5	2	18	11·5120
0	13	20·500	16	2	4	2	18	10·1846
0	13	19·875	16	2	3	2	18	8·8572
0	13	19·250	16	2	2	2	18	7·5298
0	13	18·625	16	2	1	2	18	6·2024
0	13	18·000	16	2	0	2	18	4·8750
0	13	17·375	16	1	7	2	18	3·5475
0	13	16·750	16	1	6	2	18	2·2201
0	13	16·125	16	1	5	2	18	0 8927
0	13	15·500	16	1	4	2	17	11·5653
0	13	14·875	16	1	3	2	17	10·2377
0	13	14·250	16	1	2	2	17	8·9103
0	13	13·625	16	1	1	2	17	7·5829
0	13	13·000	16	1	0	2	17	6·2554
0	13	12·375	16	0	7	2	17	4·9280
0	13	11·750	16	0	6	2	17	3·6006
0	13	11·125	16	0	5	2	17	2·2732
0	13	10·500	16	0	4	2	17	0·9458
0	13	9·875	16	0	3	2	16	11·6184
0	13	9·250	16	0	2	2	16	10·2909

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	13	8·625	16	0	1	2	16	8·9635
0	13	8·000	16	0	0	2	16	7·6363
0	13	7·375	15	3	7	2	16	6·3089
0	13	6·750	15	3	6	2	16	4·9815
0	13	6·125	15	3	5	2	16	3·6541
0	13	5·500	15	3	4	2	16	2·3267
0	13	4·875	15	3	3	2	16	0·9992
0	13	4·250	15	3	2	2	15	11·6718
0	13	3·625	15	3	1	2	15	10·3444
0	13	3·000	15	3	0	2	15	9·0170
0	13	2·373	15	2	7	2	15	7·6896
0	13	1·750	15	2	6	2	15	6·3622
0	13	1·125	15	2	5	2	15	5·0348
0	13	0·500	15	2	4	2	15	3·7073
0	12	23·875	15	2	3	2	15	2·3799
0	12	23·250	15	2	2	2	15	1·0525
0	12	22·625	15	2	1	2	14	11·7251
0	12	22·000	15	2	0	2	14	10·3976
0	12	21·375	15	1	7	2	14	9·0702
0	12	20·750	15	1	6	2	14	7·7428
0	12	20·125	15	1	5	2	14	6·4154
0	12	19·500	15	1	4	2	14	5·0880
0	12	18·875	15	1	3	2	14	3·7606
0	12	18·250	15	1	2	2	14	2·4332
0	12	17·625	15	1	1	2	14	1·1057
0	12	17·000	15	1	0	2	13	11·7783
0	12	16·375	15	0	7	2	13	10·4509
0	12	15·750	15	0	6	2	13	9·1235
0	12	15·125	15	0	5	2	13	7·7961
0	12	14·500	15	0	4	2	13	6·4687
0	12	13·875	15	0	3	2	13	5·1413
0	12	13·250	15	0	2	2	13	3·8138
0	12	12·625	15	0	1	2	13	2·4864
0	12	12·000	15	0	0	2	13	1·1591
0	12	11·375	14	3	7	2	12	11·8316
0	12	10·750	14	3	6	2	12	10·5042
0	12	10·125	14	3	5	2	12	9·1768
0	12	9·500	14	3	4	2	12	7·8494
0	12	8·875	14	3	3	2	12	6·5220
0	12	8·250	14	3	2	2	12	5·1946
0	12	7·625	14	3	1	2	12	3·8671
0	12	7·000	14	3	0	2	12	2·5397
0	12	6·375	14	2	7	2	12	1·2123
0	12	5·750	14	2	6	2	11	11·8849

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	12	5·125	14	2	5	2	11	10·5575
0	12	4·500	14	2	4	2	11	9·2301
0	12	3·875	14	2	3	2	11	7·9027
0	12	3·250	14	2	2	2	11	6·5752
0	12	2·625	14	2	1	2	11	5·2478
0	12	2·000	14	2	0	2	11	3·9204
0	12	1·375	14	1	7	2	11	2·5930
0	12	0·750	14	1	6	2	11	1·2656
0	12	0·125	14	1	5	2	10	11·9382
0	11	23·500	14	1	4	2	10	10·6107
0	11	22·875	14	1	3	2	10	9·2833
0	11	22·250	14	1	2	2	10	7·9559
0	11	21·625	14	1	1	2	10	6·6285
0	11	21·000	14	1	0	2	10	5·3011
0	11	20·375	14	0	7	2	10	3·9737
0	11	19·750	14	0	6	2	10	2·6463
0	11	19·125	14	0	5	2	10	1·3188
0	11	18·500	14	0	4	2	9	11·9914
0	11	17·875	14	0	3	2	9	10·6640
0	11	17·250	14	0	2	2	9	9·3366
0	11	16·625	14	0	1	2	9	8·0092
0	11	16·000	14	0	0	2	9	6·6818
0	11	15·375	13	3	7	2	9	5·3544
0	11	14·750	13	3	6	2	9	4·0269
0	11	14·150	13	3	5	2	9	2·6995
0	11	13·500	13	3	4	2	9	1·3721
0	11	12·875	13	3	3	2	9	0·0447
0	11	12·250	13	3	2	2	8	10·7173
0	11	11·625	13	3	1	2	8	9·3899
0	11	11·000	13	3	0	2	8	8·0625
0	11	10·375	13	2	7	2	8	6·7350
0	11	9·750	13	2	6	2	8	5·4076
0	11	9·125	13	2	5	2	8	4·0802
0	11	8·500	13	2	4	2	8	2·7528
0	11	7·875	13	2	3	2	8	1·4254
0	11	7·250	13	2	2	2	8	0·0980
0	11	6·625	13	2	1	2	7	10·7705
0	11	6·000	13	2	0	2	7	9·4431
0	11	5·375	13	1	7	2	7	8·1157
0	11	4·750	13	1	6	2	7	6·7883
0	11	4·125	13	1	5	2	7	5·4609
0	11	3·500	13	1	4	2	7	4·1335
0	11	2·875	13	1	3	2	7	2·8061
0	11	2·250	13	1	2	2	7	1·4786

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	11	1·625	13	1	1	2	7	0·1512
0	11	1·000	13	1	0	2	6	10·8238
0	11	0·375	13	0	7	2	6	9·4964
0	10	23·750	13	0	6	2	6	8·1698
0	10	23·125	13	0	5	2	6	6·8416
0	10	22·500	13	0	4	2	6	5·5142
0	10	21·875	13	0	3	2	6	4·1867
0	10	21·250	13	0	2	2	6	2·8593
0	10	20·625	13	0	1	2	6	1·5319
0	10	20·000	13	0	0	2	6	0·2045
0	10	19·375	12	3	7	2	5	10·8771
0	10	18·750	12	3	6	2	5	9·5497
0	10	18·125	12	3	5	2	5	8·2223
0	10	17·500	12	3	4	2	5	6·8948
0	10	16·875	12	3	3	2	5	5·5674
0	10	16·250	12	3	2	2	5	4·2400
0	10	15·625	12	3	1	2	5	2·9126
0	10	15·000	12	3	0	2	5	1·5852
0	10	14·375	12	2	7	2	5	0·2578
0	10	13·750	12	2	6	2	4	10·9303
0	10	13·125	12	2	5	2	4	9·6029
0	10	12·500	12	2	4	2	4	8·2755
0	10	11·875	12	2	3	2	4	6·9481
0	10	11·250	12	2	2	2	4	5·6207
0	10	10·625	12	2	1	2	4	4·2933
0	10	10·000	12	2	0	2	4	2·9659
0	10	9·375	12	1	7	2	4	1·6384
0	10	8·750	12	1	6	2	4	0·3110
0	10	8·125	12	1	5	2	3	10·8366
0	10	7·500	12	1	4	2	3	9·6562
0	10	6·875	12	1	3	2	3	8·3288
0	10	6·250	12	1	2	2	3	7·0014
0	10	5·625	12	1	1	2	3	5·6740
0	10	5·000	12	1	0	2	3	4·3465
0	10	4·375	12	0	7	2	3	3·0191
0	10	3·750	12	0	6	2	3	1·6917
0	10	3·125	12	0	5	2	3	0·3643
0	10	2·500	12	0	4	2	2	11·0369
0	10	1·875	12	0	3	2	2	9·7095
0	10	1·250	12	0	2	2	2	8·3821
0	10	0·625	12	0	1	2	2	7·0546
0	10	0·000	12	0	0	2	2	5·7272
0	9	23·375	11	3	7	2	2	4·3998
0	9	22·750	11	3	6	2	2	3·0724

FINE GOLD, Per Ounce			CARAT GOLD, Per Ounce			STERLING VALUE, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	9	22·125	11	3	5	2	2	1·7450
0	9	21·500	11	3	4	2	2	0·4176
0	9	21·875	11	3	3	2	1	11·0901
0	9	20·250	11	3	2	2	1	9·7627
0	9	19·625	11	3	1	2	1	8·4353
0	9	19·000	11	3	0	2	1	7·1079
0	9	18·375	11	2	7	2	1	5·7805
0	9	17·750	11	2	6	2	1	4·4531
0	9	17·125	11	2	5	2	1	3·1257
0	9	16·500	11	2	4	2	1	1·7982
0	9	15·875	11	2	3	2	1	0·4708
0	9	15·250	11	2	2	2	0	11·1434
0	9	14·625	11	2	1	2	0	9·8160
0	9	14·000	11	2	0	2	0	8·4886
0	9	13·375	11	1	7	2	0	7·1612
0	9	12·750	11	1	6	2	0	5·8338
0	9	12·125	11	1	5	2	0	4·5063
0	9	11·500	11	1	4	2	0	3·1789
0	9	10·875	11	1	3	2	0	1·8515
0	9	10·250	11	1	2	2	0	0·5241
0	9	9·625	11	1	1	1	19	11·1967
0	9	9·000	11	1	0	1	19	9·8693
0	9	8·375	11	0	7	1	19	8·5419
0	9	7·750	11	0	6	1	19	7·2144
0	9	7·125	11	0	5	1	19	5·8870
0	9	6·500	11	0	4	1	19	4·5596
0	9	5·875	11	0	3	1	19	3·2322
0	9	5·250	11	0	2	1	19	1·9048
0	9	4·625	11	0	1	1	19	0·5774
0	9	4·000	11	0	0	1	18	11·2500
0	9	3·375	10	3	7	1	18	9·9225
0	9	2·750	10	3	6	1	18	8·5951
0	9	2·125	10	3	5	1	18	7·2677
0	9	1·500	10	3	4	1	18	5·9403
0	9	0·875	10	3	3	1	18	4·6129
0	9	0·250	10	3	2	1	18	3·2855
0	8	23·625	10	3	1	1	18	1·9580
0	8	23·000	10	3	0	1	18	0·6306
0	8	22·375	10	2	7	1	17	11·3032
0	8	21·750	10	2	6	1	17	9·9758
0	8	21·125	10	2	5	1	17	8·6484
0	8	20·500	10	2	4	1	17	7·3210
0	8	19·875	10	2	3	1	17	5·9936
0	8	19·250	10	2	2	1	17	4·6661

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	8	18·625	10	2	1	1	17	3·3387
0	8	18·000	10	2	0	1	17	2·0113
0	8	17·375	10	1	7	1	17	0·6839
0	8	16·750	10	1	6	1	16	11·3565
0	8	16·125	10	1	5	1	16	10·0291
0	8	15·500	10	1	4	1	16	8·7017
0	8	14·875	10	1	3	1	16	7·3742
0	8	14·250	10	1	2	1	16	6·0468
0	8	13·625	10	1	1	1	16	4·7194
0	8	13·000	10	1	0	1	16	3·3920
0	8	12·375	10	0	7	1	16	2·0646
0	8	11·750	10	0	6	1	16	0·7372
0	8	11·125	10	0	5	1	15	11·4098
0	8	10·500	10	0	4	1	15	10·0823
0	8	9·875	10	0	3	1	15	8·7549
0	8	9·250	10	0	2	1	15	7·4275
0	8	8·625	10	0	1	1	15	6·1001
0	8	8·000	10	0	0	1	15	4·7728
0	8	7·375	9	3	7	1	15	3·4454
0	8	6·750	9	3	6	1	15	2·1179
0	8	6·125	9	3	5	1	15	0·7905
0	8	5·500	9	3	4	1	14	11·4631
0	8	4·875	9	3	3	1	14	10·1357
0	8	4·250	9	3	2	1	14	8·8083
0	8	3·625	9	3	1	1	14	7·4809
0	8	3·000	9	3	0	1	14	6·1535
0	8	2·375	9	2	7	1	14	4·8260
0	8	1·750	9	2	6	1	14	3·4986
0	8	1·125	9	2	5	1	14	2·1712
0	8	0·500	9	2	4	1	14	0·8438
0	7	23·875	9	2	3	1	13	11·5164
0	7	23·250	9	2	2	1	13	10·1890
0	7	22·625	9	2	1	1	13	8·8616
0	7	22·000	9	2	0	1	13	7·5341
0	7	21·375	9	1	7	1	13	6·2067
0	7	20·750	9	1	6	1	13	4·8793
0	7	20·125	9	1	5	1	13	3·5519
0	7	19·500	9	1	4	1	13	2·2245
0	7	19·875	9	1	3	1	13	0·8971
0	7	18·250	9	1	2	1	12	11·5697
0	7	17·625	9	1	1	1	12	10·2422
0	7	17·000	9	1	0	1	12	8·9168
0	7	16·375	9	0	7	1	12	7·5874
0	7	15·750	9	0	6	1	12	6·2600

FINE GOLD, Per Ounce			CARAT GOLD, Per Ounce			STERLING VALUE, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	7	15·125	9	0	5	1	12	4·9326
0	7	14·500	9	0	4	1	12	3·6052
0	7	13·875	9	0	3	1	12	2·2778
0	7	13·250	9	0	2	1	12	0·9503
0	7	12·625	9	0	1	1	11	11·6229
0	7	12·000	9	0	0	1	11	10·2954
0	7	11·375	8	3	7	1	11	8·9680
0	7	10·750	8	3	6	1	11	7·6406
0	7	10·125	8	3	5	1	11	6·3132
0	7	9·500	8	3	4	1	11	4·9857
0	7	8·875	8	3	3	1	11	3·6583
0	7	8·250	8	3	2	1	11	2·3309
0	7	7·625	8	3	1	1	11	1·0035
0	7	7·000	8	3	0	1	10	11·6761
0	7	6·375	8	2	7	1	10	10·3487
0	7	5·750	8	2	6	1	10	9·0213
0	7	5·125	8	2	5	1	10	7·6938
0	7	4·500	8	2	4	1	10	6·3664
0	7	3·875	8	2	3	1	10	5·0390
0	7	3·250	8	2	2	1	10	3·7116
0	7	2·625	8	2	1	1	10	2·3843
0	7	2·000	8	2	0	1	10	1·0568
0	7	1·375	8	1	7	1	9	11·7294
0	7	0·750	8	1	6	1	9	10·4019
0	7	0·125	8	1	5	1	9	9·0745
0	6	23·500	8	1	4	1	9	7·7471
0	6	22·875	8	1	3	1	9	6·4197
0	6	22·250	8	1	2	1	9	5·0923
0	6	21·625	8	1	1	1	9	3·7649
0	6	21·000	8	1	0	1	9	2·4375
0	6	20·375	8	0	7	1	9	1·1100
0	6	19·750	8	0	6	1	8	11·7826
0	6	19·125	8	0	5	1	8	10·4552
0	6	18·500	8	0	4	1	8	9·1278
0	6	17·875	8	0	3	1	8	7·8004
0	6	17·250	8	0	2	1	8	6·4730
0	6	16·625	8	0	1	1	8	5·1455
0	6	16·000	8	0	0	1	8	3·8181
0	6	15·375	7	3	7	1	8	2·4907
0	6	14·750	7	3	6	1	8	1·1633
0	6	14·125	7	3	5	1	7	11·8359
0	6	13·500	7	3	4	1	7	10·5085
0	6	12·875	7	3	3	1	7	9·1811
0	6	12·250	7	3	2	1	7	7·8536

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	6	11·625	7	3	1	1	7	6·5262
0	6	11·000	7	3	0	1	7	5·1988
0	6	10·375	7	2	7	1	7	3·8714
0	6	9·750	7	2	6	1	7	2·5440
0	6	9·125	7	2	5	1	7	1·2166
0	6	8·500	7	2	4	1	6	11·8892
0	6	7·875	7	2	3	1	6	10·5617
0	6	7·250	7	2	2	1	6	9·2343
0	6	6·625	7	2	1	1	6	7·8069
0	6	6·000	7	2	0	1	6	6·5795
0	6	5·375	7	1	7	1	6	5·2521
0	6	4·750	7	1	6	1	6	3·9247
0	6	4·125	7	1	5	1	6	2·5973
0	6	3·500	7	1	4	1	6	1·2698
0	6	2·875	7	1	3	1	5	11·9424
0	6	2·250	7	1	2	1	5	10·6150
0	6	1·625	7	1	1	1	5	9·2876
0	6	1·000	7	1	0	1	5	7·9602
0	6	0·375	7	0	7	1	5	6·6328
0	5	23·750	7	0	6	1	5	5·3054
0	5	23·125	7	0	5	1	5	3·9779
0	5	22·500	7	0	4	1	5	2·6505
0	5	21·875	7	0	3	1	5	1·3231
0	5	21·250	7	0	2	1	4	11·9957
0	5	20·625	7	0	1	1	4	10·6683
0	5	20·000	7	0	0	1	4	9·3409
0	5	19·375	6	3	7	1	4	8·0134
0	5	18·750	6	3	6	1	4	6·6860
0	5	18·125	6	3	5	1	4	5·3586
0	5	17·500	6	3	4	1	4	4·0312
0	5	16·875	6	3	3	1	4	2·7038
0	5	16·250	6	3	2	1	4	1·3764
0	5	15·625	6	3	1	1	4	0·0490
0	5	15·000	6	3	0	1	3	10·7216
0	5	14·375	6	2	7	1	3	9·3941
0	5	13·750	6	2	6	1	3	8·0667
0	5	13·125	6	2	5	1	3	6·7393
0	5	12·500	6	2	4	1	3	5·4119
0	5	11·875	6	2	3	1	3	4·0845
0	5	11·250	6	2	2	1	3	2·7571
0	5	10·625	6	2	1	1	3	1·4297
0	5	10·000	6	2	0	1	3	0·1022
0	5	9·375	6	1	7	1	2	10·7748
0	5	8·750	6	1	6	1	2	9·4474

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	5	8·125	6	1	5	1	2	8·1200
0	5	7·500	6	1	4	1	2	6·7926
0	5	6·875	6	1	3	1	2	5·4652
0	5	6·250	6	1	2	1	2	4·1377
0	5	5·625	6	1	1	1	2	2·8103
0	5	5·000	6	1	0	1	2	1·4829
0	5	4·375	6	0	7	1	2	0·1555
0	5	3·750	6	0	6	1	1	10·8281
0	5	3·125	6	0	5	1	1	9·5007
0	5	2·500	6	0	4	1	1	8·1733
0	5	1·875	6	0	3	1	1	6·8458
0	5	1·250	6	0	2	1	1	5·5184
0	5	0·625	6	0	1	1	1	4·1910
0	5	0·000	6	0	0	1	1	2·8636
0	4	23·375	5	3	7	1	1	1·5362
0	4	22·750	5	3	6	1	1	0·2088
0	4	22·125	5	3	5	1	0	10·8813
0	4	21·500	5	3	4	1	0	9·5539
0	4	20·875	5	3	3	1	0	8·2265
0	4	20·250	5	3	2	1	0	6·8991
0	4	19·625	5	3	1	1	0	5·5717
0	4	19·000	5	3	0	1	0	4·2443
0	4	18·375	5	2	7	1	0	2·9169
0	4	17·750	5	2	6	1	0	1·5894
0	4	17·125	5	2	5	1	0	0·2620
0	4	16·500	5	2	4	0	19	10·9346
0	4	15·875	5	2	3	0	19	9·6072
0	4	15·250	5	2	2	0	19	8·2798
0	4	14·625	5	2	1	0	19	6·9524
0	4	14·000	5	2	0	0	19	5·6250
0	4	13·375	5	1	7	0	19	4·2975
0	4	12·750	5	1	6	0	19	2·9701
0	4	12·125	5	1	5	0	19	1·6427
0	4	11·500	5	1	4	0	19	0·3153
0	4	10·875	5	1	3	0	18	10·9879
0	4	10·250	5	1	2	0	18	9·6605
0	4	9·625	5	1	1	0	18	8·3331
0	4	9·000	5	1	0	0	18	7·0056
0	4	8·375	5	0	7	0	18	5·6782
0	4	7·750	5	0	6	0	18	4·3508
0	4	7·125	5	0	5	0	18	3·0234
0	4	6·500	5	0	4	0	18	1·6960
0	4	5·875	5	0	3	0	18	0·3686
0	4	5·250	5	0	2	0	17	11·0411

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	4	4·625	5	0	1	0	17	9·7137
0	4	4·000	5	0	0	0	17	8·3863
0	4	3·375	4	3	7	0	17	7·0589
0	4	2·750	4	3	6	0	17	5·7315
0	4	2·125	4	3	5	0	17	4·4041
0	4	1·500	4	3	4	0	17	3·0767
0	4	0·875	4	3	3	0	17	1·7492
0	4	0·250	4	3	2	0	17	0·4218
0	3	23·625	4	3	1	0	16	11·0944
0	3	23·000	4	3	0	0	16	9·7670
0	3	22·375	4	2	7	0	16	8·4396
0	3	21·750	4	2	6	0	16	7·1122
0	3	21·125	4	2	5	0	16	5·7848
0	3	20·500	4	2	4	0	16	4·4573
0	3	19·875	4	2	3	0	16	3·1299
0	3	19·250	4	2	2	0	16	1·8025
0	3	18·625	4	2	1	0	16	0·4751
0	3	18·000	4	2	0	0	15	11·1477
0	3	17·375	4	1	7	0	15	9·8203
0	3	16·750	4	1	6	0	15	8·4929
0	3	16·125	4	1	5	0	15	7·1655
0	3	15·500	4	1	4	0	15	5·8380
0	3	14·875	4	1	3	0	15	4·5106
0	3	14·250	4	1	2	0	15	3·1832
0	3	13·625	4	1	1	0	15	1·8558
0	3	13·000	4	1	0	0	15	0·5284
0	3	12·375	4	0	7	0	14	11·2009
0	3	11·750	4	0	6	0	14	9·8735
0	3	11·125	4	0	5	0	14	8·5461
0	3	10·500	4	0	4	0	14	7·2187
0	3	9·875	4	0	3	0	14	5·8913
0	3	9·250	4	0	2	0	14	4·5639
0	3	8·625	4	0	1	0	14	3·2365
0	3	8·000	4	0	0	0	14	1·9090
0	3	7·375	3	3	7	0	14	0·5816
0	3	6·750	3	3	6	0	13	11·2542
0	3	6·125	3	3	5	0	13	9·9268
0	3	5·500	3	3	4	0	13	8·5994
0	3	4·875	3	3	3	0	13	7·2720
0	3	4·250	3	3	2	0	13	5·9446
0	3	3·625	3	3	1	0	13	4·6171
0	3	3·000	3	3	0	0	13	3·2897
0	3	2·375	3	2	7	0	13	1·9623
0	3	1·750	3	2	6	0	13	0·6349

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	*£*	*s.*	*d.*
0	3	1·125	3	2	5	0	12	11·3075
0	3	0·500	3	2	4	0	12	9·9801
0	2	23·875	3	2	3	0	12	8·6527
0	2	23·250	3	2	2	0	12	7·3250
0	2	22·625	3	2	1	0	12	5·9978
0	2	22·000	3	2	0	0	12	4·6704
0	2	21·375	3	1	7	0	12	3·3430
0	2	20·750	3	1	6	0	12	2·0156
0	2	20·125	3	1	5	0	12	0·6882
0	2	19·500	3	1	4	0	11	11·3607
0	2	18·875	3	1	3	0	11	10·0333
0	2	18·250	3	1	2	0	11	8·7059
0	2	17·625	3	1	1	0	11	7·3785
0	2	17·000	3	1	0	0	11	6·0511
0	2	16·375	3	0	7	0	11	4·7237
0	2	15·750	3	0	6	0	11	3·3963
0	2	15·125	3	0	5	0	11	2·0688
0	2	14·500	3	0	4	0	11	0·7414
0	2	13·875	3	0	3	0	10	11·4140
0	2	13·250	3	0	2	0	10	10·0866
0	2	12·625	3	0	1	0	10	8·7592
0	2	12·000	3	0	0	0	10	7·4318
0	2	11·375	2	3	7	0	10	6·1044
0	2	10·750	2	3	6	0	10	4·7769
0	2	10·125	2	3	5	0	10	3·4495
0	2	9·500	2	3	4	0	10	2·1221
0	2	8·875	2	3	3	0	10	0·7947
0	2	8·250	2	3	2	0	9	11·4673
0	2	7·625	2	3	1	0	9	10·1399
0	2	7·000	2	3	0	0	9	8·8125
0	2	6·375	2	2	7	0	9	7·4850
0	2	5·750	2	2	6	0	9	6·1576
0	2	5·125	2	2	5	0	9	4·8302
0	2	4·500	2	2	4	0	9	3·5028
0	2	3·875	2	2	3	0	9	2·1754
0	2	3·250	2	2	2	0	9	0·8480
0	2	2·625	2	2	1	0	8	11·5205
0	2	2·000	2	2	0	0	8	10·1931
0	2	1·375	2	1	7	0	8	8·8657
0	2	0·750	2	1	6	0	8	7·5383
0	2	0·125	2	1	5	0	8	6·2109
0	1	23·500	2	1	4	0	8	4·8835
0	1	22·875	2	1	3	0	8	3·5561
0	1	22·250	2	1	2	0	8	2·2286

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value, Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	1	21·625	2	1	1	0	8	0·9012
0	1	21·000	2	1	0	0	7	11·5738
0	1	20·375	2	0	7	0	7	10·2464
0	1	19·750	2	0	6	0	7	8·9190
0	1	19·125	2	0	5	0	7	7·5916
0	1	18·500	2	0	4	0	7	6·2642
0	1	17·875	2	0	3	0	7	4·9367
0	1	17·250	2	0	2	0	7	3·6093
0	1	16·625	2	0	1	0	7	2·2819
0	1	16·000	2	0	0	0	7	0·9545
0	1	15·375	1	3	7	0	6	11·6271
0	1	14·750	1	3	6	0	6	10·2997
0	1	14·125	1	3	5	0	6	8·9723
0	1	13·500	1	3	4	0	6	7·6448
0	1	12·875	1	3	3	0	6	6·3174
0	1	12·250	1	3	2	0	6	4·9900
0	1	11·625	1	3	1	0	6	3·6626
0	1	11·000	1	3	0	0	6	2·3352
0	1	10·375	1	2	7	0	6	1·0078
0	1	9·750	1	2	6	0	5	11·6803
0	1	9·125	1	2	5	0	5	10·3529
0	1	8·500	1	2	4	0	5	9·0255
0	1	7·875	1	2	3	0	5	7·6981
0	1	7·250	1	2	2	0	5	6·3707
0	1	6·625	1	2	1	0	5	5·0433
0	1	6·000	1	2	0	0	5	3·7159
0	1	5·375	1	1	7	0	5	2·3884
0	1	4·750	1	1	6	0	5	1·0610
0	1	4·125	1	1	5	0	4	11·7336
0	1	3·500	1	1	4	0	4	10·4062
0	1	2·875	1	1	3	0	4	9·0788
0	1	2·250	1	1	2	0	4	7·7514
0	1	1·625	1	1	1	0	4	6·4240
0	1	1·000	1	1	0	0	4	5·0965
0	1	0·375	1	0	7	0	4	3·7691
0	0	23·750	1	0	6	0	4	2·4417
0	0	23·125	1	0	5	0	4	1·1143
0	0	22·500	1	0	4	0	3	11·7869
0	0	21·875	1	0	3	0	3	10·4595
0	0	21·250	1	0	2	0	3	9·1321
0	0	20·625	1	0	1	0	3	7 8046
0	0	20·000	1	0	0	0	3	6·4772
0	0	19·375	0	3	7	0	3	5·1498
0	0	18·750	0	3	6	0	3	3·8224

Fine Gold, Per Ounce			Carat Gold, Per Ounce			Sterling Value Per Ounce		
Oz.	*Dwts.*	*Grs.*	*Carats*	*Grs.*	*Eighths*	£	*s.*	*d.*
0	0	18·125	0	3	5	0	3	2·4950
0	0	17·500	0	3	4	0	3	1·1676
0	0	16·875	0	3	3	0	2	11·8401
0	0	16·250	0	3	2	0	2	10·5127
0	0	15·625	0	3	1	0	2	9·1853
0	0	15·000	0	3	0	0	2	7·8579
0	0	14·375	0	2	7	0	2	6·5305
0	0	13·750	0	2	6	0	2	5·2031
0	0	13·125	0	2	5	0	2	3·8757
0	0	12·500	0	2	4	0	2	2·5482
0	0	11·875	0	2	3	0	2	1·2208
0	0	11·250	0	2	2	0	1	11·8934
0	0	10·625	0	2	1	0	1	10·5660
0	0	10·000	0	2	0	0	1	9·2386
0	0	9·375	0	1	7	0	1	7·9112
0	0	8·750	0	1	6	0	1	6·5838
0	0	8·125	0	1	5	0	1	5·2563
0	0	7·500	0	1	4	0	1	3·9289
0	0	6·875	0	1	3	0	1	2·6015
0	0	6·250	0	1	2	0	1	1·2741
0	0	5·625	0	1	1	0	0	11·9467
0	0	5·000	0	1	0	0	0	10·6193
0	0	4·375	0	0	7	0	0	9·2919
0	0	3·750	0	0	6	0	0	7·9644
0	0	3·125	0	0	5	0	0	6·6370
0	0	2·500	0	0	4	0	0	5·3096
0	0	1·875	0	0	3	0	0	3·9822
0	0	1·250	0	0	2	0	0	2·6548
0	0	0·625	0	0	1	0	0	1·3274

To convert MINT VALUE into BANK VALUE when the Standard is expressed in Carats, Grains, and Eighths. This can be readily accomplished for every report by the following Tables:—

TABLE A.

CARATS	VALUE IN PENCE	CARATS	VALUE IN PENCE
1	·0681	13	·8863
2	·1363	14	·9545
3	·2045	15	1·0227
4	·2727	16	1·0909
5	·3409	17	1·1590
6	·4090	18	1·2272
7	·4772	19	1·2954
8	·5454	20	1·3636
9	·6136	21	1·4318
10	·6818	22	1·5000
11	·7500	23	1·5681
12	·8181	24	1·6363

TABLE B.

CARAT GRAINS	VALUE IN PENCE	CARAT GRAINS	VALUE IN PENCE
1	·0170	3	·0511
2	·0340	4	·0681

TABLE C.

EIGHTH CARAT GRAINS	VALUE IN PENCE	EIGHTH CARAT GRAINS	VALUE IN PENCE
1	·0021	5	·0106
2	·0042	6	·0127
3	·0063	7	·0149
4	·0085	8	·0170

Table A gives the difference in price between Mint and Bank value for each carat up to fine gold; Table B the same for carat grains; and Table C the same for eighths of carat grains.

Now as the Bank value of gold is £3 17*s.* 9*d.* per oz. standard against Mint value of £3 17*s.* 10½*d.*, it follows by calculation that fine gold would fetch, Bank price, only £4 4*s.* 9·8182*d.*, instead of £4 4*s.* 11·4545*d.*, as shown by Table I. of Mint Values; and the Bank value of 1 oz. of gold, of any standard whatever, may be readily ascertained by the above Tables A, B, and C, and Table I.—the Tables A, B, and C, giving the quantities in pence to be deducted from the corresponding standard in Table I. Thus, suppose it is necessary to ascertain the Bank value of 1 oz. of gold of 14 carats 2 grains 5 eighths fine: refer to Table A, at 14 carats is found ·9545*d.*; at 2 grains in Table B is found ·0340*d.*; and at 5 eighths in Table C ·0106*d.* Now ·9545 + ·0340 + ·0106 = ·9991, which has to be deducted from £2 11*s.* 10·5575*d.* (see Table I.), leaving £2 11*s.* 9·5564*d.* as the Bank value of 1 oz. of gold of the above fineness.

TABLE II.

TABLE of relative proportions of FINE GOLD and ALLOY, with the respective Mint Values of 1 oz. of each Alloy when the Standard is expressed in Thousandths.

FINE GOLD	ALLOY	VALUE			FINE GOLD	ALLOY	VALUE		
		£	*s.*	*d.*			£	*s.*	*d.*
1000	·000	4	4	11·4545	986	·014	4	3	9·1821
999	·001	4	4	10·4350	985	·015	4	3	8·1627
998	·002	4	4	9·4156	984	·016	4	3	7·1432
997	·003	4	4	8·3961	983	·017	4	3	6·1238
996	·004	4	4	7·3767	982	·018	4	3	5·1043
995	·005	4	4	6·3572	981	·019	4	3	4·0849
994	·006	4	4	5·3378	980	·020	4	3	3·0654
993	·007	4	4	4·3183	979	·021	4	3	2·0459
992	·008	4	4	3·2989	978	·022	4	3	1·0265
991	·009	4	4	2·2793	977	·023	4	3	0·0070
990	·010	4	4	1·2600	976	·024	4	2	10·9876
989	·011	4	4	0·2405	975	·025	4	2	9·9681
988	·012	4	3	11·2210	974	·026	4	2	8·9487
987	·013	4	3	10·2016	973	·027	4	2	7·9292

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
972	·028	4	2	6·9098	929	·071	3	18	11·0732
971	·029	4	2	5·8903	928	·072	3	18	10·0538
970	·030	4	2	4·8709	927	·073	3	18	9·0343
969	·031	4	2	3·8504	926	·074	3	18	8·0149
968	·032	4	2	2·8319	925	·075	3	18	6·9954
967	·033	4	2	1·8125	924	·076	3	18	5·9759
966	·034	4	2	0·7930	923	·077	3	18	4·9565
965	·035	4	1	11·7736	922	·078	3	18	3·9370
964	·036	4	1	10·7541	921	·079	3	18	2·9176
963	·037	4	1	9·7347	920	·080	3	18	1·8981
962	·038	4	1	8·7152	919	·081	3	18	0·8787
961	·039	4	1	7·6958	918	·082	3	17	11·8592
960	·040	4	1	6·6763	917	·083	3	17	10·8398
959	·041	4	1	5·6569	916*	·084	3	17	9·8203
958	·042	4	1	4·6374	915	·085	3	17	8·8009
957	·043	4	1	3·6179	914	·086	3	17	7·7814
956	·044	4	1	2·5985	913	·087	3	17	6·7619
955	·045	4	1	1·5790	912	·088	3	17	5·7425
954	·046	4	1	0·5596	911	·089	3	17	4·7230
953	·047	4	0	11·5401	910	·090	3	17	3·7036
952	·048	4	0	10·5207	909	·091	3	17	2·6841
951	·049	4	0	9·5012	908	·092	3	17	1·6647
950	·050	4	0	8·4818	907	·093	3	17	0·6452
949	·051	4	0	7·4623	906	·094	3	16	11·6258
948	·052	4	0	6·4429	905	·095	3	16	10·6063
947	·053	4	0	5·4234	904	·096	3	16	9·5869
946	·054	4	0	4·4039	903	·097	3	16	8·5674
945	·055	4	0	3·3835	902	·098	3	16	7·5479
944	·056	4	0	2·3650	901	·099	3	16	6·5285
943	·057	4	0	1·3456	900	·100	3	16	5·5090
942	·058	4	0	0·3261	899	·101	3	16	4·4896
941	·059	3	19	11·3067	898	·102	3	16	3·4701
940	·060	3	19	10·2872	897	·103	3	16	2·4507
939	·061	3	19	9·2678	896	·104	3	16	1·4312
938	·062	3	19	8·2483	895	·105	3	16	0·4118
937	·063	3	19	7·2289	894	·106	3	15	11·3923
936	·064	3	19	6·2094	893	·107	3	15	10·3729
935	·065	3	19	5·1899	892	·108	3	15	9·3534
934	·066	3	19	4·1705	891	·109	3	15	8·3339
933	·067	3	19	3·1510	890	·110	3	15	7·3145
932	·068	3	19	2·1316	889	·111	3	15	6·2950
931	·069	3	19	1·1121	888	·112	3	15	5·2756
930	·070	3	19	0·0927	887	·113	3	15	4·2561

* 916·666 Standard ·083·333 £3 17*s.* 10·5000*d.*

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
886	·114	3	15	3·2367	841	·159	3	11	5·3612
885	·115	3	15	2·2172	840	·160	3	11	4·3418
884	·116	3	15	1·1978	839	·161	3	11	3·3223
883	·117	3	15	0·1783	838	·162	3	11	2·3029
882	·118	3	14	11·1589	837	·163	3	11	1·3834
881	·119	3	14	10·1394	836	·164	3	11	0·2639
880	·120	3	14	9·1199	835	·165	3	10	11·2445
879	·121	3	14	8·1005	834	·166	3	10	10·2250
878	·122	3	14	7·0810	833	·167	3	10	9·2056
877	·123	3	14	6·0616	832	·168	3	10	8·1861
876	·124	3	14	5·0421	831	·169	3	10	7·1667
875	·125	3	14	4·0227	830	·170	3	10	6·1472
874	·126	3	14	3·0032	829	·171	3	10	5·1278
873	·127	3	14	1·9838	828	·172	3	10	4·1083
872	·128	3	14	0·9643	827	·173	3	10	3·0889
871	·129	3	13	11·9449	826	·174	3	10	2·0694
870	·130	3	13	10·9254	825	·175	3	10	1·0499
869	·131	3	13	9·9059	824	·176	3	10	0·0305
868	·132	3	13	8·8865	823	·177	3	9	11·0110
867	·133	3	13	7·8670	822	·178	3	9	9·9916
866	·134	3	13	6·8476	821	·179	3	9	8·9721
865	·135	3	13	5·8281	820	·180	3	9	7·9527
864	·136	3	13	4·8087	819	·181	3	9	6·9332
863	·137	3	13	3·7892	818	·182	3	9	5·9138
862	·138	3	13	2·7698	817	·183	3	9	4·8943
861	·139	3	13	1·7503	816	·184	3	9	3·8749
860	·140	3	13	0·7309	815	·185	3	9	2·8554
859	·141	3	12	11·7114	814	·186	3	9	1·8359
858	·142	3	12	10·6919	813	·187	3	9	0·8165
857	·143	3	12	9·6725	812	·188	3	8	11·7970
856	·144	3	12	8·6530	811	·189	3	8	10·7776
855	·145	3	12	7·6336	810	·190	3	8	9·7581
854	·146	3	12	6·6141	809	·191	3	8	8·7387
853	·147	3	12	5·5947	808	·192	3	8	7·7192
852	·148	3	12	4·5752	807	·193	3	8	6·6998
851	·149	3	12	3·5558	806	·194	3	8	5·6803
850	·150	3	12	2·5363	805	·195	3	8	4·6609
849	·151	3	12	1·5169	804	·196	3	8	3·6414
848	·152	3	12	0·4974	803	·197	3	8	2·6219
847	·153	3	11	11·4779	802	·198	3	8	1·6025
846	·154	3	11	10·4585	801	·199	3	8	0·5830
845	·155	3	11	9·4390	800	·200	3	7	11·5636
844	·156	3	11	8·4196	799	·201	3	7	10·5441
843	·157	3	11	7·4001	798	·202	3	7	9·5247
842	·158	3	11	6·3807	797	·203	3	7	8·5052

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
796	·204	3	7	7·4858	751	·249	3	3	9·6103
795	·205	3	7	6·4663	750	·250	3	3	8·5909
794	·206	3	7	5·4469	749	·251	3	3	7·5714
793	·207	3	7	4·4274	748	·252	3	3	6·5519
792	·208	3	7	3·4979	747	·253	3	3	5·5325
791	·209	3	7	2·3885	746	·254	3	3	4·5130
790	·210	3	7	1·3690	745	·255	3	3	3·4936
789	·211	3	7	0·3496	744	·256	3	3	2·4741
788	·212	3	6	11·3301	743	·257	3	3	1·4547
787	·213	3	6	10·3107	742	·258	3	3	0·4352
786	·214	3	6	9·2912	741	·259	3	2	11·4158
785	·215	3	6	8·2718	740	·260	3	2	10·3963
784	·216	3	6	7·2523	739	·261	3	2	9·3769
783	·217	3	6	6·2329	738	·262	3	2	8·3574
782	·218	3	6	5·2134	737	·263	3	2	7·3379
781	·219	3	6	4·1939	736	·264	3	2	6·3185
780	·220	3	6	3·1745	735	·265	3	2	5·2990
779	·221	3	6	2·1550	734	·266	3	2	4·2796
778	·222	3	6	1·1356	733	·267	3	2	3·2601
777	·223	3	6	0·1161	732	·268	3	2	2·2407
776	·224	3	5	11·0967	731	·269	3	2	1·2212
775	·225	3	5	10·0772	730	·270	3	2	0·2018
774	·226	3	5	9·0578	729	·271	3	1	11·1823
773	·227	3	5	8·0383	728	·272	3	1	10·1629
772	·228	3	5	7·0189	727	·273	3	1	9·1434
771	·229	3	5	5·9994	726	·274	3	1	8·1239
770	·230	3	5	4·9799	725	·275	3	1	7·1045
769	·231	3	5	3·9605	724	·276	3	1	6·0850
768	·232	3	5	2·9410	723	·277	3	1	5·0656
767	·233	3	5	1·9216	722	·278	3	1	4·0461
766	·234	3	5	0·9021	721	·279	3	1	3·0267
765	·235	3	4	11·8827	720	·280	3	1	2·0072
764	·236	3	4	10·8632	719	·281	3	1	0·9878
763	·237	3	4	9·8438	718	·282	3	0	11·9683
762	·238	3	4	8·8243	717	·283	3	0	10·9489
761	·239	3	4	7·8049	716	·284	3	0	9·9294
760	·240	3	4	6·7854	715	·285	3	0	8·9099
759	·241	3	4	5·7659	714	·286	3	0	7·8905
758	·242	3	4	4·7465	713	·287	3	0	6·8710
757	·243	3	4	3·7270	712	·288	3	0	5·8516
756	·244	3	4	2·7076	711	·289	3	0	4·8321
755	·245	3	4	1·6881	710	·290	3	0	3·8127
754	·246	3	4	0·6687	709	·291	3	0	2·7932
753	·247	3	3	11·6492	708	·292	3	0	1·7738
752	·248	3	3	10·6298	707	·293	3	0	0·7543

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
706	·294	2	19	11·7349	661	·339	2	16	1·8594
705	·295	2	19	10·7154	660	·340	2	16	0·8399
704	·296	2	19	9·6959	659	·341	2	15	11·8205
703	·297	2	19	8·6765	658	·342	2	15	10·8010
702	·298	2	19	7·6570	657	·343	2	15	9·7816
701	·299	2	19	6·6376	656	·344	2	15	8·7621
700	·300	2	19	5·6181	655	·345	2	15	7·7427
699	·301	2	19	4·5987	654	·346	2	15	6·7232
698	·302	2	19	3·5792	653	·347	2	15	5·7038
697	·303	2	19	2·5598	652	·348	2	15	4·6843
696	·304	2	19	1·5403	651	·349	2	15	3·6649
695	·305	2	19	0·5209	650	·350	2	15	2·6454
694	·306	2	18	11·5014	649	·351	2	15	1·6259
693	·307	2	18	10·4820	648	·352	2	15	0·6065
692	·308	2	18	9·4625	647	·353	2	14	11·5870
691	·309	2	18	8·4430	646	·354	2	14	10·5676
690	·310	2	18	7·4236	645	·355	2	14	9·5481
689	·311	2	18	6·4041	644	·356	2	14	8·5287
688	·312	2	18	5·3847	643	·357	2	14	7·5092
687	·313	2	18	4·3652	642	·358	2	14	6·4898
686	·314	2	18	3·3458	641	·359	2	14	5·4703
685	·315	2	18	2·3263	640	·360	2	14	4·4509
684	·316	2	18	1·3069	639	·361	2	14	3·4314
683	·317	2	18	0·2874	638	·362	2	14	2·4120
682	·318	2	17	11·2680	637	·363	2	14	1·3925
681	·319	2	17	10·2485	636	·364	2	14	0·3730
680	·320	2	17	9·2290	635	·365	2	13	11·3536
679	·321	2	17	8·2096	634	·366	2	13	10·3341
678	·322	2	17	7·1901	633	·367	2	13	9·3147
677	·323	2	17	6·1707	632	·368	2	13	8·2952
676	·324	2	17	5·1512	631	·369	2	13	7·2758
675	·325	2	17	4·1318	630	·370	2	13	6·2563
674	·326	2	17	3·1123	629	·371	2	13	5·2369
673	·327	2	17	2·0929	628	·372	2	13	4·2174
672	·328	2	17	1·0734	627	·373	2	13	3·1979
671	·329	2	17	0·0540	626	·374	2	13	2·1785
670	·330	2	16	11·0345	625	·375	2	13	1·1590
669	·331	2	16	10·0151	624	·376	2	13	0·1396
668	·332	2	16	8·9956	623	·377	2	12	11·1201
667	·333	2	16	7·9761	622	·378	2	12	10·1007
666	·334	2	16	6·9567	621	·379	2	12	9·0812
665	·335	2	16	5·9372	620	·380	2	12	8·0618
664	·336	2	16	4·9178	619	·381	2	12	7·0423
663	·337	2	16	3·8983	618	·382	2	12	6·0229
662	·338	2	16	2·8789	617	·383	2	12	5·0034

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
616	·384	2	12	3·9839	571	·429	2	8	6·1085
615	·385	2	12	2·9645	570	·430	2	8	5·0890
614	·386	2	12	1·9451	569	·431	2	8	4·0696
613	·387	2	12	0·9256	568	·432	2	8	3·0501
612	·388	2	11	11·9061	567	·433	2	8	2·0307
611	·389	2	11	10·8867	566	·434	2	8	1·0112
610	·390	2	11	9·8672	565	·435	2	7	11·9918
609	·391	2	11	8·8478	564	·436	2	7	10·9723
608	·392	2	11	7·8283	563	·437	2	7	9·9529
607	·393	2	11	6·8089	562	·438	2	7	8·9334
606	·394	2	11	5·7894	561	·439	2	7	7·9140
605	·395	2	11	4·7699	560	·440	2	7	6·8945
604	·396	2	11	3·7505	559	·441	2	7	5·8751
603	·397	2	11	2·7311	558	·442	2	7	4·8556
602	·398	2	11	1·7116	557	·443	2	7	3·8361
601	·399	2	11	0·6921	556	·444	2	7	2·8167
600	·400	2	10	11·6727	555	·445	2	7	1·7972
599	·401	2	10	10·6532	554	·446	2	7	0·7778
598	·402	2	10	9·6338	553	·447	2	6	11·7583
597	·403	2	10	8·6143	552	·448	2	6	10·7389
596	·404	2	10	7·5949	551	·449	2	6	9·7194
595	·405	2	10	6·5754	550	·450	2	6	8·6999
594	·406	2	10	5·5559	549	·451	2	6	7·6805
593	·407	2	10	4·5365	548	·452	2	6	6·6611
592	·408	2	10	3·5170	547	·453	2	6	5·6416
591	·409	2	10	2·4976	546	·454	2	6	4·6221
590	·410	2	10	1·4781	545	·455	2	6	3·6027
589	·411	2	10	0·4587	544	·456	2	6	2·5832
588	·412	2	9	11·4392	543	·457	2	6	1·5638
587	·413	2	9	10·4198	542	·458	2	6	0·5443
586	·414	2	9	9·4003	541	·459	2	5	11·5249
585	·415	2	9	8·3809	540	·460	2	5	10·5054
584	·416	2	9	7·3614	539	·461	2	5	9·4859
583	·417	2	9	6·3419	538	·462	2	5	8·4665
582	·418	2	9	5·3225	537	·463	2	5	7·4470
581	·419	2	9	4·3030	536	·464	2	5	6·4276
580	·420	2	9	3·2836	535	·465	2	5	5·4081
579	·421	2	9	2·2641	534	·466	2	5	4·3887
578	·422	2	9	1·2447	533	·467	2	5	3·3692
577	·423	2	9	0·2252	532	·468	2	5	2·3498
576	·424	2	8	11·2058	531	·469	2	5	1·3303
575	·425	2	8	10·1863	530	·470	2	5	0·3109
574	·426	2	8	9·1669	529	·471	2	4	11·2914
573	·427	2	8	8·1474	528	·472	2	4	10·2719
572	·428	2	8	7·1279	527	·473	2	4	9·2525

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
526	·474	2	4	8·2330	481	·519	2	0	10·3576
525	·475	2	4	7·2136	480	·520	2	0	9·3381
524	·476	2	4	6·1941	479	·521	2	0	8·3187
523	·477	2	4	5·1747	478	·522	2	0	7·2992
522	·478	2	4	4·1552	477	·523	2	0	6·2798
521	·479	2	4	3·1358	476	·524	2	0	5·2603
520	·480	2	4	2·1163	475	·525	2	0	4·2409
519	·481	2	4	1·0969	474	·526	2	0	3·2214
518	·482	2	4	0·0774	473	·527	2	0	2·2020
517	·483	2	3	11·0579	472	·528	2	0	1·1825
516	·484	2	3	10·0385	471	·529	2	0	0·1630
515	·485	2	3	9·0190	470	·530	1	19	11·1436
514	·486	2	3	7·9996	469	·531	1	19	10·1241
513	·487	2	3	6·9801	468	·532	1	19	9·1047
512	·488	2	3	5·9607	467	·533	1	19	8·0852
511	·489	2	3	4·9412	466	·534	1	19	7·0658
510	·490	2	3	3·9218	465	·535	1	19	6·0463
509	·491	2	3	2·9023	464	·536	1	19	5·0269
508	·492	2	3	1·8829	463	·537	1	19	4·0074
507	·493	2	3	0·8634	462	·538	1	19	2·9879
506	·494	2	2	11·8439	461	·539	1	19	1·9685
505	·495	2	2	10·8245	460	·540	1	19	0·9490
504	·496	2	2	9·8051	459	·541	1	18	11·9296
503	·497	2	2	8·7856	458	·542	1	18	10·9101
502	·498	2	2	7·7661	457	·543	1	18	9·8907
501	·499	2	2	6·7467	456	·544	1	18	8·8712
500	·500	2	2	5·7272	455	·545	1	18	7·8518
499	·501	2	2	4·7078	454	·546	1	18	6·8323
498	·502	2	2	3·6883	453	·547	1	18	5·8129
497	·503	2	2	2·6689	452	·548	1	18	4·7934
496	·504	2	2	1·6494	451	·549	1	18	3·7739
495	·505	2	2	0·6300	450	·550	1	18	2·7545
494	·506	2	1	11·6105	449	·551	1	18	1·7351
493	·507	2	1	10·5911	448	·552	1	18	0·7156
492	·508	2	1	9·5716	447	·553	1	17	11·6961
491	·509	2	1	8·5521	446	·554	1	17	10·6767
490	·510	2	1	7·5327	445	·555	1	17	9·6572
489	·511	2	1	1·5132	444	·556	1	17	8·6378
488	·512	2	1	5·4938	443	·557	1	17	7·6183
487	·513	2	1	4·4743	442	·558	1	17	6·5989
486	·514	2	1	3·4549	441	·559	1	17	5·5794
485	·515	2	1	2·4354	440	·560	1	17	4·5599
484	·516	2	1	1·4159	439	·561	1	17	3·5405
483	·517	2	1	0·3965	438	·562	1	17	2·5211
482	·518	2	0	11·3770	437	·563	1	17	1·5016

FINE GOLD	ALLOY	VALUE £	s.	d.	FINE GOLD	ALLOY	VALUE £	s.	d.
436	·564	1	17	0·4821	391	·609	1	13	2·6067
435	·565	1	16	11·4627	390	·610	1	13	1·5872
434	·566	1	16	10·4432	389	·611	1	13	0·5678
433	·567	1	16	9·4238	388	·612	1	12	11·5483
432	·568	1	16	8·4043	387	·613	1	12	10·5289
431	·569	1	16	7·3849	386	·614	1	12	9·5094
430	·570	1	16	6·3654	385	·615	1	12	8·4899
429	·571	1	16	5·3459	384	·616	1	12	7·4705
428	·572	1	16	4·3265	383	·617	1	12	6·4511
427	·573	1	16	3·3070	382	·618	1	12	5·4316
426	·574	1	16	2·2876	381	·619	1	12	4·4121
425	·575	1	16	1·2681	380	·620	1	12	3·3927
424	·576	1	16	0·2487	379	·621	1	12	2·3732
423	·577	1	15	11·2292	378	·622	1	12	1·3538
422	·578	1	15	10·2098	377	·623	1	12	0·3343
421	·579	1	15	9·1903	376	·624	1	11	11·3142
420	·580	1	15	8·1709	375	·625	1	11	10·2954
419	·581	1	15	7·1514	374	·626	1	11	9·2759
418	·582	1	15	6·1319	373	·627	1	11	8·2565
417	·583	1	15	5·1125	372	·628	1	11	7·2370
416	·584	1	15	4·0930	371	·629	1	11	6·2176
415	·585	1	15	3·0736	370	·630	1	11	5·1981
414	·586	1	15	2·0541	369	·631	1	11	4·1787
413	·587	1	15	1·0347	368	·632	1	11	3·1592
412	·588	1	15	0·0152	367	·633	1	11	2·1398
411	·589	1	14	10·9958	366	·634	1	11	1·1203
410	·590	1	14	9·9763	365	·635	1	11	0·1009
409	·591	1	14	8·9569	364	·636	1	10	11·0814
408	·592	1	14	7·9374	363	·637	1	10	10·0620
407	·593	1	14	6·9179	362	·638	1	10	9·0425
406	·594	1	14	5·8985	361	·639	1	10	8·0230
405	·595	1	14	4·8790	360	·640	1	10	7·0036
404	·596	1	14	3·8596	359	·641	1	10	5·9841
403	·597	1	14	2·8401	358	·642	1	10	4·9647
402	·598	1	14	1·8207	357	·643	1	10	3·9452
401	·599	1	14	0·8012	356	·644	1	10	2·9258
400	.600	1	13	11·7818	355	·645	1	10	1·9063
399	·601	1	13	10·7623	354	·646	1	10	0·8869
398	·602	1	13	9·7429	353	·647	1	9	11·8674
397	·603	1	13	8·7234	352	·648	1	9	10·8479
396	·604	1	13	7·7039	351	·649	1	9	9·8285
395	·605	1	13	6·6845	350	·650	1	9	8·8090
394	·606	1	13	5·6651	349	·651	1	9	7·7896
393	·607	1	13	4·6456	348	·652	1	9	6·7701
392	·608	1	13	3·6261	347	·653	1	9	5·7507

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
346	·654	1	9	4·7312	301	·699	1	5	6·8558
345	·655	1	9	3·7118	300	·700	1	5	5·8363
344	·656	1	9	2·6923	299	·701	1	5	4·8169
343	·657	1	9	1·6729	298	·702	1	5	3·7974
342	·658	1	9	0·6534	297	·703	1	5	2·7779
341	·659	1	8	11·6339	296	·704	1	5	1·7585
340	·660	1	8	10·6145	295	·705	1	5	0·7390
339	·661	1	8	9·5951	294	·706	1	4	11·7196
338	·662	1	8	8·5756	293	·707	1	4	10·7011
337	·663	1	8	7·5561	292	·708	1	4	9·6807
336	·664	1	8	6·5367	291	·709	1	4	8·6612
335	·665	1	8	5·5172	290	·710	1	4	7·6418
334	·666	1	8	4·4978	289	·711	1	4	6·6223
333	·667	1	8	3·4783	288	·712	1	4	5·6029
332	·668	1	8	2·4589	287	·713	1	4	4·5834
331	·669	1	8	1·4394	286	·714	1	4	3·5639
330	·670	1	8	0·4199	285	·715	1	4	2·5445
329	·671	1	7	11·4005	284	·716	1	4	1·5251
328	·672	1	7	10·3811	283	·717	1	4	0·5056
327	·673	1	7	9·3616	282	·718	1	3	11·4861
326	·674	1	7	8·3421	281	·719	1	3	10·4667
325	·675	1	7	7·3227	280	·720	1	3	9·4472
324	·676	1	7	6·3032	279	·721	1	3	8·4278
323	·677	1	7	5·2838	278	·722	1	3	7·4083
322	·678	1	7	4·2643	277	·723	1	3	6·3889
321	·679	1	7	3·2449	276	·724	1	3	5·3694
320	·680	1	7	2·2254	275	·725	1	3	4·3499
319	·681	1	7	1·2059	274	·726	1	3	3·3305
318	·682	1	7	0·1865	273	·727	1	3	2·3110
317	·683	1	6	11·1670	272	·728	1	3	1·2916
316	·684	1	6	10·1476	271	·729	1	3	0·2721
315	·685	1	6	9·1281	270	·730	1	2	11·2527
314	·686	1	6	8·1087	269	·731	1	2	10·2332
313	·687	1	6	7·0892	268	·732	1	2	9·2138
312	·688	1	6	6·0698	267	·733	1	2	8·1943
311	·689	1	6	5·0503	266	·234	1	2	7·1749
310	·690	1	6	4·0309	265	·735	1	2	6·1554
309	·691	1	6	3·0114	264	·736	1	2	5·1351
308	·692	1	6	1·9919	263	·737	1	2	4·1165
307	·693	1	6	0·9725	262	·738	1	2	3·0970
306	·694	1	5	11·9530	261	·739	1	2	2·0776
305	·695	1	5	10·9336	260	·740	1	2	1·0581
304	·696	1	5	9·9141	259	·741	1	2	0·0387
303	·697	1	5	8·8947	258	·742	1	1	11·0192
302	·698	1	5	7·8752	257	·743	1	1	9·9998

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
256	·744	1	1	8·9803	211	·789	0	17	11·1049
255	·745	1	1	7·9609	210	·790	0	17	10·0854
254	·746	1	1	6·9414	209	·791	0	17	9·0659
253	·747	1	1	5·9219	208	·792	0	17	8·0465
252	·748	1	1	4·9025	207	·793	0	17	7·0270
251	·749	1	1	3·8830	206	·794	0	17	6·0076
250	·750	1	1	2·8636	205	·795	0	17	4·9881
249	·751	1	1	1·8441	204	·796	0	17	3·9687
248	·752	1	1	0·8247	203	·797	0	17	2·9492
247	·753	1	0	11·8052	202	·798	0	17	1·9298
246	·754	1	0	10·7858	201	·799	0	17	0·9103
245	·755	1	0	9·7663	200	·800	0	16	11·8909
244	·756	1	0	8·7469	199	·801	0	16	10·8714
243	·757	1	0	7·7274	198	·802	0	16	9·8519
242	·758	1	0	6·7079	197	·803	0	16	8·8325
241	·759	1	0	5·6885	196	·804	0	16	7·8130
240	·760	1	0	4·6690	195	·805	0	16	6·7936
239	·761	1	0	3·6496	194	·806	0	16	5·7741
238	·762	1	0	2·6301	193	·807	0	16	4·7547
237	·763	1	0	1·6107	192	·808	0	16	3·7352
236	·764	1	0	0·5912	191	·809	0	16	2·7158
235	·765	0	19	11·5718	190	·810	0	16	1·6963
234	·766	0	19	10·5523	189	·811	0	16	0·6769
233	·767	0	19	9·5329	188	·812	0	15	11·6574
232	·768	0	19	8·5134	187	·813	0	15	10·6379
231	·769	0	19	7·4939	186	·814	0	15	9·6185
230	·770	0	19	6·4745	185	·815	0	15	8·5990
229	·771	0	19	5·4551	184	·816	0	15	7·5796
228	·772	0	19	4·4356	183	·817	0	15	6·5601
227	·773	0	19	3·4161	182	·818	0	15	5·5407
226	·774	0	19	2·3967	181	·819	0	15	4·5212
225	·775	0	19	1·3772	180	·820	0	15	3·5018
224	·776	0	19	0·3578	179	·821	0	15	2·4823
223	·777	0	18	11·3383	178	·822	0	15	1·4629
222	·778	0	18	10·3189	177	·823	0	15	0·4434
221	·779	0	18	9·2994	176	·824	0	14	11·4239
220	·780	0	18	8·2799	175	·825	0	14	10·4045
219	·781	0	18	7·2605	174	·826	0	14	9·3851
218	·782	0	18	6·2410	173	·827	0	14	8·3656
217	·783	0	18	5·2216	172	·828	0	14	7·3461
216	·784	0	18	4·2021	171	·829	0	14	6·3267
215	·785	0	18	3·1827	170	·830	0	14	5·3072
214	·786	0	18	2·1632	169	·831	0	14	4·2878
213	·787	0	18	1·1438	168	·832	0	14	3·2683
212	·788	0	18	0·1243	167	·833	0	14	2·2489

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
166	·834	0	14	1·2294	121	·879	0	10	3·3530
165	·835	0	14	0·2099	120	·880	0	10	2·3345
164	·836	0	13	11·1905	119	·881	0	10	1·3151
163	·837	0	13	10·1710	118	·882	0	10	0·2956
162	·838	0	13	9·1516	117	·883	0	9	11·2761
161	·839	0	13	8·1321	116	·884	0	9	10·2567
160	·840	0	13	7·1127	115	·885	0	9	9·2372
159	·841	0	13	6·0932	114	·886	0	9	8·2178
158	·842	0	13	5·0738	113	·887	0	9	7·1983
157	·843	0	13	4·0543	112	·888	0	9	6·1789
156	·844	0	13	3·0349	111	·889	0	9	5·1594
155	·845	0	13	2·0154	110	·890	0	9	4·1399
154	·846	0	13	0·9959	109	·891	0	9	3·1205
153	·847	0	12	11·9765	108	·892	0	9	2·1010
152	·848	0	12	10·9570	107	·893	0	9	1·0816
151	·849	0	12	9·9376	106	·894	0	9	0·0621
150	·850	0	12	8·9181	105	·895	0	8	11·0427
149	·851	0	12	7·8987	104	·896	0	8	10·0232
148	·852	0	12	6·8792	103	·897	0	8	9·0038
147	·853	0	12	5·8598	102	·898	0	8	7·9843
146	·854	0	12	4·8403	101	·899	0	8	6·9649
145	·855	0	12	3·8209	100	·900	0	8	5·9454
144	·856	0	12	2·8014	99	·901	0	8	4·9259
143	·857	0	12	1·7819	98	·902	0	8	3·9065
142	·858	0	12	0·7625	97	·903	0	8	2·8870
141	·859	0	11	11·7430	96	·904	0	8	1·8676
140	·860	0	11	10·7236	95	·905	0	8	0·8481
139	·861	0	11	9·7041	94	·906	0	7	11·8287
138	·862	0	11	8·6847	93	·907	0	7	10·8092
137	·863	0	11	7·6652	92	·908	0	7	9·7898
136	·864	0	11	6·6458	91	·909	0	7	8·7703
135	·865	0	11	5·6263	90	·910	0	7	7·7509
134	·866	0	11	4·6069	89	·911	0	7	6·7314
133	·867	0	11	3·5874	88	·912	0	7	5·7119
132	·868	0	11	2·5679	87	·913	0	7	4·6925
131	·869	0	11	1·5485	86	·914	0	7	3·6730
130	·870	0	11	0·5290	85	·915	0	7	2·6536
129	·871	0	10	11·5096	84	·916	0	7	1·6341
128	·872	0	10	10·4901	83	·917	0	7	0·6147
127	·873	0	10	9·4707	82	·918	0	6	11·5952
126	·874	0	10	8·4512	81	·919	0	6	10·5758
125	·875	0	10	7·4318	80	·920	0	6	9·5563
124	·876	0	10	6·4123	79	·921	0	6	8·5369
123	·877	0	10	5·3929	78	·722	0	6	7·5174
122	·878	0	10	4·3734	77	·923	0	6	6·4979

Fine Gold	Alloy	Value			Fine Gold	Alloy	Value		
		£	s.	d.			£	s.	d.
76	·924	0	6	5·4785	38	·962	0	3	2·7392
75	·925	0	6	4·4590	37	·963	0	3	1·7198
74	·926	0	6	3·4396	36	·964	0	3	0·7003
73	·927	0	6	2·4201	35	·965	0	2	11·6809
72	·928	0	6	1·4007	34	·966	0	2	10·6614
71	·929	0	6	0·3812	33	·967	0	2	9·6419
70	·930	0	5	11·3618	32	·968	0	2	8·6225
69	·931	0	5	10·3423	31	·969	0	2	7·6030
68	·932	0	5	9·3229	30	·970	0	2	6·5836
67	·933	0	5	8·3034	29	·971	0	2	5·5641
66	·934	0	5	7·2839	28	·972	0	2	4·5447
65	·935	0	5	6·2645	27	·973	0	2	3·5252
64	·936	0	5	5·2451	26	·974	0	2	2·5058
63	·937	0	5	4·2256	25	·975	0	2	1·4863
62	·938	0	5	3·2061	24	·976	0	2	0·4669
61	·939	0	5	2·1867	23	·977	0	1	11·4474
60	·940	0	5	1·1672	22	·978	0	1	10·4279
59	·941	0	5	0·1478	21	·979	0	1	9·4085
58	·942	0	4	11·1283	20	·980	0	1	8·3890
57	·943	0	4	10·1089	19	·981	0	1	7·3696
56	·944	0	4	9·0894	18	·982	0	1	6·3501
55	·945	0	4	8·0699	17	·983	0	1	5·3307
54	·946	0	4	7·0505	16	·984	0	1	4·3112
53	·947	0	4	6·0310	15	·985	0	1	3·2918
52	·948	0	4	5·0116	14	·986	0	1	2·2723
51	·949	0	4	3·9921	13	·987	0	1	1·2529
50	·950	0	4	2·9727	12	·988	0	1	0·2334
49	·951	0	4	1·9532	11	·989	0	0	11·2139
48	·952	0	4	0·9338	10	·990	0	0	10·1945
47	·953	0	3	11·9143	9	·991	0	0	9·1750
46	·954	0	3	10·8949	8	·992	0	0	8·1556
45	·955	0	3	9·8754	7	·993	0	0	7·1361
44	·956	0	3	8·8559	6	·994	0	0	6·1167
43	·957	0	3	7·8365	5	·995	0	0	5·0972
42	·958	0	3	6·8170	4	·996	0	0	4·0778
41	·959	0	3	5·7976	3	·997	0	0	3·0583
40	·960	0	3	4·7781	2	·998	0	0	2·0389
39	·961	0	3	3·7587	1	·999	0	0	1·0194

To convert MINT VALUE into BANK VALUE when the Standard is expressed in Thousandths.

Thousandths	Value in Pence	Thousandths	Value in Pence
1	·001636	6	·009816
2	·003272	7	·011352
3	·004908	8	·013088
4	·006544	9	·014724
5	·008180		

To illustrate the use of the above table, gold of $\frac{500}{1000}$ths fine may be taken. As in the Table for finding the Bank value of gold when the standard is reported in carats, &c., the amounts in pence, as above, are to be deducted from the prices attached to corresponding standards in Table No. 2. Thus, the minus value of $\frac{5}{1000}$ths is ·00818 of a penny; therefore, the minus value of $\frac{500}{1000}$ths is ·818 of a penny, which amount must be deducted from the Mint price of gold at the above standard. On referring to the Table it will be found to be £2 2*s.* 5·7272*d.* per oz. Now, if ·818 be deducted, the remainder will be £2 2*s.* 4·9092*d.*, representing the Bank value of 1 oz. of gold of the fineness just mentioned.

TABLE III.

ASSAY TABLE, showing the Amount of GOLD or SILVER, in Ounces, Pennyweights, and Grains, contained in a Ton of Ore, &c. from the Weight of Metal obtained in an Assay of 200 Grains of Mineral.

If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL			If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·001	0	3	6	·031	5	1	6
·002	0	6	12	·032	5	4	12
·003	0	9	19	·033	5	7	19
·004	0	13	1	·034	5	11	1
·005	0	16	8	·035	5	14	8
·006	0	19	14	·036	5	17	14
·007	1	2	20	·037	6	0	20
·008	1	6	3	·038	6	4	3
·009	1	9	9	·039	6	7	9
·010	1	12	6	·040	6	10	16
·011	1	15	22	·041	6	13	22
·012	1	19	4	·042	6	17	4
·013	2	2	11	·043	7	0	11
·014	2	5	17	·044	7	3	17
·015	2	9	0	·045	7	7	0
·016	2	12	6	·046	7	10	6
·017	2	15	12	·047	7	13	12
·018	2	18	19	·048	7	16	19
·019	3	2	1	·049	8	0	1
·020	3	5	8	·050	8	3	8
·021	3	8	14	·051	8	6	14
·022	3	11	20	·052	8	9	20
·023	3	15	3	·053	8	13	3
·024	3	18	9	·054	8	16	9
·025	4	1	16	·055	8	19	16
·026	4	4	22	·056	9	2	22
·027	4	8	4	·057	9	6	4
·028	4	11	11	·058	9	9	11
·029	4	14	17	·059	9	12	17
·030	4	18	0	·060	9	16	0

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·061	9	19	6	·105	17	3	0
·062	10	2	12	·106	17	6	6
·063	10	5	19	·107	17	9	12
·064	10	9	1	·108	17	12	19
·065	10	12	8	·109	17	16	1
·066	10	15	14	·110	17	19	8
·067	10	18	20	·111	18	2	14
·068	11	2	3	·112	18	5	20
·069	11	5	9	·113	18	9	3
·070	11	8	16	·114	18	12	9
·071	11	11	22	·115	18	15	16
·072	11	15	4	·116	18	18	22
·073	11	18	11	·117	19	2	4
·074	12	1	17	·118	19	5	11
·075	12	5	0	·119	19	8	17
·076	12	8	6	·120	19	12	0
·077	12	11	12	·121	19	15	6
·078	12	14	19	·122	19	18	12
·079	12	18	1	·123	20	1	19
·080	13	1	8	·124	20	5	1
·081	13	4	14	·125	20	8	8
·082	13	7	20	·126	20	11	14
·083	13	11	3	·127	20	14	20
·084	13	14	9	·128	20	18	3
·085	13	17	16	·129	21	1	9
·086	14	0	22	·130	21	4	16
·087	14	4	4	·131	21	7	22
·088	14	7	11	·132	21	11	4
·089	14	10	17	·133	21	14	11
·090	14	14	0	·134	21	17	17
·091	14	17	6	·135	22	1	0
·092	15	0	12	·136	22	4	6
·093	15	3	19	·137	22	7	12
·094	15	7	1	·138	22	10	19
·095	15	10	8	·139	22	14	1
·096	15	13	14	·140	22	17	8
·097	15	16	20	·141	23	0	14
·098	16	0	3	·142	23	3	20
·099	16	3	9	·143	23	7	3
·100	16	6	16	·144	23	10	9
·101	16	9	22	·145	23	13	16
·102	16	13	4	·146	23	16	22
·103	16	16	11	·147	24	0	4
·104	16	19	17	·148	24	3	11

If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*
·149	24	6	17
·150	24	10	0
·151	24	13	6
·152	24	16	12
·153	24	19	19
·154	25	3	1
·155	25	6	8
·156	25	9	14
·157	25	12	20
·158	25	16	3
·159	25	19	9
·160	26	2	16
·161	26	5	22
·162	26	9	4
·163	26	12	11
·164	26	15	17
·165	26	19	0
·166	27	2	6
·167	27	5	12
·168	27	8	19
·169	27	12	1
·170	27	15	8
·171	27	18	14
·172	28	1	20
·173	28	5	3
·174	28	8	9
·175	28	11	16
·176	28	14	22
·177	28	18	4
·178	29	1	11
·179	29	4	17
·180	29	8	0
·181	29	11	6
·182	29	14	12
·183	29	17	19
·184	30	1	1
·185	30	4	8
·186	30	7	14
·187	30	10	20
·188	30	14	3
·189	30	17	9
·190	31	0	16
·191	31	3	22
·192	31	7	4
·193	31	10	11
·194	31	13	17
·195	31	17	0
·196	32	0	6
·197	32	3	12
·198	32	6	19
·199	32	10	1
·200	32	13	8
·201	32	16	14
·202	32	19	20
·203	33	3	3
·204	33	6	9
·205	33	9	16
·206	33	12	22
·207	33	16	4
·208	33	19	11
·209	34	2	17
·210	34	6	0
·211	34	9	6
·212	34	12	12
·213	34	15	19
·214	34	19	1
·215	35	2	8
·216	35	5	14
·217	35	8	20
·218	35	12	3
·219	35	15	9
·220	35	18	16
·221	36	1	22
·222	36	5	4
·223	36	8	11
·224	36	11	17
·225	36	15	0
·226	36	18	6
·227	37	1	12
·228	37	4	19
·229	37	8	1
·230	37	11	8
·231	37	14	14
·232	37	17	20
·233	38	1	3
·234	38	4	9
·235	38	7	16
·236	38	10	22

If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*
·237	38	14	4
·238	38	17	11
·239	39	0	17
·240	39	4	0
·241	39	7	6
·242	39	10	12
·243	39	13	18
·244	39	17	1
·245	40	0	8
·246	40	3	14
·247	40	6	20
·248	40	10	3
·249	40	13	9
·250	40	16	16
·251	40	19	22
·252	41	3	4
·253	41	6	11
·254	41	9	17
·255	41	13	0
·256	41	16	6
·257	41	19	12
·258	42	2	19
·259	42	6	1
·260	42	9	8
·261	42	12	14
·262	42	15	20
·263	42	19	3
·264	43	2	9
·265	43	5	16
·266	43	8	22
·267	43	12	4
·268	43	15	11
·269	43	18	17
·270	44	2	0
·271	44	5	6
·272	44	8	12
·273	44	11	19
·274	44	15	1
·275	44	18	8
·276	45	1	14
·277	45	4	20
·278	45	8	3
·279	45	11	9
·280	45	14	16
·281	45	17	22
·282	46	1	4
·283	46	4	11
·284	46	7	17
·285	46	11	0
·286	46	14	6
·287	46	17	12
·288	47	0	19
·289	47	4	1
·290	47	7	8
·291	47	10	14
·292	47	13	20
·293	47	17	3
·294	48	0	9
·295	48	3	16
·296	48	6	22
·297	48	10	4
·298	48	13	11
·299	48	16	17
·300	49	0	0
·301	49	3	6
·302	49	6	12
·303	49	9	19
·304	49	13	1
·305	49	16	8
·306	49	19	14
·307	50	2	20
·308	50	6	3
·309	50	9	9
·310	50	12	16
·311	50	15	22
·312	50	19	4
·313	51	2	11
·314	51	5	17
·315	51	9	0
·316	51	12	6
·317	51	15	12
·318	51	18	19
·319	52	2	1
·320	52	5	8
·321	52	8	14
·322	52	11	20
·323	52	15	3
·324	52	18	9

If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL			If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·325	53	1	16	·369	60	5	9
·326	53	4	22	·370	60	8	16
·327	53	8	4	·371	60	11	22
·328	53	11	11	·372	60	15	4
·329	53	14	17	·373	60	18	11
·330	53	18	0	·374	61	1	17
·331	54	1	6	·375	61	5	0
·332	54	4	12	·376	61	8	6
·333	54	7	19	·377	61	11	12
·334	54	11	1	·378	61	14	19
·335	54	14	8	·379	61	18	1
·336	54	17	14	·380	62	1	8
·337	55	0	20	·381	62	4	14
·338	55	4	3	·382	62	7	20
·339	55	7	9	·383	62	11	3
·340	55	10	16	·384	62	14	9
·341	55	13	22	·385	62	17	16
·342	55	17	4	·386	63	0	22
·343	56	0	11	·387	63	4	4
·344	56	3	17	·388	63	7	11
·345	56	7	0	·389	63	10	17
·346	56	10	6	·390	63	14	0
·347	56	13	12	·391	63	17	6
·348	56	16	19	·392	64	0	12
·349	57	0	1	·393	64	3	19
·350	57	3	8	·394	64	7	1
·351	57	6	14	·395	64	10	8
·352	57	9	20	·396	64	13	14
·353	57	13	3	·397	64	16	20
·354	57	16	9	·398	65	0	3
·355	57	19	16	·399	65	3	9
·356	58	2	22	·400	65	6	16
·357	58	6	4	·401	65	9	22
·358	58	9	11	·402	65	13	4
·359	58	12	17	·403	65	16	11
·360	58	16	0	·404	65	19	17
·361	58	19	6	·405	66	3	0
·362	59	9	12	·406	66	6	6
·363	59	5	19	·407	66	9	12
·364	59	9	1	·408	66	12	19
·365	59	12	8	·409	66	16	1
·366	59	15	14	·410	66	19	8
·367	59	18	20	·411	67	2	14
·368	60	2	3	·412	67	5	20

If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL			If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·413	67	9	3	·457	74	12	20
·414	67	12	9	·458	74	16	3
·415	67	15	16	·459	74	19	9
·416	67	18	22	·460	75	2	16
·417	68	2	4	·461	75	5	22
·418	68	5	11	·462	75	9	4
·419	68	8	17	·463	75	12	11
·420	68	12	0	·464	75	15	17
·421	68	15	6	·465	75	19	0
·422	68	18	12	·466	76	2	6
·423	69	1	19	·467	76	5	12
·424	69	5	1	·468	76	8	19
·425	69	8	8	·469	76	12	1
·426	69	11	14	·470	76	15	8
·427	69	14	20	·471	76	18	14
·428	69	18	3	·472	77	1	20
·429	70	1	9	·473	77	5	3
·430	70	4	16	·474	77	8	9
·431	70	7	22	·475	77	11	16
·432	70	11	4	·476	77	14	22
·433	70	14	11	·477	77	18	4
·434	70	17	17	·478	78	1	11
·435	71	1	0	·479	78	4	17
·436	71	4	6	·480	78	8	0
·437	71	7	12	·481	78	11	6
·438	71	10	19	·482	78	14	12
·439	71	14	1	·483	78	17	19
·440	71	17	8	·484	79	1	1
·441	72	0	14	·485	79	4	8
·442	72	3	20	·486	79	7	14
·443	72	7	3	·487	79	10	20
·444	72	10	9	·488	79	14	3
·445	72	13	16	·489	79	17	9
·446	72	16	22	·490	80	0	16
·447	73	0	4	·491	80	3	22
·448	73	3	11	·492	80	7	4
·449	73	6	17	·493	80	10	11
·450	73	10	0	·494	80	13	17
·451	73	13	6	·495	80	17	0
·452	73	16	12	·496	81	0	6
·453	73	19	19	·497	81	3	12
·454	74	3	1	·498	81	6	19
·455	74	6	8	·499	81	10	1
·456	74	9	14	·500	81	13	8

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·501	81	16	14	·545	89	0	8
·502	81	19	20	·546	89	3	14
·503	82	3	3	·547	89	6	20
·504	82	6	9	·548	89	10	3
·505	82	9	16	·549	89	13	9
·506	82	12	22	·550	89	16	16
·507	82	16	4	·551	89	19	22
·508	82	19	11	·552	90	3	4
·509	83	2	17	·553	90	6	11
·510	83	6	0	·554	90	9	17
·511	83	9	6	·555	90	13	0
·512	83	12	12	·556	90	16	6
·513	83	15	19	·557	90	19	12
·514	83	19	1	·558	91	2	19
·515	84	2	8	·559	91	6	1
·516	84	5	14	·560	91	9	8
·517	84	8	20	·561	91	12	14
·518	84	12	3	·562	91	15	20
·519	84	15	9	·563	91	19	3
·520	84	18	16	·564	92	2	9
·521	85	1	22	·565	92	5	16
·522	85	5	4	·566	92	8	22
·523	85	8	11	·567	92	12	4
·524	85	11	17	·568	92	15	11
·525	85	15	0	·569	92	18	17
·526	85	18	6	·570	93	2	0
·527	86	1	12	·571	93	5	6
·528	86	4	19	·572	93	8	12
·529	86	8	1	·573	93	11	19
·530	86	11	8	·574	93	15	1
·531	86	14	14	·575	93	18	8
·532	86	17	20	·576	94	1	14
·533	87	1	3	·577	94	4	20
·534	87	4	9	·578	94	8	3
·535	87	7	16	·579	94	11	9
·536	87	10	22	·580	94	14	16
·537	87	14	4	·581	94	17	22
·538	87	17	11	·582	95	1	4
·539	88	0	17	·533	95	4	11
·540	88	4	0	·584	95	7	17
·541	88	7	6	·585	95	11	0
·542	88	10	12	·586	95	14	6
·543	88	13	19	·587	95	17	12
·544	88	17	1	·588	96	0	19

If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL			If 200 Grains of Ore give of FINE METAL	One Ton of Ore will yield of FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·589	96	4	1	·633	103	7	19
·590	96	7	8	·634	103	11	1
·591	96	10	14	·635	103	14	8
·592	96	13	20	·636	103	17	14
·593	96	17	3	·637	104	0	20
·594	97	0	9	·638	104	4	3
·595	97	3	16	·639	104	7	9
·596	97	6	22	·640	104	10	16
·597	97	10	4	·641	104	13	22
·598	97	13	11	·642	104	17	4
·599	97	16	17	·643	105	0	11
·600	98	0	0	·644	105	3	17
·601	98	3	6	·645	105	7	0
·602	98	6	12	·646	105	10	6
·603	98	9	19	·647	105	13	12
·604	98	13	1	·648	105	16	19
·605	98	16	8	·649	106	0	1
·606	98	19	14	·650	106	3	8
·607	99	2	20	·651	106	6	14
·608	99	6	3	·652	106	9	20
·609	99	9	9	·653	106	13	3
·610	99	12	16	·654	106	16	9
·611	99	15	22	·655	106	19	16
·612	99	19	4	·656	107	2	22
·613	100	2	11	·657	107	6	4
·614	100	5	17	·658	107	9	11
·615	100	9	0	·659	107	12	17
·616	100	12	6	·660	107	16	0
·617	100	15	12	·661	107	19	6
·618	100	18	19	·662	108	2	12
·619	101	2	1	·663	108	5	19
·620	101	5	8	·664	108	9	1
·621	101	8	14	·665	108	12	8
·622	101	11	20	·666	108	15	14
·623	101	15	3	·667	108	18	20
·624	101	18	9	·668	109	2	3
·625	102	1	16	·669	109	5	9
·626	102	4	22	·670	109	8	16
·627	102	8	4	·671	109	11	22
·628	102	11	11	·672	109	15	4
·629	102	14	17	·673	109	18	11
·630	102	18	0	·674	110	1	17
·631	103	1	6	·675	110	5	0
·632	103	4	12	·676	110	8	6

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·677	110	11	12	·721	117	15	6
·678	110	14	19	·722	117	18	12
·679	110	18	1	·723	118	1	19
·680	111	1	8	·724	118	5	1
·681	111	4	14	·725	118	8	8
·682	111	7	20	·726	118	11	14
·683	111	11	3	·727	118	14	20
·684	111	14	9	·728	118	18	3
·685	111	17	6	·729	119	1	9
·686	112	0	22	·730	119	4	16
·687	112	4	4	·731	119	7	22
·688	112	7	11	·732	119	11	4
·689	112	10	17	·733	119	14	11
·690	112	14	0	·734	119	17	17
·691	112	17	6	·735	120	1	0
·692	113	0	12	·736	120	4	6
·693	113	3	19	·737	120	7	12
·694	113	7	1	·738	120	10	19
·695	113	10	8	·739	120	14	1
·696	113	13	14	·740	120	17	2
·697	113	16	20	·741	121	0	14
·698	114	0	3	·742	121	3	20
·699	114	3	9	·743	121	7	3
·700	114	6	16	·744	121	10	9
·701	114	9	22	·745	121	13	6
·702	114	13	4	·746	121	16	22
·703	114	16	12	·747	122	0	4
·704	114	19	17	·748	122	3	11
·705	115	3	0	·749	122	6	17
·706	115	6	6	·750	122	10	0
·707	115	9	12	·751	122	13	16
·708	115	12	19	·752	122	16	12
·709	115	16	1	·753	122	19	19
·710	115	19	8	·754	123	3	1
·711	116	2	14	·755	123	6	8
·712	116	5	20	·756	123	9	14
·713	116	9	3	·757	123	12	20
·714	116	12	9	·758	123	16	3
·715	116	15	16	·759	123	19	9
·716	116	18	22	·760	124	2	16
·717	117	2	4	·761	124	5	22
·718	117	5	11	·762	124	9	4
·719	117	8	17	·763	124	12	11
·720	117	12	0	·764	124	15	17

If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*
·765	124	19	0
·766	125	2	6
·767	125	5	12
·768	125	8	19
·769	125	12	1
·770	125	15	8
·771	125	18	14
·772	126	1	20
·773	126	5	3
·774	126	8	9
·775	126	11	16
·776	126	14	22
·777	126	18	4
·778	127	1	11
·779	127	4	17
·780	127	8	0
·781	127	11	6
·782	127	14	12
·783	127	17	19
·784	128	1	1
·785	128	4	8
·786	128	7	14
·787	128	10	20
·788	128	14	3
·789	128	17	9
·790	129	0	16
·791	129	3	22
·792	129	7	4
·793	129	10	11
·794	129	13	17
·795	129	17	0
·796	130	0	6
·797	130	3	12
·798	130	6	19
·799	130	10	1
·800	130	13	8
·801	130	16	14
·802	130	19	20
·803	131	3	3
·804	131	6	9
·805	131	9	16
·806	131	12	22
·807	131	16	4
·808	131	19	11
·809	132	2	17
·810	132	6	0
·811	132	9	6
·812	132	12	12
·813	132	15	19
·814	132	19	1
·815	133	2	8
·816	133	5	14
·817	133	8	20
·818	133	12	3
·819	133	15	9
·820	133	18	16
·821	134	1	22
·822	134	5	4
·823	134	8	11
·824	134	11	17
·825	134	15	0
·826	134	18	6
·827	135	1	12
·828	135	4	19
·829	135	8	1
·830	135	11	8
·831	135	14	14
·832	135	11	8
·833	136	1	3
·834	136	4	9
·835	136	7	16
·836	136	10	22
·837	136	14	4
·838	136	17	11
·839	137	0	17
·840	137	4	0
·841	137	7	6
·842	137	10	12
·843	137	13	19
·844	137	17	1
·845	138	0	8
·846	138	3	14
·847	138	6	20
·848	138	10	3
·849	138	13	19
·850	138	16	16
·851	138	19	22
·852	139	3	4

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·853	139	6	11	·897	146	10	4
·854	139	9	17	·898	146	13	11
·855	139	13	0	·899	146	16	17
·856	139	16	6	·900	147	0	0
·857	139	19	12	·901	147	3	6
·858	140	2	19	·902	147	6	12
·859	140	6	1	·903	147	9	19
·860	140	9	8	·904	147	13	1
·861	140	12	14	·905	147	16	8
·862	140	15	20	·906	147	19	14
·863	140	19	3	·907	148	2	2
·864	141	2	9	·908	148	6	3
·865	141	5	16	·909	148	9	9
·866	141	8	22	·910	148	12	16
·867	141	12	4	·911	148	15	21
·868	141	15	11	·912	148	19	4
·869	141	18	17	·913	149	2	11
·870	142	2	0	·914	149	5	17
·871	142	5	6	·915	149	9	0
·872	142	8	12	·916	149	12	6
·873	142	11	19	·917	149	15	12
·874	142	15	1	·918	149	18	19
·875	142	18	8	·919	150	2	1
·876	143	1	14	·920	150	5	8
·877	143	4	20	·921	150	8	14
·878	143	8	3	·922	150	11	20
·879	143	11	9	·923	150	15	3
·880	143	14	16	·924	150	18	9
·881	143	17	22	·925	151	1	16
·882	144	1	4	·926	151	4	22
·883	144	4	11	·927	151	8	4
·884	144	7	17	·928	151	11	11
·885	144	11	0	·929	151	14	17
·886	144	14	6	·930	151	18	0
·887	144	17	12	·931	152	1	6
·888	145	0	19	·932	152	4	12
·889	145	4	1	·933	152	7	19
·890	145	7	8	·934	152	11	1
·891	145	10	14	·935	152	14	8
·892	145	13	20	·936	152	17	14
·893	145	17	3	·937	153	0	20
·894	146	0	9	·938	153	4	3
·895	146	3	16	·939	153	7	9
·896	146	6	22	·940	153	10	16

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Gr.	*Oz.*	*Dwts.*	*Grs.*	*Gr.*	*Oz.*	*Dwts.*	*Grs.*
·941	153	13	22	·985	160	17	6
·942	153	17	4	·986	161	0	22
·943	154	0	11	·987	161	4	4
·944	154	3	17	·988	161	7	11
·945	154	7	0	·989	161	10	17
·946	154	10	6	·990	161	14	0
·947	154	13	12	·991	161	17	6
·948	154	16	19	·992	162	0	12
·949	155	0	1	·993	162	3	19
·950	155	3	8	·994	162	7	1
·951	155	6	14	·995	162	10	8
·952	155	9	20	·996	162	13	14
·953	155	13	3	·997	162	16	20
·954	155	16	9	·998	163	0	3
·955	155	19	16	·999	163	3	9
·956	156	2	22	1 grain	163	6	16
·957	156	6	4	2	326	13	8
·958	156	9	11	3	490	0	0
·959	156	12	17	4	653	6	16
·960	156	16	0	5	816	13	8
·961	156	19	6	6	980	0	0
·962	157	2	12	7	1143	6	16
·963	157	5	19	8	1306	13	8
·964	157	9	1	9	1470	0	0
·965	157	12	8	10	1633	6	16
·966	157	15	14	11	1796	13	8
·967	157	18	20	12	1960	0	0
·968	158	2	3	13	2123	6	16
·969	158	5	9	14	2286	13	8
·970	158	8	16	15	2450	0	0
·971	158	11	22	16	2613	6	16
·972	158	15	4	17	2776	13	8
·973	158	18	11	18	2940	0	0
·974	159	1	17	19	3103	6	16
·975	159	5	0	20	3266	13	8
·976	159	8	6	21	3430	0	0
·977	159	11	12	22	3593	6	16
·978	159	14	19	23	3756	13	8
·979	159	18	1	24	3920	0	0
·980	160	1	8	25	4083	6	16
·981	160	4	14	26	4246	13	8
·982	160	7	20	27	4410	0	0
·983	160	10	3	28	4573	6	16
·984	160	14	9	29	4736	13	8

If 200 Grains of Ore give of	One Ton of Ore will yield of			If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL			FINE METAL	FINE METAL		
Grs.	*Oz.*	*Dwts.*	*Grs.*	*Grs.*	*Oz.*	*Dwts.*	*Grs.*
30	4900	0	0	74	12086	13	8
31	5063	6	16	75	12250	0	0
32	5226	13	8	76	12413	6	16
33	5390	0	0	77	12576	13	8
34	5553	6	16	78	12740	0	0
35	5716	13	8	79	12903	6	16
36	5880	0	0	80	13066	13	8
37	6043	6	16	81	13230	0	0
38	6206	13	8	82	13393	6	16
39	6370	0	0	83	13556	13	8
40	6533	6	16	84	13720	0	0
41	6696	13	8	85	13883	6	16
42	6860	0	0	86	14046	13	8
43	7023	6	16	87	14210	0	0
44	7186	13	8	88	14373	6	16
45	7350	0	0	89	14536	13	8
46	7513	6	16	90	14700	0	0
47	7676	13	8	91	14863	6	16
48	7840	0	0	92	15026	13	8
49	8003	6	16	93	15190	0	0
50	8166	13	8	94	15353	6	16
51	8330	0	0	95	15516	13	8
52	8493	6	16	96	15680	0	0
53	8656	13	8	97	15843	6	16
54	8820	0	0	98	16006	13	8
55	8983	6	16	99	16170	0	0
56	9146	13	8	100	16333	6	16
57	9310	0	0	101	16496	13	8
58	9473	6	16	102	16660	0	0
59	9636	13	8	103	16823	6	16
60	9800	0	0	104	16986	13	8
61	9963	6	16	105	17150	0	0
62	10126	13	8	106	17313	6	16
63	10290	0	0	107	17476	13	8
64	10453	6	16	108	17640	0	0
65	10616	13	8	109	17803	6	16
66	10780	0	0	110	17966	13	8
67	10943	6	16	111	18130	0	0
68	11106	13	8	112	18293	6	16
69	11270	0	0	113	18456	13	8
70	11433	6	16	114	18620	0	0
71	11596	13	8	115	18783	6	16
72	11760	0	0	116	18946	13	8
73	11923	6	16	117	19110	0	0

If 200 Grains of Ore give of	One Ton of Ore will yield of		
FINE METAL	FINE METAL		
Grs.	*Oz.*	*Dwts.*	*Grs.*
118	19273	6	16
119	19436	13	8
120	19600	0	0
121	19763	6	16
122	19926	13	8
123	20090	0	0
124	20253	6	16
125	20416	13	8
126	20580	0	0
127	20743	6	16
128	20906	13	8
129	21070	0	0
130	21233	6	16
131	21396	13	8
132	21560	0	0
133	21723	6	16
134	21886	13	8
135	22050	0	0
136	22213	6	16
137	22376	13	8
138	22540	0	0
139	22703	6	16
140	22866	13	8
141	23030	0	0
142	23193	6	16
143	23356	13	8
144	23520	0	0
145	23683	6	16
146	23846	13	8
147	24010	0	0
148	24173	6	16
149	24336	13	8
150	24500	0	0
151	24663	6	16
152	24826	13	8
153	24990	0	0
154	25153	6	16
155	25316	13	8
156	25480	0	0
157	25643	6	16
158	25806	13	8
159	25970	0	0
160	26133	6	16
161	26296	13	8
162	26460	0	0
163	26623	6	16
164	26786	13	8
165	26950	0	0
166	27113	6	16
167	27276	13	8
168	27440	0	0
169	27603	6	16
170	27766	13	8
171	27930	0	0
172	28093	6	16
173	28256	13	8
174	28420	0	0
175	28583	6	16
176	28746	13	8
177	28910	0	0
178	29073	6	16
179	29236	13	8
180	29400	0	0
181	29563	6	16
182	29726	13	8
183	29890	0	0
184	30053	6	16
185	30216	13	8
186	30380	0	0
187	30543	6	16
188	30706	13	8
189	30870	0	0
190	31033	6	16
191	31196	13	8
192	31360	0	0
193	31523	6	16
194	31686	13	8
195	31850	0	0
196	32013	6	16
197	32176	13	8
198	32340	0	0
199	32503	6	16
200	32666	13	8

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Spottiswoode & Co., Printers, New-street Square, London.