INTERNATIONAL ATOMIC WEIGHTS FOR 1913 *

O = 16

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorine	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sm	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.07
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	172.0
Lutecium	Lu	174.0	(Neoytterbium)		
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6

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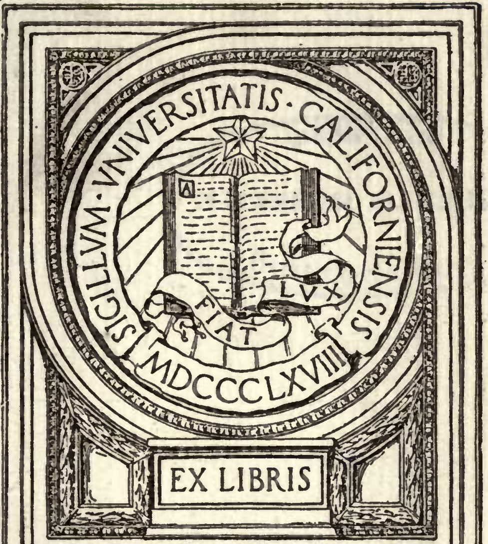
* Compiled by the International Committee on Atomic Weights consisting of F. W. Clarke, W. Ostwald, T. E. Thorpe, and G. Urbain.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METHODS

IN

METALLURGICAL ANALYSIS

BY

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PREFACE

In this volume are brought together those methods in metallurgical analysis which, owing to their fitness, seem to have been most generally adopted in American metallurgical laboratories. The procedures are given for the sake of clearness in as direct statement as possible, without regard to literary style.

Explanatory notes have been introduced where they are most needed by the beginner, but are so subdued as not to annoy the experienced reader who may wish to omit them.

From several years' experience I find that students who have had adequate preparation in qualitative analysis can take up metallurgical analysis at once without having previously taken a general course in quantitative analysis. For the benefit of such students the various operations in both gravimetric and volumetric analysis are described in detail at the beginning of the book, and the methods that such students would ordinarily take up first are given in greater detail than those which are usually assigned after considerable experience has been gained.

For more details than it is possible to give in a work of this kind, the reader should consult the references given in the footnotes, and in the bibliography on page 335.

In addition to those whose names are mentioned hereafter in these pages, I am indebted to my colleagues; Professor Albert Sauveur for many helpful suggestions, especially for the improvement of the chapter on Iron and Steel, and Professor G. S. Raymer for valuable criticism of the chapters on Sampling and Fire Assaying. I have also received generous assistance in collecting material and in preparing the illustrations from Mr. W. S. Weeks, Instructor; and Messrs. F. C. Langenberg and R. S. Cochran, Assistants, in the Harvard Mining School.

C. H. W.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.,
Jan. 2, 1915.

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METALLURGICAL ANALYSIS

Definition. Metallurgical Analysis is the application of analytical-chemical methods to the chemical problems of metallurgy, including problems of valuation and utilization as well as of production.

Purposes for which Analyses are Made. The analysis of any metallurgical material or product is made for one or more of the following reasons: (1) As a basis for the estimation of its commercial value, (2) to determine its fitness or adaptability to a certain use, or (3) as a guide in the operation of a process or in determining the efficiency of a process or treatment.

Selection of Methods. It is obvious from the above classification that analyses are made either for technical purposes or for commercial purposes. For example, the slag from a blast furnace is analyzed to determine if the furnace charge is correct. In the open-hearth process of steel making, frequent determinations of carbon are made that the heat may be terminated when the carbon has been reduced to the desired point. These determinations are for technical purposes, and, while accurate results are desirable, the important requisite is, that the results be obtained within a specified time, even if the highest degree of accuracy must thereby be sacrificed; for it is of no special value to the metallurgist to learn the composition of the slag after the whole lot of ore has been charged into the furnace; nor can the steel maker use the carbon determinations if they are not given to him within a few minutes after the samples of molten steel are taken from the furnace.

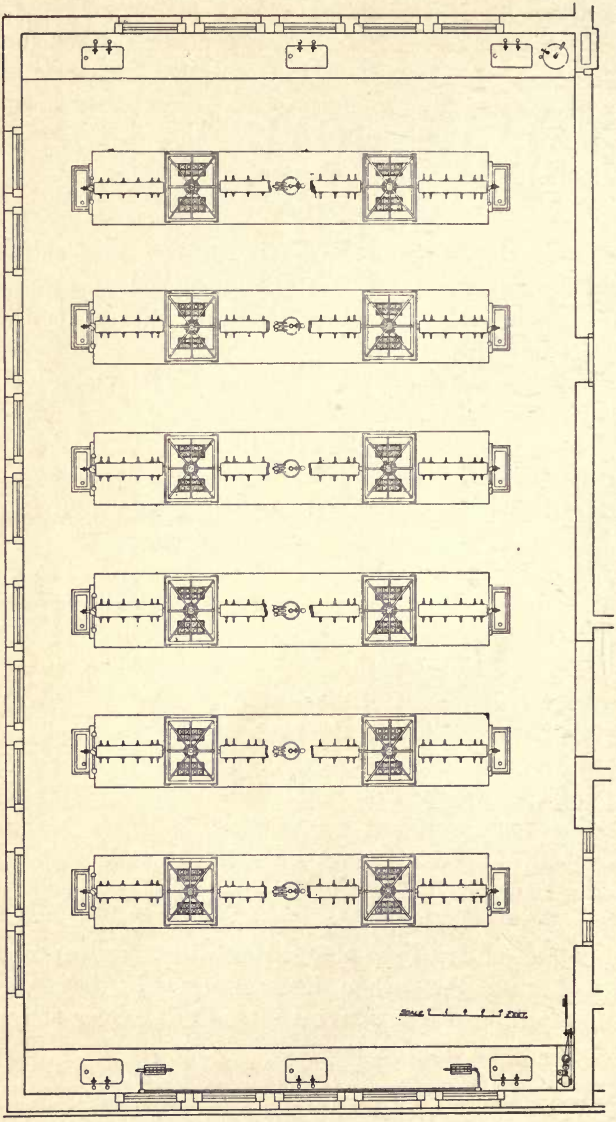


FIG. 1.—Plan of a School Laboratory for Metallurgical Chemistry.

On the other hand, buyers and sellers of blister copper must know very exactly the percentage of copper as well as the amounts of the precious metals present, in order to fix a just price for the bullion. In making determinations for commercial purposes, especially in cases where large sums of money are involved, the most accurate methods known must be applied, and should be carried out by the most skilled analysts.

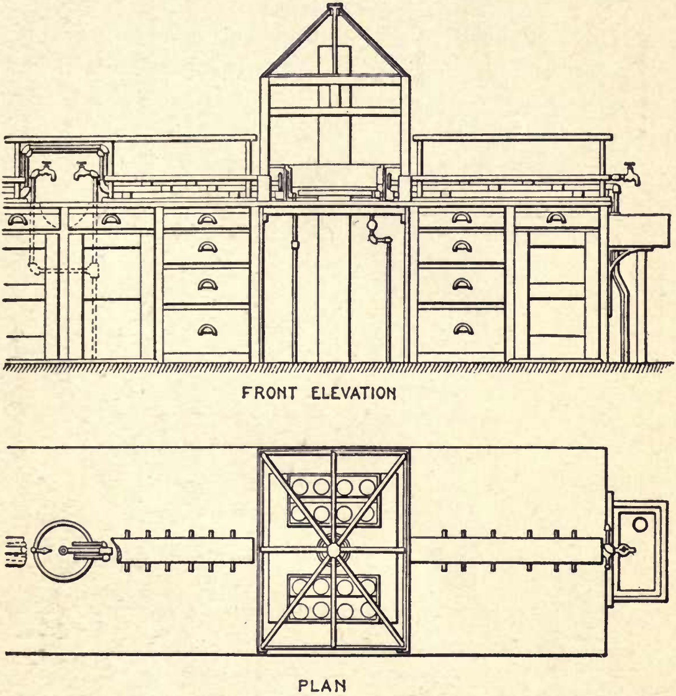
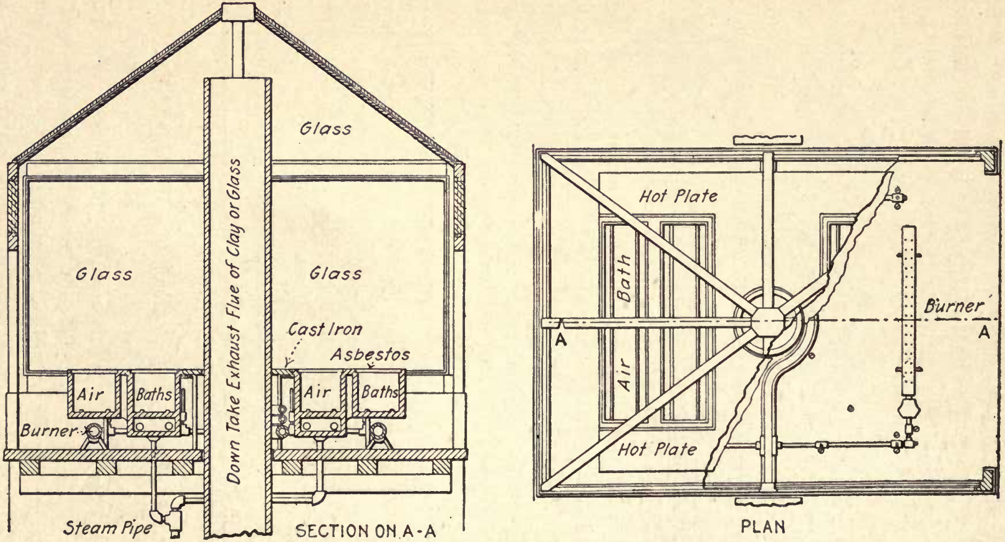


Fig. 2.—Details of Equipment of a Working Table.

The metallurgical chemist should ordinarily select, for any particular determination, the method by which he can obtain



SECTION ON A-A

PLAN

FIG. 3.—Details of Equipment of a Hood.

the most accurate result in the time allowed; but in cases where only approximations to a fair degree of accuracy are demanded, methods will be selected that are less expensive in time and materials; for the chemical department as well as the other departments of a metallurgical establishment should have regard for economy of labor and materials.

Equipment of the Laboratory. The laboratory should be designed and constructed for the special purposes for which it is to be used, and it is economy to consider the special fitness of an apparatus and the possible efficiency attainable by its use, as well as its initial cost.

Laboratories for schools and for general metallurgical analysis should have the working tables fitted for the ordinary chemical operations of solution, evaporation, filtration, and washing of precipitates, titration, etc. At each table there should be gas, water, compressed air, suction, a hood with air-bath and hot-plate.

The hoods should be conveniently placed and well ventilated. They are better made of glass and, if flues for an up-draft interfere with the light, the hoods should be provided with a down-draft with strong suction. Such hoods are easily kept clean, they do not obstruct the light, and in their use there is no danger of dust falling from the flue to spoil determinations.

A satisfactory arrangement of these details is shown in Figs. 1, 2 and 3.* In addition to the exhaust from the hoods, fresh filtered air should be supplied to the laboratory by a plenum fan. The room should be well lighted; for colorimetry, light from north windows is best.

There should also be sample grinders, drills for sampling metals, stirrers, shaking machines, centrifugal machines, and an electric current should be available for operating these machines,

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* See "The Equipment of a Laboratory for Metallurgical Chemistry in a Technical School." Trans. Am. Inst. of Mining Engineers, **35**, **117**.

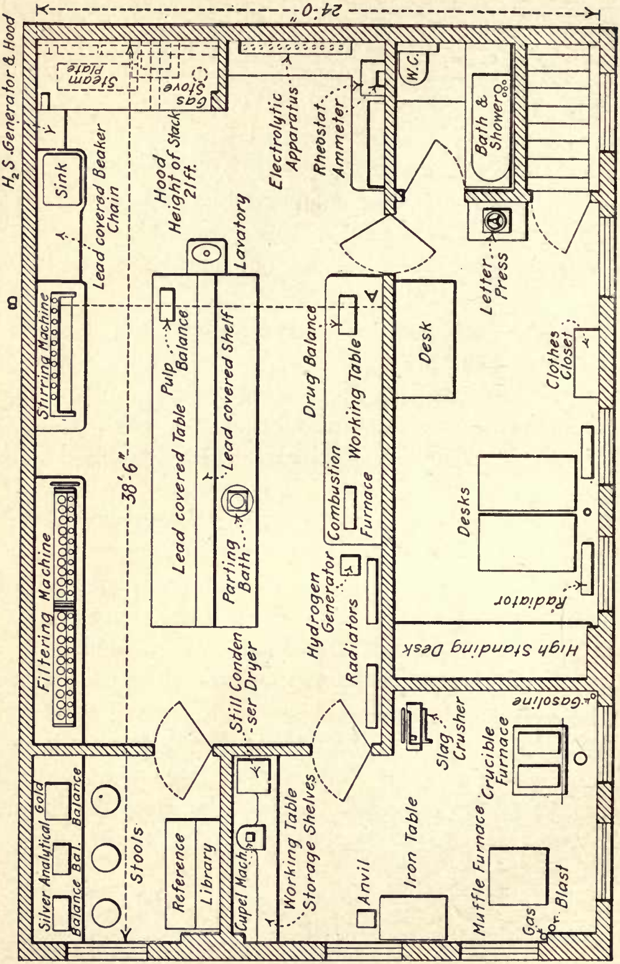

FIG. 4.—Plan of a Works Laboratory.

and for heating combustion furnaces and for electrolysis. There must also be provided the necessary balances, a still for pure water, calorimeters, colorimeters, and other special appliances that may be demanded.

The works-laboratory designed for much routine analysis may have tables or sections fitted with the necessary appliances and reagents for carrying out these special operations or determinations with the greatest facility. Figs. 4 and 5 are the plan and section of such a laboratory, described by Edward Keller.*

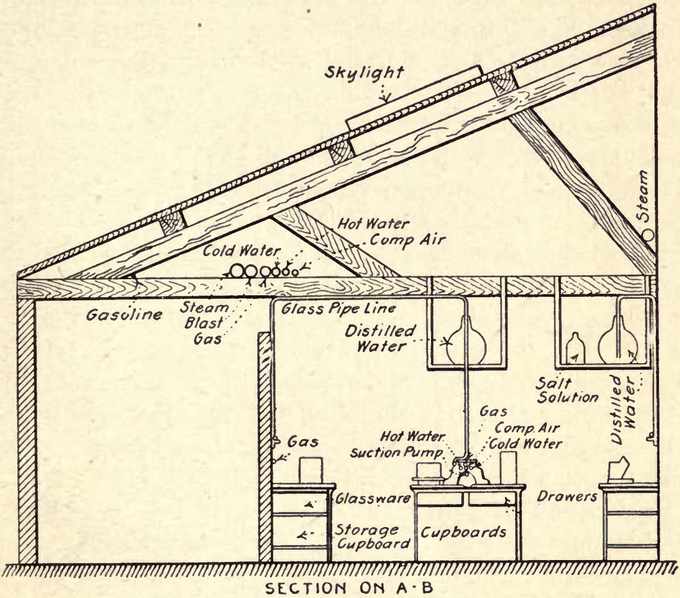

Fig. 5.—Section through the Laboratory Shown in Fig. 4.

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* Trans. Amer. Inst. Mining Engineers, **36**, 3

SAMPLING

Necessity of Correct Sampling. By chemical analysis it is only the small portion of material that is weighed, dissolved, and analyzed, whose composition is determined. If, however, the small portion analyzed has been taken from a larger quantity which is uniform throughout, then the portion analyzed was a true sample and the analysis indicates the composition of the whole. It follows that every determination to be of any value in metallurgy must consist of two distinct and equally important operations. They are sampling and chemical analysis.

The object in sampling is to separate from the whole body of the material whose composition is desired, a small quantity for analysis that shall have the same composition as the whole; for it is obvious, that if the sample is not representative, the most accurate chemical analysis cannot give the information desired, that is, the true composition of the material in question.

The sampling of ore, or mineral in place,* is not usually carried out by the chemist, but sampling for all other purposes for which metallurgical analyses are made is done by him, or under his direction, and should receive his careful consideration.

Classification of Materials. The method of sampling will depend upon the nature of the material to be sampled. For convenience in the study of sampling, metallurgical materials may be divided into the following classes:

1. Fluids (*a*) Liquids—water, oil, molten metals, slags, etc.
   (*b*) Gases—flue gas, producer gas, etc.
2. Tough or sectile materials—metals, alloys, etc.
3. Brittle or frangible materials—ores, fluxes, coal, brittle metals, alloys, etc.

General Principles of Sampling. It is practically impossible to take a theoretically perfect sample of ordinary metallurgical

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* Those interested in this subject will consult "The Sampling and Estimation of Ore in a Mine," T. A. Rickard.

materials, and the degree of perfection to be attained is usually determined by the value and uniformity of the material in question; the more uniform the material, the simpler and cheaper is the work of sampling; and the more uneven the mixture, the more difficult and expensive is the operation. For example, the smallest quantity of pure water that can be taken is a fair sample of the whole, while on the other hand it is practically impossible to take a satisfactory sample of a very "spotted" gold-ore.

To sample a *fluid* it is only necessary to mix it thoroughly and withdraw any convenient portion. The sampling of *metals* and alloys after solidification is not so easily effected as when molten on account of the segregation of impurities on cooling. It is therefore necessary to take drillings from such materials in a systematic way and mix them thoroughly before taking out the final sample. See page 197 for the sampling of blister copper.

The method of sampling *fragmental materials* like ore, coal, and limestone will be given under the analysis of each, and general principles only will be considered here. The first consideration is the quantity to be taken for the original sample. This will depend upon the value and uniformity of the material and the size of the largest particles. As has been said already, if the material is uniform in composition, only a small portion is required, and this is true regardless of the size of the lumps into which it is broken, but ores that break into lumps of great variation in size, are usually uneven in composition; that is, the large pieces are probably very different in composition from the fine. If such an ore is all crushed to a fine powder and thoroughly mixed, any small portion may be taken as a correct sample, but if it is not so crushed and mixed, the portion taken for the sample must be larger, and the quantity will depend upon the size of the largest particles of the material.

In problems of sampling there are so many unknown quantities, and these are subject to such great variation that a mathematical treatment of the subject does not yield results of a very practical nature.* The most reliable way to determine what size of sample should be taken from an unknown ore is to sample a large lot of it in duplicate. For example, if the ore is to be shoveled from one place to another, every fifth shovelful can be put alternately into two receptacles, so that when the ore is all transferred, each receptacle will contain duplicate samples, each a tenth of the ore. These samples are then properly prepared and assayed. If the assays from the two samples are not concordant, within the limits of error in assaying, the whole lot is sampled in duplicate again, every fourth or third shovelful being taken and put alternately into two receptacles as before, and the two again assayed. In this, or in a similar way, by hand or by mechanical sampler, the smallest lot that may be taken for a sample of each of various grades of ores has been determined in many mining districts. These results have been brought together and tabulated in convenient form by Prof. R. H. Richards.† In his table which is here reproduced, it will be observed that in the left-hand column is given the quantity of ore that must be taken in order to obtain a fair sample of the several grades of ore, described at the top of succeeding columns, when the largest particles have the diameters given in these columns.

For example, the sample of rich ore (column 5), whose coarsest particles measure 5 mm. in diameter, must contain 500 lbs., but that quantity will be sufficient for a sample of low-grade or uniform ore (column 2) which has its coarsest lumps as large as 18 mm. Also the sample of a rich ore whose largest particle

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* E. D. Peters, "Practice of Copper Smelting," 8. "Ore Sampling," S. A. Reed, School of Mines Quarterly **3**, 253, also **6**, 351. "The Theory and Practice of Ore-sampling," D. W. Brunton, Trans. Amer. Inst. Mining Engineers, **25**, 826. "Principles of Ore-sampling," A. Van Zwaluwenburg, Mines and Methods, Oct., 1909.

† "Ore Dressing," **2**, 852.

Weight to be Taken as Sample.		Diameter of the Largest Particle.					
Grams.	Pounds.	Very Low-grade or very Uniform Ores. 1	Low-grade or Uniform Ores. 2	Medium Ores. 3	Medium Ores. 4	Rich or "Spotted" Ores. 5	Very Rich or Excessively "Spotted" Ores. 6
		mm.	mm.	mm.	mm.	mm.	mm.
.....	20,000	207	114	76.2	50.8	31.6	5.4
.....	10,000	147	80.3	53.9	35.9	22.4	3.8
.....	5,000	104	56.8	38.1	25.4	15.8	2.7
.....	2,000	65.6	35.9	24.1	16.1	10.0	1.7
.....	1,000	46.4	25.4	17.0	11.4	7.1	1.2
.....	500	32.8	18.0	12.0	8.0	5.0	0.85
.....	200	20.7	11.4	7.6	5.1	3.2	0.54
.....	100	14.7	8.0	5.4	3.6	2.2	0.38
.....	50	10.4	5.7	3.8	2.5	1.6	0.27
.....	20	6.6	3.6	2.4	1.6	1.0	0.17
.....	10	4.6	2.5	1.7	1.1	0.71	0.12
.....	5	3.3	1.8	1.2	0.80	0.50	
.....	2	2.1	1.1	0.76	0.51	0.32	
.....	1	1.5	0.80	0.54	0.36	0.22	
.....	0.5	1.0	0.57	0.38	0.25	0.16	
90	0.2	0.66	0.36	0.24	0.16	0.10	
45	0.1	0.46	0.25	0.17	0.11		
22.5	0.05	0.33	0.18	0.12			
9	0.02	0.21	0.11				
4.5	0.01	0.15					
2.25	0.005	0.10					

measures 1 mm. in diameter must contain 20 lbs., while that of a very low-grade ore of the same size particle, would have to contain only 0.5 lb. This table shows not only how much should be taken for the original sample, but also how much must be taken from the original sample after it has been crushed finer and mixed, so that the portion taken will still be a representative portion of the whole.

After the sample has been taken either by hand or by a mechanical sampler (Fig. 6), it is successively crushed and

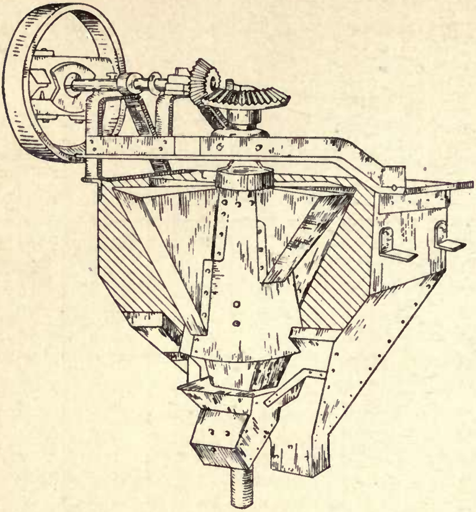

FIG. 6.—Vezin Sampler. This sampler cuts out at regular intervals a section across the stream of crushed ore and is set to take a definite fraction of the ore that passes through it.

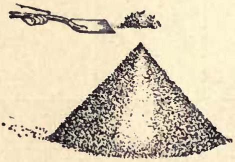

FIG. 7.

FIG. 8.

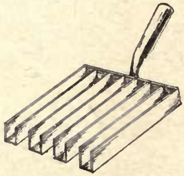

FIG. 9.

FIG. 7.—The Sample is Shoveled into a Conical Heap on the Sampling Floor. Each shovelful is dropped directly on the apex of the cone so that the ore will roll down evenly on all sides of the cone.

FIG. 8.—The Cone is Flattened by Drawing the Ore from the Center Outward with the Shovel as the Sampler Walks around the Cone. The cone is then quartered and opposite quarters are discarded.

FIG. 9.—Split Shovel for Dividing the Sample.

mixed and reduced in size—in accordance with the table—by coning and quartering (Fig. 7, 8), by the split shovel (Fig. 9),

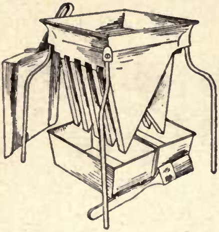

FIG. 10.—Riffle for Dividing a Crushed Sample into Halves.

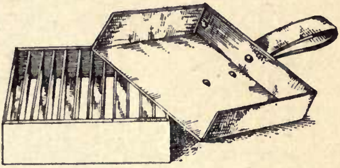

FIG. 11.—Riffle to be Placed on a Rubber Cloth when Used.

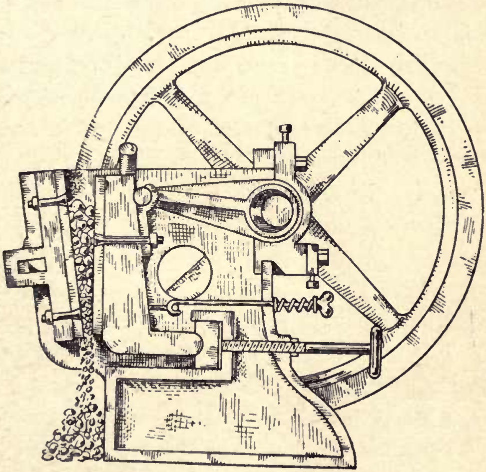

FIG. 12.—Crusher. Sectional View.

or by riffles (Fig. 10, 11), until the quantity has been reduced to a few ounces (Fig. 12, 13, 13*a*, 14), all of which will pass through a hundred-mesh sieve; and with certain ores—iron

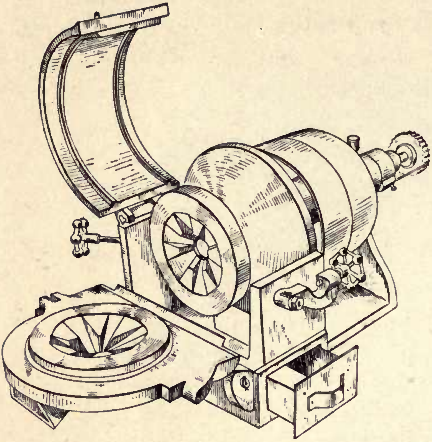

Fig. 13.—Pulverizer.

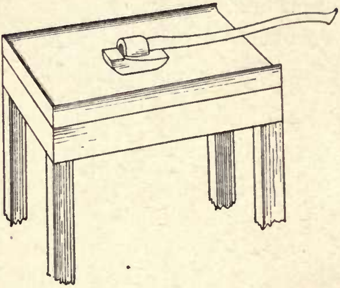

Fig. 13*a*.—Bucking Plate and Muller for Fine Grinding by Hand.

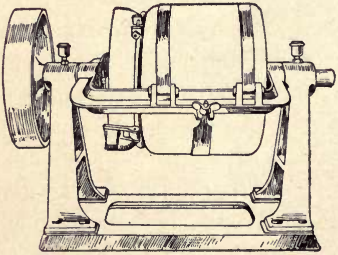

Fig. 14.—Ball Mill for Soft Ore, Coal, etc.

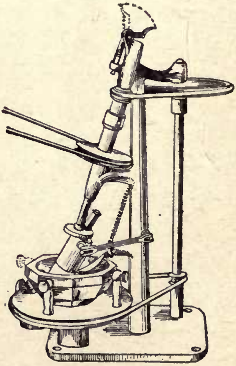

Fig. 15.—Mechanical Grinder with Agate Mortar and Pestle.

ores for instance—much time may be saved in dissolving the ore if it is ground still finer in an agate mortar. Good mechanical grinders (Fig. 15) may now be obtained that require little attention and therefore save much time and labor.

THE OPERATIONS OF ANALYSIS

Gravimetric

Weighing. The next step, after the preparation of the sample, is weighing the small portion that is to be analyzed. The quality of balance used and the care taken in weighing, as in sampling, will depend upon the values involved. With a good balance, weighing, if due care is exercised, can be made far more accurate than the other operations in chemical analysis. While a high degree of accuracy in the final result should always be kept in mind, it is unnecessary to make a great outlay to secure the highest degree of accuracy in one step of an operation when it cannot be approached in the other necessary steps.

Care and Use of the Balance. The balance should be set up level on a support free from vibration in a room of uniform temperature. It must be kept free from dust, and if, in making a weighing, anything is spilled in the case, it should be brushed out after the weighing is finished. The door of the case should always be kept closed, except when the balance is being used. The same scale of the balance should always be used for the weights, preferably the one on the right-hand side, and the one on the left is reserved for substances to be weighed. This will prevent the introduction of error, in case the arms of the balance are not of exactly equal length. Only individual objects of metal or glass should be placed directly on the metal pans of the balance; finely divided materials such as ore, dry reagents, etc., should be weighed on a watch glass, or on a platinum pan made for the purpose.

Watch glasses of approximately equal weight can be bought in pairs for use on the balance. Materials which give up moisture or gas, or absorb moisture readily, should be weighed in weighing bottles. (Fig. 16.) The small bottle containing a few grams of the material is closed with a glass stopper and weighed, a portion of the substance on which the determination is to be made is then transferred from the bottle to the beaker, or other receptacle in which the analysis is to begin, and the bottle with its remaining contents again weighed. The difference between the two weights represents the quantity taken out.


Fig. 16.—Weighing Bottle.

The Weights. The weights should be tested occasionally to see that they bear correct relations to one another. If appreciable errors are found, the weights should be returned to the instrument maker for correction, or they may be standardized by the chemist and the necessary corrections made for each weighing.

To test the weights, place upon one of the scales of a delicate balance which has arms of equal length the 1-gm. weight taken for the standard, and counterpoise it with small pieces of metal placed on the other scale. When the 1-gm. weight is thus counterpoised, transfer it to the scale with the counterbalancing metal and test the two 2-gm. weights in the other pan, one after the other. In a similar manner, test the 5-gm. weight, and the others, up to the largest, by counterpoising them with the required tested weights of lower denominations. Test the fractional weights collectively by counterpoising them with the standard gram; the inequality should not exceed 0.2 mgm. In comparing the smaller weights with one another, they should not show a difference as large as 0.1 mgm.

The Operation of Weighing. First, see that the balance and watch glasses are clean. Find the zero-point with the balance empty, as follows: let the beam down on the knife edges, release the pans, raise the door of the case an inch or so, and, with a gentle downward movement of the hand in front of the right pan of the balance, set the air in motion sufficiently to cause the balance to swing. Close the door of the balance and take the reading on the graduated scale of two consecutive swings of the pointer on one side, and the intervening swing on the other. The zero-point, or the point at which the balance, if left free to oscillate, would come to rest, is indicated by the mean of those readings. For instance, if it should swing to the right of the middle point of the scale to 6.8 and then to the left of the middle point to 4.4 and then again to the right to 6.4, we proceed thus: the mean of the readings on the right is 6.6, then the zero-point (Fig. 17) will be the point on the scale midway between 6.6 on the right and 4.4 on the left of the center of the scale, or $6.6-4.4=2.2$; $2.2\div 2=1.1$; that is, 1.1 divisions to the right of the center of the scale is the zero-point.

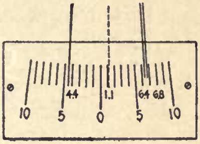

FIG. 17.—Graduated Scale of Balance Showing Method of Finding the Zero Point.

After the zero-point has been determined, arrest the pans and lift the beam from the knife edges. Place the object to be weighed on the left pan of the balance and the largest weight that is judged to be necessary to counterbalance it on the right pan. Then gently lower the beam and release the pans. If the weight tried is found to be too light, arrest the pans, lift the beam, remove the weight and try the next heavier weight. Continue in this way until the largest single weight is found that is lighter than the object being weighed; then complete the weighing by trying the lighter weights, one by one, in consecutive order down to the smallest, and finally finish with the rider with the balance door closed. The weighing is complete when the rider is so placed that the readings of the needle to the right and to the left indicate the same zero-point as when the balance is empty. Five readings may be taken instead of three, that is, three on one side and two on the other. When the rider is finally adjusted so that the oscillations indicate the original zero-point, note the vacancies in the weight-box and the position of the rider and record the weight in the weight-book opposite the name of the object weighed, in grams to the fourth decimal place. Then after arresting the pans and lifting the beam, return each weight to its proper place in the box, checking at the same time the recorded figures to make sure that they are correct.

Precautions in Weighing. The pans should always be arrested before changing the position of the rider or before changing any weight on either pan. They should be arrested when near the middle of the swing, and always before lifting the beam. The beam should be lifted before changing a weight greater than 0.5 gm. The weights should be transferred with the pincette and it should be used for nothing else. The door of the balance should always be closed when taking final readings to prevent the interference of air drafts.

Weighing for Analysis. In weighing finely divided materials such as ore, limestone, steel drillings, and the like, it is best to take a definite portion, as 1 gm., 0.5 gm., or a factor weight (see p. 32 for factor weights). In that case, the weight representing the quantity desired is placed in the watch glass on the right scale of the balance and counterbalanced by adding the material to be weighed by means of a spatula to the other scale. This method is simple and rapid; it simplifies the keeping of records and the calculation of results. For weighing steel drillings, a pointed, magnetized, steel wire, three or four inches long (Fig. 18), is useful in transferring small particles of steel to or from the balance to complete the weighing.

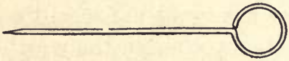
FIG. 18.—Magnetized Wire for Transferring Steel Drillings.

Dissolving. After the sample has been weighed, it is dissolved in order that the element or ion may be freed and subsequently converted into a form in which its quantity may be conveniently measured. Most metallurgical materials are soluble in acids, and those that are not may be converted into soluble form by fusing them with suitable fluxes. After weighing the sample it should be transferred, with the aid of a small camel's hair brush, from the watch glass directly to the beaker, casserole, flask, crucible, or other receptacle in which the analysis is to begin. When the acid or other solvent is added, if solution does not take place without heat, the beaker should be placed on the hot-plate or over a low burner under the hood. The quantity of the solvent to be added is usually given in the method. The solvent is measured approximately in a graduated cylinder (Fig. 19) and if its volume is considerably reduced by evaporation before the sample is dissolved, more of the solvent should be added. A hot-plate with the heat applied under the center is convenient; for, by moving the determination towards the center or away from it, any desired degree of heat may be found.

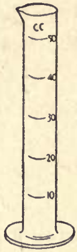

Fig. 19. — Graduated Cylinder.

Reagents. All reagents should be tested as to their purity, especially for the quantities of those impurities which would interfere with the action of the reagent, or would in any way introduce error into the result.*

The quantity of a reagent used in a determination is measured accurately only when the reagent serves as a measure, either directly or indirectly, of the element sought. In other cases when only an excess of the reagent is desired to insure the completion of a reaction, the quantity used may be measured only approximately.

In the description of the methods as given in this book, it is assumed that the following reagents are at hand: distilled water; hydrochloric acid, specific gravity 1.20; nitric acid, specific

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* "The Testing of Chemical Reagents," Van Nostrand & Co.

gravity 1.42; sulphuric acid, specific gravity 1.84; and ammonia, specific gravity 0.90. Where these reagents are mentioned without qualification, the above concentrations are meant. If other concentrations are desired, the strength is indicated either by specific gravity, or in the ratio by volume of the concentrated reagent to water. By the latter method the ratio is indicated by a colon (:), which stands between the two volumes, the volume after the colon always referring to water.

Tables on pages 332 to 334 show how to make the acids to any desired density by giving directly the volume of the concentrated acid and the volume of water necessary for each concentration.

Precipitation. It should be kept in mind that electrolytes are the more completely ionized the more dilute the solution, and that precipitates come down cleaner from a dilute solution, that is, freer from substances adsorbed from the solution.* It should also be remembered that no substance is absolutely insoluble in aqueous solution; and necessarily the larger the volume of solution, the greater quantity of the precipitate will be required for its saturation. If the solubility of the precipitate is not so small as to be negible, precautions must be taken to reduce the solubility to a minimum. This may be done by adding a liquid in which the precipitate is less soluble than in the original solution, or, in the case of an electrolyte, by adding an excess of the precipitant, or of a soluble salt containing one of the ions of the precipitate. For instance, if we wish to precipitate SO_4 from solution as $BaSO_4$, we add an excess of $BaCl_2$. The solution is saturated with Ba ions from the $BaCl_2$, which reduces to a minimum the solution and dissociation of $BaSO_4$.†

Precipitates are more easily filtered and washed if they are granular or crystalline. They should, therefore, be left in the mother liquor at a moderate temperature—but not boiling—as long as circumstances permit. By this treatment the fine

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* Ostwald: "Foundations of Analytical Chemistry," p. 18.

† Ibid., p. 73.

crystals are dissolved and redeposited upon the coarse ones. This enlargement of the crystals, as explained by Ostwald, is due to surface tension on the boundary surfaces between solids and liquids, which tends to reduce the surface, thereby enlarging the individual grains.*

Filtration. The filters used should have been washed with hydrochloric and hydrofluroic acids, and, if for gravimetric work, the average weight of ash should have been determined. Very finely divided precipitates like $BaSO_4$ will often run through ordinary filter paper. If a paper is selected whose pores are smaller than the particles of precipitate, the trouble of refiltration may be avoided. The size of the filter selected should be determined by the bulk of the precipitate, rather than by the volume of the solution to be filtered, and the paper should be folded to fit the funnel snugly. The clear supernatant solution should be decanted first and allowed to run down a glass rod into the filter while the precipitate remains undisturbed in the bottom of the beaker. (Fig. 20.) The clear solution runs through readily, after which the precipitate may be washed by decantation or transferred to the filter and washed on the filter. The filter paper should not be filled with solution nearer to the top than 5 mm. If the precipitate sticks to the beaker, it may be rubbed loose with a "policeman" (Fig. 21; a bit of small rubber tubing on the end of a

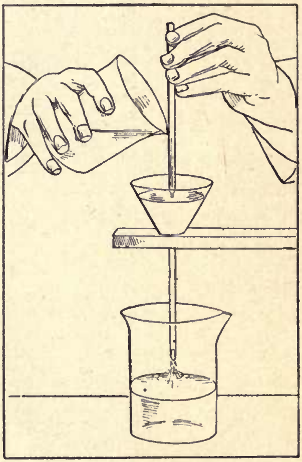

Fig. 20.—Filtering.

Fig. 21.—"Policeman."

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* Ostwald: "Foundations of Analytical Chemistry," p. 22.

glass rod) and then washed into the filter by inclining the beaker at a high angle, with a glass rod held with the left hand across the top of the beaker and resting in its lip, so that when a jet of water is directed up into the beaker with the right hand, it will flow back down the sides, carrying the precipitate with it to the lip and down the glass rod directly into the filter. In this way the last traces of precipitate are transferred to the filter. (Fig. 22.)

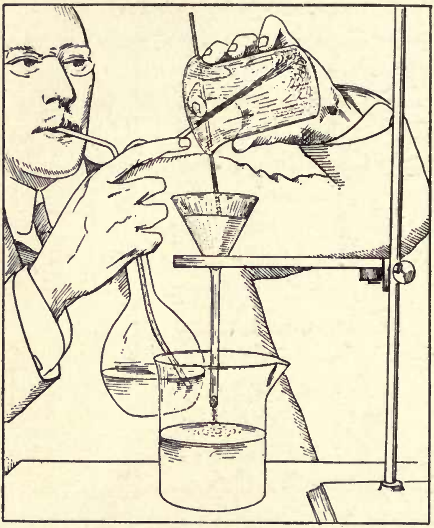

FIG. 22.—Completing the Transfer of a Precipitate to the Filter.

If filtering is to be done by gravity, the funnels should have long stems, which are kept full of solution while filtering. In laboratories where routine work is done and the same determination must be made on many samples, much time is saved by the use of multiple stirring and filtering devices such as are described by Keller and shown in Figs. 23 and 24.*

Metallurgical laboratories should be provided with apparatus for filtering by suction. Since compressed air is also needed,

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* Trans. Amer. Inst. Min. Eng., 36, 3.

it is convenient to have a pump which exhausts the air on one side of the piston and compresses it on the other, suitable equalizing tanks being provided for the compressed air and for partial vacuum. Before entering the pump the air should pass through a scrubber containing a solution of sodium hydroxide for the removal of acid fumes. In small laboratories, the Richards pump may be used for this purpose (Fig. 25), and, in connection with a Woulf bottle, the air may be compressed for a blast lamp. The stem of the funnel is put through a rubber stopper into a filter-flask which is connected with the exhaust. A perforated platinum cone (Fig. 26) should be put in the funnel under the filter to support it when the suction is turned on. To save the trouble of transferring the filtrate from the filter-flask to a beaker, by the use of a bell-jar, the filtrate may be delivered to the beaker directly. The stem of a funnel is introduced through a rubber stopper in the top of the bell-jar, under which is placed the beaker to receive the filtrate. The bell-jar

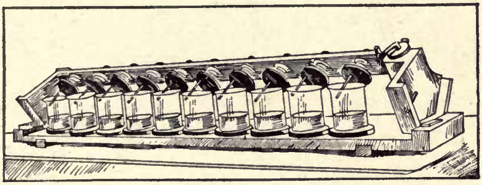

FIG. 23.—Stirring Machine in Position for Rinsing.

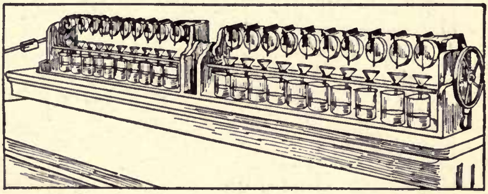

FIG. 24.—Decanting and Filtering Apparatus. Position at End of Filtration.

(Fig. 27) rests on a smooth plate and the joint between them is sealed with vaseline or grease. If the bell-jar has no side tubulure, the air may be exhausted from a tube introduced through the stopper.

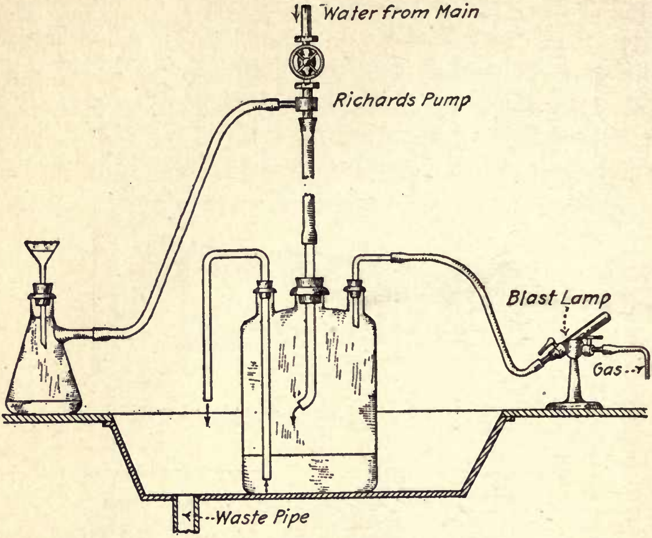

Fig. 25.—Richards Pump and Woulf Bottle Combined to Obtain Both Blast and Suction.

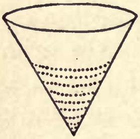

Fig. 26.—Perforated Platinum Cone.

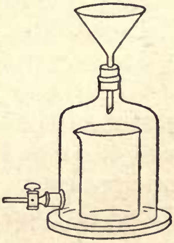

Fig. 27.—Bell Jar Arranged for Filtering by Suction Directly into a Beaker.

Use of the Gooch Crucible. Precipitates which require only drying or heating to moderate temperatures before weighing may be filtered in a Gooch crucible (Fig. 28), dried, and weighed directly. The Gooch crucible is attached to a carbon filter with a short, soft rubber tube (Fig. 29), and may be connected with suction if desired. An asbestos felt is made in the crucible, either by shaking up asbestos in distilled water and pouring into the crucible until the felt is of the desired thickness, or the asbestos fibers may be put in dry and pressed down with a glass rod. The felt is then washed with water to carry away small fibers that will pass through the perforations of the crucible. The crucible with felt is then dried for an hour in an air bath at a little above 100° C., cooled in a desiccator and weighed. It is again attached to the carbon filter, and when the filtration and washing are completed, it is dried, cooled, and weighed as before. When filtering in a Gooch crucible, very strong suction should not be applied, since it causes the asbestos felt to pack, which greatly retards the speed of filtering.

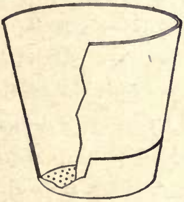
FIG. 28.—Gooch Crucible.

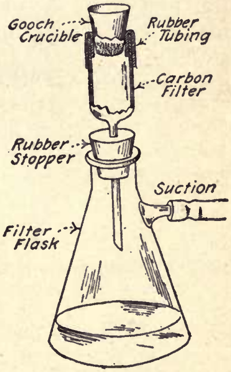

FIG. 29.—Gooch Crucible Attached to Filter Flask for Filtering by Suction.

Washing of Precipitates. Precipitates that settle readily are best washed by decantation. Let the precipitate settle, carefully decant the clear solution through the filter, leaving the precipitate in the beaker, add wash water, digest over the heat as long as desired and again decant. Repeat this treatment as often as necessary and finally transfer the precipitate to the filter. After the precipitate has been transferred to the filter, it should be washed by directing the jet of wash water down against the inside of the funnel, a little above the filter paper, carrying the jet around just above the edge of the filter and then down spirally into the filter. The wash bottle may be used, but it is simpler and more agreeable, where much work is done, to wash from a tank by gravity. This is effected by placing a tank for distilled water, which is provided with heat by gas or electricity, about three feet above the working table, from which, with a suitable rubber tube, the water is conducted to the funnels. This tube (Fig. 30) is provided at the lower end with a wash-bottle nozzle and a spring clamp for shutting off the water. By opening the clamp and directing the nozzle with the same hand the washing proceeds rapidly from one funnel to the next. The rubber tube should be long enough to permit the operator to carry the nozzle from one end of the line of funnels to the other.

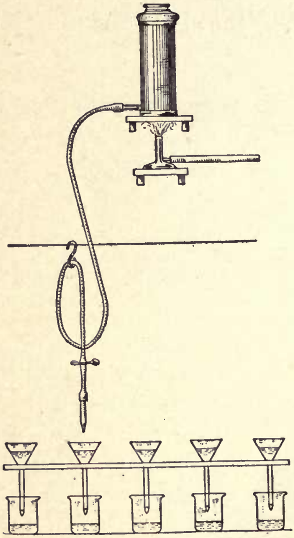

Fig. 30.—An Elevated Tin-lined Copper Tank in which Distilled Water is Heated for Washing Precipitates by Gravity.

The washing of precipitates would be a comparatively simple matter if the contaminating substances would freely leave the surface of the precipitate and diffuse evenly throughout the wash water. In this case four or five washings would ordinarily be sufficient, but, as explained by Ostwald, owing to adsorption, that is, the greater concentration of dissolved substances at the surface of the precipitated particles, the number of washings must be greatly increased, and the washing should be continued until it is found by testing the wash water as it comes through, that it no longer contains the contaminating substances. In some cases twenty or thirty washes are required. Richards considers the difficulty of freeing precipitates of contamination by washing, due to occlusion, or the enclosing of solutes in the precipitate as it is formed.

Burning Precipitates. When the washing is complete, if the precipitate is one that is to be burnt and weighed, and can be burnt in contact with the paper without danger of reduction, it can be put in the crucible and burnt without previous drying, if the heat is applied carefully at the beginning. If, on the other hand, the precipitate is a compound of lead, tin, or other metal easily reduced when in contact with hot carbon, the precipitate must be dried and transferred from the paper to the crucible (Fig. 31), where it is burnt out of contact with the paper. The paper is then held over the crucible on a platinum wire and burnt in a Bunsen flame, the ash being allowed to fall into the crucible.

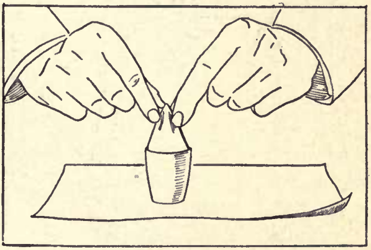

FIG. 31.—Transferring a Dried Precipitate from the Filter Paper to a Platinum Crucible.

When a wet precipitate is transferred from the funnel to the crucible to be burnt at once, the cover should be put on the crucible and kept there until all volatile matter has been driven out. Great care should be taken that the heat is increased so gradually that the precipitate is not thrown out by the escaping steam. When all volatile matter has been driven off, the cover is removed from the crucible and the temperature raised to oxidize the carbon of the filter, after which the cover is replaced and the heat of the blast-lamp applied if necessary. In burning a filter, it should be remembered that oxygen is needed as well as heat; the flame, therefore, should not envelop the crucible. but the crucible should be inclined and partially uncovered (Fig. 32), with the Bunsen flame applied only near the bottom. The cover should be so adjusted that the hot gases from the crucible can escape upward while fresh air is drawn in on each side of the cover. The carbon should be burned off at as low a temperature as possible to avoid reduction of the precipitate.

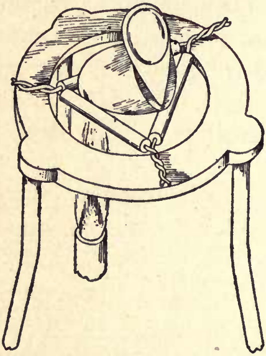

FIG. 32.—Arrangement of Crucible and Cover for Burning a Precipitate.

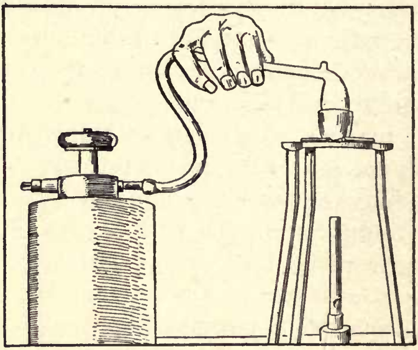

FIG. 33.—Method of Using Oxygen in Burning a Precipitate.

When rapid work is necessary, time may be saved by burning precipitates in oxygen. The oxygen may be introduced into the crucible through a clean clay tobacco-pipe (Fig. 33). Before the pipe is lowered into the crucible, the flow of oxygen must be so regulated that it will not blow the precipitate away.

The Care of Platinum. Platinum is attacked by chlorine, and, therefore, by any combination of substances that yields chlorine, as aqua regia, etc.; by mixtures of hydrobromic and nitric acids; by hydriodic acid slowly; and by boiling ferric chloride solution. Mercury will adhere to platinum, forming a plate on the surface, but it may be driven off by heat.

At high temperatures, platinum is attacked by the hydrates, nitrates, and cyanides of the alkalies and the alkaline earths; by a mixture of sulphur or sulphides with alkaline salts; by phosphorus and arsenic, and the metals that form alloys with platinum, such as lead, tin, antimony, gold, etc. Substances that contain these elements in easily reducible form should not be heated in contact with platinum.

When charcoal is burned in contact with platinum, silicon is reduced from the charcoal and combines with the platinum, making it brittle.

The reducing flame gives to platinum a dull gray appearance, and repeated heating and cooling promotes the growth of crystals which increase in size until they give the surface of the metal a spotted appearance. To prevent the growth of such crystals and the final cracking of the platinum, rub with sea-sand held on the moistened finger until the surface of the metal is bright.

To Clean Platinum. If it is known what substance produces the stain or discoloration on the platinum, use the best solvent known for that substance, which at the same time will not attack the platinum. For obstinate cases, fuse a little sodium carbonate on the stain, cool, and dissolve by boiling with hydrochloric acid, and then rub the platinum bright with sea-sand. A sand-soap may be used, but the sharp sand of the soap wears the platinum away faster than the round grains of sea-sand. Hold the sand on the moistened finger or on a damp cloth when rubbing the platinum. Do not rub the platinum against a solid lump of sand-soap.

The Desiccator. When the precipitate has been sufficiently heated in the crucible to bring it to the definite form in which it is to be weighed, the crucible is placed in a desiccator (Fig. 34) while it is still hot, but not glowing, to be left to cool before it is weighed. The desiccator may contain any good absorbent of moisture. Either concentrated sulphuric acid or calcium chloride serves the purpose well, and the desiccator should be occasionally replenished with a fresh supply of the desiccating agent to maintain its efficiency. If sulphuric acid is the dryer used in the desiccator, glass beads should be put in with the acid to prevent its flowing too easily and being thrown against the crucible when the desiccator is handled. The contact between the desiccator and its cover should be made air-tight by applying occasionally a mixture of vaseline and paraffine.

Fig. 34.—Desiccator.

Objects weighed when warm, weigh less than when cold, owing to upward currents produced in the air about them, which buoy them up; and the rate at which moisture is deposited upon them from the air depends upon the temperature; therefore, they should always be cooled in a desiccator and weighed at room temperature, or all weighings made at as nearly the same temperature as possible.

Weighing Precipitates. After the crucible has cooled in the desiccator, usually from fifteen to twenty minutes, it is carefully taken from the desiccator with a pair of clean forceps or tongs and placed upon the balance for weighing. Care should be taken not to touch the crucible with the hands until the final weighing has been made. Weigh as quickly as possible and record the weight in the weight-book. Return the crucible with its contents to the desiccator with the forceps, carry it back to the working table and heat it again for ten minutes, cool and weigh again as before, and if the weight does not agree with the former weight, repeat this treatment until the weight is constant. If a very large crucible or other large object is weighed it should be counterbalanced by a similar object on the other balance pan to neutralize the effect of deposition of moisture from the atmosphere.

Calculating Results. The results of analyses are usually expressed in parts per hundred, or per cent. If the precipitate finally weighed is in the form in which it is to be reported, it is only necessary to divide its weight by the weight of the sample taken for analysis and multiply the result by 100. For example, if the CaO from 0.5 gm. of limestone weighs 0.1931 gm., to find the percentage of lime in the limestone, the question may be simply stated thus:

If in 0.5 gm. of limestone there are 0.1931 gm. of lime, in 100 parts of limestone there are how many parts of lime?

$$0.5 : 0.1931 = 100 : x$$

$$x = \frac{0.1931 \times 100}{0.5} = 38.62.$$

It is evident in cases of this kind that the calculation is simplified by taking a definite weight of the sample that is simply expressed, as 1 gm., 0.5 gm., or 0.2 gm., because that number must be used as divisor.

When the precipitate weighed is not in the form in which it is to be reported, the quantity in the desired form must be calculated from the weight of the precipitate. For example, if the precipitate of $BaSO_4$ from 5 grams of steel weighs 0.0232 gm., what is the percentage of S in the steel? We first find the weight of S in 0.0232 gm. $BaSO_4$, and with that weight proceed as in the last example. To find the weight of S in 0.0232 gm. of $BaSO_4$, we multiply by the factor for S in $BaSO_4$. The factor is the number which expresses the weight of S in one part of $BaSO_4$, and is obtained as follows:

The molecular weight of $BaSO_4$ is 233.44, being composed of

1 atom of Ba, atomic weight		137.37
1 atom of S, atomic weight		32.07
4 atoms of O, atomic weight	16 =	64.
		233.44

Then, if in 233.44 parts of $BaSO_4$, there are 32.07 parts of S, there is in one part of $BaSO_4$ $\frac{32.07}{233.44} = 0.13738$ part of S.

The factor, then, for S in $BaSO_4$ being determined once for all as 0.13738, we proceed as follows: if one part (or gram) of $BaSO_4$ has 0.13738 part (or gram) of S, 0.0232 gm. of $BaSO_4$ will contain $0.0232 \times 0.13738 = 0.003187$ gm. of S. Then, proceeding as in the first example above, we find the percentage of S as follows:

$$\frac{0.003187 \times 100}{5} = 0.0647.$$

The whole operation may be expressed in one equation:

$$\frac{0.0232 \times 0.13738 \times 100}{5} = 0.0647.$$

Factor Weights. In the above example, if we had weighed not 5 gms. of steel, but 0.13738 gm., or better, 0.1374 gm., this latter number would become the denominator in the above equation and the solution would be simplified, for the denominator would then be the same as the factor for S in the numerator and the two would cancel. We would then only have to multiply the weight of $BaSO_4$ by 100, or move the decimal point two places to the right. A weight of this kind is called a factor weight and is used to simplify the calculation of the result. In the case above, the weight 0.1374 gm. is too small a quantity of steel for the sample, for the yield of $BaSO_4$ from that quantity of this steel (0.000637 gm.) is so small that errors in manipulation would be greatly magnified; a simple multiple as 20 or 50 times this factor weight, can be used and still the calculation remain extremely simple. Such factor weights are much used in routine gravimetric work in which the form weighed must be converted by calculation into another form before the percentage is estimated.

VOLUMETRIC ANALYSIS *

Volumetric Apparatus. Volumetric analysis demands the use of graduated flasks, pipettes, and burettes. The chemist should test such apparatus to see if it is correctly graduated, and, if it is not, he should determine the errors and make the necessary corrections. This is done by weighing the distilled water contained by the apparatus, at the temperature at which it was graduated—usually marked on the apparatus—or by comparing the volume contained with that which is held by similar specially standardized apparatus sold by dealers.

Measuring flasks (Fig. 35) are usually graduated *to hold* the quantity indicated at the temperature marked on the flask, but some flasks have a second graduation higher up on the stem to which they should be filled *to deliver* the indicated quantity. Pipettes (Fig. 36) and burettes (Figs. 37, 38) deliver the quantities indicated, and should be given half a minute to drain.

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* Titration methods and colorimetric methods are, strictly speaking, not volumetric methods in the sense that gas analysis is; for in the former we must still use the balance for weighing the sample and for standardizing the solutions, but the determination of the weight of the substance sought is accomplished through volumetric operations.

The point of the pipette should touch the side of the receiving vessel to deliver the last drop; do not blow out the last drop.

To fill a pipette, place the upper end in the mouth and draw the solution in until the meniscus stands somewhat above the graduation of the pipette. Withdraw the pipette from the mouth and quickly place the index finger of the right hand over the upper end to hold the solution in the pipette. Then turn the pipette with the left hand, admitting the air slowly until the meniscus falls to the graduation. Press firmly again with the index finger to prevent further admission of air until the pipette is brought in position to be discharged. Poisonous liquids and those giving off unpleasant gases should be drawn into the pipette by attaching the upper end of the pipette with a rubber tube to

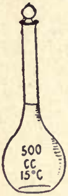

Fig. 35.

Fig. 36.

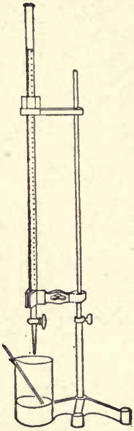

Fig. 37.

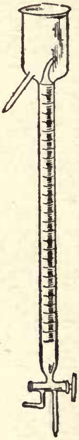

Fig. 38.

Fig. 35.—Graduated Flask. Fig. 36.—Pipette. Fig. 37.—Burette.
Fig. 38.—Burette that Fills to Zero Automatically with Overflow Cup and Side Tube for Filling from Reservoir.

the exhaust tap on the work table. The suction can be controlled by operating the tap or by pressure on the rubber tube.

For the accurate reading of the burette, some chemists prefer a burette float, but for regular routine work it is sufficiently accurate to read the bottom of the meniscus, especially if a strip of white paper be held just back of the burette. To read the burette when it contains very dark-colored solutions, such as potassium permanganate solution, it is necessary to hold a light just behind the burette to render the meniscus visible. A light may be supplied by a simple jet attached with a rubber tube to the gas tap on the table.

Cleaning Solution. All apparatus must be kept scrupulously clean. This applies especially to volumetric apparatus, which must be free from grease and all other foreign matter so that solutions will flow out evenly and not leave drops adhering to the sides. An excellent cleaning solution is made by adding 10 gms. of potassium dichromate to a liter of commercial sulphuric acid. After using the cleaning solution it should not be thrown away, but returned to the bottle for future use. The apparatus to be cleaned should be left full of the cleaning solution for several hours, and thoroughly washed with distilled water after the cleaning solution has been returned to its bottle.

Titration. Instead of precipitating, filtering out, and weighing a substance, it is better in many cases to measure it while in solution by the method of titration. For carrying out the process of titration it is necessary to prepare a solution of a reagent which will react in a definite way with the substance to be determined. This solution must have a certain determined strength and is called a *standard solution*. It is also necessary to provide means for determining when the reaction is complete. A reagent used for this purpose is called an *indicator*. To make an analysis by titration, then, we put the sample in solution in such form that the ion sought will react in a definite way with the standard solution. The standard solution is run in from a burette until the indicator shows that the reaction is complete; by noting the volume of the standard solution that has been used, and knowing its value per cubic centimeter in the substance being determined, it is easy to calculate the amount of that substance present.

Standard Solutions. Standard solutions are made to contain a definite amount of the active agent in every cubic centimeter. Two kinds of standard solutions are in general use—normal solutions, and empirical standard solutions.

Normal Solutions. A normal solution is a standard solution which has in a liter that quantity of reagent which contains 1.008 gms. (the atomic weight) of replaceable hydrogen, or the equivalent of that amount of hydrogen in some other active agent, as 35.46 gms. chlorine or 8.0 gms. of oxygen. A normal solution of hydrochloric acid will, therefore, contain 36.468 gms, of HCl per liter, and such a solution of sulphuric acid, 49.043 gms. H_2SO_4 per liter. A normal solution of potassium permanganate should contain 31.606 gms. of the salt per liter, since the weight of $K_2Mn_2O_8$ which contains, in available oxygen, the equivalent of 1.008 gms. hydrogen is $\frac{316.06}{2\times5}=31.606$ gms. (In $K_2Mn_2O_8$ there are 5 atoms of available oxygen. $K_2Mn_2O_8=K_2O+2MnO+5O$.) In like manner a normal solution of $K_2Cr_2O_7$ will contain 49.03 gms. of the salt ($K_2Cr_2O_7=K_2O+Cr_2O_3+3O$. $\frac{294.2}{2\times3}=49.03$); and such a solution of iodine will contain 126.92 gms. of iodine ($I_2+H_2O=2HI+O$).

If the normal solution is not a convenient strength, any suitable multiple as the half, fifth, tenth, hundredth, or the twice normal way be used. A normal standard solution is convenient if the one solution is to be used for different purposes and on different substances, but if the standard solution is to be used for one particular process, as is usually the case in metallurgical analysis, the empirical standard solution is the more useful and convenient.

Empirical Standard Solutions. An empirical standard solution is made so that 1 cc. of it will be equivalent to a simple definite value of the substance to be determined, as 0.01 gm. or 0.005 gm.; 1 per cent or 0.5 per cent when a sample of definite weight is worked upon. Empirical standard solutions are made by calculating, from the reaction involved, the amount of the titrating reagent required to react with 0.01 gm., 0.005 gm., or any other desired amount of the substance to be determined, and then weighing out as many times this amount as there are cubic centimeters in the whole volume of solution to be made.

Preparation of an Empirical Standard Solution. A standard solution of potassium permanganate of such value, for example, that 1 cc. will oxidize 0.01 gm. of iron from the ferrous to the ferric form is made as follows. The reaction which takes place between $KMnO_4$ and ferrous iron in the presence of H_2SO_4 is as follows:

$$10FeSO_4+2KMnO_4+8H_2SO_4= \\ 5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

If 10 atoms of Fe'' are oxidized by the available oxygen from 2 molecules of $KMnO_4$, 0.01 gm. of Fe'' will require for its oxidization 0.0056601 gm. of $KMnO_4$, as shown by the following proportion:

$$10(55.84) : 2(158.03) = 0.01 : 0.0056601,$$

55.84 being the atomic weight of iron and 158.03 the molecular weight of $KMnO_4$.

Having determined the amount of $KMnO_4$ required in 1 cc., if we wish to make a liter of such a solution, we weigh out 1000 times 0.0056601 gm., or 5.6601 gm., dissolve it in distilled water, and dilute the solution to 1 liter in a graduated flask.

Standardizing Solutions. In order that a standard solution have the strength intended, it must be made with great care. The purity of the reagent must be known, and any impurity allowed for, the weighing must be accurate, there must be no loss after weighing, the reagent must not be subjected to conditions that will change its form before or after it is put in solution, and the temperature of the solution should be the same when it is used for titration as when it was made. As a safeguard against errors from these sources, a solution that is to be used for titration should be standardized against a reagent of known purity to determine its actual strength per cubic centimeter, that is, an exact quantity of such reagent is weighed out, put in solution and titrated under as nearly as possible the same conditions as exist when determinations are made on unknown materials. There should be the same impurities present and in the same amounts, and the volume to be titrated should be the same when standardizing as when making regular determinations. See that the burette is perfectly clean, and if it is wet with distilled water, rinse it out with some of the solution that is to be standardized before filling for the test. Place the burette in a vertical position in a burette clamp attached to a stand. Nearly fill the burette with the solution to be standardized. Open the tap and let a little of the solution run out, in order to fill the point of the burette below the tap, and to bring the meniscus down to the graduations. See that a bubble of air is not held just below the tap. Now read the burette at the bottom of the meniscus and record the reading. Let the solution run from the burette into the solution to be titrated, stirring or shaking, until the reaction is complete as shown by the indicator. Care must be taken to stop the titration at the exact end-point, therefore, as the end-point is approached, the solution must be run in very slowly—drop by drop. When the end-point is reached, close the tap of the burette, and after waiting half a minute for the solution to run down the sides, read the burette and record the reading. The difference between the two readings of the burette indicates the volume used in the titration. After some practice the burette can be read to the second decimal place. The record should stand thus:

Second reading of the burette	37.58 cc.
First reading of the burette	1.24
Volume used in titration	36.34

To find the value of 1 cc. of the solution in the burette, divide the weight of the substance acted upon, after correcting for impurities, by the volume used in the titration.

Correcting a Standard Solution. If a solution is tested with a view to correcting what remains, to the exact strength desired, a definite portion, as 100 cc., should be taken out for the test, so that the remaining volume, which is to be corrected, may be known.

To indicate the method of correcting a standard solution, we will suppose that the potassium permanganate solution in the example above, when tested against a known weight of iron, is found not to have the value, 0.01 gm. of Fe per cubic centimeter, but 1 cc. proves to be equivalent to only 0.0096 gm. of Fe. If we have 900 cc. of the solution left, we may correct it as follows. If 1 cc. of the solution is equivalent to only 0.0096 gm. of iron, it does not contain 0.0056601 gm. of $KMnO_4$, but only 0.0054337 gm.

$$0.01 : 0.0056601 = 0.0096 : 0.0054337$$

There must be added, then, to each of the 900 cc. remaining (0.0056601 − .0054337) 0.0002264 gm. of the salt, or to the total volume (0.0002264 × 900) 0.0238 gm. The calculation is simplified by reducing to this form:

$$\left(\frac{1-.0096}{.01}\right).0056601\times 900 = .2038.$$

On the other hand, if the solution is too strong, it may be corrected as follows: let us suppose that 1 cc. is equivalent to 0.0107 gm. of Fe instead of 0.01 gm., then each cubic centimeter of the solution has in it, not 0.0056601 gm. of the salt, but 0.006056307 gm.

$$0.01 : 0.0107 = 0.0056601 : 0.0060563.$$

There is, therefore, in each cubic centimeter of the solution too much $KMnO_4$ by 0.0003962 gm., and in the 900 cc. remaining there are 0.35658 gm. (0.0003962×900) too much of the salt. This is a sufficient quantity of the salt to make 63 cc. of the correct strength (0.35658÷0.0056601=63). We have then only to add 63 cc. of distilled water to the solution to dilute it to the correct value. This problem stated in one equation may be reduced to the form:

$$(1.07-1)900=63.$$

Factor Weights for Standard Solutions. It is not always easy to make a standard solution of an exact predetermined value, nor is it easy to keep it at an exact value. The object of making the standard solution so that 1 cc. will be equivalent to a simple definite value, as 0.01 gm. of the substance to be determined, is, of course, to simplify the arithemtical calculation of the result after titration. If we have a standard permanganate solution of the value of 0.01 gm. of Fe per cubic centimeter, and use 1 gm. of iron-ore for analysis, the number of cubic centimeters of solution used in the titration will represent directly the percentage of iron in the ore. Suppose, for example, it is observed after titration in such a case that 62 cc. of the standard solution had been used in titration, then the calculation would be as follows:

$$\frac{62\times0.01\times100}{1}=62\%.$$

It is evident from this equation that the calculation would remain equally simple if the weight of the ore taken is always just 100 times the value of the solution. If the $KMnO_4$ solution should have the value 0.0096 instead of 0.01, we would only have to weigh out 0.96 gm. of ore instead of 1 gm. to preserve the simplicity of calculation. It is simpler then, instead of trying to make and keep a solution at an exact definite value, to standardize it as often as necessary, and, as its value changes, change the weight of ore taken to correspond with it.

Indicators. In all titrations there must be a means provided for detecting when the reaction is complete, that is, when the substance being measured has all been acted upon. This *end-point* is detected in a variety of ways, for example, by the formation of a precipitate, as in titrating cyanide with silver nitrate; by the failure of a precipitate to form, as in the Gay-Lussac method for silver; by the standard solution giving its color to the solution titrated, when the action is complete, as in the permanganate titration; by the change or disappearance of the color of the solution titrated, as in the cyanide method for copper; by a change of color in drops of a test solution, to which drops of the solution being titrated are added from time to time, as the titration proceeds, or by the change of color due to the presence of a test solution, or indicator, added to the solution titrated. The last method is the one employed when the end-point is marked by a change in the solution titrated from the alkaline to the acid condition, or *vice versa*. Several indicators are in use for detecting this change. They vary in their sensitivity and in their suitability for different uses. For convenience the more common ones are given below with their adaptability to different uses.

Phenolphthalein, colorless with acids and pink with alkalis, is good for hydrochloric, nitric, sulphuric, and the organic acids; and also for the alkalis NaOH, KOH, $Ba(OH)_2$ and $Ca(OH)_2$. It is not good for ammonia, nor in the presence of CO_2, but may be applied after expelling the CO_2 by boiling.

Methyl Orange, pink with acid and yellow with alkalis, is good for hydrochloric, nitric, and sulphuric acids; the hydrates, carbonates, and bicarbonates of the alkalis, and also for ammonia.

Cochineal, purple red with acids, and blue with alkalis, is good with ordinary mineral acids and alkalis, including ammonia. It is also reliable in the presence of CO_2, but not with the organic acids.

The reagent used for detecting the end-point will be described under each titration method.

COLORIMETRY

Many substances regularly determined in metallurgical analysis, when in solution and in certain definite forms give to the solutions characteristic colors, which may be used as a basis for the quantitative determination of these substances.

The intensity of the color of a solution depends upon three elements, or factors. They are: the quantity of coloring matter used, the volume of the solvent in which it is held, and the thickness of the solution through which the light passes before entering the eye. It is well known that if we keep two of these quantities constant and vary the third in a determinate way until two solutions are alike in color, we can estimate the quantity of coloring matter in one, if the quantity in the other is known. These three variables form the basis of three classes of methods in colorimetry, and of three types of colorimeters. When two solutions are brought to agreement in color by the addition of coloring matter to one, the amount added is the measure of that in the other. If the agreement is effected by dilution, the coloring matter is then proportional to the volumes. If they are brought to equality by changing the thickness of the sections observed, the quantity of coloring matter is then inversely proportional to the measurements of these sections.*

In laboratories where the first method is used, a series of solutions is prepared (Fig. 39) with varying amounts of the standard, representing the percentages from the lowest to the highest demanded in that laboratory. For instance, the first may contain 0.01 gm. of the color-producing substance, the second, 0.03 gm., the third, 0.05 gm., etc. Then, if the sample is dissolved and diluted to the same volume as the standards, in a similar tube, its place in the series is easily found and its value determined at once. Theoretically, this is the best colorimetric method known, but it is not so practical as some others, on account of the large number of standards required, and the necessity for frequent renewals due to their lack of permanency.

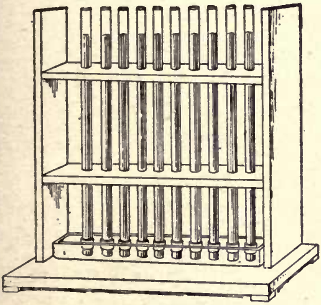

FIG. 39.—Series of Standard Solutions for Colorimetry.

FIG. 40.—Eggertz Tubes.

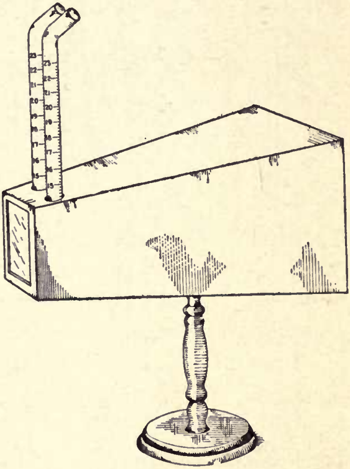

FIG. 41.—Camera for Eggertz Tubes.

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* C. H. White, Jour. Am. Chem. Soc., **34**, 639.

The second method, proposed by Eggertz,* is usually carried out in two graduated tubes of equal bore (Figs. 40, 41). The two solutions, the standard and the unknown, are diluted until the colors are the same when the tubes are held between the observer and a uniform light. The ratio existing between the quantities of coloring matter in the two tubes is then equal to the ratio between the volumes of the two solutions. Since three of these quantities are known the fourth is readily estimated.

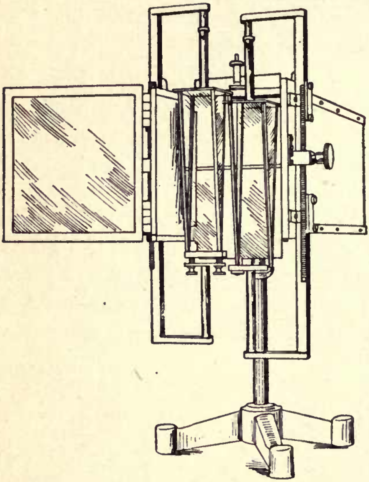

FIG. 42.

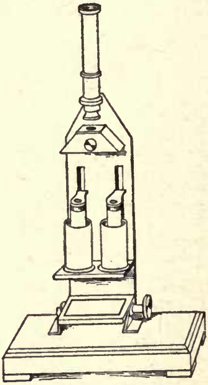

FIG. 43.

FIG. 42.—Colorimeter in which Hollow Glass Wedges are used to Vary the Depth of Solution Examined.

FIG. 43.—Colorimeter in which Solid Glass Plungers Lowered into the Solutions Change the Thickness of the Sections Compared.

In the third method, equal quantities of the standard and the unknown are dissolved in equal volumes of the solvent, and the thickness, or depth, of the solutions under examination

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* Chemical News, **44**, 173, Fern Kontorets Analer, 1862, p. 54.

is varied until the colors are the same. The percentages of coloring matter are then inversely proportional to the thickness of the sections. Several colorimeters (Figs. 42, 43) have been devised for varying and measuring the thickness of solutions under examination. These instruments are usually constructed and graduated in such a manner that the desired percentage may be read off at once. With these instruments, comparisons can be quickly made, and any number of readings may be taken and averaged without changing the volumes of the solutions. The solutions are not diluted by guess as in the Eggertz method, and preconceived notions of the value of the material cannot influence the operator, since he cannot see the graduations until the colors are matched.

METHODS OF ANALYSIS IN THE METALLURGY OF IRON AND STEEL

ANALYSIS OF ORES

Sampling Iron Ore. For the general principles of sampling see page 8, and for the quantity to be taken, and the size to which the lumps should be crushed before quartering down the sample, see the table on page 11. For the application of the table, ordinary iron ores would be classed as very uniform, low-grade material.

Fig. 44.—Sampling Trowel for Friable Ore.

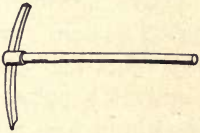
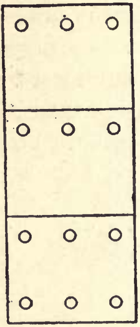


Fig. 45.—Sampling Pick for Drawing Ore from well below the Surface.

Sampling Ore in Cars. Soft ores may be sampled with a garden trowel (Fig. 44) or the sampling pick (Fig. 45). Before taking the sample, remove three inches of the surface at the point where the sample is to be taken and then dig into the ore with the trowel or sampling pick, take up the sample, and deposit it in an iron pail. Since it is not practicable to mix ore in cars previous to sampling, it should be kept in mind that the accuracy of the sample increases as the number of points from which it is taken is increased. The U. S. Steel Corporation takes at least 15 samples from 50-ton and 12 from 25-ton cars (Fig. 46),[*] of 2 to 3 ozs. each; that is, the total sample contains not less than 1½ lbs. from each small car and 2 lbs. from each large car. Samples from ten cars may be combined into one. The fact that this very small sample is representative indicates that the ore is extremely uniform in character. The points from which the samples are taken should be as evenly spaced as possible over the surface of the ore. If a lump is found at a point from which a sample is to be taken, a small piece is broken from the lump for the sample; the size of this piece will depend upon the size of the lump; if the lump is average ore in the space represented by that sample, the chip taken off for the sample will be as large as the usual sample.



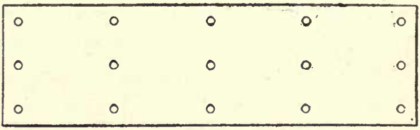


Fig. 46.—Parallel System of Sampling Ores.

The rope-net system in use at some of the hard-ore mines in the Lake Superior district is best for the even spacing of points

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[*] J. M. Camp, J. Ind. Eng. Chem., 1, 107–15. Also Electrochem. Met. Ind., 7, 65–72.

from which samples are to be taken. A rope net of 18-in. mesh (Fig. 47) is placed over the car, the knots or the squares indicating the points at which samples are to be taken.

Moisture Sample. If the regular sample is taken from well below the surface, a portion of it—2000 grams or so—may be put in a tin box or jar with tightly fitting cover for a moisture sample. If a special sample is taken for moisture, it is taken from well below the surface, and three samples, equally spaced, are taken from each car.

Sampling a Cargo. A cargo may be sampled by taking a few ounces from each grab as it is unloaded, by means of a scoop attached to a suitable handle. This method, however, is more expensive than taking samples from the surface while unloading is going on. The latter method is adopted by the U. S. Steel Corporation. Before unloading begins, samples are taken from the cone of ore under each hatch; then after unloading has proceeded far enough at a hatch to expose the bottom of the vessel, the sloping faces of ore exposed are then carefully sampled. The total sample of the cargo should be made up of at least nine-tenths from the faces, and not more than one-tenth from the surface of the cones. A cone is sampled by taking samples a foot apart along two lines which cross at the apex of the cone and end directly under the edge of the hatch midway between the center and the side of the boat as shown in Fig. 48.

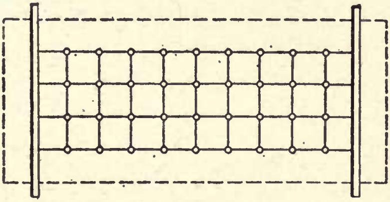

Fig. 47.—Rope Net System of Sampling for Hard Ores.

A face is sampled by climbing up the face, using a ladder, if necessary, and taking samples from points a foot apart (Fig. 49) along lines equally spaced 4 ft. apart.

Preparation of the Sample. The sample is dried, if necessary, at 100° and crushed to pass a half-inch mesh screen, or finer (see table on p. 11). Thoroughly mix the ore and quarter it alternately until only one-quarter of the original sample remains. Crush this to one-quarter inch, mix and sample it down as before until about 2 lbs remain. Grind this to pass a 20-mesh screen or finer, roll well and take out about 3 ozs., dry at 100°, grind on a bucking board to 100 mesh, or finer in an agate mortar (see p. 14) and place in a stoppered bottle and reserve for analysis.

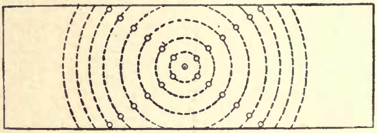

FIG. 48.—Cargo Sampling—The Cone.

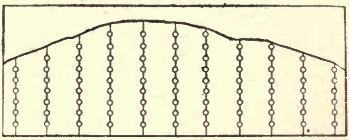

FIG. 49.—Cargo Sampling—The Face.

MOISTURE

The moisture sample should contain not less than 2000 gms., and should be carefully protected from loss of moisture until weighed (see Moisture Sample, p. 47). It is evenly spread out not more than 1 in. deep in a pan, and dried at 100° to a constant weight (4 to 6 hours, or over night). The loss in weight is moisture. Sometimes a weight of 2 lbs. is used for the moisture sample, in which case the loss in weight multiplied by 1000 gives the moisture in 1 ton.

HYGROSCOPIC WATER

To reduce the results of an analysis to the basis of dry ore, it is necessary to determine the moisture or hygroscopic water in the powdered sample when it is analyzed.

Heat a clean platinum crucible to drive off the moisture, cool it in a desiccator, weigh it, and then weigh and transfer to it about 1 gm. of the ore. Heat it about an hour on a toluene bath or in an air bath held at 105° C. to 110° C. (See p. 70.) Cool in a desiccator and weigh. The loss in weight is hygroscopic water.

COMBINED WATER *

Blow a small bulb at one end of a hard glass tube (Fig. 50) which is about 20 cm. long and 6 mm. internal diameter and another near the middle. Warm the tube to dry it thoroughly; the drying is hastened by drawing the air from it at the same time by introducing into the bulb-tube a smaller glass tube attached to the suction tap by a rubber tube. Cool and weigh the tube. Introduce into the bulb at the end, about half a gram of ore through a thistle tube, not letting the ore touch the sides of the weighed tube. Weigh the tube containing the ore. The weight of the empty tube deducted leaves the weight of the ore introduced. Hold the tube in a horizontal position and gradually heat the bulb containing the ore in the Bunsen flame, keeping the tube cool from the middle to the open end by wrapping it with cloth or filter paper wet with cold water. Do not use so much water that drops run down to the hot part of the tube. Turn the tube in the flame so that the bulb does not

FIG. 50. — Bulb Tube for Determining Combined Water.

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* Method of S. L. Penfield, Am. Jour. Sci., Third Series, 48, 31, 1894.

become soft enough to flow. The heating should be continued at least fifteen minutes, and the blast lamp should be used if minerals are known to be present that give up water with difficulty. When the water has all been driven out of the sample and has been condensed in the middle of the tube and while the bulb is still hot, grasp it with forceps or tongs and pull it away, sealing up the end of the tube with the flame. Dry the outside of the tube, cool, and weigh it. Then warm the tube to drive out the water, sucking out the moisture as before the first weighing, and then cool and weigh it again. The difference between the last two weights represents the total water. From the total water deduct moisture which has been previously determined, to find the weight of combined water. Reduce the weight to per cent in the usual way. (See p. 31.)

LOSS ON IGNITION

The sample is weighed in the same manner as for hygroscopic water and heated at the highest temperature of the blast lamp for thirty minutes. The hygroscopic water, the combined water, carbon dioxide, and other volatile substances, if present, will be driven out; carbonaceous matter burned; and ferrous compounds oxidized to ferric compounds.

It serves as a rough guide to the water and CO_2 in limestone, and to the water, in materials free from other volatile substances and from elements subject to oxidation.

IRON IN ORES

Potassium Permanganate—Margueritte Method

Outline. The iron is dissolved from the ore in hydrochloric acid. It is then reduced to the ferrous condition with zinc, sulphuric acid added, and the quantity of the iron is measured by titrating it with a standard solution of potassium permanganate.

Reagents. *Potassium chlorate*, $KClO_3$,

Pure Zinc, Zn.*

Standard Potassium Permanganate Solution. Make the permanganate solution in the manner described on page 37, using 2.83 gm. of $KMnO_4$ per liter. This solution should be equivalent to 0.005 gm. of Fe per cubic centimeter, and if it is carefully prepared with chemically pure $KMnO_4$ and distilled water that has been previously boiled with a little $KMnO_4$, the error should not be greater than one-half of 1 per cent. Freshly prepared solutions of permanganate usually contain small amounts of MnO_2, either originally in the salt as an impurity, or reduced from it by dust or other impurities in the water or in the bottle in which it is kept, and this induces the formation of more MnO_2 with a corresponding weakening of the solution. After dissolving the $KMnO_4$, the MnO_2 should be filtered on asbestos or the solution decanted from it, before diluting to the final volume.

Filter paper should not be substituted for asbestos, as it would reduce the $KMnO_4$. The container for the permanganate solution should have been previously cleansed with the cleaning solution (p. 35) and then with pure water. If, before standardizing, the solution is allowed to age for several days, the clear solution decanted into a clean bottle, and kept away from dust and sunlight, it should keep indefinitely with very little change in strength.

Standardization of Permanganate Solution. Weigh about 1 gm. of ferrous ammonium sulphate $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. Dissolve it in 20 cc. of water to which has been added 5 cc. of hydrochloric acid. Add about 3 gm. of granulated zinc and then add 10 cc. of sulphuric acid mixed with 20 cc. of water.

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* Zinc should not be used as a reducing agent for iron in ores carrying titanium, since part of the titanium is also reduced and is subsequently oxidized with the Fe by titration, vitiating the result. For titaniferous ores use either the method on p. 59 or that on p. 62.

When the zinc is all dissolved, dilute with distilled water to 500 cc. and titrate at once before the iron becomes partially oxidized by exposure to the air.

So large a quantity as 3 gms. of zinc is not necessary for the reduction of the iron for it is already in the ferrous condition except a small amount which may have become oxidized by exposure of the solution to the air, but the zinc is added to produce, as nearly as possible, the conditions which exist when the ore-solution is titrated.

Multiply the weight of ferrous ammonium sulphate taken, by its factor for iron (14.24 if it is known that the salt conforms exactly to the formula), and divide this weight of iron by the number of cubic centimeters required for the titration. This gives the value of 1 cc. of the permanganate solution in iron. Make three or four such tests that do not vary more than 0.0001 gm. from each other and average the results.

In order that the same conditions may exist when standardizing a solution as when regular titrations are made of unknown ores, iron ores in which the iron has been accurately determined are often used for standardizing, but it is evident that we must have an accurately standardized solution before we can prepare such a standard ore. It is therefore necessary to have recourse finally to a standard whose composition has been determined gravimetrically. Ferrous ammonium sulphate made and kept with ordinary care does not usually vary much from the theoretical composition, yet a quantity that is to be used for standardizing should be carefully analyzed for iron gravimetrically. The method for this determination follows.

IRON IN FERROUS AMMONIUM SULPHATE—GRAVIMETRIC METHOD

Weigh accurately about 0.5 gm. of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. Transfer it to a No. 4 beaker and dissolve in 50 cc. of water to which has been added 10 drops of hydrochloric acid.

If water alone were used for the solvent, basic salt would be precipitated by hydrolysis. HCl readily dissociates, saturating the solution with H ions, which prevents dissociation of the water into H and OH. There are therefore no OH ions available for the formation of basic salt.

Heat to boiling. Add nitric acid drop by drop until the solution turns yellow or red, through brown.

Not more than 8 or 10 drops are required if the solution is kept at the boiling-point.

$$3FeCl_2+HNO_3+3HCl=3FeCl_3+NO+2H_2O.$$

Oxidation is necessary, since NH_4OH does not completely precipitate iron in the ferrous form.

Dilute with hot water to 500 cc. Add while stirring 5 cc. ammonia.

$$FeCl_3+3NH_4OH=Fe(OH)_3+3NH_4Cl.$$

Basic ferric sulphate is precipitated in neutral solution, therefore, the ammonia should be stirred in quickly to render all portions of the solution alkaline as soon as possible.

Heat to boiling. Remove from the heat and let the ferric hydroxide settle. Decant the clear solution through a 9 cm. filter, leaving the precipitate in the beaker. Wash twice by decantation with 100 cc. hot water (see p. 21) transfer the precipitate to the filter and wash on the filter with hot water, never letting the precipitate get cold until the washing is complete. The washing is complete when the wash water comes through free from chlorides. Collect 2 or 3 cc. of the wash water on a watch glass as it runs from the funnel, add a drop of nitric acid and then test for chlorides with a solution of silver nitrate.

Nitric acid is added to neutralize ammonia, which if present would dissolve the silver chloride.

If the chlorides are not washed out, the high temperature at which the precipitate is burnt will form ferric chloride which is easily volatilized and lost.

The precipitate of ferric hydroxide should be filtered as soon as it settles; long contact of the ammoniacal solution with the glass may contaminate the precipitate with silica dissolved from the glass.

Place the moist filter with its contents in a platinum or porcelain crucible (see note below) that has been cooled in a desiccator and weighed, cover the crucible, and carefully drive off the moisture and volatile part of the filter paper at so low a temperature that the escaping gases are not ignited. When the volatile matter is all out, uncover the crucible and carefully burn the carbon at as low a temperature as possible with free access of air to prevent the reduction of ferric to magnetic oxide. When the carbon is all burnt, heat the precipitate to a high temperature for a few minutes with a small blast flame directed against the bottom of the crucible, and away from the top.

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

A high temperature is required to drive off the last traces of water-on the other hand it induces the formation of Fe_3O_4, especially if reducing gases are allowed to enter the crucible. In "Methods for the Analysis of Iron and Steel Used in the Laboratories of the American Rolling Mill Co.," page 26, it is pointed out that the ignition of ferric oxide in platinum induces the formation of Fe_3O_4, and it is suggested that the precipitate be ignited and weighed in a porcelain crucible placed inside a platinum crucible.

Cool in a desiccator and weigh. Heat again at a high temperature for a few minutes, cool and weigh. Repeat this treatment until the weight is constant. Calculate the weight of Fe in the Fe_2O_3 (Factor 0.6994) and the percentage in the salt.

Additional Methods of Standardization. Iron wire in which the iron has been carefully determined may be used for standardizing permanganate solutions. The wire is carefully cleaned, wound into a coil (on a pencil or glass rod), weighed, and treated by the method below for the determination of iron in ore.

Blair* recommends the use of a solution of ferric chloride

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* "The Chemical Analysis of Iron," seventh edition, p. 236.

made from wrought iron free from manganese and arsenic, and in which the iron and phosphorus have been accurately determined.

The oxidizing power of permanganate solution may be measured by oxalic acid, but the solution must be hot when titrated, and the other conditions under which the titration is made are not the same as when solutions of ore are titrated.

$$5H_2C_2O_4 \cdot 2H_2O + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 10H_2O.$$

This latter objection applies also to Lunge's method of standardizing the solution. By this method a measured volume of the solution is decomposed with hydrogen peroxide and sulphuric acid, the available oxygen liberated, collected and measured in a gas burette.*

Fe in Ore. Weigh 0.5 gm. of ore or a factor weight (see p. 40). Transfer it to a 300 cc. beaker or casserole.

Add 10 cc. of hydrochloric acid, cover with a watch glass, and raise the temperature but do not boil.

$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$. According to this reaction, 0.108 gm. HCl will dissolve .5 gm. Fe_2O_3. In 10 cc. of hydrochloric acid 1.20 sp.gr. at 15° there are 4.68 gm. of HCl; however, HCl is driven off by heat, and if the ore does not dissolve readily it may be necessary to add more acid.

If a solution of ferric chloride boils, iron is carried away by the vapor mechanically.

Add a few crystals of $KClO_3$ to destroy carbonaceous matter.

In the titration some permanganate would be reduced by the carbonaceous matter if it were not destroyed, and it would also give the solution a color that would persist after the iron had been reduced, making it impossible to detect by the loss of color when reduction is complete.

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* Chem. Ind., 1885, 168; Olsen, "Quantitative Analysis," p. 298.

When the solution of the iron is complete and the residue is white, or if the acid appears to have no further action, evaporate off most of the free acid (to about 5 cc.) at a low heat; do not boil.

There should be only a little HCl left, for in titration a somewhat concentrated solution of hydrochloric acid, or a weak solution if hot, reacts with $KMnO_4$ as follows:

$$2KMnO_4+16HCl=2KCl+2MnCl_2+8H_2O+5Cl_2.$$

This reaction may be prevented, however, by the addition of a few grams of manganous sulphate before titration.

If it is suspected that iron remains undissolved in the residue, as will be the case if the ore has not been finely ground or if it contains a silicate or titanate of iron, dilute with 15 cc. of hot water, filter, wash once or twice with hot water, place the filter with the residue in a platinum crucible, burn the paper, cool, add 1 cc. each of sulphuric acid and hydrofluoric acid, evaporate until sulphuric acid fumes begin to come off, and transfer the solution from the crucible to the filtrate containing the greater part of the iron.

Instead of treating the residue with sulphuric and hydrofluoric acids, the iron may be extracted from it as follows: after burning the filter paper and cooling, add 2 or 3 gms. of sodium carbonate and fuse, digest the fusion with hot water, which leaves the ferric oxide as a precipitate, filter out the ferric oxide, dissolve it in a little hydrochloric acid and add it to the main solution of iron.

When the iron is all in solution and only a little free hydrochloric acid remains, add about 3 gm. of granulated zinc to reduce the ferric to ferrous chloride.

$$Zn+2HCl=ZnCl_2+H_2,$$
$$2FeCl_3+H_2=2FeCl_2+2HCl.$$

When the brown color of ferric chloride has disappeared and the solution is clear, or if the action on the zinc ceases, add 10 cc. of sulphuric acid which has been mixed with 20 cc. of water.

When the iron is all reduced (the solution becoming colorless) and the zinc is all dissolved, transfer the solution to a large beaker or white dish, being careful to wash out all of the iron solution from the original beaker, dilute with cold distilled water to about 500 cc. and titrate with standard permanganate solution, stirring, until a faint permanent pink pervades the whole solution.

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

For the method of titrating, reading the burette, and calculating the result, see pages 35 and 39.

Reduction of the Iron by means of the Jones Reductor

If many reductions are to be made with zinc, the process is much more quickly carried out by the use of the reductor. This reductor * in its simplest form (Fig. 51) consists of a glass tube about 60 cm. in length, the upper half of which has an internal diameter of 25 mm. with a funnel top, and the lower half is drawn down to a diameter of 6 mm. The tube is provided with a glass tap at the point where the diameter is reduced. Glass wool is placed in the tube above the tap to a depth of 10 to 15 mm. to support the column of zinc. The large part of the tube is then filled to the funnel with amalgamated zinc. The zinc is amalgamated to prevent its rapid consumption. To prepare amalgamated zinc, put into a beaker enough granulated zinc (through 20- on 30-

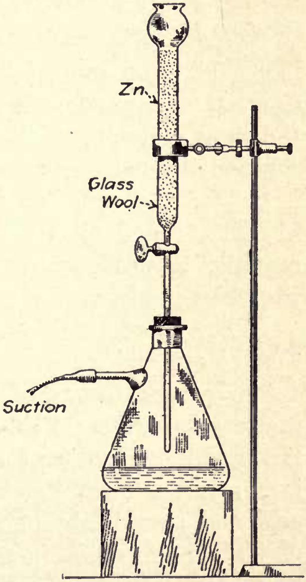

FIG. 51.—Reductor.

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* Blair, "Chemical Analysis of Iron," seventh edition, p. 94.

mesh screen) to fill the tube, cover it with distilled water, add about 5 gm. of mercury and 5 cc. sulphuric acid, and stir vigorously with a glass rod. In a few minutes the zinc is amalgamated and ready to be transferred to the reductor.

Use of the Reductor. Attach a filter flask to the reductor with a perforated rubber stopper and connect the filter flask to the suction. Prepare a dilute solution of sulphuric acid (25 cc. of sulphuric acid in a liter of water) and pass 200 cc. of it through the reductor, keeping the zinc always covered with solution.

If air comes in contact with the zinc, hydrogen peroxide is formed, which, after being absorbed by the iron solution, reacts later with the permanganate when the iron solution is titrated, vitiating the result.

Discard this wash solution, reconnect the flask and run a blank, in the manner following, to see how much permanganate solution is required, owing to traces of iron in the zinc, to produce the pink end-point. Pass 300 cc. of the dilute sulphuric acid solution through, never letting the surface of the solution in the funnel of the reductor fall down to the zinc, disconnect the filter flask and titrate directly into the flask. The quantity required to produce the end-point must be deducted from all titrations made on solutions passed through the reductor.

When the insoluble residue has been filtered from the solution of ore and most of the hydrochloric acid has been driven out by evaporation, dilute the solution to about 100 cc. with the dilute sulphuric acid solution (25 cc. acid to a liter) and pass it through the reductor into a clean filter flask. Wash all the iron solution from the beaker, with the very dilute sulphuric acid and pour it through the reductor. Follow this with more of the dilute sulphuric acid solution until 200 cc. of this solution have passed through, then follow this with 100 cc. of distilled water, never letting the air come in contact with the zinc, and finally leaving the funnel partially filled with water.

Disconnect the filter flask and titrate directly into it with the standard permanganate solution, deduct the quantity required for the blank and calculate the result.

Additional Reducing Agents. As noted on page 51, zinc should not be used for reducing iron in titaniferous ores. For such ores, stannous chloride, sulphurous acid, ammonium bisulphite, hydrogen sulphide, or some other reducing agent should be used. The method of reduction by stannous chloride is very rapid and satisfactory, and is applicable with either the potassium dichromate method or the potassium permanganate method, if, before titrating with the latter, manganous sulphate and phosphoric acid are added.

POTASSIUM PERMANGANATE METHOD FOR IRON

REDUCTION WITH STANNOUS CHLORIDE—ZIMMERMAN-REINHARDT METHOD

Reagents. *Stannous Chloride Solution.* Dissolve 250 gms. $SnCl_2$ in 100 cc. hydrochloric acid (1.2), dilute with water to 1 liter.

Mercuric chloride solution. A saturated solution of pure $HgCl_2$ in water.

"Titrating Mixture" *Manganous sulphate and phosphoric acid solution.* Dissolve 90 gms. $MnSO_4$ in 650 cc. of water, add 175 cc. sulphuric acid (1.84), and then 175 cc. phosphoric acid (1.75 sp. gr.).

Standard permanganate solution. (See p. 51.)

Fe in Ore. Weigh .5 gm. of ore and transfer it to a small porcelain crucible.

Heat over a Bunsen burner for a few minutes at low redness to destroy carbonaceous matter.

A high heat makes the ore more difficult to dissolve.

Place the crucible with the ore in a 400 cc. beaker.

Add 10 cc. of hydrochloric acid and 4 cc. of stannous chloride solution.

Stannous chloride hastens solution by reducing the iron, but care must be taken that too much stannous chloride is not added. Stop the addition when the solution clears.*

Heat to dissolve the iron. When the solution begins to turn yellow add stannous chloride solution drop by drop to reduce the iron. Finally, when all the iron is dissolved from the ore and the volume of solution has been reduced by evaporation to about 10 cc., add stannous chloride solution drop by drop until the color just disappears, then add one drop more.

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4.$$

Reduction by stannous chloride is effected best in a concentrated hot solution. If the solution is cool or dilute the reduction is slow and too much stannous chloride will be added before the color disappears.

If iron is suspected in the residue, before the final addition of stannous chloride, filter, wash twice with hot water, burn the filter in a platinum crucible, add 2 or 3 gms. of Na_2CO_3 and fuse. Cool and dissolve out the soluble salts with hot water, leaving the ferric oxide precipitated. Filter out the ferric oxide, wash it from the filter paper with a jet of hot water † (Fig. 52), dissolve it in hydrochloric acid and add to the main solution. Then proceed with the final reduction with stannous chloride.

If any platinum should be dissolved and should pass into the iron solution, it produces when stannous chloride is added a yellow color which persists after the iron is all reduced. The complete reduction of the iron can then be detected only by testing drops of the solution with a reagent such as potassium sulphocyanate.

Dilute to the capacity of the beaker with cold water and add, quickly, 5 cc. of mercuric chloride solution; stir vigorously.

$$SnCl_2+2HgCl_2=SnCl_4+2HgCl.$$

The excess of stannous chloride must be oxidized before titration. If too much stannous chloride has been added, or if the solution is warm when the mercuric chloride is added, or if it is added slowly, part of the

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* Mixer and Dubois. Jour. Am. Chem. Soc., 17, 405.

† Eng. and Min. Jour., 96, p. 695.

mercuric chloride will be reduced to metallic mercury, giving a gray color to the precipitate instead of the pure white of mercurous chloride.

$$2HgCl + SnCl_2 = SnCl_4 + Hg_2.$$

The presence of mercury spoils the determination, as it causes a reduction of the standard solution. The determination must therefore be discarded.

Add 10 cc. of the manganous sulphate and phosphoric acid solution. Stir and titrate with standard permanganate solution.

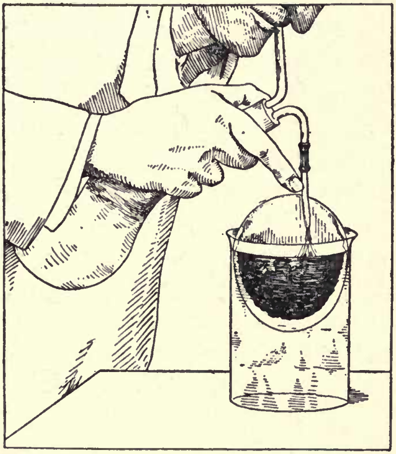

FIG. 52.—Washing a Precipitate from the Filter Paper to a Beaker.

The formation of brown ferric chloride on titration would render the detection of the end-point difficult, therefore, phosphoric acid is added in sufficient quantity to prevent the formation of ferric chloride. Manganese sulphate prevents the reduction of the permanganate by the hydrochloric acid.*

* For suggested reasons for this action see Treadwell-Hall, "Analytical Chemistry," 2, 482–3.

POTASSIUM DICHROMATE (PENNY'S) METHOD FOR IRON IN ORES

Outline. The iron is dissolved from the ore in hydrochloric acid. It is reduced to the ferrous condition with stannous chloride, the excess of stannous chloride oxidized with mercuric chloride and the quantity of the iron is then measured by titrating it with a standard solution of potassium dichromate.

Reagents.

Stannous chloride solution. (See p. 59.)

Mercuric chloride solution. (See p. 59.)

Potassium ferricyanide solution. Dissolve a small crystal, not more than 10 mgm., of $K_3Fe(CN)_6$ in 25 cc. of water. This must be made fresh just before using.

Standard solution of potassium dichromate. Dissolve 4.4 gm. $K_2Cr_2O_7$ in 1 liter of water. One cubic centimeter should be equivalent to about 0.005 gm. of Fe. Standardize this solution against an ore, iron wire, or ferrous ammonium sulphate in which the iron has been accurately determined. If ore is used for standardizing, take 0.5 gm., or if iron wire, weigh about 0.25 gm. and treat it by the process for ore (p. 63). If ferrous ammonium sulphate is used, treat it as follows:

Standardization of Potassium Dichromate Solution. Weigh accurately about 0.5 gm. of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. Dissolve it in 10 cc. of water and 5 cc. of hydrochloric acid. (See note, bottom of p. 52.) Heat to boiling and add 1 drop of stannous chloride solution. Cool and dilute to 200 cc. with cold water. Add 5 cc. of mercuric chloride solution. Stir, and titrate with the potassium dichromate solution until a blue color ceases to form when a drop of the iron solution is added to a drop of potassium ferricyanide solution on a white tile.

Before beginning the titration, place several drops of the potassium ferricyanide solution on a white tile or plate, then as titration proceeds, take out a drop of the iron solution on a glass rod and add it to a drop of the ferricyanide solution; a blue color is produced as long as any iron remains unoxidized in the solution.

The first test that fails to give a blue color indicates that all the iron is oxidized and this point is therefore the end-point. Read the burette and divide the weight of iron in the salt taken by the number of cubic centimeters used in the titration to find the value of 1 cc. of the solution in Fe.

Fe in Ore. Weigh .5 gm. of ore and transfer it to a small porcelain crucible.

Heat over a Bunsen burner for a few minutes at low redness to destroy carbonaceous matter. (See notes on p. 59.)

Place the crucible with the ore in a 400-cc. beaker.

Add 10 cc. of hydrochloric acid and 4 cc. of stannous chloride solution.

Heat to dissolve the iron. When the solution begins to turn yellow add stannous chloride solution drop by drop to reduce the iron. Finally, when all the iron is dissolved from the ore and the volume of solution has been reduced by evaporation to about 10 cc., add stannous chloride solution drop by drop until the color just disappears, then add one drop more.

If iron is suspected in the residue, before the final addition of stannous chloride, filter, wash twice with hot water, burn the filter in a platinum crucible, add 2 or 3 gms. of sodium carbonate and fuse. Cool and dissolve out the soluble salts with hot water, leaving the ferric oxide precipitated. Filter off the ferric oxide, wash it from the filter paper with a jet of hot water (Fig. 52) dissolve it in hydrochloric acid and add to the main solution. Then proceed with the final reduction with stannous chloride.

If any platinum should be dissolved and should pass into the iron solution, it produces when stannous chloride is added a yellow color which persists after the iron is all reduced. The complete reduction of the iron can then be detected only by testing drops of the solution with a reagent such as potassium sulphocyanate.

Dilute to 200 cc. with cold water and add quickly 5 cc. of mercuric chloride solution. Stir vigorously and titrate at once with standard potassium dichromate solution, testing a drop of the iron solution occasionally on a white tile with a drop of potassium ferricyanide solution, in the manner described above under the standardization of the dichromate solution, until the blue color is no longer produced. Read the burette and calculate the percentage of iron in the ore.

$$6FeCl_2+K_2Cr_2O_7+14HCl=6FeCl_3+2CrCl_3+2KCl+7H_2O.$$

The iron solution becomes green as titration proceeds, owing to the formation of chromic chloride.

When ferrous iron is added to a solution of potassium ferricyanide, Prussian, or Turnbull's, blue is formed, and the color of the tests becomes fainter as the amount of ferrous iron diminishes.

$$Fe''Cl_2+K_3Fe'''(CN)_6+2H_2O=Fe''(CN)_6KH_2Fe'''(OH)_2+2KCl.^*$$

DETERMINATION OF FERROUS IRON

By the foregoing methods the total iron in an ore is determined. It is sometimes necessary to determine the amount of iron present in the ferrous condition. This is done by dissolving the material under conditions that are neither oxidizing nor reducing, and titrating the ferrous iron at once.

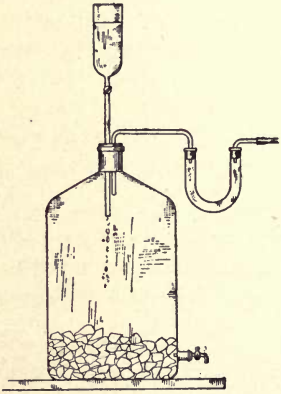

FIG. 53.—Carbon Dioxide Generator.

Reagents. *Carbon dioxide.* This may be generated in a Kipp apparatus, or in a flask (Fig. 53) provided with a separating funnel and delivery tube. Place calcium carbonate (marble or limestone fragments) in the flask and let dilute hydrochloric acid (1 : 3) drop from the funnel to produce the gas at the desired rate.

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* Treadwell-Hall, "Analytical Chemistry," Vol. 1, p. 95. Hofman, Heine, and Hochtlen, Annalen, 337 (1904), p. 1.

Hydrochloric acid (1.2) diluted with an equal volume of water.

"Titrating solution" of *manganese sulphate* and *phosphoric acid.* (See p. 59.)

A standard solution of *potassium permanganate.* (See p. 51.)

Fe in the Ferrous Condition. Weigh 0.5 gm. of ore and transfer it to a 250-cc. Florence flask. Close the flask with a two-hole stopper provided with intake and delivery tubes of glass. Let the delivery tube dip under water in a beaker. Attach the intake to the CO_2 generator and pass the gas ten minutes to displace the air. Disconnect the gas generator and attach to the intake a funnel, through which introduce 30 cc. of dilute hydrochloric acid (1 : 1). Disconnect the funnel and re-attach the gas generator to the intake and pass carbon dioxide through the flask. While the gas passes through, gently warm the flask with a Bunsen burner until the ore is dissolved and the volume has been reduced by evaporation to 15 cc. Cool, add 20 cc. of the "titrating solution," and 100 cc. of water, and titrate with standard permanganate solution.

For FeO and Fe_2O_3. If the iron is to be reported as oxides, subtract the weight of ferrous iron from the total iron, the remainder will, of course, be the weight of trivalent, or ferric iron, in the ore. Multiply the weight of ferrous iron by the factor 1.2865 to obtain the corresponding weight of ferrous oxide, and the weight of ferric iron by 1.4298 for the weight of ferric oxide. Then divide the weight of each of these oxides by the weight of ore taken to find the percentage of each present.

Materials which will not completely decompose in hydrochloric acid may be treated according to Cooke's Method.*

Weigh 0.5 gm. of the ore and place it in a large (80 cc.) platinum crucible, add a little water that has been recently boiled and about 10 cc. of dilute sulphuric acid (1 : 3). Place the

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* Bull. 422, U. S. Geolog. Survey, p. 168.

crucible under the funnel on the water bath (Fig. 54). Start the flow of CO_2 and of water through the bath. When the air under the funnel has been replaced by CO_2 raise the funnel and quickly add to the crucible about 6 cc. of strong hydrofluoric acid and replace the funnel. When steam issues freely from the funnel cut off the supply of CO_2 and continue the boiling for one hour or until the ore is all decomposed. Turn off the heat and turn on the CO_2 and the water.

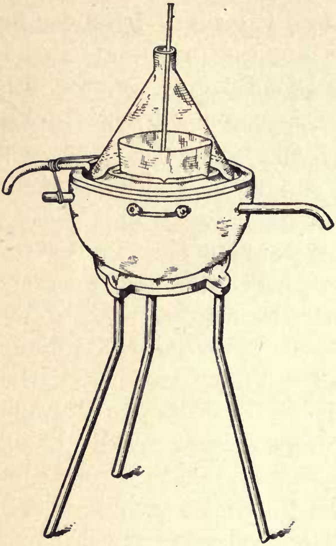

FIG. 54.—Cooke's Apparatus for Ferrous Iron Determination. The water bath has a specially made cover with circular trough in which water is kept to make an air-tight joint with the funnel which is turned over the crucible.

Place in the beaker in which the titration is to be made 300 cc. of cold freshly boiled water and 10 cc. of sulphuric acid. Now wash the contents of the crucible into the beaker and titrate with standard permanganate solution, letting the solution run in as rapidly as possible with continuous stirring until the first pink blush pervades the whole solution and persists at least two seconds. If much iron or much hydrofluoric acid is present the color fades rapidly.

DETERMINATION OF FREE METALLIC IRON

In the investigation of furnace products it is sometimes necessary to determine the quantity of iron that has been reduced to the metallic, or elementary condition. This determination may be made by dissolving the iron in a neutral solution of mercuric chloride under an atmosphere of carbon dioxide, and titrating with potassium permanganate solution; or by dissolving in dilute hydrochloric acid, collecting the evolved hydrogen and measuring it in a gas apparatus, estimating its weight and its equivalent in iron. In case iron sulphide is present, the latter method must be used, and the hydrogen sulphide generated must be absorbed by passing the gas through a solution of potassium hydroxide or other absorbent before measuring the volume of hydrogen.*

Reagents. *Neutral saturated solution of mercuric chloride.*

Solution of manganous sulphate and phosphoric acid (titrating mixture). (See p. 59.)

Carbon dioxide. (See p. 64.)

Standard solution of potassium permanganate. (See p. 51.)

Free Metallic Fe. Weigh 0.5 gm. of the sample. Transfer it to a 300-cc. flask. Add 75 cc. *neutral* saturated mercuric chloride solution and close the flask with a two-hole rubber stopper provided with intake and delivery tubes of glass. Let the delivery tube dip under water in a beaker as a seal. Pass carbon dioxide to displace air in the flask. (See p. 64 for method of generating carbon dioxide.) Heat to just below boiling and hold at this temperature for half an hour or until the metallic iron is all dissolved. Cool the flask, maintaining within it an atmosphere of CO_2.

$$Fe + 2HgCl_2 = Hg_2Cl_2 + FeCl_2.$$

When cold, filter the solution through asbestos into 30 cc. of "titrating mixture," wash with cold water, and titrate with standard permanganate solution.

Ferrous iron may be determined in this material by returning the asbestos with residue to the flask and proceeding according to the method given on page 64.

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* These methods were contributed by D. A. Lyon, metallurgist of the U. S. Bureau of Mines, in whose investigations they were used by J. F. Cullen and G. A. Reinhardt.

Free Metallic Iron in the Presence of Titanium. If metallic titanium or iron sulphide is present it is advisable to determine the metallic iron by dissolving the sample in dilute hydrochloric acid and measuring the hydrogen evolved. This is carried out in the apparatus shown in Fig. 55. From the reservoir *R*, acid is delivered to the test-tube *B* through the tube *E*. At *C* the glass tubing is connected by a rubber tube on which is a clamp. The tube *E* passes through a two-hole stopper to the lowest point in the bottom of the test-tube *B*, and is here drawn to a fine capillary opening. The test-tube *B* is connected by a capillary glass tube to the burette at *D*. The leveling tube *F* contains a solution of sodium hydroxide (250 gms. per liter) to absorb the hydrogen sulphide which is evolved with the hydrogen. Nearly fill the acid reservoir with dilute hydrochloric acid (1 : 1). Remove the test-tube *B* from its stopper and, by blowing at *A*, force the acid over to fill the tube *E*. Close the clamp *C* and wipe dry the point of the tube *E*.

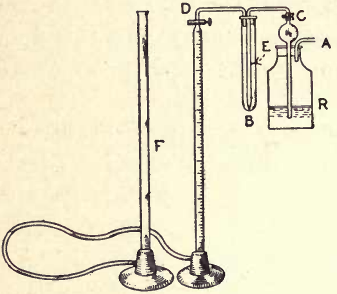

FIG. 55.—Apparatus Assembled for the Determination of Free Metallic Iron.

Weigh 0.5 gm. of the material to be analyzed and transfer it to the dry test-tube. Fit the test-tube to its stopper. Read the burette. Lower the leveling tube *F*, release the clamp at *C*, and draw in the necessary volume of acid (2 ins. or so in depth), and close the clamp at *C*. Collect the evolved hydrogen in the burette. When evolution has ceased, warm the acid in the test-tube with a very small flame for a few minutes. The acid will attack metallic titanium if the heating is continued. Pass the gas back and forth from the burette by means of the leveling tube until the absorption of hydrogen sulphide is complete and the hydrogen is at room temperature. Finally, force the acid in the test-tube back, by raising the leveling tube, until it just stands at the fine point of the tube E (its initial position), and read the burette. The increase in volume is due to the hydrogen; calculate its weight from the barometer and thermometer readings.

$$Fe+2HCl=FeCl_2+H_2.$$

One gram of hydrogen is equivalent to 27.6488 gms. of iron. 1 cc. of hydrogen at 0° C. and 760 mm. mercury weighs 0.00008987 gm.

Suppose the volume of hydrogen is 24.5 cc. at a temperature of 18° C. and a pressure of 740 mm. At 0° C. and 760 mm. this volume would become

$$\frac{273\times740\times24.5}{(273+18)760}=22.37 \text{ cc.}$$

$$.00008987\times22.37=.00201041 \text{ gm.}=\text{wt. of the hydrogen.}$$

$$27.6488\times.0020104=.055585 \text{ gm.}=\text{equivalent in iron.}$$

$$\frac{.055585\times100}{5}=11.11 \text{ per cent Fe in the material.}$$

DETERMINATION OF SILICA IN ORE

Hydrofluoric Acid, Berzelius Method

Outline. The ore is dissolved in hydrochloric acid, the solution taken to dryness and the residue heated to dehydrate the silica. The residue is treated with hydrochloric acid, filtered and weighed. The silica is volatilized with hydrofluoric acid, the residue weighed and deducted from the weight of impure silica.

Reagent. *Hydrofluoric acid,* HF.

SiO_2 in Ore. Weigh 1 gm. of ore (or 0.5 gm., if high in silica) and transfer it to a casserole or beaker. Add 20 cc. of hydrochloric acid, cover with a watch glass, and heat to dissolve.

$M_2SiO_3+2HCl=2MCl+H_2SiO_3$. *M* represents bases of soluble silicates.

Evaporate the solution to dryness and hold the residue at a temperature of about 120° C. for one hour.

$$H_2SiO_3=SiO_2+H_2O.$$

Do not heat above 130°; some SiO may recombine with bases, forming soluble silicates. A Freas electric oven (Fig. 56) is excellent for maintaining a constant temperature, but it is not difficult to adjust the heat under the air-bath, if a thermometer is fixed with its bulb opposite the bottom of the beaker (Fig. 57).

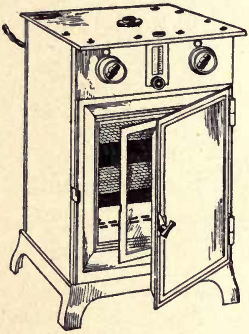

Fig. 56.—Freas Electric Oven.

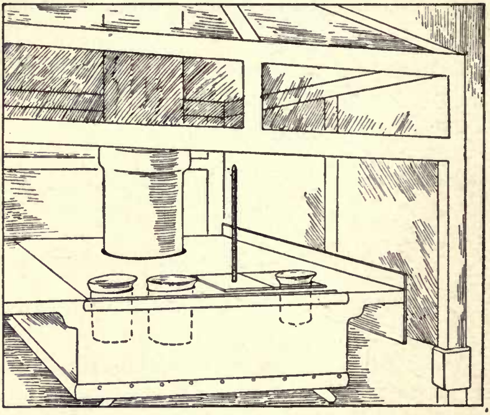

Fig. 57.—Control of the Temperature of an Air Bath.

Cool and add 10 cc. of hydrochloric acid and 10 cc. of hot water. Heat to dissolve soluble salts, dilute with a little hot water, filter, and wash (four or five times) with hot dilute hydrochloric acid (1 : 3) until the SiO_2 is free from iron, and then wash with hot water to remove the hydrochloric acid.

If washed with hot water before all the iron is out, basic salts of iron may be precipitated in the filter when the free acid has been removed. (See note p. 52.)

Place the filter with the SiO_2 in a weighed platinum crucible, carefully raise the temperature with a Bunsen burner and burn off the filter paper. Then heat with a blast lamp five minutes.

A high heat is necessary to drive off the last traces of combined water.

Cool in a desiccator and weigh.

Add to the crucible enough hydrofluoric acid to dissolve the SiO_2 (5 cc.) and two drops of sulphuric acid.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

Take care not to breathe the fumes of hydrofluoric acid, as they are extremely irritating; neither should the acid be allowed to touch the skin.

Evaporate carefully to dryness in a hood with a good draft.

Ignite with the blast lamp, cool in the desiccator and weigh. The loss in weight represents the SiO_2.

With high silica ores it may be necessary to repeat the treatment with hydrofluoric and sulphuric acids until the weight of the residue is constant.

Silicon tetrafluoride being volatile is lost on evaporation. Titanium fluoride is also volatile; therefore, sulphuric acid is added to retain titanium in the crucible as sulphate in case titanium is present. The sulphates of iron, aluminum, and titanium are broken up at a high temperature, liberating SO_3, the oxides remaining in the crucible.

SILICA IN ORE

Fusion with Sodium Carbonate

Outline. The ore is fused with a flux, dissolved in dilute hydrochloric acid, and the silica is dehydrated by evaporating the solution to dryness. The residue is treated with hydrochloric acid, and the silica is filtered from the solution and weighed.

Reagents. *Sodium carbonate*, Na_2CO_3.

Potassium carbonate, K_2CO_3.

SiO_2 in Ore. Weigh 0.5 gm. of ore and transfer it to a platinum crucible. Add about 5 gms. of fused sodium carbonate.

Put on the cover and fuse with the blast lamp. Direct the flame against the side of the crucible so that melting will begin at the top.

If heated rapidly at the bottom, the sudden expulsion of CO_2 may throw some of the charge from the crucible.

$$SiO_2+Na_2CO_3=Na_2SiO_3+CO_2.$$

The fusion should be complete within fifteen or twenty minutes.

Take the crucible in the tongs and turn it so that the fusion will run well up on the side. Continue turning it until the fusion freezes in a thin layer, covering as much of the inside of the crucible as possible. When the crucible is cool, place it on its side in a casserole which contains nearly enough water to cover the crucible, also put the crucible cover in the casserole. Cover with a watch glass and pour down the lip of the casserole hydrochloric acid to make the solution acid. Warm to hasten solution, and as the fusion dissolves add more hydrochloric acid to keep the solution always distinctly acid.

$$Na_2SiO_3+2HCl=2NaCl+H_2SiO_3.$$

Take out the crucible and cover, carefully wash them off, and let the washings run into the casserole. Evaporate the solution in the casserole to dryness, and hold at a temperature of about 120° for an hour. Add 20 cc. of dilute hydrochloric acid (1 : 1), warm to dissolve the soluble salts, dilute with 20 cc. of hot water and filter. Wash several times with warm dilute hydrochloric acid (1 : 3) and finally with hot water to remove all hydrochloric acid. Burn carefully in a weighed platinum crucible over a Bunsen burner, ignite at the highest temperature of the blast lamp five minutes, cool in a desiccator and weigh. Calculate the percentage of SiO_2.

A small amount of silica is carried through with the filtrate. For very accurate work this must be recovered by dehydration a second time. Evaporate the filtrate to dryness, take up the residue with very dilute hydrochloric acid, filter and burn the two filters together before weighing. For other notes see the method for silica pages 70 and 71.

DETERMINATION OF SULPHUR IN ORE

Outline. The ore is fused with a flux, the fusion treated with hot water to dissolve sulphates, the residue filtered off, the filtrate acidified with hydrochloric acid, evaporated to dryness and the silica dehydrated. The residue is treated with dilute hydrochloric acid and the silica is filtered out. The sulphur is precipitated from the filtrate with barium chloride, filtered and weighed.

Reagents. *Sodium carbonate,* Na_2CO_3.

Sodium nitrate, $NaNO_3$.

Alcohol, C_2H_6O.

Barium chloride, $BaCl_2$, 10 per cent solution.

S in Ore. Fuse 1 gm. (or 1.3738 gms., ten times the factor) of ore with 8–10 gms. of sodium carbonate and about 0.5 gm. of sodium nitrate in a platinum crucible.

Sodium nitrate is added to oxidize sulphur to SO_3 and is preferred to potassium nitrate, for if potassium salts are present, the precipitate of barium sulphate will contain potassium sulphate. Only a small amount of the nitrate should be added, since it attacks platinum. (See p. 29.)

If the fusion is made with a gas flame, the products of combustion which contain sulphur must not be permitted to enter the crucible. This may be prevented by inclining the crucible and allowing the lower part to project through a hole in a sheet of asbestos, as shown in the figure (Fig. 58),* or a spirit lamp may be used.

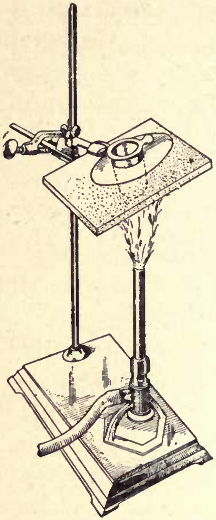

FIG. 58.—Arrangement of Crucible to Prevent the Products of Combustion of the Gas from Contaminating the Fusion.

Cool the fusion. Treat it with hot water to dissolve soluble silicates, sulphates, etc., and to precipitate the iron as oxide.

Barium sulphate when precipitated has a tendency to carry down impurities with it, some of which cannot be removed by washing. If iron is present, ferric sulphate comes down with the barium sulphate, and on ignition breaks up into ferric oxide and SO_3, the latter escaping. Other trivalent metals also, as far as possible, should be removed.

If the ore contains manganese its presence will be indicated by the green color of the fusion, and it should be removed by the addition of a few drops of alcohol, which precipitates it from the sodium manganate, as manganese dioxide. Sodium hydroxide and aldehyde are also produced by the reaction.

$$MnO_2+Na_2CO_3+O=CO_2+Na_2MnO_4,$$
$$Na_2MnO_4+C_2H_6O=2NaOH+MnO_2+C_2H_4O.$$

Decant the solution through a filter and wash twice by decantation. Acidify the filtrate with hydrochloric acid and evaporate the solution to dryness.

If nitric or chloric acid is present, the barium salts of these acids will be precipitated with the sulphate, and cannot be washed out. These acids are broken up by evaporating with hydrochloric acid. Silica, also, would contaminate the precipitate if it were not dehydrated and removed.

Cool; add a few drops of hydrochloric acid and 200 cc. of hot water.

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* Lowe, Zeit. f. Anal. Chem., 20 (1881), p. 224.

Only a very little hydrochloric acid should be used, as barium sulphate is slightly soluble in hydrochloric acid.

Filter and wash well with hot water. Heat the filtrate to boiling and add boiling barium chloride solution, drop by drop, stirring until the precipitation of barium sulphate is complete. Then add 10 cc. more of barium chloride solution and let the determination stand hot (not boiling) half an hour or more.

If barium chloride solution is added rapidly, barium chloride comes down with the sulphate. (See Precipitation, p. 20.)

Filter and wash four times by decantation. Transfer the precipitate to the filter and wash until the washings are free from barium. (Test with sulphuric acid.)

Burn carefully at a low heat with a Bunsen burner. Burning filter paper reduces some barium sulphate to the sulphide; but, if air is admitted and the heating continued, the sulphide is reoxidized.

Cool in a desiccator and weigh the $BaSO_4$. Calculate the percentage of sulphur according to the method given on page 31. If the factor weight of ore was used, the weight of $BaSO_4$ multiplied by 10 gives the percentage of sulphur in the ore.

DETERMINATION OF PHOSPHORUS IN ORE

MOLYBDATE METHOD, WEIGHING THE YELLOW PRECIPITATE

Outline. The ore is dissolved in hydrochloric acid, by previous fusion if necessary; the silica dehydrated and filtered off; the hydrochloric acid in the filtrate is replaced by nitric acid by evaporation; ammonia is added, and the phosphorus is precipitated by ammonium molybdate, filtered in a Gooch crucible and weighed.

Reagents. *Sodium carbonate,* Na_2CO_3, fused.

Dilute nitric acid, HNO_3 (2 : 3).

Alcohol, C_2H_6O (95 per cent).

Molybdate solution. Dissolve 10 gms. MoO_3 in 40 cc. of cold water and 8 cc. of ammonia. Filter, and pour this solution slowly into dilute nitric acid (40 cc. nitric acid (1.42)+60 cc. water). Stir and keep the solution cool to prevent the precipitation of molybdic acid. If a precipitate begins to form, stop the addition of the ammoniacal solution, cool by placing the beaker in cold water, and continue agitation until the precipitate dissolves. Add about 0.05 gm. of microcosmic salt to clear the solution of suspended impurities. Shake, let the solution stand twenty-four hours, and filter or decant the clear solution for use.

Wash solution of ammonium nitrate. Add to 10 cc. of nitric acid (sp.gr. 1.42), 200 gms. ammonium nitrate, and water to make one liter.

P in Ore. Weigh 1.63 gms. of ore (100 times the factor) and transfer it to a casserole.

A large precipitate of ammonium phosphomolybdate is not easy to wash and dry for weighing. A sufficient quantity of ore should be taken to yield from 0.2 gm. to 0.4 gm. of the precipitate. Therefore 1.63 gms., 100 times the factor weight, is a convenient quantity to take of ores containing from 0.2 to 0.3 per cent phosphorus. Of ores higher in phosphorus, 1 gm., or better, 50 times the factor weight, 0.815 gm., should be taken; of ores lower in phosphorus, 200 or 300 times the factor weight, that is, 3.26 gms. or 4.89 gms., would be required.

Add 30 cc. of hydrochloric acid. Digest over a moderate heat until there is no further action on the ore. Dilute with an equal volume of water and filter into a casserole. Evaporate the filtrate to dryness, and while the evaporation is going on, burn the filter paper with the residue in a platinum crucible, cool, and add sodium carbonate, in quantity about six times the weight of the residue. Fuse, place the crucible in the casserole in which the ore was dissolved, and dissolve the fusion in hot water acidulated with hydrochloric acid.

If it has been previously determined that all the phosphorus in the ore under examination is soluble, the residue need not be fused, but may be discarded after filtering and washing. In this case, before filtering, the solution should be taken to dryness, the residue baked to oxidize phosphorus, dissolved in a little hydrochloric acid, and then diluted with water.

Evaporate this solution to dryness and heat the residue as well as that from the filtrate, at about 200° C. for half an hour, or until they no longer yield an odor of hydrochloric acid.

Baking of these residues should be continued until the carbonaceous matter is destroyed and the phosphorus is oxidized to PO_4; otherwise, all the phosphorus will not be precipitated.

Cool and treat each of the residues with a little hydrochloric acid to dissolve the iron. Dilute with an equal volume of hot water, and filter both into a small Erlenmeyer flask. Wash well with hot water. Evaporate the combined filtrate until it has a syrupy consistency, or until ferric chloride begins to separate.

The washed precipitate may be burnt and weighed in the usual manner for the determination of SiO_2.

Hydrochloric acid dissolves the yellow precipitate and therefore must be removed by evaporating with nitric acid.

Add 30 cc. of nitric acid (sp.gr. 1.42) and evaporate to 15 cc. Dilute to 50 cc. with water. Add ammonia until all the iron is precipitated and there is a slight excess indicated by the odor. Add dilute nitric acid (2:3), a few drops at a time, shaking until the precipitate is just dissolved, then add about 5 cc. more, or enough to give the solution an amber color.

These proportions of nitric acid and ammonium nitrate in the solution are the best for the precipitation of the phosphomolybdate.

Heat the solution to 80° C. and add 60 cc. of molybdate solution.

$$\begin{aligned} &FePO_4+12(NH_4)_2MoO_4+24HNO_3 \\ &\qquad =(NH_4)_3PO_4\cdot 12MoO_3+21NH_4NO_3+Fe(NO_3)_3+12H_2O \end{aligned}$$

A high temperature hastens the precipitation, but if heated higher than 80° C. there is danger of bringing down molybdic acid with the yellow precipitate.

Shake five minutes, let settle one hour, and filter in a Gooch crucible; or shake ten minutes and filter at once. The solution should be shaken violently, by hand, shaking machine (Fig. 59), mechanical stirrer (see Fig. 23, p. 22, and Fig. 60, p. 98), or by a jet of compressed air.

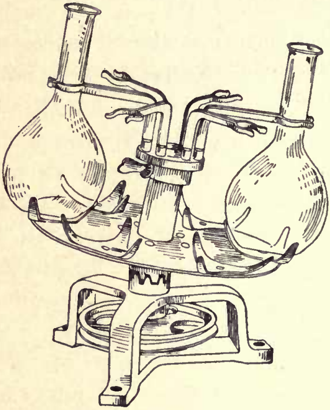

Fig. 59.—Camp's Shaking Machine.

Wash five times with the wash solution of ammonium nitrate; then wash twice with alcohol. Dry one hour in an air bath at about 130° C., cool in a desiccator, and weigh. If 100 times the factor weight (1.63 gms.) has been used, the weight of the yellow precipitate will represent the percentage of phosphorus in the ore: if any multiple of that weight is used, divide the weight of the yellow precipitate by the multiple. (See p. 32.)

The compound $(NH_4)_3PO_4 \cdot 12MoO_3$ contains theoretically 1.653 per cent phosphorus, but the precipitate formed according to this method has been found by repeated tests to contain 1.63 per cent phosphorus.

Phosphorus from the Filtrate from SiO_2. Phosphorus and silica may be determined in the same sample. Weigh the sample of ore and proceed with the determination of silica (p. 71) until the silica has been filtered from the solution. Evaporate the filtrate until solids begin to separate. Add 30 cc. of nitric acid (1.42), evaporate to 15 cc. and complete the determination in the manner described in the preceding method (p. 77) If the weight of ore used was not a factor weight for phosphorus, calculate the percentage of phosphorus in the manner described on page 31.

PHOSPHORUS IN ORE

WEIGHING AS $Mg_2P_2O_7$

If the yellow precipitate is always formed under the same conditions, its composition is constant and the method in which the yellow precipitate is weighed is a very exact one for the determination of phosphorus; but, since the conditions of precipitation are not always uniform, it is better, for very exact work, to dissolve the yellow precipitate, reprecipitate the phosphorus with magnesia mixture, and weigh as $Mg_2P_2O_7$.

Reagents. *Magnesia mixture:* Dissolve 55 gms. $MgCl_2 \cdot 6H_2O$ and 70 gms. NH_4Cl in 650 cc. of water and dilute the solution to one liter with ammonia (sp.gr. .96).

Also the reagents required for the method on page 75.

P in Ore. Weigh 2.7873 gms. ore (10 times the factor) and proceed according to the method on page 76 until the yellow precipitate is ready to be filtered. Filter on a 9-cm. filter paper and wash five times with the ammonium nitrate wash solution. Place a clean beaker under the funnel, pierce the filter paper and wash the precipitate through with a fine jet of hot water. Drop a little ammonia on the filter and wash with hot water. If any precipitate sticks to the flask in which it was formed, dissolve it out with a few drops of ammonia mixed with a little water and add the solution to that in the beaker. Keep the volume small (not greater than 50 cc.). Stir and, if the precipitate does not all dissolve, add a little more ammonia.

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 24NH_4OH = 12(NH_4)_2MoO_4 + (NH_4)_3PO_4 + 12H_2O.$$

Add hydrochloric acid to neutralize the solution and if the yellow precipitate begins to form, add ammonia to dissolve it.

If a white precipitate remains insoluble in ammonia, filter it out. Add hydrochloric acid to slight acidity and then 10 cc. of magnesia mixture. Add ammonia drop by drop, stirring constantly, until the solution is neutral. Note the depth of the solution in the beaker and add ammonia until the volume is increased by one-third. Stir and let the solution stand four hours.

$$(NH_4)_3PO_4+MgCl_2=2NH_4Cl+MgNH_4PO_4.$$

Filter and wash with dilute ammonia. Dry the precipitate. Separate the precipitate from the filter paper. (See Fig. 31.) Burn the paper on a platinum wire, letting the ash fall into a crucible; add the precipitate to the crucible and heat to low redness over a Bunsen burner until the precipitate is white. Then heat with a blast lamp ten minutes.

$$2MgNH_4PO_4=Mg_2P_2O_7+2NH_3+H_2O.$$

The temperature must not be raised until the precipitate is white. If the filter paper is burned in contact with the precipitate some phosphorus may be reduced and attack the platinum.

Cool in a desiccator and weigh. The weight of $Mg_2P_2O_7$ multiplied by 10 expresses the percentage of P in the ore.

PHOSPHORUS IN ORE

Emmerton's Volumetric Method

Outline. The ore is dissolved, the phosphorus precipitated as ammonium phosphomolybdate and filtered. The precipitate is dissolved in ammonium hydrate, the molybdic acid reduced with zinc and titrated with standard potassium permanganate solution, the quantity of phosphorus being measured indirectly.

Reagents. *Sodium carbonate.* Na_2CO_3;

Dilute nitric acid (2 : 3);

Dilute sulphuric acid; 25 cc. of sulphuric acid (1.84) diluted to one liter with water.

Standard solution of $KMnO_4$; 2.83 gms. of $KMnO_4$ dissolved in water and the solution diluted to one liter. This solution may be standardized by taking a definite weight of a phosphate in which the percentage of phosphorus is known, dissolving and precipitating the phosphorus as ammonium phosphomolybdate, filtering and dissolving the yellow precipitate in ammonia, reducing and titrating exactly as given below in the method for ore; or the permanganate solution may be standardized against iron as directed on page 51. When the value in iron has been determined multiply the value by 0.88163, the ratio of molybdic acid to iron, and the product by 0.01794, the ratio of phosphorus to molybdic acid; the result will be the value of 1 cc. of the permanganate solution in terms of phosphorus. Since the ratio of phosphorus to molybdic acid in the yellow precipitate is not constant under varying conditions of formation, great care should always be taken to produce the yellow precipitate under as nearly the same conditions as possible.

Molybdate solution. (See p. 76.)

Wash solution of acid ammonium sulphate: to one liter of water add 16 cc. of ammonia (sp.gr. 0.90) and 25 cc. sulphuric acid (sp.gr. 1.84).

A reductor charged with *amalgamated zinc.* (See pp. 57 and 58.)

P in Ore. Weigh 3 gms. of ore (or a factor weight) and proceed according to the method on page 76 until the yellow precipitate has been formed. Filter on a 9-cm. filter paper and wash with acid ammonium sulphate solution until 2 or 3 cc. of the wash water do not give a brown color on the addition of a drop of ammonium sulphide.

The precipitate must be washed free from molybdic acid because the phosphorus is measured indirectly by titrating back to molybdic acid the molybdenum oxide which has been reduced from the yellow precipitate.

Pour 5 cc. of ammonia and 20 cc. of water into the flask in which the precipitate was formed to dissolve any adhering precipitate, and then pour this solution on the precipitate in the filter, letting the filtrate to run into a 250-cc. beaker.

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 24NH_4OH = 12(NH_4)_2MoO_4 + (NH_4)_3PO_4 + 12H_2O.$$

Rinse the flask into the beaker and wash the filter with water until the solution in the beaker measures about 60 cc. Add 10 cc. of sulphuric acid (1.84) and pass the solution through the reductor, after having passed through 100 cc. of warm dilute sulphuric acid (25 cc. sulphuric acid (1.84) in 1 liter).

The equation $2MoO_3 + 3H_2 = Mo_2O_3 + 3H_2O$ expresses the complete reduction of MoO_3 to molybdic oxide, but reduction is not complete when the solution passes through the reductor in the manner here described. Emmerton gives $Mo_{12}O_{19}$ as the form he obtained, and Blair and Whitfield give $Mo_{24}O_{37}$ as the product of the method as carried out by them. It is evident, therefore, that the operator must always carry on the reduction in the same manner and under the same conditions.

Then follow with 200 cc. of the same dilute sulphuric acid in the manner described on page 58, being careful to keep the end of the small tube of the reductor below the surface of the solution in the flask to prevent reoxidation. Remove the flask from the reductor, washing into it from the reductor any adhering solution. Titrate with standard permanganate solution.

The solution, after passing through the reductor, should be bright green in color; if brown it is not sufficiently reduced and must be discarded. In titrating with permanganate, the solution of the yellow precipitate changes in color from green through brown and pinkish yellow to colorless. When the solution becomes colorless, add the permanganate solution, drop by drop—shaking—until a pink color is produced, which lasts for one minute.

Subtract from the reading of the burette the amount given by a blank determination in which the same quantities of reagents are used as in the regular process. (See p. 58.) Multiply the value of 1 cc. in phosphorus by the number of cubic centimeters thus obtained. Divide this product by the weight of ore taken and multiply the result by 100. (See p. 31.)

Reduction with Powdered Zinc. Instead of reducing the molybdic acid by means of the reductor, reduction may be effected by adding powdered zinc to the solution of yellow precipitate. This operation is best carried out by returning the solution of the yellow precipitate to the flask in which the precipitate was formed and washing the filter until the volume of solution is about 75 cc. Then add 5 gms. of powdered zinc (through 100-mesh) and 15 cc. of sulphuric acid (sp.gr. 1.84). Close the flask at once with a rubber stopper carrying a delivery tube which dips into a beaker containing a saturated solution of sodium bicarbonate. After standing thirty minutes the zinc should be in solution and the molydbic acid reduced, when it is ready to be titrated with standard permanganate solution. A blank should be run at the same time and the necessary correction made for all determinations.

When this method of reduction is used, the factor expressing the ratio of molybdic acid to iron is 0.85714 instead of 0.88163, there being this difference in the degree of reduction of the molybdic acid by the two methods.

PHOSPHORUS IN ORE

Pemberton's Alkali-metric Method

Outline. By this method the ore is treated in the manner described on page 76 to the formation of the yellow precipitate. After the yellow precipitate is filtered off it is washed to free it from acids, and its phosphorus content measured indirectly by titrating with an alkali.

Reagents. *Wash solution of nitric acid;* 13 cc. nitric acid (sp.gr. 1.42) in 1 liter of water.

Wash solution of potassium nitrate. Dissolve 1 gm. KNO_3 in 1 liter of water.

Phenolphthalein solution. Dissolve 1 gm. of $C_{20}H_{14}O_4$ in 500 cc. alcohol, C_2H_6O (95 per cent).

Standard solution of sodium hydroxide. Add to 100 gm. of pure NaOH an amount of water just insufficient to dissolve it completely. Let it settle in a tall, covered vessel. Most of the sodium carbonate which is present as an impurity remains undissolved. Add one drop of a solution of barium hydroxide to precipitate CO_2. If a precipitate forms add another drop and repeat until a precipitate ceases to form. Withdraw 17 cc. of the solution with pipette and dilute to 1 liter. This solution must be protected from the CO_2 of the air.

Standard nitric acid. Twenty-one cubic centimeters of nitric acid (sp.gr. 1.42) diluted to 1 liter.

These standard solutions must be tested against each other and the stronger one diluted until they are of equal strength, as follows:

With the pipette take out 20 cc. of the sodium hydroxide solution, dilute it with 60 cc. of water, add 3 drops of phenolphthalein solution and titrate with the standard nitric acid until the pink color just disappears.

Phenolphthalein is red with alkalies and colorless with acids. It is a weak acid and is very slightly dissociated in acid solutions. According to Ostwald's theory it is colorless when undissociated, but when combined with alkali hydroxide, the salt is dissociated, revealing the red color of the cation.*

If the solutions are not of equal strength dilute the stronger and test again.

Suppose 19.4 cc. of nitric acid solution were required to neutralize 20 cc. of sodium hydroxide solution; then the volume

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* Ostwald, "Foundations of Analytical Chemistry," 124. For another explanation of this reaction see Stieglitz, Jour. Amer. Chem. Soc., 25, 1112. Kober and Marshall, Eighth International Congress of Applied Chemistry, 6, 157.

of nitric acid solution remaining must be increased according to the ratio 19.4 : 20.

19.4 : 20 = vol. nitric acid remaining to be diluted: final vol. nitric acid.

The difference between the third and fourth terms represents the amount of water to be added.

Standardization of the Sodium Hydroxide Solution. When the solutions are of equal strength the sodium hydroxide solution is standardized by weighing 2 gms. of an ore in which the phosphorus has been previously determined, and carrying it through the process as given below. The weight of phosphorus being known and the number of cubic centimeters of sodium hydroxide solution required to complete the reaction below having been determined, the value of 1 cc. of the solution is given by dividing the weight of phosphorus by the number of cubic centimeters of sodium hydroxide solution required for the reaction.

$$2(NH_4)_3PO_4 \cdot 12MoO_3 + 46NaOH$$
$$= 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O.$$

Instead of using a standard ore, yellow precipitate may be used. This is prepared from a phosphate in the manner described for its precipitation from a solution of an ore, and carefully dried at 150° C. Weigh about 0.2 gm. of yellow precipitate, add standard sodium hydroxide solution, 10 cc. at a time, until the precipitate is dissolved. Dilute with 50 cc. of water. Add 3 drops of phenolphthalein solution and titrate with the standard nitric acid. The volume of nitric acid used, deducted from the volume of sodium hydroxide solution, leaves the number of cubic centimeters of sodium hydroxide solution required to neutralize the yellow precipitate. Multiply the weight of yellow precipitate by the factor for phosphorus, 0.0163, and divide this by the number of cubic centimeters of sodium hydroxide solution used.

P in Ore. Weigh 2 gms. of ore and proceed exactly in the manner described on page 76 until the yellow precipitate has formed and settled. Filter on a 9-cm. filter paper and wash 5 times with 1 per cent solution of nitric acid, then wash with potassium nitrate solution until the acid has all been removed. Place the filter paper and its contents in the flask in which the precipitate was made and add to the flask standard sodium hydroxide solution, 20 cc. at a time, with the pipette, shaking to disintegrate the filter, until the yellow precipitate is all dissolved. Dilute with 50 cc. of water, add 3 drops of phenolphthalein solution, and titrate the excess of alkali with the standard nitric acid. Take the difference between the number of cubic centimeters of nitric acid used in the titration and the total volume of sodium hydroxide solution added and multiply the result by the value of 1 cc. in phosphorus.

PHOSPHORUS IN THE PRESENCE OF TITANIUM

Weigh 2 gms. (or a factor weight) of ore, add 30 cc. of hydrochloric acid and heat to dissolve as much of the ore as possible. Evaporate the solution to dryness and bake. (See p. 70.) Add 25 cc. of hydrochloric acid and 25 cc. of water. Heat to dissolve the iron, and filter.

If titanium is present, when the residue is washed with water, the filtrate often runs through turbid. This can be avoided by washing with dilute nitric acid, or better, with an acid solution of ammonium nitrate (p. 76). The filtrate contains the greater part of the phosphoric acid, but a considerable part may remain with the residue.

Treatment of the Residue. Fuse the residue with sodium carbonate and extract with water.

Sodium phosphate and silicate go into solution and sodium titanate remains insoluble.

Filter, acidify the filtrate with nitric acid, evaporate the solution to dryness, and bake at 120° C. Cool, moisten the residue with nitric acid, and add water to dissolve all except silica. Filter from the silica. Concentrate the filtrate to small bulk by evaporation, nearly neutralize with ammonia, and precipitate the phosphorus with ammonium molybdate.

Treatment of the Filtrate. Evaporate the filtrate until solids begin to separate; then add nitric acid and proceed according to the method on page 77, until the yellow precipitate is filtered and washed. This yellow precipitate, and that obtained from the insoluble residue, are dissolved in ammonia according to the method on page 81. If the solution runs through turbid, and a gelatinous residue remains on the filter, heat the solution for some time and filter. Treat both these residues with nitric acid and precipitate the phosphorus from the resulting solution with ammonium molybdate. Filter out this yellow precipitate, dissolve it in ammonia, and add it to the main solution. The phosphorus may now be determined by either precipitating with magnesia mixture (p. 79), or by adding sulphuric acid, reducing and titrating by Emmerton's method (p. 80).

ALUMINA IN ORE

PHOSPHATE METHOD

Reagents. *Ammonium phosphate solution.* Dissolve 100 gms. of $(NH_4)_3PO_4$ in 1 liter of water.

Sodium thiosulphate solution. Dissolve 200 gms. $Na_2S_2O_3$ in water and dilute to 1 liter.

Acetic acid, $CH_3CO \cdot OH$, 80 per cent.

Ammonium acetate. Dissolve 200 gms. $CH_3CO \cdot ONH_4$ in water and dilute to 1 liter.

Al_2O_3 in Ore. Weigh 1 gm. of ore and proceed according to the method for silica (p. 71) until the silica has been filtered off and washed. Cool the filtrate and dilute it to about 400 cc.; add 30 cc. of ammonium phosphate solution, and then add ammonia until a faint permanent precipitate is formed. Add 1.5 cc.

of strong hydrochloric acid. Stir until the precipitate is dissolved and add 50 cc. of sodium thiosulphate solution.

$$2FeCl_3+2Na_2S_2O_3=2NaCl+2FeCl_2+Na_2S_4O_6.$$

The aluminum is precipitated as the neutral phosphate from a boiling solution faintly acid with acetic acid, and it comes down free from iron, if the iron has been reduced with sodium thiosulphate.

Heat just to the boiling-point and add 8 cc. of acetic acid mixed with 15 cc. of ammonium acetate solution and boil ten minutes. Let the precipitate settle a few minutes, filter as rapidly as possible, and wash ten times with hot water. Ignite the filter and its contents at a low temperature until the carbon is destroyed, and then at the highest temperature of the muffle furnace or the blast lamp. Cool and weigh as $AlPO_4$, multiply by 0.4184, the factor for Al_2O_3.

MANGANESE IN ORE

VOLHARD'S METHOD

Outline. The ore is dissolved in hydrochloric and nitric acids. These acids are replaced with sulphuric. The solution is diluted and nearly neutralized with sodium carbonate. An excess of zinc oxide is added and the solution is titrated hot with standard potassium permanganate solution.

Reagents. *Emulsion of pure zinc oxide.* ZnO shaken with a sufficient amount of water to form an emulsion.

Saturated solution of crystallized sodium carbonate, $Na_2CO_3 \cdot 10H_2O$.

Standard potassium permanganate solution. (See p. 51.) This solution may be made of such strength that 1 cc. equals 0.1 per cent manganese for the quantity of ore taken. It is standardized against an iron ore in which the percentage of manganese is known. Or it may be standardized against iron in the usual way and its value in manganese calculated from the following reactions.

$$6MnSO_4+4KMnO_4+5ZnSO_4+14H_2O$$
$$=4KHSO_4+7H_2SO_4+5Zn(HMnO_3)_2.$$

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

The first reaction is that upon which this method depends; the second is the familiar reaction of potassium permanganate with iron.

It will be observed that two molecules of potassium permanganate oxidize 10 atoms of iron in the one case, and 3 atoms of manganese in the other. The value of the solution in manganese, therefore, may be calculated from its value in iron by multiplying the value in iron by the factor $\frac{3(54.93)}{10(55.84)}=0.2951$.

Mn in Ore. Treat 1 gm. of ore in a casserole with 15 cc. of hydrochloric acid. Add 5 cc. of nitric acid to oxidize the iron. Heat to complete the decomposition. Add 25 cc. of water and 5 cc. of sulphuric acid. Evaporate until the sulphuric acid begins to fume. Cool, dilute to 150 cc. with water and heat to dissolve sulphates.

If it is suspected that any manganese remains undissolved, filter and burn the residue in a platinum crucible. Treat the residue with a little hydrofluoric acid (1 cc.) and a few drops of sulphuric acid and evaporate to sulphuric acid fumes. Dilute the solution in the crucible and add it to the main solution.

Nearly neutralize the sulphate solution with a solution of sodium carbonate. Transfer it to a 500-cc. graduated flask and dilute with water to the graduation. Mix well, take out 50 cc. with the pipette and let it run into a small Erlenmeyer flask. Add 50 cc. (an excess) of zinc oxide and titrate with potassium permanganate solution.

A sufficient quantity of zinc oxide is added to neutralize the solution, precipitate the iron, and provide an excess which will keep the solution neutral as titration goes on. Sulphuric acid is formed by the reaction, and the solution should be kept neutral for the reaction to proceed according to the equation given above.

Keep the solution hot while titrating, but do not let it boil. After each addition of permanganate, shake vigorously and let the precipitate settle. If kept hot it settles readily and the pink end-point can be detected in the layer of clear solution above the precipitate.

The result obtained by this titration must be multiplied by 10, since only 0.1 of the whole was titrated.

MANGANESE IN ORE

Titration with Sodium Arsenite

Outline. The hydrochloric acid in which the ore is dissolved is displaced by sulphuric. The solution is then diluted and the manganese is oxidized to permanganic acid by adding ammonium persulphate and silver nitrate. The silver is then precipitated with sodium chloride and the solution titrated with a standard solution of sodium arsenite.

Reagents. *Dilute sulphuric acid* (1 : 1).

Ammonium persulphate, $(NH_4)_2S_2O_8$.

Solution of silver nitrate. Dissolve 66.66 gms. $AgNO_3$ in one liter of water. Dilute 20 cc. of this solution to 1 liter for use. Each 15 cc. contains 0.02 gm. $AgNO_3$.

Standard solution of sodium arsenite. A stock solution is made by dissolving 30 gms. sodium carbonate in water, adding 10 gms. of arsenious acid, boiling until the acid is in solution, and diluting to 1 liter. Dilute about 125 cc. of the stock solution to 2000 cc. and standardize this solution against a steel or an ore in which the manganese has been previously determined.

Sodium chloride, 0.2 per cent solution. Dissolve 2 gms. NaCl in water and dilute the solution to 1 liter.

Mn in Ore. Weigh 1 gm. of ore and transfer it to a casserole or beaker. Add 25 cc. of hydrochloric acid and 5 cc. of sulphuric acid. Heat until the sulphuric acid fumes. Cool, add 25 cc. of water and heat until the salts are dissolved.

If the insoluble residue is suspected of containing manganese, filter and burn the residue in a platinum crucible. Add 2 or 3 drops of dilute sulphuric acid (1 : 1) and about 5 cc. of hydrofluoric acid. Evaporate until the sulphuric acid fumes. Add 5 cc. of the dilute sulphuric acid (1 : 1). Warm until the residue is in solution and add it to the main solution.

Transfer the solution to a 50-cc. graduated flask. Dilute to the mark and mix. With a pipette transfer 10 cc. of the solution to a 150-cc. Erlenmeyer flask. Add 15 cc. of the silver nitrate solution and about 1 gm. of moist ammonium persulphate; heat over a flame or water bath until the pink color of permanganic acid appears.

$$2MnSO_4+4(NH_4)_2S_2O_8+8H_2O=2H_2MnO_4+4(NH_4)_2SO_4+6H_2SO_4.$$

The silver nitrate is a catalytic agent and hastens the above reaction.*

The reaction takes place equally well in nitric acid or sulphuric acid or a mixture of the two. It is essential to have a sufficient amount of silver nitrate present.

While the permanganic acid is forming remove the flask from the heat and place it in a cold water bath. When cool, dilute to about 100 cc., add 7 cc. of sodium chloride solution, and titrate with sodium arsenite solution until the pink color is discharged.

If the silver is not precipitated with sodium chloride, the manganese is reoxidized, and the end-point is not permanent.

Since a standard solution of sodium arsenite sometimes changes in strength suddenly and unexpectedly, some chemists prefer to titrate with a standard solution of ammonium ferrous sulphate instead. See sodium bismuthate method, p. 92.

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* Marshall, Proc., Royal Soc. Edin., 1900, p. 225.

MANGANESE IN ORE

COLOR METHOD

Treat 1 gm. of ore in the manner described in the preceding method until it is dissolved and the solution is diluted to 50 cc. in a graduated flask. Mix and pour the solution through a dry filter paper. With the pipette transfer 10 cc. to an 8-in. test-tube, 1 in. in diameter. Add 15 cc. of silver nitrate solution and about 1 gm. of ammonium persulphate. Heat in a water bath and when the color of permanganic acid appears, remove the test-tube from the heat and place it in a cold water bath. Compare this solution in a colorimeter (see p. 44) with a similar solution prepared in exactly the same way from a standard ore in which the manganese is known. Instead of a standard ore a standard steel may be used, in which case dissolve 0.2 gm. of the steel in 10 cc. of nitric acid (sp.gr. 1.2), add 15 cc. of the silver nitrate solution, and 1 gm. of ammonium persulphate, and proceed according to the method given above.

MANGANESE IN ORE

SODIUM BISMUTHATE METHOD

Outline. The ore is decomposed with hydrofluric and sulphuric acids. After the hydrofluoric acid has been removed by evaporation, dilute nitric acid is added, the solution cooled and the manganese oxidized to permanganic acid with sodium bismuthate. The excess of sodium bismuthate is filtered off, a measured volume of standard ferrous sulphate solution added to the filtrate and the excess of ferrous sulphate titrated with standard potassium permanganate solution.

Reagents. *Hydrofluoric acid,* HF.

Dilute nitric acid, (1 : 3) (sp.gr. 1.135).

Dilute nitric acid, dilute 30 cc. HNO_3 (sp.gr. 1.42) to 1 liter with water.

Sodium bismuthate, $NaBiO_3$.

Standard potassium permanganate solution, 1 gm. $KMnO_4$ to the liter. After this solution has been made according to the method given on page 51, determine the exact amount of manganese it contains per cc. by standardizing it against iron in the usual way. From its iron value calculate the weight of manganese in each cubic centimeter of the permanganate solution using the following equation:

$$10\ \text{Fe} : 2\text{Mn} = \text{value in Fe per cubic centimeter} : \text{weight of Mn per cubic centimeter.}$$

Ferrous sulphate, 25.5 gms. $FeSO_4 \cdot 7H_2O$ to the liter. It is convenient to have this solution of such strength that 1 cc. is equivalent to 0.1 per cent manganese.

The value of the ferrous sulphate solution in terms of the permanganate solution is determined as follows:

Measure into a 250-cc. Erlenmeyer flask 50 cc. of cold nitric acid (sp.gr. 1.13). Add about 0.5 gm. of sodium bismuthate. Agitate and filter through asbestos. Wash the filter with 50 cc. of cold 3 per cent solution of nitric acid. Add 50 cc. of ferrous sulphate solution and titrate with potassium permanganate solution to a pink color.

Mn in Ore. Treat 1 gm. of ore (if the ore contains more than 2 per cent manganese use 0.5 gm.) in a platinum crucible with 4 cc. of strong sulphuric acid, 10 cc. of water, and 10–20 cc. of hydrofluoric acid. Evaporate until the sulphuric acid fumes freely. Cool and dissolve in 25 cc. of dilute nitric acid (1 : 3). Transfer the solution to a 200-cc. Erlenmeyer flask, using 25 cc. of nitric acid (1 : 3) to rinse the crucible. Cool and add 2 or 3 gms. of sodium bismuthate, and agitate the contents of the flask for several minutes.

Sodium bismuthate in the presence of an excess of nitric acid oxidizes the manganese to permanganic acid. The permanganic acid is stable in nitric acid of 1.135 sp.gr. if the solution is cold; if hot the excess of the bismuth salt is decomposed and the nitric acid then reacts with the permanganic acid.

Dilute the solution with 50 cc. of 3 per cent nitric acid and filter through asbestos into a 300-cc. Erlenmeyer flask. Wash the asbestos with 50 to 100 cc. of cold 3 per cent nitric acid. Run into the solution in the Erlenmeyer flask 50 cc. of standard ferrous sulphate solution from a pipette. If the permanganate color is not discharged, add more ferrous sulphate solution, accurately measured, until the color is discharged. Then titrate back to pink color with standard permanganate solution. Having thus determined the number of cubic centimeters of ferrous sulphate solution required to react with the manganese in the sample, and knowing its value per cubic centimeter in manganese, calculate the percentage of manganese in the sample.

For example, suppose 24 cc. of ferrous sulphate solution are equivalent to 100 cc. of potassium permanganate solution, and in the determination 50 cc. of ferrous sulphate solution are added to the solution and the excess titrated back with 25 cc. of potassium permanganate solution; 44 cc. of the ferrous sulphate solution were, therefore, required to react with the manganese in the sample, and this number is to be multiplied by its value in manganese.

In addition to the method of standardizing given above under reagents, after the solutions have been tested against each other, the ferrous sulphate solution may be standardized by taking an ore in which the manganese has been previously determined, and running it according to the above process.

Instead of titrating with ferrous sulphate, a standard solution of arsenious acid may be used. (See p. 90.)

MANGANESE IN ORE

JULIAN'S METHOD

Outline. The ore is decomposed with hydrochloric acid and the solution taken nearly to dryness. Nitric acid is added, the solution boiled and the manganese is oxidized to manganese dioxide by adding potassium chlorate. After the solution is cooled and diluted a measured volume of standard solution of hydrogen peroxide is added and the excess of peroxide is titrated with standard potassium permanganate solution.

Reagents. *Hydrofluoric acid*, HF.

Potassium chlorate, $KClO_3$.

Standard potassium permanganate solution, 1.7375 gms. $KMnO_4$ per liter.

Hydrogen peroxide. Dilute 1 lb. of hydrogen peroxide with about 500 cc. of water, add 200 cc. of sulphuric acid (sp.gr. 1.84), and dilute the solution to 9000 cc. with water.

Determine the relative values of these two solutions as follows:

Boil 60 cc. of strong nitric acid for about five minutes. Cool and dilute it to about 300 cc. with cold water. Add to the cold solution 50 cc. of the hydrogen peroxide solution and titrate it with the standard permanganate solution.

The hydrogen peroxide solution is standardized by weighing a sample of ore in which the manganese has been previously determined and treating it according to the method given below.

Mn in Ore. Weigh 1 gm. of ore and transfer it to a beaker. Add 20 to 30 cc. of strong hydrochloric acid and heat to dissolve the manganese. If the insoluble residue is suspected of containing manganese, add a few drops of hydrofluoric acid and evaporate the solution almost to dryness.

Manganese-free glass must be used if hydrofluoric acid is employed.

Add 75 cc. of strong nitric acid. Boil until clear. Add potassium chlorate, a little at a time, until green chlorine fumes cease to come off. Then add another crystal of potassium chlorate and boil five minutes.

$$5Mn(NO_3)_2+2KClO_3+4H_2O=5MnO_2+2KNO_3+8HNO_3+Cl_2.^*$$

Cool the solution, dilute it to about 300 cc. with cold water and add with the pipette 50 cc. of hydrogen peroxide solution.

$$MnO_2+H_2O_2+2HNO_3=Mn(NO_3)_2+2H_2O+O_2.$$

After the manganese dioxide has dissolved determine the excess of hydrogen peroxide by titrating with standard permanganate solution.

$$5H_2O_2+2KMnO_4+6HNO_3=2KNO_3+2Mn(NO_3)_2+8H_2O+5O_2.$$

The equivalent in hydrogen peroxide solution of potassium permanganate used in titration is deducted from the total volume of hydrogen peroxide solution added and the remainder which represents the quantity of hydrogen peroxide that reacted with manganese dioxide is multiplied by its value per cubic centimeter in manganese.

LIME IN ORE

Outline. The ore is decomposed by fusion with a flux. After dissolving the fusion in hydrochloric acid, the silica is dehydrated and filtered from the solution. The iron and aluminum are then precipitated from the filtrate with ammonia, and filtered. The calcium is then precipitated from the filtrate with ammonium oxalate, filtered, burnt to CaO and weighed.

Reagent. *Ammonium oxalate solution.* Dissolve 40 gms. $(NH_4)_2C_2O_4+H_2O$ in a liter of water.

CaO in Ore. Weigh 1 gm. of ore, transfer it to a platinum

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* Julian, "Quantitative Analysis," 236.

crucible, and proceed according to the method for silica (p. 71) until the silica has been filtered from the solution. Make the filtrate alkaline with ammonia to precipitate the hydrates of iron and aluminum. Boil off the excess of ammonia.

Aluminum hydrate is somewhat soluble in ammonia.

Let the precipitate settle, filter, and wash.

The precipitate may be used for the determination of iron or aluminum.

Acidulate the filtrate with hydrochloric acid and evaporate it down to 150 cc. Add 10 cc. of ammonia and 5 cc. of ammonium oxalate solution. Boil until the calcium oxalate precipitate is formed. Let the beaker stand in a warm place until the precipitate settles. Filter and wash with hot water.

Before filtering add a few drops of the precipitant to the clear supernatant solution to test for unprecipitated calcium.

See also the method of precipitation given on page 162.

Retain the filtrate for the determination of magnesia.

Burn the precipitate in a platinum crucible, cool, and weigh as CaO.

For the method of titrating calcium oxalate and for the reactions see the method for lime in limestone, pages 163 and 164.

MAGNESIA IN ORE

Reagent. *Solution of ammonium phosphate.* Dissolve 100 gms. $(NH_4)_2HPO_4$ in 1 liter of water.

MgO in Ores. Acidulate with hydrochloric acid the filtrate from the calcium oxalate; see the method above for lime. Add 5 cc. of ammonium phosphate solution and reduce the volume by evaporation to 200 cc. Cool the solution, stir the cool solution with a stirring machine (Fig. 60), and add 25 cc. of ammonia, drop by drop. Stir continuously for one hour, let settle, and filter; or, if possible, let stand over night before filtering. Wash the precipitate thoroughly with dilute ammonia (1 : 4). Dry, and separate the precipitate from the filter paper. (See Fig. 31.) Heat the precipitate in a crucible with a Bunsen burner at a low red heat until the precipitate is white. Burn the filter paper on a platinum wire and let the ash fall into the crucible. After the carbon has all been burnt and the precipitate is white, heat for a few minutes at a high temperature with the blast lamp. Cool in the desiccator and weigh the $Mg_2P_2O_7$. The factor for MgO is 0.3621.

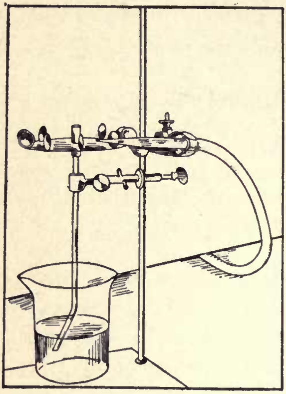

FIG. 60.—Mechanical Stirrer Driven by a Jet of Compressed Air.

For notes and precautions, see the method for magnesia in limestone page 165.

TITANIUM IN ORE

Outline. The ore is decomposed with potassium pyrosulphate and sulphuric acid, the solution diluted, and the silica filtered from it. The filtrate is nearly neutralized with ammonia, sodium sulphite added to reduce the iron, and the titanium precipitated by boiling after adding acetic acid and sodium acetate. The impure metatitanic acid is filtered and purified by decomposing it and repeating the process.*

Reagents. *Potassium pyrosulphate,* $K_2S_2O_7$.

Sodium sulphite. Dissolve 20 gms. $Na_2SO_3+7H_2O$ in 100

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* Gooch, Chem. News, p, 55. Drown, Trans. Amer. Inst. of Min. Eng., 10, p. 137.

cc. of water and add sulphuric acid to render the solution distinctly acid.

Acetic acid, $C_2H_4O_2$.

Sodium acetate, $NaC_2H_3O_2+3H_2O$.

Sodium carbonate, fused Na_2CO_3.

TiO_2 in Ore. Weigh 1 gm. of very finely pulverized ore and mix it with 15 gms. of potassium pyrosulphate in a large platinum crucible. Heat gently to melt, and raise the temperature gradually to a low red heat and keep the mass in quiet fusion thirty minutes.

Too high a temperature drives off sulphuric acid and spoils the fusion.

Cool and add about 20 cc. of strong sulphuric acid. Heat until the contents of the crucible are perfectly liquid; then cool.

If a sufficient amount of acid was added the fusion remains liquid after cooling.

Pour the solution into 400 cc. of cold water in a 600-cc. beaker. Rinse off the crucible and stir the solution until only silica remains undissolved. Filter, and to the filtrate add ammonia carefully, until the precipitate dissolves slowly on stirring. Warm and add sodium sulphite solution slowly, a little at a time, until the color, at first produced, entirely disappears.

$$Fe_2(SO_4)_3+Na_2SO_3+H_2O=2FeSO_4+Na_2SO_4+H_2SO_4.$$

Do not heat to boiling, as titanium oxide in that case would separate as a milky precipitate and render it difficult to determine when the reduction is complete.

If the precipitate forms and the solution becomes turbid, add a few drops of hydrochloric acid to clear it and continue the addition of the sulphite solution, giving plenty of time for the reaction to take place.

After the addition of about 50 cc. of the sulphite solution the titanium solution should be colorless and have a strong odor of sulphur dioxide. If the color persists, the ferric salts are not all reduced. Continue the addition of the sulphite solution and warm until the color disappears. Add 50 cc. of acetic acid and 20 gms. of sodium acetate and boil vigorously three minutes.

$$Ti(SO_4)_2+4NaC_2H_3O_2+3H_2O=2Na_2SO_4+4HC_2H_3O_2+TiO(OH)_2.$$

Let the precipitate of impure metatitanic acid settle, filter, and wash with hot water. Place the filter with residue in a platinum crucible, burn off the filter paper, and weigh the impure titanium oxide. Add to the titanium oxide ten times its weight of sodium carbonate and fuse. Boil the fusion with water until it is disintegrated. Filter and wash. Wash the residue off the filter into a beaker. Let the precipitate settle and decant the clear liquid back through the filter. Dissolve the remaining titanium precipitate adhering to the filter paper with a little hydrochloric acid, letting it run through the paper to the residue in the beaker. Burn the filter paper at a low heat and add the ash to the beaker. Dissolve the contents of the beaker in hydrochloric acid, then add 10 cc. of dilute sulphuric acid and evaporate until the sulphuric acid just begins to fume. Cool and dilute with 25 cc. of water. Boil, filter, and wash. Dilute the filtrate to 250 cc., nearly neutralize it with ammonia, and add to it about 20 cc. of sodium sulphite solution to reduce the remaining traces of iron. Add 30 cc. of acetic acid and 10 gms. of sodium acetate. Stir and let the precipitate of metatitanic acid settle, filter, wash with hot water, burn, and weigh as TiO_2.

TITANIUM IN ORE

Weller's Method

Outline. The ore is fused with potassium pyrosulphate, treated with sulphuric acid and dissolved in water. The solution is filtered and diluted to a definite volume in a graduated flask; an aliquot part is taken out and treated with hydrogen peroxide, which gives it a yellow color, the intensity of which depends upon the quantity of titanium present. This is compared with a standard solution in which the titanium is known.*

Reagents. *Hydrogen peroxide,* 3 per cent solution free from hydrofluoric acid.

Potassium pyrosulphate, $K_2S_2O_7$.

Dilute sulphuric acid, (3 : 100).

Standard solution of titanium sulphate. Weigh 0.6 gm. of potassium titanic fluoride which has been recrystallized several times in a platinum crucible with a little water and concentrated sulphuric acid, the excess of acid having been expelled by gentle ignition. Dissolve in a little concentrated sulphuric acid and add dilute sulphuric acid (3 : 100) to make the volume 100 cc. One cubic centimeter of this solution corresponds to 0.002 gm. of TiO_2.

This solution may also be prepared by igniting pure TiO_2 at a dull red heat to a constant weight, melting cautiously with potassium bisulphate until TiO_2 dissolves and the fusion becomes clear. Cool and dilute the solution to a definite volume with dilute sulphuric acid (3 : 100). Then, with the pipette, take out 20 cc. and determine the TiO_2 by the gravimetric method given on page 99 and dilute the remaining solution with weak sulphuric acid solution (3 : 100) until 1 cc. contains 1 mg. of TiO_2.

Standard solution of ferric sulphate. Prepare a dilute solution of $Fe_2(SO_4)_3$ in dilute sulphuric acid and determine its value per cubic centimeter in iron by means of standard permanganate solution. The ferric sulphate solution may be prepared from ferrous sulphate by dissolving the ferrous sulphate in dilute sulphuric acid and oxidizing it at the boiling-point with nitric acid according to the method given on page 53, evaporating

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* Berichte, 15, p. 2593. Hillebrand, Jour. Amer. Chem. Soc., 1895, p. 718.

the solution until sulphuric acid fumes are evolved and diluting with water.

TiO_2 in Ore. Weigh 0.5 gm. of ore and fuse it with 5 gms. of potassium pyrosulphate in a platinum crucible at a red heat for at least ten minutes. Cool, add 5 cc. of sulphuric acid, melt again, cool, and put the crucible with its contents in a beaker containing 200 cc. of water and 5 cc. of sulphuric acid. Warm to about 90° C. and stir to dissolve all that is soluble. Filter into a 250-cc. graduated flask and dilute the solution to the graduation with sulphuric acid solution (3 : 100).

Measure with a pipette 50 cc. of the titanium solution and transfer it to one of a pair of Nessler or other colorimetric tubes. In the other tube place that quantity of ferric sulphate solution which contains as much iron as there is in the solution of ore in the first tube.

Since the iron gives a slight color to the solution it is necessary to have an equal quantity in each tube.

Dilute the ferric sulphate solution in the second tube to 50 cc. with dilute sulphuric acid (3 : 100). Add to each tube 5 cc. of hydrogen peroxide.

Hydrogen peroxide added to a sulphuric acid solution of titanium produces a strong yellow color, the intensity of which depends on the amount of titanium present, and is independent of the excess of hydrogen peroxide. The change of color is much more sensitive with small amounts of titanium. Therefore the method is suitable only for materials low in titanium. If the titanium is high, the gravimetric method may be used; or the sulphate solution of titanium may be diluted to a large volume in a graduated flask and a suitably small portion withdrawn for the colorimetric determination.

Now run into the second tube from a burette, standard titanium solution until the color produced is the same as that in the first tube. The quantity of titanium in the volume of standard solution added to the second tube is equal to that in the solution of ore in the first tube, which represents one-fifth of the sample.

Instead of Nessler tubes, Eggertz tubes or a colorimeter may be used. If the determination is to be made with a colorimeter of the third type described on page 44, make the solutions to the same volume in the following manner. Prepare the solutions in two large test-tubes, each with a graduation to indicate a volume of 50 cc. From the 250-cc. flask containing the solution of ore transfer 50 cc. to one of the tubes; to the other, add a sufficient quantity of ferric sulphate solution to contain the same amount of iron that is contained in 50 cc. of the solution of ore. Add to this 5 cc. of the standard titanium solution (or more if necessary, accurately measured) and make up to the graduation with dilute sulphuric acid (3 : 100). Then add to each tube 5 cc. of solution of hydrogen peroxide, mix, and transfer to the colorimeter for comparison.

Rare Elements in Iron Ore. Methods for determining other elements in ores may be found by referring to the index.

ANALYSIS OF IRON AND STEEL

Sampling. Sampling is best done, as explained on page 9, while the metal is still molten. The samples are taken with an iron hand-ladle while the metal is being poured. If the metal is poured into large ladles for transfer to another part of the plant, one sample is taken from each ladle, and the drillings from these are mixed for the final sample. In the case of cast-iron, the molten metal is poured from the sampling ladle, either upon an iron plate or into a mold. If the sample is to be crushed after cooling it is best to let it cool in a thin layer. If it is to be drilled, the mold should be an inch or so in depth. A very convenient mold (Fig. 61) described by Camp * consists of two sections, which gives a casting 6 ins. long and 1¼ ins. thick, to which is attached at one end a section ½ in. thick. The latter is

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* Met. and Chem. Eng., 10, p. 668.

broken off and crushed for analysis and the large section is used for physical tests.

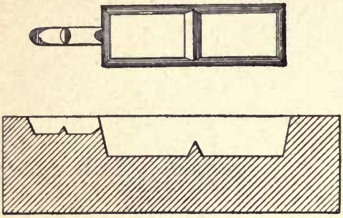

Fig. 61.—A Sample of Cast-iron and Mold in which the Sample is Cast.

As shown by Howe * and others †, the impurities in steel tend to segregate on cooling in those parts which freeze last. Therefore, to obtain a representative sample of the metal in solid form, it is necessary to drill well into the metal; and to be sure that the material comes within the specifications axial drillings should be taken, and these should be analyzed as a separate sample.

Steel drillings should be well mixed, and since the fine and the coarse differ in composition, the weight taken for analysis should consist of both fine and coarse in the same ratio that exists between them in the sample as a whole. See weighing for analysis, page 18.

If the sample of cast-iron is crushed, it should be made to pass through an 80-mesh sieve, and all that will not pass through such a sieve should be rejected.

DETECTION OF SEGREGATIONS OF SULPHUR

Sulphur occurs in steel as MnS, but if there is not enough manganese present to combine thus with all the sulphur, the excess of sulphur combines with iron as FeS. Therefore, to detect segregations of sulphur on the surface, spread a piece of white silk cloth moistened with a solution of lead acetate on the surface of the metal, and then drop dilute hydrochloric acid on the silk. The dilute hydrochloric acid liberates hydrogen

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* Trans. Amer. Inst. Min. Eng., 38, 104.

† Sauveur, "The Metallography of Iron and Steel," 6, 10.

sulphide from the metallic sulphide and this precipitates black lead sulphide on the silk directly over the segregations. Photographic printing paper moistened with dilute sulphuric acid and pressed against the surface of the polished metal serves this purpose well.

SILICON IN IRON AND STEEL *

Reagent. *Nitric acid,* HNO_3 (sp.gr. 1.2). To make 1 liter mix 391 cc. HNO_3 (1.42) with 646 cc. H_2O.

Si in Steel. Weigh 4.693 gms., transfer it to a beaker, add 40 cc. of dilute nitric acid, and warm to dissolve.

$$FeSi + 6HNO_3 = Fe(NO_3)_3 + H_2SiO_3 + 2H_2O + N_2O_3 + NO.$$

Low carbon steels dissolve very readily. If the action becomes too violent, and there is danger of loss, place the beaker in a dish of cold water.

When the metal is dissolved, evaporate the solution to dryness and raise the temperature until ferric nitrate is decomposed. Cool, add 30 cc. of hydrochloric acid and heat until the ferric oxide is dissolved. Evaporate the solution to dryness. Redissolve in 30 cc. of hydrochloric acid and dilute to 150 cc. Filter, wash with hot dilute hydrochloric acid and cold water alternately until the precipitate is free from iron.

If washed with hot water, there is danger of precipitating basic salts of iron in the filter in the absence of an excess of acid. (See p. 52.)

Burn off the carbon of the filter paper in a platinum crucible with a Bunsen burner and then drive off the last traces of water with the highest heat of the blast lamp. Cool in a desiccator and weigh the silica. The weight multiplied by 10 gives the percentage of silicon in the steel.

If the silica weighed is not pure, it may be treated with hydrofluoric acid and sulphuric acid, according to the method given on page 71, and the impurity weighed and deducted.

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* Camp. Met. and Chem. Eng., 10, p. 669.

SILICON IN STEEL

Drown's Method *

Reagents. *Silicon mixture.* Dilute 300 cc. HNO_3 (1.42) with 600 cc. of water and add to it 125 cc. H_2SO_4 (1.84).

Hydrochloric acid, HCl, dilute, (1 : 1).

Si in Steel. Weigh 4.693 gms. of steel and transfer it to casserole. Add 60 cc. of the silicon mixture. Warm to dissolve the steel, and evaporate the solution until the sulphuric acid fumes freely.

The determination should be covered with an inverted funnel to prevent loss by spattering.

Cool, add 10 cc. of dilute hydrochloric acid and 50 cc. of hot water. Warm until the soluble salts are in solution. Filter and wash, alternately, with hot dilute hydrochloric acid and cold water until the iron salts are removed, and then complete the washing with hot water. Burn the filter and residue in a platinum crucible and proceed according to the method described on page 105.

SILICON IN IRON

Drown's Method

Weigh 0.4693 gm. (twice the factor weight, 0.9386, may be taken if the iron is low in silicon), transfer it to a porcelain casserole, add 20 cc. of the silicon mixture, and proceed according to Drown's method for Si in steel. The weight of SiO_2 multiplied by 100 gives the percentage of silicon in the iron: or, if twice the factor weight was used, after multiplying by 100, divide the result by 2.

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* Trans. Amer. Inst. Min. Eng., 7, p. 346.

SILICON IN IRON

FORD'S METHOD

Weigh 0.4693 gm. of the finely pulverized sample and transfer it to a platinum dish or porcelain casserole. Add 20 cc. of concentrated hydrochloric acid, cover with a watch glass, and boil rapidly to complete dryness. Without cooling (if the determination is in platinum), add 20 cc. of dilute hydrochloric acid (1 : 1). Heat a few minutes, add 50 cc. of hot water, and continue heating to dissolve the iron. Filter, and proceed according to Drown's method.

This method is not so accurate as Drown's method, but it is rapid, and the rapidity may be increased by filtering with suction, using a perforated platinum cone to support the filter paper, and finally by burning the precipitate in an atmosphere of oxygen. (See Fig. 31.)

SILICON IN FERRO-SILICON

The silicon in ferro-silicon and other high silicon products may be determined in the same way as silicon in iron, if the material is soluble in acids. If very high in silicon the powder must be fused with an alkali or an alkaline salt and the fusion dissolved and treated according to the method for SiO_2 in ores, page 72. Since the material is high in silicon, only a small portion is necessary for the sample.

Si in Ferro-silicon. Weigh 0.4693 gm. Fuse with a mixture of 20 gms. of sodium carbonate and 4 gms. of potassium nitrate.*

Blair recommends that the material be fused with sodium peroxide,† and Preuss prefers 10 gms. of KOH in a nickel crucible.‡

When the fusion is complete, cool it and dissolve it in water and hydrochloric acid and evaporate the solution to dryness.

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* Johnson, "Chem. Anal. of Special Steels," p. 120.

† Chem. Anal. of Iron and Steel, p. 224.

‡ Z. Angew. Chem., 23, p. 201.

Dissolve the residue in hydrochloric acid and water, filter, and evaporate the filtrate to dryness, dissolve this residue in a little hydrochloric acid and water, and filter a second time. Burn the precipitates together in a platinum crucible and weigh. The silicon is then purified with hydrofluoric acid and sulphuric acid in the usual way. If the precipitate of silica is large, a second treatment with the acids will be necessary to remove all the silica. The loss in weight (SiO_2) multiplied by 100 gives the percentage of Si sought.

SULPHUR IN STEEL

OXIDATION WITH NITRIC ACID

Reagents. *Dilute hydrochloric acid* (1 : 10).

Sodium carbonate, Na_2CO_3.

Barium chloride solution. Dissolve 10 gms. $BaCl_2$ in 100 cc. of water.

S in Steel. Weigh 4.579 gms. of steel (one-third the factor multiplied by 100), transfer it to a 500-cc. beaker, and add 40 cc. of strong nitric acid.

$$3MnS+12HNO_3=Mn_2(SO_4)_3+Mn(NO_3)_3+9NO+6H_2O.$$

Low-carbon steels dissolve freely in strong nitric acid. If the action is too violent, place the beaker in cold water. High-carbon steels dissolve in strong nitric acid with great difficulty and strong hydrochloric acid should be added, a few drops at a time, to hasten the solution. If too much hydrochloric acid is added, there is danger of loss of sulphur by the formation of H_2S. If dilute nitric acid were used, the sulphur would be liberated, but not oxidized to the sulphate.

In dissolving high carbon steels, if the acid is reduced by evaporation to a small volume before solution takes place, more acid should be added.

When the steel is in solution add about 0.5 gm. of sodium carbonate and evaporate the solution to dryness in an air bath.

Silica must be dehydrated and filtered from the solution and the nitric acid replaced by hydrochloric, before precipitation of the sulphur.

Cool the residue and add 30 cc. of strong hydrochloric acid. When in solution add about 0.5 gm. of sodium carbonate and evaporate the solution to dryness in an air-bath.

If the temperature should be raised high enough to break up manganic or ferric sulphate, the sulphuric acid would be retained as sodium sulphate, which is stable at a high temperature.

Nitric acid must be removed, since it interferes with the precipitation of barium sulphate.

Redissolve the residue in hydrochloric acid and evaporate the solution until ferric chloride begins to separate, to expel the free hydrochloric acid. Add 2 cc. of hydrochloric acid.

An excess of hydrochloric acid is necessary for the formation of the precipitate, but the excess should be small, since barium sulphate is slightly soluble in hydrochloric acid.

Dilute the solution with an equal volume of water. Filter and wash with cold water.

The filtrate and washings should not exceed 100 cc., since the precipitation is better in a moderately concentrated solution; if too dilute, the iron may separate and be carried down with the barium sulphate.

Heat the filtrate to boiling and add, drop by drop, 10 cc. of hot barium chloride solution.

Then add 10 cc. more of barium chloride solution, boil a few minutes, let the precipitate settle for half an hour, or longer if convenient, in a warm place, filter and wash alternately with warm dilute hydrochloric acid and cold water, and finally wash with water until the washings are free from barium. (See p. 75.) Burn the filter and its contents in a weighed platinum crucible, cool, and weigh the $BaSO_4$. The factor for sulphur in barium sulphate is 0.13738. If the weight of steel specified at the beginning of this method was used, to obtain the percentage of sulphur, multiply the weight of barium sulphate by 3.

SULPHUR IN IRON

AMERICAN FOUNDRYMEN'S ASSOCIATION METHOD *

Outline. The iron is dissolved in concentrated nitric acid, potassium nitrate added to oxidize the sulphur, the solution evaporated to dryness and heated to drive out nitric acid, the potassium retaining the sulphur as sulphate. The residue is treated with sodium carbonate solution to dissolve sulphates, filtered, the filtrate acidified, and taken to dryness. The residue is taken up with dilute hydrochloric acid, the silica filtered from the solution and the sulphur precipitated from the filtrate with barium chloride.

Reagents. *Potassium nitrate*, KNO_3.

Solution of sodium carbonate. Dissolve 10 gms. $Na_2CO_3 \cdot 10H_2O$ in 1 liter of water.

Barium chloride solution. Dissolve 10 gms. $BaCl_2$ in 100 cc. of water.

S in Iron. Weigh 3 gms. of drillings for the sample and transfer it to a platinum dish. Cover the dish with a watch glass and dissolve the sample slowly in concentrated nitric acid. When the iron is completely dissolved add 2 gms. of potassium nitrate. (See note on sodium nitrate, p. 73.) Evaporate the solution to dryness and ignite the residue over an alcohol lamp at a red heat. Cool, add 50 cc. of the 1 per cent solution of sodium carbonate. Boil a few minutes.

The sulphate is taken into solution as alkaline sulphate and the iron left as ferric oxide.

Filter, wash the precipitate with hot 1 per cent solution of sodium carbonate, acidify the filtrate with hydrochloric acid, evaporate the solution to dryness, and dissolve the residue in 50 cc. of water and 2 cc. of hydrochloric acid. Filter and wash the SiO_2. Dilute the filtrate to 100 cc., heat it to boiling,

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* Chem. Eng., 4, p. 213.

and add barium chloride solution in the manner described in the preceding method. Filter, wash the precipitate well with hot water, ignite, and weigh. Multiply the weight of $BaSO_4$ by the factor for S, 0.13738, divide the result by 3, and multiply by 100.

SULPHUR IN IRON OR STEEL

EVOLUTION METHOD *

Outline. The steel is dissolved in hydrochloric acid in a flask and the H_2S formed is absorbed in an alkaline solution of cadmium chloride, the H_2S is liberated in the solution with hydrochloric acid and is titrated with standard iodine solution.

Reagents. *Standard iodine solution.* Place 3.958 gms. of pure iodine in a liter flask with about 6 gms. of potassium iodide and 10 cc. of water. Let the flask stand without heating until all the iodine has been dissolved, then dilute with water to the graduation. One cubic centimeter of this solution should be equivalent to 0.0005 gm. of sulphur. If 5 gms. of material are taken for analysis, 1 cc. of this solution will then be equivalent to 0.01 per cent sulphur. The solution should be standardized against a steel in which the sulphur has been previously determined, and either corrected to the above value, or a factor-weight of steel taken so that 1 cc. of the solution will be equivalent to 0.01 per cent S. (See Factor Weights for Standard Solutions, p. 40.)

Starch solution. Make an emulsion of about 1 gm. of starch in 4 cc. of cold water. Pour this slowly into about 200 cc. of boiling water and boil five minutes after the starch has been added. Cool to room temperature and add 1 gm. of zinc chloride dissolved in 10 cc. of cold water. Mix well and let it stand twenty-four hours or more, shaking it occasionally. Decant the

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* Camp, Met. and Chem. Eng., 10, p. 669. Philips, Stahl u. Eisen, 16, p. 633.

clear solution for use. The zinc chloride is added as a preservative, since it prevents the growth of vegetable molds.

The starch solution gives a much more delicate end-point if the starch, of which it is made, has been soaked twenty-four hours in very dilute hydrochloric acid, and then washed, dried, and heated three hours in an oven at 100° C.*

Cadmium chloride solution. Dissolve 5 gm. $CdCl_2$ in 375 cc. of water mixed with 625 cc. of ammonia.

Apparatus. The steel is dissolved in a Florence or Erlenmeyer flask, fitted with a 2-hole stopper, through which pass a thistle tube or separatory funnel and a delivery tube. The delivery tube above the flask should lead upward from the flask a few inches, and should be enlarged so that the condensation will return to the flask. Beyond the enlargement the delivery tube passes down through a 2-hole stopper to the bottom of a small Erlenmeyer flask or a large test-tube, containing cadmium chloride solution, in which the H_2S is absorbed. From the other hole in the stopper of the absorbent flask, a delivery tube of glass or fused quartz passes horizontally through a Bunsen flame, and then, with a right-angle bend, passes vertically

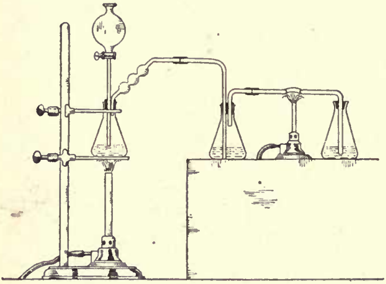

FIG. 62.—Apparatus for Determination of Sulphur. Evolution Method.

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* Chem. Abs., 4, 2617.

downward to the bottom of another similar absorbent flask or test-tube containing cadmium chloride solution. (Fig. 62.)

S in Steel. Weigh 5 gms. (or a factor weight) of steel a transfer it to the solution flask described above. Place in each of the small absorbent flasks or test-tubes 15 cc. of cadmium chloride solution diluted to 60 cc. with water. Heat the quartz tube between the two absorbent flasks to redness.

When steel, especially high-carbon steel, is dissolved in hydrochloric acid, all the sulphur is not liberated in the form of H_2S, but a considerable part is combined with hydrocarbons, one of which, $(CH_3)S_2$, has been identified by Phillips. These mercaptans are not very volatile, and when they pass over with the H_2S they are not completely absorbed by the cadmium chloride solution. These difficulties may in a measure be obviated by dissolving the steel in strong hydrochloric acid, by boiling briskly at the end of the operation, and by passing the unabsorbed gas from the first cadmium chloride flask through a red-hot tube before it enters the second flask. The sulphur in the unabsorbed compounds is changed by heat into H_2S, which is absorbed in the second cadmium chloride flask.

From the separatory funnel run into the solution flask 50 cc. of hydrochloric acid and close the tap of the funnel. Warm the flask so that the steel will dissolve briskly.

$$MnS + 2HCl = MnCl_2 + H_2S.$$

Dilute hydrochloric acid (1 : 1) is often used in this method, but the difficulties, owing to the formation of mercaptans, as mentioned above, are lessened by the use of strong acid.

After the steel is dissolved boil the solution until the vapor has carried over into the absorbent all the sulphur products that are volatile.

$$H_2S + CdCl_2 = CdS + 2HCl,$$
$$HCl + NH_4OH = NH_4Cl + H_2O.$$

Before allowing the solution-flask to cool, open the tap of the separatory funnel to prevent the formation of a partial vacuum in the flask, which would draw in the cadmium chloride solution. Disconnect the two absorbent flasks and empty them into a 500-cc. beaker, being careful to wash all of the cadmium sulphide from the delivery tubes and flasks into the beaker.

Dilute the solution to 400 cc. with cold water, add 10 cc. of starch solution, and enough hydrochloric acid to dissolve the cadmium sulphide and to render the solution acid.

$$CdS+2HCl=H_2S+CdCl_2,$$

Stir gently to mix the solution well and titrate at once with standard iodine solution to a strong blue color.

$$H_2S+I_2=2HI+S.$$

The solution should be mixed so that no part of it will be ammoniacal when titration begins. To prevent the escape of H_2S the solution should not be stirred briskly. There should be sufficient volume to hold the H_2S in solution; it should be cool and the titration should begin promptly, before there is time for H_2S to escape. The end-point is the familiar blue color produced by the combination of starch and free iodine.

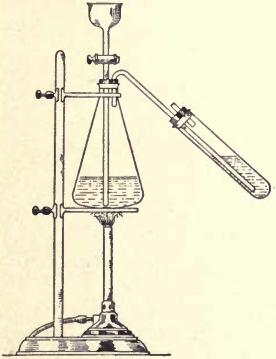

Fig. 63.—Apparatus for Sulphur. Rapid Method.

When accuracy must be sacrificed for the sake of speed, this method may be simplified by dispensing with the quartz tube and the second absorption flask. For rapid work the apparatus usually consists of an Erlenmeyer flask fitted with a 2-hole stopper which carries a thistle tube for the introduction of acid and a delivery tube, terminating in a large test-tube which contains the absorbent. (Fig. 63.)

CARBON IN STEEL

Solution and Combustion

Outline. The steel is dissolved in an acid solution of the double chloride of copper and potassium, which leaves all the carbon as a residue. The carbon is filtered from the solution and burnt to CO_2 in a combustion furnace. The CO_2 is absorbed in a solution of potassium hydroxide and weighed.

Reagents. Solvents. Solution of *copper and potassium chloride.* Dissolve 140 gms. $CuCl_2 \cdot 2KCl \cdot 2H_2O$ in 400 cc. of water and 60 cc. of hydrochloric acid (sp.gr. 1.2).

A solution of *copper and ammonium chloride* may be used as a solvent, but the potassium salt is usually freer from carbonaceous impurities.

If steel is dissolved in the ordinary acids, some of the carbon escapes in gaseous form.* The copper and potassium chloride solution dissolves the iron and leaves the carbon in solid form.

Absorbent of CO_2. *Solution of potassium hydroxide* (sp.gr. 1.2). Dissolve 300 gm. of KOH in 1 liter of water. Owing to possible impurities in the solution, which will absorb oxygen while the combustion is going on, the solution should have oxygen passed through it while it is hot, or it may be titrated while hot to a faint green with potassium permanganate solution. The potash bulbs should be filled to about two-thirds of their capacity with this solution. The bulbs should be refilled with fresh solution after they have absorbed about 0.5 gm. of CO_2.

After a bulb is filled, dry off the outside and the inside of the entrance tube. The inside may be dried with a small roll of filter paper. If the inside is not dried, a deposit of potassium carbonate may choke the tube.

Absorbents of Moisture. *Calcium chloride; dehydrated*

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* For the forms of carbon in steel, see Sauveur, "Metallography of Iron and Steel," 14, 8.

$CaCl_2$. Fused calcium chloride should not be used, since it contains some CaO, which would absorb CO_2.

Soda-lime, a mixture of sodium hydroxide and lime, is a drying agent, and is also a better absorbent of CO_2 than potassium hydroxide solution. It is not used alone, since it is soon saturated, but follows the bulb containing potassium hydroxide solution to take out the last traces of CO_2.

These drying agents should be in granular form with grains only a few millimeters in diameter and free from dust. All that will pass through a 20-mesh sieve should be discarded.

Potassium hydroxide broken up quickly and placed in a tube may be used as a drying agent. It also absorbs CO_2.

Absorbents of Hydrochloric Acid. *Anhydrous copper sulphate.* Saturate small pieces of pumice with a strong solution of $CuSO_4$ and heat in a dish to drive off all the water. This is also an absorbent of water.

A saturated solution of Ag_2SO_4 *in sulphuric acid* (sp.gr. 1.4).

Oxidizing Agents. *Copper oxide.* Make a square of copper gauze 15 cm. on the edge into a roll about 2 cm. in diameter and enclose this in a sheet of asbestos to protect the silica tube from the copper oxide formed. Place it in the combustion tube and heat it in a current of oxygen or air until the copper is converted to CuO. If a silica tube is heated in contact with copper oxide, the copper oxide combines with the silica and the tube is destroyed. Hot copper oxide converts CO to CO_2.

Platinized asbestos may be used for this purpose instead of copper oxide.

Absorbents of Chlorine. A roll of *silver foil* is placed in the cooler part of the combustion tube beyond the copper oxide. The silver foil should be taken from the combustion tube occasionally and heated in a current of hydrogen to free it from chlorine.

A bulb containing the following mixture may be used for this purpose:

0.2 gm. *pyrogallic acid* ($C_6H_6O_3$).
3 gms. neutral *oxalate of potassium* ($K_2C_2O_4+H_2O$).
4 drops concentrated *sulphuric acid.*
Add water to make 20 cc.

Apparatus. Combustion may be carried out in a fused silica combustion tube heated in either an ordinary gas combustion furnace or in an electric furnace. The silica tube should have an inside diameter of about 22 mm. and a length of 50 to 60 cm. Combustion tubes are also made of platinum, porcelain, and hard glass.

The electric furnace (Fig. 64 *C*) consists essentially of an alundum tube, about 30 mm. inside diameter (just large enough to receive the silica combustion tube) wound with nichrome or other resistance wire and imbedded in a non-conducting refractory material (magnesia and asbestos). The oxygen or air, before being admitted to the combustion tube, is passed first through a bulb *A*, containing potassium hydroxide solution, and then through the U-tube *B*, the first limb of which contains soda lime, and the second, dried calcium chloride.

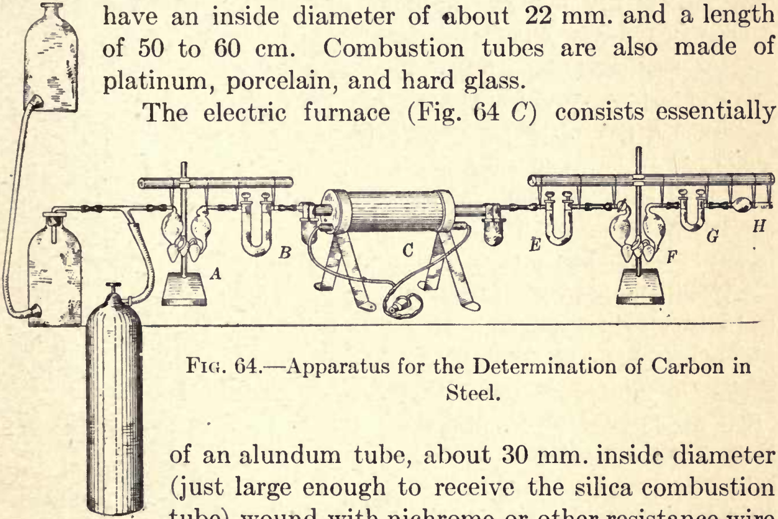

Fig. 64.—Apparatus for the Determination of Carbon in Steel.

The rubber stoppers in the combustion tube must be protected from the heat. The ends of the tube are kept cool by strips of asbestos cloth, which dip in water, and asbestos plugs held in platinum gauze are placed just inside the stoppers to protect them from radiant heat.

In the combustion tube, a little beyond its middle point, toward the exit end, is placed the roll of copper oxide enclosed in a sheet of asbestos, and beyond that, in the cooler part of the tube, a roll of silver foil to absorb chlorine. If silver is not used, the chlorine may be absorbed by passing the gases, after they leave the combustion tube, through a bulb containing potassium oxalate solution (see Reagents). The gases then pass through the U-tube *E*, which contains in the first limb dehydrated copper sulphate, and in the second, dry calcium chloride. From this tube the gas passes into the weighed potash bulb *F*, and from that to the tube *G*, which is also weighed, and which contains in the first half soda-lime, and in the second, dry calcium chloride. A larger calcium chloride tube *H* follows, which serves as a protection to *G* from moisture, in case air should be drawn in from that end of the train.

When the bulb *F* and the tube *G* are detached from the train to be weighed, they should be closed with stoppers made of small pieces of rubber tubing closed at one end with a bit of glass rod, if they are not provided with glass stopcocks.

If air is used for combustion, it may be driven through the train by aspirator bottles attached to the entrance end of the train, or it may be drawn through by attaching an aspirator bottle to the exit end. If oxygen is used, the flow is regulated by means of the valve on the oxygen tank. It is difficult to regulate the flow of oxygen through the combustion train from a tank at high pressure; it is therefore advisable to fill tanks at low pressure from a high-pressure tank for use in combustion.

Rubber absorbs appreciable amounts of CO_2; therefore the glass apparatus in the combustion train, connected by rubber tubing, should be made to touch inside the rubber tubing and thus protect the rubber from contact with the gas.

When the boat is placed in the combustion tube, the train is tested for leaks by closing the entrance end of the train and slowly exhausting the air from the exit end by suction. When the suction is removed, the atmospheric pressure will cause the caustic solution in the weighed bulb to rise in the side next the combustion tube. If there is a leak, the solution will gradually fall back to the original level.

When the train is made perfectly tight, the air or oxygen is passed through at the rate of two bubbles per second and the furnace is gradually heated to a bright red heat. After burning out the furnace fifteen minutes, detach the potash bulb and its tube, cool them in the balance case fifteen minutes, and weigh. Connect them to the train again, pass the oxygen, and burn fifteen minutes, cool and weigh again. This is repeated until the weight is constant.

In weighing the bulb and tube, they should always be counterpoised by a similar bulb and tube so that the error due to condensation of moisture on the apparatus may be avoided. Apparatus should not be weighed after it has been rubbed or wiped off with a cloth until it has stood at least thirty minutes for the dissipation of static charges of electricity. Richards and Shipley * found that a small quartz flask which was 2 mgms. too light from this cause was immediately restored to its normal weight by bringing into the balance case a very small tube of impure radium chloride.

If a gas furnace is used, the burners next the ends should be lighted first and after an interval of two minutes the burners next to these are turned on and so on until the last to be lighted are those directly under the platinum boat.

C in Steel. Weigh 3 gms. (or ten times the factor weight, 2.727 gms.) of steel, transfer it to a 500-cc. beaker, and add 200 cc. of copper and potassium chloride solution.

When ferro-alloys and chrome tungsten steels are dissolved in copper potassium solution, not all the carbon is left in the residue;

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* Jour. Am. Chem. Soc. 36 (1914) 4.

therefore a direct combustion method (see p. 121) should be adopted for carbon in these materials.

If a little fibrous asbestos is added, the finely divided carbon adheres to it, greatly facilitating filtering and washing.

Keep the temperature of the solution below 40° C., and stir with the mechanical stirrer (see Fig. 60) until the steel is dissolved.

$$Fe+CuCl_2=FeCl_2+Cu,$$
$$Cu+CuCl_2=2CuCl.$$

The copper is first precipitated on the steel and is then slowly dissolved by the solution of cupric chloride.

When the steel is dissolved, filter the solution through asbestos in a small Gooch crucible about 15 mm. in diameter or in a perforated platinum boat.

The manner of attaching the Gooch crucible to the carbon filter is shown in Fig. 29, page 25. The perforated platinum boat is most conveniently attached to the filter flask by means of a specially made holder of soft rubber which is provided with a trough-like opening in the top into which the boat is pressed to make the connection air-tight.

The asbestos should have been previously burnt to free it from carbonaceous matter.

Wash the carbon with a little dilute hydrochloric acid (1:1) and then with water until it is free from acid.

Filtering and washing should be done carefully by pouring the solution down a glass rod into the boat. A jet of water from a wash bottle may throw particles of carbon from the boat.

Dry the Gooch crucible or boat and its contents in an air-bath at a temperature not above 105° C. While the carbon is drying, prepare the combustion furnace by passing oxygen through the hot tube until the combined weight of the bulb *F* and the tube *G* is constant. Attach the weighed bulb and tube to the train, place the crucible or boat containing the carbon in the combustion tube near the copper oxide and burn the carbon in a current of oxygen or air at the rate of two bubbles per second until all the carbon has been converted to CO_2 and carried over into the absorption bulb. The operation should be complete within about thirty minutes.

After the combustion is complete, remove the absorption bulb and drying-tube and close the ends with the stoppers described on page 118.

The absorbents in the weighed bulb and tube should always be protected from moisture and CO_2 in the air by these stoppers when the bulb is not attached to the combustion train, and the stoppers should always be weighed with the bulb. The train itself should be closed with stoppers similar to those used on the bulb, when the bulb is removed for weighing.

There should always be the same amount of air (or oxygen, if that is used for combustion) in the bulb when it is weighed. If air is used for combustion, the bulb may be closed by capillary stoppers to maintain atmospheric pressure in the bulb; when oxygen is used, if the bulb is always closed when it is about the same temperature, the quantity of oxygen weighed will be the same.

Let the bulb and tube stand in the balance case fifteen minutes before weighing.

The increase in weight represents the CO_2. The factor for C in CO_2 is 0.2727 or $\frac{3}{11}$. If the factor weight was used, multiply the weight of CO_2 by 10.

TOTAL CARBON IN IRON OR STEEL

Direct Combustion

Outline. The steel is burnt directly in oxygen, the CO_2 formed by the oxidation of the carbon in the steel is absorbed in a solution of potassium hydroxide and weighed. By this method the carbon from carbonaceous gases in the steel would also be included in the determination.

Reagents. *Alundum.* Ignited alundum is placed in a platinum, nickel, alundum, porcelain, or clay boat about 7 cm.

long. A depression is made in the alundum about 3 cm. in length, in which the sample is placed to be burnt (Fig. 65).

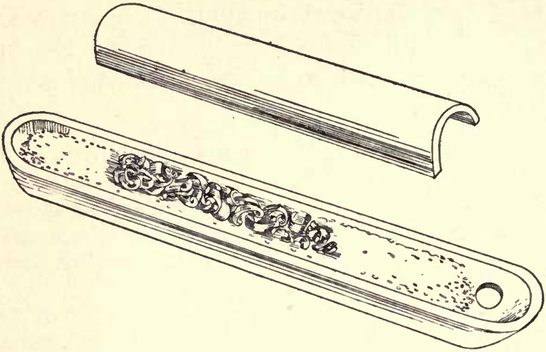

Fig. 65.—Boat with Steel Ready for Combustion and Semi-cylindrical Cover for the Protection of the Silica Tube from Iron Oxide.

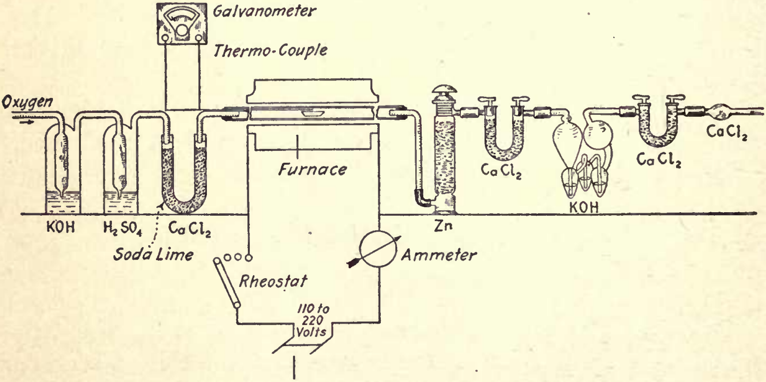

Fig. 66.—Apparatus for the Direct Combustion of Steel for Carbon.

Oxygen. The flow of oxygen is much more easily regulated if low-pressure cylinders are filled for use from the high-pressure tank.

Red lead oxide, Pb_3O_4. Pig iron and ferro-alloys burn more completely at the usual temperature of the furnace if mixed with a little red lead oxide.

Potassium hydroxide solution. Dissolve 300 gms. of KOH in 1 liter of water.

Granulated zinc for the absorption of sulphuric acid.

Calcium chloride, $CaCl_2$ dehydrated.

Apparatus. The combustion furnace (Fig. 66) is similar to that described on page 117, but in the direct combustion of steel the temperature of the furnace should be maintained at about 1000° C. It should not fall below 960° or rise above 1050° C. The furnace should, therefore, be provided with a pyrometer, or the resistance in the rheostat may be standardized once for all so that the temperature may be known approximately by the amount of resistance in the circuit. When the resistance is standardized, the hot junction of the pyrometer should be placed in the combustion tube at the point where the carbon is to be burnt.

It should be kept in mind that this latter method of controlling the temperature is only approximate and may vary as much as 40° to 50° owing to changes in room temperature, air currents, and variation in the electric current.

Before the oxygen enters the combustion tube, it is passed through potassium hydroxide solution, sulphuric acid, soda-lime, and calcium chloride. After leaving the combustion tube, the gases pass through a column of granulated zinc, which removes sulphuric acid, derived from the sulphur in the steel, and through calcium chloride, which dries them before they enter the weighed bulb and tube. A roll of copper oxide enclosed in sheet asbestos is placed in the combustion tube to oxidize CO to CO_2, or, for this purpose, plantinized asbestos may be substituted. (See p. 118.) The platinized asbestos occupies 12 to 15 cms. of the combustion tube immediately following the position of the boat and is held in place with thin plugs of platinum gauze. The stoppers in the combustion tube must be protected from heat in the way described on page 117. Before determinations begin, oxygen should be passed through the hot combustion tube at intervals and the absorption bulb and tube brought to a constant weight. (See p. 119.)

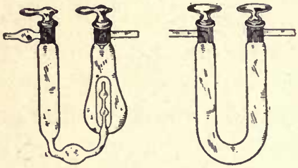

Fig. 67.—Glass-stoppered Bulb and Tube.

The absorption bulb should be provided with glass stop-cocks, and it should be filled with oxygen when weighed. (Fig. 67.) In weighing, the bulb and tube should be counterbalanced with a similar apparatus.

C in Steel. Weigh 0.2727 gm. or twice the factor, 0.5454 gm., and transfer to the boat described above. The steel drillings should lie in a continuous mass so that when combustion begins it will be propagated throughout. Turn a semi-cylindrical cover of alundum or clay over the drillings to protect the silica tube from the iron oxide which is thrown from the boat during combustion. Push the boat thus covered into place in the combustion tube, which has been heated to 1000° C. Close the combustion tube and pass the oxygen through at a uniform rate of about four bubbles per second until the steel begins to burn, when the rate is increased until the rate of flow in the forward bulb is equal to that in the first absorption bulb. The combustion should be finished in about ten minutes. The gas is cut off and the absorption bulb with its calcium chloride tube is detached from the train, cooled and weighed.

CARBON IN IRON AND STEEL

Weighing as Barium Carbonate after Direct Combustion

Outline. The steel is burnt in oxygen in a combustion furnace, the carbon of the steel is converted to CO_2 which is purified and absorbed in a solution of barium hydroxide. The precipitated barium carbonate is filtered from the solution, burnt, and weighed.

Reagents. *Barium hydroxide solution.* Dissolve 20 gms. of $Ba(OH)_2+8H_2O$ in 1 liter of freshly boiled hot water. Cover, and when cool filter as rapidly as possible into a receiver which is protected from the CO_2 of the atmosphere. The solution should be withdrawn from the container, for use through a tap or siphon, and the air which replaces it should be admitted through a tube containing soda-lime or through a bulb containing caustic potash solution.

Apparatus. Set up the combustion furnace in the manner described in the method above, except that part of the train following the column of granulated zinc is replaced by the bulb tube (Fig. 68) which should contain 30 cc. of barium hydroxide solution.

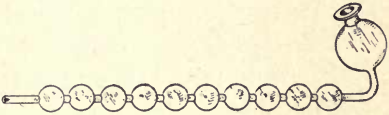

FIG. 68.—Bulb Tube for Barium Hydroxide Solution.

C in Iron and Steel. Weigh 1 gm. of the metal, or ten times the factor, 0.608 gm., and proceed in the manner described in the preceding method until combustion is complete.

$$Ba(OH)_2+CO_2=BaCO_3+H_2O.$$

Carefully wash the barium hydroxide solution with its precipitate of barium carbonate from the bulb tube. Filter and wash the precipitate several times with freshly boiled water as quickly as possible to prevent absorption of CO_2 from the atmosphere.

Burn the filter with its contents in a platinum crucible at a red heat with a Bunsen burner, cool in a desiccator, and weigh. The factor for carbon in $BaCO_3$ is 0.0608. If the factor weight, 0.608 gm., was used, multiply the weight of barium carbonate by 10.

CARBON IN IRON AND STEEL

Titration of the Excess of Barium Hydroxide

Outline. The steel is burnt in a combustion furnace with oxygen. The CO_2 formed by the oxidization of the carbon in the steel is purified and passed into a definite volume of a standard solution of $Ba(OH)_2$. The excess of $Ba(OH)_2$ is measured by titrating with standard acid and the weight of carbon is calculated.

Reagents. *Standard hydrochloric acid.* Dilute 8 cc. of HCl (sp.gr. 1.2) to 1 liter with freshly boiled water.

Standard barium hydroxide solution prepared in the manner described on page 125, and standardized according to the method given below.

Phenolphthalein solution. One gram of phenolphthalein dissolved in 1 liter of ethyl alcohol (p. 84).

To determine the relative values of the acid and alkali solutions, titrate a definite volume of the barium hydroxide solution with the dilute hydrochloric acid, after adding a few drops of phenolphthalein solution.

To determine the value of the sodium hydroxide solution in carbon, weigh a steel in which the carbon has already been determined and treat it exactly as described in this method. Divide the weight of carbon in the steel by the number of cubic centimeters of barium hydroxide solution required to combine with it to form $BaCO_3$.

C in Iron or Steel. Weigh the iron or steel and proceed according to the last method (see p. 125), with the following modification. Measure into the bulb-tube with the pipette 30 cc. of standard barium hydroxide solution. Burn the sample, passing the oxygen in the usual way (p. 124). After the combustion is complete, empty the barium hydroxide solution with the precipitate of barium carbonate into a half-liter Erlenmeyer flask and wash out the tube well with freshly-boiled water. Add 3 drops of phenolphthalein solution and titrate the excess of barium hydroxide with standard hydrochloric acid. The value of 1 cc. of the barium hydroxide solution in carbon is then multiplied by the number of cubic centimeters of the solution from which the barium had been precipitated by the CO_2.

COMBINED CARBON IN STEEL

Color Method

Outline. The steel is dissolved in a definite volume of dilute nitric acid. The intensity of the brown color of the solution depends upon the amount of carbon present. This solution is compared in a colorimeter with a solution of a standard steel prepared in the same way.

Reagent. *Dilute nitric acid* (1 : 3).

C in Steel. Weigh 0.5 gm. of steel (0.2 gm. if the steel is high in carbon) and transfer it to a large test-tube. Add 10 cc. of dilute nitric acid (1 : 3) measured with a pipette (Fig. 69). At the same time, weigh and treat in the same manner a standard steel in which the carbon has been determined by combustion. Place both test-tubes in a water bath (Figs. 70 and 71) and heat until the steel is dissolved. When in solution, remove the test-tubes and place them in cold water. Dilute the solutions to the same volume (50 cc.) and transfer to a colorimeter and read the percentage of carbon directly (see p. 44); or transfer the two solutions to Eggertz tubes and dilute until the two agree in color.

Fig. 69.—Automatic Filling Pipette.

Carbon in steel in the form known as hardening carbon does not give any color to the nitric acid solution. On the other hand, the solution is colored by copper, cobalt, and chromium. For these reasons the standard and the unknown steel should have as nearly the same composition as possible, and should have received the same treatment.

They should be annealed before sampling to convert the carbon in each to the same form.

The standard should be near the unknown in its carbon content.

The colors are matched best if the light comes directly from the sky or clouds, and it should be diffused by a ground glass.

The color fades on exposure to light; therefore the solution should be kept in the dark until ready for comparison.

If there is much difference between the standard and the unknown steel in carbon content, in using Eggertz tubes, there is a tendency to read the unknown too close to the standard. If the difference is as much as one-sixth of the standard, some chemists make a correction of 1 point for every time that one-sixth of the standard is contained in the difference between the two; for example, if the standard is 0.48 carbon and the unknown reads 0.56, the difference is 8 points, and one-sixth of the standard, that is, 8, is contained in this difference one time. Therefore add 1 to the reading of the unknown making it 0.57 as the correct percentage. If the standard were higher than the unknown, the correction would be subtracted from the reading of the unknown.

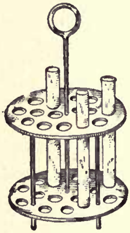

FIG. 70.—Rack Made of Copper for Holding Test Tubes in the Water Bath.

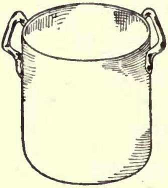

FIG. 71.—Water Bath.

A correction is also sometimes made if the standard and the unknown differ widely in manganese. Manganese causes the carbon color to be lighter, and if the unknown steel contains, for example, 10 points more of manganese than the standard, 1 point is added to the reading for carbon to give the correct percentage; if, on the other hand, the unknown were 10 points lower in manganese, 1 point would be subtracted from its carbon reading.

GRAPHITIC CARBON IN IRON

Outline. The iron is dissolved in dilute acid, the graphitic carbon filtered from the solution, dried, and weighed, or it may be burnt in a combustion furnace, the resulting CO_2 collected and weighed.

Reagents. *Dilute nitric acid* (1 : 3).

Hydrofluoric acid, HF.

Hydrochloric acid, dilute (1 : 3).

C, graphitic, in Iron. Weigh 0.608 gm. of the sample and transfer it to a small beaker or Erlenmeyer flask. Add 40 cc. of dilute nitric acid. Heat gently to dissolve the iron. Add a few drops of hydrofluoric acid to dissolve silica, and boil a few minutes. Filter the carbon on asbestos in a small Gooch crucible or in a perforated platinum boat. Wash with hot dilute hydrochloric acid and water alternately, and finally wash with hot water to remove the acid. Dry the carbon in the boat at 110° C., burn in a combustion furnace, and proceed according to the method for carbon in steel. (See p. 121.)

The graphite may be filtered on asbestos in a Gooch crucible, washed, and dried at 110° C. to a constant weight. After weighing, the graphite is burned, in the air or in oxygen, and the crucible and residue weighed. The loss in weight represents the graphite.

PHOSPHORUS IN IRON AND STEEL

Outline. The steel is dissolved in dilute nitric acid, the solution evaporated to dryness, the silica dehydrated, and the phosphorus oxidized to phosphate. The residue is taken up with hydrochloric acid, the free acid expelled by evaporation, nitric acid added, and the solution evaporated to displace all the hydrochloric acid. The solution is diluted, the silica filtered from it, and ammonia and nitric acid added to the filtrate.

The phosphorus is then precipitated with ammonium molybdate, filtered, and weighed; or it may be measured by titration.

Reagents and Notes. See phosphorus in iron ore, page 76.

P in Steel. Weigh 1,63 gm. (if the material is low in phosphorus 4.89 gm.—300 times the factor—may be used). Transfer it to a porcelain casserole or dish and add from 25 to 60 cc. of dilute nitric acid (1 : 1). Warm cautiously to dissolve the iron and evaporate the solution rapidly to dryness. Gradually increase the heat until the ferric nitrate is broken up and the acid is all expelled. Cool and add 30 cc. of strong hydrochloric acid, heat to dissolve the iron oxide, and evaporate the solution until chlorides begin to separate. Add 10 cc. of strong nitric acid and evaporate the solution to a syrupy consistency. Dilute with cold water to about 60 cc. Stir and filter into a half-liter Erlenmeyer flask. Wash alternately with 2 per cent solution of nitric acid and hot water until the residue is free from iron.

If the iron contains an appreciable amount of titanium, ignite the filter and residue in a platinum crucible. Cool and treat the residue with hydrofluoric and sulphuric acids to remove the silica. Evaporate the solution to dryness, add a little sodium carbonate, and fuse. Treat the fusion with hot water and after disintegration filter the insoluble sodium titanate from the solution and add the filtrate containing the phosphate to the main solution.

To the filtrate containing the phosphorus add 25 c. of strong ammonia.

This filtrate should be clear and should have a volume of about 150 cc.

Shake the solution vigorously, add nitric acid, and proceed according to the method for phosphorus in ores. (See p. 77.)

Instead of weighing the yellow precipitate it may be dissolved, the phosphorus precipitated with magnesia mixture, and weighed as magnesium pyrophosphate as described on page 79; or the phosphorus in the yellow precipitate may be measured by Emmerton's volumetric method (p. 80), or by Pemberton's alkalimetric method (p. 83).

PHOSPHORUS IN IRON OR STEEL

Rapid Method

Outline. The iron is dissolved in dilute nitric acid, the carbon oxidized with ammonium persulphate, the solution filtered from the residue, the phosphorus in the filtrate oxidized to phosphate with potassium permanganate, the resulting manganese dioxide reduced and dissolved and the phosphorus precipitated with ammonium molybdate, filtered, and measured by titration with standard sodium hydroxide solution.

Reagents. *Ammonium persulphate,* $(NH_4)_2S_2O_8$.

Dilute nitric acid (1 : 3).

Wash solution of nitric acid (1 : 48).

Potassium permanganate solution. Dissolve 25 gms. $KMnO_4$ in water and dilute to 1 liter.

Ammonium molybdate solution. (See p. 76.)

Reducing Agents. *Ammonium bisulphite solution.* Dissolve 5 gms. NH_4HSO_3 in 100 cc. of water.

Ferrous sulphate solution. Dissolve 5 gms. $FeSO_4+7H_2O$ in 100 cc. of water.

Sugar Solution. A saturated solution of $C_{12}H_{22}O_{11}$ in water.

P in Iron or Steel. Place 1.63 gms. (or other factor weight) of the iron in a half-liter Erlenmeyer flask. Add 40 cc. of dilute nitric acid (1 : 3) and heat until the iron is dissolved. When in solution wash down the sides of the flask, add 1 gm. of ammonium persulphate, and boil until the carbon is completely oxidized. Filter on an 11-cm. filter paper and wash alternately with 2 per cent nitric acid and hot water until the iron is all removed. Heat the filtrate to boiling, add a slight excess of potassium permanganate solution and boil until the permanganate is decomposed and manganese dioxide is precipitated. Add a saturated solution of sugar or other reducing agent until the manganese dioxide is dissolved. Cool the solution to 80° C., and add 50 cc. of ammonium molybdate solution. Shake the flask five minutes, filter, and proceed according to Pemberton's method (p. 86).

MANGANESE IN IRON AND STEEL

Walters' Color Method

Reagents. *Nitric acid* (sp.gr. 1.2).

Ammonium persulphate $(NH_4)_2S_2O_8$.

Solution of silver nitrate. (See p. 90.)

Mn in Iron or Steel. Weigh 0.2 gm. of the sample and transfer it to an 8-in. test-tube or to a small Erlenmeyer flask. Add from a pipette 10 cc. of dilute nitric acid. Heat on a water bath until the steel is in solution. Add 0.5 gm. of moist ammonium persulphate and heat to oxidize the combined carbon. If the solution is not clear, filter and wash the residue with 15 cc. of silver nitrate solution. If filtering is not necessary, add the silver nitrate solution directly to the solution of steel. Add 1 gm. of moist ammonium persulphate and heat the solution until the pink permanganic acid color develops. Cool and dilute the solution. Transfer it to a colorimeter and match the color against the standard that has been treated in exactly the same manner. (See p. 44.)

MANGANESE IN IRON AND STEEL

Titration with Sodium Arsenite

Reagents. See page 90.

Mn in Iron or Steel. Weigh 0.2 gm. of the material and treat it exactly as described in the method above to the development of the pink permanganic acid color. Add 10 cc. of sodium chloride solution and titrate with standard sodium arsenite solution to the disappearance of the pink color. (See p. 91.)

MANGANESE IN STEEL

Sodium Bismuthate Method

Reagents. See page 92.

Weigh 1 gm. of steel and transfer it to a 200-cc. Erlenmeyer flask. Add 50 cc. of dilute nitric acid (1 : 3). Heat until the steel is dissolved. When in solution, cool and add 0.5 gm. of sodium bismuthate to oxidize carbonaceous matter. Heat until the pink color disappears with or without precipitation of manganese dioxide. Add sulphurous acid until the solution clears. Boil out the excess of sulphurous acid. Cool to 15° C. and add an excess of sodium bismuthate (2 or 3 gms.). Agitate the flask for several minutes. Add 50 cc. of dilute nitric acid (3 : 100) and proceed according to the method on page 94.

MANGANESE IN FERRO-MANGANESE AND SPIEGEL

Julian's Method

Reagents. See page 95.

Weigh 0.25 gm. of ferro-manganese and transfer it to a 200-cc. beaker. Add 40 cc. of nitric acid (sp.gr. 1.2). Cover and boil the solution almost to dryness. Add 50 cc. of nitric acid (sp.gr. 1.42). Heat to boiling. Take off the cover and add potassium chlorate, a little at a time, from a glass spatula, until the green fumes suddenly disappear and are replaced by white fumes; continue boiling for three or four minutes. Cool, dilute with cold water to about 200 cc., add 50 cc. of hydrogen peroxide solution and titrate with standard permanganate solution. See the method on page 95.

MANGANESE IN STEELS CONTAINING CHROMIUM AND TUNGSTEN

WALTERS' METHOD *

Reagents. *Dilute sulphuric acid* (2 : 9).

Solution of sodium carbonate. Dissolve 200 gms. $Na_2CO_3 + 10H_2O$ in 1 liter of water.

Emulsion of zinc oxide. Suspend ZnO in distilled water by shaking in a flask.

Sodium bismuthate $NaBiO_3$.

For the preparation and standardization of *ferrous sulphate* and *potassium permanganate* solutions see page 93.

Mn in Steel. Dissolve 2 gms. of the steel in 20 cc. of dilute sulphuric acid (2 : 9) adding enough water, from time to time, to keep the ferrous sulphate in solution. When the steel is dissolved add 5 cc. of strong nitric acid. Evaporate until the sulphuric acid fumes, to destroy carbonaceous matter. Add 100 cc. of water and boil to dissolve ferric sulphate. Transfer the solution to a 500-cc. graduated flask. Add sodium carbonate solution until the solution of steel is dark in color and the precipitate dissolves slowly. Add emulsion of zinc oxide, a little at a time, and shake until the iron and chromium are precipitated. Dilute to the mark with water. Let the precipitate settle. Decant 250 cc. through a dry filter into a quarter-liter graduated flask. Transfer it to a half-liter Erlenmeyer flask and acidify with 25 cc. of nitric acid (sp.gr. 1.42). Add 1 gm. of sodium bismuthate and shake the flask several minutes. Let the residue settle. Filter through asbestos with suction. Wash the flask and filter with water acidulated with nitric acid until the washings are free from the pink color of permanganic acid. Transfer the filtrate to a beaker, add a measured volume of standard ferrous sulphate solution in excess of the permanganic acid, and titrate the excess of ferrous sulphate with standard potassium per-

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* Met. and Chem. Eng., 9, 224.

manganate solution. The ferrous sulphate solution should be of such strength that 1 cc. is equivalent to 1 cc. of the standard permanganate solution.

TITANIUM IN IRON

WELLER'S COLORIMETRIC METHOD *

Reagents. See page 90.

Ti in Iron. Weigh 5 gm. of the sample and transfer it to a No. 4 beaker. Add 50 cc. of strong hydrochloric acid, cover the beaker and heat until the iron is completely decomposed. Filter, wash with hot water, and ignite the filter in a platinum crucible. Cool, add a few drops of sulphuric acid and enough hydrofluoric acid to dissolve the silica. When the silica is dissolved, evaporate the solution to complete dryness.

A very small proportion of the titanium remains in solution and passes through with the filtrate. It may be recovered in the following way. Dilute the filtrate to 250 cc., add strong ammonia until a precipitate appears which slowly dissolves upon stirring. Add 2 per cent ammonia water until a slight, permanent precipitate is formed. Add 15 cc. of dilute hydrochloric acid (1 : 3). Stir vigorously to dissolve the precipitate. Add 100 cc. or more of a 20 per cent solution of sodium thiosulphate and stir until the iron is completely reduced and free sulphur begins to separate. Boil ten minutes. Let the precipitate settle, and filter. Wash with 2 per cent acetic acid solution and ignite in the crucible containing the silica-free titanium.

Add to the crucible 4 gm. of sodium carbonate, and fuse. Cool the fusion and disintegrate it by boiling with water. Filter the sodium titanate from the solution and wash with hot water in which has been dissolved a little sodium carbonate. Spread out the filter in a small beaker. Add to the crucible in which the fusion was made a little dilute sulphuric acid (1 : 3).

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* Camp, Met. and Chem. Eng., 10, 675.

Boil to dissolve off any adhering titanium and pour the solution upon the filter in the beaker. Wash the crucible with hot water, adding the washings to the solution in the beaker. Heat the beaker to dissolve sodium titanate. Withdraw the filter paper from the solution, washing it carefully with hot water.

If the solution contains fibers of filter paper, filter, and transfer the solution to a Nessler or other colorimeter tube. Add 5 cc. of hydrogen peroxide and compare with a standard solution in the manner described on page 92.

TITANIUM IN STEEL

Color Method

Weigh 0.5 gm. of steel (1 gm. should be taken if it contains less than 0.05 per cent Ti) and transfer to a large test-tube (10″ ×1″). At the same time place in a similar test-tube an equal amount of a steel which contains no titanium and add to it a sufficient quantity of soluble ferro-titanium, in which the titanium has been determined, to bring its Ti content to within 0.05 per cent of that in the unknown steel. Add to each, 10 cc. of dilute sulphuric acid (1 : 3), to dissolve the steel.

Add 5 cc. of concentrated nitric acid to oxidize the iron. Boil off the red fumes. Cool, add 5 cc. of hydrogen peroxide solution, dilute to the same volume, transfer to a colorimeter and compare the colors; or rinse into Eggertz tubes and dilute until the two have the same color.

Thymol is considered by Lehner and Crawford * to be more delicate for this purpose than hydrogen peroxide. The reagent is prepared by dissolving the thymol ($C_{10}H_{14}O$) in a little acetic acid and then adding sulphuric acid. The solution of thymol prepared in this manner is colorless and is fairly stable if kept out of a bright light. If exposed to a bright light it will darken in a few hours.

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* Eighth International Congress of Applied Chemistry, 1, p. 285.

NICKEL IN STEEL

ETHER METHOD

Outline. The steel is dissolved in hydrochloric acid, the iron oxidized with nitric acid, the chloride solution is shaken with ether, the ether solution containing most of the iron and the aqueous solution containing the nickel are allowed to separate in a separating funnel and the aqueous solution is drawn off. The iron and manganese are precipitated and filtered from the aqueous solution. The filtrate is acidified and if copper is present it is precipitated with hydrogen sulphide and the solution filtered, the filtrate is made ammoniacal, the nickel precipitated with hydrogen sulphide, filtered from the solution, burnt, and weighed as NiO.

Reagents. *Dilute hydrochloric acid,* (1 : 1).

Ether, $C_2H_5 \cdot O \cdot C_2H_5$.

Bromine water; water saturated with Br.

Hydrogen Sulphide. Generate H_2S by adding dilute HCl (sp.gr. 1 : 1) to FeS in a gas generator. (Fig. 53, p. 64.)

Acetic acid. 90 per cent, $CH_3 \cdot COOH$.

Ni in Steel. Dissolve 2 gm. of steel in 30 cc. of dilute hydrochloric acid (1 : 1). Add 2 cc. of strong nitric acid to oxidize the iron. Evaporate to 10 cc. Cool and pour the solution into a 150-cc. separatory funnel with short stem (Fig. 72). Wash out the beaker with dilute hydrochloric acid (1 : 1), using a small amount at a time, and adding the washings to the funnel. Do not let the volume exceed 40 cc. Cool and add 50 cc. of ether.

FIG. 72.—Separatory Funnel.

Place the stopper in the funnel and shake gently at first. Keep the funnel cool by holding it under running water. If allowed to become hot the ether would reduce some ferric chloride to ferrous chloride.

The greater part of the ferric chloride is taken up by the ether, leaving the nickel, cobalt, manganese, aluminum, and copper, and a little of the iron, in the original solution.

Set the funnel in an upright position and let the ether and aqueous solutions separate. Complete separation is indicated by a sharp line between them. Take out the stopper, open the tap, and draw off the aqueous solution, leaving the ether in the funnel. Add 5 cc. of dilute hydrochloric acid (1 : 1) to the ether in the funnel.

Only a small quantity of acid is used, because it takes some iron out of the ether solution.

Shake again and separate as before.

If the steel is high in nickel, wash a second time with hydrochloric acid.

Discard the ether solution, which contains most of the ferric chloride. Cover the beaker containing the aqueous solution and boil off the ether, taking care that it does not take fire. Dilute to 200 cc., add 3 cc. of bromine water to precipitate manganese, add a decided excess of ammonia, and boil to precipitate ferric hydrate. Filter, wash once with water, and wash the precipitate back into the beaker. Redissolve the precipitate in hydrochloric acid, add bromine water, and precipitate again with ammonia.

Filter, combine the filtrates, and boil off the ammonia. Make the solution distinctly acid with hydrochloric acid.

If copper is present, pass hydrogen sulphide through the solution and filter the precipitated copper sulphide. Evaporate the filtrate to 100 cc. and add ammonia until it is just alkaline. Saturate the hot solution with hydrogen sulphide to precipitate the sulphides of nickel and manganese. Neutralize the solution with acetic acid and then add an excess of 4 cc. to dissolve manganese sulphide. Filter off the nickel sulphide, wash well with hot water, and ignite it in an open, porcelain crucible.

Burn the paper at as low heat as possible and then heat a few minutes at the highest temperature. Cool in a desiccator and weigh as NiO. The factor for nickel in NiO is 0.78576.

If, in burning, any nickel is reduced to the metallic state, reoxidize it with a few drops of nitric acid, evaporate the excess of acid, heat to a high temperature, and weigh.

NICKEL IN STEEL

Potassium Cyanide Method*

Reagents. *Silver nitrate solution.* Dissolve 1 gm. of $AgNO_3$ in 1 liter of water.

Potassium iodide solution. Dissolve 20 gms. of KI in water and dilute to 1 liter.

Standard solution of nickel. This solution may be made by dissolving pure metallic nickel, or a pure salt of nickel. A convenient strength is about 0.0005 gm. Ni per cubic centimeter.

Standard solution of potassium cyanide. Dissolve 4 gms. KCN in 1 liter of water.

The cyanide solution is not permanent and must be standardized frequently. It is standardized in the following way:

Take 50 cc. of the standard nickel solution, dilute it to 100 cc., and add 20 cc. of hydrochloric acid. Neutralize with ammonia and add 1 cc. of ammonia in excess. Add 5 cc. each of the silver nitrate solution and the potassium iodide solution.

$$AgNO_3+KI=AgI+KNO_3.$$

The silver iodide renders the solution turbid.

Titrate with the potassium cyanide solution until the solution clears.

$$NiCl_2+4KCN=K_2Ni(CN)_4+2KCl.$$

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* Deniges, Chem. News, 69, p. 42. Moore, Chem. News, 72, p. 92.

When the reaction with the nickel is complete, the silver iodide is dissolved by the excess of potassium cyanide.

$$2KCN + AgI = KAg(CN)_2 + KI.$$

A blank should be run, leaving out the nickel and including all the reagents in the quantities given above to learn how much potassium cyanide is required to dissolve the silver iodide. The quantity of potassium cyanide thus determined should be deducted from all titrations.

Ni in Steel. Weigh 2 gms. of steel and treat it according to the ether method for nickel (p. 137) until the copper sulphide has been filtered from the solution. Evaporate the filtrate to 100 cc. Neutralize with ammonia and add 1 cc. in excess. Then add 5 cc. each of the silver and potassium iodide solutions and titrate with standard potassium cyanide solution.

NICKEL IN STEEL

Dimethylglyoxime Method*

Reagents. *Hydrofluoric acid,* HF.

Tartaric acid, $C_4H_6O_6$.

Dimethylglyoxime solution. Dissolve 1 gm. of dimethylglyoxime ($CH_3 \cdot C \cdot (: N \cdot OH)C(: N \cdot OH)CH_3$) in 100 cc. of alcohol, (C_2H_6O).

Ni in Steel. Dissolve 1 gm. of steel in 25 cc. of hydrochloric acid. Add a few cubic centimeters of nitric acid to oxidize the iron. Boil out the chlorine and most of the hydrochloric acid. If silica should be precipitated in the solution, add a little hydrofluoric acid. When solution is complete, add about 3 gms. of tartaric acid and 300 cc. of water. Make the solution slightly ammoniacal.

If iron is precipitated, acidify with hydrochloric acid, heat to dissolve the precipitate, and add more tartaric acid. When the tartaric acid is dissolved add ammonia to render the solution alkaline.

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* O. Brunck. Stahl u. Eisen, 28, 331.

If the iron remains in solution, heat nearly to boiling, and add 20 cc. of dimethylglyoxime solution. Let the solution stand for fifteen minutes at a temperature of between 80° and 90° C.

$$2C_4H_8N_2O_2+NiCl_2=C_8H_{14}N_4O_4Ni+2HCl.$$

If the flocculent precipitate of nickel stands long in the mother liquor at a high temperature, it becomes minutely crystalline and is filtered with great difficulty.

Filter while hot in a Gooch crucible. Wash with hot water until it comes through colorless. Dry forty-five minutes at a temperature of 110° to 120° C. and weigh. The dried precipitate contains 20.325 per cent Ni.

CHROMIUM AND VANADIUM IN STEEL

Outline. The steel is dissolved in sulphuric and nitric acids, the chromium and vanadium are oxidized with potassium permanganate, and the resulting manganese dioxide filtered from the solution. After adding sulphuric acid to the filtrate the chromium is titrated with a standard solution of ferrous ammonium sulphate. The excess of ferrous ammonium sulphate is titrated back with standard potassium permanganate solution, an indicator is added and the titration with standard ferrous ammonium sulphate solution is continued for the vanadium.*

Reagents. *Dilute sulphuric acid* (1 : 3).

Nitric acid (sp.gr. 1.2); add 40 cc. HNO_3 (sp.gr. 1.42) to 65 cc. of water.

A strong solution of *potassium permanganate* for oxidizing chromium and vanadium; 20 gm. of $KMnO_4$ in a liter of water.

Standard potassium permanganate solution; 2.83 gm. of $KMnO_4$ per liter. (See p. 51.)

Standard solution of ammonium ferrous sulphate; 35.09 gm. of $(NH_4)_2SO_4 \cdot FeSO_4+6H_2O$ dissolved in 300 cc. of dilute sulphuric acid (1 : 3) and diluted to 1 liter with water.

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* Johnson, "Chem. Anal. of Special Steels," p. 8.

This solution should be standardized against the permanganate solution and corrected, if necessary, to be of exactly equal value.

This solution will be equivalent to about 0.001555 gm. of chromium, but it should be standardized for chromium by taking 2 gms. of steel in which the chromium has been determined (or a steel free from Cr and adding a weighed quantity of pure $K_2Cr_2O_7$) and treating it exactly according to the method given below.

The solution should be standardized in a similar way for vanadium. Its value in vanadium should be about 0.00456.

Solution of potassium ferricyanide. Dissolve 5 gms. of $K_3Fe(CN)_6$ in 130 cc. of water.

Cr and V in Steel. Weigh 2 gm. of steel, transfer it to a 600-cc. beaker, and add 30 cc. of dilute sulphuric acid (1 : 3) and 20 cc. of water. Heat; when the first vigorous reaction is over, add 60 cc. of dilute nitric acid (sp.gr. 1.2) to complete the solution and to oxidize the iron. After it is in solution, boil two minutes and add 200 cc. of water. From a small pipette add potassium permanganate solution, a little at a time, until there is a slight precipitate of MnO_2, which does not dissolve after boiling twenty minutes.

Chromium is converted to CrO_3 and the vanadium to V_2O_5.

Remove the beaker from the heat and place it in a dish of cold water. Filter by suction on asbestos which has been previously washed with nitro-hydrochloric acid, and finally washed well with water. Wash the residue on the filter 15 times with very dilute sulphuric acid (1 : 600). Transfer the filtrate and washings, the volume of which should be about 300 cc., to the 600-cc. beaker. Add 30 cc. of dilute sulphuric acid and titrate with a standard solution of ferrous ammonium sulphate until the solution loses its brown tint and becomes practically colorless, if the steel has less than 1 per cent of chromium; and if higher in chromium (2 to 6 per cent), titrate until the chrome green no longer grows darker.

$$2CrO_3+6FeSO_4+6H_2SO_4=6H_2O+3Fe_2(SO_4)_3+Cr_2(SO_4)_3.$$

Then add 2 or 3 cc. more of the ferrous ammonium sulphate solution, to ensure the reduction of all of the chromium. Read the burette and titrate back with standard permanganate solution until a faint pink persists after stirring thirty seconds. The pink color can be detected in the chrome green solution after a little practice. The equivalent of the permanganate titration, in terms of ferrous ammonium sulphate, deducted from the total volume of ferrous ammonium sulphate solution added, represents the quantity of ammonium ferrous sulphate solution required to reduce the chromium.

V in Steel. The solution of steel in which the chromium has been titrated according to the method above may be used for the estimation of vanadium. After titrating back with permanganate solution for the determination of chromium, add, from a dropper, 12 drops of potassium ferricyanide solution (5 gms. $K_3Fe(CN)_6$ in 130 cc. of water). This gives the solution a brown color. Now titrate with ferrous ammonium sulphate solution to a green color, free from yellow tints. Do not titrate to blue.

$$V_2O_5+2FeSO_4+H_2SO_4=V_2O_4+Fe_2(SO_4)_3+H_2O.$$

If much chromium is present, titration continues until the green color begins to darken.

If as much as 0.5 per cent of copper is present, it produces a light yellow cloud of copper ferricyanide when the indicator is added. In such steels the copper should be precipitated with ferricyanide before the MnO_2 is filtered from the solution; both are then removed at the same time.

Run a blank on a steel without vanadium, and correct all titrations accordingly. The blank is from 0.3 cc. to 0.4 cc. if no chromium is present; from 0.7 cc. to 0.9 cc. if the steel has 3 per cent chromium; and from 1 cc. to 1.2 cc. if there is 4 per cent chromium.

If the steel is high in chromium and tungsten, digest the drillings until the tungstic acid is bright yellow before adding potassium permanganate. Then add enough potassium permanganate to make the tungstic acid chocolate color by the admixture of MnO_2.

VANADIUM IN STEEL

Volumetric Method

Reagents. *Standard permanganate solution.* (See p. 51.)

The permanganate solution is standardized for vanadium by weighing 2 gm. of a steel in which the vanadium is known and treating it according to the method given below.

Dilute sulphuric acid (1 : 2).

Zinc oxide, ZnO.

Zinc hydroxide, $Zn(OH)_2$ suspended in water.

Sodium hydroxide, ($NaOH$)

Potassium nitrate, (KNO_3).

Manganese chloride; a saturated solution of $MnCl_2$.

V in Steel. Dissolve 2 gms. of steel in 60 cc. of dilute sulphuric acid and 200 cc. of water. When in solution neutralize the greater part of the acid with zinc oxide. See that all of the zinc oxide is dissolved. Complete the neutralization by adding precipitated zinc hydroxide in water until some undissolved hydroxide remains. Heat, filter, and wash with hot water. The precipitate contains the whole of the vanadium and only a small amount of iron. Place the filter with the precipitate in a nickel crucible, burn the paper, and heat the precipitate to redness. Add to the burnt precipitate a few grams of sodium hydroxide and a little potassium nitrate.

$$V_2O_5 + 4NaOH = Na_4V_2O_7 + 2H_2O.$$

Extract with water. Filter and precipitate the vanadium from the filtrate with manganese chloride solution.

$$Na_4V_2O_7 + 2MnCl_2 = Mn_2V_2O_7 + 4NaCl.$$

Filter; dissolve the precipitate in hydrochloric acid. Add 10 cc. of sulphuric acid, heat, and titrate hot with standard potassium permanganate solution.

$$5V_2O_4+2KMnO_4+3H_2SO_4=5V_2O_5+K_2SO_4+2MnSO_4+3H_2O.$$

VANADIUM IN STEEL

Colorimetric Method*

Reagents. *Nitric acid* (sp.gr. 1.2).

Ammonium persulphate, $(NH_4)_2S_2O_8$.

Phosphoric acid, H_3PO_4 (sp.gr. 1.30).

Hydrogen peroxide, H_2O_2.

Standard vanadium solution. Dissolve 1 gm. ammonium vanadate (NH_4VO_3) in water. Add 20 cc. dilute sulphuric acid, (1 : 3), dilute to 1 liter and shake well. To 200 cc. of this solution add 25 cc. of dilute sulphuric acid (1 : 3), and heat to boiling. Add 30 cc. sulphurous acid (H_2SO_3), and boil to expel the excess of SO_2. Titrate the hot solution with standard permanganate solution and calculate the vanadium content.

$$V_2O_5+H_2SO_3=V_2O_4+H_2SO_4.$$

$$5V_2O_4+2KMnO_4+3H_2SO_4=5V_2O_5+K_2SO_4+2MnSO_4+3H_2O.$$

Dilute a portion of the ammonium vanadate solution remaining, so that 1 cc. will contain 0.0001 gm. vanadium.

V in Steel. Weigh 0.25 gm. of the sample and an equal amount of a steel containing no vanadium, and having about the same content of carbon. Place each in a large test-tube. Add to each 4 cc. of dilute nitric acid and heat in a water-bath until the steel is dissolved. To the clear solution add about 0.3 gm. of ammonium persulphate. Heat until the evolution of gas ceases. Cool and add to the solution containing no vanadium 1 cc. of the standard vanadium solution. Add to

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* Slawik, Chem. Zeit., 34, p. 648.

both 4 cc. of phosphoric acid and 4 cc. of hydrogen peroxide. If the color of the standard is much lighter than that of the unknown, prepare a stronger solution of the standard and compare in a colorimeter or transfer to Eggertz tubes and dilute until the colors match.

TUNGSTEN IN STEEL

Outline. The steel is dissolved in nitric and hydrochloric acids, the solution evaporated to a small volume, diluted, and filtered from the oxides of tungsten and silicon. The filter is burnt in a platinum crucible, the residue treated with hydrofluoric and sulphuric acids, and evaporated to dryness to remove the silica. The residue of WO_3 contaminated with a little ferric oxide is weighed, after which it is fused with sodium carbonate, treated with water, the ferric oxide filtered from the solution, burnt, and weighed; and this weight is deducted from the first weight of combined oxides.*

Reagents. *Hydrofluoric acid,* HF.

Dilute sulphuric acid (1 : 20).

Sodium carbonate, Na_2CO_3.

W in Steel. Weigh 2 gms. of steel. Transfer it to a porcelain casserole, and treat it with a mixture of 30 cc. of concentrated nitric acid and 30 cc. of concentrated hydrochloric acid. Heat and agitate until the steel is in solution and the precipitated tungstic acid has a bright yellow color.

Do not leave a glass rod in the solution, since tungstic acid attacks glass in hot acid solution.

Take off the cover and evaporate the solution to 20 cc. Dilute with 100 cc. of water, stir well, and remove the stirring rod. Heat to boiling and hold at the boiling-point for half an hour. Add a little paper pulp and filter. Wash with dilute

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* Johnson, "Anal. of Special Steels," p. 74.

hydrochloric acid (1 : 20) until the precipitate is free from iron, and then wash with water.

Test with potassium or ammonium sulphocyanate.

Ignite the precipitate in a platinum crucible and, if the SiO_2 is to be determined, weigh as $WO_3+SiO_2+Fe_2O_3$. Add a few drops of sulphuric acid and 10 cc. of hydrofluoric acid. Evaporate to sulphuric acid fumes and then drive off the sulphuric acid by heating the crucible from the top. Heat at a high temperature. Cool and weigh as $WO_3+Fe_2O_3$. Add 5 gms. of sodium carbonate and fuse twenty minutes. Dissolve in a casserole with water. Filter the iron from the solution, wash with water to free the precipitate from sodium (about 40 washings should be sufficient). Ignite in a platinum crucible and weigh. Deduct the weight from the combined weight of $WO_3+Fe_2O_3$. The difference is the weight of WO_3. The factor for W in WO_3 is 0.7931.

W in the Presence of Cr. If the steel contains chromium, the difference between the last two weights above will be $WO_3+Cr_2O_3$. Therefore, to determine the percentage of tungsten, the quantity of chromium which is in the filtrate with the tungsten is determined by the method described on page 141, for the determination of chromium in steel. That is, add sulphuric acid to the filtrate from the ferric oxide until the solution is acid and boil it with a slight excess of potassium permanganate. Filter, cool, and dilute to 300 cc., add 30 cc. of dilute sulphuric acid, and titrate with standard ferrous ammonium sulphate. The chromium found is calculated to Cr_2O_3 and deducted from the combined weight of $WO_3+Cr_2O_3$.

MOLYBDENUM IN STEEL

Lead Molybdate Method*

Reagents. *Solution of sodium hydroxide.* Dissolve 80 gms. NaOH in water and dilute to 1 liter.

Methyl orange. Dissolve 1 gm. $C_{14}H_{14}N_3SO_3Na$ in water and dilute to 1 liter.

Lead acetate solution. A saturated solution of $Pb(C_2H_3O_2)_2 + 3H_2O$ in water.

Ammonium acetate, $(NH_4C_2H_3O_2)$.

Mo in Steel. Weigh 2 gms. of steel, dissolve it in 40 cc. of hydrochloric acid, oxidize by adding 5 cc. of nitric acid. Nearly neutralize the acids by adding sodium hydroxide solution. If there is a precipitate (WO_3 or MoO_3), filter through a little paper pulp, transfer the pulp to a flask, and add 100 cc. of sodium hydroxide solution. Heat nearly to boiling, shake vigorously, and add, through a funnel, while shaking, the hot filtrate. Dilute the solution to 500 cc. in a graduated flask. Filter off 250 cc. Add a drop of methyl orange and hydrochloric acid to decided acidity. Then add 20 cc. of lead acetate solution (if the steel has more than 5 per cent Mo, add more of the precipitant) and a sufficient amount of ammonium acetate to combine with all the hydrochloric acid and leave an excess. Heat to boiling. Let the precipitate settle, filter, wash with hot water, ignite at a low red heat, and weigh as $PbMoO_4$. The factor for Mo in $PbMoO_4$ is 0.2615.

If the steel contains tungsten, the lead molybdate will not be pure, but will have mixed with it lead tungstate ($PbWO_4$). To separate them, dissolve the ignited precipitate in hydrochloric acid. Add a few drops of nitric acid and evaporate nearly to dryness. Add 200 cc. dilute hydrochloric acid (1 : 4). Boil,

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* Chatard, Chem. News. 24, p. 175.

and filter off WO_3. Reprecipitate the molybdenum from the filtrate with lead acetate, as in the method just described. Filter, burn and weigh it.

MOLYBDENUM IN STEEL

Weighing as MoO_3

Reagents. *Dilute nitric acid* (2 : 3).

Tartaric acid, $C_4H_6O_6$.

Dilute sulphuric acid (1 : 3).

Hydrogen sulphide, H_2S from a generator. (See Fig. 53, p. 64.)

Mo in Steel. Dissolve 2 gms. of steel in dilute nitric acid (2 : 3). Cool and add 3 or 4 gms. of tartaric acid (a sufficient quantity to keep the iron in solution, after rendering alkaline with ammonia).

Add ammonia until slightly alkaline. Dilute to 700 cc. Saturate with hydrogen sulphide by passing a current of the gas through the solution. Add dilute sulphuric acid (1 : 3), drop by drop, until the solution is slightly acid.

When the solution becomes acid, the reddish brown MoS_3 forms and settles readily.

Add a little paper pulp and pass H_2S through the solution thirty minutes. Filter and wash quickly with hydrogen sulphide water containing 2 drops of sulphuric acid per liter. Burn off the paper in a platinum crucible and roast the MoS_3 to MoO_3 at a very low red heat.

MoO_3 is volatile at a strong red heat.

Cool in a desiccator and weigh MoO_3. The factor for Mo in MoO_3 is 0.6666.

MOLYBDENUM IN MOLYBDENUM POWDERS

Weigh 0.5 gm. of the powder. Treat with aqua regia. Dilute and filter. Burn the filter and fuse the residue with sodium carbonate and a small quantity of sodium nitrate. Dissolve the fusion in dilute hydrochloric acid and add it to the main solution. Evaporate the solution to dryness. Dissolve the residue in dilute hydrochloric acid. Filter and precipitate the molybdenum from the filtrate with a solution of lead acetate and proceed according to the method given on page 148.

COPPER IN STEEL

GRAVIMETRIC METHOD

Reagents. *Dilute sulphuric acid* (1 : 3).

Sodium thiosulphate, $Na_2S_2O_3+5H_2O$.

Weigh 5 gms. (or more if low in copper). Transfer it to a 500-cc. beaker, add 50 cc. dilute of sulphuric acid (1 : 3), and heat to dissolve.

If the steel does not readily dissolve in sulphuric acid, dissolve it in dilute nitric acid (2 : 3). Add 20 cc. of sulphuric acid (1 : 1) and evaporate until the sulphuric acid fumes.

Dilute the solution to 400 cc. with hot water. Add 6 gms. of sodium thiosulphate and boil until the cloudiness due to the precipitated sulphur clears.

Hydrogen sulphide may be used as the precipitant instead of sodium thiosulphate.

Filter, wash with hot water, and ignite the filter and residue in a porcelain crucible over a Bunsen burner; cool in a desiccator and weigh CuO.

$$2CuS+3O_2=2CuO+2SO_2.$$

The temperature should not be raised high enough to melt the copper oxide.

The precipitate is usually contaminated with a little of the oxides of iron, silicon, and possibly chromium.

The impurities may be removed as follows: Dissolve the weighed precipitate in a little strong hydrochloric acid. Dilute, add an excess of ammonia, filter, burn, and weigh. Deduct the weight from the weight of the combined oxides. The difference represents the weight of copper oxide. The factor for C in CuO is 0.7989.

COPPER IN STEEL

VOLUMETRIC METHOD

Weigh the steel and proceed according to the method above until the copper sulphide is filtered from the solution and washed. Dissolve the copper sulphide in warm dilute nitric acid and proceed according to one of the volumetric methods for copper in ore. (See p. 168.)

NITROGEN IN STEEL

Outline. The steel is dissolved in hydrochloric acid, the solution distilled with sodium hydroxide sclution, the distillate containing the nitrogen is treated with Nessler reagent and compared with a standard solution similarly treated.*

Reagents. *Hydrochloric acid* (sp.gr. 1·1) free from ammonia; or the ammonia in the acid may be determined and the correction made for each estimation of nitrogen.

To prepare ammonia-free hydrochloric acid, distil strong hydrochloric acid from a flask provided with a separatory funnel and delivery tube, to which has also been added some strong sulphuric acid, free from nitrous acid. Pass the HCl gas, which distils off, through a small wash bottle containing dilute hydrochloric acid (1 : 1) and finally into distilled water free from ammonia.

If the ordinary distilled water contains ammonia, redistil, and reject the first distillate, which will contain the ammonia.

Solution of sodium hydroxide. Dissolve 300 gms. of fused NaOH in 500 cc. of distilled water. Heat for twenty-four hours

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* Allen, Chem. News, 41, 231.

at 50° C. in contact with a copper-zinc couple, prepared by rolling together about 15 $cm.^2$ each of zinc and copper foil. The copper-zinc couple decomposes nitrates, so that ammonia will be expelled in the first distillation.*

Nessler reagent. Dissolve 35 gms. potassium iodide in about 50 cc. of water. Add concentrated solution of mercuric chloride, little by little, shaking, until there is a permanent red precipitate. Filter and add to the filtrate 120 gms. of sodium hydroxide dissolved in about 200 cc. of water. Dilute to 1 liter. Add to this 5 cc. of a saturated solution of mercuric chloride in water. Mix thoroughly, let the precipitate settle, and decant the clear solution into a glass-stoppered bottle.

Standard solution of ammonia. Dissolve in 1 liter of water 0.0382 gm. NH_4Cl which has been dried at 100° C. One cubic centimeter will contain 0.01 mgm. of nitrogen.

N in Steel. Place 40 cc. of the sodium hydroxide solution, which has been prepared with the copper-zinc couple, into a 1500-cc. Erlenmeyer distilling flask, provided with a separatory funnel and a condenser. Add 500 cc. of water and about 25 gms. of tin foil, to prevent bumping, and distil until the Nessler reagent gives no reaction with the distillate.

While this is going on, weigh 3 gms. of steel free from oil and dissolve it in 30 cc. of ammonia-free hydrochloric acid. Transfer the solution to the bulb of the separatory funnel and when the soda solution is free from ammonia drop the ferrous chloride solution very slowly into the boiling solution in the flask and collect the distillate in a glass cylinder of about 160 cc. capacity. When about 50 cc. have been so collected, take away the cylinder and replace it with a fresh one. Measure the nitrogen collected as follows: Dilute the collected distillate with ammonia-free water to 100 cc. and pour it into one of the cylinders in which has been placed 1½ cc. of the Nessler reagent.

Prepare a standard solution, by adding to a similar cylinder

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* Sutton, "Volumetric Anal.," p. 446.

$1\frac{1}{2}$ cc. of Nessler reagent, 100 cc. of ammonia-free water, and 1 cc. of the standard ammonia solution. If the colors do not agree, prepare other standards, varying the amount of the ammonia solution until the color of the standard matches that of the solution from the steel.

When about 100 cc. of distillate has been collected in the second cylinder, replace it by another. Estimate its nitrogen content as before. Continue until the distillate comes over free from ammonia. Then add together the number of cubic centimeters of standard ammonium chloride solution used. Divide the sum by 3, and each cubic centimeter having the value of 0.01 mgm. of N will be equal to 0.001 per cent of N in the steel.

De Osa * found that the method above gave low results and that the method of Boussingault was more satisfactory, although it did not always give concordant results. By this method the steel is dissolved in hydrochloric acid in the presence of CO_2, the NH_3 is distilled into a measured quantity of very weak standard sulphuric acid solution (0.01 normal) and the uncombined acid measured by titrating it with a standard alkaline solution, or by treating it with a mixture of KIO_3 and KI and titrating the iodine liberated.

HYDROGEN IN STEEL†

Outline. The steel is ignited in a silica tube in a current of oxygen. Hydrogen from the steel combines with the oxygen, and the water formed is absorbed in phosphoric anhydride and weighed.

Apparatus. The operation is carried out in a combustion furnace provided with two silica tubes (Fig. 73), one above the other, each 75 cms. long. The lower one, in which the steel is placed, is 2 cms. in diameter; and the upper one, in which the oxygen is purified, 1 cm. in diameter. Each tube has placed within it a 15-cm. roll of platinum gauze to serve as a catalyzer.

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* Rev. Metal., 5, 493–504.

† "Anal. of Iron and Steel," American Rolling Mill Co., Middletown, Ohio, p. 35.

The oxygen is passed through the hot 1-cm. silica tube at the rate of 100 cc. per minute to oxidize whatever impurities it may contain. It then passes through the following purifying train: first, a wash bottle containing a strong solution of potassium hydroxide; second, through a bottle containing sticks of potassium hydroxide; third, through concentrated sulphuric acid; and finally, through a tube containing phosphoric anhydride, held loosely in glass wool. The oxygen then enters the 2-cm. silica tube containing the steel, where it combines with the hydrogen liberated from the steel, forming water. It then passes into the 4-in. U-tube provided with glass stoppers, and containing phosphoric anhydride (held loosely in glass wool) in which the water is absorbed. From this tube the gas passes through a bottle containing concentrated sulphuric acid, which shows the rate at which the gas flows.

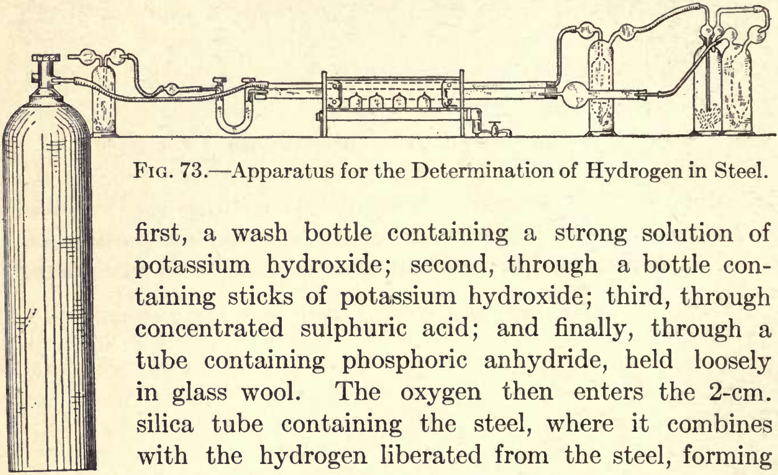

Fig. 73.—Apparatus for the Determination of Hydrogen in Steel.

H in Steel. Heat the silica tubes to redness and pass oxygen through at the rate of 100 cc. per minute. Detach the U-tube, let it cool in the balance case fifteen minutes, and weigh. Then connect it with the silica tube, through a one-hole stopper, turn on the heat, and the apparatus is ready for combustion.

Weigh from 10 to 40 gms. of the steel, in as large pieces as are available, and place the sample in a boat containing ignited alundum. Remove the stopper from the end of the silica tube at which the oxygen enters, insert the boat containing the steel into the red-hot tube. Close the tube and continue passing the oxygen, at the rate of 100 cc. per minute, for thirty minutes.

Then disconnect the U-tube, cool it in the balance case, and weigh. The weight of water, multiplied by the factor 0.1119, will give the weight of hydrogen in the steel.

It is necessary to run a blank, using the same amount of oxygen that is required for the test, and it should be run for the same length of time. The increase in weight for the blank, which is due to the oxidation of the rubber connections, should not exceed 1 mgm.

The temperature at which the combustion takes place should not be so high that the steel will absorb all the oxygen. It is not necessary to convert all the metal to oxide.

OXYGEN IN STEEL

Ledebur's Method *

Outline. The steel is ignited in a fused silica combustion tube in a current of purified hydrogen. The oxygen liberated from the steel combines with the hydrogen, and the water formed is absorbed in phosphoric anhydride and weighed.

Apparatus. The combustion furnace (Fig. 74) is the same as that described on page 154 in the Method for Hydrogen in Steel. The hydrogen is generated from hydrochloric acid on pure iron or mossy zinc. It is purified and dried by passing it first over sticks of potassium hydroxide; second, through a 30 per

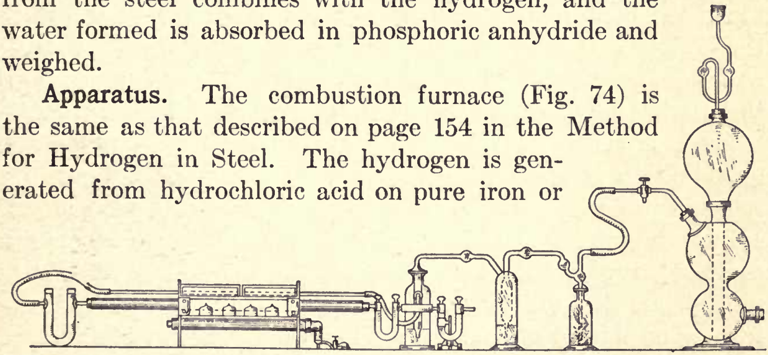

Fig. 74.—Apparatus for the Determination of Oxygen in Steel.

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* Cushman, Jour. Ind. and Eng. Chem., 3, 372. "Meth. for the Anal. of Iron and Steel," American Rolling Mill Co., Middletown, Ohio, 41.

cent solution of potassium hydroxide; and finally, before entering the 1-cm. silica tube, through concentrated sulphuric acid. From the small silica tube the gas passes through a U-tube containing phosphoric anhydride (held loosely in glass wool) to remove the water formed from the small amount of oxygen that comes over with the hydrogen. From the U-tube the hydrogen passes to the large combustion tube and combines with the oxygen of the steel to form water. The water is absorbed in phosphoric anhydride in a U-tube, and weighed. A guard tube containing phosphoric anhydride (held loosely in glass wool) follows the U-tube to protect it from moisture in the air.

Preparation of the Sample. The sample should be drilled with the machine drill, at low speed, to prevent partial oxidation. The drillings should be fine and should be free from all particles of oil or dust.

O in Steel. Weigh accurately 25 gms. of the finely divided drillings and transfer the sample to a nickel or platinum boat. Place the boat in the combustion tube, close the tube, attach the weighed U-tube (which is provided with glass stoppers) and the guard tube. Pass hydrogen through the furnace until the air has all been swept out of the furnace and connections while it is cold. Turn on the heat and raise the temperature quickly to a bright red heat (about 850° C.) and hold at this temperature while the hydrogen is passed at the rate of 100 cc. per minute, for thirty minutes. When the combustion is complete, turn off the heat and cool the furnace, as rapidly as possible, to the ordinary temperature. This may be done by turning on a blast of cold air. When the furnace is cold, detach the U-tube, with its guard tube. With an aspirator draw air into the U-tube through a drying tube to replace the hydrogen, and weigh the U-tube. The weight of water, multiplied by the factor 0.8889, will give the weight of oxygen in the steel.

A blank should be run occasionally and the necessary correction made on all determinations.

ANALYSIS OF IRON SLAGS

Sampling. If slags are chilled while hot, they are much more easily decomposed by acids than if left to cool slowly. Therefore the sample should be taken while the slag is molten and poured either into water or on a cold steel or iron plate. A steel rod may be stirred into the hot slag, withdrawn, and dipped into water, or left for the slag to cool on the rod in the air.

Since the composition of slag differs from hour to hour, a sample should be taken each time the slag is tapped and the accumulated samples for the day mixed and crushed, and properly sampled for analysis. (See p. 8.) The samples should be ground in a mechanical grinder or on a bucking-board, and finally in an agate mortar. Pass a magnet through the ground slag, to take out particles of iron that may be included in it. It is then ready for analysis.

Insoluble Residue. Weigh 0.5 gm. of slag and transfer it to a porcelain casserole. Add 20 cc. of water and stir until the slag is suspended in the water. Add 10 cc. of strong hydrochloric acid, cover, and heat to dissolve. Add a few drops of nitric acid and evaporate to dryness. Add to the residue 3 cc. of strong hydrochloric acid and evaporate again to dryness. Cool, add 30 cc. of dilute hydrochloric acid (1 : 1), heat to dissolve, and filter. Wash with hot dilute hydrochloric acid and hot water. Burn the filter with the precipitate in a platinum crucible, cool in a desiccator, and weigh as silicious residue.

SiO_2 in Slag. After the silicious residue is weighed, add a few drops of sulphuric acid, and enough hydrofluoric acid to dissolve the silica. Evaporate and weigh in the usual manner. (See p. 71.) The loss in weight represents SiO_2.

$Al_2O_3+Fe_2O_3$ in Slag. Heat the filtrate from the silicious residue to boiling and add a slight excess of ammonia. Boil until the smell of ammonia is faint. Let the precipitate settle, filter, wash with hot water, burn, and weigh as $Al_2O_3+Fe_2O_3$.

CaO in Slag. Heat the filtrate from aluminic and ferric oxides to boiling. Add 25 cc. of a saturated solution of ammonium oxalate and 10 cc. of ammonia.

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

Boil a few minutes and let the precipitate settle. Filter, and wash with hot water.

If the flux is dolomitic, for a complete separation of the magnesia, dissolve the precipitate of calcium oxalate in dilute hydrochloric acid, dilute, reprecipitate, and filter, as described above.

This precipitate may be burned and weighed as CaO, or, where many determinations are to be made, it is better to measure the lime volumetrically, as follows:

Remove the filter paper containing the precipitate of calcium oxalate from the funnel, carefully unfold it, and spread it out smoothly against the inside of a 500-cc. beaker, with the side of the paper containing the precipitate nearest the bottom of the beaker. (See Fig. 52 on p. 61.) With a jet of water carefully wash the precipitate from the paper. Withdraw the paper, add to the precipitate 100 cc. of dilute sulphuric acid (1 : 3).

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4.$$

Heat to boiling, and while hot titrate with standard potassium permanganate solution.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

By combining the two equations above and comparing it with that on page 57 for the titration of Fe, it is evident that the value of 1 cc. of permanganate solution in Fe, multiplied by 0.50205, will give its value in CaO.

$$\begin{aligned}5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 = 5CaSO_4 \\ + K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.\end{aligned}$$

MgO in Slag. Add hydrochloric acid to the filtrate from the calcium oxalate until it is slightly acid, and then add 20 cc. of 10 per cent solution of microcosmic salt. Evaporate the solution to about 250 cc. and cool it. When cold add ammonia, drop by drop, stirring, until the solution is alkaline. Then add 25 cc. of strong ammonia. Let the solution stand several hours, stirring occasionally. Filter, wash with dilute ammonia (1 : 3), burn, and weigh. (See magnesia in limestone, p. 165.)

FeO in Slag. Weigh 5 gms. of the sample and transfer it to a porcelain casserole. Add 30 cc. of water and stir until the slag is in suspension in the water. Add 30 cc. of dilute hydrochloric acid (1 : 1). Cover, and evaporate the solution to dryness. Cool, add 30 cc. of dilute hydrochloric acid (1 : 1), boil to dissolve the iron, filter, and wash. Then proceed with the reduction and titration of the iron by the potassium dichromate method given on page 62. The weight of iron, multiplied by 1.2865, will give the corresponding weight of FeO.

Al_2O_3 in Slag (by difference). From the determination of Fe above, calculate the equivalent of the Fe in Fe_2O_3 by multiplying the weight of Fe by the factor 1.4298. Deduct the weight of Fe_2O_3 from the combined weight of $Al_2O_3+Fe_2O_3$ as determined by the method on page 157, and calculate the percentage of Al_2O_3.

Al_2O_3 in Slag (Phosphate method). Weigh 0.5 gm. of the slag and treat it according to the method described above for the determination of insoluble residue. After the filtration and washing of the insoluble residue, proceed with the determination of Al_2O_3 in the filtrate according to the phosphate method given on page 87.

S in Slag. Weigh 1 gm. of slag, and transfer it to a porcelain casserole. Add 5 cc. of bromine water and 50 cc. of aqua regia. Evaporate to dryness, dissolve in a little hydrochloric acid and water, filter, and proceed in the manner described for the determination of sulphur in ore. (See p. 75.)

Mn in Slag. Weigh 1 gm. of slag and proceed according to the colorimetric method for manganese in ore (p. 92); or, if the slag is high in manganese, the bismuthate method or Julian's method may be used.

ANALYSIS OF LIMESTONE

Sampling. Limestone is sampled in a similar manner to that employed in the sampling of iron-ore (see p. 45), but usually so large a sample is not required, since it is a more uniform and less valuable material. The sample is crushed, mixed, divided, and ground to a fine powder for analysis in the usual manner.

Reagents. *Sodium carbonate.* Dry Na_2CO_3.

Dilute hydrochloric acid (1 : 1).

Oxalic acid. Dissolve 40 gms. ($H_2C_2O_4+2H_2O$ in 1 liter of water.

Sodium phosphate. Dissolve 100 gms. $HNa_2PO_4+12H_2O$ in 1 liter of water.

INSOLUBLE SILICIOUS MATTER IN LIMESTONE

Weigh 1 gm. of the powdered limestone and transfer it to a small beaker. Add 30 cc. of dilute hydrochloric acid and 1 cc. of nitric acid. Cover the beaker and heat it to dissolve as much as possible of the sample. Evaporate the solution to dryness and heat the residue in an air-bath one hour at 120° C. Cool, add 10 cc. of strong hydrochloric acid, warm gently and add 50 cc. of hot water. Filter, wash the residue with hot dilute hydrochloric acid, and then wash with hot water. Burn the filter and contents in a platinum crucible, cool in a desiccator and weigh.

SILICA IN LIMESTONE

After weighing the insoluble silicious matter (see above), add to the crucible about 0.5 gm. sodium carbonate and fuse. Cool and dissolve the fusion in a casserole with dilute hydrochloric acid. Carefully wash off the crucible and cover, letting the washings run into the casserole. Evaporate the solution to dryness and heat the residue in an air-bath one hour at 120° C. Cool, add 10 cc. of hydrochloric acid, warm and add 50 cc. of hot water. Filter, wash with dilute hydrochloric acid and then wash with hot water. Burn, cool in a desiccator, and weigh the SiO_2.

In carrying out this process about 1 per cent of the silica dissolves and passes through with the filtrate. For exact work, the filtrate should be taken to dryness again, dissolved, and filtered through a fresh paper, and the two papers burned together. If this treatment is adopted, the first heating of the residue need not be so prolonged. It is sufficient to evaporate the solution to dryness, take up the residue in dilute acid and filter.

OXIDES OF IRON, ALUMINUM, ETC., IN LIMESTONE

Combine the filtrates from the insoluble silicious matter and the silica, heat the solution to boiling and add a slight excess of ammonia. Boil until the odor of ammonia is faint.

Aluminum hydroxide is slightly soluble in ammonia, but this effect is largely neutralized by the presence of ammonium chloride.

Let the precipitate settle a few minutes, filter, and wash quickly with hot water.

The solution absorbs CO_2 from the air, which precipitates calcium as $CaCO_3$. If accurate results are required, wash the precipitate into a beaker, add hydrochloric acid, and heat to dissolve; dilute with hot water, add a slight excess of ammonia, boil until the odor is faint, let the precipitate settle, and filter and wash in the manner described above.

Burn the filter and contents in a platinum crucible. Cool in a desiccator and weigh.

The oxides weighed are chiefly those of iron and aluminum, but if the limestone contains titanium, phosphorus, vanadium, chromium, and zirconium, their oxides also will be present. For the separate determination of these elements in limestone, see the index for the methods for their determination in ores.

LIME IN LIMESTONE

Gravimetric Method

Combine the filtrates from the hydroxides of iron, aluminum, etc.

The total volume should measure about 250 cc. and there should be enough ammonium chloride present to prevent the precipitation of magnesia when the solution is near the neutral point.

Add 1 drop of methyl orange, heat to boiling, and add oxalic acid until the solution is acid. While boiling, stir, and add ammonia slowly until the solution is slightly alkaline. After the addition of the ammonia, boil and stir a few minutes. Let the precipitate settle.

$$CaCl_2+H_2C_2O_4+2NH_4OH=CaC_2O_4+2NH_4Cl+2H_2O.$$

Decant the clear solution through a filter, wash once by decantation with hot water, leaving the precipitate in the beaker. To free this precipitate of magnesium oxalate which comes down with it, dissolve it in 10 cc. of dilute hydrochloric acid, add about 100 cc. of hot water, boil, and reprecipitate the calcium oxalate with oxalic acid and ammonia. Filter on the same filter paper used for the decantation, and wash thoroughly with hot water. Reserve both filtrates for magnesia.

Place the filter and precipitate in a platinum crucible. Carefully dry, and burn off the paper with a Bunsen burner. Finally heat with a blast lamp to drive off all the CO and CO_2.

$$CaC_2O_4=CaO+CO_2+CO.$$

Cool in a desiccator and weigh quickly.

CaO readily absorbs moisture from the atmosphere. Repeat the burning and weighing until the weight is constant.

The weight of CaO multiplied by 100 represents the percentage of CaO, or lime, in the limestone. This percentage of CaO, multiplied by the factor 1.7847, will give the percentage of $CaCO_3$.

Burning large precipitates of calcium oxalate completely to CaO and weighing adds considerably to the time of making the analysis. If many determinations of lime are to be made, the following volumetric method is recommended.

LIME IN LIMESTONE

Volumetric Method

After the calcium oxalate has been transferred to the filter (see the preceding method), wash it with hot water until the wash water comes through free from oxalates.

Test by collecting a few cubic centimeters in a small beaker, acidifying with H_2SO_4, heating nearly to boiling, and adding a drop of $KMnO_4$ solution. If the color of the permanganate fades, oxalate is still present.

When thoroughly washed, transfer the precipitate from the paper to a beaker, with hot water. (See p. 61 for the method of transfer.) Then wash off the paper with a little dilute H_2SO_4 (1 : 5) from a wash bottle, and finally, with hot water. Remove the paper. Add a few cubic centimeters of sulphuric acid to dissolve the precipitate.

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4. \tag{1}$$

Dilute with hot water and, while hot (70° C.), titrate with standard potassium permanganate solution.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2. \tag{2}$$

The standard permanganate solution used for the titration of iron may be used for lime. Its value in iron, multiplied by

0.50206, will give the value per cubic centimeter in CaO, or, multiplied by 0.89604, will give the value in $CaCO_3$. These factors are calculated from the above reactions and the reaction of $KMnO_4$ with iron (p. 57). Two molecules of $KMnO_4$ react with 10 atoms of Fe in the one case (p. 57) and with 5 molecules of oxalic acid in the other (equation 2 above) which are equivalent to 5 atoms of Ca (equation 1 above). From the weight of Ca the corresponding weights of CaO and $CaCO_3$ are at once deduced.

The more accurate and desirable method, however, is to standardize the solution against a weighed quantity of pure Iceland spar, which has been treated by this method.

TITRATION OF BOTH CALCIUM AND MAGNESIUM

A method for the titration of both calcium and magnesium in the same solution has been devised by P. J. Fox,* by which the calcium is precipitated as oxalate, and the magnesium as magnesium ammonium arsenate ($MgNH_4AsO_4$), by the addition of ammonium arsenate. The precipitates are filtered together from the solution, and transferred to a flask. Sulphuric acid is added, and the calcium is measured by titrating the liberated oxalic acid, after it is heated, with $KMnO_4$ solution. The solution is cooled, KI added, and the liberated iodine titrated with standard sodium thiosulphate solution, without the addition of starch.

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2.$$

The flask should be screened from the light with black paper during the titration to prevent the liberation of iodine by the action of light.

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* Jour. Ind. and Eng. Chem., 5, 910 (1913).

MAGNESIA IN LIMESTONE

Combine in one solution the filtrates from the calcium oxalate and acidify it with hydrochloric acid. Add 20 cc. of sodium phosphate solution (100 gms. $HNa_2PO_4+12H_2O$ per liter). Evaporate the solution until a precipitate begins to form. Add hot water until the precipitate dissolves. Add ammonia, drop by drop, stirring, until the solution is alkaline. Then add a volume of ammonia (sp.gr. 0.90) equal to about one-fourth the volume of the solution. Stir well and let the precipitate settle several hours.

A mechanical stirrer is recommended. Where the stirring rod touches the sides of the beaker, the precipitate adheres and is removed with great difficulty. If the stirring is continuous, precipitation should be complete in half an hour.

$$MgCl_2+NH_4OH+HNa_2PO_4=MgNH_4PO_4+2NaCl+H_2O.$$

Filter, and if the precipitate of magnesium ammonium phosphate is large, or if other salts have crystallized with it, dissolve the precipitate in a little hydrochloric acid, dilute the solution with water, add 5 cc. of sodium phosphate solution and ammonia, in the manner described above. Stir, let the precipitate settle, and filter. Wash with water containing 100 cc. NH_4OH (sp.gr. 0.90) and 1 cc. HNO_3 per liter.

Dry the precipitate; separate it from the paper. (See Fig. 31, p. 27.) Burn the paper in a porcelain crucible. When the carbon is all burnt, add the precipitate and heat at a red heat with a Bunsen burner until the precipitate is white. Then heat at a high temperature with the blast lamp a few minutes. Cool in a desiccator and weigh $Mg_2P_2O_7$.

$$2NH_4MgPO_4=Mg_2P_2O_7+2NH_3+H_2O.$$

The factor for MgO in $Mg_2P_2O_7$ is 0.36207; and for $MgCO_3$ is 0.75718.

If the filter paper is burned in contact with the phosphate precipitate, there is danger that phosphorus will be reduced and the determination spoiled. If this takes place in a platinum crucible, the phosphorus combines with the platinum, making it brittle and causing cracks to form.

PHOSPHORUS AND SULPHUR IN LIMESTONE

For methods for the determination of phosphorus, sulphur, and other elements in limestone see the methods for these elements in iron ore.

CARBON DIOXIDE IN LIMESTONE

Apparatus and Reagents. The limestone is dissolved in a flask (Fig. 75 C), in dilute HCl.

$$CaCO_3+2HCl=CaCl_2+H_2O+CO_2.$$

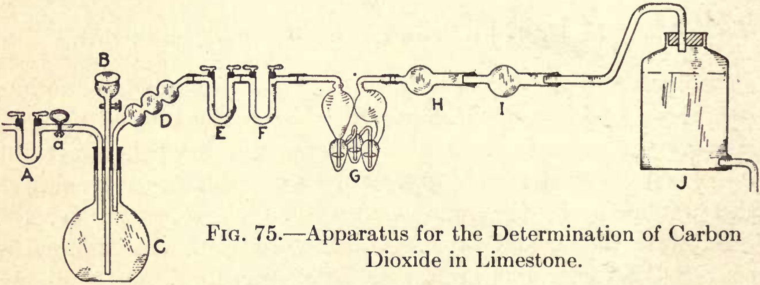

Fig. 75.—Apparatus for the Determination of Carbon Dioxide in Limestone.

The liberated CO_2, after purification, is absorbed in a KOH bulb and weighed.

A is a U-tube containing soda lime—a mixture of calcium and sodium hydroxides—which removes CO_2 from the air drawn into the apparatus.

B. A separatory funnel in which is placed 150 cc. of dilute HCl (1 : 5).

C. A Florence flask in which the sample is placed for solution.

D. A bulb tube to serve as condenser.

E. A U-tube containing a solution of silver sulphate in sulphuric acid to absorb hydrochloric acid. Sulphuric acid prevents evaporation of the silver sulphate solution.

F. A U-tube containing dried but not fused $CaCl_2$ which removes moisture from the gas. Calcium chloride sometimes contains impurities which absorb CO_2, therefore, before use, CO_2 should be passed through this tube to saturate the reagent, and then a current of air should be passed through half an hour to remove the excess of CO_2.

G. A Geissler bulb with each of the small bulbs two-thirds filled with a KOH solution (1.27 sp. gr.) for the absorption of CO_2. The solution must be concentrated to insure the absorption of CO_2 and to prevent evaporation.

H. A tube containing calcium chloride to absorb moisture that may be carried from the bulb *G.* (See Carbon in Steel, p. 117.)

I. A second calcium chloride tube added to protect *H* from moisture from the air.

J. An aspirator bottle by which air is drawn through the apparatus.

When the apparatus is set up, test for leaks in the manner described on page 119.

CO_2 in Limestone. Connect the aspirator bottle *J* and draw air through the apparatus until it is filled with air free from carbon dioxide. Weigh *G* and *H* and attach them as shown in the figure, but do not connect the aspirator bottle *J*. Weigh 1 gm. of the finely ground limestone and transfer it to the flask *C*. Open the tap of *B* and let the acid drop into the flask *C* until the gas passes through the bulb *G* at the rate of two bubbles per second. When the passage of the gas falls below that rate, add more acid. Finally, when the addition of more acid does not increase the action, attach the aspirator to *I*, and begin the aspiration very gently, and open the screw clamp *a*. Then warm the flask *C* very gradually with a Bunsen burner and boil gently half an hour. Detach *G* and *H*, place them in the balance case, and after they have stood fifteen minutes, weigh them. The same precautions must be taken in weighing that are pointed out on page 119. The increase in weight represents the CO_2 in the sample.

METHODS OF ANALYSIS IN THE METALLURGY OF COPPER AND LEAD

COPPER IN ORE

Potassium Cyanide Method

Outline. The copper is dissolved from the ore with nitric and hydrochloric acids, sulphuric acid is added and the solution is evaporated nearly to dryness. A little water is added and the copper is precipitated on metallic zinc or aluminum. The copper is separated from the solution, washed, and dissolved in nitric acid. An excess of ammonia is added and the cuprammonium nitrate is titrated with standard potassium cyanide solution.*

Reagents. *Dilute nitric acid* (1 : 4).

Bromine water; cold water saturated with Br.

Sheet zinc or *aluminum.*

Standard solution of potassium cyanide. Dissolve 21 gms. of KCN in water and dilute the solution to 1 liter. Standardize the solution as follows: Weigh accurately about 0.2 gm. of pure copper foil and transfer it to a 250-cc. Erlenmeyer flask. Add 5 cc. of strong nitric acid. When in solution, dilute with 25 cc. of water and add 5 cc. of bromine water. Boil out the bromine, and add 50 cc. of cold water and 10 cc. of ammonia. Cool to the temperature of the room, dilute to 150 cc., and titrate with the potassium cyanide solution.

The cyanide solution does not hold its strength well. It

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* For the method of sampling see p. 8.

should, therefore, be standardized frequently, the titration of the standard should be done at the same time that the ores are titrated, and all brought to the same tint for an end-point. When the blue color begins to fade, proceed more slowly with the titration, and after each addition of solution allow a little time for the reaction to take place before further additions are made. As the end-point is approached, the solution changes from pale blue to violet, and finally to faint pink. On standing, the color fades; therefore, all titrations should be made in about the same time.

Cu in Ore. Weigh 1 gm. of ore (0.5 gm. if the ore contains more than 40 per cent copper) and transfer it to a 250-cc. Erlenmeyer flask. Add 10 cc. of nitric acid, and boil gently to decompose the ore. If decomposition is not complete, add 5 cc. of hydrochloric acid and boil. Add 7 cc. of sulphuric acid and boil until dense sulphuric acid fumes are evolved.

This operation is carried on best by holding the flask by the neck with a test-tube holder and shaking it over the open Bunsen flame under a hood. (Fig. 76.) It should be boiled almost to dryness to insure the expulsion of all nitric acid.

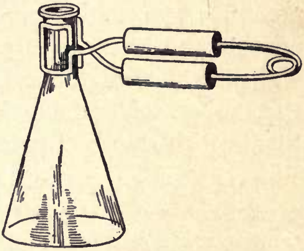

Fig. 76.—Flask for Copper Determinations.

Cool, and add 20 cc. of cold water. If the ore contains silver, add 1 drop of hydrochloric acid to precipitate the silver. Shake the flask, let it stand hot until the ferric sulphate dissolves, filter the solution into a small flask, and wash the residue with hot water, keeping the volume down to about 60 cc. Put into the flask three pieces of sheet aluminum, about 15 mm. ×40 mm., with the ends bent to prevent the sheets from lying flat on the bottom of the flask. Boil the solution to precipitate the copper. The copper is not precipitated in a weakly acid solution, but is rapidly precipitated after boiling the solution down to the proper concentration. When the copper is completely precipitated, decant the solution through a filter and wash the copper and aluminum by decantation two or three times.

A weak solution of hydrogen sulphide may be used as a wash to prevent the oxidation and solution of the finely divided copper.

Place the flask under the funnel, pour through the filter 10 cc. of warm dilute nitric acid (1 : 4). Replace the flask with a beaker. Shake the flask and warm it slightly to dissolve the copper. Empty the flask into the beaker and pour the solution back into the flask, leaving the strips of aluminum in the beaker. Wash the aluminum well with water and add the washings to the solution in the flask. Place the flask under the funnel, pour 5 cc. of cold bromine water through the filter to oxidize arsenic and antimony, and then wash the filter with a little hot water. Boil the solution to expel the bromine, cool, and add 10 cc. of ammonia. Dilute the solution to 150 cc. and titrate with standard potassium cyanide solution.

This method is not accurate unless the titrations of ore-solutions are carried out under exactly the same conditions as exist when the potassium cyanide solution is standardized; therefore, the volume of solution, the excess of ammonia, the temperature, and the time required for titration should always be as nearly the same as possible.

Sheet zinc may be used instead of aluminum for the precipitation of the copper. In this case, after the copper is precipitated, add 20 cc. of dilute sulphuric acid (1 : 1) to hasten the solution of the zinc. When the zinc is dissolved, fill the flask to the neck with cold water, let the copper settle, decant the clear solution, and fill and decant a second and a third time.

Add 5 cc. of nitric acid to the copper in the flask and boil to expel red fumes. Add 50 cc. of water and 10 cc. of ammonia. Cool, dilute to 150 cc., and titrate with standard potassium cyanide solution.

COPPER IN ORE

POTASSIUM IODIDE METHOD

Outline. The copper is dissolved from the ore with nitric and hydrochloric acids, sulphuric acid is added and the solution evaporated nearly to dryness. A little water is added and the copper is precipitated on metallic aluminum. The copper is separated from the solution, dissolved in nitric acid, the excess of acid neutralized with ammonia. Acetic acid and potassium iodide are added, and the iodine liberated is titrated with a standard solution of sodium thiosulphate, which measures the quantity of copper indirectly.

Reagents. *Acetic acid* ($C_2H_4O_2$; sp.gr. 1.04).

Starch solution. (See p. 111.)

Potassium iodide, KI.

Standard solution of sodium thiosulphate. Dissolve 19 gms. $Na_2S_2O_3$ in water and dilute the solution to 1 liter. To standardize this solution, dissolve about 0.2 gm. of pure copper foil in 5 cc. of strong nitric acid; dilute the solution with 25 cc. of water, and add 5 cc. of bromine water. Boil off the excess of bromine, remove from the heat, and add a slight excess of ammonia. Boil off the excess of ammonia, and acidify with acetic acid.

Too great a concentration of ammonium salts interferes with the reaction between the copper and acetic acid.

Boil until any precipitate present is dissolved, cool, add 3 gms. of potassium iodide, and titrate at once with sodium thiosulphate solution to a faint brown color. Add a few drops of starch solution and continue the titration until the blue color disappears.

$$2Cu(C_2H_3O_2)_2+4KI=Cu_2I_2+4KC_2H_3O_2+I_2.$$

$$I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6.$$

Cu in Ore. Weigh 1 gm. of ore (0.5 gm. if the ore contains more than 40 per cent copper) and transfer it to a 250-cc. Erlenmeyer flask. Add 10 cc. of nitric acid, and boil gently to decompose the ore. If decomposition is not complete, add 5 cc. of hydrochloric acid and boil. Add 7 cc. of sulphuric acid and boil until dense sulphuric acid fumes are evolved. (See the preceding method for notes.)

Cool, and add 20 cc. of cold water. If the ore contains silver, add 1 drop of hydrochloric acid to precipitate the silver. Shake the flask, let it stand hot until the ferric sulphate dissolves, filter the solution into a small flask, and wash the residue with hot water, keeping the volume down to about 60 cc. Put into the flask three pieces of sheet aluminum, about 15 mm. ×40 mm., with the ends bent to prevent the sheets from lying flat on the bottom of the flask. Boil the solution to precipitate the copper. The copper is not precipitated in a weakly acid solution, but is rapidly precipitated after boiling the solution down to the proper concentration. When the copper is completely precipitated, decant the solution through a filter and wash the copper and aluminum by decantation two or three times.

Place the flask under the funnel, pour through the filter 10 cc. of warm dilute nitric acid (1 : 4). Replace the flask with a beaker. Shake the flask and warm it slightly to dissolve the copper. Empty the flask into the beaker and pour the solution back into the flask, leaving the strips of aluminum in the beaker. Wash the aluminum well with water and add the washings to the solution in the flask. Place the flask under the funnel, pour 5 cc. of cold bromine water through the filter to oxidize arsenic and antimony, and then wash the filter with a little hot water. Boil the solution to expel the bromine, cool, and add a slight excess of ammonia. Boil off the ammonia, acidify the solution with acetic acid, and boil until any precipitate present is dissolved. Cool, add 3 gms. of potassium iodide, and titrate with standard sodium thiosulphate solution to a faint brown color. Add a few drops of starch solution, and continue the titration until the blue color changes suddenly to white or light cream color.

COPPER IN ORE

ELECTROLYTIC METHOD*

Outline. The ore is dissolved in acids, and after adding sulphuric acid the solution is boiled nearly to dryness. A little nitric acid is added, the solution diluted and the copper precipitated by electrolysis.

Cu in Ore. Weigh the ore and dissolve it according to the method described for the potassium cyanide assay of copper. After boiling until dense sulphuric acid fumes are evolved, cool, add 20 cc. of cold water, and warm the solution to dissolve the soluble sulphates. Add 1 drop of hydrochloric acid to precipitate silver. Filter the solution into a No. 4 beaker, add 2 cc. of nitric acid and electrolyze.

$$2CuSO_4+2H_2O+\text{electric current}$$
$$=2H_2SO_4+Cu_2+O_2.$$

The electrodes are of platinum. The most satisfactory cathode is made of platinum gauze in cylindrical form, with platinum wire attached, by which it is connected to the negative pole of an electric circuit. The anode may be a coiled platinum wire, about 16 gauge. (Fig. 77.)

Before use the electrodes should be cleaned with nitric acid and washed with water, and the cathode must be dried and weighed.

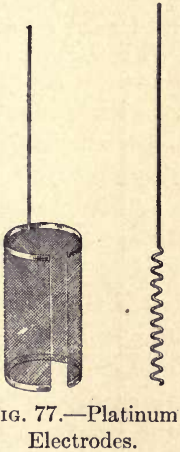

FIG. 77.—Platinum Electrodes.

The electrodes should be held firmly by a support so that they do not touch, and the solution should be diluted to cover the cathode.

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* Stoddard, Jour. Amer. Chem. Soc., 31, 385. Price and Meade, "Tech. Anal. of Brass," 71. Smith, "Electro-analysis," 63.

The solution may be electrolyzed in a platinum dish. The dish is connected by a wire to the negative pole and serves as the cathode. A platinum crucible cover partly submerged in the solution and connected by a wire with the positive pole serves as anode.

The current should have a density per hundred square centimeters of cathode surface (D/100) of 0.5 ampere at 2.5 volts, and twelve hours should be a sufficient time for the complete precipitation of the copper.

The ordinary 110-volt current may be conveniently and economically reduced for this purpose by the use of a motor-generator set. The motor which drives the generator takes the current at 110 volts; the current from the generator is regulated by an easily variable resistance which controls the current in its field. For the proper regulation of the current a voltmeter and an ammeter are connected with the generator circuit.

Ordinary electric batteries may be used for this purpose. Two or three gravity cells in good working order supply a satisfactory current for one set of electrodes of the usual size.

When the current passes through the electrolyte, oxygen is set free at the anode and the copper should be deposited on the cathode in a smooth, bright copper-colored plate. If the copper is dull in color or granular in appearance, it is easily washed off and is also readily oxidized when dried in the air.

When the solution has lost its blue color, test it to determine if all the copper has been precipitated, by taking out 1 cc. of the solution and adding to it a little strong solution of hydrogen sulphide.

If copper is still present, continue the electrolysis until the solution gives no reaction for copper.

If the resistance of the solution is high and the deposition of the copper is too slow, add a little ammonia to reduce the resistance.

Fig. 78.—Anode Suitable for Rotating.

The time of deposition may be very much shortened by increasing the current to 6–8 amperes and 3–4 volts; but under these conditions the copper will be deposited in a granular condition, or some of it may be deposited as copper sulphide, unless the anode or the cathode or the solution be rotated at a high speed. With this provision the copper will be deposited as a smooth adherent plate even with a current strong enough to completely precipitate it in half an hour. Fig. 78 shows a suitable form of anode for rotating. It may be attached directly to the shaft of a small motor or to a belt-driven pulley.

When deposition is complete, withdraw the electrodes from the beaker before breaking the current, at the same time washing them off with distilled water to prevent re-solution of the copper. Disconnect the cathode from the circuit, wet it with a little alcohol, dry, and weigh it. From the combined weight of the cathode and copper must be deducted the weight of the cathode.

If the copper plate is smooth with a fine metallic luster, it may be dried by burning off the alcohol, without danger of oxidizing the copper. After the copper has been weighed, it is dissolved from the cathode in a little warm nitric acid.

LEAD IN ORE

Molybdate Method

Outline. The ore is treated with hydrochloric, nitric, and sulphuric acids and the solution evaporated until the sulphuric acid fumes; water is added to take up soluble sulphates. The lead sulphate with other insoluble matter is filtered from the solution; the lead sulphate is dissolved in ammonium acetate and the lead measured by titrating it with a standard solution of ammonium molybdate.

Reagents. *Sulphuric acid,* dilute (1 : 1).

Sulphuric acid, dilute (1 : 10).

Ammonium acetate; saturated solution of $NH_4C_2H_3O_2$ in water.

Solution of tannin. Dissolve 1 gm. of $C_{14}H_{10}O_9$ in 200 cc. of water.

Standard solution of ammonium molybdate. Dissolve 4.3 gms. $(NH_4)_6Mo_7O_{24}+4H_2O$ in 300 cc. of water, add a few drops of ammonia, and dilute to 1 liter. One cubic centimeter is equivalent to about 0.005 gm. of lead. To standardize this solution, weigh 0.2 gm. of pure lead foil. Dissolve it in dilute nitric acid, add ammonia until the solution is alkaline, boil, acidify the solution with acetic acid, and titrate with the ammonium molybdate solution, using tannin solution on a porcelain plate as indicator.

Run a blank, by titrating the same volume of solution containing all the reagents used in the standardization, to determine how much molybdate solution is required to give the yellow color to the tannin when no lead is present. This amount is to be deducted from all titrations.

Pb in Ore. Weigh 0.5 gm. of ore (1 gm. if it contains less than 30 per cent lead), and transfer it to a 200-cc. Erlenmeyer flask. Add 10 cc. of hydrochloric acid and boil.

Hydrochloric acid attacks galena, ferric oxide, etc.

Continue boiling and add, at short intervals, 20 cc. of water, 10 cc. of nitric acid, and 10 cc. of dilute sulphuric acid (1 : 1).

Nitric acid is added to attack those sulphides not dissolved by hydrochloric acid.

Boil over the open flame (see p. 169) until dense sulphuric acid fumes are evolved. Cool, add 25 cc. of cold water, heat to the boiling-point, and let it stand to dissolve ferric sulphate. Cool, filter, and wash the residue with dilute sulphuric acid (1 : 10), and then with water. Spread the filter paper against the inside of a beaker, (Fig. 52, p. 61), and wash off the precipitate with hot water, followed by hot ammonium acetate solution, and add a sufficient amount of ammonium acetate to dissolve all the lead sulphate.

One part of lead sulphate is soluble in 47 parts of ammonium acetate solution of specific gravity 1.036.

$$PbSO_4+2NH_4C_2H_3O_2=Pb(C_2H_3O_2)_2+(NH_4)_2SO_4.$$

Heat to boiling and titrate with standard solution of ammonium molybdate until a drop of the solution titrated tested with a drop of tannin solution on a porcelain plate gives a yellow color.

LEAD IN ORE

FIRE METHOD *

This method for the assay of lead, although much used, is inaccurate. It gives too low results with pure ores, and too high results with ores containing arsenic, antimony, bismuth, etc.

Flux. *Sodium bicarbonate,* $NaHCO_3$, 64 parts.

Potassium carbonate, K_2CO_3, 50 parts.

Borax glass, $Na_2B_4O_7$, 25 parts.

Flour, 25 parts. The reducing power of the flour should be tested, and if found to be below 3, the quantity added to the flux should be increased. Mix the reagents thoroughly by rolling on a rubber cloth.

Pb in Ore. Weigh 10 gms. of ore and mix it in a crucible (see Fig. 84, page 225) with 20 gms. of flux. Cover with 10 gms. of flux, and if the ore is low in sulphur, put into the charge one tenpenny nail; if it is high in sulphur, put in two tenpenny nails. Put the crucible into a muffle heated to a moderately low temperature and raise the heat to a light yellow and fuse for thirty minutes.

$$7PbS+4K_2CO_3=4Pb+K_2S+3(K_2S\cdot PbS)+4CO_2.$$

$$PbS+Fe=Pb+FeS.$$

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

When the fusion is complete, withdraw the crucible from the muffle, take out the nails with a pair of short tongs, taking care to shake off into the crucible any adhering globules of lead. Shake the crucible and tap it gently several times to

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* See Fire Assaying, page 224.

concentrate the lead in the bottom, and pour the fusion into the mold.

When cold, break the slag from the lead button and weigh the lead. If the lead button is hard or brittle, it is alloyed with other metals and the assay is not accurate.

ZINC IN ORE

Outline. The ore is treated with hydrochloric and nitric acids, then with potassium chlorate and a fresh portion of nitric acid, after which the solution is evaporated to dryness. The residue is treated with ammonia, ammonium chloride, bromine, and water; zinc and copper are taken into solution and are filtered from the residue, which contains the other metals and the insoluble part of the ore. The solution is then acidified with hydrochloric acid, the copper precipitated, and the zinc titrated with a standard solution of potassium ferrocyanide.*

Reagents. *Potassium chlorate*, $KClO_3$.

Ammonium chloride, NH_4Cl.

Bromine water; water saturated with Br.

Standard solution of potassium ferrocyanide. Dissolve 21.63 gms. $K_4Fe(CN)_6$ and 7 gms. $Na_2SO_3+7H_2O$ in water, and dilute the solution to 1 liter. One cubic centimeter is equivalent to about 0.005 gm. Zn. To standardize, dissolve 0.2 gm. of chemically pure zinc or freshly ignited chemically pure zinc oxide in 15 cc. of hydrochloric acid, add 7 gms. of ammonium chloride, dilute to 200 cc. with boiling water, and titrate, using uranium nitrate solution on a porcelain plate as indicator.

Indicators: uranium nitrate solution; 1 gm. $UO_2(NO_3)_2+6H_2O$ dissolved in 10 cc. of water. Other indicators are:

Ammonium molybdate solution, 1 gm. dissolved in 100 cc. of water; or a saturated solution of *uranium acetate*.

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* Sutton, "Volumetric Analysis," 356. Low, "Tech. Meth. of Ore Anal.," 210.

Run a blank in the usual manner and make the necessary correction.

Zn in Ore. Weigh 1 gm. of ore, transfer it to a 200-cc. Erlenmeyer flask, add 15 cc. of hydrochloric acid, and boil. Add 25 cc. of nitric acid and boil down to a volume of 10 cc. Then add 10 cc. of nitric acid and 5 gms. of potassium chlorate, a little at a time. Evaporate just to dryness.

A high heat after the mass is dry will volatilize zinc chloride.

Cool, add 10 gms. of ammonium chloride, 15 cc. of ammonia, 25 cc. of water, and 10 cc. of bromine water.

Instead of adding ammonium chloride, ammonia, and bromine water, Demorest * precipitates Fe, Mn, Pb, and Cd by adding 0.5 gm. KOH and 7 gms. $(NH_4)_2CO_3$ with 50 cc. H_2O, filtering, dissolving the precipitate in HCl, reprecipitating in the same manner and filtering.

Boil two minutes, filter, and wash well with a hot solution of ammonium chloride (10 gms. NH_4Cl+2 drops $NH_4OH+1000$ cc. of water).

Acidify the filtrate with hydrochloric acid, dilute to 150 cc., add 20 gms. of granulated lead, and boil to precipitate copper. Remove from the heat, dilute again to 150 cc. with water, heat to 70° C. and titrate immediately with a standard solution of potassium ferrocyanide. (See zinc in matte, p. 186.)

Hydrogen sulphide may be used as the precipitant of copper instead of granulated lead. If no copper is present, this step may be omitted.

The solution, when titrated, should be at about 70° C., and there should be an excess of about 3 cc. of hydrochloric acid in the whole volume of 150 cc.

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* J. Ind. and Eng. Chem., 5, 302.

ARSENIC

SKINNER AND HAWLEY'S METHOD

Reagents. *Hydrogen sulphide;* H_2S from a generator.

Sodium sulphite, Na_2SO_3.

Distilling solution: Mix 500 cc. of water with 1200 cc. of hydrochloric acid (sp.gr. 1.2), add the mixture gradually to 400 gms. of pure zinc, and heat to dissolve the zinc. Evaporate the solution to 1100 cc. and add to it a solution of 300 gms. of pure cupric chloride crystals in 1 liter of hydrochloric acid (sp.gr., 1.2).

Sodium bicarbonate, $NaHCO_3$.

Starch solution. (See p. 111).

Standard iodine solution. Weigh 16.932 gms. of pure iodine. Transfer it to a liter flask, add 30 gms. of potassium iodide, add water, and when the iodine is dissolved, dilute the solution to 1 liter. One cubic centimeter should be equivalent to about 0.005 gm. of arsenic.

The solution may be standardized by weighing accurately about 0.2 gm. As_2O_3, dissolving it in dilute hydrochloric acid, neutralizing with ammonia, just acidifying the solution with hydrochloric acid, and adding sodium bicarbonate and starch solution, and titrating with the iodine solution.

As in Ores and Furnace Products. Weigh 0.5 gm. of the sample (if the material is low in arsenic, as much as 5 gms. may be used) and transfer it to a small beaker. Add 5 cc. of nitric acid and a little potassium chlorate. When vigorous action has ceased, add 8 cc. of hydrochloric acid and evaporate the solution to dryness at about 100° C. Add 5 cc. of hydrochloric acid and 25 cc. of water, boil, and filter. Dilute the filtrate to 200 cc. with boiling water. Add sodium sulphite, a little at a time, until the solution becomes colorless.

$$As_2O_5+3H_2O+2Na_2SO_3=2As(OH)_3+2Na_2SO_4.$$

$$Na_2SO_3+2HCl=2NaCl+H_2O+SO_2.$$

Boil off the excess of SO_2, add 15 cc. of hydrochloric acid, and pass a current of hydrogen sulphide through the solution until the sulphides are completely precipitated.

$$2As(OH)_3+3H_2S=6H_2O+As_2S_3.$$

If there are present only small quantities of other hydrogen sulphide metals, the precipitation of the arsenic is hastened by adding, to the sample 0.1 gm. of pure copper.

Filter and wash the sulphide. Place the precipitate in a flask fitted with a thermometer and connected with a condenser (8-in. Allihn, Fig. 79, is satisfactory), add 50 cc. of distilling solution, and distil carefully until the thermometer reads 115° C., letting the distillate run into a flask which contains dilute sulphuric acid (1 : 20).* Remove from the heat and add 25 cc. of hydrochloric acid, and distil again until the thermometer reads 115° C.

FIG. 79.—Allihn Condenser.

$$As_2S_3+3CuCl_2=2AsCl_3+3CuS.$$

$$2AsCl_3+6H_2O=2As(OH)_3+6HCl$$

Arsenious trichloride is volatile when boiled in a concentrated solution of hydrochloric acid.

Pour the distillate into a No. 3 beaker. Add ammonia until the solution is alkaline; then just acidify it with dilute sulphuric acid. Cool, add about 10 gms. of sodium bicarbonate, 4 drops of a 10 per cent solution of KI, and a little starch solution, and titrate with standard iodine solution.

$$2As(OH)_3+4I+4NaHCO_3=As_2O_5+4NaI+5H_2O+4CO_2.$$

Sodium bicarbonate must be used, since the hydroxyl ion resulting from the use of caustic or neutral alkali reacts with iodine.

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* Price and Meade, "Tech. Anal. of Brass," p. 257.

ARSENIC IN INSOLUBLE ORES AND FURNACE PRODUCTS.*

Reagents. *Sodium carbonate,* Na_2CO_3, and potassium nitrate, KNO_3, mixed in equal parts.

Acetic acid, $C_2H_4O_2$, (sp.gr. 1.04).

Solution of phenolphthalein. (See p. 84.)

Solution of sodium hydroxide. Dissolve 10 gms. NaOH in 100 cc. of water.

Saturated solution of silver nitrate ($AgNO_3$) in water.

Granulated lead, Pb.

As in Ore. Weigh 0.5 gm. of the sample, mix it with 3 gms. of the sodium carbonate and potassium nitrate flux. Transfer the mixture to a porcelain crucible, and add as a cover 2 gms. of the same fusion mixture. Gradually raise the temperature and fuse for a few minutes.

$$As+3KNO_3=K_3AsO_4+2NO_2+NO.$$

Cool, treat the fusion with hot water, and filter. Strongly acidify the filtrate which contains the arsenic, with acetic acid. Boil to expel CO_2. Cool, add a few drops of phenolphthalein solution, and make alkaline with sodium hydroxide solution. Acidify with acetic acid, add a slight excess of silver nitrate solution and stir vigorously.

$$K_3AsO_4+3AgNO_3=3KNO_3+Ag_3AsO_4.$$

Let the precipitate settle away from direct sunlight. Filter, and wash by decantation with cold water. Transfer the precipitate to the filter and wash it well. Place the filter with precipitate in a scorifier, dry, add granulated lead and borax, and make a scorification assay for silver. (See p. 234.) The weight

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* Bennett, Jour. Amer. Chem. Soc., 21, 431.

of silver, multiplied by the factor 0.2316, will give the weight of arsenic.

$$\text{Wt. Ag.} : \text{Wt. As.} = 3(107.88) : 74.96.$$

If the ore contains soluble chlorides, they must be washed out before making the fusion.

ARSENIC IN ORE BY TITRATING WITH AMMONIUM THIOCYANATE

After obtaining the precipitate of Ag_3AsO_4, according to the method above, instead of determining the silver by a scorification assay, it may be determined as follows: Dissolve the precipitate of Ag_3AsO_4 in dilute nitric acid.

This leaves silver chloride, if present, undissolved.

$$Ag_3AsO_4 + 3HNO_3 = 3AgNO_3 + H_3AsO_4.$$

Filter, add 5 cc. of a saturated solution of ammonium ferric sulphate, as indicator, and titrate with a standard solution of ammonium thiocyanate until brown ferric thiocyanate remains after shaking.

$$AgNO_3 + NH_4CNS = AgCNS + NH_4NO_3.$$

When the silver thiocyanate has all been precipitated, the ammonium thiocyanate then combines with the ammonium ferric sulphate to form brown ferric thiocyanate.

$$Fe_2(SO_4)_3 + 6NH_4CNS = 2Fe(CNS)_3 + 3(NH_4)_2SO_4.$$

The ammonium thiocyanate solution is standardized against silver nitrate.

ANALYSIS OF COPPER MATTE

COPPER IN MATTE

Electrolytic Method

Weigh 1 gm. of matte and transfer it to a No. 4 beaker. Moisten it with a few drops of water, add 8 cc. of nitric acid and 1 cc. of sulphuric acid. Evaporate the solution to dryness. Dissolve the residue in 8 cc. of nitric acid. Dilute the solution, filter, and electrolyze. (See Copper in Ore, p. 173.)

COPPER IN MATTE

Potassium Iodide Method

Weigh 0.5 gm. of matte, transfer it to a 150-cc. Erlenmeyer flask, add 5 cc. of nitric acid, and heat until the mass is pasty and red fumes have ceased to come off. Remove from the heat, add 15 cc. of water, and boil five minutes. Add ammonia to make the solution slightly alkaline, boil out the excess of ammonia, remove from the heat, make strongly acid with acetic acid, and cool. When cold, add 3 gms. of potassium iodide, shake, and titrate at once with standard sodium thiosulphate solution until the yellow color begins to fade. Add 20 cc. of starch solution and continue the titration until the bluish green color disappears and does not return for ten seconds.

For reagents and notes see Copper in Ore, p. 171.

Owing to impurities in the matte, the end-point is not permanent and a little experience is required to enable the operator to detect the correct end.

COPPER IN MATTE

Potassium Cyanide Method

Weigh 0.5 gm. of matte, transfer it to a small Erlenmeyer flask, add 5 cc. of nitric acid, and proceed according to the potassium cyanide method for copper in ore (see p. 168); or the somewhat more rapid method given below may be used.

Weigh 0.5 gm. of the matte and transfer it to a small beaker. Add 15 cc. of nitric acid and boil ten minutes. Remove from the heat, add 35 cc. of cold water, and make the solution strongly alkaline with ammonia to precipitate the iron. Filter rapidly, wash the precipitate back into the original beaker with as little hot water as possible, and redissolve in as small quantity as possible of dilute sulphuric acid (1 : 3). Reprecipitate the iron with ammonia and filter, letting this filtrate run into the first filtrate. Wash well with hot water, cool, and titrate with a standard solution of potassium cyanide. (See p. 168.)

IRON IN MATTE

Potassium Dichromate Method

Weigh 0.5 gm. of matte, transfer it to a small beaker, add 15 cc. of nitric acid, dissolve at a moderate heat, and evaporate the solution to dryness. When free from nitrous fumes, cool, add 25 cc. of hydrochloric acid, cover with a watch glass, and heat until the solution is clear and globules of sulphur float on the surface. Add 25 cc. of hot water and about 20 gms. of granulated lead, and boil until the copper is precipitated on the lead and the ferric chloride is reduced to ferrous chloride, leaving the solution clear. Remove from the heat and wash all particles of test lead to the bottom of the beaker. Decant the solution into a beaker, wash the lead with hot water by decantation, cool the solution to the temperature of the room, and titrate with a standard solution of potassium dichromate. (See Iron in Ores, p. 62.)

ZINC IN MATTE

Reagents. See Zinc in Ore (p. 178).

Weigh 0.5 gm. of matte, transfer it to a small beaker, add 20 cc. of chlorate solution (saturated solution of $KClO_3$ in HNO_3, sp.gr. 1.42). Heat to dissolve, and evaporate the solution at a moderate heat to dryness. Add about 10 gms. of ammonium chloride, 25 cc. of ammonia, and 25 cc. of boiling water. Cover, and boil two minutes. Filter and wash well with a hot solution of ammonium chloride (10 gms. NH_4Cl+2 drops of NH_4OH $+1000$ cc. of water). Acidify the filtrate with hydrochloric acid, dilute the solution to 150 cc., add 20 gms. of granulated lead, and boil until the copper is all precipitated on the lead and the solution is clear. Remove from the heat and dilute again to 150 cc. with cold water and titrate immediately with a standard solution of potassium ferrocyanide, using a solution of uranium nitrate or acetate as indicator. (See p. 178.)

While titrating, if a brownish or red precipitate forms, it indicates that the solution was not boiled long enough with the granulated lead to precipitate all the copper, and the determination must be discarded.

LEAD IN MATTE

Reagents. See Reagents for Lead in Ore (p. 175).

Weigh 0.5 gm. of matte and transfer it to a 250-cc. Erlenmeyer flask, add 10 cc. of hydrochloric acid, and heat to boiling. Add 5 cc. of nitric acid and 7 cc. of sulphuric acid and boil over the open flame of the Bunsen burner (see p. 169) until dense white fumes of sulphuric acid are given off freely and the volume is reduced to only a few cubic centimeters. It is essential that all the nitric acid be expelled.

Cool, add 50 cc. of cold water, heat, and let the solution stand at the boiling-point five minutes. Filter, and wash well with hot water. Spread out the filter paper with its contents on the inside of a beaker and wash off the precipitate with a jet of hot water, using about 25 cc.; discard the filter paper.

Pour 20 cc. of a saturated solution of ammonium acetate into the flask in which the precipitation was made, shake to dissolve any adhering lead sulphate, and pour the solution into the beaker containing the main precipitate of lead sulphate. Wash out the flask, using about 25 cc. of hot water, and add it to the lead sulphate solution. Heat the solution to boiling and titrate it hot with the standard solution of ammonium molybdate, using tannin solution as an indicator. (See p. 176.)

SULPHUR IN MATTE

Weigh 0.5 gm. of the matte and transfer it to a porcelain casserole. Sprinkle 1 gm. of potassium chlorate over the sample, add 15 cc. of chlorate solution (saturated solution of $KClO_3$ in strong nitric acid), cover, and keep it cool until the sulphur is oxidized. Heat gradually and evaporate slowly to dryness. When thoroughly dry, cool, add 25 cc. of water and 15 cc. hydrochloric acid and boil until the solution is clear. Filter hot and wash with hot water. Add 5 cc. of a saturated solution of barium chloride and heat to the boiling-point.

If the matte contains much lead, boil at least five minutes to dissolve lead chloride, and filter hot to prevent the contamination of barium sulphate with lead chloride.

Remove from the heat and let the barium sulphate settle. Filter, wash with hot water, burn in an annealing cup in a muffle, or in a platinum crucible and weigh. The factor for S in $BaSO_4$ is 0.13738.

MANGANESE IN MATTE

Weigh 0.5 gm. of matte and transfer it to a small beaker. Add 35 cc. of water, boil, add 15 cc. of hydrochloric acid, and boil ten minutes. Add 5 cc. of nitric acid and continue boiling ten minutes. Remove the beaker from the heat, add an emulsion of zinc oxide until the solution when stirred is almost white. Dilute the solution to 150 cc. with hot water, heat to the boiling-point, and titrate hot, according to the Volhard method, with a standard solution of potassium permanganate. (See p. 88.)

GOLD AND SILVER IN MATTE

Weigh 0.1 assay-ton. Place it in a scorifier, add 70 gms. of granulated lead, a little borax glass, and a little silica. Place the scorifier in a hot muffle. After melting, reduce the temperature and complete the scorification at a moderate temperature. Cupel the lead button, weigh the bead of silver combined with gold, part in the usual way with nitric acid, and weigh the gold. The difference between the weight of gold and the combined weight of gold and silver will give the weight of silver. (See Fire Assaying, p. 224.)

ANALYSIS OF CHILLED BLAST FURNACE SLAGS

Sampling. Granulate the slag by dipping a sample from the molten slag with an iron ladle and pouring it into a pail of water. Then take out the granulated slag with the ladle and place it near the heat to dry. When the slag is dry, crush it and prepare the sample for analysis in the usual way. (See p. 8.)

SILICA IN SLAG

Weigh 0.5 gm. of slag and transfer it to a casserole. Moisten it with a few drops (6 or 7) of water. Stir with a glass rod, and while stirring add slowly about 4 cc. of hydrochloric acid. Continue stirring until the slag gelatinizes.

The slag is treated first with hydrochloric acid alone to insure the escape of sulphur as H_2S. If nitric acid were added at the same time, the H_2S would be oxidized and would combine with barium to form barium sulphate, which would come down with the SiO_2.

Add about 1 cc. of nitric acid and stir, spreading the gelatinous precipitate smoothly on the inside of the casserole.

This permits rapid dehydration without loss.

Nitric acid is added to oxidize the lead and copper sulphides, which are not completely decomposed by hydrochloric acid. The lead will be dissolved by the hot acids and pass through the filter.

Take the cover off the casserole and heat until the acid has all evaporated.

Do not prolong the heating at too high a temperature, since there is danger of recombining some of the silica with alumina, giving a gray-colored residue after ignition, and a high result.

Cool the casserole, add about 15 cc. of hydrochloric acid, and boil. Dilute with a little hot water and filter hot. Wash the precipitate with hot water until it is free from chlorides.

The residue may be black, owing to the presence of carbon.

Place the filter and residue in a porcelain crucible, burn fifteen minutes in a hot muffle, cool, and weigh.

By this method the result is *insoluble silicious residue*, but it is usually reported as silica, unless a fusion silica is especially asked for. In the latter case, follow the method for silica in ore, page 71, or purify the insoluble silicious residue with hydrofluoric and sulphuric acids.

LIME IN SLAG

Add to the filtrate from the silica, which should measure about 150 cc., ammonia in slight excess. Add just enough hot saturated solution of oxalic acid to dissolve the iron precipitate. Add ammonia again until a slight precipitate of iron is obtained, and then add oxalic acid to dissolve the iron. There should now be a white precipitate of calcium oxalate, and the solution should be slightly acid, and should have a clear greenish-yellow color.

Boil, and let the precipitate settle ten minutes or more. Filter, wash the precipitate once by decantation with hot water, and then wash it on the filter until all the oxalic acid is removed.

Test the wash water for oxalic acid by collecting a few cubic centimeters as it runs from the funnel, heating it and adding a little sulphuric acid, and a drop of potassium permanganate solution. If the color of the permanganate fades, oxalic acid is present and the washing must be continued and the test repeated until no oxalic acid remains.

Spread the filter paper, with the precipitate, on the inside of a beaker. Wash the precipitate from the paper with 200 cc. of hot water, using a strong jet from a wash bottle. Add 40 cc. of dilute sulphuric acid (1 : 1). Stir to dissolve the precipitate and titrate the hot solution with standard potassium permanganate solution.

For reactions and method of calculating the result, see Lime in Limestone, page 163.

IRON IN SLAG

Weigh 0.5 gm. of slag, transfer it to a small beaker, add 30 cc. of water, cover, and boil. While boiling, add 20 cc. of hydrochloric acid and continue to boil until the solution is clear. Add 2 or 3 drops of stannous chloride solution to the hot solution and stir. Cool, and when cold add 20 cc. of mercuric chloride solution and titrate with standard potassium dichromate solution. (See Iron in Ore, p. 62.)

MAGNESIA IN SLAG

Weigh 0.5 gm. of slag and treat it according to the method for the determination of silica. To the filtrate from the silica add an excess of ammonia, and ammonium chloride. Add 10 cc. of bromine water and 0.03 gm. of ammonium persulphate for every 0.01 gm. of manganese in the solution. Boil to precipitate iron, alumina, and manganese. Filter, redissolve the precipitate in hydrochloric acid, and add ammonia, bromine water, and ammonium persulphate, as before. Boil and filter.

Combine the filtrates and add ammonium oxalate to precipitate calcium. Filter, and wash the precipitate well. To the filtrate add a solution of sodium phosphate, or microcosmic salt, and proceed according to the method for the determination of magnesia in limestone. (See p. 165.)

MANGANESE IN SLAG

Weigh 0.5 gm. of the slag and transfer it to a small beaker. Add 30 cc. of water and 20 cc. of hydrochloric acid. Boil until the solution is clear. Add 5 cc. of nitric acid and boil five minutes. Remove from the heat and add very slowly, while stirring vigorously, an emulsion of zinc oxide, and proceed according to Volhard's method for manganese in matte. (See p. 187.)

ALUMINA IN SLAG

Weigh 0.5 gm. of slag and treat it according to the method for the determination of silica. To the filtrate from the silica add ammonia to distinct alkaline reaction. Boil fifteen minutes and filter to remove the small amount of copper present. Spread the filter paper, with the precipitate, against the inside of a beaker, wash off the precipitate with a jet of hot water, dissolve in hydrochloric acid, dilute the solution to 400 cc., and proceed according to the phosphate method for alumina. (See p. 87.)

ZINC IN SLAG

Weigh 0.5 gm. of slag (if low in zinc, weigh 1 gm.), transfer it to a casserole, add 3 cc. of water, 5 cc. of hydrochloric acid, and 2 cc. of nitric acid. Stir, and when completely gelatinized, add 4 gms. of ammonium chloride and stir. Evaporate just to dryness.

Heating at a high temperature when dry will volatilize zinc chloride.

Remove from the heat and add 30 cc. of water. Boil, filter, and wash well with boiling water. Add to the filtrate 0.03 gm. of ammonium persulphate and 10 cc. of bromine water for every 0.01 gm. of manganese in the solution. Then add a slight excess of ammonia. Boil a few minutes, filter, and wash with a solution of ammonium chloride (100 gms. NH_4Cl+50 cc. $NH_4OH+1000$ cc. H_2O). Redissolve the precipitate in dilute hydrochloric acid, add ammonium persulphate, bromine water, and ammonia, as before. Boil and filter. Combine the two filtrates, neutralize with hydrochloric acid, and add 5 cc. in excess. Add 2 gms. of granulated lead and boil fifteen minutes. Add 10 cc. of hydrochloric acid and titrate at a temperature of 60° C. with a standard solution of potassium ferrocyanide. (See the method for zinc in ore, p. 178.)

LEAD IN SLAG

Weigh 5 gms. of slag, transfer it to a casserole, add 10 cc. of water, stir and add 10 cc. of hydrochloric acid, and continue stirring until the slag is gelatinized. Add 5 cc. of nitric acid. Slowly increase the heat, stirring to break up lumps, and gradually evaporate the mass to dryness. When thoroughly dehydrated continue the heat a few minutes until the mass turns dark brown. Cool, add 20 cc. of water and 15 cc. of hydrochloric acid. Boil at least ten minutes. Filter while hot and let the filtrate run into a 500-cc. beaker. Dilute the filtrate to 400 cc., add 15 gms. of ammonium chloride, and add ammonia very slowly, stirring, until the solution becomes dark cherry red, without the precipitation of iron. Pass hydrogen sulphide through the solution for half an hour. Filter, spread the filter paper, with the precipitate, against the inside of a beaker, and wash off the precipitate with as little hot water as possible. Drop 10 cc. of nitric acid on the paper and wash off, with water, all traces of the precipitate. Remove the paper, add to the solution 5 cc. of hydrochloric acid and 10 cc. of sulphuric acid.

Boil the solution until dense white fumes of sulphuric acid are evolved. Cool, dilute with 40 cc. of cold water, boil five minutes, filter the lead sulphate, and wash it with hot water. Wash the lead sulphate back into the beaker with 40 cc. of hot water. Add 15 cc. of a saturated solution of ammonium acetate. Heat the solution to boiling, and titrate it while hot with standard solution of ammonium molybdate. (See the method for lead in ore, p. 175.)

COPPER IN SLAG

Potassium Iodide Method

To the filtrate from the precipitate of lead sulphate (see the method above), add 15 cc. of a saturated solution of sodium thiosulphate and boil until the sulphides are precipitated and the solution is clear. Filter, place the filter paper, with the precipitate, in a porcelain annealing cup, and burn carefully at a very low heat until there is no longer a flame of burning sulphur. Transfer the mass to a flask, and add a little potassium chlorate and 5 cc. of nitric acid. Boil until the solution is pasty. Add 20 cc. of water and boil out all traces of nitrous fumes. Make the solution slightly alkaline with ammonia, boil out the excess of ammonia, remove from the heat, and acidify with acetic acid. When cold, add 3 gms. of potassium iodide and titrate with a standard solution of sodium thiosulphate. (See the iodide method for copper in matte, p. 184.)

After the copper sulphide has been filtered from the solution and dissolved, according to the method above, instead of following the iodide method, the copper may be measured either by electrolysis, or by the potassium cyanide method, as described for the determination of copper in matte. (See p. 185.) The copper may also be determined according to the following colorimetric method.

COPPER IN SLAG

Colorimetric Method

Weigh 3 gms. of the sample, moisten it with water, add 10 cc. of nitric acid and 1 cc. of hydrochloric acid, and heat a few minutes on a steam bath. Dilute with 100 cc. of water. Add a slight excess of dilute ammonia (1 : 1) and filter the solution into a colorimetric tube or bottle and wash the precipitate free from copper.

For a standard, weigh 3 gms. of a sample in which the copper has been determined electrolytically and treat it exactly as described above for the unknown sample. Filter the solution into a similar tube or bottle, and match the colors in a colorimeter, or dilute in Eggertz tubes.

For colorimetric determinations of copper, it is convenient to prepare a set of standards, increasing in strength by 0.002 gm. of copper from the lowest to the highest required for low-grade materials. The unknown solution is placed in a bottle similar to those containing the standards, and diluted to the same volume, when its place in the series is easily found and its content in copper determined directly. (See p. 42.)

BARYTA IN SLAG

Weigh 1 gm. of slag, transfer it to a casserole, add potassium sulphate, moisten the contents of the casserole with water, and add nitric and hydrochloric acids. Heat to dissolve the slag, and evaporate the solution to dryness. Dissolve the residue in dilute hydrochloric acid, filter, wash, ignite, and weigh SiO_2+BaSO_4. Deduct the SiO_2, which has already been determined in the slag, and multiply the remainder, which represents $BaSO_4$, by the factor for BaO, 0.65699.

ARSENIC IN SLAG

Treat 5 to 10 gms. of the slag with 10 cc. of nitric acid, 2 cc. of sulphuric acid, and, if the slag has not been chilled, add 10 cc. of hydrofluoric acid. Evaporate the solution until sulphuric acid fumes are evolved. Cool, add 10 cc. of hydrochloric acid and 25 cc. of water, and boil. Filter, wash, and dilute the filtrate to 500 cc. Add ammonia until the solution is almost neutral. Reduce with sodium sulphite and proceed according to the method for arsenic in ores, etc., on page 180.

ANALYSIS OF REVERBERATORY SLAG

SiO_2 in Slag. Weigh 0.5 gm. of the slag and transfer it to a platinum crucible or dish. Add about 6 gms. of sodium carbonate, mix, cover with 1 or 2 gms. of sodium carbonate and fuse. Raise the temperature gradually and keep the crucible at a bright red heat about fifteen minutes. Cool and dissolve the fusion in a casserole in hydrochloric acid and water.

If the color of the fusion indicates the presence of much manganese, the fusion should be dissolved in water and the platinum removed from the solution before the addition of hydrochloric acid. The platinum would be attacked by chlorine liberated from the hydrochloric acid by the manganese.

Evaporate the solution to dryness to dehydrate the silica. (See p. 70.) Cool, add 10 cc. of hydrochloric acid and 30 cc. of water to the residue, and boil. Filter, wash, ignite, and weigh SiO_2.

FeO in Slag. To the filtrate from the silica, add a slight excess of ammonia. Boil, filter, and wash. Dissolve the precipitate in dilute hydrochloric acid, reduce the iron and titrate it according to the method for iron described on page 62. The factor for converting Fe to FeO is 1.2865.

CaO in Slag. To the filtrate from the hydrates of iron and aluminum obtained in the method for FeO, add ammonium oxalate and a little ammonia. Boil, let the precipitate settle, filter, and wash. Dissolve the precipitate of calcium oxalate in sulphuric acid and titrate the oxalic acid while the solution is hot with standard solution of potassium permanganate. (See p. 163.)

Gold and Silver in Slag. Gold and silver are determined by crucible assay. Weigh 1 assay-ton, transfer it to a fire-clay crucible, and mix it with the following charge:

	gms.
Litharge	80
Sodium bicarbonate	50
Flour	3½

(or other reducing agent to yield an 18-gm. button).

Mix thoroughly and cover with borax. Fuse in a muffle and complete the assay according to the method given on page 229.

ANALYSIS OF BRIQUETTES AND OTHER INSOLUBLE COPPER-BEARING PRODUCTS

SiO_2, FeO, and CaO. Weigh 0.5 gm. of the sample, and transfer it to a casserole. Add 6 cc. of hydrochloric acid and 3 cc. of nitric acid. Cover and slowly heat to boiling. Dilute the solution with boiling water, filter into a casserole, and wash. Ignite the filter in an annealing cup and place the filtrate on the heat to evaporate.

Mix with the ignited residue in the annealing cup 8 gms. of sodium carbonate and transfer the mixture to a platinum crucible. Cover with 2 gms. of sodium carbonate and proceed with the fusion according to the method above for the analysis of slag.

When the filtrate in the casserole has been evaporated to dryness, dissolve the fusion from the crucible and add it to the casserole. Evaporate the contents of the casserole to dryness, and proceed with the determination of SiO_2, FeO, and CaO according to the method described above for the analysis of slag.

GOLD AND SILVER IN COPPER-BEARING CONCENTRATES

Mix 1 assay-ton of the concentrates in a fire-clay crucible with 150 gms. of litharge, 35 gms. of sodium bicarbonate, 10 gms. of silica, and 40 gms. of potassium nitrate. Cover with salt to a depth of half an inch, fuse, and complete the assay according to the method given on page 229.

ANALYSIS OF COPPER BULLION

Sampling. At the furnace, the metal is sampled in the molten condition while it is being poured. The sample is taken at regular intervals; the first is taken thirty minutes after the pouring begins, and the others at intervals of an hour, by batting the stream of molten metal with a wooden paddle, driving from 150 to 200 gms. of the molten metal into a pail of water, where it solidifies in the form of shot. The samples are collected, mixed, and screened through a 4-mesh screen, and then through a 10-mesh screen; that remaining on the latter is reserved for the sample. It is then halved with a riffle and one-half of the sample is sent to the laboratory for analysis.*

When bullion cools, the impurities are not evenly distributed throughout the mass, but, according to Keller,† are segregated, either in those parts which cool first, if the impurities are high, or in those parts which cool last if the impurities are low.

Converter copper, having more than 97 per cent of copper, usually has its impurities, including gold and silver, concentrated

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* Wraith, Trans. Amer. Inst. Min. Eng., 41, p. 318.

† Trans. Amer. Inst. Min. Eng., 27, p. 106; 42, p. 905.

in that part which cools last; while black copper, from the blast furnace, usually has its impurities concentrated in those parts that cool first. The sampling of plates and bars, therefore, requires great care. This is best done by taking the samples with a drilling-template. For sampling anodes, 36.75 ins. long, 28 ins. wide, and about 2 ins. thick, Kellar uses a 99-hole template (Fig. 80). Every fourth anode in the lot is sampled, one sample being taken from each. The first anode is carefully swept, the template laid upon it, and drilled through with a $\frac{1}{2}$-in. drill at the first hole in the template and all the drillings saved. The succeeding anodes are treated in the same way, the holes of the template being used in consecutive order, one hole to the anode. The drillings from the entire lot are then ground to pass through a 16-mesh screen. The sample is then mixed and quartered. The final sample of about 1 lb. is screened over a 40-mesh screen. The oversize and undersize are then weighed to determine the ratio of coarse to fine, the same ratio being maintained in the assay-ton made up for analysis.

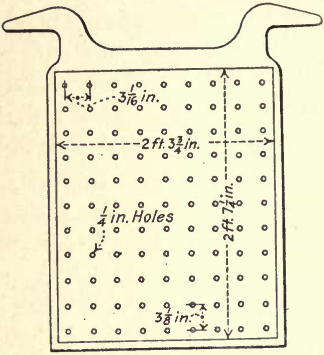

Fig. 80.—Template for Sampling Anodes.

MOISTURE IN PIG COPPER

When copper is cast into pigs in a casting machine, and left to cool under water, the water is taken into the pores of the metal. The pores are so small that the ordinary temperature at which moisture is determined (100° C. to 110° C.) is not sufficient to overcome the surface tension and expel it. Therefore, the sample of copper in which moisture is to be determined should be weighed and heated to about 200° C., until the steam is observed to escape from the metal, and then cooled in a desiccator and weighed again. The loss in weight represents the moisture.

COPPER IN COPPER BULLION *

Weigh accurately about 10 gms. of the bullion and transfer it to a beaker. Add a drop or two of hydrochloric acid to precipitate silver. Add 50 cc. of water and 50 cc. of nitric acid. When in solution, let the silver chloride settle, filter into a carefully weighed flask, and dilute with water to about 300 cc. Weigh the flask. This requires a special balance. Take out about 25 cc. of the solution and reweigh the flask. Dilute the portion taken out and precipitate the copper from it by electrolysis. (See electrolytic method for copper, p. 173.)

SILVER IN COPPER BULLION

Weigh one assay-ton (the quantity depends upon the content of silver). Divide it into ten nearly equal parts and transfer each part to a beaker. Dissolve in nitric acid, dilute, and add a sufficient amount of a solution of sodium chloride to precipitate the silver. Let the silver chloride settle over night, filter, place the filter papers with their contents in ten scorifiers, sprinkle with litharge, and burn the papers, Add granulated lead and scorify. (See assay of silver ores, p. 234.) Cupel, assemble the beads, and weigh. Part with nitric acid and weigh. The difference in the two weights represents the silver.

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* This method for copper and the following one for silver were communicated to the author by D. W. Buckly, Butte, Mont.

SILVER IN COPPER BULLION

Washoe Method

Weigh a one assay-ton sample of the drillings and transfer it to a beaker. Add 160 cc. of cold water and 110 cc. of nitric acid (sp.gr. 1.42). Cover; when in solution, wash off the cover, add 100 cc. of cold water and 10 cc. of sodium chloride solution (2 gms. NaCl in 250 cc. of water).

If the bullion carries more than 100 ounces of silver per ton, add more sodium chloride solution.

Stir, and let the precipitate settle twelve hours. Filter and wash. Wipe out the beaker with pieces of filter paper and add these to the filter containing the silver chloride. Place the filter, with the precipitate of silver chloride, on a scorifier, add 3 gms. of litharge, and burn off the filter in a muffle, at a very low temperature. When the paper is burnt, add 35 gms. of granulated lead and a little borax glass, and scorify at a low heat. Cupel and weigh.

Crush the top of the cupel containing lead oxide on a bucking-board, and mix it in a crucible with

	Gms.
Sodium carbonate	35
Borax glass	60
Litharge	30
Calcium fluoride	1
Flour	5

(or other reducing agent to yield a 15-gm. button).

Cover with borax glass, fuse at a high temperature, and, after separating the lead button from the slag, cupel and weigh the silver bead, and add, as a correction, to the silver already found. (See Fire Assaying, p. 224.)

GOLD IN COPPER BULLION

Weigh 10 portions of drillings, each 1/20 of an assay-ton, place each portion in a cupel, 38 mm. in diameter and 28 mm. in height. Fill the cupel with test lead, place it in a very hot muffle to melt the lead, reduce the heat as quickly as possible, and finish the cupellation at a moderate temperature. Assemble the beads, part, and weigh. The weight, multiplied by 2, will give the number of ounces of gold per ton of bullion.

SILVER AND GOLD IN COPPER BULLION *

Reagents. *Solution of mercuric nitrate.* Dissolve 40 gms. $Hg(NO_3)_2$ in 1 liter of water.

Solution of sodium chloride. Dissolve 19 gms. NaCl in 1 liter of water (1 cc. will precipitate about 0.35 gm. of silver).

Au and Ag in Copper-bullion. Weigh one assay-ton of the drillings which have been ground and divided into coarse and fine with a 40-mesh sieve, the assay-ton being made up of the coarse and fine in the ratio that exists in the sample as a whole. Transfer it to an 800-cc. Jena beaker. Add 30 cc. of water and 10 cc. of the mercuric nitrate solution (=0.25 gm. Hg).

For comparatively pure copper the amount of mercuric nitrate may be reduced; but copper high in sulphur will require more than 10 cc. of the mercuric nitrate solution.

Shake the beaker until the copper is amalgamated with mercury. Add 100 cc. of strong sulphuric acid, cover the beaker, and place it on a hot plate.

The solution appears to boil, owing to the reduction of sulphuric acid and the evolution of sulphur dioxide gas. This continues about an hour.

When this reaction is complete, the liquid is dark green in color, and finally changes to a light grayish blue. At this point,

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* Edward Keller, Trans. Amer. Inst. Min. Eng., Vol. 46, Bull. 80, 2101.

remove the beaker and add 450 cc. of water and a sufficient amount of sodium chloride solution to precipitate the silver and the mercury (30 cc. will be sufficient for 100 mgms. of silver and 0.25 gm. of mercury. Heat the solution to the boiling-point to dissolve copper sulphate and to coagulate the silver chloride. Remove the beaker from the heat and add to its contents 150 cc. of water. Let the precipitate settle over night, if convenient, and filter. Place the filter with the precipitate in a scorifier, sprinkle with litharge, and burn the paper. Add granulated lead and scorify. Cupel and weigh the combined gold and silver. Part, and weigh the gold. (See Fire Assaying, p. 224.)

COPPER, ARSENIC, AND ANTIMONY IN SILVER BULLION

Outline. The bullion is treated with nitric acid and the insoluble residue (Au, Sn, part of the Sb, a little Pb, etc.) filtered from the solution. The antimony is extracted from the residue with tartaric acid and added to the first filtrate after silver and lead have been removed from it. The copper, arsenic, and antimony are then precipitated with hydrogen sulphide. The arsenic and antimony sulphides are dissolved in a solution of potassium hydroxide, the copper sulphide filtered from the solution, and the copper determined by electrolysis. From the solution of arsenic and antimony sulphides, the arsenic is precipitated and filtered as magnesium ammonium arsenate. It is burnt and weighed. The antimony is measured in the filtrate by adding potassium iodide and titrating with standard solution of sodium thiosulphate.*

Cu in Bullion. Weigh 10 gms. of the bullion and dissolve it in 50 cc. of dilute nitric acid (1 : 4), free from chlorine. Evaporate the solution to 25 cc. and add 25 cc. of hot water. Boil,

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* Method communicated to the author by Oliver C. Martin, Denver, Colo.

filter, and wash by decantation. Reserve this as Filtrate No. 1. Treat the residue in the original beaker with 10 cc. of water, 2 cc. of hydrochloric acid, and 1 cc. of nitric acid. When in solution, filter, and evaporate the filtrate to dryness.

Do not heat to a high temperature when dry, since that treatment would form insoluble lead antimonate.

Dissolve the residue in a solution of tartaric acid (1 gm. in 10 cc. of water) and reserve as Solution No. 2.

To Filtrate No. 1 add a sufficient quantity of hydrochloric acid to precipitate the silver present. Then add the calculated quantity of sulphuric acid to precipitate the lead present. Add immediately 50 cc. of alcohol and stir vigorously.

Lead sulphate is insoluble in alcohol.

Let the precipitate settle, filter, by suction, wash the precipitate with a mixture of alcohol and hydrochloric acid (4 : 1), first by decantation, and finally, on the filter.

Evaporate the filtrate until most of the alcohol has been removed and the volume has been reduced to about 125 cc. Then filter into it the tartaric acid solution (No. 2), and wash well. Neutralize the solution with ammonia. Add 2 cc. of hydrochloric acid, boil, and pass H_2S through the solution at the boiling temperature for forty-five minutes to precipitate the sulphides of copper, arsenic, and antimony. Filter at once and wash. Spread the filter paper on the inside of a beaker and wash off the precipitate with as little water as possible. Treat the precipitate with a solution of potassium hydroxide (2 gms. KOH dissolved in 10 cc. of water) to dissolve the sulphides of arsenic and antimony. Heat until the precipitate is black, and filter.

Dissolve the copper sulphide with nitric acid and determine the copper by electrolysis. (See p. 173.)

As in Bullion. To the filtrate from the copper sulphide, obtained according to the preceding method, which should not measure more than 40 cc., add 1 gm. $KClO_3$ and 50 cc. of hydrochloric acid. Boil until the solution is clear and the chlorine is expelled.

The sulphides are oxidized to sulphates.

Cool, neutralize with ammonia, and let the solution stand to permit the separation of the small quantity of lead sulphate which may be present. Filter, and add ammonia, in quantity equal to one-third the volume of the solution. Add magnesia mixture. (See p. 79.)

$$K_2HAsO_4+MgCl_2+NH_3+6H_2O=2KCl+MgNH_4AsO_4\cdot 6H_2O.$$

Let the solution stand twenty-four hours or more. Filter in a porcelain Gooch crucible. Reserve the filtrate for antimony and burn the precipitate to convert the magnesium ammonium arsenate to magnesium pyroarsenate.

$$2MgNH_4AsO_4\cdot 6H_2O=Mg_2As_2O_7+2NH_3+7H_2O.$$

The factor for As in $Mg_2As_2O_7$ is 0.4828.

Sb in Bullion. Boil off the excess of ammonia from the filtrate from the arsenic precipitate, cool, and add 50 cc. of hydrochloric acid and 3 gms. of potassium iodide.

$$SbCl_5+2KI=2KCl+SbCl_3+I_2.$$

Add a little starch solution and titrate with standard solution of sodium thiosulphate.

$$I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6.$$

For the method of making and standardizing the solution of sodium thiosulphate, see iodide method for copper, page 171. The solution may be standardized against copper and its value in antimony determined by multiplying its value in copper by the factor 0.9454. It will be observed in the reaction on page 171, that 2 atoms of copper, in the form of copper acetate, liberate 2 atoms of iodine from potassium iodide; and the equation above indicates that 2 atoms of iodine are liberated by one atom of antimony. The ratio of the value of this standard solution in copper to its value in antimony will, therefore, be equal to the ratio of twice the atomic weight of copper (2×63.57) to the atomic weight of antimony (120.2), and this ratio is expressed by the factor 0.9454.

COPPER IN CONVERTER COPPER

Weigh 0.5 gm. of the sample and transfer it to a No. 4 beaker. Add 8 cc. of nitric acid, 8 cc. of water, and 1 cc. of sulphuric acid, and keep the beaker covered during the solution of the sample. When the metal is in solution, boil out the fumes, dilute the solution with water, and precipitate the copper by electrolysis. The silver present is precipitated with the copper on the cathode and the weight of silver, which has been previously determined by the fire assay, should be deducted from the total weight (291.66 ounces = 1 per cent). The silver may be removed prior to the precipitation of copper by adding just enough hydrochloric acid to precipitate it, letting the chloride settle, and filtering it off. The solution is then electrolyzed and the copper weighed directly.

ARSENIC AND ANTIMONY IN CONVERTER COPPER

Outline. The sample is dissolved in sulphuric and nitric acids and most of the copper is precipitated from the solution by electrolysis; the remaining copper, with the antimony and arsenic, is precipitated with hydrogen sulphide, the sulphides of arsenic and antimony are extracted with potassium hydroxide solution, and the antimony determined by electrolysis.

After the antimony has been withdrawn from the solution, the arsenic is precipitated with hydrogen sulphide, filtered from the solution, and dissolved in ammonia. Sulphuric acid is added, the solution evaporated, diluted, the acid neutralized with ammonia, hydrochloric acid added, and the solution filtered. An excess of sodium bicarbonate is added to the filtrate, and the arsenic is titrated with standard iodine solution.*

Reagents. *Standard iodine solution.* Dissolve 5.2 gms. of iodine and 9 gms. of potassium iodide in 10 cc. of water and dilute the solution to 1 liter. Each cubic centimeter should be equivalent to about 0.0015 gm. of arsenic.

To standardize the solution, dissolve 0.1 gm. of pure As_2O_3 and 1 gm. of potassium hydroxide in about 30 cc. of water. Acidify the solution with hydrochloric acid, add sodium bicarbonate to render the solution alkaline, and then add about 4 gms. in excess. Add a little starch solution, and titrate with the iodine solution. The factor for As in As_2O_3 is 0.7574.

Starch solution. (See p. 111.)

Hydrogen sulphide, H_2S from a generator.

Potassium hydroxide, KOH.

Sodium sulphide solution. Dissolve 25 gms. Na_2S+9H_2O in 100 cc. of water.

Sb in Copper. Weigh 10 gms. of the sample (20 gms. if it contains less than 5 per cent of arsenic) and transfer it to a No. 5 beaker. Add 30 cc. of sulphuric acid, 20 cc. of nitric acid, and 50 cc. of water. When in solution, heat to drive off nitrous fumes, dilute with water, and electrolyze 2.5 hours at 4 amperes, using a cylindrical platinum gauze cathode about 75 mm. high and 50 mm. in diameter. The precipitation of the copper should be stopped when about 0.25 gm. of copper remains in solution, indicated by a faint blue color. Remove the cathode, rinsing back into the beaker the adhering solution with water from a jet.

Neutralize the solution with ammonia and then acidify it with 3 cc. of hydrochloric acid. Pass hydrogen sulphide through the solution rapidly for thirty minutes and let the sulphides of

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* E. E. Brownson, Trans. Amer. Inst. Min. Eng., 46, Bull. 80, 1489.

copper, arsenic, antimony, etc., settle thirty minutes. Filter and discard the filtrate. Wash the precipitate once on the paper, and then wash the sulphides into a No. 5 beaker with the smallest possible amount of water. Add to the precipitate in the beaker 10 cc. of aqua regia and place the beaker under the funnel. In another beaker, mix 5 cc. of water and 20 cc. of aqua regia, heat to boiling, and pour through the filter to dissolve the small amount of sulphides adhering to the paper. Wash the paper with a small amount of water, and keep the bulk of the solution low to save time in evaporating. Cover the beaker and boil the solution thirty minutes. Remove the cover, and, with a fine jet of water, wash off the cover and wash down the sides of the beaker. Evaporate the solution to dryness at a temperature low enough not to cause loss by spattering. The residue should be heated until there is no longer an odor of acid.

Add about 5 gms. of potassium hydroxide and 30 cc. of water and boil vigorously about fifteen minutes. The arsenic and antimony will pass into solution. Add 25 cc. of sodium sulphide solution (25 gms. Na_2S+9H_2O in 100 cc. of water) and boil vigorously about ten minutes. Cool, decant the clear solution through a filter paper into a No. 2 beaker. Again add 25 cc. of sodium sulphide solution to the black precipitate in the beaker, stir well, and transfer the precipitate to the filter paper. Wash well with a dilute solution of sodium sulphide (5 gms. Na_2S+9H_2O in 100 cc. of water) from a wash bottle.

This precipitate may be washed with hot water if care is taken that it be kept wet. If allowed to dry, copper will be oxidized and dissolved.

Add to the filtrate, which should measure about 160 cc., 5 cc. of hydrogen peroxide and heat until the yellow color of the solution fades.

The solution will become nearly colorless unless the aqua regia used on the filter paper was strong enough to attack it.

Cool, and precipitate the antimony by electrolysis, at 0.1 to 0.15 ampere. The antimony should be precipitated in about twelve hours.

Remove the cathode, carefully washing off the solution which contains arsenic. Then wash in alcohol, dry carefully over an alcohol flame, and weigh. The increase in weight is Sb.

As in Copper. Add to the solution containing the arsenic (from which the antimony has been precipitated) dilute sulphuric acid (1 : 4) to distinct acidity. Pass through the solution a rapid stream of hydrogen sulphide about ten minutes.

$$As_2(SO_4)_3+3H_2S=3H_2SO_4+As_2S_3.$$

Let the precipitate settle twenty-five minutes and decant the solution through a filter (some sulphur will run through the filter). Transfer the precipitate and remaining solution directly to a No. 2 beaker. Now decant again through the filter and place the beaker containing the arsenic sulphide under the funnel. Wash out the beaker in which the arsenic was precipitated with 15 cc. of dilute ammonia (1 : 4), pour this through the filter to dissolve the small amount of arsenic sulphide which it contains, let the solution run into the beaker with the main precipitate, and finally, wash with a little water.

$$As_2S_3+6NH_4OH=2H_3AsO_3+3(NH_4)_2S.$$

To the solution of arsenic add sulphuric acid to neutralize ammonia, and about 8 cc. in excess. Evaporate until the sulphuric acid fumes and then heat the solution at a high temperature about 1.5 hours. Cool, wash down the sides of the beaker with water, and add water to half fill the beaker. Neutralize the acid with ammonia, add hydrochloric acid to distinct acidity, and filter into a No. 4 beaker. Wash thoroughly with hot water. Add water to about half fill the beaker. Neutralize the acid with sodium bicarbonate, and then add 4 gms. in excess.

$$AsCl_3+3NaHCO_3=H_3AsO_3+3NaCl+3CO_2.$$

The solution must be neutral, but NaOH must not be used, since it reacts with I.

Cool to the temperature of the room, add starch solution, and titrate with standard iodine solution.

$$H_3AsO_3+I_2+H_2O=H_3AsO_4+2HI.$$

$$HI+NaHCO_3=NaI+H_2O+CO_2.$$

COPPER IN MATERIALS CONTAINING ARSENIC, ANTIMONY, TELLURIUM, AND SELENIUM

Weigh 0.5 gm. of the sample and transfer it to a beaker. Dissolve in nitric acid, dilute with water, and add just enough hydrochloric acid to precipitate the silver. Filter and wash. To the filtrate, add 0.1 gm. of iron. When the iron is dissolved add ammonia to precipitate the iron, boil, let the precipitate settle, and filter. Dissolve the precipitate in nitric acid, dilute, and precipitate, as before. To insure the separation of all the copper, dissolve the precipitate, reprecipitate, and filter a third time.

The precipitate of ferric hydroxide carries down with it arsenic, antimony, selenium, and tellurium, leaving the copper in solution.

Combine the filtrates and precipitate the copper by electrolysis

SELENIUM AND TELLURIUM IN COPPER

KELLER'S METHOD*

Se in Copper. Weigh 5 to 100 gms. of copper, the quantity depending upon the amount of Se and Te present. Dissolve it in nitric acid and add an excess of ammonia to precipitate P, As, Sb, Sn, Bi, Se, Te, and Fe. Filter and wash the precipitate with dilute ammonia water to remove all the copper.

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* Jour. Amer. Chem. Soc., 19, 771; and 22, 242.

Dissolve the precipitate in hydrochloric acid and saturate the solution with hydrogen sulphide in the cold to precipitate Se, Te, As, Sb, Sn, and Bi as sulphides. Filter the sulphides from the iron and phosphorus. Treat the precipitate with sodium sulphide and filter. The filtrate contains all the Se and Te with some As, Sb, and Sn. Acidify the filtrate with nitric acid and evaporate carefully to dryness. Dissolve the residue in 200 cc. of hydrochloric acid (1.175 sp.gr.) and boil to remove nitric acid. Saturate the solution with sulphur dioxide and filter the elementary selenium in a Gooch crucible. Tellurium is not precipitated in a strongly acid solution. Wash the precipitate with a mixture of hydrochloric acid (1.175) and water (9 : 1), followed by dilute hydrochloric acid, then by water to remove the hydrochloric acid, and finally with absolute alcohol. Dry at 105° C. and weigh the selenium.

Te in Copper. Dilute the filtrate from the selenium with an equal volume of water. Heat it to boiling and add sulphur dioxide to precipitate the tellurium. Filter in a Gooch crucible and treat the precipitate of tellurium in the manner described above for selenium.

ANALYSIS OF ALLOYS

BRASS AND BRONZE

METHOD FOR THE DETERMINATION OF SN, PB, CU, ZN, AL, AND FE

This is a rapid method, which yields only approximately accurate results. Methods for the more accurate separation of these metals are given on pages 215 and 220.

Sn in Bronze. Weigh 1 gm. of fine drillings for the sample, transfer it to a small beaker, and add 15 cc. of dilute nitric acid (2 : 3). Heat to dissolve the alloy and to convert the tin to metastannic acid.

$$5Sn + 10HNO_3 = H_{10}Sn_5O_{15} + 5NO_2 + 5NO.$$

Evaporate the solution nearly to dryness. Add 50 cc. of water and 5 cc. of nitric acid (sp.gr. 1.42). Boil, and let the precipitate settle. Filter, and wash by decantation four or five times. Transfer the precipitate to the filter and wash with boiling water. Dry, separate the precipitate from the filter (Fig. 31, p. 27), burn the filter in a porcelain crucible, add the precipitate, and ignite.

$$H_{10}Sn_5O_{15} = 5SnO_2 + 5H_2O.$$

Cool in a desiccator and weigh. The factor for Sn in SnO_2 is 0.788.

Pb in Alloy. To the filtrate from the metastannic acid, add 15 cc. of sulphuric acid.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$

Evaporate the solution nearly to dryness, cool, add 10 cc. of sulphuric acid, and dilute to 50 cc. with water. Filter, wash with dilute sulphuric acid (1 : 10), and finally, with water. Dry and ignite the filter and residue separately in a porcelain crucible. Cool in a desiccator and weigh $PbSO_4$. The factor for Pb in $PbSO_4$ is 0.68311.

Cu in Alloy. Boil the filtrate from the lead sulphate and pass a current of hydrogen sulphide through the solution for half an hour. Filter, and wash the precipitate with a solution of hydrogen sulphide water. Dissolve the copper sulphide on the filter with a little warm, dilute nitric acid, boil the solution, and if sulphur is still present, filter. To the solution add 5 cc. of sulphuric acid and 3 cc. of nitric acid. Dilute the solution and precipitate the copper by electrolysis.

Fe_2O_3 and Al_2O_3 in Alloy. Boil the filtrate from the copper sulphide to expel hydrogen sulphide. Add a few drops of nitric acid and boil. Add ammonia until the solution is alkaline. Heat to the boiling-point, filter, wash with hot water, burn, and weigh as $Al_2O_3 + Fe_2O_3$.

Zn in Alloy. Heat the filtrate from the hydrates of iron and aluminum to the boiling-point and pass through it a current of hydrogen sulphide to precipitate the zinc.

$$ZnSO_4 + H_2S = ZnS + H_2SO_4.$$

Filter, dissolve the precipitate in about 50 cc. of dilute hydrochloric acid (1 : 4), dilute the solution, and boil to expel hydrogen sulphide.

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$

Cool, and add to the cold solution a large excess (50 cc.) of a 10 per cent solution of sodium ammonium phosphate ($NH_4NaHPO_4 + 4H_2O$). Add ammonia carefully to neutralize the solution, using litmus as an indicator. Add two drops of ammonia in excess and then 1 cc. of acetic acid. Test with litmus to be sure the solution is acid. Heat for one hour, but do not boil. After the precipitate has become granular and has settled, filter, and wash it with hot water. Dry the precipitate and separate it from the paper (Fig. 31). Dissolve the precipitate which adheres to the filter paper in a little dilute nitric acid and collect the solution in a small, weighed porcelain dish. Evaporate the solution to dryness, add the dry precipitate which was separated from the paper and heat gently to a low red heat. Cool in a desiccator and weigh as zinc pyrophosphate ($Zn_2P_2O_7$). The factor for Zn is 0.4289.

Instead of filtering on filter paper in the manner described above the zinc ammonium phosphate may be filtered in a porcelain Gooch crucible, dried at 100° C. and weighed directly. (See p. 25.)

The zinc may also be determined by the volumetric method described on page 178. After the zinc sulphide has been filtered from the solution and dissolved in 50 cc. of hydrochloric acid (1 : 4), about 4 gms. of ammonium chloride are added, the solution diluted with 250 cc. of hot water, heated to 60° C. and titrated with a standard solution of potassium ferrocyanide.

Fe in Alloy. The precipitate formed by adding ammonia (see $Al_2O_3 + Fe_2O_3$ in alloy, p. 211) may consist of aluminic hydrate or ferric hydrate or a mixture of the two. If it is brown in color, iron is present. To determine the iron in the alloy, weigh 1 gm. of the sample and treat it according to the process described above until the hydroxides of iron and aluminum have been filtered from the solution. Dissolve the precipitate in a little hydrochloric acid, reduce the iron with a little stannous chloride solution, add mercuric chloride solution, and titrate the iron with standard potassium dichromate solution; or the iron may be reduced with zinc in the presence of an excess of sulphuric acid, and titrated with standard permanganate solution. See Methods for iron in ores, page 50 et seq.

Al in Alloy. From the weight of Fe, as determined above, calculate its value in Fe_2O_3 by multiplying by the factor 1.4298. Deduct this weight from the weight of the combined oxides of iron and aluminum, and multiply the weight of Al_2O_3 remaining by the factor 0.5303 to obtain the weight of Al.

WHITE ALLOYS CONTAINING TIN, LEAD, COPPER, PHOSPHORUS AND ANTIMONY

Sn in Alloys. Weigh 1 gm. of the sample and transfer it to a small beaker. Add 20 cc. of dilute nitric acid (1 : 1), evaporate the solution nearly to dryness, add 50 cc. of boiling water, boil, filter, and wash the precipitate with hot 2 per cent solution of nitric acid. Burn the filter and precipitate separately in a porcelain crucible, cool in a desiccator, and weigh SnO_2. The factor for Sn in SnO_2 is 0.788.

If the alloy contains phosphorus, the phosphorus will come down with the tin, providing the ratio of tin to phosphorus is as great as 8 to 1. The phosphorus should be determined (see P in alloy, p. 214) and its equivalent in P_2O_5 deducted from the weight of impure SnO_2.

Pb in Alloy. To the filtrate from the metastannic acid, add 5 cc. of sulphuric acid, evaporate the solution until dense fumes of sulphuric acid are evolved, cool, add 50 cc. of cold water, stir, and let the precipitate settle half an hour. Filter in a Gooch crucible, and wash with dilute sulphuric acid (1 : 9).

Remove the filtrate and reserve it for the determination of copper and zinc. Then wash the lead sulphate once with alcohol. Dry the precipitate at about 250° C. and weigh the $PbSO_4$. The factor for Pb in $PbSO_4$ is 0.6831.

Cu in Alloy. To the filtrate from lead sulphate add 1 cc. of nitric acid, and determine the copper by electrolysis. (See p. 173.)

Zn in Alloy. To the solution from which the copper has been precipitated add bromine water, ammonium persulphate, and ammonium chloride. Then add an excess of ammonia and heat to the boiling-point. If a precipitate forms—$Fe(OH)_3$, MnO_2—filter, and add to the solution an excess of ammonium phosphate. Heat to the boiling-point and add dilute hydrochloric acid until the solution is nearly neutral. Boil ten minutes, filter in a weighed Gooch crucible, and wash well with hot water. Dry at 100° C. to a constant weight. The factor for Zn in $ZnNH_4PO_4$ is 0.3663. For other methods see page 178.

P in Alloy. Weigh 1 gm. of the alloy and treat it according to the method described above for the determination of Sn, until the precipitate of tin and phosphorus has been ignited in a porcelain crucible. Add to the crucible 3 gms. of potassium cyanide, cover, fuse, and keep at a dull red heat for five minutes.

$$SnO_2 + 2KCN = 2KCNO + Sn.$$

Cool, treat the fusion with boiling water, and filter the tin from the solution. Add to the filtrate 20 cc. of strong hydrochloric acid and boil.

This should be done under the hood.

Then add 30 cc. of nitric acid and evaporate to dryness. Cool, treat the residue with nitric acid and water, filter, and determine the phosphorus in the filtrate by precipitating with ammonium molybdate solution and weighing the yellow precipitate. (See p. 75.)

Sb in Alloy. (See p. 218.)

ALLOY CONTAINING TIN, COPPER, ANTIMONY, LEAD AND ZINC *

Reagents. Dilute *nitric acid* (3 : 7).
Sodium carbonate, Na_2CO_3.
Sulphur, S.
Sodium sulphite, Na_2SO_3.
Solution of *hydrogen sulphide*. Water saturated with H_2S.
Dilute *sulphuric acid* (1 : 1).
Ammonium acetate, $NH_4C_2H_3O_2$.
Acetic acid, $C_2H_4O_2$ (sp.gr. 1.04).
Standard ammonium molybdate solution, page 175.
Potassium iodide, KI.
Standard solution of sodium thiosulphate, page 171.
Starch solution, page 111.
Solution of *sodium ammonium hydrogen phosphate*.
Dissolve $Na(NH_4)HPO_4 \cdot 4H_2O$ in water.

Sn in Alloy. Weigh 1 gm. of the sample and transfer it to a small beaker. Add 20 cc. of dilute nitric acid (3 : 7). Cover, and when the sample is in solution, remove the cover and evaporate the solution to dryness on a water-bath. Heat in an air-bath at 120° C. for an hour. Cool, moisten the residue with 4 cc. of nitric acid, and then add 30 cc. of water. Heat, filter, and wash the precipitate until the acid is all removed. Dry the precipitate and separate it from the paper. Ignite the paper in a weighed porcelain crucible, moisten the ash with a few drops of nitric acid, and ignite gently. Add the precipitate to the ash in the crucible and ignite at a red heat. Weigh as impure $Sb_2O_4 + SnO_2$.

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* Meade, Chem. Eng., 8, 45.

Add to the crucible a mixture of dry sodium carbonate and sulphur, in equal parts, in quantity about six times the weight of the oxides in the crucible. Fuse at a low temperature until burning sulphur ceases to escape between the crucible and its cover. Cool, and dissolve the fusion in hot water; add sodium sulphite to the dark-brown-colored solution until the iron and copper sulphides are precipitated and the solution changes to a light yellow color. Filter off the iron and copper sulphides, wash well with water containing hydrogen sulphide, ignite and weigh the residue as CuO and Fe_2O_3. Subtract this weight from the weight of impure Sb_2O_4 and SnO_2 already determined. Dissolve the copper and iron oxides in a little strong hydrochloric acid, dilute the solution to 25 cc., add an excess of ammonia to precipitate the ferric hydroxide, filter, and wash with water. Ignite and weigh the precipitate as Fe_2O_3. The factor for Fe in Fe_2O_3 is 0.69939. Acidify the filtrate from the ferric hydroxide with dilute sulphuric acid and add it to the main solution for the copper.

Determine the antimony according to the method described below, calculate its equivalent in Sb_2O_4, and subtract it from the combined weight of Sb_2O_4 and SnO_2 to give the weight of SnO_2. The factor for Sn in SnO_2 is 0.7881.

Pb in Alloy. To the filtrate from the antimony and tin, add 10 cc. of dilute sulphuric acid (1 : 1) and evaporate the solution until dense white fumes of sulphuric acid are evolved. Cool, and dilute the solution. Heat it, let the precipitate settle, decant the clear solution through a filter, wash the precipitate by decantation with 2 per cent sulphuric acid, and then wash it with cold water. Dissolve 10 gms. of ammonium acetate in 50 cc. of hot water, and pour it through the filter to dissolve the small amount of lead sulphate deposited on the paper by decantation, letting the solution run into the beaker containing the main part of the precipitate. Wash the paper with hot water, and place the beaker over the heat until the lead sulphate is dissolved. Dilute the solution to 200 cc., make it slightly acid with acetic acid, and titrate the lead with standard ammonium molybdate solution. (See p. 175.)

Cu in Alloy. To the filtrate from the lead sulphate add ammonia until the solution is faintly alkaline, and then add 8 cc. of acetic acid and 3 gms. of potassium iodide. When the potassium iodide is in solution add a little starch solution and titrate with standard sodium thiosulphate solution. (See p. 171.)

Cu in Alloy Containing Zinc. Heat the filtrate from the lead sulphate to boiling and pass through it a current of hydrogen sulphide until it becomes cold. Filter by suction and wash the precipitate with hydrogen sulphide water. Dissolve the precipitate in a little warm dilute nitric acid, evaporate the solution to 2 or 3 cc., dilute slightly, add ammonia until the solution is faintly alkaline, and then add 8 cc. of acetic acid, 3 gms. of potassium iodide, and a little starch solution, and titrate with standard sodium thiosulphate solution.

The copper may also be determined in the filtrate from the lead sulphate by electrolysis.

Zn in Alloy. To the cold filtrate from the copper, add 50 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate. Carefully neutralize the solution with ammonia, using litmus paper, and add 2 drops of ammonia in excess. Acidify the solution with acetic acid (1 cc. or more if necessary). Heat for one hour, but do not boil. Filter and wash the precipitate with hot water, dry, and transfer it to a watch glass. Dissolve the small amount of the precipitate on the filter in dilute nitric acid and let the solution run into a small. weighed, porcelain dish. Evaporate the solution to dryness, add the main precipitate from the watch glass, and heat gently at first, and then for a few minutes at a low red heat. Cool and weigh as $Zn_2P_2O_7$. The factor for zinc is 0.4289.

The zinc may also be determined volumetrically by the method described on page 178.

Sb in Alloy.* Weigh 1 gm. of the sample, transfer it to a beaker, add 1 gm. of potassium iodide, 40 cc. of water, 40 cc. of concentrated hydrochloric acid, and boil gently one hour.

The residue is metallic antimony precipitated from $SbCl_3$ by the metals not yet dissolved. KI reduces $SbCl_5$ to $SbCl_3$.

Filter on asbestos and wash five or six times with hot dilute hydrochloric acid (1 : 10). Wash the precipitate and asbestos into a small beaker with a little water and add 25 cc. of concentrated hydrochloric acid and a few crystals of potassium chlorate. Cover and warm gently, stirring occasionally. When the antimony is dissolved, dilute the solution to 100 cc. and filter out the asbestos, washing it free of hydrochloric acid. Boil the solution vigorously five minutes to drive off the chlorine. The Sb is oxidized to $SbCl_5$. Cool to room temperature, add 1 gm. of potassium iodide, and titrate with standard sodium thiosulphate solution. (See p. 204.)

BISMUTH IN ALLOYS

Outline. The alloy is dissolved in acids and all the metals converted to sulphates. Insoluble sulphates are filtered from the solution. From the filtrate bismuth and the other metals of that group are precipitated with hydrogen sulphide. The sulphides of copper, arsenic, and antimony are dissolved from the precipitate with potassium cyanide solution; the remaining sulphides are dissolved and the bismuth precipitated and weighed as the oxychloride.

Reagents. Dilute *sulphuric acid* (1 : 10).

Hydrogen sulphide; H_2S from a generator.

Solution of *potassium cyanide*; concentrated solution of KCN in water.

Dilute *nitric acid* (1 : 1)

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* H. Yockey, Jour. Amer. Chem. Soc., 28, 646 and 1435. Walters and Apfelder, Ibid., 25, 635.

Dilute *ammonia* (1 : 2).

Dilute *hydrochloric acid* (1 : 2).

Bi in Alloy. Weigh 1 gm. of the alloy, transfer it to a 250-cc. Erlenmeyer flask, add 10 cc. of nitric acid, and evaporate the solution until the residue is pasty, but do not let it boil. Add 7 cc. of hydrochloric acid and heat to complete the decomposition of the alloy. Then add 8 cc. of sulphuric acid and boil until dense white fumes of sulphuric acid are evolved. Cool the solution, add 30 cc. of water, and boil until the bismuth sulphate dissolves. Cool, filter quickly before there is time for basic bismuth sulphate to precipitate, and wash with 10 per cent solution of sulphuric acid. Dilute the filtrate to 100 cc. and pass a current of hydrogen sulphide through the solution to precipitate bismuth, copper, arsenic, and antimony—also lead if any remains. Filter and wash the precipitate with hydrogen sulphide water. Place the filter with its contents in a 250-cc. beaker, add a concentrated solution of potassium cyanide, using as little as possible to dissolve the sulphides of copper, arsenic, and antimony. Warm the solution for a few minutes, filter, and wash the sulphides with hot water. Dissolve the sulphides of bismuth, lead, and cadmium by placing the filter and precipitate in a 250-cc. beaker, and heating with 10 cc. of dilute nitric acid (1 : 1). Add 20 cc. of water and filter in a porcelain Gooch crucible. Wash the precipitate with dilute nitric acid. Transfer the filtrate to a 400-cc. beaker, dilute it to 300 cc., and heat the solution to boiling. Remove it from the heat and neutralize it by adding dilute ammonia (1 : 2), testing with litmus paper. Continue adding ammonia, cautiously, drop by drop, until the solution becomes slightly cloudy. Add 1 cc. of dilute hydrochloric acid and let the determination stand on the hot-plate for an hour, but do not let it boil. Filter the bismuth oxychloride in a porcelain Gooch crucible, wash with hot water, dry at 100° C., and weigh as $BiOCl$. The factor for Bi is 0.80166.

ANALYSIS OF COPPER CONTAINING LEAD, ANTIMONY, ARSENIC, TIN, IRON, COBALT, AND NICKEL, WHEN ONLY A SMALL SAMPLE OF THE MATERIAL IS AVAILABLE *

Reagents. *Sodium carbonate* (Na_2CO_3).

Sulphur, S.

Hydrogen sulphide (H_2S from a generator).

Solution of *sodium sulphide;* Na_2S dissolved in water.

Sodium dioxide (Na_2O_2).

Alcohol (C_2H_6O—sp.gr. 0.84).

Tartaric acid ($C_4H_6O_6$).

Ammonium nitrate (NH_4NO_3).

Solution of *ammonium nitrate.* Dissolve 10 gms. NH_4NO_3 in 1 liter of water.

Ammonium carbonate, $(NH_4)_2CO_3$.

Ammonium acid sulphide, $(NH_4)HS$.

Solution of *ammonium sulpho-cyanate.* Dissolve 10 gms. NH_4SCN in 1 liter of water.

Bromine water; water saturated with Br.

A. Weigh 0.5 gm. of the sample, transfer it to a small beaker, cover, and pour down the lip into the beaker 10 cc. of nitric acid (sp.gr. 1.42). Heat, or cool, to dissolve, at a moderate rate. Evaporate the solution to dryness and heat the residue at 110° C. Cool, moisten the deposit with nitric acid, add 50 cc. of water and then add ammonia to render the solution slightly alkaline and to precipitate the tin completely. Heat the solution to boiling, acidify it with nitric acid, filter, wash the precipitate, burn it in a porcelain crucible, and weigh it. Reserve the filtrate for separate treatment (see *E* below).

B. Cover the residue with a mixture of sodium carbonate and sulphur, in equal parts. Cover the crucible and fuse until sulphur has ceased to be volatilized. Cool, place the crucible in a beaker with water, and boil. Remove the crucible after

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* F. A. Gooch, Carnegie Publication, 1, 235.

it has been washed off. Filter and wash the residue. If the precipitate is large, repeat this treatment. Combine the filtrates for treatment under *D*.

C. Ignite the precipitate—which may contain sulphides of lead, copper, and iron—in a porcelain crucible. Cool, treat the residue with aqua regia and a little sulphuric acid. Evaporate the solution until sulphuric acid fumes are evolved. Cool, add a little water, filter off the lead sulphate in a Gooch crucible, dry, and weigh the $PbSO_4$.

To the filtrate add ammonia to precipitate ferric hydroxide. Boil, filter, burn, and weigh the Fe_2O_3.

Through the filtrate from the iron pass a current of hydrogen sulphide, filter from the solution the copper sulphide, burn it in a crucible to CuO, and weigh it.

D. Acidify the filtrate from *B*, containing arsenic, antimony, and tin, with hydrochloric acid. Filter, and reject the filtrate. Dissolve the precipitate on the filter with the smallest amount possible of warm solution of sodium sulphide. Concentrate the solution by evaporation. Cool and add sodium dioxide, a little at a time, until the liquid becomes colorless and oxygen is liberated freely. Add to the solution one-third of its volume of alcohol (sp.gr. .84). Filter, and wash with alcohol, gradually increasing the strength (1 : 2), (1 : 1), and then with (3 : 1). The precipitate should contain antimony as sodium antimonate; and the filtrate, sodium arsenate and sodium stannate in solution. Dissolve the precipitate of sodium antimonate in a mixture of dilute hydrochloric acid (1 : 4) and 5 to 10 per cent of its weight of tartaric acid. Dilute and pass through the solution a current of hydrogen sulphide. Filter on asbestos, and dry in an atmosphere of CO_2 at 240° C. (Paul's apparatus) and weigh as antimony trisulphide.

Acidulate the filtrate containing arsenic and tin with hydrochloric acid. Cool to 0° C. Treat with twice its volume of hydrochloric acid (sp.gr. 1.2) also cooled to 0° C. Filter out sodium chloride on asbestos and pass a current of hydrogen sulphide through the solution 1.5 hours. Let the precipitate settle for two hours, filter on asbestos, wash with dilute hydrochloric acid (1 : 2), and then with hot alcohol. Dry at 110° C. and weigh as As_2S_5.

To drive off most of the acid evaporate the filtrate from the arsenic pentasulphide. Dilute the solution largely and pass through it a current of hydrogen sulphide. Add ammonium nitrate to aid coagulation. Filter, and wash the precipitate with the solution of ammonium nitrate. Ignite with ammonium carbonate and weigh as SnO_2.

E. To the filtrate from the residue, after the first solution of the metal, add 5 cc. of sulphuric acid, and evaporate until the sulphuric acid fumes. Dilute to 50 cc., filter on asbestos, wash with dilute sulphuric acid (1 : 3), ignite, and weigh as $PbSO_4$. Proceed with the filtrate as follows.

F. To the filtrate add 1 gm. of tartaric acid, nearly neutralize with ammonia, heat to boiling, and add 5 cc. of dilute sulphuric acid (1 : 4), 5 cc. of ammonium acid sulphide, and 100 cc. of solution of ammonium sulphocyanate. Let the determination stand over night, decant the solution through asbestos in a Gooch crucible, and wash twice by decantation, leaving most of the precipitate of cuprous sulphocyanate in the beaker. Reserve the filtrate for treatment under *G.*

Place the Gooch crucible in the beaker with the greater part of the precipitate and dissolve the precipitate in a mixture of sulphuric and nitric acids. After the precipitate has dissolved, dilute the solution and filter the asbestos from it. Evaporate the solution to the evolution of sulphuric acid fumes. Dilute a little and neutralize with ammonia. Acidify with sulphuric acid, and precipitate the copper by electrolysis.

G. Boil down the filtrate from the cuprous sulphocyanate to one-third its volume, in order to remove sulphur dioxide; and pass through the hot solution a current of hydrogen sulphide to precipitate antimony, arsenic, lead, copper, and tin, if present. Filter, and reserve the filtrate for treatment under *I*.

H. Treat the precipitate obtained above (under *G*) on the filter with sodium sulphide solution to dissolve arsenic, antimony, and tin, and wash the filter. Treat the filtrate according to the methods of section *D*. Burn the filter and treat the residue according to section *C* for lead sulphate and copper oxide.

I. Carefully neutralize the filtrate from *G* with ammonia and pass through it a current of hydrogen sulphide to precipitate iron, nickel, cobalt, and possibly copper. Reject the filtrate. Treat the precipitate on the filter with dilute hydrochloric acid and wash the residue. Reserve the filtrate for the estimation of iron. Ignite the filter and residue. Treat the residue with aqua regia, evaporate the solution to dryness, dissolve the deposit in hydrochloric acid, and pass through the solution a current of hydrogen sulphide. Filter from the solution the copper sulphide, ignite it, and weigh as copper oxide. Carefully make the filtrate from the copper sulphide ammoniacal, pass through it a current of hydrogen sulphide, filter, ignite, and weigh as $NiO+CoO$. If the precipitate is large, the nickel and cobalt should be separated.

To the filtrate reserved for the determination of iron, add bromine water, and then make the solution alkaline with ammonia, boil to precipitate the ferric hydroxide; filter, ignite, and weigh as Fe_2O_3.

METHODS OF ANALYSIS IN THE PRODUCTION OF THE PRECIOUS METALS. FIRE ASSAYING

ASSAY OF GOLD AND SILVER ORES

Sampling. It is extremely difficult to take a satisfactory sample of a high grade gold ore, since such ores usually lack uniformity in composition For the quantity of ore required for the sample, and for the fineness of crushing before dividing, see Richards' table, page 11. The sample is finally crushed on a bucking-board to pass an 80-mesh or a 100-mesh screen.

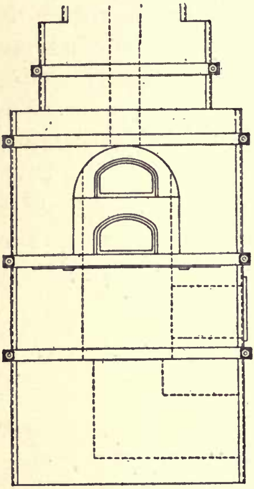

Fig. 81.—Two-muffle Assay Furnace Designed for the Use of Coal.

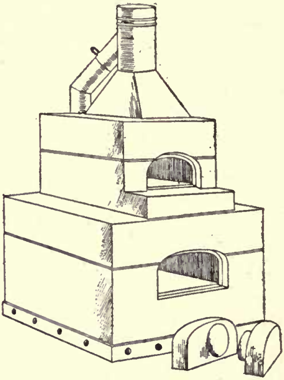

Fig. 82.—Assay Furnace for Liquid or Gaseous Fuel.

If any particles of free gold or silver in the ore (metallics) cannot be crushed to pass the screen, they are collected, weighed and assayed separately by scorification assay (see below). The values thus found are properly apportioned to the whole of the sample.

Methods of Assaying. In the fire assay for gold and silver, the ore is fused in a muffle (Figs. 81 and 82) by the aid of fluxes in the presence of lead, and the gold and silver are collected by the lead. The lead "button" is separated from the slag and cupeled.

By *cupellation*, the lead button containing the gold and silver is melted on a bone ash cup called a cupel (Fig. 83), the lead is oxidized to PbO, which is volatilized in part, and the remainder, and larger part, is absorbed by the bone ash, leaving the bead of gold and silver on the cupel. The bead is weighed and the silver dissolved from it with nitric acid, and the gold which remains is weighed.

The gold and silver may be absorbed by lead and separated from the gangue by either the crucible method, or the scorification method of assay.

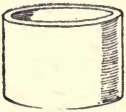

Fig. 83.—Cupel.

Fig. 84.—Crucible.

By the *crucible method*, the ore is mixed with flux, lead oxide, and a reducing agent, and melted in a fire-clay crucible. (Fig. 84.) The flux combines with the gangue to make a fusible slag, at the same time liberating the gold and silver. These metals are then absorbed by the metallic lead, which has been reduced from the lead oxide by the reducing agent. When the fusion is complete, the charge is poured from the crucible into a cast-iron conical mold (Fig. 85) and allowed to cool. The lead button, which settles to the bottom, is separated from the slag and is hammered into shape (usually a cube) for the cupel.

By a *scorification assay* the ore is mixed in a scorifier (Fig.

86) with granulated lead, a little borax glass added, and the charge is placed in a hot muffle and scorified; that is, the lead melts, the ore floats on its surface, is roasted and oxidized, the basic elements combining with the borax glass, and the acid elements with the lead oxide, which form a slag on the surface of the molten lead. When the slag thus formed increases until it completely covers the surface of the lead, the charge is poured into a mold, and the assay finished as in the crucible method.

In the scorification method of assay, only a very small quantity of ore can be used. It is, therefore, not a satisfactory method for low-grade ores. Neither is it satisfactory for basic ores, owing to the small amount of acid flux that can be used.

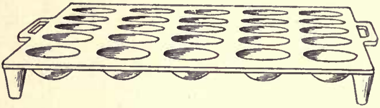

Fig. 85.—Cast Iron Mold for Receiving the Fusions.

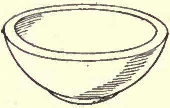

Fig. 86.—Scorifier.

It is, however, satisfactory for ordinary silver ores, and for rich gold ores and furnace products, though the losses are usually somewhat higher than in the crucible method.

The Assay-ton. Gold and silver ores are usually weighed in tons of 2000 lbs. avoirdupois, and the value of the ore is expressed in troy ounces per ton. In making the assay, gold and silver are weighed in milligrams. To avoid the necessity of changing milligrams into ounces per ton by calculation, Prof. Chandler devised the assay-ton. The assay-ton is that quantity of ore whose content of precious metal, weighed in milligrams, expresses the number of troy ounces of precious metal contained in a ton of ore of 2000 lbs. avoirdupois.

One ton avoirdupois contains 14,000,000 grains troy; and 1 oz. troy contains 480 grains. Therefore, there are 29,166 oz.

troy in 1 ton avoirdupois. If 1 ton contains 29,166 oz., 1 assay-ton must contain 29,166 mgm., or 29.166 gms., that is, 1 mgm. bears the same relation to 1 assay-ton that 1 oz. troy does to 1 ton of 2000 pounds avoirdupois. The troy ounce of gold is worth $20.67.

The Metric Ton. In those countries where the metric system has been adopted, ore is weighed in metric tons of 1000 kgms. each, and the assay-ton is not necessary. The sample taken is usually 10 gms. for the crucible assay, and every 0.01 mgm. of the metal found in the assay equals the number of grams per metric ton. A gram of gold is worth $0.66.

Reagents. *Reducing agents.* The reducing agent combines with the oxygen of the litharge (PbO), setting free metallic lead throughout all parts of the charge, the lead falling through the molten mass to the bottom of the crucible collects the gold and silver. Various carbonaceous substances are used as reducing agents. The principal ones are *charcoal*, *argols*, and *flour.*

$$2PbO+C=Pb_2+CO_2.$$

Reducing power. The power of a reducing agent must be known before it is used in a charge. To determine the reducing power, weigh 1 gm. of the reducing agent and mix it in a crucible with 60 gms. of sodium bicarbonate, 5 gms. of borax glass, and 30 gms. of litharge; cover with salt, fuse in a hot muffle, pour the fusion into a cast-iron mold, cool, separate the lead button from the slag, and weigh it.

In making up a charge for assay, put in enough reducing agent to produce a lead button that weighs about 18 gms.

Oxidizing agents. Oxidizing agents are added to the assay to take sulphur from the sulphides of the metals and to oxidize the base metals. In this form they are slagged by acid fluxes. The chief oxidizers are the *nitrates of potassium and sodium.*

$$4ZnS+6KNO_3=4ZnO+3K_2SO_4+SO_2+3N_2.$$

Desulphurizing agents. In addition to the *nitrates of the alkalies, iron, alkaline carbonates,* and *litharge* are reagents that reduce metallic sulphides.

$$PbS+Fe=FeS+Pb.$$
$$7PbS+4K_2CO_3=4Pb+3(K_2S\cdot PbS)+K_2SO_4+4CO_2.$$
$$K_2S\cdot PbS+Fe=Pb+K_2S\cdot FeS.$$
$$PbS+2PbO=3Pb+SO_2.$$

Fluxes. Fluxes are added to the charge to combine with the gangue and form an easily fusible liquid slag, through which the metallic particles can readily settle. If the gangue is basic, the flux should be acid; and if the gangue is acid, the flux should be basic. The principal basic fluxes are:

	Melting-point.
Litharge (PbO)	906° C.
Sodium carbonate (Na_2CO_3)	814° C.
Sodium bicarbonate ($NaHCO_3$) loses CO_2 and melts at	270° C.
Potassium carbonate (K_2CO_3)	885° C.

$$PbO+SiO_2=PbSiO_3,$$
$$Na_2CO_3+SiO_2=Na_2SiO_3+CO_2.$$

The principal acid fluxes are:

	Melting-point.
Silica (SiO_2)	1775° C.
Borax glass ($Na_2B_4O_7$)	560° C.

$$SiO_2+CaCO_3=CaSiO_3+CO_2.$$

The cover. After the charge is mixed in the crucible, it is covered with a reagent of low melting-point to catch any particles that would otherwise be thrown out by the escape of gases and to protect the charge from the air. The agent often used for this purpose is *salt* (NaCl), which is neutral; but sometimes, however, an acid cover, borax, is used; and sometimes, especially in the assay of telluride ores, *litharge* is used.

Metals as reagents. In addition to the reagents given above, pure granulated *lead* is used in scorification, pure *silver* for inquartation, and pure *sheet lead* in connection with silver for inquarting on a cupel.

Purity of reagents. Litharge and lead usually contain small amounts of silver. Tests must be run to determine the amount of silver the reagents contain, and the proper correction made for each assay. It is also necessary to test all the reagents used for gold and silver. This is done by making up a crucible charge, with the same quantities of reagents that are used in the assay of an ore, but with the ore left out, and putting it through the regular process, as given below for ores.

GOLD AND SILVER IN ORE

The nature of the charge that is mixed with the ore will depend upon the character of the ore. If the gangue is silicious, and does not contain reducing agents, such as sulphides and arsenides, the charge taken may be as follows.

Sodium bicarbonate	60 gm.
Borax	5 gm.
Litharge	30 gm.
Ore	1 assay-ton
Charcoal	1 gm.

(if another reducing agent is used, the quantity taken should be sufficient to produce a lead button weighing about 18 gms.).

Place the ore on the charge in a crucible, mix in the crucible with a spatula, and cover the mixture to the depth of half an inch with salt. Place the charged crucible in a hot muffle, using the crucible tongs (Fig. 87) and fuse for about thirty minutes.

When fusion is complete, withdraw the crucible with the tongs (asbestos gloves should be worn to protect the hands), shake the crucible by giving it a rotary motion in a horizontal plane, and tap it gently to settle the lead in one mass. Pour the fusion into a mold and let it freeze. Separate the slag from the lead button and hammer the lead into a convenient form (usually a cube) for cupellation.

Cupellation. Heat the cupel in a muffle, and with the cupel tongs (Fig. 88) place the lead button on the hot cupel. Close the muffle until the lead melts. Then reduce the heat and open the muffle so that the fumes of lead oxide are slowly carried from the cupel. Cupellation should be carried on at a moderately low temperature to prevent loss of the precious metals by volatilization. The temperature should be low enough to permit the formation of lead oxide crystals, "feathers," on the cupel. When the lead is all oxidized, and only the gold and silver bead remains, it suddenly glows, or "blicks." After the blick the cupel is withdrawn from the furnace.

Fig. 87.—Crucible Tongs.

Fig. 88.—Types of Cupel Tongs.

If the bead is large, it should be cooled gradually to prevent "sprouting." This may be accomplished by covering the cupel before withdrawing it from the furnace with an empty hot cupel or scorifier.

Weighing and Parting. When the metallic bead is cold, take it from the cupel with a pair of strong, pointed pliers, and carefully brush it with a stiff brush to remove adhering litharge or bone ash. Then flatten the bead with a small hammer to break off any adhering particles of bone ash, and weigh it as Ag+Au. Transfer the weighed bead to a porcelain crucible

(Fig. 89) and add about 2 cc. of water from a wash bottle. Drop in nitric acid slowly, until the bead turns dark and begins to dissolve. Stop the addition of acid and warm gently. When the action ceases, add more nitric acid, and heat the solution to boiling. Fill the crucible with water from a wash bottle and carefully empty it by pouring the solution down a glass rod, leaving the gold behind. The crucible is then filled with water and emptied in the same way a second and a third time to free the gold from all traces of silver nitrate. After the final decantation, carefully remove the last drop of water from the crucible with blotting paper or filter paper and carefully dry the crucible over a Bunsen burner, and then heat it until the black particle of gold is annealed and turns yellow. The gold is then transferred to the gold balance and weighed. The difference between the weight of gold and the combined weight of gold and silver represents the weight of silver.


Fig. 89.—Porcelain Annealing Cup.

In parting by the above method the gold is sometimes left in a powdered condition, especially if the ratio of silver to gold is high. In this condition there is danger of loss in washing the gold to free it from silver nitrate.

A more convenient method of parting, especially if many assays are to be made at the same time, and one which leaves the gold in a more coherent mass, consists in placing the metallic bead in hot dilute nitric acid (1 : 9) at once and boiling it at least fifteen minutes. Place 20 cc. of the dilute acid in each of the test-tubes (Fig. 90); heat in the bath until the acid boils; then add the metallic beads and continue boiling fifteen minutes. Fill each test-tube with distilled water; turn an annealing cup (Fig. 91) over the top of each test-tube. Invert the test-tube and let the particle of gold fall into the annealing cup. Fill up the annealing cup with distilled water from a wash bottle. Carefully raise the inverted test-tube to the top of the annealing cup, letting the cup fill with the solution, then quickly draw the test-tube to one side so that the remaining solution in the tube will flow into a receptacle below and leave the particle of gold undisturbed in the annealing cup. Give the gold three successive washings with warm distilled water. Take the last drop of water out of the cup with clean blotting paper, anneal the gold and weigh it.

Inquartation. If the gold-silver bead has a higher ratio of gold to silver than 1 to 4, the silver is not readily dissolved from it with nitric acid. Therefore, when there is not four times as much silver as gold present, or, in other words, if the total quantity of silver present is less than four times the amount of gold, a sufficient amount of silver should be added to the assay to produce this ratio. If silver is to be determined in the ore, as well as gold, the additional silver for inquartation must not be introduced until after the gold-silver bead has been weighed. The bead is then wrapped in a small piece of pure lead foil, together with the necessary weight of pure silver for inquartation, returned to the muffle, and cupeled.* The bead is then parted and the gold weighed. If the assay is for gold alone, and it is known that there is not a sufficient amount of silver in the ore to yield a button that will part readily, the necessary silver

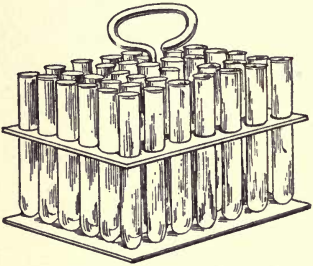

FIG. 90.—Test Tubes for Parting Ready for the Bath.

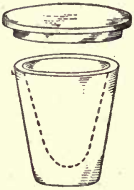

FIG. 91.—Clay Annealing Cup.

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* The silver may be alloyed with the bead on charcoal before the blow-pipe.

for inquartation may be added, either to the crucible, or to the cupel, since the gold in that case is not weighed until after parting.

ASSAY OF SULPHIDE ORE

Sulphide ores after they are weighed for the assay may be roasted in a roasting dish in a muffle, mixed with a charge similar to that given in the preceding method, and assayed in the same way. Roasting, however, may be avoided by making up a crucible charge, in which is included a desulphurizing agent. The following charge may be used.

	Gms.
Sodium carbonate	60
Litharge	30
Borax	8
Silica	2

Place the flux in the crucible, add 1 assay-ton of ore, and mix thoroughly with a spatula. Add three twenty-penny iron nails. Put the nails in, points downward, and press them well into the charge. Add a half-inch cover of salt and fuse.

For ores high in sulphur, reduce the sodium bicarbonate to 50 gms. and increase the borax to 20 gms. and the silica to 10 gms. For low sulphur ores, reduce the borax to 5 gms., leave out the silica and iron nails, and add 2 gms. of argols.

After fusing about twenty minutes, it is advisable to inspect the nails to see if there is danger of their breaking, through corrosion, at the surface of the slag. If they are much corroded, they should be removed, and fresh nails added, since the fusion cannot be poured satisfactorily if it includes fragments of nails. When the fusion is complete, withdraw the crucible from the muffle, and with short tongs, take out the nail, shaking from them into the crucible any globules of adhering lead. Shake the crucible and settle the lead to the bottom. Pour the charge into a mold.

When cold, separate the lead from the slag and hammer the lead into the usual form for cupellation. If the lead is soft complete the assay according to the method given above for silicious ores.

If the lead is brittle, place it in a scorifier, add granulated lead, and a pinch of borax glass and scorify. When the scorification is complete, pour the contents of the scorifier into a mold and complete the assay in the usual way.

Ores high in copper, arsenic or antimony should he done by the nitre method. The charge for one assay-ton would consist of 120 gms. litharge, 35 gms. sodium carbonate, 10 gms. silica, and from 10 to 20 gms. of nitre; the quantity of nitre depending upon the reducing power of the ore.*

ASSAY OF TELLURIDE ORE

Charge:

	Gms.
Sodium carbonate	25
Potassium carbonate	25
Litharge	50
Borax glass	14
Flour	$2\frac{1}{2}$ or more.
(See Reducing Power, p. 227.)	
Ore	0.5 assay-ton

The ore is placed on top of the charge and then thoroughly mixed with the spatula. Cover with 40 gms. of litharge. Place the crucible in a moderately hot muffle and complete the fusion at about 1000° C. Pour the charge into a mold and complete the assay according to the method for silicious ores.

SILVER IN ORE

Scorification Method

Weigh 0.1 assay-ton and mix it in a scorifier with 20 gms. of granulated lead. Cover with 20 gms. of granulated lead;

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* C. H. Fulton, "Fire Assaying," pp. 61 and 115.

sprinkle about 1 gm. of borax glass over the surface, and with the scorifier tongs (Fig. 92) place in a hot muffle, and scorify. Keep the door of the muffle closed until the lead is thoroughly melted, then open the door of the muffle to admit air for the oxidation of the lead, as well as of sulphur, arsenic, antimony, etc. When the slag completely covers the lead, the scorification is complete. The assay is then poured into a mold, and when cold, the lead is separated from the slag. If the lead is soft, it is hammered into a cube, and cupeled. If it is hard and brittle, it is rescorified with a sufficient amount of granulated lead added to make a total of 60 gms. A second scorification should slag off the impurities sufficiently to give a soft lead button, which is cupeled, and the resulting silver bead cleaned and weighed in the usual manner.

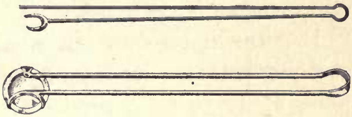

FIG. 92.—Types of Scorifier Tongs.

ASSAY OF BULLION

Sampling. The bullion is melted and cast into bars. Chips are taken from diagonally opposite corners of the bars, the chips rolled into fillets, and each fillet assayed separately.

Base bullion is best sampled while it is molten. The sample is dipped from the molten bullion with a graphite ladle and poured slowly into warm water. The granules are collected and assayed.

SILVER IN BULLION

FIRE METHOD

Silver in bullion is determined by cupeling a weighed sample of the bullion with pure lead, weighing the gold-silver bead, parting, and weighing the gold. The difference between the two weights represents the weight of silver.

When bullion is thus cupeled, considerable quantities of the precious metals are lost, the extent of the loss depending upon the amount and kind of base metals present and the temperature at which the bullion is cupeled. To make an accurate assay of bullion, it is, therefore, necessary to run at the same time a check assay in which the losses are determined, from which the bullion assay is corrected.

It is necessary to make a preliminary assay of the bullion, to determine its approximate composition. The alloy for the check assay is then made to agree with the approximate composition of the bullion. The quantities of the precious metals added must, of course, be accurately determined. The loss in cupellation is then determined by weighing the precious metals after cupellation.

The Preliminary Assay. Weigh 0.5 gm. of bullion, wrap it in 5 gms. of pure lead foil and cupel carefully, at a temperature low enough for the formation of " feathers " on the cupel. Clean, hammer, and weigh the bead. Part and weigh the gold.

The check assay is now made up to correspond in composition with the bullion, except that about 5 mgms. more of silver are put in the check than were found in the bullion, because that amount of silver is usually lost under these conditions from such an assay in cupellation.

Suppose the weight of the silver determined by preliminary assay on 500 mgms., of the bullion is 478 mgms., and the gold 2 mgms.; there is a loss then of 20 mgms. (500 − 480).

Experience indicates that of this loss about 5 mgms. are silver and the remaining 15, probably copper (indicated by the color of the cupel). The check is then made by weighing very accurately 483 mgms. of silver, 15 mgms. of pure sheet copper, and 2 mgms. of gold, or the gold bead obtained in the preliminary assay. These metals are wrapped as closely as possible in pure lead foil and cupeled in the muffle with the bullion.

The weight of lead foil required depends upon the amount of copper in the bullion. If there is less than 50 mgms. of copper in 500 mgms. of the bullion, add 5 gms. of lead foil. If the bullion contains more than 50 mgms. of copper increase the amount of lead as the copper increases; about 5 gms. of lead for each 50 mgms. of copper. It is better, however, not to add more than 20 gms. of lead at once. If the copper is not all removed at one cupellation, add fresh lead and cupel again.

Ag in Bullion. After making the preliminary assay, weigh two portions of the bullion, of 500 mgms. each, and make up a check assay in the manner described above; wrap each of the three assays closely in that weight of lead foil required for the copper in the bullion as determined in the preliminary assay. Place them in three hot cupels, arranged in a line across the muffle, the check assay being placed between the duplicates of the bullion. Close the muffle until the charges are melted; then open the muffle and cupel at a sufficiently low temperature to form feathers. When the beads "blick," cover them with hot cupels and cool slowly to prevent sprouting. If a bead sprouts, it must be discarded. Clean, hammer, and weigh the beads. The loss of silver in the check assay is supposed to be sustained in the same ratio by the bullion. This correction is added to each of the duplicate bullion assays and the results added.

SILVER IN BULLION

GAY-LUSSAC METHOD *

Standard Solutions. (1) *Solution of silver.* Dissolve 1 gm. of pure silver in 10 cc. of nitric acid and dilute the solution to 1 liter. One cubic centimeter of this solution will contain 0.001 gm. of silver. The solution should be kept in a green glass bottle which is covered with black paper.

(2) *Standard solution of sodium chloride.* Dry NaCl at 125° C. and weigh 5.4167 gms. Dissolve it in distilled water and

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* Frederick P. Dewey, Jour. Ind. and Eng. Chem., 5, 209.

dilute the solution to 1 liter. One cubic centimeter of this solution, if properly prepared, will precipitate 0.01 gm. of silver.

(3) *Decime salt solution.* Measure 10 cc. of solution No. 2 and dilute it to 100 cc. If correct, 1 cc. of this solution will precipitate 0.001 gm. of silver.

Care should be taken that the temperature of these solutions is the same when they are prepared.

The sodium chloride solution (No. 2), is standardized as follows. Weigh 1 gm. of pure silver, dissolve it in 10 cc. of nitric acid, dilute the solution to about 80 cc., add 100 cc. (measured with a pipette) of No. 2 solution, agitate violently, and let the silver chloride settle. Then add 1 cc. of the decime solution. If a precipitate appears, shake vigorously, let the precipitate settle and add another cubic centimeter. Shake and let the precipitate settle, and continue adding this solution, 1 cc. at a time, until no precipitate is produced. Then add 1 cc. of the silver solution (No. 1 above), and continue adding 1 cc. at a time until no precipitate forms. Suppose 100 cc. of the strong solution of sodium chloride are run in; then 7 cc. of the decime solution are added before a precipitate ceases to form. Now, if on adding the solution of silver, 1 cc. at a time, the first produces a precipitate and the second does not, 1 gm. of silver would be equivalent to 100.6 cc. of No. 2 solution.

The solution is corrected as follows: 100 cc. of the sodium chloride solution should contain 0.54167 gm. of salt; but it requires 100.6 cc. of the solution to contain that amount. Therefore, 100 cc. contains $\frac{0.54167\times 100}{100\ 6}=0.53844$; that is, 0.00323 gm. $(0.54167-0.53844)$ per 100 cc. should be added.

If the solution is too strong, it may be corrected according to the method in the following example. Suppose after adding 100 cc. of No. 2 solution and 1 cc. of the decime solution we titrate back with 8 cc. of the silver solution; then

99.4 cc. [100.1 − (0.8 − 0.1)] would contain 0.54167 gm. NaCl; and that is the amount of NaCl which should be contained in every 100 cc. Therefore, add 0.6 cc. (100 − 99.4) for every 99.4 cc. of solution left.

After correcting the solution No. 2, make another decime solution from it, test again and correct, if necessary, until it is exactly right.

Ag in Bullion. Make a preliminary test as follows: Weigh 0.5 gm. of bullion, dissolve it in dilute nitric acid, and titrate first with the standard sodium chloride solution, and finally with the decime solution. When the approximate fineness is determined, weigh that quantity of bullion which contains 1 gm. of silver, dissolve it in a 250-cc. flask in dilute nitric acid, and dilute with water to 80 cc. Add 100 cc. of the standard sodium chloride solution, shake vigorously, and let the precipitate settle Add decime sodium chloride solution, 1 cc. at a time, until no precipitate forms, shaking after each addition. Then add standard silver solution in the same way until a precipitate ceases to form.

Example. Suppose we weigh and dissolve 1.02 gms. of bullion and add 100 cc. of standard sodium chloride solution and 9.5 cc. of decime solution, and then titrate back with 3 cc. of standard silver solution, the third producing no precipitate.

The result is calculated as follows:

	Mgms. silver.
100 cc. standard salt solution are equivalent to..	1000
9.5 cc. decime salt solution are equivalent to..	9.5
	1009.5
Less 2 cc. standard silver solution.............	2
	1007.5

1.02 gms. of bullion then contain 1.0075 gms. of silver. One gram of the bullion contains $\left(\frac{1.0075}{1.02}\right).9878$ gm. of silver, and 1000 gms. of the bullion would contain 987.8 gms. of silver. The bullion is, therefore, 987.8 fine.

GOLD IN BULLION

Make a preliminary assay of the bullion to determine its approximate composition and make a check assay in a muffle similar to that described for preliminary assay of silver bullion (see p. 236). Weigh 0.5 gm. of the bullion and add enough pure silver to make the ratio of silver to gold 2 to 1; an experienced assayer can estimate this from the color of the bullion. Wrap the bullion and silver in about 8 gms. of pure lead foil and cupel, clean the button, and weigh. Part and weigh the gold.

Suppose, for example, that from 0.5 gm. of bullion we obtain 380 mgms. of gold and 15 mgms. of silver. Since experience indicates that 0.3 mgm.* of gold is lost in the cupellation of 500 mgms., 395.3 mgms. of the bullion are made up of gold and silver, leaving 104.7 mgms. for base metal—probably copper.

To make the check assay, weigh 380.3 mgms. of pure gold, 760.6 mgms. of silver (380.3 ×2), and 104.7 mgms. of pure copper. Wrap in 10 gms. of lead and cupel with the bullion.

Au in Bullion. Weigh 500 mgms. of the bullion in duplicate. Add enough silver to make the ratio of silver to gold 2 to 1, as determined by the preliminary assay. $[(380.3\times2)-15=745.6]$. Wrap in lead foil, the weight of lead taken depending upon the amount of base metal in the bullion. For the quantity required, see assay of silver bullion (p. 236) Place the duplicate assay with the check in hot cupels in the muffle and cupel according to the method described for the fire assay of silver.

T. K. Rose † has found that the losses of gold are slightl

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* Rose, "Metallurgical of Gold," p. 448.

† Eng. and Min. Jour., 80, 492.

greater from the cupels next to the sides of the muffle than from those in the center, and recommends that the check assays be distributed throughout the muffle.

After cupeling, each button is cleaned, hammered, annealed, rolled into a thin sheet, and then coiled into a "cornet." The cornets are parted, annealed, and weighed, and the weight of the gold found in the bullion corrected from the loss or gain in weight of the gold in the check assay.

The results are reported as parts of gold in 1000 parts of the bullion. Bullion, for instance, which contains 984.6 parts gold in 1000 parts of the bullion is said to be 984.6 fine.

GOLD AND SILVER IN LEAD BULLION

Weigh four portions of the bullion, 0.5 assay-ton each, and mix each portion with 30 gms. of granulated lead in a scorifier. Add 1.5 gms. of borax glass and 0.5 gm. of silica and scorify. (See p. 234.)

Separate the slag from the button and save it. Cupel the lead button and assay the scorifier slag and the cupel in a crucible, using the following charge: 15 gms. of sodium carbonate, 45 gms. of borax glass, 80 gms. of litharge, and 2 gms. of argols. Mix and cover with a little litharge. Complete the assay in the usual way and correct the original assay accordingly.

If the bullion is free from copper, arsenic, antimony, zinc, sulphur, etc., it may be cupeled without scorification as follows: Weigh 0.5 assay-ton and wrap it in about 8 gms. of sheet lead and cupel. To correct the assay, the cupels are crushed and assayed by the crucible method, using the charge given above. The weights of the precious metals obtained in the correction assay are added to the weights obtained by the original assay.

GOLD AND SILVER IN CYANIDE SOLUTIONS

Measure 300 cc. of the solution and transfer it to a porcelain evaporating dish. Sprinkle 40 gms. of litharge over the surface of the solution. Evaporate the solution, without boiling, to dryness. When dry, scrape out the residue with a spatula and mix it in a fire-clay crucible with the following charge:

	Gms.
Sodium carbonate	30
Borax glass	10
Silica	20
Charcoal	1

If any of the residue sticks to the dish, wipe it out with a moistened piece of filter paper and add it to the charge in the crucible. Cover the charge with litharge, fuse it in a muffle, and complete the assay in the usual way (See p. 229.)

PREPARATION OF PURE SILVER

Dissolve pure silver foil in nitric acid. Filter, dilute the filtrate, and precipitate the silver with hydrochloric acid. Filter and wash the silver chloride with dilute hydrochloric acid. Transfer the silver chloride to a beaker, and add pure sheet aluminum and hydrochloric acid. When the silver has been precipitated as metallic silver, and the aluminum is all dissolved, wash by decantation, dry, and fuse the silver in a cupel. The melting-point of silver is 960° C.*

PREPARATION OF PURE GOLD

Dissolve the purest gold obtainable (cornets) in aqua regia. Dilute and let the solution stand several days to allow the silver chloride to settle. Siphon off the clear solution and evaporate

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* Day and Sosman, 1910.

it nearly to dryness. Dilute the solution largely with distilled water, add a little sodium bromide dissolved in water, and let the solution stand several days. Again siphon off the clear solution and precipitate the gold on aluminum by letting the solution drop slowly from a burette into a beaker containing pure aluminum foil. When the gold is precipitated, add hydrochloric acid to dissolve the aluminum. Decant, and wash the gold by decantation. Dry, and melt it into a bead in a cupel. The melting-point of gold is 1062° C.*

TESTING CYANIDE SOLUTIONS

FREE CYANIDE IN CYANIDE SOLUTIONS

Reagents. Standard solution of *silver nitrate.* Dissolve 13.04 gms. $AgNO_3$ in water and dilute the solution to 1 liter. One cubic centimeter of this solution is equivalent to 0.004 gm. CN or 0.01 gm. KCN.

Solution of *potassium iodide.* Dissolve 10 gms. KI in a liter of water.

FREE CYANIDE

Measure 10 cc. of the cyanide solution with a pipette (if the solution is weak, take 50 cc.), and transfer it to a beaker. Add about 8 cc. of potassium iodide solution as an indicator and titrate with standard silver nitrate solution until a yellow tinge is given to the solution by silver iodide.

$$AgNO_3 + KCN = AgCN + KNO_3.$$

$$AgCN + KCN = KAg(CN)_2.$$

$$AgNO_3 + KI = AgI + KNO_3.$$

If 10 cc. of the cyanide solution are tested, every cubic centimeter of the standard silver nitrate solution used will repre-

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* Day and Sosman, 1910.

sent 0.04 per cent CN, or 0.1 per cent KCN, which is equivalent to 1 kilogram KCN per metric ton of 1000 kg. or 2 lbs. per ton avoir. If 50 cc. are titrated every cubic centimeter of the standard solution will represent 0.008 per cent CN or 0.02 per cent KCN.

When gold is dissolved in a solution of an alkaline cyanide, the double cyanide of the alkali and gold is formed. A given weight of cyanogen, then, whether combined with sodium or potassium, should always dissolve the same amount of gold, other conditions being the same, and, owing to the fact that sodium has a smaller atomic weight than potassium, a smaller quantity of sodium cyanide than of potassium cyanide will be required to dissolve a given weight of gold.

In the method above, it is the quantity of cyanogen only that is measured by titration, but its equivalent in potassium cyanide is usually reported. This is due to the fact that potassium cyanide was the only cyanide available when the cyanide process was developed. Now that sodium cyanide is much used for this purpose, it is not accurate to report as potassium cyanide the equivalent of the cyanogen found.

From the molecular weights KCN (65.11), NaCN (49.01), and CN (26.01), we find that the percentage of CN in pure KCN is 40, and in NaCN it is 53.

If 40 per cent of cyanogen is found in cyanide, it is not correct to assume that the material is pure KCN (100 per cent); for, if the cyanide were NaCN, it would only have to be 75.5 per cent pure to yield that amount of CN. The remainder might consist of any adulterant wholly free from cyanogen. It is to be regretted that the cyanide process is not conducted on the basis of the active cyanogen present, instead of its equivalent in potassium cyanide.

TOTAL CYANIDE

Total cyanide has been defined as "the equivalent, in terms of potassium cyanide, of all the cyanogen existing as simple cyanides and easily decomposable double cyanides, such as $K_2Zn(CN)_4$." * It might be termed *available cyanogen,* since it is the cyanogen existing as a simple cyanide after the addition of an excess of sodium hydroxide.

* Clennell, "The Cyanide Handbook," 440.

Reagents. *Standard silver nitrate solution.* (See p. 243.)

Alkaline indicator: Take 100 cc. of the potassium iodide solution (p. 243) and add to it 4 gms. NaOH.

Total Cyanide. Measure 50 cc. of the solution to be tested, add to it 10 cc. of the alkaline indicator solution, and titrate with the standard silver nitrate solution to a faint yellow turbidity.

$$Na_2Zn(CN)_4+2NaOH=4NaCN+Zn(OH)_2.$$

Also see reactions on page 243.

PROTECTIVE ALKALI IN MILL SOLUTIONS

Reagents. *Standard acid.* Nitric, hydrochloric, sulphuric, or oxalic, acid may be used, and it is convenient to make the solution equivalent to 0.001 gm. of the alkali per cubic centimeter.

If nitric acid is used, a solution containing 2.257 gms. HNO_3 (sp.gr. 1.42) per liter, will be equivalent per cubic centimeter to about 0.001 gm. of NaOH, or, a solution of the same strength is made if 1 cc. of nitric acid (sp.gr. 1.42) be added to 625 cc. of water.

$$NaOH+HNO_3=NaNO_3+H_2O.$$

Nitric acid (sp.gr. 1.42) contains 69.77 per cent of HNO_3 by weight.

If oxalic acid is used, 1.5753 gms. of crystallized $H_2C_2O_4+2H_2O$ per liter will give a solution of the same strength; that is, 1 cc. will be equivalent to 0.001 gm. NaOH.

$$2NaOH+H_2C_2O_4\cdot 2H_2O=Na_2C_2O_4+4H_2O.$$

Phenolphthalein solution: 1 gm. $C_{20}H_{14}O_4$ dissolved in 500 cc. alcohol (95 per cent C_2H_6O).

Silver nitrate solution. (See p. 243.)

Alkali. Measure with a pipette a convenient volume of the solution to be tested (50 cc.) and, if it contains no zinc, add to it a solution of silver nitrate until a slight permanent turbidity is produced.

$$2KCN + AgNO_3 = KNO_3 + KAg(CN)_2.$$

If the simple cyanides were not broken up, they, as well as the free alkali, would react with the standard acid in titration.

Add 3 drops of phenolphthalein solution and titrate with standard acid until the pink color disappears (See p. 84.)

PROTECTIVE ALKALI IN THE PRESENCE OF ZINC

Reagents. *Potassium ferrocyanide solution.* Dissolve 5 gms. $K_4Fe(CN)_6$ in 100 cc. of water. For other reagents see the preceding method.

Alkali. Measure with a pipette 50 cc. of the solution to be tested, add 10 cc. (an excess) of potassium ferrocyanide solution.

If the solution contains zinc as well as an alkali, when silver nitrate is added the hydroxide is precipitated, according to Clennell,* in the following way.

$$K_2Zn(CN)_4 + 2KOH + 2AgNO_3 = Zn(OH)_2 + 2KAg(CN)_2 + 2KNO_3.$$

The potassium ferrocyanide is added to liberate the alkali.

$$2Zn(OH)_2 + K_4Fe(CN)_6 = Zn_2Fe(CN)_6 + 4KOH.$$

Proceed according to the method above (p. 245) by adding silver nitrate to a slight turbidity and titrating with standard acid after the addition of phenolphthalein solution.

ACIDITY OF ORE

Reagents. *Standard acid.* (See p. 245.)

Standard alkali: a solution of sodium or calcium hydroxide equivalent to the standard acid.

Phenolphthalein solution. (See p. 245.)

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* "The Cyanide Hand Book," 439.

Weigh 200 gms. of ore, transfer it to a suitable bottle for agitation, add 400 cc. of the standard alkali solution and agitate one hour. Filter 100 cc. of this solution from the bottle, add to it two drops of phenolphthalein solution, and titrate with standard acid.

If the standard acid and alkali solutions are exactly equal in value, deduct the number of cubic centimeters of standard acid used in the titration from 100, and multiply the remainder by 4, since 400 cc. were used. The result, multiplied by 0.001, will give the acidity of 200 gms. of ore, or the weight in grams of the alkali required to neutralize the acid in 200 gms. of ore. This quantity multiplied by 5 will give the weight of the alkali in kilograms, required for a metric ton of the ore; or multiplied by 10, will give the number of pounds required for one ton avoirdupois.

CYANOGEN IN COMMERCIAL CYANIDE

Sampling. When a case of cyanide is opened, break off and select from many places small lumps of the cyanide to a weight of about 200 gms. Grind it quickly in a porcelain mortar, taking great care not to inhale the dust. It is well to grind it in a hood which is provided with a strong exhaust. Mix the powder and transfer a few grams for analysis to a well-stoppered bottle.

Reagent. *Standard silver nitrate solution.* (See p. 243.)

CN in Commercial Cyanide. Weigh from a weighing bottle about 0.5 gm. of the cyanide, transferring it directly from the weighing bottle to a quarter-liter Erlenmeyer flask. Add 100 cc. of water to dissolve the cyanide. Add 5 cc. of potassium iodide solution and titrate with standard silver nitrate solution.

The result may be reported in CN or in its equivalent of KCN or NaCN. (See free cyanide in mill solutions, p. 243.)

If the cyanide contains soluble sulphides, before titrating with silver nitrate solution, agitate the cyanide solution with a little alkaline solution of lead acetate and filter, to prevent the darkening of the solution while titration goes on.

WEIGHT OF ORE IN SLIME

The percentage of ore in mill pulp may be conveniently estimated at any time by weighing a flask or bottle filled with the pulp and calculating the percentage in the manner given below, by the use of the following data, previously determined, once for all:

Weight of the bottle empty.........$=b$
Weight of the bottle filled with water$=B$

Determine the specific gravity of the dry slime as follows:

Dry a quantity of the slime and weigh 200 gms. or any convenient quantity (S). Boil it in a small quantity of water to liberate entangled air, cool and wash it into the empty bottle. Add water to fill the bottle, and weigh. Let the weight equal C. The specific gravity (G) is calculated from the equation $G=\frac{S}{B+S-C}$.

Then to find the percentage of ore in pulp, fill the bottle with the pulp and weigh it. Let the weight$=S'$. Then $\frac{100(S'-B)G}{(G-1)(S'-b)}$ equals the percentage of ore in the pulp.

THE PLATINUM METALS

PLATINUM

Dewey's Method*

Weigh one assay-ton of the material (or 0.5 assay-ton if much platinum is present) and treat it according to the method for the assay of gold ore, page 229, until the metallic bead has been parted with nitric acid.

If only a small quantity of platinum is present, it will be dissolved with the silver. If there is much platinum present, some will remain with the gold; in this case, the residue is annealed, inquarted and parted again, and perhaps a third time to insure the complete separation of the platinum.

If the nitric acid solution containing the silver and platinum is strongly acid, dilute it. It may be evaporated to a small bulk before dilution if the volume is large.

Now add slowly to the diluted nitric acid solution containing the silver and platinum, while stirring, 15 cc. hydrogen sulphide solution, made by diluting 1 cc. of concentrated hydrogen sulphide water to 15 cc.

The hydrogen sulphide precipitates all the platinum, if the amount is small, and enough silver to produce a bead of suitable size.

If much platinum is present, it will be necessary to add 2 cc. of strong hydrogen sulphide water, diluted to 30 cc.

Stir occasionally and let the precipitate collect three to four hours or over night, if convenient. Filter and reserve the filtrate for a second precipitation of platinum if the quantity of the metal should be large. Dry the filter in a porcelain crucible and burn at a low heat. Wrap the metallic sponge in a thin sheet of lead foil and cupel. Part the bead in strong sulphuric

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* Trans. Amer. Inst. Min. Eng., 43, 578.

acid. If necessary, boil a second time in strong sulphuric acid, wash by decantation, anneal and weigh.

If there is doubt as to the identity of the metal, it may be dissolved in aqua regia and qualitative tests applied. See page 319.

PLATINUM [*]

Weigh 1 gm. of the sample and treat it in a 250 cc. Jena beaker with 10 cc. of nitric acid, 10 cc. of hydrochloric acid, and 5 cc. of water in a water-bath until action ceases; then boil on the hot plate with repeated additions of hydrochloric acid until all the nitric acid is expelled. Evaporate the solution to 40 cc., dilute to 100 cc. with water and filter. Evaporate the filtrate to 40 cc., add 25 cc. of ethyl alcohol and 25 cc. of saturated solution of ammonium chloride. Stir well, heat to boiling, and let the precipitate settle over night in a cool place. Filter $(NH_4)_2PtCl_6$ in a weighed Gooch crucible, wash with a 20 per cent solution of ammonium chloride, dry, ignite, and weigh as Pt.

If the material is low in platinum, begin with 8 or 10 determinations of 1 gm. each and combine them at the end to obtain a convenient quantity to weigh.

The precipitate of $(NH_4)_2PtCl_6$ should be ignited very carefully to prevent loss of Pt mechanically by the sudden expulsion of gas.[†]

PALLADIUM [‡]

Weigh 0.5 gm. of the material and transfer it to a 250-cc. Jena beaker. Add 10 cc. of nitric acid, 5 cc. of hydrochloric acid, and 5 cc. of water and heat on the water-bath until the action ceases. Boil on the hot plate, dilute to 100 cc. with water, and filter.

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[*] Greenwood, Eng. and Min. Jour., 96, 1175.

[†] Smoot, Eng. and Mining Jour., 96, 1175.

[‡] Greenwood, Eng. and Min. Jour., 76, 1175.

The residue may contain palladium oxides; it should, therefore, be boiled with 3 cc. of formic acid (CH_2O_2) and 5 cc. of water to reduce the oxides to metallic palladium, which is then dissolved by the treatment above.

Evaporate the filtrate with repeated additions of nitric acid to expel all hydrochloric acid, dilute the solution to 100 cc. and add 25 cc. of a 10 per cent solution of mercuric cyanide, $Hg(CN)_2$. Boil a few minutes and let it stand over night.

$$Pd(NO_3)_2+Hg(CN)_2=Pd(CN)_2+Hg(NO_3)_2.$$

Filter and wash with a 1 per cent solution of mercuric cyanide. Burn in a porcelain or silica crucible.

$$Pd(CN)_2+O_2=PdO_2+2CN.$$

Boil the residue with 50 cc. of a 20 per cent solution of formic acid, filter in a weighed Gooch crucible and weigh as Pd.

$$PdO_2+2CH_2O_2=Pd+2H_2O+2CO_2.$$

If the material is low in Pd, begin the determination with several portions of 0.5 gm. each and combine them at the end to obtain a weighable quantity of Pd.

THE PLATINUM METALS

Method of Deville and Stas *

Fuse 5 gms. of the alloy with 50 gms. of lead in a crucible of purified retort carbon. Hold at a temperature of at least 1000° C. for four or five hours. Boil the resulting alloy with very dilute nitric acid, filter and wash. Retain the filtrate (see below). Boil the black residue with very dilute aqua regia; nitric acid (1) : hydrochloric acid (4) : water (45). Filter and add the filtrate to the nitric acid solution above.

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* Menschutkin, "Anal. Chem.," 164.

Fuse the residue of lustrous flakes which contains all the iridium and ruthenium with 3 gms. of potassium nitrate and 10 gms. potassium carbonate. Cool and extract the fusion with water. Transfer the solution and residue to a tall cylinder and let the residue settle. Decant the clear solution and wash the residue with a dilute solution of sodium carbonate and sodium hypochlorite until the wash is no longer yellow. Pour these solutions into a retort, pass chlorine gas into the solution to saturate it, and distill into a flask containing water, hydrohloric acid and alcohol (purified by distillation over potassium oxide).

Perruthenic acid passes over into the flask and is converted to ruthenium chloride. Evaporate the distillate to dryness and reduce to metallic ruthenium in hydrogen. The residue in the retort and that on the filter contain all the iridium. Boil them in sodium hydroxide and alcohol; the iridium oxide obtained is purified, reduced in hydrogen, and weighed as iridium.

Analysis of Nitric Acid and Aqua Regia Solutions. Add to these solutions combined (which contain all the Pb, Cu, Pd, Rh, Os) just enough H_2SO_4 from a burette to precipitate the lead. Evaporate the solution to dryness. Treat the residue with hydrochloric acid. Filter off the lead sulphate. To the filtrate add ammonium chloride, filter, dry the precipitate at a low temperature and reduce to metals with hydrogen. Fuse the spongy metals with acid potassium sulphate. Platinum is not dissolved. Dissolve the fusion with cold water and filter off the platinum and weigh it. To the filtrate add mercuric cyanide to precipitate $Pd(Cn)_2$. Filter, and complete the determination for palladium according to the method on p. 250.

Add formic acid to the filtrate to precipitate Rh, filter, and weigh as Rh.*

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* Mylius and Forster, Berichte der deutschen chem. Gesellschaft, 25, 665.

ANALYSIS OF FLUXES

Limestone. For the analysis of limestone see page 160.

Silica. Materials high in silica and silicates generally may be analyzed by following the method for clay, page 286. For the determination of silica in such materials a sample of 0.5 gm. should be taken.

Iron Oxide. Fluxes high in ferric oxide are analyzed by the methods used for iron-ore, page 50, et seq. The quantity of Fe multiplied by the factor 1.4298 will give the weight of Fe_2O_3.

For methods for other materials see the Index.

ANALYSIS OF FUELS

COAL

Sampling.[*] The sampling of coal, if the determinations of ash are to agree within 1 per cent, requires greater care than is usually exercised in the sampling of iron ore; that is, the total original sample should be larger and it should be made up of a greater number of individual samples.

Iron ores are usually not sampled with so much care as is demanded of the lowest grade material referred to in the table on page 11, but by numerous tests it has been shown that analyses of coal are practically worthless if the coal has not been sampled at least as carefully as is required for " low-grade or uniform ore." Therefore, the figures in column 2, page 11, should be the guide in taking the original sample and in crushing for its reduction. The method for the crushing, dividing, and final grinding of iron ore, page 48, should be used for the preparation of the sample of coal. For the fine grinding of coal, it should first be air-dried and care should be taken that the grinder does not become heated,

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[*] Bailey, Jour. Ind. and Eng. Chem., 1, 176 (1909). J. A. Holmes, U. S. Bureau of Mines, Technical Paper 1, 1911.

since oxidation of some of the constituents of the coal begin at a comparatively low temperature. A ball mill of porcelain is recommended for the fine grinding (see Fig. 14 p. 14). After the coal passes a 12-mesh screen, it is put in the jar with inch quartz pebbles, or porcelain balls, and the jar is rotated until the coal will pass a 60-mesh sieve.

PROXIMATE ANALYSIS OF COAL

In the valuation of coal for technical purposes it is much more desirable to know how much of the coal is ash, fixed carbon, and volatile matter than to know the percentage of the several component chemical elements. By the proximate analysis, the moisture, volatile matter, fixed carbon, and ash are determined. It also usually includes the determination of sulphur.*

Moisture. Weigh 1 gm. of the finely powdered coal and transfer it to a porcelain crucible (18 mm.×40 mm.). Place it in an air-bath and heat one hour at 105° C. in a current of dry air. Remove the crucible from the air-bath, cover it, place it in a desiccator over sulphuric acid and, when it is cool, weigh it. The loss in weight multiplied by 100 gives the percentage of moisture.

Volatile Matter.

The quantity of volatile matter that a coal yields depends upon the degree of heat and the length of time it is applied, the size of the crucible in which it is heated, etc.; therefore, in order that results may have a comparative value, it is necessary, always, to carry out the operation, as nearly as possible, under the same conditions.

A committee appointed by the American Chemical Society to standardize coal analysis recommended the following method:

Weigh 1 gm. of the fresh, powdered, undried sample and place it in a 20-gm. or 30-gm. platinum crucible which has a tightly fitting cover. Heat over the full flame of the Bunsen

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* U. S. Bureau of Mines, Technical Paper 8.

burner seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be 20 cms. high, when burning free, and should be protected from draughts. The carbon which collects on the outside of the cover should be burnt off, but not that which is deposited on the inside. Cool and weigh. From the loss in weight subtract the *moisture* previously determined to obtain *volatile combustible matter*.

In 1913 the Committee recommended the following methods: **Volatile Matter.** 1. Weigh 1 gm. of coal and place it in a 10-gm. crucible with a capsule cover, that is, one that fits inside the crucible, and not on top. Place the crucible on a platinum or nichrome wire tripod in a muffle maintained at a heat of approximately 950° C. and leave it there seven minutes. When the flame from the volatile combustible matter disappears, gently tap the cover to seal the crucible and exclude the air. At the expiration of seven minutes withdraw the crucible, cool in a desiccator, and weigh.

2. Weigh 1 gm. of coal and place it in a 20-gm. crucible with capsule cover. Place the crucible in the flame of a No. 4 Meker burner, which gives a flame 15 cms. high. The bottom of the crucible should be 1 cm. above the top of the burner and the temperature inside the crucible should be from 900° to 950° C. When the flame from the volatile combustible matter disappears, tap the cover gently to exclude the air. At the expiration of seven minutes, place the crucible in a desiccator to cool. When cool, weigh. From the loss in weight deduct the moisture previously determined.

Coke. If the residue in the crucible is a firm coherent mass, the coal is a coking coal and the wieght of the mass may be used to calculate the percentage of coke the coal will produce.

Ash. If coal is free from the carbonates of calcium, magnesium, etc., the ash may be determined by burning off, with the crucible uncovered, all the carbonaceous matter from the sample in which moisture was determined, or from a fresh sample, and weighing the residue. The burning should begin over a very low flame. The carbon is more easily burned from this sample than from the compact mass of coke.

If the sample contains carbonates, some of the CO_2 will be driven off when the carbon is burned; the residue will, therefore, not truly represent the ash. It is necessary in such a case to determine the CO_2 in a separate sample, by taking a 5-gm. sample of the coal and treating it according to the method on on page 166 for the determination of CO_2 in limestone. From the weight of CO_2 calculate its equivalent in C. The factor is 0.2727.

When the carbon has been burned from a 1-gm. sample. the ash is moistened with a few drops of dilute H_2SO_4 (1 : 1) and carefully heated to a temperature of 750° C. and held at that temperature five minutes. It is then cooled in a desiccator and weighed. Multiply the equivalent of the CO_2 in C by 3 and subtract this from the weight of the ash to convert the weight of sulphate to its equivalent weight of carbonate, since that is the form in which it exists in the coal.

Fixed Carbon. The weight of ash subtracted from the weight of coke will give the fixed carbon; or the sum of the moisture, volatile matter, and ash deducted from the original weight of the sample (1 gm.) will give the fixed carbon.

SULPHUR IN COAL

The proximate analysis of coal usually includes the determination of sulphur. The method of Eschka, as modified by the Committee of the American Chemical Society on Coal Analysis, is an excellent one.*

Reagents. *Eschka mixture.* Two parts of light dry mag-

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* G. L. Heath, Jour. Amer. Chem. Soc., 20, 630; 21, 1127. A. H. White, "Gas and Fuel Analysis," 205.

nesium oxide (MgO) and 1 part dry sodium carbonate (Na_2CO_3) thoroughly mixed by passing them at the same time through a 40-mesh screen.

Bromine water. Water saturated with Br.

Barium chloride solution. A 10 per cent solution of $BaCl_2$ in water.

S in Coal. Weigh 1.3737 gms. and mix it on glazed paper with 6 gms. of the Eschka mixture.

As the sulphur in the coal burns, it is absorbed by the sodium carbonate. Magnesium oxide renders the mixture porous, so that air is more freely admitted. It also prevents any tendency of the coal to cake.

Transfer the mixture to a 25 cc. porcelain crucible and add, as a cover, about 2 gms. of the Eschka mixture. Heat the crucible gently with an alcohol lamp, stirring occasionally with a platinum wire, for about thirty minutes, or until the black particles of carbon have disappeared.

The sulphur, being oxidized, replaces CO_2 in the Na_2CO_3 and forms the sulphate, and probably some sulphite, of sodium.

Instead of using an alcohol lamp, the burning out of the carbon may be accomplished in a gas muffle, if it is heated gradually, and if a blank is run in the muffle, at the same time, to determine the quantity of sulphur absorbed from the gas. It is desirable, in any case, to run a blank to determine the amount of sulphur in the reagents.

Cool the crucible and transfer the contents to a beaker, using hot water. Add about 200 cc. of hot water, and digest for thirty to forty minutes at the boiling-point or near it, stirring occasionally. Filter and wash the residue several times by decantation with hot water, and finally, transfer and wash the residue on the filter.

Parr * has found that all the sulphur is not extracted by treatment with water alone. After extraction with water he treats the residue with acid to recover the remaining sulphur.

* J. Ind. and Eng. Chem., 1, 690.

To the filtrate add 20 cc. of bromine water and enough concentrated hydrochloric acid to make the solution slightly acid.

Bromine oxidizes sodium sulphite to sulphate.
See sulphur in ore, page 73.

Heat the solution to boiling and add, drop by drop, while stirring, 10 cc. of hot barium chloride solution. Boil the solution gently fifteen minutes and let it stand, a little below the boiling-point, two hours or longer. Filter and wash, first with hot water acidulated with hydrochloric acid (1 : 1000), and then with hot water, until the washings are free from hydrochloric acid. Burn the filter in a platinum crucible, cool in a desiccator, and weigh. Make the correction indicated by the blank and multiply the result by 10.

RAPID METHOD FOR SULPHUR IN COAL BY THE TURBIDIMETER *

After the determination of the calorific power of the coal with the bomb calorimeter (see p. 262), wash out the bomb carefully with hot water. Titrate for acidity. Add 5 cc. of hydrochloric acid (1 : 2) and heat to boiling. Cool and precipitate the sulphur in the cold with a solution of barium chloride to which has been added a little oxalic acid.

The precipitate is very finely divided and does not settle readily.

Dilute to the mark in a graduated flask, mix, and take out an aliquot part of the turbid solution and compare it with a standard which has been prepared in the same way from a sample in which the sulphur is known. (See Colorimetry p. 42.) This method gives somewhat lower results than the Eschka method. The sulphur in the standard, therefore, should have been determined by the Eschka method and the standard burnt in the calorimeter in the usual way.

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* Parr, Jour. Amer. Chem. Sec., 26, 1139 (1904); Jour. Ind. and Chem. Eng., 1, 689 (1909).

ULTIMATE ANALYSIS OF COAL

HYDROGEN AND OXYGEN IN COAL AND COKE

Weigh about 0.25 gm. of the coal, place it in a combustion boat, and burn in a combustion furnace in a current of pure dry oxygen. Pass the products of combustion through, first, an absorption bulb containing H_2SO_4, which removes the water, and then through a similar bulb containing KOH solution, which absorbs the CO_2. The bulbs are weighed before and after combustion. From the weights of H_2O and CO_2 found the H and C are calculated.

NITROGEN IN COAL

The percentage of nitrogen in coal indicates the quantity of ammonia that may be recovered as a by-product in coke-making. Nitrogen is determined by the Kjeldahl method.*

N in Coal. Place 1 gm. of coal in a 500-cc. Kjeldahl flask with 30 cc. of dilute sulphuric acid (1 : 84) and 0.6 gm. of mercury and boil until the solution is nearly colorless (three hours). Add potassium permanganate crystals gradually until the solution becomes permanently green.

Cool, dilute the solution to about 200 cc. with cold water. Add 25 cc. of potassium sulphide solution (40 gms. K_2S per liter) to precipitate the mercury. Add 1 gm. of granulated zinc to prevent bumping and about 0.5 gm. of paraffine to prevent frothing. Add saturated solution of sodium hydroxide to distinct alkalinity (80 cc. to 100 cc.).

Connect the flask at once with the condenser and distil the ammonia into a measured quantity of standard sulphuric acid solution (1 cc. equivalent to 0.05 gm. N) to which has been added cochineal indicator. Continue the distillation until

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* Technical Paper 8, U. S. Bureau of Mines.

200 cc. have passed over, then titrate the excess acid with standard ammonia solution. The two solutions should be made so that 20 cc. NH_4OH solution = 10 cc. H_2SO_4 solution.

OXYGEN IN COAL

Oxygen is determined by difference. The sum of the percentages of carbon, hydrogen, nitrogen, sulphur, and ash are deducted from 100; the remainder is assumed to be oxygen.

PHOSPHORUS IN COAL

Weigh 6.52 gms. of the coal and transfer it to a platinum crucible. Place the crucible in a muffle and burn the carbon. Add to the ash about six times its weight of sodium carbonate and 0.2 gm. of sodium nitrate. Fuse with a blast lamp. Cool and dissolve the fusion in water and hydrochloric acid. Evaporate the solution to dryness. Dissolve the residue in dilute hydrochloric acid, filter, and determine the phosphorus in the filtrate according to one of the methods for phosphorus in ore (p. 75.)

CALORIFIC POWER OF COAL

The calorie is the quantity of heat required to raise 1 gm. of water 1° C. (between 0° and 100°). The calorific value, or power, of a coal is expressed by the number of calories that 1 gm. of the coal will yield when burnt in a calorimeter. A calorimeter of the usual type consists of a bomb of steel or alloy in which the coal is burnt, and its enclosing vessel of about 4 liters capacity which holds a definite weight of water, in which the bomb is submerged while a determination is being made. This vessel is usually made of copper, plated with nickel to diminish the loss of heat by radiation, and is provided with a stirrer and an accurate thermometer graduated to hundredths of a degree centigrade. The bomb in some calorimeters is held in place centrally in the inner of two concentric fiber pails to render the passage of heat between the water in the calorimeter and the atmosphere of the room slow and uniform.

The bomb is usually made of steel and is lined with enamel or nickel, or, for very accurate work, with gold or platinum. Parr * has made a bomb of an alloy of nickel, copper, tungsten, etc., which resists well the action of nitric and sulphuric acids and, therefore, needs no lining. It is provided with rubber gaskets, well protected from the heat, and is therefore more satisfactory to operate and to keep in working condition than are other types of bombs, which have metal valves and gaskets. (Figs. 93 and 94.)

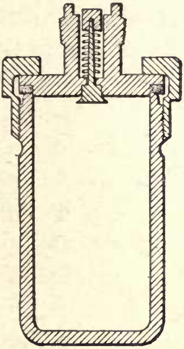

FIG. 93.—Bomb for Calorimeter.

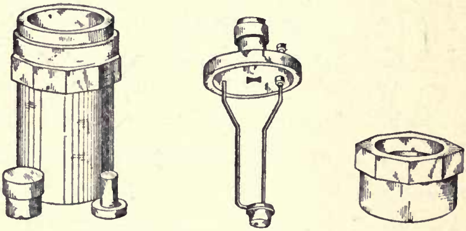

FIG. 94.—Calorimeter Bomb with Fittings.

The bomb is provided with a tightly fitting cover, held firmly in place on the gasket by a collar screwed down on the outside. Through a valve in the cover, oxygen is admitted for combustion. The capsule in which the coal is placed for combustion is supported, near the center of the bomb, on one of the electrodes, which, in turn, is attached to the cover. The other electrode pierces the cover and is insulated from it.

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* Jour. Ind. and Eng. Chem., 4, 746 (1912).

In the calorimeter vessel, a weighed quantity of water is placed (usually about 2000 cc.), in which the bomb is submerged for the combustion. Midway between the bomb and the side of the vessel, an accurate thermometer, which, with the aid of a cathetometer and telescope may be read to thousandths of a degree, is introduced through the cover of the calorimeter and fixed in place with the bulb of the thermometer opposite the center of the bomb. While a determination is being made, the water is thoroughly stirred at a uniform rate with a stirrer which projects through a hole in the cover. The air space between the inner and outer pails serves as an insulation from the heat of the room. For accurate work, this space is also filled with water, and, in that case, it also is provided with stirrer and thermometer.

Calorific Power of Coal. Weigh in a shallow platinum capsule about 1 gm. of coal, and place it in position on the electrode. Weigh a length of about 5 cms. of 36 B. & S. gauge iron wire and with it connect the two electrodes above the capsule, bending a loop of wire down to touch the coal, but not the capsule.

Powdered bituminous coal burns so violently that some of the dust may be thrown from the capsule before it is burnt. The powder should, therefore, be compressed into a pellet before weighing.

Place in the bomb a few drops of water to absorb the nitric acid which is produced by the combustion. Put the cover in place on the bomb, taking care not to disturb the position of the capsule. With the spanner, screw the ring down to hold the cover firmly in place, attach the oxygen tank with a flexible metal tube provided with a pressure gauge, open the valve of the bomb and then the valve of the oxygen cylinder, and let the oxygen flow in gently until the gauge indicates 20 to 25 atmospheres. Close the valve of the oxygen tank and then the valve of the bomb and disconnect the cylinder. Weigh in the calorimeter 2000 gms. of water, which should be about 2° or 3° C. above the room temperature. The quantity of water used may be such that when combined with the water value of the calorimeter the total will be equivalent to 3000 gms. of water.

If only an approximate determination is to be made, and no correction for loss of heat, the water in the calorimeter should be about 3° C. below the room temperature, but not low enough to precipitate moisture from the atmosphere on the outside of the calorimeter.

The gain and loss of heat due to the deposition and later evaporation of this moisture would interfere with the gradual and uniform change of temperature which is desirable within the calorimeter.

Place the bomb in the center of the calorimeter, attaching the electric wires for ignition. Put on the cover, and adjust the thermometer and the stirrer.

The thermometer must be made especially for this purpose and must be carefully calibrated. After recording the readings of the thermometer, the corrected readings from the certificate must be added.

Stir two minutes and then read the thermometer and record the reading. Continue the stirring at a uniform rate and read the thermometer each minute for five minutes. The thermometer should gradually fall, as the heat of the water passes out to the air of the room. On the minute that the fifth reading of the thermometer is taken, close the electric circuit to ignite the coal. The current from dry cells at about 12 volts ignites the coal promptly by heating the small iron wire. Continue stirring and read the thermometer every minute, for at least ten minutes after ignition. Note carefully the maximum temperature and the time of its occurrence.

After all the readings have been taken and recorded, remove the bomb from the calorimeter, open the valve to relieve the pressure, and take off the cover. Rinse out the bomb carefully with hot water and titrate the acid in the solution with a standard alkali solution.

If the sulphur in the coal has not been determined, after titrating the acid, which is a combination of nitric and sulphuric acids, make the solution acid with hydrochloric acid and determine the sulphur by precipitating it with barium chloride. (See p. 73.)

Weigh the lengths of unburnt wire to determine how much has been burnt.

To prevent rusting of the valve, the bomb should not stand wet too long, but should be carefully dried in an air-bath.

Corrections. The maximum reading of the thermometer cannot be taken as the correct figure by which to multiply the weight of water in the calorimeter and its water value, for there has been (1) a loss of heat from the calorimeter while the thermometer has been rising; on the other hand deductions must be made (2) for the sulphur, which in ordinary combustion is oxidized chiefly to SO_2, but in the bomb is oxidized almost entirely to SO_3; (3) for oxidation of some nitrogen to nitric acid, which would not take place in the ordinary burning of the fuel on a grate; and (4) for the burning of the iron ignition wire.

1. The correction for the loss of heat by radiation may be done graphically by the method of Holman * described by Howe.† Plot on cross-section paper, on a large scale, the corrected readings of the thermometer as ordinates, and the times of the readings as abscissas, and draw a line through these points, as shown in Fig. 95. The line *i-m-o-p-r* shows the maximum reading at *o*. Through *o* draw a line parallel to *pr* and project it to cut the ordinate through *m* at *n*. The number of degrees represented by the line *mn* is the corrected rise in temperature due to the combustion. Multiply the weight of water in the calorimeter added to the water value of the calorimeter by the rise in temperature represented by the line *mn*; the result will be the total number of calories produced by the combustion. From

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* "Physical Laboratory Notes," 46 (1887).

† "Metallurgical Laboratory Notes," 35 (1902).

this total must be deducted the heat of formation of the acids and of the magnetic oxide produced by the burning of the iron wire.

2. The correction for the higher oxidation of sulphur in the bomb cannot be made with absolute accuracy, for the quantity of heat produced depends not only upon the quantity of sulphur present, but upon the form in which it occurs and the completeness of oxidation. It is customary, however, to assume that all the sulphur in the coal is in the form of pyrite, and to deduct for each milligram of sulphur 2 calories.*

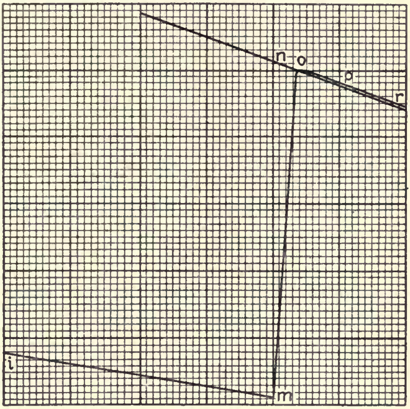

FIG. 95.—Graph for Correcting Total Rise in Temperature.

3. When the sulphur present has been calculated to sulphuric acid, deduct it from the total acidity; the remainder is nitric acid formed by the oxidation of nitrogen. The formation of 1 gm. of HNO_3 produces 238 calories. The correction is usually not more than 8 calories.†

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* A. H. White, "Gas and Fuel Analysis," 231 (1913).

† Ibid., 230.

4. When 1 gm. of iron is burnt to Fe_3O_4, it yields 1600 calories; therefore, 1.6 calories must be deducted for every milligram of fuse wire burnt.

Water Value of the Calorimeter. Burn in the calorimeter exactly in the manner described for coal, either 2 gms. of pure cane-sugar, $C_{12}H_{22}O_{11}$ (3945 calories per gm.), 1.5 gms. benzoic acid, $C_7H_6O_2$ (6321 calories per gm.), or 1 gm. camphor, $C_9H_{16}CO$ (9290 calories per gm.) and make the corrections which are made in the method for coal, except that for sulphuric acid, which is omitted. Deduct the number of calories thus determined from the calculated value, using the values given above. The difference represents the heat absorbed by the calorimeter. Divide this number by the total corrected rise in temperature (*mn.* Fig. 95, p. 22) and the quotient represents the equivalent in water of the calorimeter, or its water value.

Formula for Calorific Power. The method for calculating the calorific power may be indicated by the formula

$$C=\frac{r(W+w)-(.238N+2a+1.6F)}{S},$$

C = the calorific power of the material. (Calories produced by burning 1 gm.);
r = the corrected rise in temperature;
W = the weight of water in the calorimeter in grams;
w = the water value of the calorimeter;
N = mgm. of nitric acid;
a = mgm. of sulphuric acid;
F = mgm. of iron wire burnt;
S = weight of the sample of coal burnt.

If approximate determinations are to be made, and no corrections applied for loss or gain from the heat of the room, the error will be reduced by beginning the operation with the water in the calorimeter about 3° C. below the temperature of the room, for, since the rise of temperature due to combustion, under this condition, will bring the calorimeter to about room temperature, there will be only a slight tendency for gain or loss to the calorimeter.

Dickinson's Formula. For calculating the calorific power by Dickinson's formula, the water in the calorimeter should be about 3° C. below room temperature when the operation begins.

The thermometer is read every minute for five minutes, or until the rise in temperature is uniform; then, on the fifth minute, close the circuit to ignite the coal and note the time a and the temperature t. To the temperature t (corrected) add 60 per cent of the expected total rise in temperature and call it t_2.

The total rise of the thermometer for any calorimeter is nearly constant if the tests are always made on the same quantity of coal—60 per cent of the expected rise is therefore based upon previous determinations.

When the thermometer has risen to t_2, note the time b.

Continue reading the thermometer every minute for about ten minutes until the change of temperature has become uniform. Observe which of these readings is the first one in the period of uniform change and mark it c.

Now find the rate of rise in temperature r_1 for the preliminary period, that is, from the first reading up to a, and the rate of cooling per minute, r_2, during the final period, that is, from c to the end.

Open the bomb, wash it out, and determine the amount of acid formed and the weight of wire burnt as directed on page 263.

From the above data calculate the calorific power according to the formula given below.

r_1 = rate of rise in temperature (preliminary);
a = time of last reading preliminary period;
t = temperature at time a;
$t_2 = t + 60$ per cent of expected rise;

b = time when thermometer reads t_2;
c = time when change in temperature has become uniform after combustion;
t_3 = temperature at time c;
r_2 = rate of cooling in final period;
$[r_2(c-b)+t_3]-[r_1(b-a)+t]$ = total temperature rise T.

The intervals of time $c-b$ and $b-a$ are to be expressed in minutes and tenths of minutes.

T multiplied by the weight of water in the calorimeter plus its water value equals the total amount of heat liberated. This quantity corrected for the acid and Fe_3O_4 formed, and divided by the weight of coal taken, will give the calorific power.

CALORIFIC POWER OF COAL BY THE PARR CALORIMETER *

In the Parr calorimeter the coal is burnt, not by oxygen under compression, but by oxygen furnished by sodium peroxide and potassium chlorate, which are mixed with the coal.

The following reactions are believed to take place:

$$2Na_2O_2 + C = Na_2CO_3 + Na_2O.$$
$$Na_2O_2 + H_2 = 2NaOH.$$

Since there is no gas under compression, either before or after the combustion, a strong bomb is not required, but only a comparatively light "cartridge." The cartridge is placed in a cylindrical brass calorimeter vessel, which is insulated from the heat of the room by two concentric fiber pails. The temperature of the water in the calorimeter is taken with an accurate thermometer, graduated to hundredths of a degree, and the water is stirred by rotating the cartridge, to which are clamped

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* Jour. Amer. Chem. Soc., 22, 646; Jour. Ind. and Eng. Chem., 1, 673.

propeller-like wings. A belt from a motor drives the pulley attached to the stem of the cartridge, the cartridge turning on a pivot fixed in the bottom of the calorimeter vessel. (Fig. 96.)

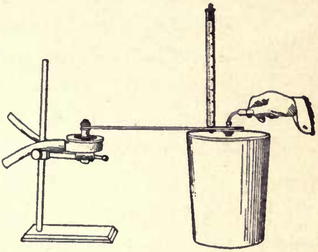

FIG. 96.—Parr Calorimeter.

Operation of the Calorimeter. Weigh 0.5 gm. of the coal which has been ground to pass a 100-mesh screen, and transfer it to the cartridge, in which has already been placed 1 gm. of finely ground $KClO_3$. Add about 10 gm. of Na_2O_2 (measured in a scoop furnished with the calorimeter). Close the cartridge with the false cover and shake to mix the coal and reagents thoroughly.

The Na_2O_2 must be fresh. It deteriorates rapidly on exposure to air and moisture.

The cartridge must be thoroughly dry before putting in the charge.

Attach a loop of 34 or 36 B. & S. gauge iron wire to the terminals so that it will be pressed down into the charge when the cap is put on. Screw the cap on, making sure there are no leaks, for a little water in the bomb would spoil the determination and might cause an explosion. Put in the calorimeter 2000 gms. of water at about 2° C. below room temperature.

Place the cartridge on its pivot, adjust the cover, thermometer, electric wires for firing, and the belt on the pulley. Start the cartridge rotating at about 100 revolutions per minute and read the thermometer every minute (see p. 263). After four or five minutes, when the rise in temperature has become uniform, close the circuit to ignite the charge, and continue reading the thermometer for about eight minutes after ignition, noting the maximum temperature reached. The rise in temperature may be corrected according to the method given on page 265. According to Professor Parr * the increase in temperature should be further corrected by " a factor made up of the following components ":

Each per cent of ash is multiplied by	0.00275° C.
Each per cent of sulphur is multiplied by	0.005° C.
Correction for heat reaction of 1 gm. $KClO_3$	0.130° C.
Heat of combustion of fuse wire	0.008° C.

The corrected rise in temperature T is multiplied by the water in the calorimeter (2000 gms.) added to its water value, which is for the Parr calorimeter 135. Professor Parr found, by careful tests, that the heat evolved in burning coal in oxygen is 73 per cent of that produced when the coal is burnt in Na_2O_2; therefore, the calorific power C may be calculated from the following equation:

$$C=\frac{T(2135)0.73}{W},$$

in which T represents the corrected rise in temperature and W the weight of the sample. When W equals 0.5 gm. the calorific power equals $T3117$.

CALORIFIC POWER FROM THE ULTIMATE ANALYSIS

The calorific power of coal may be calculated from its ultimate analysis by multiplying the percentage of each of its constituent combustible elements by its calorific power and taking the sum of the products. The following correction, however, must be made for hydrogen. It is assumed (Dulong's formula) that all the oxygen in coal exists in combination with hydrogen as water; therefore, a sufficient quantity of hydrogen to combine with all

* Jour Ind. and Eng. Chem., 1, 673.

the oxygen present as H_2O, is deducted from the total hydrogen before multiplying by its calorific power. Since the weight of the hydrogen in water is equal to one-eighth of the weight of the oxygen, deduct from the percentage of hydrogen one-eighth of the percentage of the oxygen in the coal; and then calculate the calorific power as follows:

Percentage $C \times 8100$(C to CO_2) = calories produced by carbon.
" $H - (\frac{1}{8}$ percentage of $O) \times 34,500$ (H to H_2O, liquid) = calories produced by hydrogen.
" $S \times 2164$(S to SO_2) = calories produced by sulphur.
Take the sum of these products for the total calories produced by 1 gm. of the coal.

This method usually gives lower results than those obtained with the calorimeter. The difference is not uniform, but the average for more than 50 determinations made by the U. S. Geological Survey is about 1 per cent.

To convert calories to British thermal units multiply by 1.8.

PETROLEUM

Sampling. If the oil can be sampled while it is flowing from a pipe, the samples should be taken at regular intervals with a small dipper and collected in a pail. If the oil is in tanks or barrels, lower a long tube, which is open at both ends, vertically into the oil until it touches the bottom of the container, close the lower end of the tube by pressing into it a stopper held on the end of wire which passes through the tube; or, if the tube is small, close tightly the upper end and withdraw it with the sample. Instead of a tube, a bottle attached to a rod or stick may be depressed well into the oil, the stopper withdrawn by a string, and the bottle allowed to fill.

FRACTIONAL DISTILLATION OF CRUDE PETROLEUM

In the examination of crude petroleum the oil is divided into various products by fractional distillation and the quantity, specific gravity, color, etc., of the several products determined.

The crude oil is placed in a still provided with a thermometer which has its bulb opposite the outlet of the still. The temperature is raised gradually and the distillate of light oil, naphtha, gasolene, etc., is collected, until the temperature reaches 150° C. This distillate is removed and another receiver is attached to collect the illuminating oil, which distils over while the heat is gradually increased from 150° to 300° C. After the illuminating oil, the lubricating oil is collected until there is only coke left in the still.

For the test, Gray * recommends the following method: Measure from 2 to 4 liters of the crude petroleum and distil it at the rate of 5 to 10 cc. per minute and collect the distillate in 1 per cent fractions. Take the fractions of more than 58° B. for the naphtha fraction, all those between 58° and 36° B. for burning oils, and those below 36° B. for lubricating distillate; the residue is coke.

Sulphur in Petroleum. Sulphur is best determined in petroleum by burning the oil in a calorimeter with oxygen under a pressure of 25 to 30 atmospheres, washing out the bomb, acidifying the washings with HCl, and precipitating the S as $BaSO_4$ with $BaCl_2$ solution.

Calorific Power of Liquid Fuels. Place a weighed quantity of the liquid in a narrow platinum crucible.†

If the liquid is burnt in a shallow capsule, combustion is not always complete.

Above the liquid, on a glass platform in the crucible, place a weighed quantity of powdered sugar (3945 calories per gm.).

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* "Industrial Chemistry," p. 522.

† Richards and Jesse: Jour. Amer. Chem. Soc., 32, 268.

Place the crucible in the bomb of a calorimeter with the fuse wire adjusted in the sugar and carry out the operation in the manner described for determining the calorific power of coal on page 262. Of course the number of calories produced by the burning of the sugar must be deducted from the total.

WATER IN OIL

Distil 200 gms. of the oil in a small still and collect the distillate until the temperature reaches 150° C. Collect the water from the distillate with a micropipette and weigh it. If any drops of water adhere to the inside of the condenser and do not run into the receiver, wet a small pellet of absorbent cotton,* squeeze it as dry as possible, weigh it, fasten it to a wire, and run it into the condenser to collect the drops, weigh it again and add the increase in weight to that of the water found in the receiver.

GAS ANALYSIS

Sampling. A tube of porcelain, fused quartz, or glass is inserted through an opening in the side of the flue or chamber containing the gas and the sample is withdrawn through it, usually by aspirator bottles. The sample should be taken across the whole section of the moving gas, the greater portion from the central, or more rapidly moving part of the column. This may be accomplished by closing the inward end of the tube and admitting the gas through perforations along the side so spaced that the gas will enter in the proper proportion at different points in the cross-section of the flue.

The same result may be accomplished by wiring together a number of small tubes of different lengths so that they terminate at different points in the flue. The end of the bundle of tubes which projects out of the flue is set with cement in an iron tube

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* U. S. Bureau of Mines, Technical Paper, 25, 10.

just large enough to receive it. The iron tube is connected by a reducer to a rubber tube through which the gas is delivered to the receiver.*

An iron sampling tube may be used for cool or moderately warm gases. The composition of gas is changed by contact with hot iron.

The water used in the aspirator bottles should be thoroughly shaken with a quantity of the gas to be sampled before the sample is taken, to saturate it completely with the several component gases; otherwise the composition of the sample would be changed by the varying degrees of solublity of the components.

The Gas Burette. Gas is measured for analysis in a burette, (Fig. 97) usually of 100 cc. capacity, provided with a stopcock and capillary, at the upper end. To dispense with the necessity of correcting the volume of gas for changes of temperature while the analysis is going on, due to changes in the temperature of the surrounding air, the burette is enclosed in a large glass tube which is filled with water and closed at each end with a rubber stopper, through which the burette projects. The water in the tube is allowed to attain the temperature of the room before the analyis begins.

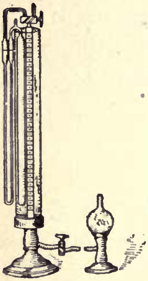

Fig. 97.—Gas Burette.

Gas Pipettes. A gas pipette is a bulb or tube, or a combination of these, in which gaseous mixtures are brought into contact with absorbents. Each pipette contains an absorbent for a single gas or group of similar gases and is provided with a capillary tubular outlet, through which the gas is passed to the burette for measurement. (Figs. 98 and 99.)

Explosion Pipette. For the determination of methane and hydrogen a measured quantity of the gas, which has had removed from it CO_2, heavy hydrocarbons, O_2, and CO, is mixed with

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* A. H. White, "Gas and Fuel Analysis," p. 10.

an excess of air and exploded over mercury in a pipette of heavy glass (Fig. 100), provided with stopcocks and fused-in electric terminals for the passage of an electric spark for the ignition of the mixture.

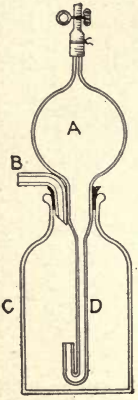

FIG. 98.—Gas Pipette (Richards).

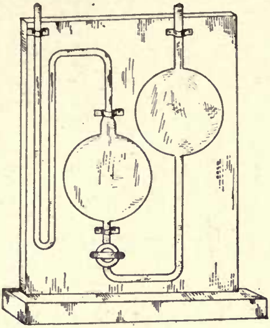

FIG. 99.—Gas Pipette (Hempel).

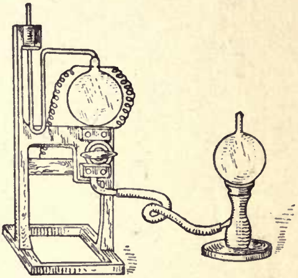

FIG. 100.—Explosion Pipette.

The Gases in Gaseous Mixtures. In technical gas analysis the following gases are separated and measured:

(1) Carbon dioxide, CO_2;

(2) Heavy hydrocarbons of the series

$$\left\{\begin{array}{ll} C_nH_{2n} & \left\{\begin{array}{l}\text{ethylene, } C_2H_4\\ \text{propylene, } C_3H_6 \\ \text{butylene, } C_4H_8\end{array}\right. \\ C_nH_{2n-2} & \text{acetylene, } C_2H_2 \\ C_nH_{2n-6} & \left\{\begin{array}{l}\text{benzine, } C_6H_6\\ \text{toluene, } C_7H_8{}^*\end{array}\right.\end{array}\right.$$

(3) Oxygen, O_2; (4) Carbon monoxide, CO; (5) Hydrogen, H_2; (6) Methane, CH_4; and (7) Nitrogen, N_2.

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[*] Winkler and Lunge, "Technical Gas Analysis," 66.

Absorbents. Absorbent for CO_2. Solution of potassium hydroxide. Dissolve 250 gms. of commercial potassium hydroxide (KOH) in 1 liter of water; 1 cc. contains 0.21 gm. KOH and absorbs 0.083 gm., or 42 cc. of CO_2. Absorption should be complete within two or three minutes. This solution also absorbs acid fumes if they are present.

Absorbent for Heavy Hydrocarbons. Fuming sulphuric acid, sp.gr. 1.938, which contains 24 per cent free SO_3. Shake the acid in the pipette with the gas for five minutes.

Absorbent for Oxygen. Alkaline solution of pyrogallol. Dissolve 250 gms. of KOH in a liter of water and add to it 50 gms. of $C_6H_3(OH)_3$. Agitate the absorbent with the gas in the pipette five minutes. One cubic centimeter will absorb about 10 cc. of oxygen.

If the solution is not fresh, it gives up CO after taking up oxygen, giving incorrect results for both oxygen and CO.

Yellow phosphorus in sticks may be used for the absorption of oxygen, but under certain conditions it is not satisfactory.* Phosphorus does not absorb oxygen readily if the temperature is low, 12° to 15° C. or lower; if the oxygen is not well diluted with nitrogen; and if certain gases are present, among the number being acetylene, ethylene, etc.

Absorbent for CO. Cuprous chloride solution. Dissolve 250 gms. HN_4Cl in 750 cc. of water in a bottle provided with a rubber stopper. Add 200 gms. CuCl and a small strip of sheet copper to prevent oxidation to cupric chloride. For use in the pipette, add 50 cc. of ammonia to 150 cc. of the cuprous chloride solution. One cubic centimeter of this solution will absorb 16 cc. of CO.

The gas should be passed into two pipettes of this solution in succession; the second one should contain very fresh solution, to effect complete absorption of all the CO.

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* Winkler and Lunge: "Technical Gas Analysis," 69.

Methane and **hydrogen** are best determined by explosion over mercury in an explosion pipette, in the manner described on page 278, and **nitrogen** is estimated by difference.

ANALYSIS OF A GAS

Measuring the Gas. Set up the burette with leveling tube attached to its lower end by means of a long rubber tube. Pour enough water into the leveling tube to bring the water surface near the lower end of the tube when the burette is full. The water should be rendered slightly acid and should be saturated with the gas to be analyzed before the analysis begins.

Open the stopcock of the burette and raise the leveling tube until the water fills the burette and the capillary from the stopcock. Close the stopcock. With a small rubber tube, attach the burette to the capillary leading to the aspirator bottle, or other container of the gas to be analyzed. Open the stopcock and lower the leveling tube to draw the gas into the burette. When the burette has been filled, close the stopcock and hold the leveling tube alongside the burette to bring the surface of the water in the burette and in the leveling tube to the same level. Read the burette.

CO_2 in Gas. Fill the bulb of the pipette and its capillary tube with the absorbent. Attach the pipette to the burette with a small rubber tube, open the stopcock, and raise the leveling tube to drive the gas into the pipette. When all the gas has been driven over and the water of the burette fills the capillary of the pipette, close the stopcock and shake the pipette carefully for four or five minutes. Open the stopcock, lower the leveling tube, and draw the gas into the burette until the absorbent in the pipette approaches the stopcock. Close the stopcock, bring the water in the burette and leveling tube to the same level, and read the burette. The loss in volume represents the CO_2 and this divided by the original volume gives the percentage of CO_2 in the gas.

Heavy Hydrocarbons in Gas. After the absorption of the CO_2, pass the remaining volume of gas from the burette into the pipette containing the absorbent of heavy hydrocarbons and agitate the pipette about five minutes. Return the gas to the burette and, since it may contain fumes of sulphuric acid, it should be passed into the KOH pipette, shaken, and returned to the burette before the volume is read. The decrease in volume represents the heavy hydrocarbons.

Oxygen in Gas. After the determination of heavy hydrocarbons, pass the remaining gaseous mixture into the pipette for the absorption of oxygen in the manner described above for the determination of CO_2, and, after agitation, return the remaining gas to the burette and note the diminution in volume, which represents the oxygen in the gas.

The absorbent must be frequently renewed. See note under *absorbent for oxygen.*

CO in Gas. Pass the gas next into the first absorption pipette for CO and, after agitation, pass it into the second pipette for CO containing fresh ammoniacal cuprous chloride solution, and, finally, return the remaining gas to the burette and read its volume for the estimation of CO.

Nitrogen in Gas. If the gaseous mixture contains no hydrogen or methane, the volume in the burette, after the absorption of CO, is read and recorded as nitrogen.

H and CH_4 in Gas. If the gaseous mixture contains either or both of these gases, after the CO has been determined, a suitable volume—10 to 15 cc.—of the remaining gas is measured in the burette, the stopcock closed, the leveling tube lowered, and the stopcock opened to admit 60 cc. to 70 cc. of air; the quantity must be sufficient to furnish more than enough oxygen to combine with the hydrogen and methane present. The volume of the total mixture is read; it is passed into an explosion pipette containing mercury and is exploded by passing an electric spark through it.

$$CH_4+2O_2=CO_2+2H_2O.$$
$$2H_2+O_2 = 2H_2O.$$

One volume of CH_4 combines with two volumes of oxygen to form one volume of CO_2 and two volumes of water (in the gaseous form), but the water condenses, leaving only the one volume of CO_2.

The free hydrogen combines with oxygen in the proportion of two volumes of the former to one of the latter, the three disappearing when the resulting water condenses.

Pass the gas back into the burette and read its volume. Note the diminution in volume owing to the formation of water.

Pass the gas now into the CO_2 pipette, agitate, return the gas to the burette, and read its volume. This diminution in volume is due to absorption of CO_2 formed from the methane and is equal to the volume of the methane. Twice the volume of the methane represents the volume of oxygen withdrawn from the mixture by the hydrogen of the methane. The remaining diminution of volume, owing to the formation of water, is due to the burning of the free hydrogen, and two-thirds of this reduction represents the volume of hydrogen.

Example.	Readings of Burette.	Volume of Gas. cc.
Sample of gas taken	98.8	98.8
After absorption of CO_2	97.2	....
Volume of CO_2	....	1.6
After absorption of heavy hydrocarbons	93.4	....
Volume of heavy hydrocarbons	....	3.8
After absorption of oxygen	93.0	....
Volume of oxygen	....	0.4
After absorption of CO	84.2	....
Volume of CO	....	8.8

Example.	Readings of Burette.	Volume of Gas. cc.
Retained in the burette for determination of CH_4 and H_2	12.4	....
Air drawn in for explosion mixture	96.4	....
After explosion and cooling	74.8	....
Contraction due to formation of H_2O	....	21.6
After absorption of CO_2 resulting from CH_4	68.0	....
Volume of CH_4	....	6.8
Contraction due to withdrawal of O_2 to combine with CH_4 to form H_2O (2×6.8)	....	13.6
Contraction due to H_2O formed from free H_2 and O $(21.6 - 13.6)$	....	8.0
Contraction due to H_2 $(\frac{2}{3} \times 8)$	....	5.3
Volume of CH_4 in original sample $\left(\frac{6.8 \times 84.2}{12.4}\right)$	....	46.2
Volume of H_2 in original sample $\left(\frac{5.3 \times 84.2}{12.4}\right)$	....	36.0

The composition of the gaseous mixture is therefore as follows:

CO_2	1.6
Heavy hydrocarbons	3.8
O_2	0.4
CO	8.9
CH_4	46.7
H_2	36.4
N_2	2.0

EXPLOSION METHOD FOR CARBON MONOXIDE, METHANE, AND HYDROGEN

In the laboratories of the United States Steel Corporation * CO, CH_4, and H_2 are determined as follows:

Explode a sample of the gas with a known quantity of a definite mixture of nitrogen and oxygen; note the contraction (I). Pass the gas into a KOH pipette to absorb the CO_2 and measure

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* Met. and Chem. Eng., 9, 302 and 356.

the residue; note the contraction (II). Add a definite volume of hydrogen (sufficient to combine with all the remaining O_2 as H_2O) and explode with an electric spark. Measure the residue of nitrogen and hydrogen and note the contraction (III).

From these data taken in conjunction with the reactions,

$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O,$$

the following equations are formed:

Contraction I $= \frac{1}{2}$ carbon monoxide $+ \frac{3}{2}$ hydrogen $+ 2$ methane.

Carbon dioxide formed = carbon monoxide + methane.

Oxygen consumed $= \frac{1}{2}$ carbon monoxide $+ \frac{1}{2}$ hydrogen $+ 2$ methane.

From these equations the following formulæ for calculating the components of the original sample are derived:

Oxygen consumed = oxygen added $- \frac{1}{3}$ Contraction III.

Hydrogen = Contraction I − oxygen consumed.

Carbon monoxide

$$= \frac{\text{Con. I} + (4 \times \text{Con. II}) + \text{Con. III} - \text{oxygen added}}{3}.$$

Methane = Contraction II − carbon monoxide present.

The Orsat Apparatus. This is a compact arrangement of a gas burette, absorption pipettes, etc., in a portable case (Fig. 101). The burette is attached permanently to the pipettes with capillary tubing provided with the necessary stopcocks. The manipulation in the process of analysis is practically the same as that described on page 277.

Many modifications of the original Orsat apparatus have been described. Among them may be mentioned those of Allen and Moyer,* Williams,† and Burrel.‡

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* Trans. Amer. Soc. Mech. Eng., 18, 901.

† Jour. of Ind. and Eng. Chem., 4, 387 (1911).

‡ Jour. of Ind. and Eng. Chem., 4, 297 (1911).

Automatic Analysis of Gas. Apparatus of various types are in use for measuring and recording mechanically the percentage of a single gas in a gaseous mixture. They have been adapted to the estimation of CO_2, SO_2, HCl, and Cl_2.

In the Simmance-Abady Automatic Gas Analyzer (Fig. 102)* the gas is drawn into a bulb in measured portions from the flue, from which it is forced through an absorbent into a second bulb which rises to a point on a scale indicating the volume of gas that has been absorbed. A pen records the percentage on a chart actuated by a clock, and the gas is automatically discharged as the bulb descends in position to receive the succeeding sample.

The Uehling carbon dioxide meter

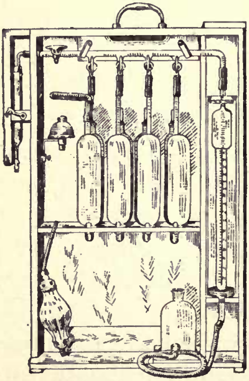

Fig. 101.—Orsat Apparatus.

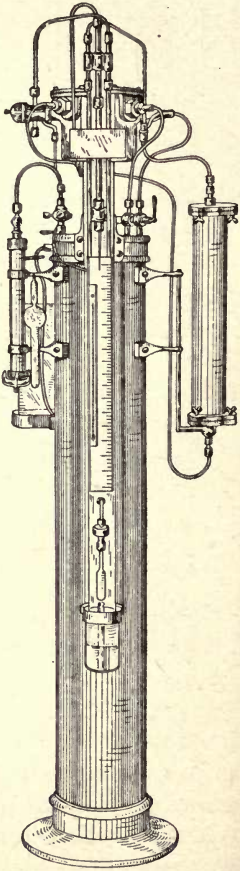

Fig. 102.—Simmance-Abady Automatic Gas Analyzer.

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[*] Met. and Chem. Eng., 9, 327, and 10, 121.

(Fig. 103)* measures and records the drop in pressure between the orifices of admission and exit to the absorbent chamber.

With this instrument the per cent of CO_2 may be indicated at the boiler front and a continuous record made elsewhere at the same time, of both the CO_2 and the temperature.

Calorific Power of Gas. The calorific power of gas is usually determined in a calorimeter of the Junkers type (Fig. 104).

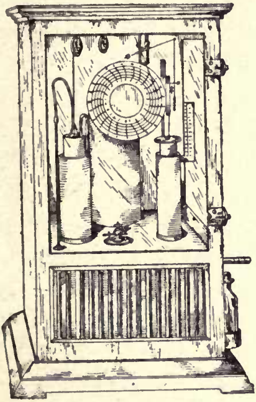

FIG. 103.—Uehling Carbon Dioxide Meter.

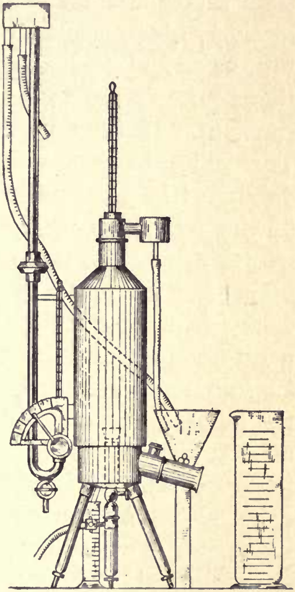

FIG. 104.—Junkers Gas Calorimeter.

A definite volume of the gas is burnt in a Bunsen burner, at a uniform rate, the flame being surrounded by a jacket, through which water flows at a rate regulated so as to absorb all the heat of the flame. A thermometer is fixed in the stream of water at its inlet and one at the outlet.

To make a test, the gas is ignited and, while it is burning at a definite and uniform rate shown by the meter, and the

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* Met. and Chem. Eng., 9, 329, and 10, 497.

water is flowing uniformly through the calorimeter, the two thermometers are observed until the readings have become constant. When the hand of the meter passes a certain point, the zero, for instance, the tube through which the water flows from the calorimeter is quickly turned to deliver the water to a receiver, where it is allowed to collect until the hand of the meter returns to the point selected for the beginning of the test. The thermometers are to be read frequently to see if they remain constant. If they do not, the readings are to be averaged. The water is then weighed and its weight multiplied by the difference in temperature between the inflowing and the outflowing water. This gives the quantity of heat produced by the gas that was burnt while the water was being collected. In order that tests may be comparable, one with another, it is necessary in each test to correct the volume of the gas for temperature and pressure to a uniform standard; usually, when English units are used, to 60° F. and 30 ins. of mercury. In the laboratories of the United States Steel Corporation, 62° F. and 30 ins. of mercury have been adopted as the standard. A table for reducing volumes of gas to this standard is given on page 330.* At the time a test is made, a thermometer and barometer are read which give the conditions under which the gas is burned. The measured volume of gas is then reduced to standard conditions (usually expressed in cubic feet) and the total heat produced, divided by this corrected volume, gives the heating power in British thermal units if English units have been used throughout, and in calories if 15° C. and 760 mm. of mercury are taken as the standard, and the gram and centimeter as the units.

Automatic Recording Gas Calorimeter. If the water is made to flow into a calorimeter at a constant temperature and uniform rate, and the gas is burnt at a constant rate, then any change in the heating value of the gas will be expressed by a change

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* Met. and Chem., Eng., 9, 358.

in temperature of the water flowing from the calorimeter. A calorimeter, then, which has a self-registering thermometer to record continuously the temperature of the outflowing water becomes a self-registering calorimeter.

CALCULATION OF THE CALORIFIC POWER OF A GAS FROM ITS ANALYSIS

The heating value of a gas may be calculated with a fair degree of accuracy from its analysis, if, in addition to the H_2, CH_4, and CO, the components of the heavy hydrocarbons are identified and the quantity of each determined. This presents no difficulty with blast-furnace gas which is devoid of heavy hydrocarbons, and little difficulty is experienced with producer gas and natural gas, since the former usually contains only a very small quantity of such, and that is ethylene, C_2H_4, and the latter is composed chiefly of methane, CH_4, and ethane, C_2H_6.

The quantity of each combustible component in a cubic foot of the mixture is multiplied by its heating value and the sum taken as the calorific power of the gas. The heating values of these gases are given below in B.t.u.'s per cubic foot at 62° F. and a pressure of 30 ins. of mercury, based on Earnshaw's calculations.*

	B. t. u.'s per cu. ft. at 62° and 30″ mercury.
Hydrogen, H_2	325.0
Methane, CH_4	1005.3
Carbon monoxide, CO	322.2
Ethylene, C_2H_4	1581.9
Ethane, C_2H_6	1757.6

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* Jour. Franklin Inst., 146, 161.

ANALYSIS OF CLAY

The Sample. Clays should be sampled and the sample prepared for analysis according to the method described for sampling limestone, page 160. The clay must be dried before grinding.

Moisture. Weigh 1 gm. of the sample, transfer it to a 30-gm. platinum crucible, heat at 110° C. for an hour, cool in a desiccator and weigh. The loss in weight represents the moisture.

Combined water is best determined with the bulb tube (method of Brush and Penfield) described on page 49.

Loss on Ignition. Weigh 1 gm., transfer it to a 30-gm. platinum crucible, cover, and heat with a blast lamp thirty minutes, cool in a desiccator and weigh. The loss in weight is reported as the *loss on ignition.*

SiO_2. To 1 gm. of the sample in a 30-gm. platinum crucible (or to the residue after the determination of *moisture* or *loss on ignition*) add 6 gms. of dry sodium carbonate, fuse, and complete the determination according to the method for SiO_2 on page 71.

Fe_2O_3. To the filtrate from the SiO_2 (above) add ammonia to precipitate the hydroxides of iron, aluminum, etc. Filter, wash the precipitate into a beaker (see p. 61), dissolve it in sulphuric acid, reduce the iron with zinc to the ferrous condition, and titrate it with standard potassium permanganate solution (see p. 55); or the precipitate may be dissolved in hydrochloric acid and titrated with standard potassium dichromate solution after reduction with stannous chloride (see p. 62). If the latter method is used, see note in regard to effect of platinum (p. 63).

CaO. To the filtrate from the precipitate of iron and aluminum hydroxides add ammonium oxalate and complete the determination according to the method described on page 162.

MgO. Precipitate the magnesium as magnesium ammonium phosphate and proceed according to the method for the determination of magnesia in limestone, page 165.

Al_2O_3. Weigh a separate portion and proceed according to the method (phosphate) described on page 87.

ALKALIES IN CLAY

J. LAWRENCE SMITH METHOD *

Reagents. *Pure dry ammonium chloride*, NH_4Cl.

Pure calcium carbonate, $CaCO_3$.

Ammonium carbonate, $(NH_4)_2CO_3$.

Ammonium oxalate solution. Dissolve 40 gms. $(NH_4)_2C_2O_4 + 2H_2O$ in 1 liter of water.

Alcohol, 80 per cent strength.

Solution of chlorplatinic acid.

Weigh 1 gm. of the clay and transfer it to an agate mortar; add 1 gm. of ammonium chloride and grind well to mix. Add nearly all of 8 gms. of calcium carbonate and grind.

Place a little calcium carbonate in a large platinum crucible, or better, in a long narrow crucible with close fitting cap, designed for the purpose (Fig. 106).

The calcium carbonate prevents the sintered cake from sticking.†

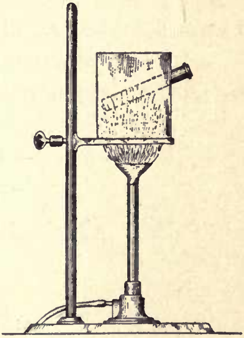

FIG. 105.—Lawrence Smith Crucible for Alkali Determination.

Transfer the charge from the agate mortar to the crucible. Grind the remaining part of the 8 gms. of calcium carbonate in the mortar to clean out the charge, and add it to the crucible. Put on the cover and heat

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* Amer. Jour. Sci., Second Series, 50, 269 (1871). Hillebrand, Bull. 422, U. S. Geological Survey, p. 171 (1910).

† Schaller, Bull. U. S. G. S., 422, 173.

gently the lower two-fifths of the crucible, keeping the top cool to prevent loss by volatilization of the alkaline chlorides formed.

If an ordinary crucible is used, let it project through a hole in an asbestos board (see Fig. 58, p. 74) to protect the top from the heat of the flame.

Keep the heat low for about ten minutes until the odor of ammonia no longer comes from the crucible, then heat the lower part of the crucible to redness and continue the heating at that temperature for about forty-five minutes.

This converts the alkalies, and much of the calcium, to chlorides.

Transfer the sintered cake to a platinum dish, and add 1 or 2 cc. of hot water.* When the cake is slaked, add hot water and stir to disintegrate thoroughly. Filter and wash by decantation and finally wash thoroughly on the filter with hot water.

Add to the filtrate ammonia and about 1.5 gm. ammonium carbonate, which will precipitate nearly all the calcium.

$$CaCl_2+(NH_4)_2CO_3=CaCO_3+2NH_4Cl.$$

Filter and wash. Evaporate the filtrate to dryness in a platinum dish and carefully heat to dull redness to drive off salts of ammonia.

The dish should be fitted into a hole in an asbestos board to prevent the admission of sulphur to the solution from the gas flame.

Dissolve the alkaline chlorides in a very little water.

If the sample contains sulphur or if sulphur has been introduced from the flame, add a drop of $BaCl_2$ solution. Then add a little ammonium carbonate solution to precipitate the remaining Ba, and finally, add a little ammonium oxalate solution to precipitate the remaining calcium. Filter into a platinum crucible and evaporate the filtrate to dryness, taking precautions in regard to the introduction of sulphur from the flame.

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* Steiger, loc. cit., 173.

Cool in a desiccator and weigh. Dissolve in a little water and, if there is an insoluble residue, filter into a small porcelain dish, wash, ignite the paper with the residue, cool, weigh, and deduct from the previous weight. The difference represents the combined weight of potassium and sodium chlorides.

K_2O. To the solution of the chlorides in the porcelain dish add an excess of a solution of chlorplatinic acid.

Any precipitate which forms should dissolve when heated on the water-bath.

Evaporate the solution until the residue solidifies on cooling Now treat the mass with 80 per cent alcohol, filter through a very small filter, and wash by decantation with more of the alcohol, retaining as much as possible of the precipitate in the dish.

Dry the dish and filter a few minutes to drive off the alcohol. Transfer the precipitate to a weighed platinum crucible. Dissolve with hot water any precipitate that adheres to the dish and wash it through the filter into the crucible.

Evaporate the solution to dryness on a water-bath, cover the crucible to prevent loss by decrepitation and heat to 135° C. Cool in a desiccator and weigh K_2PtCl_6. The factor for KCl in K_2PtCl_2 is 0.30674 and the factor for K_2O in K_2PtCl_6 is 0.19376.

Na_2O. Deduct the weight of KCl from the combined weight of KCl and NaCl and multiply the difference by the factor for Na_2O in NaCl, which is 0.53028.

The sodium may be determined directly from the filtrate from the potassium platinic chloride by evaporating the solution and precipitating the platinum with H_2S, filtering and evaporating the filtrate to dryness and weighing as NaCl.

METHODS FOR THE DETERMINATION OF SOME OF THE MINOR METALS

CHROMIUM *

Weigh 1 gm. of the sample, which must be ground extremely fine, and fuse it one hour in a platinum crucible with about 10 gms. of a basic mixture composed of 4 parts of lime or magnesia and 1 part each of potassium and sodium carbonates. Transfer the sintered mass to a beaker and dissolve it in water and sulphuric acid.

If any black particles remain undissolved, filter them off and fuse them again with the basic mixture; dissolve and add to the first solution. Add an excess of standard ferrous ammonium sulphate solution, accurately measured, and titrate the excess with standard potassium permanganate solution. (See p. 141.)

NICKEL AND COBALT

Add to 1 gm. of the sample in a 200-cc. Erlenmeyer flask 15 cc. of NHO_3 and boil until the solution becomes syrupy. Add 10 cc. NHO_3 and 5 gms. $KClO_3$ and boil ten minutes. Add 5 cc. more of HNO_3 and 5 gms. $KClO_3$ and boil until yellow fumes are no longer produced. Cool, add 40 cc. of hot water, filter, and wash. Reserve the filtrate (*a*). Wash into the flask the residue on the filter. Place the flask under the funnel and pour through the filter 15 cc. of warm dilute hydrochloric acid (1 : 2) and wash with a little hot water. Heat the flask to dissolve the residue. Add 20 cc. bromine water and an excess of ammonia. Boil, let the precipitate settle, filter, and wash with hot water. Combine this filtrate with the filtrate (*a*), and boil off the excess of ammonia. Neutralize the solution with hydrochloric acid and add 10 cc. in excess. Boil, dilute

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* Sutton, "Volumetric Analysis," p. 182.

to 300 cc. and saturate the solution with hydrogen sulphide by passing through it a current of the gas. Filter and wash the precipitate with dilute hydrogen sulphide water. Boil the solution down to about 25 cc. and add NaOH to neutralize the acid. Pour this solution, which contains the nickel, cobalt, and zinc, slowly into 50 cc. of a 10 per cent solution of sodium hydroxide, stirring constantly. Dilute the solution with an equal volume of water and filter. Dissolve the precipitate in a little hydrochloric acid, nearly neutralize with sodium hydroxide, and pour again into a 10 per cent solution of sodium hydroxide, stirring. Dilute and filter. Dissolve the hydroxides of nickel and cobalt, in a little dilute H_2SO_4; wash the filter free from acid. Dilute the filtrate to 125 cc., add 5 gms. ammonium sulphate and 40 cc. of ammonia. Electrolyze several hours with a current of $D_{100}=0.5$ to 0.7 amperes and 2.8 to 3.3 volts.

When precipitation is complete, a few drops on a porcelain plate with ammonium sulphide should show no trace of black color.

With rotating anode or cathode the current may be increased to $D_{100}=4$ amperes and 5.5 volts and the time of deposition thereby shortened to about half an hour.

Ni. After weighing, dissolve the nickel and cobalt in nitric acid. Add hydrochloric acid and boil the solution down to convert nitrates to chlorides. Dilute so that there will be not more than 0.1 gm. cobalt per 100 cc. to prevent solution of the precipitate.* Heat to boiling, precipitate the nickel with dimethylglyoxime, and complete the determination according to the method on page 140.

Co. When the nickel has been determined by the dimethylgloxime method, deduct its weight from the combined weight of nickel and cobalt and calculate the percentage of Co.

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* Price and Meade, " Brass Analysis," p. 115.

CADMIUM

METHOD OF BEILSTEIN AND JAWEIN *

Add 10 cc. of nitric acid to 0.5 gm. of the ore in a 250-cc. Erlenmeyer flask. Boil down to about 5 cc., add 7 cc. of sulphuric acid and boil over a free flame to dense fumes of sulphuric acid. Cool, add 25 cc. of water, heat to boiling, and let it stand hot to dissolve iron sulphate. Cool, filter, and wash with dilute sulphuric acid (1 : 1). Dilute the filtrate to 200 cc. and pass through it a current of hydrogen sulphide. Filter and wash with dilute hydrogen sulphide water acidulated with hydrochloric acid. Wash the precipitate into a beaker, using as little water as possible. Place the beaker under the funnel and pour through the filter a strong cold solution of potassium cyanide. Use as little potassium cyanide solution as possible to dissolve the sulphides of copper, etc., that may be present and leave the yellow or orange sulphide of cadmium. Filter through the same paper and wash with dilute hydrogen sulphide water. Dissolve the cadmium sulphide on the filter with as little hot dilute hydrochloric acid (1 : 1) as possible. Add 5 cc. of sulphuric acid and boil to white fumes. Cool and dilute to 20 cc. Add a drop of phenolphthalein solution and then add pure sodium hydroxide solution until a permanent red color is produced. Stir and add a solution of potassium cyanide slowly, until the cadmium hydroxide dissolves, being very careful not to add an excess. Dilute to a volume of 100 to 150 cc. and electrolyze in the cold five to six hours with a current of $D_{100} = 0.5$ to 0.7 amperes and 4.8 to 5 volts. After the expiration of this time, increase the current to about 1 or 1.2 amperes and continue the electrolysis one hour more. Wash the cathode successively with water, alcohol, and ether. Dry and weigh.

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* Berichte, 12, 466, through Treadwell-Hall, "Analytical Chemistry," Vol. 2, 150.

If the stronger current is run from the beginning, the metal will be spongy; if the weaker current is continued, more than twelve hours will be required for total precipitation.

MERCURY *

Treat 1 gm. of the ore with 15 cc. of nitric acid and 10 cc. of hydrochloric acid at a gentle heat until the ore is decomposed.

Add more nitric acid if necessary, but do not evaporate to too small a volume, since there is danger of volatilizing some mercuric chloride. Filter into an Erlenmeyer flask and wash. Nearly neutralize the filtrate with sodium carbonate and add a slight excess of freshly prepared ammonium sulphide. Shake the flask to rotate the solution and add a solution of pure sodium hydroxide until the dark liquid begins to clear. Heat to boiling and add more NaOH until the solution is perfectly clear. The mercury is now in solution as $Hg(SNa)_2$. If any precipitate forms, filter; precipitate the mercury from the filtrate by adding ammonium nitrate. Boil until the odor of ammonia is very faint.

Let the precipitate settle.

$$Hg(SNa)_2+2NH_4NO_3=2NaNO_3+(NH_4)_2S+HgS.$$

If any free sulphur has precipitated with the sulphide of mercury, before filtering, boil with a little sodium sulphite to remove the sulphur.

$$Na_2SO_3+S=Na_2S_2O_3.$$

The sulphur may be dissolved from the precipitate with carbon disulphide after filtering. Filter in a Gooch crucible and wash by decantation with hot water until the washings do not react with silver nitrate solution. Transfer the precipitate to the crucible, dry at 110° C. and weigh as HgS.

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* Treadwell-Hall, "Analytical Chemistry," 2, 134.

TIN

If the ore is practically pure cassiterite the metallic tin may be reduced and recovered in a suitable bead for weighing by fusing the finely ground ore with potassium cyanide in a porcelain crucible. The fused mass, after cooling, is dissolved in water, and the metallic tin is dried and weighed.

If the ore is impure, other metals may be reduced with the tin, and if silica is present, some of the tin will combine with it and go into the slag.

The following method by Milon and Fouret * is recommended.

Sn in Ore. Mix 2 gms. of the finely ground sample with 20 gms. of sodium dioxide in a 6-cm. sheet-iron crucible. Fuse carefully twenty minutes, cool and place in a 500-cc. beaker with 150 cc. of water. Cover with a watch glass and when the action becomes quiet, add, a little at a time, 70 cc. of hydrochloric acid. When the mass is decomposed take out the crucible and wash it off. Heat the solution to 60° C. and add 4 gms. of iron filings to precipitate arsenic, antimony, and copper, and to reduce the stannic to stannous chloride. This operation requires about half an hour.

Filter into a 500-cc. Erlenmeyer flask and wash the residue well with hot water. Heat the filtrate to 95° C. and add 10 gms. of pure zinc to precipitate the tin. Drops of the solution should be tested from time to time on a porcelain plate with hydrogen sulphide water. A brown precipitate indicates that tin is still in solution.

When the tin is all precipitated, decant the solution through a funnel containing a plug of glass wool, leaving most of the tin and the zinc in the flask. Put the glass wool with the tin, which was carried over, into the flask. Fit the flask with a two-hole rubber stopper carrying glass tubes for the passage of CO_2. Pass CO_2 through the flask several minutes. Remove

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* Eighth International Congress of Applied Chemistry, 1, 373.

the stopper and pour into the flask 30 cc. of hydrochloric acid. Replace the stopper and warm the flask gently until the tin and zinc are completely dissolved. Close the exit tube and cool the flask. When cold, disconnect the CO_2 generator, remove the stopper and wash off the tubes with water from which the air has been expelled by CO_2 (1 liter of water+3 gms. $NaHCO_3+HCl$), dilute the solution to 250 cc. with the same water, add a few drops of starch solution, and titrate with standard iodine solution.

Low * fuses 0.5 gm. of the ore mixed with a little charcoal in an iron crucible with sodium hydroxide, dissolves in hydrochloric acid, reduces the stannic to stannous chloride with metallic iron, and titrates with standard iodine solution (9.7 gms. iodine per liter = about 1 per cent Sn per cubic centimeter when 0.5 gm. of ore is used).

TIN

Gravimetric Method

Mix 1 gm. of the finely ground ore in a porcelain crucible with 3 gms. of dry Na_2CO_3 and 3 gms. of S. Cover the crucible and heat gently over a low flame until the sulphur has ceased to escape and burn (about twenty minutes). Cool the crucible and treat the fusion with hot water in a casserole. The tin should dissolve as sodium sulpho-stannate.

$$2SnO_2+2Na_2CO_3+9S=3SO_2+2Na_2SnS_3+2CO_2.\dagger$$

Filter and wash the precipitate with hot water.

If the residue feels gritty under the glass rod, burn the filter, add sodium carbonate and sulphur and repeat the process described above. Add the filtrate containing the residue of tin to the first filtrate.

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* "Technical Methods of Ore Analysis," 164a.

† Treadwell-Hall, "Analyt. Chem.," 1, 222.

Acidify the filtrate with sulphuric acid to precipitate the tin as SnS_2. Keep the solution warm while the precipitate settles. Decant the clear solution through a filter and wash by decantation with ammonium acetate solution—made by adding an excess of acetic acid to dilute ammonia—to prevent the precipitate from running through the filter. Transfer the precipitate to the filter and finally wash it with hot water. Place the filter and its contents in a weighed porcelain crucible. Heat very gently with free access of air until there is no longer an odor of burning sulphur. Gradually increase the heat to a high temperature.

A high temperature at first may volatilize SnS_2.

Add about half a gram of ammonium carbonate and heat to drive out sulphuric acid completely. Cool, weigh, and repeat the treatment with ammonium carbonate several times until the weight of SnO_2 is constant. The factor for Sn in SnO_2 is 0.78808.

TIN IN CONCENTRATES

Tin in cassiterite concentrates may be determined by the fire assay.

Mix 5 gms. of the ore in a fire-clay crucible with 2 gms. of charcoal, 12 gms. of $NaHCO_3$, and 1 gm. of borax glass. Cover with salt and place on top of the charge several lumps of charcoal. Fuse in a muffle at a little below white heat for about one hour. Withdraw the crucible from the furnace. When cool break the crucible and remove the slag from the tin button and weigh the tin.

TUNGSTEN

Fuse 1 gm. of the ore in a platinum crucible with 4 gms. of sodium carbonate for about forty minutes. Cool and extract the fusion by boiling in water. Filter.

The tungstate and silicate of sodium are soluble.

Add to the filtrate an excess of nitric acid and evaporate the solution to dryness. Add a little hydrochloric acid, warm, and dilute with hot water. Boil and filter. Burn the residue in a platinum crucible to SiO_2+WO_3. Add hydrofluoric acid and sulphuric acid to the crucible and evaporate to dryness to volatilize the silica. If necessary, repeat the treatment to volatilize the silica completely.

Burn with the blast lamp and weigh as WO_3.

VANADIUM

HILLEBRAND'S METHOD *

Fuse 1 to 5 gms. of the ore with 4 to 20 gms. of sodium carbonate and 0.5 to 3 gms. of potassium nitrate. Treat the fusion with hot water, add a few drops of alcohol to precipitate manganese, and filter.

If the ore contains much vanadium, some will be retained by the residue on the filter. In this case, burn the filter with the residue and fuse it again in the manner directed above.

Nearly neutralize the filtrate containing all the vanadium with nitric acid to precipitate aluminum hydroxide and silicic acid.

Be careful not to make the solution acid on account of the reducing action of nitrous acid formed from nitrates in the fusion.

The quantity of acid required to neutralize the sodium carbonate in the fusion can be determined on a separate portion.

Evaporate the solution nearly to dryness. Treat with hot water and filter. When the filtrate is cold, add a nearly neutral solution of mercurous nitrate to precipitate vanadium.

It also precipitates mercurous carbonate and, if the elements are present, the chromate, molybdate, arsenate, and phosphate.

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* Amer. Jour. Science, 6, 209; Treadwell-Hall, "Analytical Chemistry," 2, 277.

Heat to boiling, filter, wash with a dilute solution of ammonium nitrate. Dry and burn in a platinum crucible at as low a temperature as possible. Add a little sodium carbonate and fuse. Cool and treat with hot water.

If a determination of chromium is desired, filter and determine it colorimetrically, using potassium chromate for a standard.

Then acidify the solution slightly with sulphuric acid and precipitate the molybdenum, arsenic, and platinum with hydrogen sulphide. Filter, boil the filtrate, and pass a current of CO_2 through it to remove H_2S. Titrate the *hot* solution with standard potassium permanganate solution.

For the most accurate work, reduce the solution with sulphur dioxide, titrate again, and average the two titrations.

For reactions see page 143.

URANIUM

Treat 1 gm. of ore with strong nitric acid until there is no further action; add 5 cc. of hydrochloric acid and evaporate the solution to dryness. Cool, add 3 cc. of hydrochloric and 25 cc. of hot water. Boil, filter, and wash with hot water. Dilute the filtrate to 150 cc. and pass a current of hydrogen sulphide through the solution. Filter, and wash with hydrogen sulphide water. Boil the filtrate to expel the hydrogen sulphide and oxidize by adding strong nitric acid. Add ammonia until nearly neutral. Pour the solution into 50 cc. of a 20 per cent solution of ammonium carbonate. Boil, let the precipitate settle, filter, and wash. Acidify the filtrate with hydrochloric acid and boil off all the carbon dioxide. Add an excess of ammonia, boil a few minutes, filter, wash with ammonium chloride solution and once with water. Burn and weigh U_3O_8.

The U may be measured by titration as follows:

Dissolve the precipitate of ammonium uranate in dilute sulphuric acid, reduce with zinc for thirty minutes, completely dissolve the zinc, and titrate with standard permanganate solution.

$$UO_2SO_4+H_2+H_2SO_4=U(SO_4)_2+2H_2O.$$

$$5U(SO_4)_2+2KMnO_4+2H_2O=5UO_2SO_4+K_2SO_4+2MnSO_4+2H_2SO_4.$$

The permanganate solution may be standardized against iron and its value in uranium calculated.

The value of the solution in iron multiplied by $\frac{238.5}{2(55.84)}$ gives the value in uranium.

METHODS FOR THE DETERMINATION OF SOME OF THE RARER METALS

LITHIUM

Gooch's Method *

Reagent. *Amyl alcohol.* $C_5H_{12}O$ (boiling-point 131° C.).

Weigh and treat the sample according to the Lawrence Smith method for alkalies in clay, p. 287, until the alkaline chlorides have been weighed. Evaporate the solution of the alkaline chlorides, which should not contain more than 0.2 gm. lithium chloride, to a very small bulk. Transfer the solution to a 50-cc. Erlenmeyer flask, add 6 cc. amyl alcohol, and carefully heat the mixture to boil off the water.

It is advisable to fit the flask with a two-hole stopper provided with intake and delivery tubes and draw a current of dry air through the flask to assist in the removal of water vapor and thereby prevent bumping.

When the water has all been boiled out, the chlorides of potassium and sodium being insoluble in amyl alcohol, are

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* Proceedings Amer. Acad. of Arts and Sci., N. S., 14, 177.

precipitated. Add 2 to 3 drops of strong HCl to convert to chloride the small amount of LiOH that has been produced by hydrolysis. Boil a few minutes and filter while hot on asbestos. Wash with hot amyl alcohol that has been boiled. The filtrate, which contains the lithium and a very small amount of potassium and sodium, if they were present in the original material, is evaporated to dryness. Add a little dilute sulphuric acid, and filter the solution from the carbonaceous residue into a weighed platinum crucible. Evaporate the solution to dryness, ignite and weigh the Li_2SO_4. Deduct from this weight, if K and Na were present, 0.00041 gm. for Na and 0.00051 for K and 0.00092 gm. if both were present for each 10 cc. of amyl alcohol in the filtrate. The factor for Li_2O in Li_2SO_4 is 0.27176.

STRONTIUM *

Reagent. A mixture of *absolute alcohol* and *ether* in equal parts.

Strontium is precipitated with calcium as oxalate. Therefore, after obtaining the oxalate precipitate according to the method for limestone (p. 162), or for clay (p. 286), burn the oxalates to the oxides in a platinum crucible and weigh. Then dissolve the oxides in nitric acid and transfer the solution to a 20-cc. flask. Evaporate the solution to dryness and raise the temperature to between 150° and 160° C. Cool and add about 2 cc. of a mixture of equal parts of absolute alcohol and ether (as small a quantity is used as will dissolve the calcium nitrate). Agitate to hasten solution of the calcium nitrate. Cork the flask and let it stand over night. Filter on a very small paper and wash with the mixture of absolute alcohol and ether. Let the filter dry and dissolve the strontium nitrate on the filter in a few cubic centimeters of hot water, letting the solution run into a small beaker. After washing the filter, precipitate

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* Hillebrand, Bull. 422, U. S. Geological Survey, p. 119.

the strontium by adding to the filtrate a few drops of sulphuric acid. Add to the solution an equal volume of alcohol. Let the precipitate settle twelve hours, filter, burn, and weigh as $SrSO_4$. The factor for SrO in $SrSO_4$ is 0.5641.

If the material under examination contains only a small quantity of barium, it will all pass into solution if the precipitation of the oxalates of calcium and strontium is repeated in a fresh solution. If a considerable quantity of barium is present, a little will come down with the strontium. After weighing the strontium precipitate, it should be tested for barium.

BARIUM

Treat 1 gm. of the material according to the method for the analysis of clay (p. 286) until the oxalates are filtered from the solution. If the oxalates are dissolved and reprecipitated in fresh solution once or twice, all the barium will pass into solution with the magnesium.

Evaporate the solution to dryness and drive off the ammonium salts by heat. Dissolve the residue in a little water, add a little hydrochloric acid and a few drops of sulphuric acid. Let it stand in a warm place over night, filter, burn, and weigh $BaSO_4$. The factor for BaO in $BaSO_4$ is 0.65699.

COLUMBIUM AND TANTALUM

Fuse the sample with acid potassium sulphate until the ore is in solution. Cool, add water, and boil for some time. Columbic acid remains as a precipitate (impure). Filter by decantation and digest with ammonium sulphite to dissolve stannic and tungstic acids. Wash with water and treat the precipitate on the filter with very dilute hydrochloric acid to dissolve iron sulphide.

Ignite the filter after adding ammonium carbonate and weigh as Cb_2O_5 and Ta_2O_5.

CAESIUM *

The alkalies are obtained as chlorides. (See the Lawrence Smith Method, p. 287.) Add to the cold, strongly acid solution of the chlorides a cold solution of antimonous chloride acidified with hydrochloric acid. Filter off the white precipitate of $CsC\ SbCl_3$ and wash with cold concentrated hydrochloric acid. Wash the precipitate into a beaker with warm water and warm to decompose it. Pass a current of hydrogen sulphide through the solution to precipitate antimony sulphide. Filter off the sulphide, evaporate the filtrate to dryness and weigh the residue as $CsCl$.

Caesium chloride melts at a dull red heat and is volatile; therefore, after evaporating to dryness, the temperature should not be raised.

GERMANIUM

Fuse the ore in a porcelain crucible with 2 parts of sulphur and 5 parts of sodium carbonate. Cool the fusion, treat it with boiling water, and filter. Add to the filtrate an excess of hydrochloric acid to precipitate germanium disulphide. Filter and wash with dilute hydrochloric acid (5 : 100). Dry the precipitate and heat it in a current of hydrogen or coal gas to reduce it to germanous sulphide. Dissolve the sulphide in hot hydrochloric acid and pass through the solution a current of hydrogen sulphide. Filter and treat the precipitate with nitric acid to convert the sulphide to insoluble GeO_2, which is recovered in a Gooch crucible and weighed.

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* Cahen and Wootton, "The Mineralogy of the Rare Metals," 180.

GLUCINUM (BERYLLIUM) *

Weigh 1 gm. of the sample and treat it according to the method for the analysis of clay, page 286, to the precipitation of iron and aluminum as hydroxides. Dissolve this precipitate, which also contains the glucinum hydroxide, in as little hydrochloric acid as possible and oxidize by adding a little nitric acid. Nearly neutralize the solution with ammonia and evaporate it to 25 cc. While hot, pour this solution into 75 cc. of a 20 per cent solution pure sodium bicarbonate, heated to 75° C. Boil for one-half minute after all the carbon dioxide has escaped. Let the solution cool and the precipitate settle. Filter off the hydroxides of iron and aluminum, which will contain a little glucinum. Wash with a 10 per cent solution of sodium bicarbonate heated to 75° C. Dissolve the precipitate in hydrochloric acid, reprecipitate as before, and filter into the first filtrate. Acidify the filtrate with hydrochloric acid, boil off the carbon dioxide, add only a slight excess of ammonia to precipitate the $Gl(OH)_2$, filter, and wash by decantation. Redissolve the precipitate in a little hydrochloric acid and precipitate again with ammonia to free it from sodium. Filter and wash the precipitate free from chlorides with a 2 per cent solution of ammonium nitrate or acetate. Ignite and weigh as GlO.

THALLIUM

Treat 1 gm. of the sample with 10 cc. of nitric acid and 5 cc. of hydrochloric acid; then add 7 cc. of sulphuric acid and boil until the fumes of sulphuric acid are evolved. Dilute, filter, wash, pass a current of hydrogen sulphide through the filtrate, filter, boil off the excess of hydrogen sulphide, nearly neutralize with sodium carbonate and add an excess of potassium iodide. The thallium is precipitated as bright yellow TlI. Let the

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* Parsons, " The Chemistry and Literature of Beryllium."

precipitate settle, filter in a Gooch crucible, wash with cold water and then with a little alcohol. Dry at 100° C. and weigh.

CERIUM

Decompose the sample by several partial evaporations with hydrofluoric acid. Filter off the fluorides and silicofluorides, supporting the paper on a platinum cone; wash the residue with water acidulated with hydrofluoric acid, and then wash it into a platinum crucible, add sulphuric acid, and evaporate to complete dryness to expel all the fluorine. Burn the filter paper and add the ash to the crucible. Dissolve the contents of the crucible in dilute hydrochloric acid, filter, add ammonia to the filtrate to precipitate the rare earths with possibly some alumina, filter, wash the precipitate, dissolve it in hydrochloric acid, and evaporate the resulting solution to dryness. Add a little oxalic acid solution and heat. Filter off the oxalates of the rare earths and burn them to oxides. Dissolve the oxides in dilute sulphuric acid. When cold, add an excess of standard hydrogen peroxide solution and titrate the excess of H_2O_2 with standard permanganate solution.

$$2Ce(SO_4)_2+H_2O_2=Ce(SO_4)_3+H_2SO_4+O_2.$$

If the permanganate solution has been standardized against iron, the ratio of the value in cerium to its value in iron will be as 140 is to 56.

THORIUM IN MONAZITE *

Heat gradually to a gentle fusion 0.5 gm. of the sample with 10 gms. of potassium bisulphate and 0.5 gm. of sodium fluoride in a platinum crucible. Cool and dissolve in water and a little hydrochloric acid. Filter by decantation, add hydro-

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* Benz, Zeit. f. Angew. Chem., 15, 297 (1902).

chloric acid to the residue, and boil. Dilute and filter. Nearly neutralize the combined filtrate with ammonia, being careful not to produce a precipitate. Heat to boiling, add about 4 gms. of ammonium oxalate (the salt) and stir vigorously. Let the precipitated oxalates of the rare earths stand twelve hours, filter, wash once with water acidulated with nitric acid. With the wash bottle wash the precipitate into a porcelain dish, using strong hot nitric acid to dissolve off the last traces. Evaporate the solution to dryness. Add to the residue 10 cc. of nitric acid (1.42) and 20 cc. of fuming nitric acid, cover and heat on the water-bath. When the oxalates are decomposed, wash off the cover and wash down the sides of the dish. Evaporate the solution to dryness. Cool, add a little water, boil, and filter. Dilute the filtrate to 100 cc. with a 10 per cent solution of ammonium nitrate. Heat to about 70° C., and add 20 cc. of a 3 per cent solution of hydrogen peroxide. Filter at once and wash with hot water containing ammonium nitrate. The precipitate may be yellow owing to traces of cerium peroxide.

Ignite in a platinum crucible and weigh as ThO_2.

YTTRIUM

Treat 5 gms. of the sample in a porcelain dish with aqua regia and evaporate the solution to dryness. Cool, add water and a little hydrochloric acid and boil. Dilute the solution and filter. Add ammonium oxalate to the filtrate until a precipitate ceases to form. Filter off the oxalates of yttrium and cerium with a little of the oxalates of calcium and manganese. Dry and ignite the precipitate and redissolve it in a little hydrochloric acid. Add a saturated solution of potassium sulphate to precipitate cerium. Filter and wash the precipitate with a saturated solution of potassium sulphate. Add to the filtrate a solution of potassium hydroxide or ammonium oxalate to precipitate the yttrium. Filter and—to remove calcium and manganese, which contaminate the precipitate—dissolve in a little nitric acid, evaporate to dryness, and bake to decompose the manganese salt. Cool, add hot water, boil, and filter. Add ammonia to the filtrate to precipitate yttrium. Stir well until the calcium is dissolved, filter, wash, dry, burn, and weigh as Y_2O_3.

ZIRCONIUM *

Fuse 2 gms. of the sample in a platinum crucible with Na_2CO_3. Cool and digest the fusion with hot water, filter, and wash the residue with a dilute solution of Na_2CO_3. The zirconium is filtered off with the residue. Wash the precipitate into a small beaker and treat it with a little more than enough warm dilute sulphuric acid to take up all that is soluble. Do not digest it so long that dissolved silica gelatinizes.

Filter through the same paper used for the first filtration and let the filtrate run into a 100 or 150-cc. Erlenmeyer flask, wash the residue, ignite it in a platinum crucible, add to the residue hydrofluoric and sulphuric acids, and evaporate. Dilute the solution and filter off barium, strontium, and calcium sulphates and add the filtrate to the last filtrate, which will now contain all the zirconium and rare earths. Add to the combined filtrates hydrogen peroxide to oxidize titanium, and a few drops of a solution of disodium phosphate. Let the precipitate settle twenty-four to forty-eight hours; all the zirconium is precipitated as phosphate with a little titanium.

If the yellow color of the solution should fade and disappear, add more H_2O_2.

Filter and treat the residue as follows to free it from titanium:

Ignite the precipitate, fuse it with Na_2CO_3, cool the fusion and treat it with hot water, filter, ignite the precipitate, and fuse with potassium pyrosulphate. Dissolve the fusion in hot water

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* Hillebrand, Bull. 422, U. S., Geological Survey, p. 140.

to which has been added a few drops of dilute H_2SO_4. Pour the solution into a 20-cc. Erlenmeyer flask, add a few drops of 4 per cent H_2O_2 solution and a few drops of solution of disodium phosphate. Let the precipitate settle one to two days, filter, ignite the precipitate and weigh as zirconium phosphate, 50 per cent of which is taken as ZrO_2, although the theoretical factor is 0.518.

LUBRICATING OIL

Viscosity. The viscosity of oil is determined by a test with the viscosimeter, and is expressed by the time required for a given quantity of oil at a definite temperature to run through an orifice of definite dimensions. The lighter oils are tested at 100° F. or lower and the heavier at 210° to 212° F. Viscosimeters of many designs can be had of dealers in chemical supplies.

Flashing-point and Fire Test. The oil is very gradually heated in a cup in which is placed a thermometer so that the bulb is submerged. At regular intervals a flame or electric spark is passed near the surface of the oil and the temperature noted when the first flash is observed. The heating is continued until the oil burns, and the temperature is recorded as the burning test, which is usually 60° to 80° F. above the flash-point.

Cold Test. A four-ounce bottle of thin glass is filled one-third full of the oil. The bottle is closed with a stopper which carries a thermometer so adjusted that the bulb is just submerged in oil. The oil is now cooled down gradually, being finally placed in a freezing mixture of ice and salt. The bottle is frequently withdrawn and examined to see when the oil ceases to flow. The temperature at which it just ceases to flow is taken as the setting point, or *cold test.*

Cold Test for Lighter Oils. To determine the setting point of lighter oils (solidifying above 45° F.), it is customary to cool the oil to about 20° F. below its freezing-point and then gradually warm it until it just begins to flow, at which point the temperature is taken as the *cold test.*

EXAMINATION OF BOILER WATER

Total Solids. Evaporate 1 liter of the water to dryness in a weighed platinum dish on a water-bath.

If the water is low in total solids, 2 liters or more should be taken; if high in total solids, half a liter may be used. The water is added to the dish, a little at a time.

When dry, weigh the dish and contents; the weight of the empty dish deducted leaves the weight of the total solids.

Mineral Matter. Ignite the residue (Total Solids above) in the platinum dish.

This burns organic matter, expels combined water and CO_2 from calcium and magnesium carbonates.

Moisten the residue with a very little water and place it in an atmosphere of CO_2 for an hour.* Dry at 100° C., cool in a desiccator and weigh. This gives the total mineral matter as it existed in the water.

Organic Matter. Deduct the total mineral matter from the total solids and the difference represents the organic matter.

Scale-forming Constituents. Treat the total mineral matter with hot water free from CO_2, a little at a time, filter and wash with boiling water, using not more than 50 cc. in all. Burn the filter in the platinum dish and weigh. The weight of the residue represents the scale-forming constituents.

Non-scale-forming Constituents. The difference between the total mineral matter and the scale-forming constituents represents the non-scale-forming constituents.

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* Stillman, "Engineering Chemistry," p. 57.

SiO_2, Fe_2O_3, Al_2O_3, CaO, and MgO in the Scale-forming Constituents. Dissolve the scale-forming constituents in hydrochloric acid and proceed according to the method for limestone (p. 160), for the determination of insoluble silicious matter, iron and aluminum oxides, lime, and magnesia.

SO_3 in the Scale-forming Constituents. Acidify the filtrate from the magnesium ammonium phosphate with hydrochloric acid, add barium chloride solution, boil, let the precipitate settle, filter, burn, and weigh the $BaSO_4$, from which calculate the percentage of SO_3. The factor for SO_3 in $BaSO_4$ is 0.343.

Composition of the Scale-forming Constituents. The SO_3 is combined with CaO to form $CaSO_4$. The remaining CaO and the MgO are calculated to carbonates. The sum of the $CaSO_4$, $CaCO_3$, $MgCO_3$, insoluble siliceous matter, Fe_2O_3, and Al_2O_3 should be equal to the weight of scale-forming constituents.

For a complete report on the total solids, the filtrate from the scale-forming constituents should also be analyzed for iron, lime, and magnesia.

Cl in Water. Add to 100 cc. of the water two or three drops of 20 per cent solution of K_2CrO_4 and titrate with standard $AgNO_3$ solution to the faint reddish color due to silver chromate.

$$NaCl+AgNO_3=AgCl+NaNO_3,$$

$$2AgNO_3+K_2CrO_4=Ag_2CrO_4+2KNO_3.$$

Run a blank with 100 cc. of distilled water and a few drops of 20 per cent solution of potassium dichromate to determine how much $AgNO_3$ solution is required to produce the red color in the absence of Cl.

Total SO_3 in Water. Add to 100 cc. of the water 5 cc. of hydrochloric acid and 20 cc. $BaCl_2$ solution. (See p. 73.) Boil and let the solution stand in a warm place several hours. Filter, burn, and weigh $BaSO_4$, from which calculate the percentage of SO_3. The factor for SO_3 in $BaSO_4$ is 0.343.

NO_2 in Water. Sprengel's Color Method, modified by Gill.*

Reagents. *Phenoldisulphonic acid.* Mix 3 gms. of pure phenol (C_6H_5OH) with 37 gms. (20.1 cc.) of pure sulphuric acid (1.84) in a flask and heat six hours on a water bath at 100° C.

$$C_6H_5OH + 2H_2SO_4 = C_6H_3OH(SO_3H)_2 + 2H_2O.$$

If the acid crystallizes out on cooling, it will be redissolved when heated.

Standard potassium nitrate solution. Dissolve 2.197 gms. of KNO_3 in 1 liter of water. One cubic centimeter of the solution will contain 1 mgm. of NO_2. To avoid errors of measuring 1 cc. dilute 100 cc. to a liter and take out 10 cc. for the analysis. Place the 10 cc. in a small evaporating dish and treat it exactly in the manner described below for the sample of water.

NO_2. Take 5 cc. of the water, add to it enough pure silver sulphate to precipitate all the Cl from the water. Filter into a small porcelain dish and wash. Evaporate the filtrate on a steam bath until only a drop of water remains. Add 1 cc. of pure phenoldisulphonic acid and stir; add 7 cc. of distilled water and stir. Add an excess of ammonia (about 20 cc. of sp.gr. 0.96), dilute to 100 cc. with distilled water, and compare the solution in a colorimeter with a standard, similarly treated, or place the solution in a Nessler tube and match it with a standard.

$$C_6H_3OH(SO_3H)_2 + 3HNO_3 + 5NH_4OH = NH_4C_6H_2(NO_2)_3O \\ + 2(NH_4)_2SO_4 + 6H_2O.$$

Treating phenoldisulphonic acid with nitric acid and ammonia produces ammonium picrate, which gives the solution a distinctly yellow color.

Free CO_2 in Water. (Seyler's method.)

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* Tech. Quarterly, 7, 55.

Reagents. N/50 *solution of sodium carbonate.* Dissolve 1.06 gm. of freshly ignited Na_2CO_3 in freshly boiled water and dilute to 1 liter with cold water, free from air. This solution must be protected from the air.

Phenolphthalein solution. (See page 84.)

Measure 50 cc. of the water into a Nessler tube.

Add 25 to 30 drops of phenolphthalein solution and titrate with the standard sodium carbonate solution, stirring with a glass rod bent at the lower end into a circle at right angles to the rod.

The end-point is more easily detected if another Nessler tube containing water is placed alongside the tube containing the test.

TEMPORARY HARDNESS OF WATER

Reagents. N/10 *solution of hydrochloric acid.* Dilute 8 cc. of hydrochloric acid to 1 liter, test it against N/10 *sodium carbonate solution,* and correct it if necessary. (See the method below.)

Hydrochloric acid of 1.20 sp.gr. at 15° C. contains 469 gms. HCl per liter.

Measure 100 cc. of the water, add 5 drops of methyl orange solution and titrate with N/10 hydrochloric acid. At the same time, run a blank on 100 cc. of distilled water and 5 drops of methyl orange, titrating both to the same color.

PERMANENT HARDNESS OF WATER

Reagents. N/10 alkaline solution made of equal parts of *sodium, carbonate* and *sodium hydroxide* solution, as follows:

Make a N/10 solution of sodium hydroxide (4.0008 gms. NaOH per liter), and a N/10 solution of sodium carbonate (5.3 gms. Na_2CO_3 per liter). Take 25 cc. of each solution for the test.

Measure 200 cc. of the water into a platinum or porcelain dish, or a Jena flask (not ordinary glass). Add to it 50 cc. of N/10 alkaline solution (mixed Na_2CO_3 and NaOH solutions). Boil until the volume is reduced to a little less than 200 cc.

$$CaH_2(CO_3)_2+2NaOH=CaCO_3+Na_2CO_3+2H_2O$$
$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

$$MgH_2(CO_3)_2+4NaOH=Mg(OH)_2+2Na_2CO_3+2H_2O.$$
$$MgSO_4+2NaOH=Mg(OH)_2+Na_2SO_4.$$

Dilute with water to make the volume just 200 cc. when cold. Let the precipitate of calcium carbonate and magnesium hydroxide settle. Filter or siphon off 100 cc. of the clear solution.

If filtered, discard the first 50 cc. of the filtrate, since filter papers are usually not neutral.

Add 5 drops of methyl orange solution and titrate with N/10 hydrochloric acid, running a blank at the same time. The difference between the titration and 25 represents the amount of alkali used in the reactions above. Multiply this difference by 5 to give milligrams per 100,000 in terms of $CaCO_3$.*

SOFTENING WATER

Water is usually softened by adding lime and sodium carbonate. The lime precipitates calcium from solution as carbonate and the magnesium as hydroxide.

$$CaH_2(CO_3)_2+CaO=2CaCO_3+H_2O.$$
$$MgH_2(CO_3)_2+2CaO=2CaCO_3+Mg(OH)$$
$$MgSO_4+CaO+H_2O=CaSO_4+Mg(OH)_2.$$

The sodium carbonate precipitates calcium as carbonate.

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

* Procter, Jour. Soc. Chem. Ind., 23, 8.

To determine how much of these reagents to use, boil an accurately measured sample of the water with a measured volume of standard solution of $Ca(OH)_2$. Let it cool and settle; then filter and titrate the excess of $Ca(OH)_2$ with standard acid, as described above for permanent hardness.

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

Then add to the titrated solution a measured volume of a standard solution of sodium carbonate, boil, cool, settle, filter, and titrate the excess of Na_2CO_3 in the filtrate.

It must be kept in mind that the sodium carbonate reacts, not only with the sulphates originally in the water, but also with the $CaCl_2$ formed in the previous titration for the excess of lime, and the necessary correction must, therefore, be made.*

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

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* Drawe, Zeit. Angew. Chem., 23, 52.

DETECTION OF THE METALS

Aluminum is precipitated as white gelatinous hydroxide by ammonia. When the oxide is strongly heated on charcoal with cobalt nitrate a bright blue mass is obtained.

Antimony. When a small quantity of an antimony compound is heated in the upper reduction zone of a Bunsen burner on a thread of asbestos, the flame is given a bluish tinge and when a small porcelain basin filled with cold water is held above it, a brownish black deposit of metallic antimony is deposited upon the basin, and this is but slightly attacked by cold nitric acid and is insoluble in sodium hypochlorite. Arsenic gives a similar reaction, but arsenic gives a garlic-like odor during the reduction, and the metallic film is readily soluble in the hypochlorite. Antimony compounds may be obtained in solution by treating with HCl or by fusing first with potassium carbonate and potassium nitrate. Hydrogen sulphide produces in acid solution a very characteristic orange-red colored precipitate of antimony trisulphide.

Arsenic. Mix with sodium carbonate and heat on charcoal with the blowpipe. All arsenic compounds give a garlic odor.

Add to concentrated hydrochloric acid a few drops of an arsenite solution and half a cubic centimeter of saturated solution of stannous chloride in hydrochloric acid, warm, and the solution turns brown, then black.

Barium. The Bunsen flame is colored a yellowish-green tint when any volatile barium compound is brought into it.

Soluble barium salts are distinguished from those of strontium and calcium inasmuch as they are immediately precipitated by a solution of calcium sulphate.

Bismuth. On charcoal with soda, bismuth gives a very characteristic orange-yellow sublimate. Brittle globules of the metal are also reduced on the charcoal when treated with soda.

Hydrogen sulphide precipitates from solutions of bismuth salts a blackish brown sulphide (Bi_2S_3) insoluble in ammonium sulphide and easily soluble in nitric acid. Ammonia throws down a white basic salt insoluble in excess.

Cadmium. Cadmium is precipitated as a yellow sulphide by hydrogen sulphide. The sulphide is insoluble in ammonium sulphide and in the caustic alkalies. On charcoal with soda, compounds of cadmium give a characteristic sublimate of the reddish-brown oxide.

To test for cadmium in a sulphide, roast it to oxide, and reduce some of the oxide in the upper reducing flame of the Bunsen burner, at the same time holding a glazed porcelain dish which contains water just above the flame to receive a brown coating. To the brown coating add a drop of $AgNO_3$ solution; if Cd is present, black metallic silver will be deposited.

Caesium. H_2PtCl_6 produces a bright yellow crystalline precipitate, a brighter color than the potassium salt thus produced, and is much more soluble than the potassium salt. The flame test is reddish violet, similar to potassium.

Calcium. Calcium compounds moistened with hydrochloric acid and placed on a platinum wire in the hottest part of a Bunsen flame, impart a red color to the flame.

Calcium may be precipitated from solution as oxalate by first making the solution ammoniacal and then adding ammonium oxalate or oxalic acid.

Cerium. Fuse with sodium carbonate. Treat with dilute hydrochloric acid, evaporate to dryness and bake. Take up with dilute hydrochloric acid, filter. Add ammonia to the filtrate, filter. Dissolve the precipitate in hydrochloric acid, add ammonia and oxalic acid, filter. Dissolve the precipitate in concentrated hydrochloric acid, nearly neutralize with ammonia; add 1 cc. of hydrogen peroxide and then ammonia, drop by drop, until just alkaline. When just neutral, white thorium peroxide is precipitated; when ammoniacal, the orange cerium peroxide is precipitated.

Chromium. Chromium oxide is detected in its insoluble compounds by its characteristic green color. It forms an emerald-green head with borax or microcosmic salt. Caustic potash or soda gives a green precipitate in solutions of chromic salts. This dissolves in an excess of alkali in the cold, but is precipitated on boiling the solution. The detection of chromic acid is rendered easy by the bright yellow color of its salts. The yellow color of the normal chromates becomes red on the addition of an acid, and again yellow when made alkaline.

Cobalt. Ammonium sulphide produces a black precipitate (CoS) insoluble in acetic acid and in dilute hydrochloric acid.

Ammonium sulphocyanate produces a beautiful blue color, $Co(CNS)_2$.

With a borax bead cobalt gives the characteristic cobalt-blue color.

Columbium. Fuse with potassium bisulphate. Pulverize the fusion and treat it with hot water; then treat it with dilute hydrochloric acid. Digest the residue with ammonium sulphide to remove W, Sn, etc. Wash and treat again with dilute hydrochloric acid. The residue should be colorless and contain only silica and the oxides of columbium and tantalum. This residue in a bead of microcosmic salt is colorless if no columbium is present or if heated in the oxidizing flame; but if heated in the reducing flame, columbium imparts a violet color to the bead, or blue if saturated with oxide. Adding ferrous sulphate turns the bead blood red.

If, when the mixed oxides are boiled in dilute sulphuric acid with metallic zinc, the white precipitate turns intensely blue, and remains so on dilution, columbium is present; if it turns bluish gray and colorless on dilution, tantalum is predominant.

Copper. Copper can easily be detected by the reduction to the red metallic bead on charcoal before the blowpipe.

Copper compounds moistened with HCl color the non-luminous flame green.

An excess of ammonia added to a nitric acid solution of copper produces an azure-blue color.

Erbium. Erbium oxide heated on a platinum wire colors the flame distinctly green.

Gallium. If a neutral solution of gallium chloride be warmed with zinc, gallium oxide or basic salt separates but not the metal.

Germanium. Fuse with sulphur and sodium carbonate. Treat with hot water, filter, add a few drops of hydrochloric acid to the filtrate to precipitate white germanium sulphide. Filter and heat the residue in a current of hydrogen to reduce it to gray-black crystalline germanous sulphide. Dissolve the crystals in hydrochloric acid and pass hydrogen sulphide into the solution to precipitate reddish-brown germanous sulphide.

Glucinum. Ammonium carbonate produces a white precipitate, $GlCO_3$, soluble in an excess of the reagent; by boiling the solution it is precipitated as a basic carbonate.

Gold. Gold may be reduced from its ores on charcoal to a yellow malleable bead which is soluble in aqua regia; if the solution be dropped on filter paper and one drop of stannous chloride added, a purple-red color is produced.

Indium. Heated on charcoal before the blowpipe it colors the flame blue, and gives an incrustation of the oxide. It slowly dissolves in hydrochloric and dilute sulphuric acids, but readily in nitric acid.

Iridium. Ammonium chloride produces in a tolerably concentrated solution of iridium a dark-red crystalline precipitate. Iridium is distinguished from platinum by the formation of a colorless solution of potassium chloriridiate when caustic potash is added to the chloride of the metal, and on exposure to the air this colorless solution first becomes red colored and afterward blue.

Hydrogen sulphide precipitates brown iridium sulphide, which is soluble in ammonium sulphide.

Iron. Ferrous salts with potassium ferricyanide produce a dark-blue precipitate.

Ferric salts with ammonia or the fixed alkalies produce a brown precipitate.

Ferric salts with potassium or ammonium sulphocyanate produce a blood-red colored precipitate. Ferrous salts with a bead of microcosmic salt or borax is colored dark green. This color readily changes to yellow or reddish brown by oxidation.

Lead. With soda on charcoal a malleable globule of metallic lead is obtained from lead compounds; the coating has a yellow color near the assay.

In nitric acid solution dilute sulphuric acid gives a white precipitate of lead sulphate.

Lithium. In the Bunsen flame a fine carmine-red color is produced, visible if sodium is present by viewing the flame through cobalt glass.

Magnesium. To a solution of magnesium add ammonium chloride, ammonia, and sodium phosphate; a white precipitate ($MgNH_4PO_4$) forms. The action is hastened by rubbing the sides of the beaker with a glass rod.

Manganese. Ammonium sulphide produces a flesh-colored precipitate.

A solution containing traces of manganese boiled in concentrated nitric acid with lead peroxide or sodium bismuthate and allowed to settle gives a violet-red colored solution ($HMnO_4$).

The borax bead with manganese in the oxidizing flame gives an amethyst-colored bead, and this in the reducing flame becomes colorless.

Mercury. Stannous chloride heated with a solution of mercury precipitates gray metallic Hg.

Mercury compounds mixed with sodium carbonate and heated in a closed tube produce a gray mirror of metallic Hg.

Molybdenum. To a strong nitric acid solution of molybdenum add nearly enough ammonia to neutralize the acid and then add a few drops of sodium phosphate solution. A bright yellow crystalline precipitate forms when the solution is warmed.

A hydrochloric or sulphuric acid solution of molybdenum, to which zinc or stannous chloride is added, turns first blue, then green, and finally brown.

Neodymium. The didymium salts are violet and are identified by a characteristic absorption spectrum.

Nickel. Potassium cyanide produces a bright green precipitate, $Ni(CN)_2$.

When nickel compounds are heated with reducing agents before the blowpipe, an infusible magnetic powder is produced. If this powder is dissolved in a drop or two of dilute nitric acid and evaporated to complete dryness, a characteristic green stain is obtained which becomes yellow on further heating. Nickel compounds color the borax bead brownish yellow in the oxidizing flame, the bead becoming gray and opaque in the reducing flame, owing to the separation of the metallic nickel. Nickel is precipitated in alkaline solution by ammonium sulphide, which dissolves in an excess of ammonium sulphide, forming a dark-colored solution.

Osmium. It is dissolved in fuming nitric acid, or by fusing with sodium hydroxide and potassium nitrate and then treating with nitric acid and distilling. Osmic oxide (OsO_4), which sublimes at a moderately low temperature, passes over and condenses as a colorless crystalline mass. The osmic oxide has an odor similar to chlorine and is poisonous.

Palladium. Dissolve in nitric acid or aqua regia. Potassium iodide added produces a black precipitate, palladous iodide (PdI_2), soluble in an excess of the reagent, but not soluble in water, alcohol, or ether. Mercuric cyanide, $Hg(CN)_2$, produces a yellowish-white gelatinous precipitate, $Pd(CN)_2$, which, on ignition, leaves the spongy metal.

Platinum. When heated with sodium carbonate on charcoal, gray spongy metal is reduced. This, rubbed on a mortar with a pestle, gives a metallic luster and is insoluble in any single acid.

Potassium. A solution of H_2PtCl_6 added to concentrated solutions of potassium gives a yellow precipitate K_2PtCl_6. In the Bunsen flame potassium gives a violet color, visible if sodium also is present if viewed through cobalt glass.

Praseodymium. See Neodymium.

Radium. To the Bunsen flame a radium salt imparts an intense carmine-red color.

Radium rays discharge a charged eletroscope and may be used for making photographs on ordinary X-ray plates.

Rhodium. Before the blowpipe on charcoal with sodium carbonate the salts of rhodium are reduced to the metal, which is insoluble in aqua regai, but may be dissolved by fusing it with potassium pyrosulphate and then treating the fusion with water. By adding to this solution potassium hydroxide and a little alcohol the brown rhodium hydroxide is formed.

Rubidium. A solution of H_2PtCl_6 produces a white crystalline precipitate, Rb_2PtCl_6, which is less soluble than the corresponding potassium salt and more soluble than the caesium salt.

The flame test gives a color similar to the caesium test.

Ruthenium. Ruthenium is practically insoluble in all acids and in aqua regia. Fuse it with potassium hydroxide and potassium nitrate. The resulting K_2RuO_4 heated with NaCl in a current of chlorine yields soluble K_2RuCl_6. The greenish-black fusion treated with water yields an orange-yellow solution, which stains the skin black.

Scandium. A hydrochloric acid solution of scandium treated with solid sodium silicofluoride and boiled thirty minutes gives a precipitate containing scandium free from the rare earth metals.

Silver. When fused with sodium carbonate on charcoal before the blowpipe, a bright metallic silver bead is produced, which may be dissolved in nitric acid and precipitated from the solution by hydrochloric acid as a curdy precipitate of silver chloride, or, if only a trace of silver is present, as a mere opalescence.

Sodium. To a neutral or weakly alkaline solution add potassium pyroantimonate, $K_2H_2Sb_2O_3$, and a heavy white crystalline precipitate, $Na_2H_2Sb_2O_3$, is quickly formed by rubbing the sides of the beaker with a glass rod.

Solutions of sodium on a platinum wire in a Bunsen flame give a yellow color.

Strontium. Solutions on a platinum wire color the Bunsen flame carmine red.

Strontium sulphate is less soluble than calcuim sulphate, but more soluble than barium sulphate.

Tantalum. See Columbium.

Thallium. Dissolve in dilute acid, add H_2S, filter. Add to the filtrate ammonium sulphide, and filter. If thallium is present in the precipitate it will color the Bunsen flame emerald green.

Thorium. Fuse in a platinum crucible with sodium carbonate. Cool, dissolve in water and hydrochloric acid. Evaporate to dryness and bake. Take up with dilute hydrochloric acid, filter. Add ammonia to the filtrate, filter. Dissolve the precipitate in hydrochloric acid; reprecipitate with oxalic acid, filter, ignite the residue. Dissolve in hydrochloric acid. Evaporate to dryness. Take up with water. Add an excess of sodium thiosulphate and boil to precipitate.

Tin. Mercuric chloride added to a solution of a stannous salt precipitates white mercurous chloride.

A trace of stannous chloride in solution added to a solution of gold chloride precipitates finely divided gold, brown by transmitted light and bluish green by reflected light.

Metallic zinc precipitates tin from solution as a spongy mass, which adheres to the zinc.

Heat the ore on charcoal with sodium carbonate or potassium cyanide; a metallic bead is produced which is coated with white oxide when the flame is removed.

Casserite in lumps in a test-tube with metallic zinc and dilute sulphuric acid is soon coated with metallic tin.

Titanium. Titanium sulphate with hydrogen peroxide in a slightly acid solution produces an orange-red color, or a clear yellow with small amounts of titanium. Vanadic acid with hydrogen peroxide produces a similar effect.

Tin or zinc in hydrochloric acid solutions of titanium produces a violet color, Ti_2Cl_2.

Tungsten. Treat with hydrochloric and nitric acids (4 : 1) and take to dryness, wash by decantation, add dilute hydrochloric acid and metallic zinc, aluminum, or tin and shake; a fine blue coloration or precipitate is produced, W_2O_5; the color disappears when diluted with water.

Fuse in platinum with potassium bisulphate, digest with a solution of ammonium carbonate, filter, add to the filtrate a few drops of $SnCl_2$ solution, acidify with hydrochloric acid, warm gently; a fine blue color is produced.

The microcosmic salt bead made in the reducing flame is clear blue; if iron is also present, the bead will be red-brown. In the oxidizing flame the bead is colorless.

Uranium. Potassium ferrocyanide produces a brown precipitate, in dilute solution a brownish-red coloration.

The borax (or microcosmic salt) bead is yellow in the oxidizing flame and green in the reducing flame.

Vanadium. Vanadium compounds can be dissolved by a treatment with acids or alkalies. The hydrochloric acid solution assumes a bright blue color on addition of zinc. A solution of hydrovanadic sulphate cannot be distinguished in color from one of copper sulphate when sufficiently diluted with water, but, of course, does not become colorless in the presence of metallic iron.

Solutions of certain vanadates also closely resemble solutions of the chromates. For instance, a solution of the tetravanadate of potassium, $K_2V_4O_{11}$, does not differ in appearance from one of potassium dichromate. They may, however, be distinguished from one another, since the vanadate solution becomes blue and the chromate assumes a green color on deoxidation. When a solution of vanadic acid or an acid solution of an alkali vanadate is shaken up with ether containing hydrogen peroxide, the aqueous solution assumes a red color like that of ferric acetate. This reaction serves to detect one part of vanadic acid in 4000 parts of the liquid. Chromic acid does not interfere with the reaction.

Yttrium. Extract the yttrium in the manner described under Cerium and separate it from the other rare earths in a solution of their sulphates by adding a saturated solution of potassium sulphate. Yttrium sulphate is soluble; the others are not.

Zinc. Ammonium sulphide precipitates ZnS. Potassium ferrocyanide produces a white precipitate, $Zn_2Fe(CN)_6$. Before the blowpipe on charcoal with sodium carbonate a coating of oxide is produced which is yellow while hot and white when cold. With cobalt nitrate on charcoal an infusible green mass is produced.

Zirconium. Treat with dilute sulphuric acid (2 : 1), filter, add ammonia to the cold filtrate, filter; wash, dissolve the precipitate in hydrochloric acid, evaporate to dryness. Take up with a little water and add to the cold saturated solution hydrochloric acid, drop by drop; if zirconium is present, the oxychloride will be precipitated. Heat to dissolve the precipitate. Cool and after some time fine silky needles of $ZrOCl_2+8H_2O$ will precipitate.

PROPERTIES OF THE ELEMENTS

	Symbol.	Atomic Weight.	Melting-point.	Boiling-point. 760 mm.	Density at Ordinary Temp. unless otherwise Stated.
Aluminum.........	Al	27.1	658.7	1800	2.65
Antimony.........	Sb	120.2	630	1440	6.62
Argon.............	A	39.88	−188	−186	liq. −185° 1.4
Arsenic............	As	74.96	850?	Sublimes 450	5.73
Barium...........	Ba	137.37	850	....	3.75
Bismuth...........	Bi	208.0	271	1420	9.80
Boron.............	B	11.0	2200–2500	Sublimes 3500?	2.5?
Bromine...........	Br	79.92	−7.3	63	25° 3.102
Cadmium.........	Cd	112.40	320.9	778	8.64
Caesium...........	Cs	132.81	26	670	1.87
Calcium...........	Ca	40.07	810	....	29° 1.55
Carbon............	C	12.00	> 3600	....	Diamond 3.52 Graphite 2.3
Cerium............	Ce	140.25	640	....	6.68
Chlorine...........	Cl	35.46	−101.5	−33.6	liq. 0° 2.49
Chromium.........	Cr	52.0	1510	2200	6.50
Cobalt............	Co	58.97	1490	....	8.6
Columbium (Niobium)......	Cb	93.5	2200?	....	12.75
Copper............	Cu	63.57	1083	2310	8.93
Dysprosium.......	Dy	162.5			
Erbium...........	Er	167.7	....	....	4.77?
Europium.........	Eu	152.0			
Fluorine..........	F	19.0	−223	−187	liq. −187 1.11?
Gadolinium........	Gd	157.3			

PROPERTIES OF THE ELEMENTS—*Continued*

	Symbol.	Atomic Weight.	Melting-point.	Boiling-point. 760 mm.	Density at Ordinary Temp. unless otherwise Stated.
Gallium	Ga	69.9	30	....	5.95
Germanium	Ge	72.5	958	....	5.47
Glucinum (Beryllium)	Gl	9.1	> 1800?	....	1.93
Gold	Au	197.2	1063	2530?	19.32
Helium	He	3.99	< −271	−268.6	
Holmium	Ho	163.5			
Hydrogen	H	1.008	−259	−252.7	
Indium	In	114.8	155	1000?	7.12
Iodine	I	126.92	113.5	184.4	4.95
Iridium	Ir	193.1	2300?	2550?	22.41
Iron	Fe	55.84	1520	2450	7.86
Krypton	Kr	82.92	−169	−151.7	liq. 2.16
Lanthanum	La	139.0	810?	....	6.12
Lead	Pb	207.10	327.4	1525	11.37
Lithium	Li	6.94	186	> 1400	.534
Lutecium	Lu	174.0			
Magnesium	Mg	24.32	651	1120	1.74
Manganese	Mn	54.93	1225	1900	7.39
Mercury	Hg	200.6	−38.7	356.7	13.56
Molybdenum	Mo	96.0	2500?	3200?	8.6
Neodymium	Nd	144.3	840?	....	6.96
Neon	Ne	20.2	−253?	−239	
Nickel	Ni	58.68	1452	2330?	8.9
Niton (radium emanation)	Nt	222.4			
Nitrogen	N	14.01	−210	−195.7	
Osmium	Os	190.9	2700?	....	22.5
Oxygen	O	16.00	−218	−182.9	
Palladium	Pd	106.7	1549	2540	11.4
Phosphorus	P	31.04	44	287	Yellow 1.83 Red 2.20
Platinum	Pt	195.2	1755	2450?	21.50
Potassium	K	39.10	62.3	758	.862
Praseodymium	Pr	140.6	940?	....	6.48

PROPERTIES OF THE ELEMENTS—*Continued*

	Symbol.	Atomic Weight.	Melting-point.	Boiling-point. 760 mm.	Density at Ordinary Temp. unless otherwise Stated.
Radium...........	Ra	226.4			
Rhodium..........	Rh	102.9	1940	2500?	12.44
Rubidium.........	Rb	85.45	38	696	1.532
Ruthenium........	Ru	101.7	> 1950	2520?	12.3
Samarium.........	Sa	150.4	1300–1400	....	7.8
Scandium.........	Sc	44.1			
Selenium.........	Se	79.2	217–220	690	4.8
Silicon............	Si	28.3	1420	3500?	2.3
Silver..............	Ag	107.88	960.5	1955	10.5
Sodium............	Na	23.00	97.5	877	.971
Strontium.........	Sr	87.63	....	....	2.54
Sulphur...........	S	32.07	S_I 112.8 S_{II} 119.2 S_{III} 106.8	444.7	2.07 1.96 1.92
Tantalum.........	Ta	181.5	2850	....	16.6
Tellurium.........	Te	127.5	452	1390	6.25
Terbium..........	Tb	159.2			
Thallium..........	Tl	204.0	302	1280?	11.9
Thorium..........	Th	232.4	> 1700	....	11.3
Thulium..........	Tm	168.5			
Tin................	Sn	119.0	231.9	2270	7.29
Titanium..........	Ti	48.1	1900?	....	3.54
Tungsten..........	W	184.0	3000	3700?	17–18 8
Uranium..........	U	238.5	....	....	18.7
Vanadium.........	V	51.0	1730?	....	5.5
Xenon............	Xe	130.2	−140	−109	
Ytterbium (Neoytterbium)..	Yb	172.0			
Yttrium...........	Yt	89.0	....	.. ..	3.8?
Zinc..............	Zn	65.37	419.4	918	7.1
Zirconium.........	Zr	90.6	1700?	....	4.15

TABLE OF FACTORS

Sought.	Found.	Factor.	Log.
Ag	AgCl	0.7526	87,656
Al	Al_2O_3	0.5303	72,455
	$AlPO_4$	0.22187	34,610
Al_2O_3	$AlPO_4$	0.41873	62,193
Ba	$BaSO_4$	0.58846	76,972
BaO	$BaSO_4$	0.65699	81,756
Bi	BiOCl	0.8017	90,401
C	CO_2	0.27273	43.573
($BaCO_3$)	$BaSO_4$	0.05154	71,214
	$BaCO_3$	0.06080	78,390
CaO	$CaSO_4$	0.4118	61,469
$CaCO_3$	CaO	1.7847	25,156
Cl	AgCl	0.2474	39,340
Fe	Fe_2O_3	0.6994	84,472
FeO	Fe	1.2865	10,942
Fe_2O_3	Fe	1.4298	15,527
K_2O	KCl	0.6317	80,051
	K_2PtCl_6	0.19376	28,727
KCl	K_2PtCl_6	0.30674	48,676
MgO	$Mg_2P_2O_7$	0.3621	55,879
Li_2O	Li_2SO_4	0.27176	43,418
Na_2O	NaCl	0.53028	72,450
Ni	NiO	0.78576	89,529
P	$Mg_2P_2O_7$	0.27873	44,518
P_2O_5	$Mg_2P_2O_7$	0.6379	80,475
Pb	$PbSO_4$	0.6831	83,449
S	$BaSO_4$	0.13738	13,793
SO_3	$BaSO_4$	0.34300	53,529
Si	SiO_2	0.46932	67,147
Sn	SnO_2	0.78808	89,657
Sr	$SrSO_4$	0.47703	67,855
SrO	$SrSO_4$	0.5641	75,136
Ti	TiO_2	0.60051	77,852
W	WO_3	0.7931	89,933

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	13	17	21	25	29	33	38
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Table of Factors for Correcting the Volumes of Gas to Standard Conditions of 62° F. and 30″ Mercury.*

	BAROMETER IN INCHES OF MERCURY.																				
TEMPERATURE IN DEGREES FAHRENHEIT.	28.5	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
40	992	995	999	1002	1006	1009	1013	1016	1020	1023	1027	1030	1034	1037	1041	1044	1047	1051	1054	1058	1061
41	990	993	997	1000	1004	1007	1011	1014	1018	1021	1025	1028	1032	1035	1039	1042	1045	1049	1052	1056	1060
42	988	991	995	998	1002	1005	1009	1012	1016	1019	1022	1026	1030	1033	1036	1040	1043	1047	1050	1054	1057
43	986	989	993	996	1000	1003	1007	1010	1013	1017	1020	1024	1027	1031	1034	1038	1041	1045	1048	1052	1055
44	984	988	991	994	998	1001	1005	1008	1012	1015	1019	1022	1026	1029	1032	1036	1039	1043	1046	1050	1053
45	982	986	989	992	996	999	1003	1006	1010	1013	1017	1020	1023	1027	1030	1034	1037	1041	1044	1048	1051
46	980	984	987	990	994	997	1001	1004	1008	1011	1015	1018	1021	1025	1028	1032	1035	1039	1042	1045	1049
47	978	982	985	989	992	996	999	1002	1006	1009	1013	1016	1020	1023	1026	1030	1033	1037	1040	1044	1047
48	976	980	983	986	990	993	997	1000	1004	1007	1010	1014	1017	1021	1024	1028	1031	1034	1038	1041	1045
49	974	978	981	985	988	992	995	998	1002	1005	1009	1012	1015	1019	1022	1026	1029	1033	1036	1039	1043
50	972	976	979	983	986	989	993	996	1000	1003	1007	1010	1013	1017	1020	1024	1027	1030	1034	1037	1041
51	970	974	977	981	984	987	991	994	998	1001	1004	1008	1011	1015	1018	1022	1025	1028	1032	1035	1039
52	969	972	976	979	982	986	989	992	996	999	1003	1006	1010	1013	1016	1020	1023	1026	1030	1033	1037
53	967	970	973	977	980	984	987	990	994	997	1001	1004	1007	1011	1014	1018	1021	1024	1028	1031	1035
54	965	968	972	975	978	982	985	988	992	995	999	1002	1005	1009	1012	1016	1019	1022	1026	1029	1032
55	963	966	970	973	977	980	983	987	990	993	997	1000	1004	1007	1010	1014	1017	1020	1024	1027	1031
56	961	964	968	971	975	978	981	985	988	991	995	998	1001	1005	1008	1012	1015	1018	1022	1025	1028
57	959	963	966	969	973	976	980	983	986	990	993	996	1000	1003	1006	1010	1013	1016	1020	1023	1027
58	957	961	964	967	971	974	977	981	984	988	991	994	998	1001	1004	1008	1011	1014	1018	1021	1025
59	956	959	962	966	969	972	976	979	982	986	989	992	996	999	1003	1006	1009	1013	1016	1019	1023
60	954	957	960	964	967	970	974	977	980	984	987	990	994	997	1000	1004	1007	1010	1014	1017	1021
61	952	955	959	962	965	969	972	975	979	982	985	989	992	995	999	1002	1005	1009	1012	1015	1019
62	950	953	957	960	963	967	970	973	977	980	983	987	990	993	997	....	1003	1007	1010	1013	1017
63	948	952	955	958	962	965	968	971	975	978	981	985	988	991	995	998	1001	1005	1008	1011	1015
64	946	950	953	956	960	963	966	970	973	976	980	983	986	990	993	996	1000	1003	1006	1009	1013
65	944	948	951	954	958	961	964	968	971	974	978	981	984	988	991	994	998	1001	1004	1007	1011
66	943	946	949	953	956	959	963	966	969	973	976	979	982	986	989	992	996	999	1002	1006	1009
67	941	944	948	951	954	958	961	964	967	971	974	977	981	984	987	991	994	997	1001	1004	1007
68	939	942	946	949	952	956	959	962	965	969	972	975	979	982	985	989	992	995	998	1002	1005
69	937	941	944	947	951	954	957	960	964	967	970	974	977	980	983	987	990	993	997	1000	1003

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* J.M.Camp. Met. and Chem. Eng. 9. 358.

Table of Factors for Correcting the Volumes of Gas to Standard Conditions of 62° F. and 30″ Mercury—Continued.

TEMPERATURE IN DEGREES FAHRENHEIT.	BAROMETER IN INCHES OF MERCURY.																				
	28.5	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
70	936	939	942	946	949	952	955	959	962	965	968	972	975	978	982	985	988	991	995	998	1001
71	934	937	940	944	947	950	954	957	960	963	967	970	973	977	980	983	986	990	993	996	999
72	932	936	939	942	945	949	952	955	958	962	965	968	971	975	978	981	985	988	991	994	998
73	930	933	937	940	943	947	950	953	956	960	963	966	969	973	976	979	982	986	989	992	996
74	929	932	935	938	942	945	948	951	955	958	961	964	968	971	974	977	981	984	987	990	994
75	927	930	933	937	940	943	946	950	953	956	959	963	966	969	972	976	979	982	985	989	992
76	925	928	932	935	938	941	945	948	951	954	958	961	964	967	971	974	977	980	984	987	990
77	923	927	930	933	936	940	943	946	949	953	956	959	962	966	969	972	975	978	982	985	988
78	922	925	928	931	935	938	941	944	948	951	954	957	960	964	967	970	973	977	980	983	986
79	920	923	926	929	933	936	939	943	946	949	952	955	959	962	965	968	972	975	978	981	985
80	918	921	925	928	931	934	938	941	944	947	950	954	957	960	963	967	970	973	976	979	983
81	917	920	923	926	929	933	936	939	942	945	949	952	955	958	962	965	968	971	974	978	981
82	915	918	921	924	928	931	934	937	941	944	947	950	953	957	960	963	966	969	973	976	979
83	913	916	920	923	926	929	932	936	939	942	945	948	952	955	958	961	964	968	971	974	977
84	911	915	918	921	924	927	931	934	937	940	943	947	950	953	956	959	963	966	969	972	975
85	910	913	916	919	922	926	929	932	935	938	942	945	948	951	954	958	961	964	967	970	974
86	908	911	915	918	921	924	927	930	934	937	940	943	946	950	953	956	959	962	965	969	972
87	907	910	912	916	919	922	926	929	931	935	938	942	945	948	951	954	957	961	964	967	970
88	905	908	911	914	918	921	924	927	930	933	937	940	943	946	949	952	956	959	962	965	968
89	903	906	909	913	916	919	922	925	929	932	935	938	941	944	948	951	954	957	960	963	967
90	901	905	908	911	914	917	920	924	927	930	933	936	939	943	946	949	952	955	958	962	965
91	900	903	906	909	913	916	919	922	925	928	932	935	938	941	944	947	951	954	957	960	963
92	898	901	905	908	911	914	917	920	924	927	930	933	936	939	942	946	949	952	955	958	961
93	897	900	903	906	909	912	915	919	922	925	928	931	934	937	941	944	947	950	953	956	960
94	895	898	901	904	907	911	914	917	920	923	926	929	933	936	939	942	945	948	951	955	958
95	893	897	900	903	906	909	912	915	919	922	925	928	931	934	937	940	944	947	950	953	956
96	892	895	898	901	904	907	911	914	917	920	923	926	929	932	936	939	942	945	948	951	954
97	890	893	896	900	903	906	909	912	915	918	921	925	928	931	934	937	940	943	946	949	953
98	889	892	895	898	901	904	907	910	914	917	920	923	926	929	932	935	939	942	945	948	951
99	887	890	893	896	899	902	906	909	912	915	918	921	924	927	930	934	937	940	943	946	949
100	885	889	892	895	898	901	904	907	910	913	917	920	923	926	929	932	935	938	941	945	948

HYDROCHLORIC ACID—DENSITY

Table showing the approximate quantities of hydrochloric acid (sp.gr. 1.20), and water required to make 1 liter of any desired density at 15° C., and also the weight of HCl per liter for each density.

Density.	Cubic Centimeters Required for 1 Liter.		Grams HCl in 1 Liter.*
	HCl 1.20.	Water, Approx.	
1.01	50	950	22
1.02	100	900	42
1.03	150	850	64
1.04	200	800	85
1.05	250	750	107
1.06	300	700	129
1.07	350	650	152
1.08	400	600	174
1.09	450	550	197
1.10	500	500	220
1.11	550	450	243
1.12	600	400	267
1.13	650	350	291
1.14	700	300	315
1.15	750	250	340
1.16	800	200	366
1.17	850	150	392
1.18	900	100	418
1.19	950	50	443
1.20	1000	...	469

* Lunge and Marchlewski, 1891.

SULPHURIC ACID—DENSITY

Table showing the approximate quantities of sulphuric acid (sp.gr. 1.84), and water required to make 1 liter of any desired density at 15° C., and also the weight of H_2SO_4 per liter for each density.

Density.	Cubic Centimeters Required for 1 Liter.		Grams * H_2SO_4 in 1 Liter.	Density.	Cubic Centimeters Required for 1 Liter.		Grams H_2SO_4 in 1 Liter.
	H_2SO_4 1.84.	Water.			H_2SO_4 1.84.	Water.	
1.02	18	987	31	1.44	443	624	779
1.04	35	976	62	1.46	465	604	817
1.06	53	960	93	1.48	487	584	856
1.08	71	949	125	1.50	509	564	896
1.10	90	934	158	1.52	532	540	936
1.12	108	921	191	1.54	555	521	977
1.14	126	908	223	1.56	575	502	1015
1.16	146	891	257	1.58	598	479	1054
1.18	166	874	292	1.60	621	457	1096
1.20	186	858	328	1.62	646	432	1139
1.22	207	839	364	1.64	671	406	1181
1.24	227	822	400	1.66	695	382	1222
1.26	247	805	435	1.68	720	356	1267
1.28	268	786	472	1.70	745	329	1312
1.30	290	767	510	1.72	772	298	1357
1.32	312	746	548	1.74	798	271	1404
1.34	333	726	586	1.76	823	245	1451
1.36	354	709	624	1.78	854	208	1504
1.38	376	688	662	1.80	893	157	1564
1.40	399	665	702	1.82	932	105	1639
1.42	421	645	740	1.84	1000	...	1759

* Lunge and Isler, 1895.

NITRIC ACID—DENSITY

Table showing the quantities of nitric acid (sp.gr. 1.42), and water required to make 1 liter of any desired density at 15° C., and also the weight of HNO_3 per liter for each density.

Density, sp.gr.	Cubic Centimeters Required for 1 Liter.		Grams * HNO_3 in 1 Liter.	Density, sp.gr.	Cubic Centimeters Required for 1 Liter.		Grams HNO_3 in 1 Liter.
	HNO_3 1.42.	Water.			HNO_3 1.42.	Water.	
1.01	19	983	19	1.22	434	605	430
1.02	38	966	38	1.23	456	584	452
1.03	57	949	57	1.24	479	562	475
1.04	76	932	75	1.25	503	538	499
1.05	95	915	94	1.26	527	514	521
1.06	114	898	113	1.27	550	491	545
1.07	133	881	132	1.28	573	468	568
1.08	152	864	151	1.29	598	442	592
1.09	171	847	170	1.30	623	417	617
1.10	190	830	188	1.31	649	389	643
1.11	209	813	207	1.32	675	362	669
1.12	229	795	227	1.33	701	334	695
1.13	248	777	246	1.34	732	302	725
1.14	268	759	266	1.35	761	271	754
1.15	288	741	286	1.36	790	239	783
1.16	309	722	306	1.37	822	203	814
1.17	329	704	326	1.38	854	168	846
1.18	350	684	347	1.39	888	129	880
1.19	370	665	367	1.40	922	90	914
1.20	391	646	388	1.41	961	45	953
1.21	412	626	409	1.42	1000	...	991

* Lunge and Rey, 1891.

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