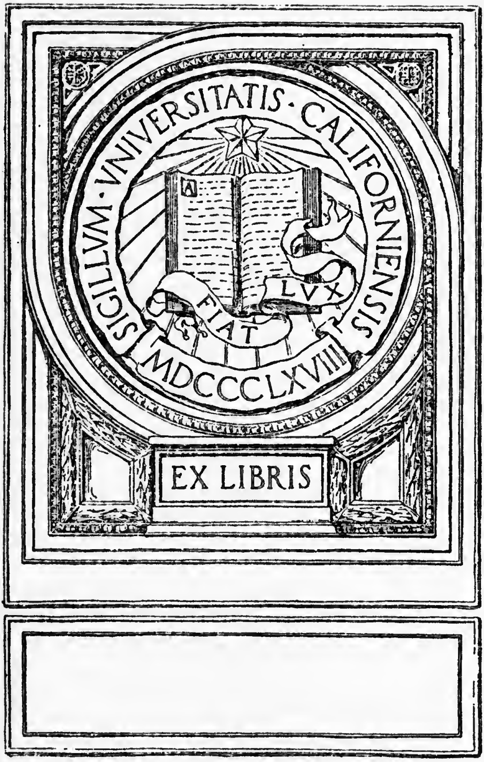

THE CHEMICAL ANALYSIS OF STEEL-WORKS' MATERIALS

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BY

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BREARLEY AND IBBOTSON'S "ANALYSIS OF STEEL WORKS' MATERIALS"

WITH DIAGRAMS

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PREFACE

SINCE the publication of *The Analysis of Steel-Works' Materials* in 1902, quite a number of text-books on pyrometry and microscopy have appeared, in response to the rapid growth and development of these highly important branches of metallurgy. This little volume, therefore, purports to be a new and revised edition, long overdue, of that section only of the work referred to, which treated of the analytical chemistry of the raw materials and finished products of ferrous metallurgy.

Compiled at infrequent intervals, and under difficult circumstances, its defects are doubtless not few, and none the less because the author's esteemed friend, Harry Brearley, was unable to collaborate in its production.

The author gratefully acknowledges the assistance of Drs. L. Aitchison and F. C. Thompson, and of Messrs. B. W. Methley, F.I.C., S. G. Clark, T. F. Russell, and E. V. Nicholson.

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PART I. GENERAL PROCESSES AND MISCELLANEOUS NOTES.

REAGENTS.

In the following pages the expression ‘hydrochloric acid’ refers to the concentrated aqueous solution of hydrogen chloride of spec. grav. 1·21. The terms ‘nitric acid’ and ‘sulphuric acid’ refer to the liquids of spec. grav. 1·42 and 1·84 respectively. ‘Acetic acid’ refers to the B.P. preparation containing approximately 33 per cent. of the pure acid. ‘Hydrofluoric acid’ is used to describe the aqueous solution of hydrogen fluoride; the solution should leave no residue on evaporation to dryness. ‘Ammonium hydrate’ is used to indicate the strong aqueous solution of ammonia of spec. grav. 0·880.

The strength of more dilute solutions of the above reagents is indicated in the context; when it is expressed as a percentage, the composition by volume is to be understood.

Nitric acid of spec. grav. 1·2 is obtained by mixing approximately 9 volumes of the strong acid with 13 volumes of water.

‘Ammonium acetate’ describes the solution obtained by the neutralisation of acetic acid with ammonium hydrate, each of the strength indicated above; the proportions are approximately 3 volumes acid, 1 volume alkali. ‘Sulphurous acid’ is made by saturating water with sulphur dioxide delivered from a syphon of the liquefied gas.

SEPARATIONS OF IRON FROM OTHER METALS.

The number of metals which occur in steel, and which, in the majority of cases have been purposely added, is large, and embraces nearly all the common ones which fall into the same group as iron itself in the ordinary schemes of qualitative analysis. Although methods for their estimation involving no separation from iron are applicable in many cases, separations frequently must be made. The most suitable methods of separation for each particular element are indicated in their respective places in the following pages, but as some are of a general character, affecting groups of metals rather than individual members, an account of them is introduced at the outset.

In the analysis of steel, the separation of iron from another metal is generally that of a very large amount of it from a small amount of the other metal. A separation which carries the iron into the filtrate from a precipitate containing the other metal is therefore usually not only easier of manipulation, but also more accurate than its converse, in which adsorption, for instance, is given full play by the large volume of the precipitated compound of iron. The latter form is nevertheless frequently used, and quite satisfactory results are obtained, *e.g.*, in the 'Basic Acetate' separation, without resorting to the repetition of the precipitation which is so often recommended.

Separations by means of Ammonium Hydrate.—Ammonium hydrate, added in excess to solutions of ferric iron, aluminium, and chromium, precipitates these metals quantitatively as hydroxides, and, after the previous addition of ammonium chloride, is the reagent commonly employed in qualitative analysis for separating them from manganese, zinc, nickel and cobalt. The latter, with the exception of zinc, are all used in the manufacture of steel for various purposes, and this method of separation is still used by works' chemists, since it is capable of quantitative application.

The difficulty in the way of an accurate separation is due to adsorption by the precipitate of salts that should pass into the filtrate. The amount of adsorbed substance is obviously dependent upon the volume of solid matter constituting the precipitate; it is not so obvious why the means adopted for the prevention of adsorption actually do so.

One of these is the introduction of ammonium salts, and most commonly, the chloride; the sulphate, oxalate, borate, etc., have also been suggested and used, and their action has been attributed to the formation in the solution of double salts of ammonium and the metal. The loss by adsorption and the comparative values of three ammonium salts as correctives are shewn in the following specific case. In each test a solution containing one gram of ferric iron and one decigram of nickel, was treated with the same excess of ammonium hydrate in the presence of the ammonium salt obtained by neutralising 50 c.c. of ammonium hydrate s.g. 0·880.

Ammonium Salt.	Grm. Nickel in filtrate.
Chloride - - -	0·0607
Nitrate - - -	0·0584
Sulphate - - -	0·0573
None - - -	0·0083

The yields are improved by increasing the amount of ammonium salt until, in the particular case of nickel, they become quantitative. For instance, a method still practised in the determination of nickel in steels, chiefly because the separation of the iron provides in the filtrate an electrolyte very suitable for the deposition of the nickel, consists in running the solution (from one gram of steel) in drops, from a funnel provided with a tap, into an excess of ammonium hydrate in which have been dissolved 8 to 10 grams of ammonium sulphate, whilst the latter solution is briskly stirred or shaken. The mixture is then made up to a definite volume, and a suitable fraction of the filtrate electrolysed.

The results given above for nickel are typical also of the behaviour of cobalt-ammonium and manganese-ammonium salts in the prevention of adsorption effects.

A more striking example is provided by the so-called double cyanides with potassium of nickel and cobalt. Thus Brearley found that a perfect separation of one decigram of nickel from one gram of ferric iron can be made when very little more potassium cyanide is present than is required to form the compound $K_2Ni(CN)_4$. The amount of this was 66·4 c.c. of the solution used, and the following results were obtained when the iron-nickel mixture containing the cyanide was poured into an excess of ammonium hydrate.

C.c. KCN used.	Grm. Ni recovered.
70	0·0999
100	0·0998
150	0·0999

In these tests the nickel was determined cyanometrically. The filtrate is not a suitable solution from which to deposit nickel electrolytically, but the metal can be determined gravimetrically, after boiling with an excess of hydrochloric acid, by precipitation with bromine and potassium hydroxide. If potassium cyanide of known strength is used, it is quite easy to estimate the excess in an aliquot part of the filtrate by means of silver nitrate and potassium iodide. In this form the process is the most rapid of all those in use for the estimation of nickel and which involve a separation of the iron. Taking care always to dissolve in the same amount of acid, and to use reagents of known strength, the operations may be concluded in the same time as is needed to make a colour carbon test on the furnace stage, and as the process is not influenced by the presence of chromium, it is well suited to the circumstances under which such tests are required.

The cyanometric assay is not suitable for the determination of cobalt (*q.v.*).

Another factor which determines the amount of adsorbed salt is the degree of alkalinity of the solution, particularly in the absence of an electrolyte. If hydrochloric acid be added cautiously and with constant stirring, to the mixture obtained by adding an excess of ammonium hydrate to a solution of ferric and nickel chlorides, until the liquid is rendered just acid, the adsorbed nickel salt passes into solution again before the ferric hydrate is appreciably attacked. Similarly, when the iron is precipitated by using so little ammonium hydrate that the filtrate is faintly acid, the separation is good ; this is, in fact, the principle of the well known Schwarzenberg separation.

The least troublesome way of precipitating the iron with so little ammonium hydrate that the solution still remains distinctly acid is as follows : The acid solution of the iron and nickel is heated to boiling ; at this temperature the ferric hydrate first precipitated is easily dissolved by the ferric chloride, and very little time is lost in obtaining a turbid solution, which, however, does not hold any filtrable precipitate, and is really obtained with less ammonia or ammonium carbonate than would be needed to form a lasting precipitate in the cold solution. From this point a solution of ammonium carbonate only should be used, and when the total amount of ammonia added is equal to or somewhat less in amount than would have been needed to form a permanent precipitate if the addition had been made to the cold solution, the iron is precipitated. The operation requires considerable care and attention, but is not otherwise a difficult one ; its success depends entirely on keeping the solution acid throughout, for if the solution be ever so slightly alkaline the separation is imperfect.

Appended are examples of separations : made as above (II.) ; in the same way, but adding 2 or 3 c.c. acetic acid after precipitating (I. and IV.) ; as in II., but adding a few c.c. acetic acid before precipitating (III.). The process could be advantageously modified in various other ways.

	Present.		Found.
	Grms. Fe.	Grms. Ni.	Grms. Ni.
I.	1	0·20	0·1999
II.	1	·10	0·0998
III.	1	·05	0·0497
IV.	2	·10	0·1002
V.	2	·03	0·0298

In all forms of the separation by means of ammonium hydrate the precipitated hydroxides of iron, aluminium, and chromium, contain, wholly or in part, the following metals, if present in the original solution:—zirconium, uranium, vanadium, titanium, molybdenum and tungsten.

The ‘ Barium Carbonate ’ Separation.—The separation of iron (ferric), aluminium and chromium from manganese, nickel, etc., by means of barium carbonate and similar reagents depends upon the fact that the salts of the former are much more easily hydrolysed than those of the latter. The substitution of hydroxyl for chlorine which may be represented by :— $FeCl_3 + HOH \rightarrow Fe(OH)Cl_2 + HCl$

takes place readily on the gradual addition of an alkali or alkaline carbonate to a cold solution of ferric chloride, and is referred to at greater length in the section immediately following. Complete hydrolysis, however, according to the equation :—

$$FeCl_3 + 3H.OH \rightarrow Fe(OH)_3 + 3HCl$$

is impossible without the assistance of a hydrolytic agent other than water. The reaction is, in fact, reversible, and, as in all such reactions, a condition of equilibrium is reached which depends upon the relative proportions of the reacting substances. Dilute solutions of ferric salts are obviously hydrolysed to a greater extent than when concentrated, and salts of weak acids to a greater extent than those of the strong ones. Temperature also is of considerable influence; the separation of the trivalent from the bivalent metals of the same group depends, in fact, upon the circumstance that solutions of salts of the latter undergo no hydrolysis in the cold.

The function of the barium carbonate is to neutralise the free acid generated by the hydrolysis, which then proceeds to completion thus :—

$$2FeCl_3 + 6HOH + 3BaCO_3 \rightarrow 2Fe(OH)_3 + 3H_2O + 3CO_2 + 3BaCl_2.$$

The process is carried out by adding first a solution of sodium carbonate to the cold solution containing the metals in the form of chlorides or nitrates, but not sulphates, until a slight but permanent turbidity is produced. The liquid is then just cleared by the addition of hydrochloric acid, added drop by drop, the solution diluted freely, and an emulsion of barium carbonate in water added until, after shaking, an excess is seen to be present at the bottom of the vessel. The latter, a flask, is then closed and the mixture allowed to stand for several hours with shaking at frequent intervals.

The precipitate contains all the iron, aluminium and chromium, together with any titanium, uranium and vanadium that may be present, and the excess of barium carbonate, whilst the solution holds the manganese, zinc, nickel, cobalt, iron (-ous) and barium chloride. The separation from zinc and manganese is more complete than from nickel and cobalt; the yield of the latter is improved by the presence of ammonium chloride, and is quantitative if a sufficient amount of this salt is added.

This method is one which is not often practised in steel-works' laboratories because of the time required for complete precipitation, and the possible necessity of removing barium from the filtrate before proceeding to the determination of the contained metals. It may be found useful, however, in the analysis of cobalt-chromium alloys ('stellite') for the separation of the two chief constituents as well as the smaller amounts of iron and manganese which are invariably present.

Zinc oxide suspended in water is more frequently used than barium carbonate as the hydrolytic agent in the analysis of steel. The procedure is the same, and is obviously applicable in the presence of sulphates. A method often practised for the determination of manganese in chrome-steels, for example, may be briefly described as follows:—

Decompose 2·2 grams of the drillings with about 50 c.c. of ten per cent. sulphuric acid, and evaporate to fumes. Take up with a little water, add 3 c.c. of concentrated nitric acid to oxidize the iron, and dilute largely. Neutralise the free acid as above described with sodium carbonate and then add an excess of the zinc oxide emulsion. Dilute to a measured volume (500 c.c.), shake, allow to settle, filter off 250 c.c. of the supernatant liquid through a dry filter, and apply the 'bismuthate process' (*q.v.*) to the filtrate.

It will be noticed in the above method that no considerable time is allowed for the hydrolysis after the addition of the zinc oxide, and it is more than probable that long standing is unnecessary in the case of barium carbonate. It was found, in fact, by Cain,[1] and the observation confirmed by others, that precipitation may be completed in a few minutes from *hot* solutions in the case of both hydrolytes, the particular case in hand being, however, the hydrolysis of small amounts of chromium and vanadium from a solution containing relatively large amounts of ferrous iron. The same observer found also that an emulsion of cadmium carbonate rapidly precipitates vanadium and chromium from boiling solutions containing the iron as ferrous sulphate, the excess cadmium being easily removed, after dissolving the precipitate, by means of hydrogen sulphide passed through the slightly acid solution.

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[1] *Journ. Ind. and Eng. Chem.* iii. No. 7, and *Chem. News,* 105, 125.

The 'Basic Acetate' Separation.—The 'basic acetate' separation of ferric iron from manganese, nickel, etc., is one of the best and most reliable processes used in the analysis of steel and ferrous alloys. Involving, as it does, the precipitation of the iron, it succeeds equally well in the separation of large or of small amounts of this element, and, when properly executed, yields quantitative results by one precipitation only. Much work has been done by various chemists on this separation and notably by Brearley.[1]

The first stage of the operation is usually described as a 'neutralisation,' a term which does not, however, define it accurately. On adding an alkali a little at a time to a *cold* acid solution of a ferric salt the free acid is certainly first of all neutralised, but afterwards the ferric hydroxide precipitated by repeated additions of the alkali dissolves on shaking, and readily at first, accompanied by a progressive darkening in the colour of the liquid. This operation takes place most quickly when a carbonated alkali is used because the carbon dioxide liberated by the reaction

$$2FeCl_3+3(NH_4)_2CO_3+3H_2O \rightarrow 2Fe(HO)_3+3CO_2+6NH_4Cl$$

breaks up and aerates the precipitated flocks, rendering them easier of solution. But whether the alkali be carbonate or hydroxide, a point is reached at which a precipitate, if formed, does not dissolve on shaking or standing for any length of time. A solution to which so much alkali has been added that any further addition would result in the formation of a permanent precipitate is said to be 'neutralised.' The operation having been performed upon a solution initially at laboratory temperatures, the weight of iron hydrolysed is about eight-ninths of the total amount present, if it existed originally as chloride, so that the expression $8Fe(HO)_3+FeCl_3$ may be taken to represent approximately the composition of the neutralised solution. Cold solutions of ferric nitrate can similarly be hydrolysed to the extent of ninety-five per cent. of the iron present without producing a permanent precipitate.

Dilute solutions of ferric chloride are decomposed and become turbid on heating. Similarly, when neutralised solutions are diluted and heated, the eight or nine molecules of ferric hydroxide are precipitated because the remaining molecule of ferric chloride in which they are dissolved is decomposed. Hence by heating a dilute solution of ferric chloride saturated with its own hydrate, all the iron may be precipitated without the assistance of acetates, succinates, sulphates or phosphates, but it requires both patience and skill to do this effectively and repeatedly, with all kinds of ferric solutions.

The function of sodium or ammonium acetate in the basic acetate

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[1] *Chem. News*, 75-253 and 76-49, 165, 175, 210, 222.

separation is to effect a complete precipitation of the iron by formation of an acetate easily hydrolysed to a basic compound insoluble in the acetic acid formed by the hydrolysis. In solutions previously neutralised, acetate sufficient only to precipitate that portion of the iron not changed to hydroxide is required, even if no account be taken of the decomposition of dilute solutions of ferric chloride on boiling.

The temperature at which solutions of ferric acetate decompose depends to some extent on the amount of alkaline salts present such as chlorides or nitrates, but mainly upon the amount of acetate in excess of that required to convert the ferric chloride to ferric acetate.

The separation of iron (or aluminium) from nickel (cobalt, zinc, manganese or copper) depends upon the fact that solutions of the acetates of the latter metals are not decomposed (hydrolysed) at, or about, the boiling point of water, but require a temperature some seventy degrees higher. The temperature of decomposition is lowered, however, by the presence of excesses of alkaline acetates, so that ferric acetate, *e.g.*, becomes decomposable at ordinary temperatures and similarly the acetates of nickel and cobalt may be decomposed at boiling point or below. This circumstance would obviously result in an imperfect separation, so that the amount of acetate tolerable is of great importance. In this connection it may be observed that manganese passes wholly into the filtrate when twenty times the necessary amount of acetate is added; the order of the yields in the cases of the other metals is zinc, cobalt, nickel, copper, a perfect separation of copper being almost impossible by a single precipitation of the iron.

In the following table is set out a summary of the behaviour of the various elements when separated by the addition of varying amounts of acetate to the solution previously neutralised and then treated with 10 c.c. of 33 per cent. acetic acid. In each case Brearley made the separations upon solutions containing one gram of iron and one decigram of the other metal. The acetate used was in some cases the sodium and in others the ammonium salt. The former was a solution of 50 grams of the crystals in a litre of water and the latter was made by the neutralisation of 33 per cent. acetic acid with ·880 ammonium hydrate, and dilution of 75 c.c. of the resulting solution to one litre.

Acetate used.	Percentage Separation from Iron of				
	Mn.	Zn.	Co.	Ni.	Cu.
10 c.c.	100·0	—	100·0	100·0	98·0
20 c.c.	100·0	100·8	99·0	99·0	92·9
50 c.c.	100·0	97·6	97·5	95·2	69·6
100 c.c.	100·0	—	93·8	90·0	53·1

It has been repeatedly recommended that the acetate should be added to the cold solution, and the mixture then raised to boiling. This procedure is supposed in some degree to compensate for the addition of any injurious excess of acetate. This is, however, not merely a useless and troublesome, but actually a harmful recommendation. The mischief is apparent if one considers the causes from which an imperfect separation may arise, viz. : the excess of alkaline acetate, and the ferric compound in *the act of precipitating*. When acetate is added to the cold solution both these factors exert their maximum influence, but on adding it to the boiling solution the first portion completes the precipitation of the iron, and the remainder is added to a solution in which the iron is suspended merely. Thus by precipitating with a purposed excess of acetate at 16° C., only 83·3 per cent. of the nickel present remained in solution ; at 60° 86·3 per cent., at 80° 91·0 per cent., and at boiling point 94·7 per cent. of the nickel was found in the filtrate. This difference is an important one to those who prefer to use reagents in " a free and easy " manner, for, on comparing the influence exerted by increasing amounts of acetate when added to the cold (I.) and boiling solutions (II.), the advantage is seen to lie with the latter procedure ; in fact, the acetate could not be added at a more unfavourable moment than when the solution is cold.

Dilute Acetate Used.	Percentage Nickel Recovered.	
	I.	II.
10	100·0	—
20	99·0	99·8
50	95·2	98·1
100	90·0	94·8

The following is a description of the method of manipulation, which the author, after a long experience of the process, finds most satisfactory in the hands of inexperienced operators, though expert analysts may effect a separation in less time by slight modifications.

Assuming that it is desired to make a determination of manganese, nickel or cobalt in steel, weigh out two to four grams of drillings, transfer to a large conical flask (32 oz.) and decompose with 20-40 c.c. of hydrochloric acid. Add to the solution 2 to 5 c.c. of nitric acid and, when the vigorous oxidation effects are spent, dilute to a volume of 400 to 500 c.c. with cold water. Next add dilute ammonium hydrate (1 : 3) a little at a time, with vigorous shaking between each addition, until a noticeable reddening of colour takes place without the production, however, of a permanent precipitate. Next add similarly a saturated solution of ammonium carbonate, resulting at each addition in the formation of a brown precipitate, which dissolves on shaking with the production of an ever deepening colour, until the liquid in the bulk appears almost black. When on further additions a permanent and unmistakable brown precipitate is obtained, add 10 to 20 c.c. of 33 per cent. acetic acid, again shaking between each addition, until the brown precipitate is dissolved and the liquid resumes its former black colour. Dilute then with hot water nearly to a litre and heat the mixture to boiling, at which point the iron should not be more than partly precipitated. If the mixture during the heating develops a turbidity before a temperature of 70° C. is reached, too large an excess of ammonium carbonate was added, too much acetic acid required for dissolving the induced precipitate, and too much ammonium acetate thereby generated in the solution. An imperfect separation may thus result; the corrective is the careful addition of a few drops of hydrochloric acid. At or near the boiling point add one c.c. of ammonium acetate per gram of steel weighed out, and maintain the mixture in ebullition for two or three minutes. Transfer the mixture to a litre flask and make up to the mark (or beyond it) with boiling water, mix by returning to the original flask, and filter through a large dry folded filter, collecting 500 c.c. of the filtrate, and discarding the remainder.

Corrections may be made, if considered necessary, for the volume of the solid matter at the rate of 2·5 c.c. per gram of steel, also for contraction due to cooling during filtration; 500 c.c. at 60° C. occupy a volume of 513 c.c. at 100° C. The filtration should not occupy more than three minutes.

The treatment of the filtrate for the determination of the contained metal is described later in the section appertaining to the particular element.

The 'Ether Separation' (Rothé).—The separation of one substance from another is, in the great majority of cases, that of a solid from a liquid, because it is easier of execution and generally gives better results than any other possible separation. A notable exception is furnished by the Rothé ether method, which is an application of the law that when a substance is brought into intimate contact with two immiscible liquids in each of which it is soluble, it is distributed between them so that, after equilibrium is established, the ratio of its concentration in the one to that in the other is constant at any given temperature. Thus if c_1 and c_2 represent the concentrations, *i.e.*, the weight of solute in unit volume of solvent, $c_1/c_2 = k$. When the value of k, the co-efficient of distribution, differs greatly from unity, the almost complete removal of the solute from one solvent to the other becomes a practical proposition. Thus, after separating the two immiscible solutions and shaking the one of weaker concentration with a fresh portion of the other's solvent, the latter again abstracts its share of the solute according to the law of distribution, so that the progression of the separation is of the geometric order.

Iron can be separated in this way from most of the other elements that occur in steel, because of the much greater solubility in ether than in water (or dilute hydrochloric acid) of ferric chloride, whilst the chlorides of the other elements are insoluble in the former medium. When, therefore, an aqueous or dilute hydrochloric acid solution of ferric chloride is shaken with ether and the mixture allowed to separate into two layers, the upper one is essentially an ethereal solution of ferric chloride and the lower an aqueous solution of the remaining much smaller amount of it, together with the whole of the chlorides of other metals that may have been present in the original solution. (This statement is not strictly true, because ether and water are not completely immiscible, having a small range of mutual solubility, so that the upper ethereal layer contains some water and the lower aqueous layer some ether.)

The metals whose chlorides remain in the aqueous layer include copper, aluminium, chromium, titanium, nickel, cobalt, manganese, vanadium (vanadyl), and uranium (uranyl). In addition sulphuric and phosphoric acids remain in the lower menstruum, but molybdic acid passes almost entirely into the ethereal layer.

An almost complete separation can be made by a second shaking of the aqueous layer with more ether, though in practice this may not be necessary. The necessity or otherwise, of a complete removal of the iron is determined primarily by the methods to be employed for the determination of the other elements.

The essential requirements for the practical conduct of the process consist of a separating funnel or funnels, pure ethyl ether and dilute hydrochloric acid of specific gravity 1·1 to 1·12. To these may be added, with advantage, a solution made by saturating the dilute acid with ether, of which about 30 c.c. can be dissolved in 100 c.c. of the acid.

As applied to the determination in steel of one of the elements mentioned above, the following is perhaps the simplest of the various forms of procedure.

Two grams of drillings are decomposed in a beaker with about 20 c.c. of hydrochloric acid, and the ferrous chloride oxidised by the usual addition of about 3 c.c. of nitric acid. The solution is evaporated to a paste which is then taken up in as small a volume as possible of dilute hydrochloric acid, s.g. 1·1. (A more complete elimination of the nitric acid is obtained by taking to dryness, baking, and again extracting with hydrochloric acid, the solution being then filtered to remove silica and the filtrate concentrated to a pasty condition.) The solution is then transferred by means of the dilute acid to a stoppered separating funnel of about 200 c.c. capacity; the volume of the liquid should then not exceed 40 c.c. After cooling under the water tap, at least an equal volume of pure ether is added, the stopper inserted, and the funnel vigorously shaken under cold running water for about 3 minutes. The stopper is then momentarily removed in order to release the pressure of the ether vapour, the funnel clamped to a burette stand, and the mixture allowed to separate into two layers. The lower one is then drawn off, care being taken to close the tap before any of the ethereal layer enters the capillary. The stopper and funnel are then rinsed twice, with not more than 10 c.c. at a time, of the ether-hydrochloric acid mixture, and the washings drawn off into the main aqueous solution.

After one such separation, not more than 2 per cent. of the iron is usually found in the solution along with the other metals, and, as stated above, a repetition of the operation is frequently unnecessary. Should a more complete separation be required, the solution may conveniently be drawn off into another similar separating funnel, and the treatment with ether repeated. Special forms of apparatus consisting of two-bulbed funnels with suitable adjuncts are often used for this purpose.

The points to be observed carefully are, the use of alcohol-free ether and cold solutions throughout; rise of temperature and the presence of alcohol result in some reduction of the iron, which passes as ferrous chloride into the aqueous layer. Finally, the volume of the original solution should be as small as possible: this is obviously conditioned by the amount of material opened out in the first instance. From one gram of steel, the resulting ferric chloride can be transferred to the separating funnel as a solution of not more than 15 c.c. in volume, and at one shaking with 20 to 25 c.c. of ether, 99 per cent. of the iron can be extracted.

The ether separation is particularly useful in the determination of the small amounts of vanadium which occur in chrome-nickel steels, and is referred to later in connection with the determination of vanadium.

Partial Separations.—When the determination of very small amounts of a constituent of a mixture of it with very large amounts of another necessitates a separation of the two, it is often found advantageous to conduct a preliminary and partial separation, having for its object the removal of the greater part of the latter constituent; the manipulation of the mixture which results is obviously simplified considerably. The analysis of steel furnishes several examples of this kind.

The Rothé ether separation just described is a case in point, one extraction with ether sufficing to remove most of the iron from a mixture of its chloride with the chlorides of other metals.

The partial separation of iron from phosphoric acid, as applied to the determination of phosphorus in steel (*q.v.*), is one in which the greater part of the iron is held in solution as a ferrous compound, the remaining small portion being precipitated as ferric phosphate.

Similarly small quantities of vanadium may be precipitated as a ferric compound, whilst the main portion of the iron is removed in the filtrate as a ferrous salt. The procedure is exactly the same as in the case of phosphorus, and is very useful in the determination of small amounts of vanadium in steel.

Johnson [1] applies the principle of a preliminary partial separation of iron to the determination of uranium, zirconium, chromium, vanadium and aluminium in steel. The solution, which contains the iron as ferrous sulphate and some free sulphuric acid, is treated with dilute ammonium hydrate added very slowly and with constant stirring. When that point of the neutralisation is reached at which a slight reddish precipitate is obtained, the addition of a few drops more of the alkali causes the precipitate to darken considerably and assume a blackish tint. At this stage, the small quantities that are usually present in steel of such metals as uranium, zirconium, and aluminium, are completely precipitated whilst as much as 99 per cent. of the iron is still in solution. The author is able to confirm this observation, except the minor point of the amount of iron separated.

REDUCTIONS BY MEANS OF ‘NASCENT’ HYDROGEN.

The Jones Reductor.—The use of a reducing agent in quantitative analysis involves the subsequent removal or oxidation of the excess of it when the reduced solution is to be titrated with a standardised oxidant. Gaseous reducing agents such as sulphur dioxide and hydrogen sulphide are easily and completely expelled from solutions by boiling, stannous chloride is oxidised by the addition of mercuric chloride, etc. In the case of reduction by means of a metal in acid solution, the excess of

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[1] *Chem. and Met. Engineering*, xx. Nos. 10 and 11 (1919).

metal is either removed by filtration or allowed to dissolve completely in the solution.

The Jones reductor is an instrument which effects the reduction and filtration at the same time, and without exposing the reduced substance to the atmosphere, which is a point of immense importance. A very efficient form of the apparatus is shewn in the accompanying figure. The narrow part AB of the tube ABC is about 2 cm. in diameter and 24 cm. long, and the wide upper part BC is 4 cm. in diameter and 8 cm. in length. A layer of ignited asbestos, several millimetres thick and resting on a filter plate, is placed at A in order to arrest small particles of zinc as they accumulate by use of the apparatus. The solution after reduction is received in a flask or bottle connected with a simple form of aspirator such as that depicted in Fig. 6; the rest of the apparatus needs no description.

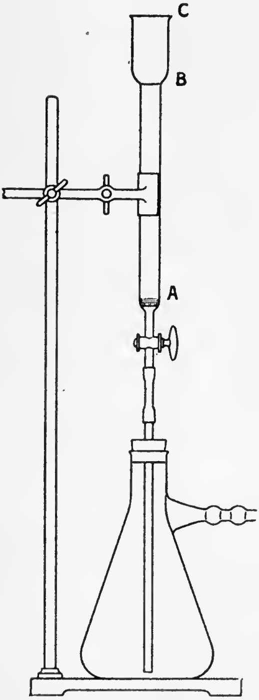

FIG. 1.

The metal used is zinc in the form of small granules which will pass through a sieve of 20, but are retained by one of 30 meshes to the inch; about 150 grams are required to charge the portion AB of the tube. The zinc is first amalgamated by vigorous shaking with a solution in very dilute sulphuric acid of sufficient mercuric sulphate to yield one gram of metallic mercury per 100 grams of zinc. It is then washed several times with water and transferred to the reductor tube without packing, except to the extent of securing, by gentle tapping, the uniform distribution of the zinc throughout the column. The metal is never allowed to be exposed to the air during a reduction or afterwards; when the apparatus is not in use, a head of water is retained above the top of the column of zinc. Neglect of this precaution is stated to result in the formation of hydrogen peroxide.

When, after considerable use, the zinc packs too tightly near the bottom of the column on account of the accumulation of small particles, the tube should be emptied and recharged, the smaller particles being rejected. Occasionally also a very dilute solution of mercuric sulphate may be passed through the reductor when the zinc near the top is seen to require re-amalgamation.

Reductions are made in the following manner:—About 100 c.c. of $2\frac{1}{2}$ per cent. sulphuric acid are passed through the reductor first of all, in order to activate the zinc, then the solution to be reduced (containing also about $2\frac{1}{2}$ per cent. of its volume of sulphuric acid and heated to a temperature of about 30° C.), next 100 c.c. more of the dilute acid, and lastly 100-150 c.c. of water. The flask is then disconnected from the reductor and the aspirator, and the solution titrated with standard permanganate. A blank determination is made occasionally by passing the same quantities of reagents through the reductor; a titration of the solution, if the zinc has the necessary degree of purity, should not require more than 0·2 c.c. of decinormal permanganate.

In the case of reduced solutions containing, *e.g.*, vanadium or molybdenum, which cannot be exposed to the air, even momentarily, without undergoing some oxidation, the receiver is charged at the beginning of the operation with a solution of some oxidising agent into which the end of the tube dips so as to ensure the delivery of the product of reduction directly into it. A suitable solution is obtained by dissolving about 70 grams of ferric ammonium sulphate (ammonium iron alum) in a litre of $2\frac{1}{2}$ per cent. sulphuric acid; 25 c.c. of this solution contain approximately 0·2 grams of iron, which is quite ample for most purposes. The subsequent titration with permanganate is thus not that of the unstable product of the reduction with 'nascent' hydrogen, but of ferrous sulphate equivalent to it in reducing power as measured by the permanganate consumed. (More exactly stated, the titration is generally that of a mixture of ferrous sulphate with a substance oxidisable by permanganate but not by ferric sulphate.) The permanganate used is in any case a measure of the actual 'oxygen exchange' due to the original reduction.

Of the various applications of the reductor, the following are particularly useful in the analysis of special steels and alloys.

Determination of Iron.—Acid solutions of ferric sulphate are easily reduced and may be collected in an empty receiver. Less than half an hour suffices for the reduction of from two to three decigrams of iron in 100 c.c. of solution.

Determination of Molybdenum.—The reduction of molybdic acid may be expressed thus:—

$$2MoO_3 + 3H_2 \rightarrow Mo_2O_3 + 3H_2O.$$

From this it follows that $2Mo = 6H = \frac{6}{5}KMnO_4$

$$\text{or, 1 c.c. } \frac{N}{10} KMnO_4 = 0{\cdot}0032 \text{ gm. Mo.}$$

The reduction is quantitative, but the reduced compound suffers oxidation by contact with the atmosphere, so that ferric alum solution must be charged into the receiver. The titration with permanganate is made at laboratory temperature with the usual indication of the end point. The intermediate colour changes, which do not promise a clearly defined end point, may safely be ignored.

Determination of Vanadium.—The reduction of vanadic acid by means of zinc and sulphuric acid proceeds according to the expression

$$V_2O_5+3H_2 \rightarrow V_2O_2+3H_2O$$

and, as the subsequent titration with permanganate re-oxidises to vanadic acid, 1 c.c. $\frac{N}{10}KMnO_4=0{\cdot}0017$ g. V. The hypovanadious (V_2O_2) solution is remarkably sensitive to free oxygen by which it is quickly oxidised to the hypovanadic (V_2O_4) condition. Ferric salts produce the same result, so that the titration with permanganate is that of a mixture of ferrous and vanadyl sulphates. It is conducted in the cold until the colour of the permanganate is seen to be discharged lazily, whereupon the solution is heated to 70° C. and the titration finished at or about that temperature.

Determination of Uranium.—The reduction of uranyl to uranous sulphate according to the equation

$$UO_2SO_4+H_2SO_4+H_2 \rightarrow U(SO_4)_2+2H_2O$$

is more than accomplished by passing the solution through a column of amalgamated zinc. A titration of the product of reduction, which possesses a brownish green colour instead of the paler and clearer green of dilute uranous sulphate solutions, shews that the uranyl sulphate has been reduced below the uranous condition,[1] and also that the amount of excess reduction is not constant.[2]

The difficulty thus created is overcome easily by exposing the reduced solution to the atmosphere for a short time before titrating it, or by aspirating a current of air through the solution for a minute or so, until the brownish green colour, indicative of excess reduction, is replaced by the paler green of the uranous salt. Obviously the reduced solution is received in an empty flask.

Titanium.—Solutions of titanic sulphate are reduced according to the equation $2Ti(SO_4)_2+H_2 \rightarrow Ti_2(SO_4)_3+H_2SO_4$. The Jones reductor does not constitute a suitable means of effecting the reduction with a view to the determination of the element, because hydrolysis of titanic sulphate (with separation of the hydroxide) takes place from solutions containing as little as 2½ per cent. of sulphuric acid, and stronger acid solutions exert a too vigorous action on the zinc.

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[1] Pulman, *Amer. Journ. Sci.* (4), xvi. 229.

[2] Author and Clark, *Chem. News*, 103, 146.

Titanium may be present in small quantities in solutions containing other metals whose salts are reducible, and the determination of these would be vitiated by its presence unless its amount were known or a corrective applied. The difficulty is overcome in the case of iron and uranium determinations[1] by the addition of the reduced solution of a small quantity of bismuth trioxide, the excess of which, together with the metallic bismuth formed by the reoxidation of the titanous compound, is removed by filtration prior to the titration with permanganate.

Mixtures containing two Metals.—The most useful application of the Jones reductor is found in the analysis of a mixture containing two reducible substances, one (or both) of which is also reducible, but to a different degree, by another reagent, preferably gaseous. Several important cases of this kind arise in the analysis of steel works' materials. Thus, mixtures containing two of the elements mentioned above can be accurately assayed for each by reducing first with sulphur dioxide, titrating, reducing the reoxidised products by passing them through the reductor, and titrating again with the same standard solution of potassium permanganate. The two permanganate readings suffice to determine both metals.

Several cases of this kind were investigated by Edgar,[2] the results of which the author has found extremely useful in the analysis of ferro-molybdenum, ferro-vanadium, and special high-speed steels containing both molybdenum and vanadium.

Molybdenum and Vanadium.—Sulphur dioxide does not reduce molybdic acid from an acid solution containing not less than 1 c.c. of the strong acid (s.g. 1·84) per 50 c.c. of solution, with as much as two decigrammes of MoO_3 present. If then a mixture of molybdic and vanadic acids containing sufficient free sulphuric acid be treated with sulphurous acid and the excess of sulphur dioxide expelled, after the blue colour is fully developed, the vanadium is determined by titrating the vanadyl sulphate with permanganate at 70° C. The acidity of the titrated solution being then adjusted to about 2·5 per cent. and the liquid, after cooling to about 30° C., passed through the reductor into ferric alum, the contents of the receiver are titrated again. The titration is performed in the cold at first, and is finished at 70° C.

If 'm' and 'n' are the number of cubic centimetres of decinormal permanganate used in the two titrations, then

$$\text{amount of vanadium} = m \times {\cdot}0051 \text{ grams}$$

$$\text{and amount of molybdenum} = (n - 3m) \times {\cdot}0032 \text{ grams.}$$

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[1] Gooch and Newton, *Amer. Journ. Sci.* (4), 23. 365.

[2] *Amer. Journ. Sci.* xxv. 332, and xxvi. 79.

Vanadium and Iron.—The solution containing vanadium and iron is treated with dilute ammonium hydrate until a small but permanent turbidity or precipitate is obtained, and an excess of strong sulphurous acid then added. The mixture is heated and when a clear greenish blue solution is obtained, dilute sulphuric acid is added and the liquid boiled vigorously to expel the excess of sulphur dioxide. The remaining operations are those already described, with the following slight modification. As the amount of iron usually present is considerable, the yellow colour of the solution makes it rather difficult to determine the exact end point in the second titration in such a large volume of solution, and one or two cubic centimetres of syrupy phosphoric acid are therefore added in order to decolourise it.

If the number of c.c. of decinormal permanganate used in the first titration is m (of which x are due to the iron and y to the vanadium) and n c.c., after deducting the blank, are used in the second titration, then

$$x+y=m$$
$$x+3y=n$$
$$2y=n-m$$

and amount of vanadium in grams $=\left(\frac{n-m}{2}\right)\times\cdot0051$.

The application of the process to the analysis of ferro-vanadium is described later.

Molybdenum and Iron.—The assay of a mixture of ferric sulphate and molybdic acid is conducted exactly as just described, except that the titrations may be done in the cold. The first titration determines the iron only, and the second determines the sum of the two, from which the molybdenum is obtained by difference.

Note.—The three cases cited above are the most important of those which arise in the analysis of steel and steel-making alloys; other applications of the same principles will be obvious. The presence of reducible impurities in the solutions influences the results seriously. Titanium has been referred to in this connection, but the influence of arsenic necessitates special mention. Alloys of iron and vanadium not infrequently contain appreciable quantities of this element, the amount of which is included by the permanganate (m) used in the first titration. The second reduction by 'nascent hydrogen' eliminates the arsenic entirely in the form of its gaseous hydride, and its amount is therefore not included in the n c.c. of permanganate. Arsenic must therefore be separated from the solutions before the determination of the contained metals by the above method.

THE 'MERCUROUS NITRATE' PRECIPITATION.

The higher oxides of tungsten, chromium, molybdenum and vanadium are acidic in character, and are quantitatively precipitated from solutions containing them by a soluble mercurous salt. As the conditions of precipitation are nearly the same in every case, a description of them may fairly claim a place under the heading of 'general methods.'

Ores and rich ferro-alloys of these metals are frequently 'opened out' by a fusion with carbonates of sodium and potassium together with an oxidant such as potassium nitrate or sodium peroxide. An aqueous extract of the fusion yields a solution of the sodium and potassium salts of the acids, from which the precipitation is made by the following procedure.

To the solution is added dilute nitric acid until neutrality, or the faintest degree of acidity, is indicated by methyl orange, and the solution is then boiled in order to expel carbon dioxide. A freshly prepared dilute aqueous solution of pure mercurous nitrate crystals is then added with stirring, until the precipitation is apparently complete. A small quantity of an aqueous emulsion of precipitated mercuric oxide may then be added in order to neutralise the slight excess of nitric acid. The mixture is digested over the corner of the hot plate for an hour or so, the precipitate collected on paper pulp, washed with water containing a small quantity of mercurous nitrate, dried and ignited. The ignition should be conducted cautiously at first in order to prevent mechanical loss in the escaping mercury vapours, and finished at a red heat except in the case of molybdenum. The residues frequently contain small amounts of silica, which should be eliminated by adding hydrofluoric and a drop or two of sulphuric acid, evaporating to dryness and igniting again.

Vanadic Acid.—The precipitation of vanadic acid with a salt of mercury was used by Berzelius, v. Hauer, Rammelsberg, Rose, Classen and others, and in several cases found unsatisfactory as a method for the estimation of vanadium. Radau,[1] however, and many later investigators obtained excellent results by the following modification of the above procedure. The original solution is adjusted to very faint acidity by means of nitric acid, carbon dioxide expelled, and the liquid cooled. The mercurous nitrate is added in drops, the orange-yellow vanadate allowed to settle, and the supernatant liquid tested. When the precipitation is apparently complete, very dilute ammonium hydrate is added until the liquid is rendered just alkaline, whereupon the

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[1] *Ann. Chem. Pharm.* 251, 153 (1889).

precipitate blackens and settles very quickly after stirring. The filtration and washing are conducted as previously described, and the ignition completed at a red heat. The residue is V_2O_5, but may contain traces of V_2O_4 formed by reduction during the combustion of the filter. It should therefore be moistened with a few drops of concentrated nitric acid and again ignited.

If a nitrate is employed in the original fusion mixture, the subsequent acidification of the aqueous extract with nitric acid liberates nitrous acid in the solution. The effect of this is a partial reduction of vanadic acid to a vanadyl salt, which is not precipitated by mercurous nitrate, and low results therefore follow. Hillebrand[1] directs attention to this important point, and recommends that the addition of nitric acid be stopped before the solution becomes acid, the mercury precipitation being thus made in a slightly alkaline solution.

The author finds that in the analysis of ferro-vanadiums a suitable oxidant is potassium permanganate, a few crystals of which when powdered and mixed with the alkaline carbonates effect the complete oxidation of the metals, and provide a solution which may be treated according to the method of Radau.

The removal of silica from a residue of vanadic oxide requires a modification of the treatment with hydrofluoric and sulphuric acids. A fluoride or oxyfluoride of vanadium is formed, which is visibly expelled by ignition at a red heat following upon the evaporation of the excess acid. To prevent this, the residue should be moistened with concentrated nitric acid, the excess removed by gentle evaporation, and the treatment repeated before final ignition.

Molybdic Acid.—No departure from the method of precipitation and collection of the mercurous molybdate is necessary in this case. The ignition must be conducted at a much lower temperature, however, in order to avoid loss of MoO_3, which is volatile at a red heat. Gibbs avoids possible loss by mixing the dried precipitate with a weighed amount of pure lead oxide, which is deducted from the weight of the final residue of lead molybdate and excess of oxide.

Tungstic and Chromic Acids.—The ignition may be conducted in both these cases at a bright red heat. The final residue in the case of chromium is the basic oxide Cr_2O_3.

SAMPLING.

Steel is generally sampled in the form of drillings or millings taken with a dry tool, surface drillings being rejected, more particularly in the

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[1] *U.S. Geol. Survey Bull.* 411.

case of samples taken from bars or billets. Hardened or tempered steel is softened before drilling by heating for a quarter of an hour or so to a dull red heat (750°-800° C.), and allowing to cool in air. Thin wire is sheared into small pieces and thicker samples dealt with similarly after flattening out under a hammer. High-speed steels may be softened by packing in lime, heating to a temperature of about 800° C., and allowing to cool slowly in the furnace.

A representative sample of a grey iron is not so easily obtained, since the fine particles are much richer in carbon than the coarse. Pigs should be drilled right through, and the whole of the drillings mixed well together. For very exact purposes, the sample thus obtained should be weighed and divided into three portions by graded sieving, and the weight of each portion then taken. For the analysis, an amount proportional to the total should be weighed from each lot, and the three samples mixed together.

For crushing metallic alloys a steel mortar is indispensable. One of a convenient shape is shown in Fig. 2. It wears well if made from the best procurable chisel steel containing about 1·10 per cent. carbon. The separate parts are made to fit easily, and the faces of the mortar and pestle are hardened.

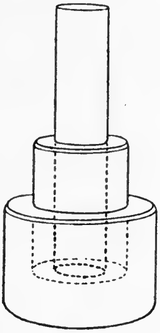

FIG. 2.

The pestle of an agate mortar can be used more effectively and with less labour if it is fitted into a file handle and fastened with shellac. The grinding of some powders in the 'agate' is much facilitated by moistening with water.

Earthenware mortars are generally too soft to be safely used for grinding samples; but it must not be forgotten that in this respect even they should sometimes be used in preference to the common bowl-shaped iron mortar. Both kinds are apt to be considerably abraded by the samples ground in them, and the nature of the impurity thus introduced is sometimes of great moment. For instance, magnesia or silica bricks crushed—as is by no means uncommon—in an iron mortar pick up a considerable amount of metallic iron: the harder portion of the magnesia may be quite grey through admixed iron before it is fine enough to pass a sixty-mesh sieve. In the subsequent analysis the ferric oxide would be considerably increased by this means, and a determination of the ferrous oxide would be hopelessly wrong. To minimise this error one may

1. Use a mortar made of hardened steel.
2. Powder as much as possible by stamping rather than grinding.

3. Go through the powdered sample with a magnet if it contains no other magnetic constituents.

By grinding ten grams of glass to a uniform size in mortars made of agate, bottle glass, hardened steel, and cast iron, Hempel found hardened steel to be undoubtedly the best material. The agate mortar lost eight times as much in weight as the steel mortar.

Bottle Labels.

The ordinary unprotected adhesive label does not long resist the attack of damp acid fumes which are always in the air of an active laboratory. Of the varnishes, balsams, etc., used to coat the surface, paraffin wax is about the most handy and serviceable. This may be brushed over the label after melting, or the label itself after it has dried on the bottle may be heated in the bunsen flame and rubbed over with a piece of wax. Faraday recommended a mixture of Brunswick black with half its bulk of oil of turpentine.

A most elegant label may be made by grinding sealing wax first dry and then mixed with a little alcohol and ether in such proportions as make a thick liquid. The lettering is done by means of a piece of glass tube drawn out at one end, the other end being attached to the mouth by a piece of rubber tubing, so that the wax can be gently forced out as needed.

The Care of Platinum Apparatus.

Salts of easily reducible metals, such as tin, antimony, lead, etc., should never be heated in platinum vessels ; nor should phosphates, as they tend to make the metal brittle. The element silicon, or rich ferro-silicon alloy, together with a flux, may also destroy platinum. Tungsten powders, too, or some constituent of them, will sometimes superficially attack or alloy with the platinum dish in which the roasting is made. Stains on crucibles and dishes are generally removed by digesting with hydrochloric acid alone, by digesting with hydrochloric acid after fusion with sodium carbonate, or by fusion with acid potassium sulphate.

The grey appearance of platinum which has been ignited for a long time has been shown by Erdmann to be really a superficial loosening of the texture of the platinum in consequence of the strong heat. This grey coating, which under the microscope appears rough and almost warty, disappears when the utensil is polished with fine sand, the weight lost in the operation being really insignificant. The regular cleaning of crucibles, therefore, not only retains a beautiful, smooth surface, pleasant to work with, but also preserves the metal.

Dishes and crucibles should never be needlessly bent out of shape. Small plugs or lasts for straightening them when crooked are cheap luxuries which the mental stimulus of working with trim and clean apparatus makes it worth while obtaining.

Small holes in the sides or other accessible places on dishes and crucibles can easily be patched with platinum foil as follows: Support the crucible over a clean iron rod of about its own curvature, clean with sand, lay on a piece of foil considerably larger than the hole, and direct a blow-pipe flame on the spot. By gently tapping with a hammer the weld becomes so perfect as to be scarcely distinguishable. In the same way scrap platinum can be made to serve many a useful end.

Filters and Filtering Operations.

Pulp Filters.—In some cases, mainly when large sticky precipitates are being dealt with, the cone filter, plain or ribbed, is very necessary, but for the majority of operations the pulp filter does the work more quickly and better. The pulp is made by tearing soft-textured ashless paper into small pieces and shaking well with water in a stoppered flask; or to make large quantities the paper is kneaded in a jar with water and the small flask filled up as required. To make a filter, place a porcelain disc (a button is useful when discs are scarce) in the throat of the funnel, cover it with water and pour on the pulp; when the excess of water has run away press down the edges of the filter to prevent rising during the filtration. If the filter is made at twice, it is easy when removing it from the funnel to split it, the upper part holding all the precipitate, and the lower being quite clean paper; it is sometimes convenient to do this.

The special advantages of pulp filters are:

1. A filtering medium of any desired texture according to pressure applied in constructing it;
2. The greater effect of a given amount of wash water, since every portion must pass through the precipitate;
3. No loss of precipitate by ‘creeping.’

One drawback to the use of pulp is the impossibility of separating the precipitate from the paper. Happily the necessity of doing so is comparatively rare; much rarer in fact than is generally believed. Having regard to the ignition of a precipitate, pulp has this advantage: that by thorough aspiration the precipitate is sucked firmly on if not into the paper and is much less likely to spatter when dried hurriedly at the mouth of the muffle.

In transferring the filter to the crucible, which is done by turning up one edge of the filter with the leg of a pair of forceps, lifting it out, and cleaning with a piece of paper pressed against the revolving funnel, it is by no means easy to prevent the precipitate from touching the crucible at some point, and in this way the glaze is soon destroyed. To avoid this a piece of ashless filter paper is placed in the crucible and the filter laid on it.

In handling an appreciably soluble precipitate, the beaker or flask should be cleaned with portions of the filtrate (which are already saturated solutions so far as the precipitate is concerned), and water or other wash liquid proper used to displace the mother liquor. It is better to wash many times with small quantities of liquid rather than a few times with large quantities.

Preparing Asbestos for Filters.—Cut the asbestos fibre into pieces half an inch long, cover with concentrated hydrochloric acid and keep in a warm place for several hours. Then transfer the asbestos to a funnel which contains a large filter plate, drain off and squeeze out the excess of acid. Transfer the asbestos to a sieve of about twenty meshes to the inch and vigorously agitate with a strong current of water until all free acid is washed out. Now squeeze as dry as possible, break into small pieces and ignite very strongly in the muffle. The ignited material may be used at once after shaking up with water; or if a more open filter is desired it is again washed into the sieve to get rid of the powdered portion. A filter made up with hot water acts more rapidly than if made with cold.

Adsorption of Salts by Filters.—The adsorption of a salt from a solution during filtration can only very rarely occur to a noticeable extent. During fractional filtrations, however, it is well to bear the possibility of it in mind. Paper, for instance, adsorbs (*i.e.*, takes up proportionally more of the salt than of the solution it is dissolved in) nickel and lead acetate; and sand filters adsorb the acetates of chromium, iron, and copper. It sometimes happens that a salt adsorbed in this way cannot be removed by washing, and almost invariably it happens that when a precipitate has been washed with water whose volume is $(m-1)$ times the mother liquor held by the precipitate and filter the impurity still remaining has not been reduced to the mth part. The reason for this is that in contact surfaces between solids and liquids the concentration of the dissolved substance is different from and always greater than in the rest of the solution.

TABLE OF FACTORS.

Element.	Found.	Required.	Factor.	Log. of Factor.
Aluminium	Al_2O_3	Al	0·5303	$\bar{1}$·72455
Aluminium	$AlPO_4$	Al	0·2219	$\bar{1}$·34625
Aluminium	$AlPO_4$	Al_2O_3	0·4185	$\bar{1}$·62170
Calcium	CaO	Ca	0·7148	$\bar{1}$·85418
Calcium	$CaSO_4$	CaO	0·4119	$\bar{1}$·61478
Calcium	$CaSO_4$	Ca	0·2944	$\bar{1}$·46896
Carbon	CO_2	C	0·2727	$\bar{1}$·43573
Chromium	Cr_2O_3	Cr	0·6842	$\bar{1}$·83519
Chromium	Cr	Cr_2O_3	1·4615	0·16481
Cobalt	Co_3O_4	Co	0·7344	$\bar{1}$·86595
Cobalt	CoO	Co	0·7867	$\bar{1}$·89579
Cobalt	$Co_2P_2O_7$	Co	0·4041	$\bar{1}$·60650
Copper	CuO	Cu	0·7990	$\bar{1}$·90255
Copper	Cu_2S	Cu	0·7985	$\bar{1}$·90225
Hydrogen	H_2O	H	0·1111	$\bar{1}$·04576
Iron	Fe_2O_3	Fe	0·6993	$\bar{1}$·84463
Iron	Fe_2O_3	FeO	0·8998	$\bar{1}$·95412
Lead	$PbSO_4$	Pb	0·6831	$\bar{1}$·83445
Lead	$PbMoO_4$	Pb	0·5642	$\bar{1}$·75140
Magnesium	$Mg_2P_2O_7$	MgO	0·3621	$\bar{1}$·55881
Manganese	Mn_3O_4	Mn	0·7201	$\bar{1}$·85742
Manganese	Mn_3O_4	MnO	0·9300	$\bar{1}$·96850
Manganese	Mn	MnO	1·2915	0·11108
Molybdenum	$PbMoO_4$	Mo	0·2613	$\bar{1}$·41749
Molybdenum	MoO_3	Mo	0·6667	$\bar{1}$·82391
Nickel	$NiC_8H_{14}N_4O_4$	Ni	0·2033	$\bar{1}$·30819
Nickel	NiO	Ni	0·7859	$\bar{1}$·89532
Phosphorus	$PbMoO_4$	P	0·007	3·84739
Phophorus	$PbMoO_4$	P_2O_5	0·0161	$\bar{2}$·20729
Phosphorus	$Pb_3(PO_4)_2 \cdot 24PbMoO_4$	P	0·00644	$\bar{3}$·80914
Phosphorus	$Pb_3(PO_4)_2 \cdot 24PbMoO_4$	P_2O_5	0·0148	$\bar{2}$·16904
Phosphorus	$(NH_4)_3PO_4 \cdot 12MoO_3$	P	0·0165	$\bar{2}$·21790
Phosphorus	$(NH_4)_3PO_4 \cdot 12MoO_3$	P_2O_5	0·0378	$\bar{2}$·57780
Potassium	K_2PtCl_6	K	0·1610	1·20675
Silicon	SiO_2	Si	0·4693	$\bar{1}$·67147
Sulphur	$BaSO_4$	S	0·1375	$\bar{1}$·13822
Sulphur	$BaSO_4$	SO_3	0·3430	$\bar{1}$·53534
Titanium	TiO_2	Ti	0·6005	$\bar{1}$·77852
Titanium	TiO_2	$TiO_2 \cdot P_2O_5$	2·773	0·44292
Tungsten	WO_3	W	0·7931	$\bar{1}$·89933
Tungsten	WO_3	Na_2WO_4	1·267	0·10286
Uranium	$(UO_2)_2P_2O_7$	U	0·6671	$\bar{1}$·82421
Uranium	U_3O_8	U	0·8482	$\bar{1}$·92849
Vanadium	V_2O_5	V	0·5604	$\bar{1}$·74853
Zirconium	ZrO_2	Zr	0·7390	$\bar{1}$·86864

TABLE OF APPROXIMATE ATOMIC WEIGHTS AND MELTING POINTS.[1]

Element.	Atomic Weight.	Melting Point.	Element.	Atomic Weight.	Melting Point.
Aluminium	27·1	658·7° C.	Mercury	200·6	–38·87° C.
Antimony	120·2	630·0	Molybdenum	96·0	2550·0 (?)
Arsenic	75·0	850·0	Nickel	58·7	1452·0
Barium	137·4	850·0	Nitrogen	14·0	–210·0
Bismuth	208·0	271·0	Oxygen	16·00	–218·0
Boron	11·0	2200-2500 (?)	Phosphorus	31·0	44·0
Cadmium	112·4	320·9	Platinum	195·2	1755·0
Calcium	40·1	810·0	Potassium	39·1	62·3
Carbon	12·0	>3600	Silicon	28·3	1420·0
Chlorine	35·4	–101·5	Silver	107·9	960·5
Chromium	52·0	1615·0	Sodium	23·0	97·5
Cobalt	59·0	1480·0	Sulphur	32·1	106·8, 112·8, 119·2
Copper	63·6	1083·0	Tantalum	181·5	2900·0 (?)
Fluorine	19·0	–223·0	Tin	119·0	231·9
Hydrogen	1·008	–259·0	Titanium	48·1	1800·0 (?)
Iodine	126·9	113·5	Tungsten	184·0	3400·0 (?)
Iron	55·8	1530·0	Uranium	238·5	<1850·0
Lead	207·1	327·4	Vanadium	51·0	1720·0 (?)
Magnesium	24·3	651·0	Zinc	65·4	419·4
Manganese	54·9	1230·0	Zirconium	90·6	1700·0 (?)

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[1] The melting points are taken from the U.S. Bureau of Standards (Circular No. 35, 3rd edition. Revised July 15, 1918).

PART II. THE ANALYSIS OF STEEL AND PIG IRON.

CARBON ($C=12{\cdot}00$).

CARBON is estimated in steel more frequently than any other element. Although its amount is often many times less than that of the elements, other than iron, with which it is associated, its influence upon the physical properties of iron is profound. The difference between iron and steel is, in fact, a difference of carbon content, just as is the difference between the soft steel of a boiler plate and the hard steel of a file or razor.

Carbon may be present in steel and ferrous alloys in several different forms. It may exist in the free condition as graphite, which is the usual form of occurrence in grey pig irons, though comparatively rare in sound steel. Most usually it is present in the plain alloys of carbon and iron, which constitute by far the greater proportion of the world's output of steel, as carbide of iron. Again, in hardened steels it may be present as a mixture of carbide of iron with a solid solution of this carbide in excess of iron, and, moreover, the carbide of iron may exist in one or more of several states, dependent upon the heat treatment to which the steel has been subjected, and recognisable microscopically in a polished and etched sample. It is evident therefore that a perfect separation of these various constituents is a matter of the greatest difficulty; and, in fact, except by burning the carbon out, it is, to all intents and purposes, an impossibility to separate the carbon and iron in the case of hardened steel.

Separation from Iron.—(1) By means of the selective action of chlorine upon the alloy, a perfect separation of carbon from the iron can be effected, the metal being removed as ferric chloride, leaving the carbon. The operation consists in the passage of a current of chlorine over the metal heated in a tube. The gas should be quite dry and free from oxygen, hence it is passed over heated charcoal before reaching the steel. This separation was formerly used largely in the determination of carbon in highly refractory alloys, such as ferro-chromium, which require a very high temperature to effect complete decarbonisation by a direct combustion in oxygen.

(2) The electrolytic method, due to Binks and Weyl, is also, for ordinary steels, an accurate and reliable process. It consists in making a rod or bar of the steel the anode of an electrolytic cell, a plate of platinum being the cathode. The electrolyte is generally dilute hydrochloric or sulphuric acid. The carbon is left behind as a carbide of iron in the case of pure carbon steels, the iron being taken, for the most part, into solution. Much work upon this form of separation has been done by Arnold and Read,[1] upon various alloy steels. Reference to their work shews that the separation results frequently in a loss of carbon in the form of gaseous hydrocarbons, and yields a carbonaceous residue containing considerable amounts of the alloying element along with the carbon. This is particularly true in the case of tungsten, molybdenum, chromium, manganese and vanadium steels.

In order to hasten the decomposition, drillings may be used instead of a solid rod; these are placed on a platinum plate fixed horizontally in the electrolyte. Blount corrects for the loss of carbon during the decomposition by using a solution of copper as electrolyte and placing the drillings on a platinum plate above which a copper plate is suspended.

(3) Both of the above methods require somewhat specialised apparatus and are obviously unsatisfactory if many samples have to be decomposed at the same time. They are not therefore used so frequently as the method of dissolving out the iron by solutions of salts of metals possessing a lower solution pressure than that of iron. Of these the one always used is copper, and, in order to prevent the separation of cuprous salts by reduction, a solution of copper ammonium or copper potassium chloride with some hydrochloric acid is used instead of a simple salt of the metal. In the absence of hydrochloric acid this solution precipitates metallic copper on the ferrous alloy and so delays or even stops the action before its completion. The amount of acid must not be too great, for then there is a loss of carbon as hydrocarbons, whilst conversely, neutral solutions are not only slow of action but are found in practice not to give a quantitative yield of carbon in the insoluble residue. This is particularly the case with tungsten-steels.

The decomposition is generally started in cold solution, and results

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[1] *Journ. Iron and S. I.* 1911, 249; 1912, 215; *Proc. Inst. Mech. E.*, 1914, 223; 1915, 629.

in a slight rise of temperature, which does not endanger the success of the operation, since there is no loss of carbon below a temperature of 70° C. The action is accelerated considerably by agitation of the mixture, and may then be completed with fine drillings in an hour or less. A simple arrangement for this purpose, consisting of a current of air induced by a water pump, is shown in the description of the process given below, Fig. 7.

The device of adding ferric chloride to the solution in order to prevent the separation of metallic copper is not to be recommended, as it results in a small loss of carbon.

Gravimetric Determination of Carbon.—The determination of carbon is generally made gravimetrically, and consists in its oxidation to carbon dioxide and absorption of the latter by a tared reagent. The principal variations amongst the methods are those due to the different ways of converting the carbon into carbon dioxide. This may be done with or without the previous separation of the carbon from the whole or greater portion of the iron. Modern practice eliminates the preliminary separation and is simply a direct oxidation of the material by means of oxygen at a high temperature.

In order to effect this satisfactorily it is imperative that the material should be in a fine state of division, and it is customary to use drillings which are caught between sieves of thirty and sixty meshes per square inch. It is found useful also to mix with the drillings some reagent free from carbon, in order to ensure the full advantage of their contact with the oxygen. A large number of such reagents has been employed, some of them preferable in view of their possible catalytic action; *e.g.*, powdered pumice, 'alundum' powder, alumina, lead chromate, lead peroxide, red lead, bismuth trioxide, cupric oxide, trimanganic tetroxide, zinc oxide, etc. Lead chromate and oxides are much used because they take up the sulphur of the steel, and thus obviate the necessity of an external absorption tube for sulphur dioxide. The chromate necessitates a higher temperature for combustion than litharge or red lead.

It is of importance that the amount of carbon dioxide coming from these reagents be known and hence a blank determination must be carried out at frequent intervals; litharge, for example, absorbs carbon dioxide from the air and its blank is therefore inconstant; strongly ignited manganese dioxide, *i.e.*, trimanganic tetroxide, and bismuth trioxide, on the other hand, have a very small and constant blank, or even none at all. Red lead, which the author prefers, may be purchased of a high degree of purity and with an almost constant small blank.

The temperature of the combustion is of the greatest importance; ordinary steels and pig irons can be burned at 950° to 1000° completely, and in ten to fifteen minutes. In the case of some alloys, *e.g.*, ferro-chromium, the highest temperature available should be obtained, and red lead should be mixed with the finely divided sample. Spiegels can be treated successfully in much the same way, but it is better to mix a ferro-manganese with freshly ignited zinc oxide.

The oxygen used during the combustion and the air afterwards used for 'sweeping out' are passed through washing towers containing a solution of caustic potash as well as the solid itself in order to free them from carbon dioxide before admission to the combustion tube. After passing through the tube, which contains cupric oxide to effect complete oxidation, the gases are passed first through a solution of chromium trioxide in sulphuric acid for removing any sulphur dioxide that may be present, then through a bulb containing concentrated sulphuric acid and lastly a calcium chloride tube, before reaching the vessels for absorbing the carbon dioxide resulting from the combustion of the alloy.

For collecting the carbon dioxide, solutions of barium, sodium or potassium hydroxide may be used, and also soda lime. The latter is very hygroscopic, and being solid, does not make such intimate contact with the gases as a solution does; on the other hand it possesses the advantage of being easily charged into a straight tube along with calcium chloride or phosphorus pentoxide, thus providing a compact and strong arrangement. Caustic potash is largely used as the absorbent in the form of a 50 per cent. solution; and the absorption bulbs are usually provided with a trap for moisture in the shape of a small tube containing calcium chloride. This arrangement provides a full and complete contact between the gases and the absorbing medium, and the reagents are not so hygroscopic as to cause trouble due to the absorption of atmospheric moisture during the weighing, etc.

It is sometimes convenient to separate the carbon from the iron by means of copper ammonium chloride as described above. The resulting residue may be submitted to a wet or a dry oxidation. In the latter case the procedure is practically identical with the method just described. The carbonaceous residue is filtered out on to asbestos, washed, and transferred, filter and all, to a boat, dried in a steam oven and then burnt. There is no necessity to add any oxidising agent, and the temperature required for a complete oxidation is much lower than in the case of a direct combustion of the metals. It has been stated that the drying of the washed residue at 100° C. may cause a loss of carbon and direct ignition of the wet residue is recommended accordingly. The author's experience does not confirm this observation.

Oxidation in the wet way may be applied to the metal itself or the carbonaceous residue after decomposition with the double copper salt. The furnace and accessories are thereby dispensed with. The reagent used is a mixture of chromium trioxide and sulphuric acid to which copper sulphate is added. This mixture will oxidise the carbon of the steel to carbon dioxide in an hour or less if suitable drillings are employed.

It has been pointed out that even with such a strong oxidising mixture there is a possibility of the existence in the evolved gases of hydrocarbons; ordinary practice shows that loss of carbon due to this is negligible.

Volumetric Determination of Carbon.—For this class of estimation three distinct suggestions have been adopted in practice. The first of these consists in the conversion of the carbon into carbon dioxide either in the wet or the dry way, and with or without a previous separation of carbides by the 'copper attack.' The carbon dioxide is passed through a solution of a known quantity of barium hydroxide, the resulting precipitate of barium carbonate is filtered out, and the excess of baryta determined by titration with a standard solution of an acid.

The second type of estimation is quite different and is really a modification of the wet oxidation process. The carbides are obtained first by decomposition of the metal with cuprammonium chloride, and they are then filtered out and washed with hot dilute sulphuric acid until the washings show no evidence of the presence of ferrous salts when tested with a dilute solution of potassium permanganate. The oxidation is readily carried out in small beakers by means of $\frac{2N}{5}$ solution of potassium bichromate in 50 per cent. sulphuric acid.

$$3C + 4CrO_3 + 6H_2SO_4 \rightarrow 3CO_2 + 2Cr_2(SO_4)_3 + 6H_2O.$$

The beakers are immersed in a bath of boiling water, or in special cases in a concentrated solution of calcium chloride, which can be heated up to 130° or thereabouts. During the oxidation the asbestos of the filter upon which the carbide residue has been collected entangles liberated carbon dioxide, and is floated to the surface of the liquid. This necessitates occasional stirring, but at the same time it provides longer contact with the oxidant, and thereby promotes the complete oxidation of carbon monoxide that may be generated. When the asbestos lies quietly *in* the solution, and gentle stirring causes no appearance of bubbles, the reaction is at an end. The solution may then be diluted and titrated with ferrous ammonium sulphate solution and the bichromate used for the oxidation.

The rate of oxidation depends on the temperature and the amount of stirring. In a calcium chloride bath at 130° C., and with constant stirring, the carbon from three grams of a 1·25 per cent. carbon steel may be oxidised in ten minutes. In a water bath at 100° C. the time occupied is twice as much, whilst with such occasional stirring as could be given to a batch of eight or ten samples in a water bath at once, an hour's digestion is ample.

Larger amounts of carbon, requiring more of the standard bichromate solution than can be accommodated in the small beakers, may have powdered bichromate, free from organic matter, added along with 30 to 50 c.c. of the acid solution.

Any class of material which is decomposed by the double copper salt without leaving reducing matter in the residue may be successfully assayed for carbon by this process. The metallic tungsten from tungsten steels reduces bichromate solutions at an appreciable rate only when the sulphuric acid is dilute, so that if the digestion with the half and half sulphuric acid solution of the bichromate is not unduly prolonged, and the titration after dilution completed rapidly, the results are only a few hundredths per cent. too large. The oxidation of the metallic tungsten is very much lessened by using concentrated sulphuric acid along with powdered bichromate, but in such a solution the carbon is oxidized much less speedily. The process is not applicable to chromium steels.

The graphitic carbon of pig irons is much less readily oxidized than combined carbon, using the half and half sulphuric acid solution. Ninety parts of sulphuric acid, with ten parts of water, is the best strength of solution to use for graphite, but curiously enough the combined carbon is as badly oxidised by the stronger acid solution as graphite by the weaker. This fact should considerably modify the practice of using as strongly acid solution as possible in the ordinary wet combustion of the residue, and the experimental results upon which it is established are of sufficient interest to merit special mention.

Amounts of combined carbon and of graphite, liberated from steel and pig iron respectively, and equivalent in each case to 1·18 per cent. when calculated on three grams of the metal, were digested with 0·7 grams of powdered bichromate and 30 c.c. sulphuric acid solution of the strengths specified in the following table. The digestions were made at 100° C. in batches of four, the samples being stirred continuously in succession :

Parts Concentrated Sulphuric Acid in 100.	Percentage Oxidised of		
	Combined Carbon.		Graphite.
	Digested 30 mins.	Digested 15 mins.	Digested 30 mins.
10	0·58	—	0·04
20	0·77	—	0·09
30	0·90	—	0·12
40	1·05	—	0·17
50	1·17	1·04	0·31
60	1·19	1·12	0·47
70	1·20	1·08	0·62
80	1·10	0·81	0·78
90	0·59	—	1·07
100	0·35	—	1·00

The volume of sulphuric acid used has very little influence on the speed of the oxidation. so long as there is sufficient bulk of liquid to permit free movement of the carbonaceous residue and the filtering medium on which it is collected.

Of importance also in this connection is the following table, showing the spontaneous reduction of chromic acid by sulphuric acid when kept at varying temperatures for three hours. The figures show the percentage of chromic acid undecomposed at the end of the operation :

Parts Concentrated H_2SO_4 in 100.	Temperature of Digestion.				100° for 16 hours.
	130°	120°	110°	100°	
30	100·0	—	—	—	—
40	100·1	—	—	—	—
50	100·1	—	—	—	99·9
60	98·6	99·2	99·6	99·9	99·0
70	91·3	98·2	99·0	99·6	97·6
80	88·7	95·1	96·5	98·1	88·7
90	91·3	95·8	96·8	98·2	92·6
100	94·8	—	—	—	97·6

At 130° C., in a bath of calcium chloride, the residue from 1·5 grams of a highly graphitic iron was completely oxidised by the weaker acid solution in an hour and a half ; the same time was occupied in the strong acid at 100° C., whilst at 130° C. the time required was less. Both of these latter procedures introduce a positive error due to the action already mentioned, and exemplified by the table given above.

The third process for the volumetric estimation of carbon consists in the direct measurement of the volume of carbon dioxide evolved by the combustion of the steel. This process is usually conducted in solution upon the carbide separated by means of the copper attack, and as the apparatus required is not elaborate, is often found useful when approximate results only are required. Unoxidised carbon monoxide is obviously registered as carbon dioxide, without error.

Determination of Carbon by Colour.—The combined carbon in steel, that is, the carbon present as a carbide, imparts a brown colour to the solution obtained by dissolving the steel in dilute nitric acid, due to the nitration of an organic compound. The intensity of colour is evidently due to the proportion of colouring matter produced by the nitrated carbon compound, and this fact has been for a very long time the basis of a ready and simple process for the determination of carbon in steel by comparing the colour obtained from a standard steel with that from the unknown.

Theoretically the principle is sound, but in practice it is found that the process is anything but good except under precisely defined conditions. Since the colour of the solution depends, except for that due to the ferric nitrate, upon the nitrated carbon compound, any carbon that is present in another form, such as graphite or as the solid solution of carbide in iron, will not be registered. Hence the heat treatment of the steel and the standard must be normal heat treatment, not quenched or tempered in any way. The presence in the steel of any element giving a coloured solution also interferes with the successful conduct of the process, which is therefore of little value for chrome-nickel and similar steels.

Standard and sample should be treated identically throughout; the same quantity of each should be dissolved in the same quantity of acid, the solutions digested together for the same length of time, cooled off together and compared at the same temperature. These details are essential to success, since the colour of the solution is distinctly affected by the rapidity of the solution, being darker if the steel is dissolved quickly, and also since the colour diminishes in intensity by continued action of hot nitric acid, on account of slow oxidation of the nitro-compound. Another point to which importance is attached is the necessity of the carbon percentage in the standard being as nearly as possible that in the unknown steel. Even a standard steel containing, say, 1·2 per cent. carbon does not shew the same intensity of colour when its solution is diluted to twice the volume of a solution obtained from a standard containing 0·6 per cent.; in other words, the colour intensity is not strictly proportional to the percentage of carbon.

The influence of ferric nitrate on this fact is not generally taken into consideration. Beneker,[1] however, finds that the colours due to carbon only are about strictly proportional to the carbon percentage, when that due to the iron is discharged by the addition of 0·5 c.c. of 85 per cent. phosphoric acid.

Stead [2] has proposed a modification of the ordinary Eggertz process, and he precipitates the iron from the dissolved steels by means of sodium hydrate and compares the colours in the filtrate, which are of greater intensity than in an acid solution.

In general the colour process is only suitable to the determination of carbon very approximately. It is good for rapid furnace tests to indicate roughly the percentage of carbon in the bath and it is satisfactory for the rapid checking of goods that are supposed to be of an approximately standard carbon, any serious divergence from the normal being detected at once.

Determination of Graphite.—A direct combustion of an ordinary steel or iron yields the total carbon, whether it is combined or in solid solution or as graphite. It is important, however, to know whether free carbon is present, as, in the case of steel, its presence makes the material practically useless. Such material is known technically as "black steel." In the case of pig irons the proportion of graphitic to carbide carbon helps to decide the kind of iron, and its uses.

The only reliable process for the estimation of graphite is to separate it first from the steel or iron, and then to burn it in the usual way. Dilute nitric acid, s.g. 1·2, has no action upon the graphite of an alloy, and at the same time it takes into solution the carbide carbon without causing any separation of its carbon. Hydrochloric acid, on the other hand, evolves the carbide carbon as a mixture of hydrocarbons with the possibility of their partial decomposition and precipitation of the element. Moreover, nitric acid carries silicon into solution, whilst hydrochloric causes it to precipitate in a gelatinous form on the graphite, necessitating its removal by washing with a caustic alkali. After having opened out with dilute nitric, therefore, the mixture is digested for some time, the insoluble graphite filtered through asbestos, washed, dried and burned in the ordinary way.

GRAVIMETRIC ESTIMATION IN STEEL.

1. Direct Dry Combustion.—For this process the two most important pieces of apparatus are the combustion tube and the furnace required for heating it.

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[1] *Chemist-Analyst,* No. 22, 1917.

[2] *Chem. News,* 47, 285.

The choice of the latter is a matter of convenience and individual taste. Furnaces heated electrically are now very largely used and may be purchased directly from the manufacturers, whose catalogues render a description unnecessary.[1] Gas-heated furnaces of many different patterns are also available, any one of which may be used provided always that it fulfils the fundamental condition of providing a sufficiently high temperature. The Huxley furnace shown in Figure 3 possesses one or two advantages over many of the others. The flame is not allowed to come into direct contact with the tube, thereby reducing the chances of cracking the latter during the heating up of the furnace; this protection is attained by the use of the inner fireclay cylinder. In addition the ends of the combustion tube are excellently protected from heat, and are kept comparatively cool during the combustion. Lastly, the furnace accommodates four combustion tubes and its daily output of work can thus be varied as occasion requires.

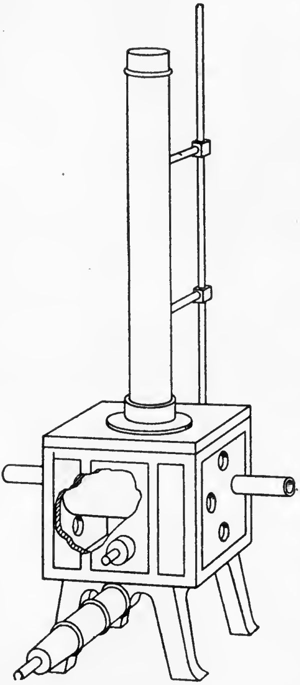

Fig. 3.

The best combustion tubes for iron and steel analysis are those made of porcelain or silica, though glass tubes and iron tubes with brass taps were formerly often used; platinum tubes, for an obvious reason, are not in general use.

Each end of the tube is fitted with a tight rubber bung pierced by one hole; tube and bungs should be tested for air tightness before using. As a further protection against cracking during the heating of the furnace the tube may be wrapped in asbestos. This may either be thin woven asbestos or a thin sheet that has been wetted, pressed tightly round the tube and allowed to dry in this position. These precautions are not so necessary with the Huxley

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[1] Tube furnaces of this kind are not difficult of construction to a skilled workman. The winding consists of nichrome wire, approximately 2 mm. in diameter, from which a sufficiently high temperature is induced by a current of 4·5 to 5 amperes, at a pressure of 100-150 volts. Nichrome is also made up into thin ribbon, which makes a better winding than the wire.

furnace as with those in which the flames impinge directly on the combustion tube.

Combustion tubes should be at least twenty inches in length, thus allowing about five inches to project from the furnace at either end, and providing a length of ten inches in the furnace. About half of the latter is packed with copper oxide, held in position by short wads of ignited asbestos packed in loosely at either end. The copper oxide may be the granulated material prepared by the ignition of fragments of copper wire, or it may, preferably, be made from fine copper gauze. A cylinder of this is easily made by folding the gauze in upon itself, and wrapping over it one or two layers of wetted asbestos paper. After drying, the cylinder is pushed into position in the tube, the asbestos wads introduced, and the copper oxidised by passing a slow current of air through the tube at a low red heat. The remaining five inches of the tube are reserved for the boat.

Regarding the whole train in order, the first item is the oxygen supply. This may be taken directly from a cylinder or collected in a holder and used therefrom; in the former case the trouble of filling the holder at frequent intervals is removed.

The oxygen and air used are washed free from carbon dioxide by passing them through towers containing caustic potash. Suitable vessels for this purpose are shown in Fig. 4. The lower wider part of the tower, designed by Dufty, is charged with a fifty per cent. solution of the alkali and the upper part with solid pieces or sticks of the reagent, in order to remove aqueous vapour brought from below. The gases pass from these direct to the tube and through it.

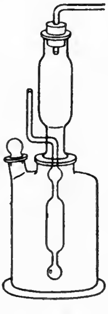

FIG 4.

On the other side of the furnace there is placed first an Arnold bulb or other vessel containing a solution of chromic acid for the purpose of absorbing any escaping sulphur dioxide. The reagent is a saturated solution of the solid in 50 per cent. sulphuric acid. The gases are next dried thoroughly by passing them first through sulphuric acid and next through a U-tube charged with calcium chloride in the form of small granules and free from powder. The gases then pass into the weighed potash bulbs or soda lime tubes for the absorption of the carbon dioxide generated by the combustion.

Numerous forms of bulb are used for containing the potash solution. As it is essential that the gases after passing through the solution should be thoroughly desiccated, many forms of apparatus are provided with an attachment or prolong containing granulated calcium chloride; this is the case with the old Geissler bulb still in favour, Fig. 5*a*. A stronger form is the Arnold bulb shown in Fig. 5*b*; this is connected by rubber tubing to an external calcium chloride tube which must therefore be weighed also before and after combustion. The form of bulb shewn in Fig. 5*c* is the Lansiedle bulb, made by Orme, which is also much less fragile than the Geissler bulb, is more compact, and stands easily on its own base during absorption and weighing.

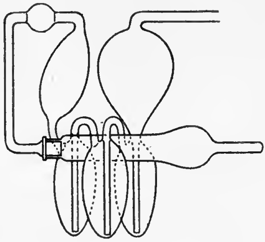

FIG. 5*a*.

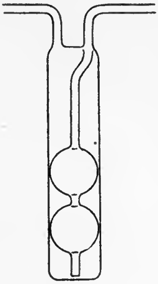

FIG. 5*b*.

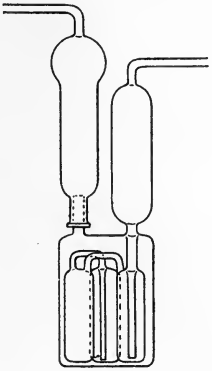

FIG. 5*c*.

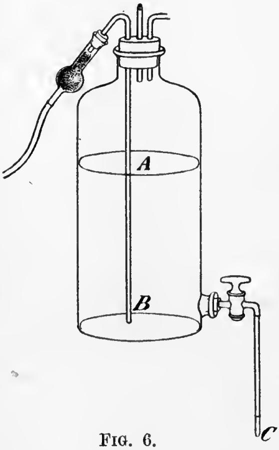

FIG. 6.

From the absorption bulb the gases pass through a U-tube containing calcium chloride to act as a trap for moisture between the absorption bulb and the aspirator, then finally into the aspirator. The latter is shewn separately in Fig. 6, with the calcium chloride tube referred to in position; this arrangement exercises a constant and adjustable pull on the train, the amount of which is determined by the length of the column of water BC.

Boats to contain the metal may be of glazed or unglazed porcelain or of good fireclay; they should be protected by a wrapping of asbestos paper, wetted and pressed round the boats, to which it will closely adhere after drying and heating to redness in the muffle. This prevents such a flux as red lead from coming out of the boat and sticking to it and to the tube, and, at the same time, facilitates the removal of the contents entirely, whilst they are still hot, immediately after the combustion is at an end. Boats can thus be used more than once, but a cracked one should be incontinently rejected.

For the combustion of steel sievings, two grams are weighed off and mixed by shaking in a glass-stoppered bottle with five grams of red lead or with one gram of ignited oxide of manganese. The mixture is emptied into the lined boat and, with or without a covering of finely divided and ignited ' alundum ' powder, the boat is pushed into the hot tube up to the asbestos plug, by means of a thick iron or copper wire. The tube is immediately closed and oxygen fed into it. The rate of its admission is determined by observation of the rate at which gas bubbles through the absorption train at the exit side. During the oxidation of the iron and its contained carbon, oxygen is copiously absorbed, and the supply should be fed in accordingly. Ten to fifteen minutes suffice to effect the oxidation during which time one or two litres of oxygen may be used up. The supply is then shut off and the whole apparatus swept out by a current of air, passed for about fifteen minutes. The absorption bulbs are then removed, placed in the balance case to cool with their ends closed up, and weighed with the ends open. The increase in weight is carbon dioxide which contains 27·27 per cent. of carbon.

One combustion may follow immediately upon another, and in regular daily practice even without sweeping out the apparatus with air.

2. Dry Combustion after Separation of Carbon.—Five grams of steel drillings are placed in a conical flask with about 200 c.c. of a solution of cuprammonium chloride containing five per cent. of hydrochloric acid. The solution is an approximately saturated one made by dissolving about 400 grams of the solid in a litre of water containing 50 c.c. of hydrochloric acid; it is always filtered through asbestos for use. The contents of the flask are kept in motion vigorously until the metal is decomposed. If several samples are to be opened out, the flasks are arranged in series as shown in Fig. 7, and connected with a water pump. A mercury trap is placed in the series in order to prevent any sucking back from one flask to another. By this means the water pump pulls

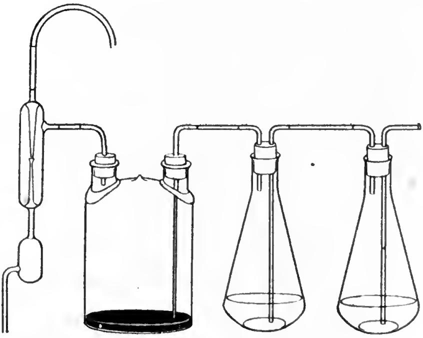

Fig. 7.

through the flasks a stream of air which keeps the drillings in continual movement. With such an arrangement it is quite safe and convenient to leave a series of estimations in this condition over a night. The residue is collected on an asbestos filter, washed with very dilute hydrochloric acid and finally with water. It has been recommended to filter through an asbestos plug placed in the combustion tube, an operation which is obviously only suitable in the case of a single estimation. Various other devices, more or less complicated, of funnels and tubes for filtering have been evolved and used to a limited extent, but there is no reason why the filtration should not take place through an ordinary asbestos pulp filter in a plain glass funnel. After washing, the filter is sucked dry at the pump and then transferred to the prepared boat in which it is placed face downwards and packed neatly with forceps. The small residue left on the sides of the funnel is transferred to the boat by cleaning it off with moistened asbestos. This is held by the forceps and pressed against the sides of the funnel whilst the latter is rotated so as to draw the asbestos towards the rim. The boat and contents are then dried in the steam oven for an hour or more. The combustion is performed as above, but a much lower temperature suffices.

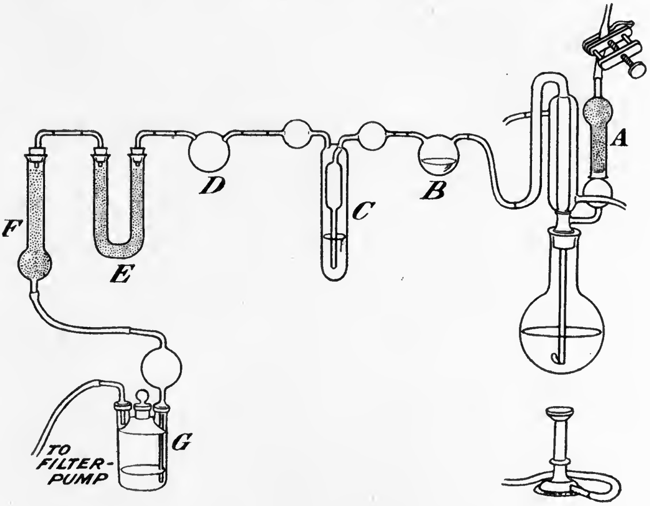

FIG. 8.

A contains calcium chloride in the bulb and powdered soda lime in the stem; it is fitted with a screw clip for regulating the air supply.
B is an empty bulb.
C contains strong sulphuric acid.
D is an empty bulb whose object is to prevent any spray of acid getting to E.
E contains dry calcium chloride.
F is a soda lime tube for absorbing the carbon dioxide.
G is a sulphuric acid trap for the suction arrangement.

3. Direct Wet Combustion.—A suitable apparatus for this process which, however, has been almost entirely displaced in works' practice by the direct dry combustion process, is shewn in the accompanying Fig. 8

A stock solution of the oxidising mixture is made by dissolving about 450 grams of pure chromic acid and the same weight of recrystallised copper sulphate in water, and diluting the mixed solutions to 3 litres. Of this mixture, filtered through asbestos for use, 170 c.c. are placed in the evolution flask together with 185 c.c. of concentrated sulphuric acid. The flask is then placed in position on a wire gauze, the screw clip for regulating the air supply closed, and the filter pump started. All joints in the apparatus being found gas-tight, the liquid is heated to boiling, the screw clip loosened, and a steady current of air allowed to pass for half an hour; the flame is then turned out and the pump stopped. After cooling for 15 minutes, the flask is removed, the weighed soda lime tube attached, 5·4544 grams of the sieved drillings are added to the mixture in the flask, and the latter quickly replaced. The mixture is then heated up in the same order of procedure as before. The decomposition is usually complete in about an hour, whereupon air is admitted for a few minutes to sweep out the last traces of carbon dioxide. Five times the increase in the weight of the soda lime tube is the percentage of carbon in the steel.

ESTIMATION BY COLOUR IN STEEL.

Weigh off 0·10, 0·15 or 0·2 grams of the steel and the same weight of the standard steel, according to the percentage of carbon in the latter. Place the drillings in dry test tubes and add 3 c.c. of nitric acid (specific gravity 1·20) to each. Allow the first vigorous action to subside and then immerse the tubes in a bath of hot water. Continue the heating, with occasional shaking, until the brown flocks which float in the liquid have dissolved, then remove the tubes and cool them off under the tap. When cold, transfer to the paired "comparison tubes," graduated in tenths of a cubic centimetre. By dilution of one or other of the solutions, bring the depth of colour in the two solutions to the same, when viewed against an opaque screen; the percentage of carbon in the two steels is proportional to the volumes of the solutions. A damp filter paper stuck on a window pane makes a good background. In comparing colours the tubes are held close up to the screen, side by side, and with the graduations invisible.

GRAVIMETRIC ESTIMATION OF GRAPHITE IN STEEL.

To 5 grams of the steel add about 100 c.c of nitric acid s.g. 1·20, in small amounts at a time, allowing the vigorous reactions to subside between each addition. Digest the mixture short of boiling point until all the flocks of nitrated carbonaceous matter pass into solution. Filter off the graphite through asbestos, wash with cold water and finally with very dilute ammonium hydrate. Transfer to a boat, dry in steam oven, and burn as above. Instead of digesting until the carbonaceous flocks are taken into solution, the latter may be more quickly disposed of by adding a solution of potassium permanganate until a brown precipitate of hydrated manganic oxide persists in the hot solution. The precipitate is then removed by the addition of a few drops of sulphurous acid. It is worthy of note that a representative sample for the estimation of graphite is not secured by sieving. Sievings are likely either to be deficient in free carbon if the larger pieces are taken, and too rich if the finer dust is selected.

ESTIMATION OF CARBON IN PIG IRON.

The total carbon in pig irons is determined on a one gram sample by direct combustion, using red lead as a flux. The remarks above respecting sampling apply with greater force to the case of pig iron.

Graphite is also determined as in steel. An approximate estimation which does not require a combustion furnace is effected by separating the graphite with dilute nitric acid, filtering through a hardened paper, washing with a solution of sodium or potassium hydrate to dissolve out silica, then with acidulated water, and finally with water only. The graphite is then washed from the paper into a weighed dish, the excess of water evaporated and the dish and contents dried in a steam oven.

This method is not accurate, but it does not require such close attention as the combustion process. Grey irons which are highly siliceous frequently yield a residue which clogs the filter. This difficulty is removed by the occasional addition to the solution of a few drops of hydrofluoric acid.

ESTIMATION OF CARBON IN SPECIAL STEELS.

High speed steels, and steels in general containing special elements such as nickel, cobalt, vanadium, etc., are not suitable materials for the estimation of carbon in the wet way, nor for the previous wet separation of carbon followed by a combustion. Without exception, however, the direct combustion may be applied and red lead is particularly recommended as a flux.

Free carbon is very seldom encountered in these steels except in the case of such as contain large amounts of silicon, and known as 'silicon steels'; these are treated for the estimation of graphite as described above.

SILICON (Si = 28·3.)

All methods practised in the determination of silicon in steel or pig iron are gravimetric, involving the final weighing of the oxide, SiO_2, and almost all of them effect the separation of silicon from the associated iron by taking advantage of the fact that the oxide is insoluble in the ordinary mineral acids (and in mixtures of them)—with the exception of hydrofluoric acid. The usual procedure in the estimation of silicon consists therefore of (1) a conversion of the silicon of the metal into silicic acid, (2) the dehydration of the latter, and (3) dissolving out the basic iron compounds from the solid mixture by means of hydrochloric acid.

Most mineral acids and mixtures of them have been recommended for the first operation—hydrochloric, nitric, aqua regia, sulphuric, and mixtures of sulphuric with nitric or with aqua regia. It was formerly thought and believed that decomposition of the metal with hydrochloric or sulphuric acid singly resulted in a loss of silicon in the form of its volatile hydride, SiH_4, hence the employment of an oxidant in the form of nitric acid, alone or in a mixture. This belief proved not to be founded on fact, and hydrochloric acid is now commonly used for 'opening out' ordinary steels.

Silicon exists in steel as a solid solution of iron silicide in excess of iron, but there may also be present a very small amount in the form of a silicate, constituting slag involved in the steel or iron during casting operations. The acid or acid mixture decomposes the iron silicide, and part of the silicon passes into solution in the form of silicic acid (and probably also silico-chloroform, $SiHCl_3$, when hydrochloric acid is used for opening out the metal). The amount taken into solution depends upon the acid used—reducing acids such as hydrochloric and sulphuric leave a larger undissolved portion than nitric acid. The insoluble part consists of coagulated silicic acid.

The second operation, that of dehydrating the silicic acid, is performed in one of two ways, both of which commence with an evaporation of the mixture. The first method consists in a continuation of the evaporation to complete dryness, and is followed by a roasting of the dry ' cake ' on the hot plate. Solutions in hydrochloric acid usually give little trouble, due to spattering, when they reach pastiness, and, moreover, there is no danger of overheating the dry residue, an operation which requires from 10 to 15 minutes over the hottest part of the plate for the complete dehydration of silicic acid. On the other hand, solutions of ferric nitrate are much more liable to spattering when the solid begins to separate out, and overheating of the residue may yield basic compounds not easy to dissolve in the next operation.

The second method of dehydration is always and necessarily utilised when sulphuric acid is a constituent of the original acid mixture. In this case the evaporation and heating are continued until the excess of the more volatile acid, nitric or hydrochloric, is completely expelled, as indicated by the copious fumes of sulphur trioxide which rise from the semi-solid mass of ferric sulphate. By this treatment silicic acid is dehydrated without any fear of overheating.

Grey and mottled pig irons contain much more silicon than steels, and the separation of silicic acid during the decomposition of the metal is therefore much more copious and obvious; the drillings, in fact, frequently become coated with gelatinous silica, thereby retarding the decomposition. The remedy is to employ finely divided material, a large excess of acid, and vigorous boiling.

Plain carbon steels yield a residue of pure silica ultimately, but special steels which may contain, *e.g.*, tungsten, molybdenum, vanadium, chromium, nickel, cobalt, etc., may yield an impure product. This is always the case with steels containing tungsten, an invariable and abundant constituent of high-speed steels. Titanium is seldom present in steels, though frequently found in pig irons—it also separates almost completely as TiO_2 along with the silica. Alumina and phosphide of iron occasionally have also to be reckoned with.

The determination of the exact amount of silica in these impure residues is made usually by treating them, after ignition in a platinum vessel and weighing, with a slight excess of hydrofluoric acid, which converts the oxide into the volatile tetrafluoride of silicon.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O.$$

The excess of acid is removed by evaporation on the hot plate, and this is followed by ignition at a red heat for a few minutes in order to convert the fluoride of the contaminating metal into oxide again—the loss of weight due to this treatment is evidently a measure of the silica.

Obviously metals whose fluorides are volatile or undecomposable at a red heat should not be present in residues thus treated. Aluminium and titanium fluorides are examples of the former and calcium fluoride of the latter type. In such cases a few drops of sulphuric acid are added along with the hydrofluoric acid. The sulphates thus formed remain during the evaporation of the excess of hydrofluoric acid and expulsion of silicon tetrafluoride, but are decomposed subsequently into oxides by ignition, which should be conducted at a high temperature, to remove the last traces of sulphur trioxide.

Siliceous residues containing vanadium, as V_2O_5, the presence of which is betrayed by the reddish brown tint which it imparts to them (either diffused through the mass or in coloured patches), require special treatment. At a red heat, with or without the addition of sulphuric acid, vanadium is visibly expelled in the form of a brown vapour. To prevent this, the excess of sulphuric acid which remains after that of the hydrofluoric acid has been expelled, is removed on the hot plate, a few drops of nitric acid added, and the mixture again taken to dryness. A repetition of the treatment with nitric acid, followed by a final ignition at a dull red heat leaves the whole of the vanadium in the form of its pentoxide again.

Another method of purifying siliceous residues, and one which possesses the advantage of providing a direct determination of the silica in them, consists of a fusion with potassium pyrosulphate or bisulphate. The latter is decomposed thus :—

$$2KHSO_4 \rightarrow K_2SO_4 + H_2SO_4,$$

and the sulphuric acid generated under these conditions possesses an enhanced solvent action on the impurities. Lixiviation of the cooled melt with water, filtration, and washing, leave pure silica on the filter.

Several methods of minor importance for the determination of silicon call for brief mention.

(1) The metal is decomposed in a heated tube by means of a current of chlorine, the volatile ferric chloride and silicon tetrachloride being carried forward into water, in which the former dissolves and by which the latter is hydrolysed to silicic acid. It is claimed that a separation is thus made of the silicon in the metal from that existent in involved slag.

(2) The metal is fused with potassium bisulphate, the melt extracted with acid, and the insoluble silica filtered off.

(3) The metal, in a fine state of division, is roasted in the muffle in order to oxidise the silicon to silica, and the roasted mass extracted with hydrochloric acid.

GRAVIMETRIC ESTIMATION IN STEEL.

1. **Hydrochloric Acid Method.**—Five grams of drillings are treated with about 50 c.c. of hydrochloric acid in a covered beaker, and when decomposition is complete, or nearly so, the liquid is boiled briskly over the middle of the hot plate until solid ferrous chloride begins to separate. Evaporation is then allowed to proceed more slowly and cautiously, so as to avoid spattering, until the residue is almost dry, whereupon the cover is removed and the temperature gradually raised again until the yellowish green 'cake' is quite dry. The beaker is finally heated over the hottest part of the plate until the solid contents assume a reddish brown colour; it is then removed and allowed to cool after replacing the cover. When cold, or nearly so, 30 c.c. of hydrochloric acid are added, the mixture heated until the iron compounds have completely dissolved, an equal volume of water added so as to rinse the cover glass and sides of the beaker, the mixture brought to boiling point and filtered at once through paper pulp. Washing, which must be very thorough, is done alternately with cold water and hot 50 per cent. hydrochloric acid, the latter being prepared conveniently in the beaker and used along with a 'policeman' for detaching the last traces of silica which cling tenaciously to the glass. The filter and contents are then transferred to a crucible, dried rapidly in front of the muffle or on the hot plate, and finally ignited in the hottest part of the muffle. The residue should be perfectly white—it contains 46·93 per cent. of silicon.

Silica is very hygroscopic unless it has been subjected to a very high temperature, so that in the case of steels of high silicon contents, a second ignition and weighing are necessary. Purification of the residue by one or other of the methods described above is seldom necessary in the case of plain carbon steels.

2. **'Nitro-sulphuric' Method.**—Dissolve 5 grams of drillings in about 80 c.c. of the following mixture.

Sulphuric Acid (s.g. 1·84) - - - - -	250 c.c.
Nitric Acid (s.g. 1·42) - - - - - -	450 c.c.
Water - - - - - - -	1000 c.c.

Place the beaker at once over the hottest part of the plate and allow the liquid to boil briskly to dryness with the cover in position. When the frothing, which occurs towards the end of the evaporation, is followed by the expulsion of thick fumes of sulphur trioxide, add immediately warm water to the pale yellow mass of ferric sulphate. [The addition of cold water to the hot 'cake', or of either hot or cold water after waiting until the beaker is quite cold, results frequently in a cracked vessel and a wrecked assay.] Next add from 20 to 30 c.c. hydrochloric acid and heat the mixture until the ferric sulphate is completely dissolved, and then finish the operation, which should occupy not more than an hour, as above.

ESTIMATION IN PIG IRON.

Of white irons, weigh the same amount as for steels; in the case of mottled and grey irons, one gram is ample, and the amount of acids used is proportionately diminished. The nitro-sulphuric mixture is the better one to employ, and the procedure is exactly the same as for steels up to the process of ignition. This operation in the case of grey irons requires a longer time in order to burn out the associated graphitic carbon completely, and ought in all cases to be followed by a treatment of the residue with hydrofluoric and sulphuric acids.

ESTIMATION IN HIGH-SPEED STEELS.

High-speed steels and steels for the manufacture of permanent magnets contain comparatively large amounts of tungsten. The determination of silicon in this class of material is always made in conjunction with that of tungsten, for which see p. 136.

PHOSPHORUS (P = 31·0).

Numerous investigators in the fields of analytical chemistry have busied themselves with the determination of phosphorus, and the published papers on the subject outnumber those relating to the determination of any other element, with the possible exception of vanadium. Fortunately the processes in use at the present time are comparatively few, and the conditions making for success in their application to the analysis of the raw materials and finished products of metallurgical and other operations, have been precisely determined. Nothing more than a brief reference to a few of the others is therefore necessary, nor is it possible to attempt more within the compass of this work.

Separation from Iron.—The separation of phosphorus from iron, and also its determination, are almost invariably made from solutions containing the element in the oxidised form of orthophosphoric acid or a salt of it. A notable exception to this is furnished by the method of opening out steels with solutions of copper. A warm neutral solution of potassio-cupric chloride, *e.g.*, leaves all the phosphorus in an unoxidised form in the carbonaceous residue, associated with a small quantity of the iron, with the sulphur, etc., but free from arsenic ; this method of attack was formerly used by a number of operators.

The precipitation of the phosphorus as a phosphate from hot neutralised solutions containing the iron sometimes as a ferrous, at other times as a ferric salt, was formerly made with solutions of silver, lead, antimony, etc. Conversely the precipitation of the iron as ferrocyanide was made the basis of other and less satisfactory separations of the two elements. These, and fusion with an oxidising mixture of potassium and sodium salts, followed by an aqueous extraction of the soluble phosphate, are methods which have fallen completely into disuse, though in many cases they were originally devised as improvements upon those which are in use at the present time.

There are now practically only two processes in general use. The most important of these is the precipitation of orthophosphoric acid from solutions, containing also free nitric acid, by means of ammonium molybdate solution, which separates phosphorus completely from iron or any other metallic bases that may be present. As the precipitate provides in itself a direct method for the determination of the element, a fuller account of the process is given below in that connection.

The other method, known frequently as the 'acetate process,' is one in which nearly all the iron is held in solution as a ferrous salt, and the whole of the phosphorus precipitated together with the remaining small portion of iron as a mixture of ferric phosphate with basic ferric acetate. The process is not easy of execution, but as it provides at one stage of the operation a suitable solution from which to eliminate arsenic when present, and is, moreover, extremely useful in certain other respects, a description of it, as applied, *e.g.*, to the determination of phosphorus in steel, is appended.

Five grams of the drillings are opened out in a wide beaker with nitric acid s.g. 1·20, the mixture taken to dryness and the residue baked strongly over the hottest part of the plate in order to decompose the ferric nitrate. The residue is dissolved in hydrochloric acid and the solution again evaporated to low bulk. After dilution, the liquid is transferred to a large conical flask, with or without filtration of the separated silica, and made up to about 300 c.c. with hot water. To the hot solution dilute ammonium hydrate is added a little at a time, with vigorous shaking between each addition, until a small but permanent precipitate is obtained, whereupon about 100 c.c. of a saturated solution of sulphur dioxide in water are added. The colour of the solution rapidly changes from red to a very pale green, due to the reduction of the iron. The liquid is then boiled vigorously to expel the excess of sulphur dioxide, and at this stage it is convenient to remove arsenic, if present. This is done by passing a current of hydrogen sulphide through the solution or by adding a few decigrams of pure zinc sulphide. The precipitated arsenic sulphide is filtered out after digesting for a short time, and the excess of hydrogen sulphide expelled from the filtrate by boiling.

The precipitation of the phosphoric acid is then made in one or other of several ways, all of which depend upon the presence in the solution of sufficient or just more than sufficient ferric iron to form ferric phosphate, any excess of iron being precipitated at the same time as a basic acetate. A procedure frequently recommended is that of generating the ferric iron required by the addition to the solution, after cooling, of one or two c.c. of chlorine or bromine water. The precipitation is then made by the cautious addition of very dilute ammonium hydrate, with vigorous agitation of the solution, until the greenish precipitate which forms at first dissolves with difficulty, is then followed by a distinct red or brownish red precipitate, and finally by a permanent green precipitate. The last is then dissolved by adding dilute acetic acid (s.g. 1·04) drop by drop, leaving the red precipitate, whereupon an excess of 1 c.c. of the acetic acid is added, the solution heated to boiling, and maintained in ebullition for a minute or so.

Another form of precipitation, preferred by the author, differs somewhat from the above. The solution, after the expulsion of the excess of sulphur dioxide (which need not be perfectly complete unless arsenic is to be removed), contains a considerable amount of free acid resulting from the reduction of such a large amount as nearly 5 grams of iron in the form of ferric chloride.

$$2FeCl_3 + SO_2 + 2H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl.$$

It is accordingly again treated with dilute ammonium hydrate, added cautiously, until a faint but permanent turbidity or precipitate is obtained, about 20 c.c. of saturated sulphurous acid are added, and the liquid boiled until sulphur dioxide can be no longer detected by smell in the escaping vapour. To the hot solution there are then added a solution of ferric chloride, free from phosphorus and equivalent to about 5 centigrams of the metal, and about 20 c.c. of hot ammonium acetate solution. The mixture is then boiled for a minute or so and the precipitate allowed to settle for about 2 minutes.

By either of these two methods the whole of the phosphoric acid present is secured in the precipitate, which is filtered out as rapidly as possible, and, without washing, is dissolved as described below, along with that part of it left on the sides of the flask.

The filtrate containing nearly all the iron as ferrous chloride, passes through the filter perfectly clear, but rapidly becomes brown and turbid with a surface scum due to the separation of insoluble basic ferric compounds. This separation is more pronounced in the second method of precipitation than the first; in both cases suction should be used in the filtration.

The above method of separating ferrous from ferric iron is applicable also to its separation from chromium and aluminium, as the phosphates of these metals, like ferric phosphate, are also insoluble in acetic acid solution. The addition therefore to the solution containing the ferrous chloride of a crystal or two of potash alum instead of ferric chloride is quite as satisfactory, though obviously the colour changes which provide a guide to the addition of the correct amount of alkali, are missing. (See ' Aluminium ' p. 104.)

Determination of Phosphorus. 1. The ' Magnesia Process.'—The precipitation of phosphoric acid by means of magnesia mixture is one of the oldest methods employed for the determination of phosphorus in irons. The process has been made the subject of many investigations resulting in more or less conflicting recommendations in the past. In its present form, whether applied to the determination of phosphorus or of magnesium, it gives excellent results.

The solution must contain the phosphorus in the form of an orthophosphate and be free from the heavy metals or alkaline earths. In order to obtain the characteristic crystalline precipitate of the composition $MgNH_4PO_4 \cdot 6H_2O$, the precipitation should be made from a hot[1] and not from a cold solution, as formerly recommended. Obtained from a cold solution the precipitate is liable to contamination with the orthophosphate $Mg_3(PO_4)_2$, and also with the double phosphate $Mg(NH_4)_2(PO_4)_2$, both of which separate in a non-crystalline form.

The ' magnesia mixture ' used as the precipitant should be made from the chloride and not the sulphate. A considerable excess of magnesia mixture is first added to the solution, which should contain a little hydrochloric acid, then about 15 c.c. of a saturated solution of ammonium chloride. The liquid is then heated to boiling and, whilst stirring continuously, very dilute ammonium hydrate of strength not greater than 3 per cent., is added cautiously until the precipitate begins to form. The addition of the alkali is then continued in drops at intervals of about

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[1] Gooch, *Zeit. anorg. Chem.*, 20. 135.

15 seconds, until the mixture is faintly but distinctly ammoniacal to the smell. It may happen that the precipitate which first forms is not the crystalline one desired, but a milky turbidity; in such an event, the solution should be cleared with hydrochloric acid and the operation repeated. When the mixture is cold, one-fifth of its volume of ammonium hydrate (0·880) is added and the beaker set aside for not less than 15 minutes.

The precipitate may be collected on paper pulp; it is washed with 3 per cent. ammonium hydrate until the washings yield no reaction for chlorides, transferred to a crucible, and dried on the hot plate before ignition. The ignition should be conducted at a low temperature at first so as to prevent loss of material mechanically carried away with the escaping ammonia, and completed finally at the back of the muffle. The residue of magnesium pyrophosphate should be quite white throughout its entire mass. This is almost invariably the case with small amounts, but large residues frequently contain charred, unburnt portions of the filter enclosed by the outer white layer of completely ignited material. It is necessary to break up such residues with a rounded glass rod or stiff platinum wire, and re-ignite them until they are perfectly white, with the addition, in obstinate cases, of a little ammonium nitrate. Magnesium pyrophosphate, $Mg_2P_2O_7$, contains 27·85 per cent. of phosphorus, equivalent to 63·79 per cent. of P_2O_5.

The above method when applied to the estimation of phosphorus in steels involves a preliminary separation of the whole or greater portion of the iron. This separation is made either by the ammonium molybdate precipitation next described or by the ‘acetate process’ described above.

In the latter case, the precipitate of ferric phosphate mixed with basic acetate is dissolved from the filter by means of a hot mixture of equal volumes of hydrochloric acid and water prepared in the unrinsed flask in which the precipitation was made. The solution and washings are concentrated by evaporation to a volume of about 5 c.c., the same amount of a 50 per cent. solution of citric acid added, and the solution treated, as described above, with magnesia mixture, etc. The amount of concentrated ammonium hydrate added in the determination of such small amounts of phosphorus should be increased to about one-half the volume of the mixture, and the whole allowed to stand overnight.

When the separation from iron is made by precipitation with ammonium molybdate, the yellow precipitate obtained is collected, washed, and then dissolved from the filter with very dilute ammonium hydrate (about 3 per cent.), and the solution treated with dilute hydrochloric acid until the precipitate which forms dissolves with difficulty on stirring. An excess of magnesia mixture is then added, the solution heated to boiling, and the precipitation completed as described above.

2. The 'Molybdate Process.'—The precipitation of orthophosphoric acid from solutions containing it and free nitric acid by means of ammonium molybdate, followed by direct weighing of the yellow compound obtained is very extensively used for the determination of phosphorus; as a means of separating iron and phosphorus it has almost entirely superseded the 'acetate process.' This has doubtless resulted from the facts that the separation is perfect, is easy and rapid of execution, and yields, moreover, a weight of precipitate more than 60 times that of the phosphorus contained in it. No account of the process is complete without a reference to the classical research of Hundeshagen—"Analytical Studies on Phospho-dodecamolybdic Acid, the Conditions of its Formation, and its Separation as an Ammonium Salt." (*Zeit. f. anal. Chem.*, 28. 14, and *Chem. News*, 50. 169, 177, 188, 201 and 215.) From it, the following principal findings are abstracted.

(1) The yellow precipitate obtained by the addition of ammonium molybdate solution to a solution containing orthophosphoric acid and an excess of nitric acid, after being washed with cold dilute nitric acid and dried to constant weight in the desiccator over calcium chloride or caustic potash, has the composition

$$12MoO_3 \cdot (NH_4)_3PO_4 \cdot 2HNO_3 \cdot H_2O.$$

At 130°-150° it loses water and nitric acid, becoming $(NH_4)_3PO_4 \cdot 12MoO_3$, containing 1·65 per cent. of phosphorus.

(2) The formation of the precipitate is facilitated and hastened by the presence of from 5 to 10 per cent. of ammonium nitrate in the solution.

(3) Precipitation is more rapid from hot than from cold solutions and the precipitate is denser and more crystalline. Obtained from a cold solution it consists of spheroidal granules and is not so easily and quickly filtered and washed. Agitation of the reacting mixture assists the separation.

(4) An excess of nitric acid is necessary. The minimum amount is 26 molecules for each molecule of P_2O_5 in the solution, and as much as 80 molecules is permissible. When present in still larger amounts the acid decomposes and partially dissolves the precipitate. This action is perceptible with 100 molecules, from which point it increases rapidly, dissociation being complete when 1900 molecules of acid to 1 molecule of P_2O_5 are present.

A sufficient excess of ammonium molybdate prevents the solvent action of the acid, as also does ammonium nitrate.

(5) Perfectly neutral and cold solutions of ammonium nitrate or chloride do not dissolve any appreciable quantities of ammonium phospho-molybdate, but they eliminate the combined acid, so that the precipitate after washing with such solutions has the same composition as when dried at 130°-150°. Very dilute solutions dissolve the yellow precipitate without decomposition of it; the addition of ammonium nitrate to the solution effects a re-precipitation.

Nitrate and chloride of sodium, and of potassium in less degree, dissolve the precipitate, which can be re-formed also by the addition of ammonium salts.

By heating with water, considerable amounts of the yellow precipitate can be dissolved in a short time: ammonium nitrate and nitric acid again effect a re-precipitation. Salts of organic acids dissolve the phospho-molybdate; it is re-formed, however, when the organic acid is monobasic if it be liberated by a mineral acid in the presence of ammonium salts. Dibasic acids, *e.g.*, oxalic and tartaric, entirely prevent the reunion of the constituents of the compound.

In the particular case of the analysis of steel and of iron alloys, there remain other points which are not covered by the preceding generalisations. The influence of the elements invariably present in steel upon the precipitation must first be considered; of these carbon is the most important.

Steel and iron are often dissolved by dilute nitric acid for the purpose of a phosphorus determination. The nitrated carbon compounds formed were at one time supposed to cause an imperfect separation of the phospho-molybdate, and this led to the practice of evaporating the solution to dryness and baking the residue. It is now generally understood that the nitrated carbon compound exerts little or no influence upon the precipitation, which is really due to the fact that metaphosphoric acid is first formed when the metal is dissolved. The subsequent evaporation to dryness and baking of the residue convert the meta- to the ortho- compound and incidentally decompose the organic matter. The conversion to ortho-phosphoric acid and the oxidation of the carbonaceous matter are therefore now generally effected in the solution by the addition to it, at boiling point, of potassium permanganate, the excess of which, or of its decomposition product (hydrated manganese peroxide) is afterwards decomposed. Any one of such reducing agents as ferrous sulphate, oxalic acid, sulphurous acid, sugar, hydrogen peroxide, tartaric acid, potassium nitrite, or hydrochloric acid may be used for this purpose.

Manganese and sulphur do not affect the precipitation in any way.

Silicon also does not retard the precipitation but traces of silica may be incorporated in the precipitate, and would therefore lead to high results if the estimation is completed by a direct weighing of the yellow compound. From dilute solutions that are kept just warm only, a precipitate practically free from silica can be secured even when the material is highly siliceous.

Arsenic is a not uncommon constituent of steel, though the amount of it is small. It is precipitated, more or less, along with the phosphorus compound, and in the form also of a yellow compound of analogous composition. The amount of arsenic carried down depends upon the temperature at which the precipitation is made and also upon the time allowed before filtration. At a temperature not exceeding 30° C. the amount precipitated in a comparatively long time is negligible, and this is true also of a precipitation at 70° C. with vigorous shaking for about five minutes, which suffice for a complete separation of the phospho-molybdate. The elimination of arsenic from the solution by means of zinc sulphide or hydrogen sulphide prior to the precipitation of the phosphorus has been referred to previously. Metallic zinc is also used for the same purpose, the arsenic being thus removed in the form of gaseous arsine.

With the exception of vanadium, metallic elements in general are without influence upon the precipitation of ammonium phospho-molybdate. The determination of phosphorus in vanadium steels is treated below.

There remains at least one other point that calls for notice, viz., the temperature factor. A high temperature not only favours the co-precipitation of silica and arsenic acid, but also promotes the separation of molybdic acid by decomposition of the ammonium molybdate reagent. Under the most favourable conditions, the maximum temperature of precipitation should not exceed 80° C.

The ultimate determination of the phosphorus is made in a variety of ways, gravimetric and volumetric. In connection with the gravimetric assay, it is mentioned previously that the yellow compound after being dried at 130°-150° C. has the composition $(NH_4)_3PO_4.12MoO_3$. In ordinary practice, the precipitate is filtered off, washed with 2 per cent. nitric acid and dried at a temperature of 100° C. or thereabouts, and is found then to contain 1·63 per cent. of phosphorus instead of 1·65 required by the above formula. In order to make a direct weighing the following methods are in use.

1. Brushing from the dried filter paper.
2. Using counterpoised filter papers.
3. Washing from the paper into a weighed dish and drying.
4. Collecting in a Gooch crucible.

The drying in (1) and (2) is often hastened by a final washing of the precipitate with alcohol, but the devices are subject to such obvious errors as the incomplete removal of the precipitate from the paper, and the possibility of the balanced papers taking up unequal amounts of water vapour. The darkening of the paper, which is sometimes referred to as an indication that the precipitate has been sufficiently dried, is also an indication that some reduction has taken place or that ammonia has been lost from the compound. The third method is so tedious that for works' purposes the first or second means are more extensively used, notwithstanding the possible sources of error mentioned. Filtration through a felting of asbestos in a Gooch crucible is obviously the best procedure; its use in works is limited, however, by the all-important time factor.

The hygroscopic character of the dried precipitate must always be taken into account, and in the case of large amounts of it, two weighings should always be made, the second one following upon a second drying for a few minutes, and made with the greatest possible speed.

Another form of gravimetric estimation consists in an ignition of the ammonium phospho-molybdate. The ignition must be carefully controlled, however, and yields a residue of the composition $P_2O_5 . 24MoO_3$, if the temperature does not exceed 450° C.[1] The yellow precipitate is collected in a Gooch crucible, and after a preliminary drying, the crucible is covered with a watch glass and placed inside a larger nickel crucible on a filter disc or thin layer of ignited asbestos. The ignition is then conducted over a small flame, the temperature of the bottom of the outer crucible not being allowed to exceed that of dull redness, until the precipitate assumes a homogeneous blue-black colour throughout. The residue contains 1·72 per cent. of phosphorus.

The most satisfactory method of treating the yellow precipitate by way of a gravimetric determination of phosphorus consists in the conversion of the molybdic acid in it to lead molybdate. A long experience of the method, during which thousands of estimations have been done or observed by the author, has convinced him that the process is the most reliable and exact of all, gravimetric and volumetric alike.

In some papers on the analysis of molybdenum compounds Brearley[2] showed that when a hot solution containing molybdic and phosphoric acids is treated with hydrochloric acid sufficient in quantity to prevent a precipitate from forming on adding next at least enough lead acetate to form the lead salts of the first two acids, the hot mixture so obtained, when poured into another containing ammonium chloride and ammonium

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[1] *Chem. Zeit.* 21. 442.

[2] *Chem. News*, 78. 203.

acetate, yields the whole of the molybdenum as a precipitate of lead molybdate, the phosphoric acid remaining in solution. The advantage of transforming the phospho-molybdate into lead molybdate in this way is that the latter separates at once in a form which is rapidly filtered, washed and ignited without decomposition. Moreover, its weight is more than 140 times that of the phosphorus which it represents, thus :—

$$\begin{array}{ccccc} P & \rightarrow & (NH_4)_3PO_4 \cdot 12MoO_3 & \rightarrow & 12PbMoO_4 \\ 31 & & 1877 & & 4404 \end{array}$$

The details of the process are given below.

The volumetric estimation of phosphorus in the yellow precipitate can be made in two ways, each depending upon the determination of the molybdic acid contents. The first of these, due to Handy,[1] consists in decomposing the compound with a standard solution of sodium hydroxide and measuring the excess of alkali by titration with an acid. The method is very rapid, and is therefore extensively used ; it is described in detail below.

The second method consists in the reduction of the molybdic oxide to the sesquioxide (Mo_2O_3), followed by a titration of the solution with standard potassium permanganate. For this purpose, the yellow precipitate is collected on filter paper or pulp and washed thoroughly with an acid solution of ammonium sulphate, made by dissolving about 17 grams of the solid in 1000 c.c. of 2·5 per cent. sulphuric acid. The precipitate is then dissolved from the filter with about 20 to 30 c.c. of water containing 5 c.c. of ammonium hydrate (0·880), and the solution treated with sulphuric acid until it contains approximately 2·5 per cent. of its volume of free acid (1·84). The acid solution is passed through the reductor, according to the procedure described on p. 15, and is received in a solution of ferric alum. The usual titration with permanganate completes the determination.

$$P \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 \rightarrow 6Mo_2O_3 \rightarrow \tfrac{36}{5}(KMnO_4).$$

From the above formulation it follows that 31 parts by weight of phosphorus correspond to $\tfrac{36}{5} \times 158$ parts of potassium permanganate, or 1 part of phosphorus to 36·696 parts of permanganate. One cubic centimeter of a solution of the latter, containing 1·8348 grams of the pure solid per litre, is therefore equivalent to 0·00005 gram of phosphorus, *i.e.*, 0·01 per cent., working upon a two-gram sample of the steel.

A solution containing about two grams of the solid per litre is frequently used instead, and is standardised by means of a steel of known phos-

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[1] *Chem. News*, 76. 324.

phorus contents. The figure thus obtained obviously dispenses with a blank determination on the reductor and the reagents.

A number of other methods are employed for the purpose of an approximate estimation of phosphorus in steel. They are useful for purposes of control and when information is wanted in the quickest possible time. They depend upon:

1. Comparison of the turbidities formed when a solution of the steel is shaken with ammonium molybdate.
2. The colour formed when the dissolved phospho-molybdate is poured into an acid solution of stannous chloride or sodium thiosulphate; or the colour formed with ferrocyanide.
3. The volume occupied by a precipitate when it is settled in a graduated taper tube by whirling in a centrifugal machine.

Each of these processes must be worked under the conditions obtaining when the standards are prepared or the apparatus calibrated.

Of less interest from a steel-works' point of view are various other volumetric processes which in most cases are useful for estimating large amounts of phosphorus only. They may be briefly tabulated:

1. Direct titration with a neutral solution of ammonium molybdate until a precipitate of phospho-molybdate is no longer formed.
2. Iodometric estimation of the combined molybdic oxide by distilling with potassium iodide and hydrochloric acid or with potassium bromate.
3. Titration of the molybdic acid with lead acetate and tannin after eliminating phosphoric acid with magnesia.
4. Addition of silver nitrate, lead acetate, etc., and estimation of excess of metal in the filtrate, or its amount in the precipitated phosphate.
5. Formation of ammonium magnesium phosphate and estimation of the excess of standard ammonium hydrate added, or of the ammonia in the precipitate.
6. Titration with uranium nitrate using ferrocyanide or cochineal as indicator.
7. Titration with ferric oxychloride or iron alum solution, using gallic or salicylic acid as indicator.
8. Precipitation as ammonium manganese phosphate and estimating the manganese after transforming to dioxide.
9. Measuring the amount of soda required to transform the monosodic to the disodic phosphate, using methyl-orange and phenolphthalein as indicators.

GRAVIMETRIC ESTIMATION IN STEEL.

Ammonium Molybdate Reagent.—Prepare a stock solution of the molybdate reagent by dissolving 100 grams of molybdic oxide in a mixture of 240 c.c. of water and 170 c.c. of ammonium hydrate (0·880) and pouring the solution with constant stirring, into 1250 c.c. of nitric acid s.g. 1·20. Filter off the required amount when wanted for each determination.

I. **Weighing as Lead Molybdate.**—Dissolve two grams of steel in 45 c.c. of nitric acid 1·20, expel the nitrous fumes by boiling, and add a solution of potassium permanganate until a pink colour or a brown precipitate of hydrated manganese dioxide persists for a minute in the boiling solution. Clear the liquid with a few drops of sulphurous acid, add carefully 4 or 5 c.c. of ammonium hydrate, dissolve any ‘ splashings ’ of ferric hydrate from the sides of the flask into the main solution, and then add 30 c.c. of the molybdate reagent. Allow the mixture to digest at about 70° C. for about 20 minutes, with occasional shaking, until the yellow precipitate settles to the bottom leaving a clear supernatant liquid. Filter through paper pulp, transferring the last traces of the precipitate to the filter with cold 2 per cent. nitric acid, and wash the precipitate well with the same reagent. Dissolve the precipitate from the filter in 4 c.c. of strong ammonium hydrate, wash once with hot water, pass the solution through the same filter again, and wash several times with hot water. Set the liquid to boil on the hot plate side by side with a mixture of 50 c.c. of ammonium acetate and 10 grams of ammonium chloride contained conveniently in the original flask. When both solutions boil, add to the ammoniacal solution of the yellow precipitate 10 c.c. of hydrochloric acid, 10 c.c. of a 4 per cent. solution of lead acetate, and pour at once into the boiling mixture in the other flask. Lead molybdate is precipitated and may be filtered at once through pulp, washed with hot water, and ignited.

$$PbMoO_4 \times \cdot 007 = \text{Phosphorus.}$$

Notes.—The above process is very accurate, though it is not so rapid as the volumetric method described below. A single estimation needs at least half an hour from the time the drillings are weighed out, but a series of estimations can be made in proportionally less time; *e.g.* thirty estimations have been done in a working day of seven hours by an experienced operator. This output, needless to say, is not attainable by the majority of workers.

The ability to deal with large numbers of assays depends to a great extent upon the peculiar fitness of the apparatus for the work; the following particulars, therefore, may be found useful in this connection.

Registered conical flasks such as are shewn in Fig. 7 are used throughout the operation. A smooth funnel 3¼ inches in diameter is large enough to hold the whole of the solution and yellow precipitate, which may therefore be poured on at once. The flask is washed twice, and then the filter twice more, each time allowing all the solution to run through; about 100 c.c. of 2 per cent. nitric acid in all should be used. Using pulp, the filtration is very rapid and the washing particularly effective. The filters holding the final precipitate of lead molybdate are transferred to marked crucibles and placed six or eight at a time in the hot muffle; under this severe treatment the precipitate never spatters.

The final precipitation may be modified and time saved in the act, by pouring the ammoniacal solution into 50 c.c. of a solution made by dissolving 8 grams of lead acetate crystals in 400 c.c. of B.P. acetic acid and 600 c.c. of water. The composition of the precipitate thus obtained is approximately $Pb_3(PO_4)_2 \cdot 24PbMoO_4$ which contains 0·644 per cent. of phosphorus.

II. **Direct weighing of the 'yellow precipitate.'**—The precipitate of ammonium phospho-molybdate obtained in the preceding method may be collected and weighed directly. It is customary, however, to obtain it in a different manner, and particularly in the case of material containing arsenic, because the process provides at one stage a solution from which this element may be eliminated.

Dissolve 2 grams of drillings in about 30 c.c. of nitric acid of s.g. 1·20, evaporate to dryness, and bake the residue at a moderate heat (about 200°-250° C.) for half an hour. Dissolve up with 15 c.c. of hydrochloric acid, dilute to about 40 c.c. with water and filter off the silica. Evaporate filtrate and washings to a volume not exceeding 10 c.c., add dilute ammonium hydrate (1 to 1) until the iron is precipitated as hydrate, re-dissolve the precipitate in strong nitric acid added in drops at a time and add then an excess of about 3 c.c. Dilute to a volume of about 50 c.c., and shake round continuously whilst 30 c.c. of the filtered solution of molybdate reagent is delivered into the centre of the solution. Digest as before at 70°-80° C. The precipitate is collected on a tared or counterpoised filter paper, or best of all, on asbestos in a Gooch crucible, dried at 100°-110° C. and weighed, with due attention to the hygroscopic nature of the product. The residue contains 1·63 per cent. of phosphorus.

VOLUMETRIC ESTIMATION IN STEEL.

The following reagents are required for this process :—

1. A solution of sodium hydrate, made by dissolving approximately 15·5 grams of the pure solid in 2000 c.c. of distilled water.
2. Nitric acid of strength approximately equal to that of the alkali, and made by diluting 20 c.c. of the strong acid s.g. 1·4 to 2000 c.c. with water.
3. A solution of phenol-phthalein, made by dissolving 0·2 gram of the solid in about 200 c.c. of 95 per cent. alcohol.

Weigh off 2 grams of steel and proceed exactly as described in the 'lead molybdate method' described above up to the end of the washing of the yellow precipitate with 2 per cent. nitric acid, and then wash the precipitate with a 2 per cent. solution of potassium nitrate until the washings show no acid reaction. Transfer the precipitate and filter to a clean flask, add about 30 c.c. of freshly distilled water, and run in an excess (10 to 15 c.c.) of the sodium hydrate solution from a burette. Shake until the yellow precipitate is decomposed and dissolved, as shewn by the perfectly white condition of the pulp. Add three drops of the phenol-phthalein indicator and titrate the liquid with the nitric acid solution until the pink colour is just discharged. Read the burettes, and without rinsing out the flask, add next about 20 c.c. of the sodium hydrate solution and titrate again with nitric acid.

Notes.—The second pair of readings gives the relative strengths of the acid and alkali, determined under the conditions obtaining in the assay of the steel. From these, the amount of alkali required to neutralise the molybdic oxide of the yellow precipitate is easily calculated, since the excess of it added is given by the nitric acid of the first titration. The value of the sodium hydrate in terms of phosphorus remains finally to be obtained.

The decomposition of the ammonium phospho-molybdate precipitate by the alkali may be symbolised thus :—

$$2[(NH_4)_3PO_4 \cdot 12MoO_3] + 46NaHO = 2Na_2HPO_4 + 21Na_2MoO_4 + 3(NH_4)_2MoO_4 + 22H_2O.$$

From the above it follows that

$$\begin{array}{ccccc} P & \rightarrow & (NH_4)_3PO_4 \cdot 12MoO_3 & \rightarrow & 23NaHO \\ 31 & & 1877 & & 920 \end{array}$$

The sodium hydrate solution may therefore be made up according to the above figures, and standardised by a direct titration with a standard solution of a mineral acid. It is frequently standardised also by means of a definite weight of pure ammonium phospho-molybdate, prepared by precipitation from a solution of pure sodium phosphate. A weighed amount, freshly dried, is dissolved in an excess of the alkali, and the solution titrated with a standard acid.

Most frequently the standardisation is made by means of a steel of known phosphorus contents. An assay of this is conducted along with a batch of the unknowns, and the relative strengths of the acid and alkali determined on this particular one of the set. This is the method preferred by the author, hence the stock solutions of acid and alkali are not made up with any great care. The main objection to standardisations of solutions and processes by means of material of 'known' composition is obvious, but the objection disappears when reliable material can be obtained. In respect of this matter, the American Bureau of Standards has done valuable work; similar work has been and is now being done also in this country.

ESTIMATION IN PIG IRON.

The processes described for steel apply equally well to pig iron, after removal of the contained graphite. If the iron is highly siliceous, a few drops of hydrofluoric acid should be added when the material is decomposed, so as to facilitate the filtration of the graphite. The filtrate should be concentrated to approximately the volume obtaining before the filtration, before proceeding to the precipitation.

High Phosphorus Irons.—In the case of highly phosphoric irons, less than 2 grams may be weighed off and the process modified accordingly. When the ammonium phospho-molybdate precipitate is the first indication that much phosphorus is present, the lead molybdate process is modified, after dissolving the precipitate in ammonium hydrate, by making the solution up to a definite volume and using a measured fraction of it for the remaining operations. The quantities of reagents specified are suitable for percentages of phosphorus up to 0·1, working upon a 2 gram sample, and larger amounts may be accurately estimated by increasing the amount of hydrochloric acid added to the boiling ammoniacal solution of the yellow precipitate, in order to hold molybdic acid in solution, the amount of ammonium acetate being also correspondingly increased. It is safer, however, to confine the process within the prescribed limit, and fractionate at an earlier stage of the operation.

Titanium in Irons.—The insoluble residue obtained by dissolving titanic pig irons in nitric acid contains phosphorus, which may be recovered in several ways. Thus, after evaporating to dryness, baking, dissolving in hydrochloric acid and filtering, the insoluble residue is ignited to burn off the graphite, and the residue fused with sodium carbonate. The mass is extracted with hot water and the insoluble sodium titanate filtered out. The filtrate is acidified, a few cubic centimetres of the first filtrate containing the iron added to it, and the mixture treated with a slight excess of ammonium hydrate. The precipitate of ferric hydrate and phosphate is filtered out, washed, dissolved in acid, and the solution added to the main filtrate.

Another method, due to Pattinson, is as follows. The iron is dissolved up as before in hydrochloric acid. Without filtering, the ferric chloride is then reduced by means of sulphurous acid, and the phosphorus obtained from the solution as aluminium phosphate by the addition of sufficient dissolved alum. This precipitation has been described at some length under the heading 'separation from iron' on pp. 48-50. The precipitate is ignited and the residue fused with sodium carbonate as above. The filtrate from an aqueous extract of the fusion contains the whole of the phosphorus, which may be precipitated as ferric phosphate, as just described, after adding a solution of ferric chloride free from phosphorus.

Influence and Removal of Arsenic.—Ammonium molybdate precipitates arsenic from solutions of arsenic acid and its salts, hence the element must be eliminated before an accurate determination of phosphorus can be made. The amount usually present in most steels is so small that the phosphorus value is not seriously affected, particularly when the precipitation of the phospho-molybdate is effected rapidly. Wrought iron and pig irons frequently contain amounts of arsenic, however, which make it absolutely necessary to eliminate the element.

In the section dealing with the separation of phosphorus from iron the precipitation of arsenic as sulphide from the solution containing the iron as a ferrous salt is mentioned, hydrogen sulphide or zinc sulphide being employed for this purpose. Similarly in Method II. described above, the solution obtained by dissolving the baked residue in hydrochloric acid may be utilised. By adding metallic zinc, the arsenic is volatilised entirely or partly as arsine, the ferric being at the same time reduced to ferrous chloride. Complete removal of arsenic in the form of its tribromide is then obtained by adding a pure solution of hydrobromic acid (about 10 c.c. of 1·4 s.g. acid), and evaporating the solution carefully to dryness. Ridsdale[1] uses 5 grams of ammonium bromide instead of hydrobromic acid. The residue is taken up again with hydrochloric acid, silica filtered out and the process carried forward as usual, extra nitric acid being required for the re-oxidation of the iron.

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[1] *Chem. News*, 118. 100.

When the precipitation of phospho-molybdate is made in the presence of arsenic, the freedom of the compound from arsenic is best assured by increasing the acidity of the solution and diminishing the amount of contained ammonium nitrate. Chlorides and sulphates should be absent from the solution, and the temperature of the precipitation should not exceed 60°C. These are substantially the conditions obtaining in Method I. described above. For sulphurous acid, however, potassium nitrite or ammonium oxalate may be advantageously substituted.

ESTIMATION IN SPECIAL STEELS.

Steels containing either chromium, nickel, cobalt, large amounts of manganese or small amounts of tungsten may be assayed for phosphorus without any serious modification of the ordinary processes.

Chromium steels require more permanganate in the preliminary operation, the resulting chromic acid being afterwards reduced by the sulphurous acid. When the chromium present amounts to 2 or 3 per cent., the material is not always decomposed completely by 1·20 nitric acid, even after digestion with permanganate. On adding a few cubic centimetres of dilute sulphuric acid, however, the action recommences, frequently with a slight explosion, and then ends quickly ; in such cases, 6 or 7 c.c. of ammonium hydrate should be added before precipitating with the molybdate reagent.

In the case of low tungsten steels tungstic oxide may separate during the preliminary operations, and should be removed by filtration before proceeding.

Tungsten Steels.—High-speed steels, containing usually not less than 10 and often as much as 18 per cent. of tungsten, cannot be decomposed by dilute nitric acid. For the determination of phosphorus, 2 grams of the drillings are decomposed with 40 c.c. of a mixture of equal volumes of strong hydrochloric and nitric acids, added a few cubic centimetres at a time. The mixture is digested until the tungstic oxide which separates is quite yellow, and is then taken to a pasty condition by evaporation of the excess of acid. The paste is boiled up with 50 c.c. of dilute hydrochloric acid (1 to 4), the tungstic oxide filtered off and washed with 5 per cent. hydrochloric acid, and the filtrate set to evaporate. The tungstic oxide contains phosphorus, as shewn by Gray and Smith.[1] The amount of the contained phosphorus is of no moment with regard to the determination of tungsten, since high-speed steels rarely contain more than a total of 0·05 per cent., but it is obviously of

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[1] *Chem. News,* 118. 258.

considerable importance in this connection. The ignited tungstic oxide is therefore fused with sodium carbonate, and the melt extracted with water. Any slight residue is filtered off, the paper burnt, the residue dissolved in a few drops of hydrochloric acid, and the solution rinsed into the original filtrate under evaporation. The alkaline solution of sodium tungstate is made freely acid with hydrochloric acid, ammonium hydrate added until the precipitated tungstic oxide is dissolved, and a further excess equal to one-fourth the volume of the liquid. The phosphorus is then recovered from the solution by precipitation with 3 c.c. of magnesia mixture. The ignited pyrophosphate is dissolved in acid and the solution combined with the original filtrate, which is then taken to dryness, the residue re-dissolved in 10 c.c. of hydrochloric acid, an excess of ammonium hydrate added, the ferric hydrate precipitate just dissolved in nitric acid, 3 c.c. more added, and lastly, the molybdate reagent.

Vanadium Steels.—The phospho-molybdate precipitate obtained from vanadium steels by the ordinary methods is orange-red in colour instead of yellow, and contains vanadium. Brearley and the author[1] called attention to this fact and pointed out also that though the precipitate contains vanadium, it does not contain the whole of the phosphorus. The presence of vanadium evidently retards the formation of the phospho-molybdate, and thus leads to low results when the estimation of phosphorus is conducted as usual. The deficiency is not very serious, as it is partially compensated by the vanadium, which is ultimately weighed as a basic pyrovanadate of lead and included in the calculation as lead molybdate when the first of the three methods is used. Vanadium may be eliminated from the precipitate in several ways. Brearley and the author originally employed the following method :—

Dissolve 2 grams of the steel in 45 c.c. nitric acid (1·20), add an excess of permanganate and clear with ferrous sulphate, as in the estimation of phosphorus in ordinary steels. Then cool and add a small excess of a strong solution of ferrous sulphate, so that a drop of the solution tested with ferri-cyanide gives an *immediate and marked* blue colour. Then add 6 or 7 c.c. concentrated ammonium hydrate, the usual amount of molybdate reagent, and shake occasionally over a period of half an hour. Numerous tests of the above process, made since its publication, have convinced the author that it is not quite satisfactory. The results are usually low.

Johnson[2] obtains accurate results from steels containing as much as

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[1] *Analysis of Steel Works' Materials.*

[2] *Journ. Ind. and Eng. Chem.* xi. No. 2, and *Chem. News,* 118. 113.

2·6 per cent. of vanadium by precipitation from solutions containing an excess of nitric acid, using a faintly ammoniacal solution of ammonium molybdate instead of the usual acid reagent. It is prepared by dissolving 55 grams of the solid and 50 grams of ammonium nitrate in 40 c.c. of ammonium hydrate (0·95 s.g.), diluted to 700 c.c. with water. The mixture is heated for about half an hour with occasional stirring until complete solution is obtained, water up to 1000 c.c. is added and the mixture allowed to stand over night. Insoluble matter is then removed by filtration and the clear solution bottled for use. The method of precipitation follows the ordinary lines, thus :—

Dissolve 1·63 grams in 45 c.c. nitric acid s.g. 1.13. When brown fumes have been expelled, add 3 c.c. permanganate solution (50 grams per litre), boil, and clear with a slight excess of ferrous sulphate solution. Add 40-50 c.c. of nitric acid (1·42), heat to boiling, add 50 c.c. of the molybdate reagent, stir for a minute or two and allow to stand over night.

Johnson recommends the volumetric method for finishing the estimation.

Of the other methods which have been proposed for the determination of phosphorus in vanadium steels that of Hagmaier[1] merits a brief description, though the cost of material precludes its general adoption in works. The metal is decomposed with aqua regia, the solution evaporated to dryness, the residue baked, taken up with hydrochloric acid and silica filtered out. The iron is reduced with sulphurous acid, 5 c.c. of 90 per cent. acetic acid and 10 c.c. of a saturated solution of cerium chloride added. Dilute ammonium hydrate is then added cautiously with constant stirring, up to the formation of a turbidity. The mixture is heated to boiling, and the precipitated cerium phosphate filtered off, washed with hot water, dissolved in hot 1·20 nitric acid, and the phosphorus precipitated from the solution with the molybdate reagent.

SULPHUR (S = 32·1).

Separation from Iron.—As the separation of sulphur from iron is always accomplished in the course of the actual estimation of the element, there is no necessity for a distinct and separate account of the various processes.

An exception to the above is the method of opening out with a solution of copper ammonium chloride, since this is followed by a second quite distinct process for the actual estimation of the sulphur. The insoluble

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[1] *Met. and Chem. Eng.* xi. p. 28.

carbonaceous residue left by the decomposition of steel in this way contains the whole of the sulphur, and upon it the determination of sulphur is made by fusing with a mixture of sodium carbonate and sodium peroxide. From the aqueous extract, after filtration and acidification, the sulphate in solution is precipitated and estimated as barium sulphate. Franklin[1] rightly claims that this process yields consistently higher results than any other. That this is so is evident from the fact that certain materials only yield their total sulphur content by a fusion, and the preliminary removal of the greater part of the iron by the attack with copper ammonium chloride considerably facilitates this operation.

Gravimetric Determination of Sulphur.—The gravimetric methods of estimating the element may be divided into two classes, accordingly as the element is weighed as a sulphate or as a sulphide. The latter are the more numerous, but the former are, perhaps, more frequently employed. Of the few so-called insoluble sulphates of metals, that of barium is very much less soluble than the others, particularly in the presence of acids, and it is almost exclusively the one selected for precipitation from solution after sulphuric acid has been generated in it.

The conversion of the sulphur from a steel or alloy (in which it does not exist in the form of an oxidised compound) into sulphuric acid is, obviously, a point of extreme importance. This is done in the initial decomposition of the steel, and loss of sulphur as hydrogen sulphide must therefore be prevented by attacking with powerful oxidants. Many mixtures may be employed that oxidise the sulphur partially, the remainder escaping as hydride, but only few effect a complete oxidation. Mixtures of hydrochloric acid and bromine, and hydrochloric acid and potassium chlorate have been recommended and used, but the best mixture is undoubtedly that of nitric with hydrochloric acid, if properly applied.

The resulting solution is not suitable for an immediate precipitation with a solution of barium, as the nitric acid present retards the formation of barium sulphate. It is customary therefore to evaporate the solution to dryness and bake the residue thoroughly. This removes the nitric acid and renders the silica insoluble, incidentally providing a means of estimating silicon at the same time.

Thorough baking for the purpose of removing nitric acid is a matter of some importance. At too high a temperature there is a danger of loss of sulphur as sulphur trioxide, due to the decomposition of the sulphate in the dried mass. Ferric sulphate is decomposed at a lower temperature (530°C.) than the sulphates of sodium and potassium,

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[1] *Journ. Ind. and Eng. Chemistry*, 5. 839.

hence it is customary to introduce with the drillings, or at any time previous to the baking, a small quantity of a potassium salt such as the nitrate or chlorate.

The various instructions as to time, temperature, and degree of acidity for the precipitation of the sulphur as barium sulphate are very numerous, and have resulted largely from the following facts.

If the amount of free acid present is too little, there is great probability of contamination of the barium sulphate with basic iron compounds; on the other hand, strongly acid solutions of ferric chloride exert a marked solvent action on barium sulphate. Moreover, it is not easy, in any case, to obtain a precipitate of pure barium sulphate as it so readily occludes any possible impurities that may be present in the form, for example, of salts of the alkali metals, and increased acidity is the corrective of this. Hence the adjustment of the amount of acid is a matter of primary importance. It is certainly now well established that the precipitation should be made in a solution containing only a moderate amount of free hydrochloric acid, about 10 per cent., and from a total bulk of about 100 c.c.

Complete separation and filtration of the small amount of barium sulphate obtained from steel is facilitated by the addition to the solution, before precipitation, of a definite quantity of a soluble sulphate, and is strongly recommended (*vide infra*). As an aid to filtration also, Krak has proposed the use of ammonium acetate. Most of the supernatant liquid is poured upon the filter without disturbing the precipitate and then a few cubic centimetres of ammonium acetate are added, the mixture stirred well and poured upon the filter. This procedure also defeats the tendency of the precipitate to pass through the filter.

Barium sulphate is stable up to a temperature of about 1500° C. according to Hofmann and Wanjukow,[1] but when ignited along with a paper filter there may be some reduction. This is not much in the case of the comparatively small weight of barium sulphate obtained in the analysis of steel, and is lessened by completing the ignition at the back of the muffle with a good draught. With larger amounts of precipitate, however, it is desirable to add a drop or two of sulphuric and nitric acid, after ashing the paper completely, and re-ignite.

One of the oldest methods of estimating sulphur as a sulphate is due to Fresenius and consists in the evolution of hydrogen sulphide by dissolving the steel in hydrochloric or sulphuric acid, and the subsequent oxidation to sulphuric acid. The oxidation is done by passing the evolved gases through bromine in bromine water, thus separating the

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[1] *Met. and Chem. Engineering*, 10. 1912. 172.

sulphur from the iron, and providing a solution from which it is only necessary to expel the excess of bromine before precipitating out with barium chloride.

The other gravimetric methods which finish with barium sulphate are, firstly, those in which the separation from the greater part of the iron is effected by opening out with copper ammonium chloride, already referred to. The residue is then either fused as outlined above or treated with brominised hydrochloric acid for effecting oxidation. The second class employs the raw material in a finely divided condition for the fusion.

The evolution of hydrogen sulphide has been used for gravimetric purposes in other ways. For instance, the gases are passed through a solution of a metallic salt, the resulting sulphide decomposed with an oxidant and the sulphur precipitated from the solution as before. Or the precipitated sulphide may be collected directly, and weighed after drying or igniting. An ammoniacal solution of a cadmium salt is frequently used for this purpose; the resulting cadmium sulphide is collected on a Gooch crucible, dried and weighed as such. Similarly copper sulphide may be precipitated out, collected and ignited to oxide.

Volumetric Determination of Sulphur.—All the methods for the volumetric estimation of sulphur in steel depend upon the evolution in the form of sulphide by attacking the steel with hydrochloric or sulphuric acid or with a mixture of the two.

It is obvious that oxidising agents must be excluded during the decomposition of the metal in order to prevent the formation of sulphuric acid or even sulphur resulting from atmospheric oxidation.

The decomposition is sometimes started in an atmosphere of hydrogen or carbon dioxide generated externally: the precaution is unnecessary if the solution of the steel be effected quickly, as the evolution of hydrogen which then takes place sweeps out the air very quickly from the apparatus. The question of the speed of evolution is, in fact, of considerable importance. Experience has shewn that the more rapidly the steel is attacked, the more complete is the delivery of the sulphur as hydrogen sulphide. From this it follows that an elevated temperature, finely divided drillings, and, in the case of hydrochloric, fairly strong acid are the best conditions for the attack. Under these circumstances, it is found also to be unnecessary to sweep out the apparatus at the conclusion of the decomposition, by means of hydrogen or carbon dioxide.

Another point in connection with the evolution of hydrogen sulphide is of importance, though it is not very often observed in works' practice, and has, indeed, not been fully investigated. It has been pointed out that when alloys such as steel, which contain carbon as well as sulphur, are attacked by acids there is a probability of the evolution of organic sulphur compounds, which may not be absorbed by the medium usually employed. In the case of pig irons this probability is enhanced by the presence of so much carbon in them, and it is certain that many cases of discrepancy between the results obtained on the same sample gravimetrically and volumetrically are due to this cause. The decomposition of the organic sulphides is resorted to by many operators, and is accomplished by passing the evolved gases through a heated tube before their delivery into the absorption vessels. Rapid modes of evolution appear to lead to the formation of less of these compounds than do the slower methods.

The condition of the steel, as regards its previous treatment, is a matter of some importance, particularly in the case of alloy steels. Elliot[1] obtains more uniform results by annealing the steel. He mixes 5 grams of the drillings with 0·25 grams of potassium ferro-cyanide, wraps the mixture in paper and heats in a crucible for twenty minutes in the muffle; similarly Gregory and Macfarlane,[2] in the case of pig irons, mix the finely divided drillings (5 grams) with acid potassium tartrate (0·5 gram) and anneal for fifteen minutes prior to decomposition.

The methods employed for absorbing the hydrogen sulphide are very numerous. One of the oldest and best is that of Arnold and Hardy,[3] in which the hydrogen sulphide is passed through a series of bulbs each containing a known amount of a standard lead acetate solution. One bulb at a time is attacked, and hence the quantity of sulphur may be read off directly by counting the number of bulbs completely blackened and estimating the proportion of the last that has been attacked. Another method is to pass the hydrogen sulphide into a solution of sodium hydrate, to liberate it again by adding an excess of acid and then to titrate the solution with a standard solution of iodine. Instead of sodium hydrate an ammoniacal solution of cadmium chloride is often employed, the resulting cadmium sulphide, without filtration, being treated exactly as in the preceding case. This is a very satisfactory method and gives excellent results. Klinder[4] adopts a modification of the last method by filtering out the cadmium sulphide. It is then placed in a solution of potassium iodide to which has been added an excess of sulphuric acid and a known amount of potassium permanganate. The excess of iodine is titrated with sodium thiosulphate.

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[1] *Chem. News*, 104. 298.

[2] *Chem. News*, 93. 201.

[3] *Chem. News*, 58. 41.

[4] *Stahl u. Eisen*, 31. 1838.

$$10KI + 2KMnO_4 + 8H_2SO_4 \rightarrow 5I_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O$$
$$H_2S + I_2 \rightarrow 2HI + S.$$

The following proposals do not appear to have been generally adopted:

1. The evolved gases are passed through a solution containing lead, copper or arsenic, the precipitated sulphide removed and the solution assayed for the amount of metal left.
2. The hydrogen sulphide is absorbed in a solution of an alkali and the solution is titrated with a standard solution of lead acetate.
3. The hydrogen sulphide is absorbed by a neutral solution of a metallic salt and the acid thereby liberated measured.

GRAVIMETRIC ESTIMATION IN STEEL.

Place 5 grams of the steel in a 20 oz. covered beaker and add 30 c.c. of nitric acid s.g. 1·42. Warm the mixture and then add a few drops of hydrochloric acid. Allow the vigorous action to complete itself and then add a little more hydrochloric acid, repeating the addition similarly until the steel is all dissolved. Not more than 30 c.c. of hydrochloric acid are required in any case. To the solution add a crystal or two of pure potassium chlorate or nitrate and evaporate the liquid as quickly as possible to dryness, taking care to avoid spattering at low bulk. Bake the residue for about half an hour and allow to cool. When cold dissolve in 25 c.c. of hydrochloric acid, evaporate to a low bulk (about 10 c.c.), add 50 c.c. of water and heat to boiling. Filter off the silica and wash well, or, alternatively, make up the solution to 90 c.c. and collect 75 c.c. of filtrate passed through a dry filter, thereby avoiding the washing. To the solution add 20 c.c. of a 10 per cent. solution of barium chloride, bring the liquid to a boil and then set aside for the precipitate to form and settle. This may be complete in a few hours, but it is preferable to allow the estimation to stand overnight to ensure the complete precipitation of the barium sulphate. Filter the solution through a tightly packed pulp filter and wash thoroughly with five per cent. hydrochloric acid. Dry and ignite, in the ordinary manner and weigh the precipitate. The precipitate is $BaSO_4$ and contains 13·7 per cent. of sulphur.

It has been found to be of great advantage to this method to increase the weight of the precipitate of barium sulphate by adding a known weight of a sulphate to the solution at some definite stage, and then deducting this weight from that of the final precipitate. A standard solution is prepared by dissolving a definite weight of either potash alum, ferric alum, or potassium sulphate in water. A suitable solution is one containing 1·36 grams of potassium sulphate crystals per litre. Of this solution add 10 c.c. (from a burette) to the solution obtained after filtering off the silica and before the addition of the barium chloride solution. In order to standardise the potassium sulphate solution a standard steel should be employed, the sulphur content of which is known. If a number of sulphur estimations are being made at the same time, this standard steel should be worked upon with each batch of estimations. Perform the estimation on this steel exactly as above and obtain the precipitate of sulphate from the steel and from the added sulphate. Calculate the sulphur in the steel to barium sulphate, deduct this weight from that of the precipitate, the difference representing the weight of barium sulphate obtained from 10 c.c. of the standard solution, and the reagents employed. This weight should then be deducted from that obtained in the case of the unknown steel, and the difference calculated for the percentage of sulphur in the steel.

The reagents employed in this process, whether more sulphate is added or not, have usually a blank sulphur value. If the modification of adding sulphur is adopted, the standardisation of the potassium sulphate includes the determination of the blank, but if the simple estimation be carried out, the quantity of sulphur in the reagents must be found. To determine this it is not sufficient to mix all the quantities used with some alkali and then to precipitate the sulphate. It is essential to carry out an estimation under the exact conditions of the usual determination on a steel of known sulphur content, and by calculation of this content to barium sulphate to obtain the value of the blank. Another way is to operate on two different quantities of the same steel, *e.g.*, 2·5 and 7·5 grams, and to take the difference in the weights of the precipitates as representing the sulphur from 5 grams of the steel.

VOLUMETRIC ESTIMATION IN STEEL.

Many different forms of apparatus for decomposing the steel and absorbing the hydrogen sulphide evolved are in use; some of these are elaborate and others very simple in construction. Any of them may be used, but as a particular arrangement is usually associated with a particular absorbent, a brief description is included in the following three methods, which are typical of general works' practice.

1. Cadmium Sulphide Process.—Prepare an evolution flask from a large wash bottle, fitting it with a rubber bung pierced by two holes. Through one hole pass a thistle funnel tube with a stem reaching nearly to the bottom of the flask and through the other an evolution tube bent twice at right angles. This tube should be of such dimensions that the horizontal arm is long enough to protrude over the edge of the hot plate and clear the flask if the latter is placed a little distance from the edge of the plate. The further vertical part of the tube should be divided into two parts, one short (the upper part) and the other of length sufficient to reach to the bottom of a tall glass cylinder placed on the working bench, whilst the flask is on the hot plate. These two parts of the tube should be joined by a piece of rubber tubing.

Place 20 c.c. of the ammoniacal cadmium chloride solution (*vide infra*) in the cylinder and dilute to about 200 c.c. with water so as to provide a long column of absorbent. In the evolution flask place 5 grams of drillings and just cover these with 20 c.c. of water. Arrange the thistle funnel tube to dip under the surface of the water and connect up the evolution tube with the exit tube in the cylinder. Heat 50 c.c. of hydrochloric acid almost to boiling, place the evolution flask on the corner of the hot plate and pour the hot acid down the funnel. When all the acid has been added heat the contents of the flask to boiling point and maintain the action at a vigorous rate until all the steel is dissolved. When this has happened, boil for a minute or so, and then without removing the flask from the plate, disconnect the larger part of the exit tube at the rubber joint. Then remove the flask from the plate. Pour the contents of the cylinder into a 30 oz. flask, washing all the precipitate from the cylinder and the evolution tube into the flask. Add hydrochloric acid, a little at a time, keeping the mixture cold, until the yellow cadmium sulphide is all dissolved and a clear colourless solution is obtained. Add a few c.c. of starch solution and titrate at once with a standard solution of iodine containing 2 grams of iodine and 6 grams of potassium iodide per litre, until the full purple blue of iodide of starch indicates an excess.

The end point of the reaction is reached when a full blue colour is obtained, intermediate pink and red colours being disregarded. The iodine solution should be standardised against a standard steel of definite and known sulphur contents. The following reactions are involved in the process ;—

$$\begin{aligned}
&MnS + 2HCl \rightarrow MnCl_2 + H_2S.\\
&H_2S + CdCl_2 4NH_3 \rightarrow CdS + 2NH_4Cl + 2NH_3\\
&CdS + 2HCl \rightarrow CdCl_2 + H_2S\\
&H_2S + I_2 \rightarrow 2HI + S.
\end{aligned}$$

A stock solution of cadmium chloride is made by dissolving 10 grams of the solid in 500 c.c. of water mixed with an equal volume of ammonium hydrate s.g. 0·880.

2. Sodium Sulphide Process.—In this method the hydrogen sulphide evolved is absorbed in sodium hydroxide solution, and after being liberated again by acidification is titrated as in the preceding method by means of iodine. The apparatus used is shewn in Fig. 9.

Weigh off 5 grams of drillings and place them in the evolution flask (20 oz.) fitted with a two-bulbed thistle funnel and a 50 c.c. blank pipette bent as shewn, the latter being connected with a three-bulbed U tube (5 ins. by $\frac{5}{8}$ in.). Charge the U tube with 7 c.c. of the sodium hydroxide solution and pour through the thistle funnel a hot mixture of 50 c.c. of hydrochloric acid with 50 c.c. of water. Maintain the heat until all drillings have dissolved and finally boil to expel all traces of hydrogen sulphide from the flask and until the delivery tube is too hot to touch at the top of the bend. The U tube or its contents should not be allowed to become hot. Rinse out the contents of the U tube into a beaker containing 25 c.c. of 20 per cent. sulphuric acid and a measured amount of the standard iodine solution and titrate the excess of iodine with a standard solution of sodium thiosulphate.

The sodium hydroxide solution contains 280 grams of the solid sticks in one litre of solution. A blank test should be made upon it by acidifying 7 c.c. of it and testing the solution with the standard iodine. If more than 0·5 c.c. of the latter are used the soda solution is unfit for use, and a fitter sample should be secured.

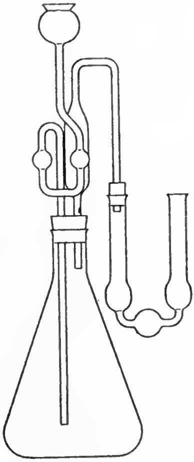
FIG. 9.

The iodine solution is made by dissolving about 4 grams of iodine and 12 grams of potassium iodide in as small a quantity of water as possible and then diluting to a litre.

The sodium thiosulphate solution contains about 8 grams of the pure crystals and 4 grams of sodium bicarbonate in one litre of solution.

3. Zinc Sulphide Process.—Place 5 grams of drillings in the evolution flask shewn in Fig. 10, insert the condenser and connect up with the two absorption flasks, each previously charged with about 100 c.c. of a zinc solution. Add a hot mixture of 50 c.c. hydrochloric acid and 50 c.c. water by means of the small funnel shewn on the left side of the figure, start the flow of water through the condenser and apply heat to the flask. When solution of the drillings is complete, remove the funnel, attach the wash bottle containing a solution of lead acetate, open the screw clamp and sweep out with a current of air induced by a water pump. To the first absorption flask, which alone need be considered if the second remains clear, add an excess of iodine, shake for a minute or two in order to promote decomposition of the zinc sulphide, and titrate the excess of iodine by means of sodium thiosulphate.

As in the preceding methods, the solutions are standardised by operating upon a steel of known sulphur contents, and therefore under exactly the same conditions that obtain in the assay of unknown steels.

A suitable absorbing solution is made by dissolving 20 grams of pure zinc in hydrochloric acid, adding ammonium hydrate until a precipitate forms, redissolving in acetic acid, and diluting with water to a litre.

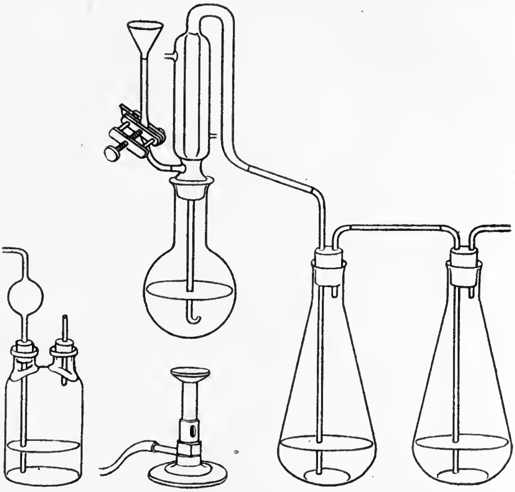

FIG. 10.

ESTIMATION IN PIG IRON.

Any of the above methods may be applied to the assay of pig iron for sulphur; the volumetric process employing cadmium ammonium chloride as the absorbent is particularly recommended. The preliminary annealing with potassium ferrocyanide or cream of tartar referred to in the summary may be necessary with certain irons. Instances are not unknown in which the gravimetric process must be modified somewhat, because the graphitic residue left after the initial attack with the acids may contain sulphur. The amount of this is determined by the method adopted for coal or coke (*q.v.*).

ESTIMATION IN SPECIAL STEELS.

For steels containing nickel, chromium, vanadium, or molybdenum either the volumetric or gravimetric process may be employed with equally good results. If tungsten is present, and for high-speed steels generally, the volumetric process is unsatisfactory. The tungstic oxide is filtered out along with the silica in the gravimetric method.

MANGANESE (Mn = 54·9).

Separation from Iron.—Most of the processes used in the separation of iron from manganese are of a general character and have been described previously. Such are the ether separation, the barium carbonate separation, and the basic acetate separation. See p. 5 *et seq.*

Of those methods in which the manganese is thrown out of solution, the most important is known to steel works' chemists as the chlorate process. It is frequently referred to also as the Ford and Williams[1] method, and is described also by Hampe.[2] The method is based upon the conversion of a manganous salt in nitric acid solution to the dioxide by means of potassium chlorate.

$$Mn(NO_3)_2+2KClO_3 \rightarrow MnO_2+2KNO_3+2ClO_2.$$

Traces of iron are washed from the precipitate with difficulty, hence the determination of manganese, when made by this method, is usually volumetric, *vide infra.*

Methods of minor importance, and seldom used for technical purposes, are :—Volatilisation of the iron as chloride by a current of chlorine, precipitation of the iron with nitroso-β-naphthol, precipitation of the manganese by means of iodine or hydrogen peroxide from solutions containing potassium cyanide, and as potassium manganous oxalate, by a neutral solution of potassium oxalate, etc.

Gravimetric Determination.—Manganese is determined gravimetrically in the form of its sulphide, sulphate, pyrophosphate, and oxide (Mn_3O_4).

1. **As Oxide.**—The separation of iron as basic acetate is nearly always associated with the precipitation of the manganese from the filtrate as peroxide, by means of an oxidant such as bromine, chlorine, or hydrogen peroxide. The reaction

$$MnCl_2+Br_2+2H_2O \rightarrow MnO_2+2HCl+2HBr$$

is readily accomplished in solution containing a soluble acetate, which is decomposed by the liberated halogen acids with formation of neutral

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[1] *Trans. Inst. Min. Eng.* 10. 100.

[2] *Chem. Zeitg.* 7. 73 and 9. 1478.

salts. In the presence of larger amounts of ammonium salts, however, the quantity of acetate may not be sufficient to neutralise the acids set free by the reaction

$$2NH_4Cl + 3Br_2 \rightarrow N_2 + 2HCl + 6HBr$$

and accordingly the precipitation must be made in ammoniacal solution. The reaction may then be expressed by the following equation :—

$$MnCl_2 + Br_2 + 4NH_4OH \rightarrow MnO_2 . H_2O + 2NH_4Cl + 2NH_4Br + H_2O.$$

Bromine alone was used by the first steel analysts. The modern method is to dissolve a few cubic centimetres of bromine in the solution, not necessarily to saturation, and then add sufficient ammonium hydrate to render the solution distinctly alkaline. After digestion for a short time, the precipitate collects into flocks and may then be filtered, washed with hot water, dried and ignited.

Much discussion arose in the past respecting the composition of the ignited residue, and when the ignition is conducted in a platinum vessel over a flame, as was generally the case, the composition is undoubtedly subject to variation. Ignition at a temperature above 950° in a muffle furnace, however, invariably yields trimanganic tetroxide (Mn_3O_4), which contains 71·92 per cent. of manganese.

2. **As Sulphate.**—The determination of manganese as sulphate generally involves a previous precipitation in the form of carbonate, sulphide or hydrated peroxide, and though very accurate, is not rapid enough for technical purposes. The process is very easy to work, and is conducted as follows. The residue obtained by the ignition in a porcelain crucible of one or other of the compounds mentioned is dissolved in dilute sulphuric acid containing some dissolved sulphur dioxide, and the excess of acid removed by evaporation. The last traces are removed over a small flame, and the residue of manganous sulphate is finally heated to redness. $MnSO_4$ contains 36·36 per cent. of manganese.

3. **As Pyrophosphate.**—The solution, which should not contain more than 0·2 gram of manganese, is made slightly acid, treated with a large excess of ammonium chloride (10 to 20 grams), and about 10 c.c. of a saturated solution of sodium phosphate. Ammonium hydrate is then added in drops until the liquid smells distinctly of ammonia after mixing, the cold mixture is then heated to boiling and maintained for a few minutes at that temperature until the pink silky-looking crystalline ammonium manganese phosphate forms. After cooling again, the precipitate is collected on paper pulp, washed with cold water containing

ammonium nitrate, dried and ignited in the muffle at full redness. The residue is $Mn_2P_2O_7$ and contains 38·69 per cent. of manganese.

Volumetric Determination.—The volumetric processes are divisible into two groups, the first containing those in which a salt of manganese is oxidised to the hydrated peroxide (manganous acid), and the second those in which the oxidation is carried to permanganic acid. The former include the chlorate process and Volhard's method, and the latter the bismuthate, persulphate, and red lead processes.

1. **The "Chlorate Process."**—Referred to above in connection with the separation of manganese from iron, this method was formerly very largely used in the analysis of steel, and is still in use, though not to the same extent as the bismuthate process.

The precipitate of hydrated peroxide, obtained by the oxidation, is filtered off, washed, and transferred, filter and all, to a known amount of ferrous ammonium sulphate solution in dilute sulphuric acid. It is thus decomposed, according to the reaction

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O,$$

and the excess of ferrous salt is finally titrated with a standard solution of potassium bichromate or permanganate.

The process is accurate enough for the determination of comparatively small amounts of manganese, but large quantities of the precipitated oxide contain rather less oxygen than is demanded by the formula MnO_2, and this fact should be borne in mind in the assay of spiegel or ferro-manganese.

2. **The Volhard[1] Method.**—The oxidation to manganous acid is made in this process by adding a standard solution of potassium permanganate drop by drop to the boiling and slightly acid solution of the manganese salt. Guyard expressed the reaction thus:—

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + 2KHSO_4 + H_2SO_4.$$

Accordingly two molecules of permanganate are decomposed thus:—

$$2KMnO_4 \rightarrow K_2O + 2MnO_2 + 3(O),$$

and yield oxygen sufficient for the oxidation of 3 atoms of manganese

$$3MnO + 3(O) = 3MnO_2.$$

By weight 316 parts of permanganate are a measure of 164·7 parts of manganese, or 1 c.c. of $\frac{N}{10}$ solution $= 0·001647$ gram manganese.

The above equation and deductions therefrom do not represent the actual facts when the reaction takes place in pure solutions. The cause

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[1] *Ann. d. Chem. u. Pharm.* 198. 318.

of this is to be found in the fact that the oxidation product is not MnO_2 or H_2MnO_3, but more probably an acid manganous manganite. Volhard shewed that by introducing salts of calcium, barium, and particularly zinc, the precipitate obtained consists of a manganite (or acid manganite) of one of these metals, and the reaction could be expressed thus :—

$$2KMnO_4+3MnSO_4+5ZnSO_4+7H_2O \rightarrow 5ZnMnO_3+2KHSO_4+6H_2SO_4.$$

The ratio of permanganate to manganous salt is then the same as in the Guyard equation.

The process involves a previous separation of manganese from iron, and in the analysis of steel and of iron alloys is conducted as follows.

The metal is decomposed by nitric acid s.g. 1·20, about 10 c.c. of sulphuric acid added and the mixture evaporated to fumes. The residue of ferric and manganous sulphates is dissolved in water, the solution neutralised, short of the formation of a precipitate, with sodium carbonate, and transferred to a graduated flask. An excess of an emulsion of zinc oxide in water is then added, the contents of the flask made up to the mark and mixed, and a measured fraction strained off through a dry filter. To the filtrate a solution of about 8 grams of zinc sulphate is added, the liquid heated to boiling, and titrated with the potassium permanganate, with constant shaking, until the supernatant liquid is coloured pink.

3. The 'Bismuthate Process.'—The oxidation of a salt of manganese in nitric acid solution to permanganic acid by means of bismuth tetroxide was introduced by Schneider.[1] This reagent, which by virtue of the method of preparing it is seldom free from chlorine, is now displaced by sodium bismuthate. The latter is an amorphous brown powder, and is prepared, according to the instructions of Reddrop and Ramage [2] by heating 20 parts of sodium hydrate nearly to redness in an iron crucible, and adding, in small quantities at a time, 10 parts of dried basic nitrate of bismuth. Two parts of sodium peroxide are then added and the brownish yellow fused mass poured out on an iron plate to cool; when cold, it is broken up in a mortar, extracted with water, and the residue collected on an asbestos filter. The brown mass is washed several times with water, dried in a steam oven, ground and sieved finely. Its oxidising power is determined by adding half a gram of it to a known amount of ferrous sulphate or hydrogen peroxide, and titrating the excess with a decinormal solution of potassium permanganate.

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[1] *Ding. poly. J.*, 269. 224.

[2] *Trans. Chem. Soc.*, 1895. 268.

Purchased samples of sodium bismuthate seldom have an oxidising value equivalent to the formula $Na_2O.Bi_2O_5$. One molecule of this substance contains two atoms of available oxygen, so that the oxidation is expressible by the equation

$$4Mn(NO_3)_2+10NaBiO_3+28HNO_3 \rightarrow 4NaMn\cancel{N}O_4+6NaNO_3 \\ +10Bi(NO_3)_3+14H_2O.$$

The oxidation is effected in the cold, the excess of sodium bismuthate filtered off, and the sodium permanganate in the filtrate titrated with a standard solution of a reducing agent. The latter is generally ferrous ammonium sulphate, which is added in slight excess and the excess measured by a back titration with standard permanganate. The ferrous solution suffers no oxidation by the nitric acid in the cold and dilute solution.

The results are very accurate and the method is undoubtedly the best of the numerous processes for the determination of manganese, gravimetric or volumetric.

4. ‘ **The Persulphate Method.**’—Two forms of the persulphate process are in use. In one, the oxidation of the manganous salt is effected in sulphuric acid solution at the boiling point, whereby hydrated manganic oxide is precipitated according to the reaction

$$MnSO_4+(NH_4)_2S_2O_8+3H_2O \rightarrow MnO_2 . H_2O+2H_2SO_4+(NH_4)_2SO_4.$$

The precipitate is filtered off, and treated for the determination of the manganese, exactly as in the Ford and Williams ‘ chlorate method.’

In the other, the oxidation is effected in nitric acid solution by adding an excess of ammonium persulphate and heating the mixture until the permanganate colour is fully developed and oxygen is copiously evolved by the decomposition of the excess of oxidant. The reaction is hastened, catalytically, by the addition of a small quantity of silver nitrate.

$$2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O \rightarrow 2HMnO_4 \\ +5(NH_4)_2SO_4+5H_2SO_4+4HNO_3.$$

The solution is cooled quickly, the silver thrown out of solution by the addition of a small quantity of common salt, and the permanganic acid titrated with a standardised reducing agent.

Colorimetric Determination.—Small quantities of manganese are determined with a sufficient degree of accuracy by matching the pink colour of permanganic acid with that yielded by standardised material, just as in the Eggertz colour test for carbon. Ammonium persulphate, sodium bismuthate and red lead are the oxidants used.

GRAVIMETRIC ESTIMATION IN STEEL.

Four grams of drillings are dissolved in a 32 oz. conical flask in 40 c.c. hydrochloric acid, the iron oxidised with 5 c.c. of nitric acid, and a basic acetate precipitation of the iron made exactly as described on pp. 9-10. The volume of the mixture is made up to 1000 c.c. and 500 c.c., representing therefore two grams of the material, filtered off through a thick dry paper, the first runnings being discarded. An allowance of about 5 c.c. for the volume of the solid matter, and a temperature correction for contraction during the filtration may be made, though both are almost negligible factors. In the following table, calculated from Kopp's figures for the expansion of water by rise of temperature, the first vertical column shows the temperature of the half-litre filtrate, the top horizontal column the temperature of the mixture (1005 c.c.) before filtration, and the intersection of a pair shews the volume which the half-litre would occupy at the 'litre temperature.'

500 c.c. at	Equivalent at							
	65°.	70°.	75°.	80°.	85°.	90°.	95°.	100°.
60° C.	501·4	502·8	504·4	506·0	507·6	509·4	511·2	513·2
65°	—	501·5	503·1	504·6	506·3	508·1	509·9	511·3
70°	—	—	501·6	503·4	504·8	506·6	508·4	510·3
75°	—	—	—	501·6	503·2	505·0	506·8	508·8
80°	—	—	—	—	501·7	503·4	505·3	507·2
85°	—	—	—	—	—	501·8	503·6	505·6
90°	—	—	—	—	—	—	501·9	503·8
95°	—	—	—	—	—	—	—	502·0

The filtrate is cooled, a few cubic centimetres of bromine added and dissolved by shaking, and ammonium hydrate until the liquid smells distinctly of ammonia. The mixture is boiled, the manganese hydrate filtered through paper pulp, partially dried by suction, and ignited with the filter at a bright red heat. The brown residue is Mn_3O_4; its weight, when multiplied by 36, gives the percentage of manganese in the steel.

For very exact work the precipitate should always be examined for ferric oxide, silica, and also for oxides of nickel and copper if these metals are present in the steel.

The most important impurity is ferric oxide, the amount of which is most conveniently determined colorimetrically. For this purpose the residue of mangano-manganic oxide is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, filtered if necessary from traces of silica, and a solution of ammonium thiocyanate added. The red colour obtained is then matched by that obtained from a known amount of a slightly acid solution of ferric chloride similarly treated with the thiocyanate. The amount of iron found should never exceed one milligram.

VOLUMETRIC ESTIMATION IN STEEL.

I. '**The Chlorate Process.**'—Two grams of drillings are decomposed in a flask with a mixture of 40 c.c. of water and 20 c.c. of nitric acid (1·4), and a few drops of hydrogen fluoride solution. The solution is boiled, 30 c.c. of strong nitric acid and 3 grams of potassium chlorate added, and the mixture boiled until manganic hydrate separates out. The same amounts of acid and chlorate are then again added and the boiling continued for half an hour. The mixture is then cooled, diluted, and the precipitate filtered off. Filter and precipitate are washed well with hot water and then transferred to the original flask. A solution of ferrous sulphate is run from a burette, water added, and the filter broken by shaking. When the precipitate is completely decomposed, the excess of ferrous sulphate is titrated with potassium dichromate if the filter was paper or paper pulp, or with permanganate if the filter was made of asbestos pulp. From the equation

$$MnO_2+2FeSO_4+2H_2SO_4 \rightarrow MnSO_4+Fe_2(SO_4)_3+2H_2O$$

54·9 parts of manganese are equivalent to 112 parts of iron, or 1 gram Mn = 2·04 gram Fe = 14·28 grams of ferrous ammonium sulphate crystals. A solution containing this weight of crystals in 1 litre of dilute sulphuric acid is equivalent to a dichromate solution of 1·786 gram per litre, and of permanganate at 1·1511 gram per litre. One cubic centimetre of either of these is a measure of 0·001 gram of manganese, representing 0·05 per cent. on a two-gram sample of steel. The ferrous solution is standardised daily along with each batch of samples.

II. **The** '**Bismuthate Process.**'—The sample, weighing 1·1 grams, is dissolved in 35 c.c. of nitric acid of s.g. 1·20, and nitrous fumes expelled by boiling. To the hot solution sodium bismuthate is added a little at a time until the nitrated carbon compounds are oxidised; about half a gram suffices except in the case of high carbon steels or white irons. Should a brown precipitate of hydrated manganese dioxide separate, it is removed by the addition of a few drops of a strong solution of sulphurous acid, and the clear solution cooled off at once. An excess of bismuthate, 1·5 to 2 grams, is added, the mixture shaken, and allowed to stand. The supernatant liquid is decanted through an asbestos filter, the excess of bismuthate washed by decantation several times with 3 per cent. nitric acid or until the filtered washings are colourless. The liquid is then titrated by adding decinormal ferrous solution until a clear pale green colour is obtained, and the excess determined with permanganate. The ferrous solution is then standardised by permanganate in the flask containing the finished assay.

$$1 \text{ c.c. } \frac{N}{10} \text{ solution} = 0{\cdot}1 \text{ per cent. of manganese.}$$

Notes.—As the above process is now generally regarded as the standard manganese method, a few additional notes are worthy of record. The solution of manganese nitrate should contain not less than one half its volume of 1·20 nitric acid. Fairly strong nitric acid solutions are necessary for the oxidation in the cold to prevent the formation of manganese peroxide. The point is not of great importance in the assay of steels, but must not be neglected in the case of manganese alloys. Hydrochloric acid must not be present, but sulphuric up to normal strength is tolerable.

Chromium is oxidised to chromate in the hot solution by the bismuthate, and care must be taken to add sufficient sulphurous acid to reduce it again before proceeding with the estimation. To reduce the amount of chromate formed after adding the excess of bismuthate to the cold solution to a minimum, no time should be lost in the filtration and washing. By shaking vigorously for a few seconds after adding the bismuthate to the quite cold solution, and filtering rapidly, 0·52 per cent. of manganese was obtained from a steel containing 0·50, and 3 per cent. chromium. By allowing to stand before filtering for 5 minutes in one case, and 10 minutes in another, the percentages found were respectively 0·55 and 0·57. Steels containing chromium are not always decomposed by 1·20 nitric acid ; digestion with 10 c.c. of dilute sulphuric acid (1 to 3), followed by nitric acid is usually efficacious. The determination of manganese in very rich chromium steels should be preceded by a separation of the chromium, *vide infra.*

The process is not influenced by the presence of tungsten if the amount is not sufficient to prevent complete decomposition of the steel with nitric acid. Nor do molybdenum, vanadium and titanium interfere when ferrous sulphate (and not hydrogen peroxide) is used for titrating the sodium permanganate. The only evidence of the presence of these elements is furnished in the titration, when on adding excess of ferrous solution, the blue colour of the solution shews the presence of vanadium, but the subsequent titration with permanganate is not seriously affected ; see pp. 113 and 151.

COLORIMETRIC ESTIMATION IN STEEL.

The colorimetric estimation of manganese in steel conveniently follows directly upon the colour carbon test, and gives most satisfactory results when conducted as described by Dufty.[1]

The solution, after estimating the carbon, is transferred to a graduated ‘test-mixer,’ provided with a glass stopper, and diluted with 1·20 nitric acid to 25 c.c. The same weight (0·1 gram) of a standard manganese steel, which may also serve in many cases as a carbon standard, is similarly treated, 0·2 gram of bismuthate added to each, the contents mixed and the mixers set aside in a dark cupboard for about half an hour. Exactly 5 c.c. of the clear supernatant liquid are withdrawn from each cylinder, transferred to graduated comparison tubes and the colours matched by diluting the one or other as required.

ESTIMATION IN PIG IRONS.

Manganese may be estimated in pig irons gravimetrically or volumetrically after removal of the graphite by filtration, fractionally or otherwise. In the bismuthate process the solution should be boiled for some time after the formation of a brown precipitate of manganese dioxide. The nitrated organic compounds from white iron in particular appear to be much more difficult to oxidise than in the case of steels.

ESTIMATION IN SPECIAL STEELS.

The gravimetric process requires modification when copper, nickel or cobalt are present in the steel, since these metals pass wholly or partially into the filtrate from the iron precipitate. They may be removed as sulphides by saturating the solution with sulphuretted hydrogen. The filtrate from the sulphides is boiled to expel the excess of sulphuretted hydrogen, filtered, cooled, and treated with bromine and ammonium hydrate.

Steels containing much chromium do not yield such a sharp separation of the iron, and the manganic hydrate precipitate is therefore never pure.

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[1] *Chem. News*, 84, 248.

It may be dissolved from the filter with sulphurous acid, the solution boiled to expel the excess of sulphur dioxide, 1·20 nitric acid added and the determination completed by the bismuthate process.

High-speed steels, which contain large amounts of tungsten, are opened out with hydrochloric and nitric acids as in the determination of this element, page 135, and the tungstic oxide removed by filtration. The filtrate may then be assayed for manganese gravimetrically, after adding to it the solution in hydrochloric acid of the small quantity of ferric and manganic oxides recovered from the impure tungstic oxide residue. As these steels also contain about 3 per cent. chromium, the modification referred to above should be applied.

Better results are secured, and in less time, by the bismuthate process. Thus, in the case of high-speed steels, the filtrate from the tungstic oxide may be evaporated to fumes with sulphuric acid, the residue taken up in 1·20 nitric acid and the estimation completed. Or, the residue of sulphates may be dissolved up in water, the solution partially neutralised and the iron and chromium precipitated with an emulsion of zinc oxide. A measured fraction of the filtrate is taken, concentrated, the acidity adjusted up to about 1·20 strength by adding strong nitric acid, and so on.

The following process also gives good results with this class of material. Dissolve 1·1 gram in hydrochloric and nitric acids, evaporate to pastiness, add carefully about 8 c.c. of strong sulphuric acid, and fume for 10 minutes. Cool, add 30 c.c. of 1·20 nitric acid and an equal volume of water, boil, and filter off WO_3. Wash with 2 per cent. nitric acid, and apply the bismuthate process to the filtrate.

The so-called rustless or stainless steels, containing 12 per cent. or more of chromium are assayed for manganese on similar lines. Good results are obtained by a zinc oxide hydrolysis of the iron and chromium, followed by the volumetric determination of the manganese in the filtrate.

IRON (Fe = 55·8).

Gravimetric Determination.—The solitary method for the determination of iron gravimetrically is the precipitation as ferric hydrate followed by ignition to the oxide; the usual precipitant is ammonium hydrate. The process is applicable only when the iron is present in practically pure solutions, and it is therefore not often employed in the analysis of steel and alloys. The higher oxides of phosphorus, arsenic tungsten, molybdenum, vanadium, etc., form fairly stable ferric salts in neutral or faintly alkaline solutions, whilst the salts of metals such as nickel, cobalt, copper, etc., are adsorbed by the ferric hydrate precipitate. Hence the precipitation of ferric iron by means of ammonium hydrate is generally used only as a means of extracting it from solution.

For the determination of iron, the precipitation is made from a hot (but not boiling) solution containing some ammonium chloride, and by means of a slight excess only of the precipitant. After washing with hot water, the precipitate is dried and ignited at not too high a temperature. A dull red heat suffices to decompose the hydrate, leaving a brownish red residue of ferric oxide. At higher temperatures small amounts of the magnetic oxide, Fe_3O_4, may be formed, and the product is more difficult to dissolve in hydrochloric acid.

$$Fe_2O_3 \times 0{\cdot}6993 = Fe.$$

Volumetric Determination.—The direct titration of ferric solutions, and the conditions under which it gives accurate results, have been extensively studied, but not adopted in works' laboratories, with the exception of the titration with stannous chloride. This operation is performed in strongly acid solutions, and is at an end when the yellow colour of the solution disappears. A known amount of copper chloride may be added so as to render the end of the titration more distinct; or a mixture of mercuric with platinic chloride added, and the formation of a dark turbidity, due to the separation of reduced metals, looked for.

Acid solutions of ferric chloride may also be titrated in the presence of potassium thiocyanate, the end point being determined by the disappearance of the red colour. In the presence of a thiocyanate, the titration may also be made with cuprous chloride, a turbidity of cuprous thiocyanate marking the end point of the reduction.

Iodometric methods have assumed various forms :—

(*a*) The neutralised ferric solution is treated with an excess of sodium thiosulphate, and the excess determined by means of iodine.

(*b*) The faintly acid solution is treated with an excess of potassium iodide, and the liberated iodine titrated with thiosulphate.

(*c*) The acid solution of ferric chloride is treated with potassium iodide, the mixture distilled, and the liberated iodine absorbed and determined.

Iron is almost invariably determined by titration of a ferrous salt with a standard oxidising agent. When, as generally happens, the solution obtained in the preliminary operations of opening out the material contains the iron wholly or partially in the ferric condition, the reduction to the ferrous state can be made in a number of ways.

(1) Zinc in acid solution rapidly reduces ferric to ferrous salts. The use of this reagent for this purpose is described at some length on pp. 13-18.

(2) Hydrogen sulphide is a very effective reducing agent in weak or in strongly acid solutions. It removes at the same time metals of the 'second group' by precipitating them as sulphides, and, moreover, does not reduce titanic acid. The excess of hydrogen sulphide is easily expelled from the solution by boiling, and it is quite unnecessary to filter off the sulphur which separates during the reduction.

(3) Sulphurous acid does not effect a speedy or complete reduction in the presence of much free acid. The solution of the ferric salt is therefore treated with dilute ammonium hydrate until a dark brown colour or a slight precipitate is obtained, before adding the reducing agent. The mixture is then heated until the solution is colourless, *made freely acid again*, and the excess of sulphur dioxide expelled by boiling. The boiling should be continued for a minute or so after sulphur dioxide can no longer be detected by smell in the escaping steam. Re-oxidation of the iron does not take place if the operation is performed as described, nor is it necessary to introduce the precaution, so frequently recommended, of passing a current of carbon dioxide through the solution during the boiling. A few cubic centimetres of a saturated solution of sodium bicarbonate may, with advantage, be added before cooling under the water tap, and titrating.

(4) Stannous chloride is extensively used as a reducing agent in the assay of iron ores. The reduction is conducted in hydrochloric acid solution, hence potassium permanganate is not used for titrating the reduced solution unless the latter contains a considerable amount of manganese sulphate.

The solution to be reduced should contain approximately half its volume of concentrated hydrochloric acid, and the stannous chloride solution is added drop by drop until the liquid is decolourised. A few cubic centimetres of a saturated solution of mercuric chloride are then added to oxidise the excess of the reducing agent. A solution of stannous chloride suitable for comparatively large amounts of iron, is made by dissolving 10 grams of the solid in 20 c.c. of hydrochloric acid and diluting to 200 c.c. with water. For the estimation of small amounts of iron, this solution is diluted with 10 per cent. hydrochloric acid.

If permanganate is used for titrating the reduced solution, not only should the latter contain a gram or two of manganous sulphate, but also some sodium phosphate or a few cubic centimetres of syrupy phosphoric acid; otherwise, the colour of the ferric chloride regenerated during the titration makes the detection of the end point difficult. The use of dichromate does not call for these precautions.

Standard decinormal solutions of potassium permanganate and potassium dichromate contain 3·161 and 4·903 grams of the respective substances per litre of solution.

A solution of the former is made by dissolving approximately 3·2 grams of the crystals in about 300 c.c. of water, hot or cold, allowing the solution to stand for at least a day, filtering through freshly ignited asbestos into the litre flask, and diluting to the mark with distilled water. The solution so obtained retains its strength over a very long period of time, having been freed from the small quantity of manganese dioxide which is generally present in the best samples of permanganate, and may be observed as a brown stain on the asbestos filter. If not removed, it sets up a decomposition with slow evolution of oxygen, thereby necessitating frequent standardisation of the solution.

Permanganate solutions are standardised by means of metallic iron, ferrous ammonium sulphate, sodium oxalate, oxalic acid, etc.

(*a*) **Metallic Iron.**—A carefully weighed amount of electrolytic iron, or of fine and nearly pure iron wire, is dissolved in dilute sulphuric acid in a flask provided with a bunsen valve, and the solution of ferrous sulphate thus obtained is titrated with the permanganate. As the best iron wire is not chemically pure, an allowance of from two to four-tenths per cent. is usually made for impurities; that is to say, the weight of iron taken is multiplied by from 0·996 to 0·998 in calculating the strength of permanganate. This correction obviously implies that the impurities have no influence upon the titration. If iron wire is used, the small particles of carbonaceous matter which may be seen floating in the solution when the metal is all dissolved are oxidised by the permanganate, and a positive correction of from one to two per cent. may become necessary. On this account, solutions of permanganate are more frequently standardised as described below.

From the expressions

$$2KMnO_4 \rightarrow K_2O + 2MnO + 5(O)$$

and

$$2FeO + O \rightarrow Fe_2O_3$$

it follows that

$$2KMnO_4(316) = 10Fe(558{\cdot}5)$$

and

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = 0{\cdot}005585\text{g. Fe.}$$

(*b*) **Ferrous Ammonium Sulphate.**—Exactly 1·96 grams of the pure crystals are dissolved in about 70 c.c. of water and 5 c.c. of sulphuric acid, and the solution titrated at once with the permanganate. If exactly decinormal, 50 c.c. of the latter will be required in the titration.

Ferrous ammonium sulphate obtained by crystallisation from aqueous solution is not always reliable. A better sample is readily obtained by adding to a strong aqueous solution containing a few cubic centimetres of sulphuric acid, an excess of alcohol. The fine crystals which are thrown out of solution are collected, washed with alcohol and dried. The results obtained with this preparation agree closely with those of the Sörensen titration[1] against sodium oxalate.

(*c*) **Sodium Oxalate.**—This substance possesses several advantages over the two preceding. It may be purchased in a state of purity, (or can be easily prepared), crystallises without water of crystallisation, and is not hygroscopic. From the expressions

$$Na_2C_2O_4 + O \rightarrow Na_2O + 2CO_2$$

and

$$2KMnO_4 \rightarrow K_2O + 2MnO + 5(O)$$

it follows that

$$5Na_2C_2O_4 = 2KMnO_4.$$

The reaction in sulphuric acid solution is therefore

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

From the above, exactly 0·335 grams of sodium oxalate require 50 c.c. of decinormal permanganate. This amount of the solid is weighed off, transferred to a beaker or flask, and dissolved in about 200 c.c. of distilled water heated to 70° C. or thereabouts. Two or three cubic centimetres of sulphuric acid are added, and the solution titrated with the permanganate, which is run in very slowly at first. The reaction becomes very brisk after the delivery of the first few cubic centimetres, and the permanganate may then be run in a rapid stream until the end point is approached.

A decinormal solution of potassium dichromate is made up at once by dissolving 4·903 grams of the crystals in water, and diluting to one litre. The solution retains its strength indefinitely, and as the solid may be purchased in a state of purity, standardisation of the solution becomes almost unnecessary. The reagents used for the purpose are metallic iron or ferrous ammonium sulphate.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Dichromate may be used for titrating ferrous salts in hydrochloric as well as in sulphuric acid solution. It can also be used in the titration of solutions holding suspended matter, or even paper filters.

On the other hand, the titration may be interfered with by a number of commonly occurring elements which form an insoluble ferricyanide

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[1] *Zeit. f. anal. Chem.*, 42. 352. 512 and 45. 272.

with the indicator. The presence of considerable amounts of manganese, for instance, as in Stead's method for the determination of chromium, produces a brown colour with the indicator, which may mask the reaction with dilute ferrous solutions. Nickel and copper act similarly. This interference is reduced to a minimum by making the solution of the indicator very dilute. The latter is made freshly for each determination by washing a crystal or two of the solid before dissolving it, so as to remove any trace of ferrocyanide.

The blue colour is developed rather slowly with dilute ferrous solutions so that a premature finish is generally obtained. The error is not serious, and is eliminated by standardising the dichromate in the same manner or by covering the mixed test drops with a porcelain crucible so as to shut out the light, and allowing to stand for a few minutes.

ESTIMATION IN STEELS AND PIG IRONS.

When the amount of iron in steel is considered at all, the percentage is obtained by difference between 100 and the sum of the percentages of the other elements. With comparatively pure plain carbon steels this procedure is quite as accurate as a direct determination of the iron, which is conveniently made as follows.

Weigh out 0·28 gram of the drillings into a conical flask, add 20 c.c. of 50 per cent. hydrochloric acid, and heat until the metal is decomposed, leaving only carbonaceous matter. Add half a gram of solid potassium chlorate, expel the excess of chlorine and chlorine peroxide, and repeat the treatment twice. Dilute to about 60 c.c., neutralise the excess of acid with dilute ammonium hydrate and reduce the ferric to ferrous chloride by means of sulphurous acid. After expelling the excess of reducing agent, titrate with decinormal dichromate. Twice the number of cubic centimetres used is the percentage of iron in the steel.

For pig irons, open out in the same manner, filter off the graphite and silica, wash well and ignite in a platinum crucible. Remove the silica with hydrofluoric acid and dissolve any slight residue in hydrochloric acid, adding the solution to the original filtrate.

The process is also applicable to alloy steels that yield a perfect solution with hydrochloric acid and potassium chlorate. When vanadium is present, it exists as vanadyl chloride after the reduction with sulphurous acid and is not oxidised by the dichromate, but its action on the ferricyanide indicator must be taken into consideration when the end of the titration is approached. This is discussed in connection with the determination of vanadium, page 149.

In the case of high-speed steels containing tungsten, the tungstic oxide residue obtained in the initial decomposition is filtered off, washed and ignited. It is then fused with sodium carbonate, the melt boiled out with water, and any insoluble residue of ferric oxide dissolved and added to the main filtrate.

COPPER (Cu = 63·6).

Separation from Iron.—Copper is found in steels and irons in very small amounts only. As a separation from iron is necessary for the estimation of the element, one which yields the copper as an insoluble compound is therefore much to be preferred to the converse.

Of the latter type the precipitation of the iron with ammonium hydrate or as a ' basic acetate ' are both valueless in this case. The soluble dark blue copper compounds of the type cuprammonium chloride or cuprammonium sulphate, which are obtained by adding an excess of ammonium hydrate to copper solutions, are readily adsorbed by the precipitated ferric hydroxide, and, neither the fixation of the copper as a double compound with a salt of sodium or potassium before adding ammonium hydrate, nor repeated precipitations, provide a sufficiently good separation of small quantities of copper from large quantities of iron. Similarly the basic acetate precipitation fails to secure the whole of the copper in the filtrate, though a complete separation can be obtained by substituting a soluble chromate for the acetate.

Precipitation of the copper as a sulphide gives much better results ; this is done either by means of hydrogen sulphide or sodium thiosulphate. In the former case a rapid stream of the gas is conducted through the hot acid solution containing the iron, preferably in the ferrous condition. Sodium thiosulphate forms first of all cupric thiosulphate and next a soluble thiosulphate of copper and sodium ; both of these are decomposed on boiling the liquid with precipitation of cuprous sulphide and free sulphur. In both forms of precipitation the copper sulphide is always found to be contaminated with more or less iron, depending chiefly upon the degree of acidity of the solution, a factor which determines also the freedom or otherwise of the precipitate from such metals as aluminium, chromium, and vanadium. Arsenic and tin sometimes occurring in small quantities in steel, and molybdenum in larger quantity, are all precipitated along with copper as sulphides, and are separated by dissolving these out with sodium sulphide. Ammonium sulphide should not be used for this purpose as it dissolves small quantities of copper sulphide, and larger amounts when associated with molybdenum sulphide.

By dissolving steel in dilute sulphuric acid copper is found in the insoluble residue. The amount of this depends largely upon the presence of oxygen in the solution, and by the use of freshly boiled acid and an inert atmosphere a perfect yield of copper may be obtained. Zinberg,[1] for example, uses a large excess of dilute sulphuric acid and effects the decomposition in a current of carbon dioxide; the copper is filtered off after complete decomposition and ignited to cupric oxide.

The precipitation, upon a sheet of platinum, of metallic copper from its solution by the addition of another metal such as zinc is not suited to the analysis of steel.

Gravimetric Determination of Copper.—The gravimetric processes in general are not so convenient and reliable as the volumetric. After separation from iron, copper may be precipitated by potassium or sodium hydroxide and the precipitate ignited to cupric oxide. This method is invested with the usual difficulties of slow filtration and washing, and is of little or no practical value. Similarly. copper sulphide obtained by precipitation with sodium sulphide is not suitable for a direct determination of the copper. Obtained, however, from acid solution, copper sulphide may be weighed directly. Washing with hydrogen sulphide water to prevent loss, and ignition of the dried precipitate after mixing with flowers of sulphur in a Rose crucible in a current of hydrogen, constitute the vital points of the manipulation.

Much more satisfactory than the above, is the precipitation, in the presence of a reducing agent, with potassium or ammonium thiocyanate. From hot solutions of copper containing hydrochloric acid or sulphuric acid together with sulphurous acid or ammonium bisulphite, a quantitative precipitation in the form of white cuprous thiocyanate $Cu_2(SCN)_2$ is effected by adding an excess of ammonium thiocyanate solution. The precipitate may be filtered almost immediately through a Gooch crucible, dried at 100°-110° C., and weighed, or it may be collected on paper pulp and ignited, along with the filter, to a mixture of cupric oxide and cuprous sulphide.

Volumetric Determination of Copper.—The volumetric determination of copper is easily performed by one of several methods.

One of the oldest is based upon the fact that ammoniacal solutions of cuprammonium compounds react quantitatively with potassium cyanide with formation of the double cyanide. Solutions of the latter being almost colourless, the complete discharge of the blue colour of the original solution marks the end of the reaction. The usual procedure consists first in the removal of any free mineral acid

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[1] *Zeit. f. anal. Chem.*, 51. 19.

in the solution by evaporating to dryness, the residue being then taken into solution with water. Next the solution is treated with ammonium-hydrate at the rate of 10 c.c. per 0·1 gram of copper, and finally titrated with standardised potassium cyanide solution. The end point of the titration is usually taken when the original blue colour of the solution changes to a pale lavender; this indication is used in the standardisation of the potassium cyanide empirically against a solution of known copper contents.

The method most frequently practised is iodometric, and depends upon the reduction of cupric to cuprous salts. If potassium iodide is added in excess to a faintly acid solution of a cupric salt, cuprous iodide is precipitated (and may dissolve in excess of potassium iodide) with separation of iodine. The reaction

$$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 + 2K_2SO_4$$

is absolutely quantitative, so that a titration of the liberated iodine with sodium thiosulphate, without filtering out the cuprous iodide precipitate, measures the amount of copper present, each unit of which liberates almost exactly twice its own weight of iodine from the potassium iodide.

Limitations to the application of this excellent process are imposed by the susceptibility of iodides and iodine to react with other substances. On the one hand, comparatively feeble oxidising agents liberate iodine from iodides, and reducing agents act conversely upon free iodine: hence ferric iron must be entirely removed on the one hand, and gaseous reducing agents such as hydrogen sulphide and sulphur dioxide, on the other, are not tolerable in the immediate atmosphere during titration. Moreover, there is a limit to the amount of mineral acids that may be present, since they readily decompose sodium thiosulphate; also the excess of potassium iodide used, according to Gooch and Heath[1] is not without influence upon the results. These workers have shewn that in 50 c.c. of solution up to 2 c.c. of strong mineral acids exert no appreciable influence, but that 3 c.c. of either strong nitric, sulphuric or hydrochloric acids in the same volume will result in the liberation of iodine from potassium iodide. The quantity of iodine set free depends upon the proportion of acid present. In 100 c.c. of liquid 20 c.c. of glacial acetic acid may be present with 5 grams of potassium iodide without causing any error. The amount of potassium iodide that should be present depends upon the volume of the solution; too small an excess results in too small an amount of liberated iodine. The volume of the solution should be kept as small as possible, as at large dilution the results

[1] *Amer. Journ. Sci.*, 24. 68, and *Chem. News*, 97. 174.

are erratic ; in 50 c.c. of solution an excess of at least 0·6 gram must be present. Two grams of potassium iodide in 50 c.c. of solution or 5 grams in 100 c.c. are recommended for the assay of 0·2 grams of copper.

Other workers have directed attention to sources of error incidental to the method. Carbon dioxide must be entirely eliminated from the solution before titration and Kendale[1] accordingly precipitates the copper and redissolves the precipitate in acetic acid. Sujiura and Kober[2] for the same reason and also to eliminate free mineral acids and nitrates, which last also cause an uncertain end point, precipitate the copper with sodium hydrate, filter, wash and dissolve the precipitate in acetic acid.

Several other volumetric methods for the determination of copper are in use, but more often for comparatively large amounts of the element, as in the assay of copper ores and alloys, than for steel.

Parr[3] precipitates cuprous thiocyanate and titrates the washed precipitate with permanganate.

Jamieson, Levy and Wells[4] operate similarly but use potassium iodate for the titration. This reagent first of all liberates iodine and afterwards oxidises it to iodine monochloride ; the complete reaction may be expressed thus :

$$2Cu_2(SCN)_2+7KIO_3+14HCl \rightarrow 4CuSO_4+7ICl+4HCN+7KCl+5H_2O.$$

Rhead[5] utilises the reaction between cupric salts and titanous chloride, which is applied also by Knecht and Hibbert[6] as follows. The solution containing hydrochloric or sulphuric acid is treated with a known amount of ferric alum and some ammonium thiocyanate and the mixture titrated with titanous chloride until the red colour of ferric thiocyanate disappears. The amount of titanous chloride solution required measures the amount of iron and copper present and from this is deducted the amount, previously determined, required by the iron.

$$2CuCl_2+2TiCl_3 \rightarrow Cu_2Cl_2+TiCl_4.$$

Colorimetric Determination of Copper.—Small quantities of copper are conveniently determined by a colour test, using a standard solution of copper for comparison.

1. The blue colour of ammoniacal copper solutions is sometimes utilised for this purpose. Organic matter and metals such as nickel

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[1] *Journ. Amer. Chem. Soc.*, 1911. 1947.

[2] *Journ. Amer. Chem. Soc.*, 1912. 422.

[3] *Journ. Amer. Chem. Soc.*, 22. 685.

[4] *Journ. Amer. Chem. Soc.*, 30. 760.

[5] *Trans. Chem. Soc.*, 1906. 1491.

[6] "Reduction Methods in Volumetric Analysis."

and cobalt, which yield coloured solutions, must not be present; the maximum amount of copper should not exceed one centigram. The standard solution of copper is made from pure recrystallised copper sulphate.

2. Amounts of copper less than one milligram may be conveniently estimated by treating a cold acidified solution with hydrogen sulphide, and comparing the brown colour thus obtained with a standard.

3. A very sensitive test is furnished by the reaction of copper salts with potassium ferrocyanide, one part of copper in more than two millions of water being thus revealed. In applying the test for the estimation of copper, iron must obviously be absent and the solution should be neutral. Solutions containing free acid are neutralised with ammonium hydrate, those containing fixed alkalies are first neutralised with acid and the excess of the latter then removed by ammonium hydrate; in both cases any excess of ammonium hydrate is expelled by boiling before adding ferrocyanide. A convenient standard copper solution is made by dissolving 0·393 grams of crystallised copper sulphate and diluting to a litre; 1 c.c. of this = 0·1 milligram of copper.

4. Copper salts in solution give a yellow precipitate of copper xanthate on the addition of a solution of potassium ethyl xanthate, and small amounts a colouration only. This reaction is utilised for the colorimetric determination of copper and possesses the advantage that it is not disturbed by the presence of small quantities of iron and manganese.

Electrolytic Determination of Copper.—Copper is one of the few metals occurring in steel which can be conveniently assayed electrolytically. Of the numerous sets of conditions for the deposition the most suitable for ordinary purposes is the deposition from solutions containing nitrate or sulphate. With a nitric acid solution the percentage of free acid should not exceed ten for stationary electrodes but may be increased up to three times that amount with rotating electrodes. In the former case a current density of one ampere per square decimetre and an E.M.F. of between 2·5 and 3 volts across the electrodes are suitable conditions; in the latter these values may be considerably increased and the time of deposition thus lessened. For sulphate solutions the percentage of free acid should be less than ten, the other conditions remaining practically the same.

The completion of the deposition is ascertained by the application of the ferrocyanide or sulphide test referred to above.

Solutions from which iron has been completely separated may be treated by either of these methods of determination.

GRAVIMETRIC ESTIMATION IN STEEL.

Attack 5 grams of drillings in a 20 oz. beaker with a mixture of 10 c.c. of sulphuric acid and 50 c.c. of water, boil until the steel is all dissolved and add a solution in water of about 5 grams of sodium thiosulphate. Boil the liquid containing now a mixture of precipitated cuprous sulphide and free sulphur, until the latter is coagulated and an almost clear solution is obtained. Filter through paper pulp, wash thoroughly with hot water, dry, and ignite at a low red heat until the paper is ashed and all the sulphur is burnt off. Weigh the impure residue, dissolve in a small quantity of dilute hydrochloric acid, dilute, and add ammonium hydrate until distinctly alkaline. Filter off the precipitated ferric hydrate, wash well, and retain the blue filtrate containing the copper. If more than a few milligrams of precipitate are judged to be present, re-dissolve in acid and re-precipitate, mixing the filtrate thus obtained with the first. Ignite and weigh the residue of ferric oxide and deduct the weight from the original weight of the impure residue. The difference is the weight of the mixed cupric oxide and cuprous sulphide, the relative proportions of which are of no consequence since each compound contains 79·8 per cent. of copper. The process yields fairly good results, but, obviously, does not provide a direct determination of the copper.

VOLUMETRIC ESTIMATION IN STEEL.

The blue solution obtained from the preceding process as a filtrate from the ferric hydroxide provides the starting point of a direct volumetric determination. Acidify it with nitric acid and concentrate to a volume of about 10 c.c. Next add sodium carbonate, solid or concentrated solution, until a pale blue precipitate or a darker blue solution is obtained, and then make acid again with acetic acid. Boil off carbon dioxide, cool thoroughly and add one gram of potassium iodide. Shake the mixture until the crystals have dissolved and titrate the liberated iodine with standard sodium thiosulphate solution. The following reactions occur:

$$4KI + 2Cu(C_2H_3O_2)_2 \rightarrow Cu_2I_2 + I_2 + 4KC_2H_3O_2$$
$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6.$$

From these reactions it follows that

$$\begin{array}{ccccc} 2Cu & = & I_2 & = & 2Na_2S_2O_3{\cdot}5H_2O. \\ 127{\cdot}2 & & 253{\cdot}8 & & 496{\cdot}4 \end{array}$$

$$1 \text{ gram } Cu = 3{\cdot}925 \text{ grams } Na_2S_2O_3{\cdot}5H_2O.$$

3·925 grams of pure thiosulphate crystals in a litre of solution, therefore, provide a solution, one cubic centimetre of which is equivalent to one milligram of copper. The solution, if not exposed to acid fumes, remains almost constant in strength for a long time; the works' chemist will find it necessary, however, to standardise from time to time. This is best done by the above process on a solution of copper nitrate, prepared from pure electrotype copper foil.

ESTIMATION IN PIG IRON.

Open out as for steels and proceed without filtering off graphite and silica. The results obtained by the gravimetric process are unreliable, so that the estimation should be made volumetrically on the blue filtrate from the ferric oxide (and silica).

ESTIMATION IN SPECIAL STEELS.

The precipitation of copper by means of sodium thiosulphate separates most of the special elements of steel, but modifications are necessary in a few cases.

Tungsten should be removed before the precipitation of copper by oxidising the solution, evaporating to low bulk, diluting and filtering off the separated tungstic oxide fractionally. The iron of the filtrate is reduced with sulphur dioxide before proceeding.

From steels containing much silicon there is a separation of silicic acid, as in the case of pig irons, when the metal is dissolved, and this is, of course, collected with the cuprous sulphide. The gravimetric process is, therefore, either discarded, or the silica must be removed by means of hydrofluoric acid.

Chromium, if present, is revealed in the insoluble residue after treating the ignited precipitate with hydrochloric acid, and a certain amount of copper is invariably associated with it. For the recovery of the latter fuse the residue with sodium carbonate, extract with dilute sulphuric acid, and repeat the precipitation with thiosulphate.

Molybdenum is precipitated with copper by the addition of sodium thiosulphate to a solution containing both. The mixed sulphides are washed by decantation, and as little of them as possible transferred to the filter. The residue is then digested in the original beaker or flask with a solution of sodium sulphide, the supernatant liquid poured through the same filter, and the undissolved copper sulphide finally transferred. After washing, the residue is treated as above for the removal of the small amount of iron present and for the determination of the copper.

ARSENIC ($As = 75 \cdot 0$).

Arsenic is frequently separated as sulphide in the estimation of phosphorus in steel, but it is not often regularly estimated in the daily produce of a furnace, even when it is known to be present. Mainly on this account, the methods of separation and determination of the element, which have been treated at some length in the case of others, are not described.

ESTIMATION IN STEEL.

Five grams of steel are placed in a flask provided with a stopper and an absorption bulb, such as that shewn in Fig. 11, which is charged with saturated bromine water and a few cubic centimetres of bromine. A mixture of 30 c.c. of hydrochloric acid with 20 c.c. of hot water is added to the drillings, the stopper quickly replaced, the mixture heated gently until the steel is dissolved, and finally boiled for about a minute.

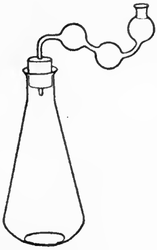

FIG. 11.

Part of the arsenic is evolved as arsine, which is oxidised by the bromine and retained as arsenic acid in the absorption bulb.

$$AsH_3 + 4Br_2 + 4H_2O = H_3AsO_4 + 8HBr.$$

The remainder passes into solution, or, in the case of material containing more than very small percentages of the element, may be seen as a scum on the surface of the liquid and sides of the flask, resembling graphite in appearance and consisting of elementary arsenic or of arsenide of iron. The volatile portion varies from 5 to 15 per cent. of the total, according to the rate at which the metal is dissolved.

When decomposition is complete, the flask and absorption bulb are disconnected, the contents of the latter transferred to a beaker and boiled until the excess of bromine is expelled. The solution and the ferrous chloride in the flask are transferred to a distillation flask connected with a condenser, as shewn in the accompanying Fig. 12.

The receiver is charged with water into which the end of the condenser just dips before commencing the distillation. Boiling is maintained until the contents of the flask are reduced to about 10 c.c., whereupon 25 c.c. of hydrochloric acid of s.g. 1·16 are introduced and the distillation repeated. The treatment with hydrochloric acid and boiling are again repeated so as to ensure the complete expulsion of the arsenic in the form of its trichloride. (Compounds of arsenic, including arsenates, are converted by boiling them with hydrochloric acid and a ferrous salt into volatile $AsCl_3$, which is hydrolysed by the water in the receiver.)

$$2AsCl_3 + 6H_2O = 2H_3AsO_3 + 6HCl.$$

The contents of the receiver are treated with ammonium hydrate until alkaline, and the solution then made faintly acid again with hydrochloric acid. Twenty c.c. of a cold saturated solution of sodium bicarbonate are then added, a few c.c. of starch solution, and the mixture titrated with a standard solution of iodine.

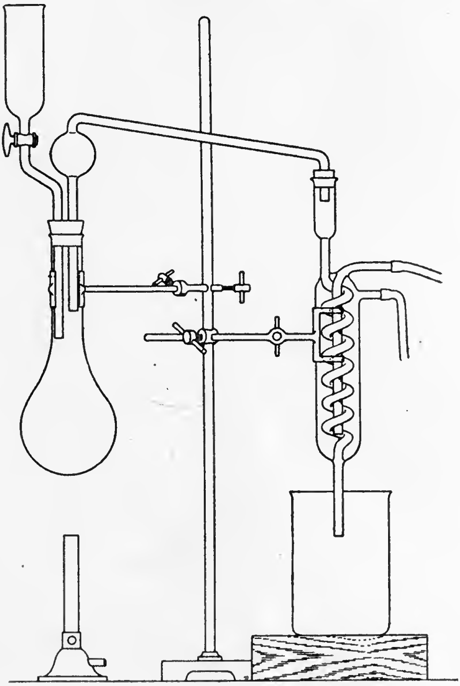

FIG. 12.

$$H_3AsO_3 + 2NaHCO_3 + I_2 = H_3AsO_4 + 2NaI + 2CO_2 + H_2O.$$

The iodine solution is made by dissolving 1·7 grams of the re-sublimed solid in water containing 2 grams of potassium iodide, and making up to 1 litre. It is standardised at intervals by means of a standard solution of arsenic, containing 0·66 gram of the pure trioxide. The latter solution is made by boiling the solid with about 200 c.c. of water containing 2 grams of sodium bicarbonate, and diluting the solution so obtained, after cooling, to 1 litre, with water in which another 2 grams of sodium bicarbonate have been dissolved. The solution contains 0·0005 gram of arsenic per c.c., representing therefore 0·01 per cent. on a 5-gram sample of the steel; it remains constant in strength indefinitely.

The results obtained by the above process are subject to a deduction of the amount of arsenic in the reagents, particularly the hydrochloric acid. The blank is determined by distilling the same amount of hydrochloric acid as used in the process with about a gram of bar iron, free from arsenic. A further deduction from the amount of iodine used in the titration is also necessary. This is the quantity required to develop a colour with starch, and is appreciable because of the large volume of the solution under titration, and the low concentration of the iodine.

For occasional estimations of arsenic the distillation apparatus may be dispensed with by proceeding as follows:

Cool the solution after the steel is dissolved, add 5 c.c. of hydrochloric acid and about 0·5 gram of pure zinc sulphide. Stopper the flask so as to retain the hydrogen sulphide under pressure, and shake for two or three minutes before allowing the precipitate to settle. Collect the precipitate of zinc sulphide, iron arsenide and carbonaceous matter on a small pulp filter and wash with 5 per cent. hydrochloric acid. Return the filter to the flask, add 10 c.c. of hydrochloric acid and the bromine water from the absorption bulb. Break up the filter by shaking, and, if necessary, add more bromine until a slight excess is present. Filter, and wash with water. Expel the bromine from the filtrate, which should not exceed 70 c.c. in bulk, add about half a gram of potassium iodide, and a slight excess of sulphurous acid. Boil off the excess, cool, add half a gram of zinc sulphide, collect and wash the re-precipitated arsenious sulphide. According to the amount of the latter, one or other of the following procedures may be adopted:

(1) In most estimations, which are those of small amounts of arsenic, the filter and precipitate are transferred to a large beaker, 600-700 c.c. of water added, and the liquid reduced to about 20 c.c. by vigorous boiling. In this way the arsenic sulphide is hydrolysed—$As_2S_3+6H_2O=2H_3AsO_3+3H_2O$. The filter paper and insoluble residue (carbonaceous matter, iron and copper sulphides) are filtered off, washed with hot water and the filtrate cooled. Ten to 20 c.c. of a saturated solution of sodium bicarbonate are added, and the solution titrated with iodine.

(2) Larger quantities may be assayed as follows. The filter with the impure arsenic sulphide is transferred to the original flask, treated with about 10 c.c. of normal sodium hydrate which has been saturated with

hydrogen sulphide, and the mixture shaken to effect the complete solution of the arsenious sulphide and the separation of it from the very small amounts of sulphide of iron (and copper). A small quantity of ammonium chloride is added to accelerate the filtration, and washing is done with water containing the same salt and a few drops of ammonium hydrate.

The filtrate is neutralised, about one-tenth of its volume of hydrochloric acid and a slight excess of bromine added, then a few drops of potassium iodide, and an excess of sulphurous acid. Free iodine imparts a colour to the solution if the excess of sulphur dioxide is boiled off before the reduction of the arsenic acid is completed; in any case a crystal of potassium iodide dropped into the solution should give no permanent colour.

When the solution is free from sulphurous dioxide and quite cold, a few cubic centimetres of starch solution and one or two drops of the standard iodine solution are added. If more than two drops of iodine are required, the sulphur dioxide has not been completely expelled, but this is of no moment if iodine is added until a blue colour persists. The latter is then discharged by the addition of sodium or ammonium hydrate, and the solution made faintly acid with hydrochloric acid. Excess of sodium bicarbonate is then added and the solution titrated as above.

ALUMINIUM (Al = 27·1).

Separation from Iron.—The chief chemical reactions of aluminium salts closely resemble those of ferric iron but differ markedly in certain particulars from those of ferrous salts. Upon this fact are based several methods for the separation of the two metals, which consist of a precipitation of aluminium as a compound that is insoluble under conditions which hold the ferrous compound in solution. Another class of separations take advantage of the fact that alumina with strong alkalies forms salts, the so-called aluminates, in which the aluminium constitutes a part of the acid radicle. Ferric oxide does not form such compounds except under special circumstances, and even then they may be readily decomposed again, yielding the base, which can be separated by filtration from the soluble aluminate.

The most suitable compound of aluminium to employ in the first of these methods of separation is the phosphate. Aluminium and ferric phosphates are both insoluble in very weak acid solutions, whilst ferrous phosphate is soluble. Hence the usual method of procedure is to reduce the iron to the ferrous condition and then to precipitate the aluminium as phosphate by the addition of sodium or ammonium phosphate and also some reagent that is easily decomposed by any strong acid that may be present in the solution. Such reagents are to be found in ammonium acetate and sodium thiosulphate. The use of the latter may result in the precipitation, along with the aluminium phosphate, of sulphides of copper, etc.; in both cases small quantities of iron may be carried into the precipitate, resulting from a slight oxidation of the ferrous salt during the precipitation and subsequent boiling. The complete removal of the iron is accomplished either by a re-precipitation under the same conditions, or by the application of the other method of separation.

This separation may be made either in the dry or wet way. If a mixture of aluminium and ferric oxides (or phosphates) be fused together with sodium carbonate, the former is converted into sodium aluminate. On leaching out the fusion with water, ferric oxide remains and the aluminate passes into solution. A similar result is obtained by the action of sodium or potassium hydrate upon the precipitated hydroxides, the aluminium compound being re-dissolved and the ferric hydrate left. If the separation be attempted by forming the precipitate of the hydroxide with caustic alkali, by simply pouring the latter in excess into the solution containing the two metals and digesting, it is generally imperfect; a much better result is obtained by pouring the solution containing the metals into the alkali. A variation of this procedure is the use of sodium peroxide as the precipitant; the mixture is boiled well in order to decompose the soluble sodium ferrite which is first formed.

Separations made by the use of caustic alkalies are open to the objection that these reagents are not themselves always free from aluminium, the amount of which must therefore be found by a 'blank' determination. Barium hydroxide, which can be obtained free from aluminium, is therefore used by some operators instead.

The following are the most important of the remaining methods that are employed in the analysis of a mixture of aluminium with iron:

(1) The Ether Separation described on p. 10.

(2) The solution is treated with an excess of tartaric acid, about three times the combined weights of the aluminium and iron present, calculated as oxides. Hydrogen sulphide is passed through the solution to saturation, and ammonium hydrate then added until just alkaline. The iron is precipitated as sulphide (which may then be redissolved for a volumetric determination), and the aluminium passes into the

filtrate. The latter is evaporated to dryness after adding some sodium carbonate and a little potassium nitrate, the residue gently ignited to decompose the tartrate and dissolved in dilute nitric acid. After filtering out the separated carbon the aluminium is determined gravimetrically.

(3) The solution containing the iron in the ferrous condition is made neutral or feebly alkaline with sodium bicarbonate and is then poured into an excess of potassium cyanide. After allowing to stand for some time so that the iron is all converted into potassium ferrocyanide, the aluminium is precipitated by the addition of ammonium carbonate solution. This process also separates nickel and cobalt from aluminium.

The following methods of separation are of minor importance, particularly from the point of view of the works' chemist:

(4) The solution is treated with a large excess of tri-methylamine and allowed to stand for twenty-four hours. Aluminium hydroxide is precipitated at first, but dissolves again, on standing, in the excess of reagent.

(5) The neutral solution containing the iron in the ferrous condition is treated with phenyl hydrazine; aluminium hydroxide (or phosphate) is precipitated.

(6) The solution, free from nitrates, is neutralised and treated with a large excess of nitroso-β-naphthol. This reagent precipitates the iron free from aluminium, and also chromium or nickel.

Gravimetric Determination of Aluminium.—From solutions of its salts aluminium is almost exclusively precipitated as hydroxide or phosphate. The former is thrown down by various reagents, several of which are used in order to facilitate the subsequent manipulative operations. Aluminium hydroxide precipitated by means of strong alkalies is soluble in an excess of them, and the same property manifests itself in the case of ammonium hydrate, which is the reagent usually employed. This is due to the fact that the compound exists not only in an insoluble, colloidal form (hydrogel), but also in a soluble form (hydrosol), in the presence of an excess of the precipitant. The hydrosol may be coagulated by the addition to the solution of an electrolyte such as ammonium chloride or ammonium nitrate, and if a large excess of this be present with only a small excess of ammonium hydrate the aluminium is completely precipitated.

The gelatinous precipitate is slow of filtration and difficult to wash, hence the water for washing should always contain an electrolyte such as ammonium nitrate. Coagulation of the precipitate prior to filtering is effected in various ways by different workers. Divine used tannin, Guyard glycerol, Liebermann starch, and Zulkowsky ether.

The precipitation of aluminium hydroxide by reagents other than ammonia is most satisfactorily accomplished after a neutralisation of the solution as described under the ‘ basic acetate separation ’ on p. 7. In other words, the hydrolysis of the aluminium salt, which is carried as far as possible by the addition of an alkali just short of the formation of a precipitate, is completed by the reagent. Sodium thiosulphate is a favourite reagent for this purpose, possessing the additional advantage of providing a precipitate of sulphur in the solution, which, on boiling, coagulates round the aluminium hydroxide, ‘ balling ’ it up and rendering it more easy to filter. Ammonium nitrite is another suitable reagent for this purpose by virtue of its decomposition by the free acid resulting from the hydrolysis.

$$2HCl + 2NH_4NO_2 \rightarrow 2NH_4Cl + NO + NO_2 + H_2O.$$

Wynkoop and Schirm [1] recommend this reagent, which is added to the solution after careful neutralisation with ammonium hydrate or ammonium carbonate, followed by large dilution. The mixture is boiled until oxides of nitrogen are completely expelled and a few drops only of ammonium hydrate are then added before filtration.

Another reagent for the completion of the hydrolysis is furnished by a mixture of potassium iodide and potassium iodate. In the presence of a free acid this mixture is decomposed with the liberation of free iodine according to the equation

$$KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3H_2O + 3I_2.$$

Stock,[2] who worked out the details of the process, uses equal volumes of a 25 per cent. solution of potassium iodide and a saturated solution (*i.e.*, about 7 per cent.) of iodate. The free iodine is taken into solution with a 20 per cent. solution of sodium thiosulphate before proceeding to the filtration of the aluminium hydroxide.

The solution of sodium aluminate obtained by the addition of an excess of sodium hydrate to solutions containing aluminium may also be used for the gravimetric determination of the element. The compound is easily decomposed by weak acids and by simply passing a current of carbon dioxide through the solution, there results a quantitative precipitation of the aluminium as a basic carbonate which may be quickly filtered and washed.

For the analysis of steel and ferrous alloys the precipitation of aluminium as phosphate is much to be preferred to that as hydrate—the details of this process are given below.

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[1] *Journ. Amer. Chem. Soc.*, 19. 434.

[2] *Ber.*, 1900. 548.

It is essential to the success of the method that the excess of sodium phosphate added should be very large. The quantitative separation of the aluminium will take place without a large excess, but the composition of the resulting precipitate is then not in correspondence with the formula $AlPO_4$, being, in fact, indefinite. The precipitate is much more satisfactory to wash and filter than the hydroxide; the wash water should, as before, contain a small quantity of ammonium nitrate and in this case also a little sodium phosphate, in order to prevent slight decomposition of the precipitate. The solution used need not exceed one hundredth per cent. in strength, and is therefore without appreciable effect on the weight of the ignited phosphate.

GRAVIMETRIC ESTIMATION IN STEEL.

To 10 grams of drillings contained in a 30 oz. conical flask add 60 c.c. of hydrochloric acid and warm the mixture to effect decomposition as quickly as possible. Without filtering off carbonaceous matter or any silicic acid which may separate, add about 300 c.c. of hot water and about 2 grams of sodium phosphate. Next add dilute ammonium hydrate (1 to 3), or a saturated solution of ammonium carbonate until a small but permanent precipitate of ferrous hydrate is obtained, and then just dissolve the latter in hydrochloric acid, adding afterwards about 1 c.c. in excess. To the clear solution add next 15 c.c. of acetic acid, then 10 c.c. of saturated sulphurous acid, and heat the mixture to boiling. At incipient boiling add 10 grams of sodium thiosulphate, a crystal or two at a time at first, until a white precipitate begins to form, and then the remainder at one addition. Boil until sulphur dioxide can no longer be detected in the issuing steam, and filter at once through paper pulp, washing thoroughly with hot water. Ignite in a porcelain crucible near the mouth of the muffle until the filter is completely ashed; overheating should be avoided.

The residue of aluminium phosphate is white if pure, but this is seldom the case, because it almost invariably contains more or less iron, depending upon the amount of oxidation which occurs in the hot solution, and also upon the degree of thoroughness of the washing. In order, therefore, to eliminate the iron, the residue is dissolved in a few c.c. of hydrochloric acid, the solution diluted and filtered into a smaller flask. One gram of sodium phosphate is dissolved in the liquid, and the neutralisation, reduction, etc., repeated, the final precipitation being made with about 3 grams of thiosulphate. The ignited residue is the orthophosphate, $AlPO_4$, and contains 22·19 per cent. of aluminium.

ESTIMATION IN PIG IRON.

Pig irons are decomposed like steels, the solution made up to 300 c.c. in a graduated flask, and 250 c.c. filtered off from the graphite and silica through a dry paper. The estimation is then conducted on the filtrate exactly as for steels.

The insoluble residue obtained in this way does not contain aluminium present as metal in the pig iron, but in certain cases it may contain traces of alumina. The determination of this is obviously not provided for in the process described. The necessary modification is to collect the whole of the filtrate, ignite the washed residue, fuse with sodium carbonate, extract with hydrochloric acid, and add the solution thus obtained to the main filtrate.

ESTIMATION IN SPECIAL STEELS.

Several elements found in special steels are not without influence upon the estimation of aluminium. Nickel and manganese are eliminated completely by the double precipitation of aluminium phosphate, but copper is precipitated as sulphide by these operations, and should therefore be removed by means of hydrogen sulphide from the original solution after dilution of it. Tungsten also should be removed at the outset, by opening out as for the estimation of that element in steel, and filtering out the tungstic oxide by fractionation.

Of the metals which cannot conveniently be separated at the beginning, chromium, vanadium and titanium require special treatment.

Chromium accompanies the aluminium as phosphate, and is removed by fusion of the mixed phosphates with sodium carbonate and a little peroxide. The filtrate from an aqueous extract of the melt, containing sodium aluminate and chromate, is then rendered just acid and treated with sodium phosphate and ammonium acetate solutions, whereby aluminium phosphate is again precipitated and chromium left in solution. Another method of precipitating the aluminium from the alkaline mixture of aluminate and chromate consists in passing a current of carbon dioxide through the solution.

Vanadium also is carried wholly or partly into the aluminium phosphate. It is removed by dissolving the precipitate in hydrochloric acid, diluting, adding one gram of sodium phosphate, then sodium peroxide until the reddish brown colour of pervanadic acid is fully developed, and finally adding to the heated solution a very slight excess of ammonium hydrate. After boiling for a few minutes, the aluminium phosphate is filtered out. The filtrate is acidified, boiled until the colour is discharged, and ammonium hydrate again added in slight excess. If no precipitate is formed, the solution is rejected. If there is a precipitate, both are dissolved again, the solutions mixed and the aluminium phosphate re-precipitated. (See determination of aluminium in ferro-vanadium.)

Titanium is not often found in steel, but when present is precipitated with aluminium. The amount of it may be determined by dissolving the precipitate and applying the colorimetric test with hydrogen peroxide. An approximate separation can also be made by fusion with sodium carbonate and extraction with water. After filtering and washing with a dilute solution of sodium hydrate, the aluminium can be determined in the filtrate after acidification, by re-precipitation as phosphate.

CHROMIUM (Cr = 52·0).

The compounds of chromium correspond to three different states of oxidation—CrO, Cr_2O_3, and CrO_3. The first of these oxides is basic, giving rise to very unstable and oxidisable chromous salts, of no importance whatever to the analytical chemist. Chromic oxide, Cr_2O_3, is also a weak base; the green salts to which it gives rise are soluble in water and are easily hydrolysed. The oxide CrO_3 is an acid, and its salts are the most stable of the compounds of chromium. They are easily produced from chromic salts by quite a number of oxidising agents, are quantitatively reduced again by several standard reducing agents, and are therefore very largely used for the volumetric determination of the element.

Separation from Iron.—The separation of chromium from iron depends upon whether the former exists as a chromic salt or as a chromate, and also whether the iron is present as a ferrous or a ferric salt.

The hydrolysis of chromium salts by means of barium carbonate, zinc oxide, magnesium oxide, etc., is obviously only applicable to solutions containing ferrous iron. The precipitation of the chromic hydrate is not so perfect as that of ferric hydrate, and its repetition, particularly when barium carbonate is used, is generally necessary. Much more satisfactory is the separation of chromium from ferrous iron by precipitation of the former as a basic phosphate, under the conditions which obtain in the case of aluminium.

When the iron is present as a ferric salt, the 'Rothe ether separation' is generally used. The precipitation of the iron with nitroso-β-naphthol, or the chromium with phenyl-hydrazine are of little importance to the steel-works' chemist, though the latter form of separation is useful on occasion. Digestion with hydrochloric acid of a mixture of the ignited oxides carries the iron into solution slowly, but the separation is not by any means perfect. Ferric oxide is converted into the chloride and volatilised in that form, at a temperature of 300° C., by passing a current of dry hydrogen chloride over it, and may thus be separated from chromic oxide.

Neither of the last two methods is as exact or convenient as the precipitation of the iron as ferrous sulphide from ammoniacal solutions containing a relatively large amount of ammonium tartrate, by means of a solution of freshly prepared ammonium sulphide. Chromium (and aluminium) may be recovered quantitatively from the filtrate, though the operation generally entails an evaporation to dryness and a destruction of the excess of ammonium tartrate by careful ignition of the residue.

The separation of iron from chromic acid and chromates is much more convenient than any of the preceding processes. Any compound of chromium is converted into a soluble chromate by fusion with sodium or potassium carbonate mixed with an oxidant; ferric oxide is left undissolved on boiling the 'melt' with water.

In the wet way, the separation usually is a precipitation of the iron as hydroxide. All such separations are subject to error on account of the formation of basic ferric chromates. These compounds form so readily that a soluble normal chromate may be used instead of acetate, phosphate, succinate, etc., for precipitating iron from its 'neutralised' solutions in making a separation from manganese, nickel or cobalt. The best results are obtained by pouring the mixture of ferric iron and chromic acid into the alkali. A caustic alkali is to be preferred, as will be seen from the following results obtained by Brearley from mixtures of 1 gram of iron as ferric chloride, with 0·1 gram of chromium, as potassium chromate.

2N alkali in excess.	Percentage separation.		
	$(NH_4)HO$.	Na_2CO_3.	NaHO.
0 c.c.	24·8	54·6	69·3
10 c.c.	70·4	90·4	100·0
20 c.c.	77·0	97·5	99·8
30 c.c.	83·6	98·7	100·1
50 c.c.	87·8	100·1	—

Gravimetric Determination.—From solutions containing a salt of chromic oxide, the hydroxide is quantitatively precipitated by most of the reagents which are used for the determination of aluminium.

Ammonium hydrate should be added in slight excess only, and the mixture digested for some time before filtration. Large excesses yield pink solutions containing chromium, which is precipitated from them completely only after long heating. The green hydroxide is slow of filtration and obstinately retains salts adsorbed from solution, even after prolonged washing. The washing water should contain a small quantity of ammonium nitrate. Filter and precipitate are ignited together at a full red heat. The residue Cr_2O_3 contains 68·50 per cent. of chromium.

Ammonium sulphide may with advantage replace the hydrate as the precipitant, but the reagent should only be used immediately after its preparation.

Ammonium nitrate, and a mixture of potassium iodide and iodate, both of which are used for the determination of aluminium (*q.v.*), act equally well in the case of chromium; the conditions are the same as for aluminium.

Similarly, the precipitation as phosphate may be utilised for the determination of chromium. The adsorption of dissolved salts is practically negligible, and the process is therefore not confined to pure solutions. The precipitate is a basic phosphate $3Cr_2O_3 \cdot 2P_2O_5$, and is quite definite in composition when formed in the presence of a large excess of ammonium phosphate. The conditions of precipitation are again the same as for aluminium.

In solutions of chromates, the metal may be determined by precipitation with a solution of silver, lead, barium, or mercurous salt. The 'mercury precipitation' is described on p. 19.

In the case of barium, the solution containing the chromate is made neutral or faintly acid with acetic acid, brought to boiling, and an excess of barium acetate solution added drop by drop. (If the precipitant is added quickly, the barium chromate may not be of the exact composition $BaCrO_4$.) Dilute alcohol is used for washing the yellow precipitate, which is afterwards ignited cautiously at first, and finally at a red heat. $BaCrO_4$ contains 54·22 per cent. of chromium.

Volumetric Determination.—In point of accuracy, as well as speed, the volumetric methods of determining chromium are superior to the gravimetric; particularly is this so in the analysis of steel-works' materials.

The majority of the processes in use depend upon a preliminary oxidation of a salt of chromic oxide to a chromate, thus:

$$Cr_2O_3+3(O)=2CrO_3.$$

The oxidised compound is then titrated with a standard solution of a reducing agent such as ferrous ammonium sulphate, and from the expression $Cr_2=3(O)=6Fe''$ it follows that

$$1 \text{ c.c. } \frac{N}{10} \text{ ferrous solution} = 0{\cdot}001733 \text{ gram of chromium.}$$

In the dry way, the oxidation to chromate is generally obtained by mixing a chlorate, nitrate, or peroxide with the carbonates of sodium and potassium. By a wet reaction, the change is easily made by the addition of such reagents as chlorine, bromine, hydrogen and sodium peroxides, manganese dioxide, permanganates, persulphates, sodium bismuthate, and a mixture of potassium chlorate with nitric acid.

Besides ferrous sulphate, stannous chloride and sodium thiosulphate (following upon the addition to the chromate of an excess of potassium iodide) are sometimes used as standard reducing agents.

The conditions which make for success in the volumetric determination of chromium in steel are discussed at some length below. Other methods for the volumetric determination of chromic acid include: (1) addition of barium hydrate, the excess of which is precipitated with carbon dioxide, and followed by a titration of the resulting free alkali; (2) precipitation with a salt of lead, the excess of which is afterwards determined; and (3) distillation with hydrochloric acid and potassium bromide, the liberated bromine being absorbed in a solution of potassium iodide and the resulting free iodine titrated with sodium thiosulphate.

VOLUMETRIC ESTIMATION IN STEEL.

Ordinary chromium steels are decomposed by dilute sulphuric acid, and the metal passes into solution as chromic sulphate except the small amount contained by the carbonaceous particles, which are quickly decomposed in the next operation. This is the addition of potassium permanganate to the solution which oxidises the iron only at first, according to the equation,

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

When this reaction is completed, the further addition of permanganate oxidises the chromic sulphate to potassium bichromate thus:—

$$Cr_2(SO_4)_3+2KMnO_4+3H_2O \rightarrow K_2Cr_2O_7+2MnO_2+3H_2SO_4.$$

Before this reaction is completed, however, the permanganate reacts with the manganous sulphate (introduced by the steel and generated by the first reaction), precipitating manganese dioxide,

$$2KMnO_4+3MnSO_4+2H_2O \rightarrow 5MnO_2+2KHSO_4+H_2SO_4,$$

and the completion of the oxidation of the chromium is brought about by this precipitate.

The speed of oxidation depends on the temperature, the excess of permanganate or peroxide of manganese, and the degree of acidity of the solution. The change can be effected by a very small excess of permanganate over theoretical demands if the mixture be boiled for a long time. Increased acidity favours the oxidation, but this advantage is discounted by the fact that in strongly acid solutions a small amount of manganese dioxide apparently assumes a colloidal form, and when, as in some methods, the oxide is removed by filtration, the amount of chromium found in the filtrate is therefore in slight excess of the truth. This fact probably accounts for the 'blank' to which such processes are subject.

That the precipitated manganic oxide readily oxidises a chromium salt in a boiling solution appears to have been overlooked when the permanganate oxidation process was first introduced, and it was customary to add the oxidant until an excess was indicated by the pink colour of the boiling mixture. Since no such indication is obtained until all the manganous sulphate present is converted to dioxide, the result is a bulky precipitate, which is never free from chromium when the aqueous washings of it are quite colourless.

The loss of chromium in this way is obviated by following the aqueous washing with a solution of a caustic alkali, which dissolves the chromium out of the precipitate as chromate. This procedure is a feature of the 'Galbraith method,' dating to 1863. Later, Stead obviated the difficulty by dissolving the manganic oxide in dilute hydrochloric, and expelled the resulting chlorine by boiling the solution vigorously before titrating. The following is a brief outline of his method.

The 'Stead Process.'—Two grams of the steel are dissolved in dilute sulphuric acid (1 to 3), the ferrous sulphate oxidised with potassium permanganate, the liquid diluted to 300 c.c., and about half a gram more of permanganate added. The mixture is boiled for 10 minutes, 80 c.c. of hot dilute hydrochloric acid (1 to 1) added, and the boiling continued until the manganese dioxide is just decomposed and the liquid thereby 'cleared.' About 150 c.c. of boiling water are then added and the boiling continued vigorously until chlorine is completely expelled, which is usually the case after the volume of the solution has been reduced by about 100 c.c. After cooling, ferrous ammonium sulphate solution is added to more than reduce the chromate, and the excess titrated with a standard solution of potassium bichromate.

The process is fairly accurate, though the end point of the titration is not satisfactory. It precludes the use of permanganate for titrating the excess of ferrous iron, however, and it does not admit of an easy means of detecting and determining vanadium, when present.

The best of the volumetric methods in which potassium permanganate is used for the oxidation of the chromium is one in which the ferrous sulphate formed by the initial decomposition of the steel is oxidised first of all by means of nitric acid. Thus the amount of manganese in solution is considerably reduced, and it is therefore impossible to form a bulky precipitate of peroxide before a permanent pink colour is obtained. This is the principle of the 'Vignal method,' which is now generally practised. In the following adaptation of it, due to Russell,[1] the acidity of the solution and amount of manganic oxide formed lead to results that do not necessitate the deduction of a 'blank.'

The 'Vignal Process.'—Two grams of drillings are decomposed by a mixture of 30 c.c. of water with 6 c.c. of sulphuric acid, and the oxidation of ferrous sulphate made by adding 2½ c.c. of nitric acid (1·4). When nitrogen peroxide is completely expelled, hot water up to about 200 c.c. is added, and to the liquid, boiling gently, a dilute solution of potassium permanganate (about 4 grams per litre) is added a few drops at a time, until a brown precipitate is obtained and remains for 10 minutes after the last addition. The mixture is cooled, filtered through asbestos and the precipitate washed with hot water. To the filtrate 30 c.c. of dilute sulphuric acid (1 to 4) are added, then an approximately decinormal solution of ferrous ammonium sulphate, until the complete reduction of chromic acid is indicated by the green colour of the liquid, and the excess of iron finally titrated with standard permanganate.

The above process differs from ordinary practice of the Vignal method on one important point. It is customary to add a concentrated solution of permanganate freely until an excess is obviously indicated, and to decompose the excess by the addition of a small quantity of solid manganous sulphate, a procedure which, as shewn above, necessitates a blank determination.

For amounts of chromium up to 2·5 per cent. a suitable solution of permanganate is made by dissolving 1·825 grams of the pure solid in a litre of distilled water. An equivalent solution of ferrous ammonium

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[1] *Iron and Coal Trades Review*, 95. 491 (1917).

sulphate, which should contain about 20 c.c. of sulphuric acid in each litre, is made from 22·64 grams of the solid. One cubic centimetre is equivalent to 0·05 per cent. of chromium, working upon a 2 gram sample.

Decinormal solutions are suitable for larger percentages of chromium than 2·5.

COLORIMETRIC ESTIMATION.

In the manufacture of plain carbon tool steels, a very small amount of chromium (less than 0·1 per cent.) is frequently introduced, and its amount is best estimated by a colorimetric process. The yellow colour of a soluble chromate may be utilised for this purpose, and in the manner described by Russell as follows:

Prepare a solution of potassium dichromate, 0·283 gram per litre. Weigh out 0·2 gram of the sample and 0·2 gram of a steel free from chromium into small beakers. To the latter add 2 c.c. of the standard dichromate solution, representing therefore 0·1 per cent. of chromium. Dissolve in 3 c.c. of hydrochloric acid and oxidise the iron with a few drops of nitric acid. Rinse down once with cold water, then add sodium peroxide, a little at a time, and shaking well after each addition, until the iron is precipitated, and the chromium oxidised to sodium chromate. Boil, rinse down once more, filter into test tubes 6 in. × $\frac{3}{8}$ in., and wash. Dilute the one or the other filtrate until the tints just match when the tubes are held up to a white background. Measure the volumes of the solutions and calculate the percentage of chromium.

The above method is applicable to steels containing up to 0·15 per cent. of chromium and gives results, accurate to within 0·005 per cent., in less than half an hour.

ESTIMATION IN SPECIAL STEELS.

The Vignal process is applicable to any alloy steel, but slight modifications are imposed by the presence of tungsten and vanadium. In the case of the former some tungstic oxide may separate immediately after oxidising the iron with nitric acid, in the form of a dirty green precipitate containing undecomposed carbides. The mixture should then be digested short of boiling until the precipitate assumes a bright yellow colour, whereupon the hot water is added and the process finished as described. Vanadium passes into the filtrate from the manganese dioxide precipitate, in the form of vanadic acid, which is reduced later to vanadyl sulphate by the ferrous solution. In the final titration of the excess of ferrous iron with permanganate the vanadium is re-oxidised after the iron, and hence does not affect the calculated results. As, however, the reaction between permanganate and a vanadyl salt in cold solution is sluggish, the end of the titration is not reached until a pink colour is obtained which persists for at least a minute. This point, and the determination of the amount of vanadium present, are fully discussed later.

NICKEL (Ni = 58·7).

Separation from Iron.—Quite a number of processes may be used for separating iron from nickel. The most serviceable in steel analysis are described at length in Part I.; of these, the basic acetate method, in which the iron is precipitated by a small amount of ammonium acetate added to a ‘ neutralised ’ solution, is particularly recommended. For ammonium acetate may be substituted a soluble chromate,[1] of which an excess may safely be added without loss of even a trace of nickel in the iron precipitate.

The remaining methods which effect the separation by precipitating the iron, are now seldom practised. Perhaps the two most important are Eastwick's,[2] which depends upon the separation as sulphide from acid solutions containing ammonium sulphate, and Rosenblatt's,[3] in which the iron is removed by means of potassium thio-carbonate.

When the separation is effected by precipitating the nickel, the method now most generally used is the precipitation from an ammoniacal solution containing a tartrate or citrate by means of dimethyl glyoxime; it is dealt with below.

The precipitation from a similar solution can also be made by means of potassium iodide; a pale violet nickelous ammonium iodide separates. This method, discarded by the author some years ago in favour of the glyoxime precipitation, is recommended by Schoeller and Powell,[4] who utilise it with success in the determination of nickel (and cobalt) in steel. For retaining the iron in solution, older methods made use of a pyrophosphate or converted the iron to ferrocyanide, the nickel being precipitated by means of bromine and a caustic alkali.

Gravimetric Determination. 1. Precipitation as Hydroxide.—Nickel is precipitated quantitatively from solutions of its salts by sodium or potassium hydrate. The pale green nickelous hydrate filters slowly and obstinately retains sodium and potassium salts. Saturation of the solution with chlorine or bromine before the addition of the alkali leads

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[1] Brearley, *Chem. News*, 78. 15.

[2] *Journ. I. S. Inst.*, 1894, 1. 615.

[3] *J. C. S.*, 50. 492.

[4] *Journ. I. S. Inst.*, 1918, 1. 441.

to the formation of black nickelic hydrate which can be filtered more quickly and washed more effectively. Both compounds yield on ignition the green oxide, NiO, containing small quantities of alkaline salts and also silica.

2. **Precipitation as Sulphide.**—The determination as oxide is much more satisfactory, however, when the nickel is thrown out of solution as its sulphide NiS. When the conditions of precipitation are suitably adjusted, the method is most reliable. If free mineral acid is present in the solution it should be neutralised with ammonium hydrate, an excess of 10 to 15 c.c. of B.P. acetic acid added, and then 20-30 c.c. of ammonium acetate. The solution is heated to boiling and a rapid current of hydrogen sulphide passed to saturation. If the solution has been allowed to cool during this operation, the mixture is brought to the boiling point before filtration, otherwise traces of nickel may be left in solution. The precipitate is collected on paper pulp, and washed with hydrogen sulphide water containing a few drops of ammonium acetate. The filter is partially dried by suction at the pump, transferred to a crucible, and ignited in the muffle. Large amounts require some time for the complete conversion of the sulphide to oxide; the change is facilitated by interrupting the ignition shortly after the filter is completely 'ashed,' and grinding the residue with a rounded glass rod. A further ignition at a red heat for half an hour completes the operation.

3. **Precipitation as 'Glyoxime.'**—The favourite gravimetric method for the determination of nickel is the precipitation by means of dimethyl—or diphenyl—glyoxime. The use of the former reagent was advocated by Tschugaeff [1] in 1905, and the method was investigated and improved by Krant,[2] Brunck [3] and others.[4] Its particular merit is that of providing not only a means of determining nickel, but also of separating it at the same time from iron and several other metals, including cobalt.

The solution, at weak concentration of any one of the soluble salts of nickel, is made slightly alkaline with ammonium hydrate, and precipitated at a temperature of 50° C. by an excess of a 1 per cent. solution, in 95 per cent. alcohol, of dimethyl glyoxime. The mixture is digested at the same temperature for at least 15 minutes, and the bright red voluminous precipitate filtered, either through paper pulp or upon asbestos contained in a weighed Gooch crucible. The precipitate is washed with water containing a small quantity of ammonium nitrate;

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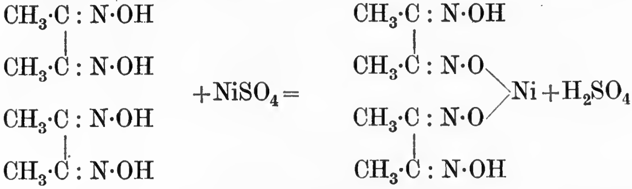
[1] *Zeit. anorg. Chem.*, 46. 144. and *Ber.* 38. 2520.

[2] *Zeit. angew. Chem.*, 19. 1793.

[3] *Ibid.*, 20. 834.

[4] *Chem. News*, 104. 58 and 224.

during this operation it becomes much more compact. If collected on a Gooch crucible it is dried at 110°-120° C. and weighed as 'nickel glyoxime,' $NiC_8H_{14}N_4O_4$, containing 20·32 per cent. of nickel.



$$\begin{array}{l} CH_3\cdot C:N\cdot OH \\ \quad | \\ CH_3\cdot C:N\cdot OH \\ CH_3\cdot C:N\cdot OH \\ \quad | \\ CH_3\cdot C:N\cdot OH \end{array} + NiSO_4 = \begin{array}{l} CH_3\cdot C:N\cdot OH \\ \quad | \\ CH_3\cdot C:N\cdot O \\ CH_3\cdot C:N\cdot O \\ \quad | \\ CH_3\cdot C:N\cdot OH \end{array} \rangle Ni + H_2SO_4$$

The precipitate is soluble in strong acids, hence the addition of ammonium hydrate to neutralise the acid generated in the above reaction. Dilute acetic acid has little action on the precipitate, however, and solutions containing ammonium acetate may therefore be used for the precipitation.

Direct weighing of the glyoxime precipitate is particularly suited to the determination of small amounts of nickel, on account of the high molecular weight of the compound. Large precipitates are more conveniently ignited at a red heat, yielding NiO, but precaution must be taken to prevent loss. This is due to the fact that at a temperature of about 250° C. nickel-glyoxime sublimes. Some 20 or 30 degrees higher, however, the compound decomposes, so that if loss by volatilisation is prevented before the decomposition temperature is reached, the complete removal of the organic products may safely be conducted at a red heat. The pulp filter is accordingly enclosed whilst still wet in two 'ashless' papers, also wetted, and transferred to the crucible. The crucible and contents are then placed near the mouth of the muffle until the enclosing papers are thoroughly charred without taking fire, by which time the enclosed compound has decomposed, and the ignition may then be completed at a full red heat.

$$NiO \times 0{\cdot}7857 = \text{Nickel}.$$

Volumetric Determination.—Two of the preceding methods of precipitating nickel have been utilised for the volumetric determination of the element. Thus, the black hydrate obtained by bromine and an alkali may be filtered out, washed and added, filter and all, to an acid solution of a known amount of ferrous sulphate. When the precipitate is completely dissolved, according to the following reaction, the excess of ferrous iron is titrated with potassium permanganate or bichromate.

$$Ni_2O_3 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NiSO_4 + 3H_2O.$$

Similarly the hydrated oxide may be dissolved in an excess of dilute sulphuric acid containing potassium iodide, and the liberated iodine titrated with thiosulphate.

$$Ni_2O_3+2KI+3H_2SO_4 \rightarrow 2NiSO_4+K_2SO_4+I_2+3H_2O.$$

The results yielded by the above processes are not perfectly reliable, however, because the hydrate obtained in the first instance is not quite of the theoretical composition corresponding to the sesquioxide Ni_2O_3, though it approximates closely to it.

Another simple volumetric method consists in dissolving the washed precipitate of nickel-glyoxime in a measured excess of standard sulphuric acid, followed by a titration of the excess with potassium hydrate. Parr and Lindgren [1] employ this method, and determine the end point of the reaction by the appearance in the liquid of a faint yellow turbidity, indicative of the re-precipitation of nickel glyoxime.

The most important volumetric method for the determination of nickel is the cyanometric titration. Potassium cyanide and nickel salts react quantitatively according to the following equations:

$$NiSO_4+2KCN \rightarrow Ni(CN)_2+K_2SO_4$$
$$Ni(CN)_2+2KCN \rightarrow K_2Ni(CN)_4.$$

According to the above, $Ni=4KCN$.

As the exact end point of the second reaction, which is the conversion of the insoluble $Ni(CN)_2$ into a soluble potassium nickelo-cyanide, is not sufficiently well marked, a turbidity of silver iodide is generated in the solution before the titration is commenced, by adding potassium iodide and a known amount of silver nitrate. The excess of the latter reacts with the potassium cyanide according to the equations

$$AgNO_3+KCN \rightarrow AgCN+KNO_3$$
$$AgCN+KCN \rightarrow KAg(CN)_2.$$

Similarly the turbidity of silver iodide is decomposed, and the solution thereby cleared according to the reaction

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

The last reaction takes place after the nickel and the excess, if any, of dissolved silver have been converted into the double compounds, and thus furnishes the end point of the titration.

The operation is usually conducted as follows:—The solution to be titrated is made slightly alkaline with ammonium hydrate, and a gram or two of ammonium sulphate either dissolved in it, or generated in it by adding a few cubic centimetres of dilute sulphuric acid before making

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[1] *Trans. Amer. Brass Founders' Ass.* (1911), 5. 120.

alkaline. A small quantity of potassium iodide is added and about 5 c.c. of a standard solution of silver nitrate from a burette. The potassium cyanide solution is then run in, a few cubic centimetres at a time, but as quickly as possible consistent with a shaking between each addition, until the solution is cleared. The exact end point of the reaction is found by re-forming a turbidity with a few drops of the silver solution and discharging it again with the cyanide. The last operations may obviously be repeated as often as desired. The potassium cyanide solution is next standardised in the finished titration mixture, in terms of silver, by the addition of 20 to 25 c.c. of the silver nitrate solution and repeating the above operations.

$$\mathrm{Ni} = 4\mathrm{KCN} = 2\mathrm{Ag}.$$

Notes.—The above method is one of the most exact processes of quantitative analysis, and is capable of application in the presence of quite a number of other substances. The following additional observations may be found useful.

A large excess of ammonium hydrate should be avoided, not merely because of its solvent action upon the silver iodide indicator, but because it interferes with the formation of potassium nickelo-cyanide. A solution containing 2 per cent. of its volume of 2N ammonium hydrate titrates perfectly, and several times this amount are allowable.

The intensity of the iodide turbidity is increased by the presence of an ammonium salt, of which the sulphate is most effective. The indicator is the more sensitive the less potassium iodide added in excess of what is needed for the formation of a working turbidity; a suitable amount to add is 2 c.c. of a 2 per cent. solution in a volume of 500 c.c. of liquid.

Hydrolysis and consequent loss of strength of the potassium cyanide solution is prevented by the addition to it of a small quantity of sodium hydrate.

Moderate amounts of alkaline carbonates and other salts of the alkalies exert no appreciable influence upon the cyanometric estimation of nickel.

Manganese is slowly precipitated from ammoniacal solutions, and so it is impossible to take full advantage of the delicacy of the indicator even by repeated filtrations, but the precipitated hydrate does not react in any way with the cyanide. Manganese may be held in solution by the addition of ammonium chloride, though this procedure is only necessary in the analysis of ferro-nickel alloys or of high nickel steels which frequently contain comparatively large amounts of manganese. If time is not unnecessarily lost in the titration after making the solution alkaline, the end point is not difficult of determination.

Iron, Aluminium and Chromium are frequently separated from the nickel, before proceeding to the cyanometric estimation, by the basic acetate process or by precipitation with ammonium hydrate from a solution previously treated with an excess of potassium cyanide. In the latter case the nickel is determined by titration of the excess of cyanide in the filtrate. These metals are also held in solution by the use of tartaric and citric acids, which do not, however, give quite satisfactory results in the presence of much chromium, if present as a chromium salt. Chromates exert no interference.

Cobalt must be absent from the solution to be titrated for nickel. The metal forms soluble double cyanides with potassium, but the reaction between its soluble salts and potassium cyanide is not capable of exact quantitative measurement.

Copper is present in such small amounts in steel and steel-making alloys that its effect on the results of a nickel assay is practically negligible. Moreover, the reaction between its salts and potassium cyanide is quantitative according to the expression

$$CuSO_4 + 4KCN \rightarrow K_2Cu(CN)_4 + K_2SO_4$$

and the amount of cyanide consumed may be subtracted from the total amount used in the assay for nickel, when the percentage of copper has been previously determined.

Electrolytic Determination.—Nickel is determined electrolytically by deposition from ammoniacal solutions containing sulphate or oxalate of ammonium. In the former case, if the solution does not contain the nickel in the form of sulphate, it should be evaporated to fumes after adding about 3 c.c. of concentrated sulphuric acid, the residue taken up in water and about 8 grams of ammonium sulphate dissolved in the solution. The mixture is then treated with ammonium hydrate sufficient to yield an excess of about 30 per cent. of the total volume of the solution. A current of 1 ampère, with an E.M.F. of about 4 volts, will deposit 0·2 gram of nickel in about 3½ hours. The electrolyte may be warmed with advantage, loss by evaporation being corrected by the addition of 50 per cent. ammonium hydrate. The end of the deposition is determined by testing a few drops of the electrolyte with colourless ammonium sulphide solution. The absence of any brown colouration indicates freedom from nickel. The deposit is washed with water, then with absolute alcohol, and is dried and weighed at once. After weighing, the nickel is dissolved from the platinum dish without delay, by means of dilute nitric acid.

In the second form of deposition, the solution should contain about

8 grams of ammonium oxalate, and a slight excess only of ammonium hydrate at the outset. The alkalinity increases during the course of the deposition. The other conditions are substantially the same as above.

VOLUMETRIC ESTIMATION IN STEEL.

With Separation of Iron.—I. Two grams of steel are decomposed with 20 to 30 c.c. of hydrochloric acid, the ferrous oxidised to ferric chloride with 2 or 3 c.c. of nitric acid, the solution diluted with cold water to about 400 c.c., 'neutralised,' and the iron precipitated exactly as described under the 'basic acetate separation' on p. 9. Not more than 2 c.c. (or 20 c.c. of the dilute) ammonium acetate should be added for completing the precipitation at or near the boiling point. The mixture is made up to a litre, with a correction for the volume of the solid matter, and 500 c.c. filtered off through a dry fluted paper.

The filtrate is cooled off rapidly, 1 c.c. of sulphuric acid added, the liquid made faintly alkaline with ammonium hydrate, and titrated as described above. Suitable solutions for the titration are (1) potassium cyanide, about 1·5 grams per litre of water containing a gram or two of sodium hydrate; (2) silver nitrate, made by dissolving exactly 3·398 grams of the crystals in a litre of distilled water. One c.c. of the latter contains 0·002158 gram of silver, equivalent to 0·000587 gram of nickel.

In an actual assay, 5·4 c.c. of $AgNO_3$ and 49·8 c.c. of KCN solution were used in the titration. On standardising the cyanide in the same solution, a further amount of 24·5 c.c. of $AgNO_3$ were titrated by 20·2 c.c. of the cyanide, from which it follows that

$$1 \text{ c.c. KCN} = 1{\cdot}21 \text{ c.c. } AgNO_3.$$

Therefore $$49{\cdot}8 \text{ c.c. KCN} = 60{\cdot}3 \text{ c.c. } AgNO_3$$

and $(60{\cdot}3 - 5{\cdot}4) \times 0{\cdot}000587 = 0{\cdot}0322$ gram of nickel.

Percentage of nickel in steel = 3·22.

II. Dissolve one gram of the sample as before, pour into a half litre flask already partly filled with cold water, and containing also nearly half the 70 c.c. of binormal ammonium hydrate which is to be used for precipitating the iron. Run in an excess of cyanide from a burette and add the remaining portion of the alkali, which should be sufficient to precipitate all the iron, and leave the filtered solution suitably alkaline for the subsequent titration. Make up to 500 c.c., mix well, and filter 250 c.c. through a fluted paper. During filtration add 2 c.c. potassium iodide solution and a little ammonium sulphate to a clean flask, empty the filtered solution into this, and add silver nitrate from a burette until a turbidity appears.

If 5·789 grams of silver nitrate are dissolved in a litre of water, each cubic centimetre of the solution is equivalent to 0·001 gram nickel, or equal to a tenth per cent. nickel if one gram of the steel is used. The potassium cyanide and silver nitrate should be of equal strength, or their relative strengths known. In the former case the percentage of nickel in the steel is at once found by deducting twice the amount of silver nitrate used from the amount of cyanide added and dividing by ten.

Rather more cyanide must be added than is required to combine with the expected amount of nickel. In making furnace tests the amount of nickel present is known to within half per cent. or so. But supposing it were otherwise, there is no disadvantage in using larger excesses of cyanide than are required. This is shewn by the following results, obtained by operating with similar amounts of a one per cent. nickel steel, and adding varying excesses of potassium cyanide. The cyanide required theoretically was 10 c.c.

KCN added.	Per cent. Nickel.	Per cent. Nickel Corrected.
13·3 c.c.	1·01	1·00
16·0 c.c.	1·02	0·99
18·9 c.c.	1·05	1·01
22·8 c.c.	1·06	1·00
27·0 c.c.	1·06	0·98
32·5 c.c.	1·11	1·01

Large excesses of potassium cyanide, it is seen, cause high results. The error, however, causes no serious inconvenience, because when a large amount of silver nitrate is required to form the turbidity, it would be known that the calculated result was too great. Happily, the error is fairly proportionate, as may be seen from the third column of the table, where a correction has been made by increasing the amount of silver nitrate actually used by ·5 per cent.

The process is a very rapid one, the manipulations requiring less than 15 minutes, and it is as exact as any other if a preliminary test is made when the approximate percentage of nickel is not known.

Without Separation of the Iron.—Weigh off one gram of the sample and add 10 c.c. hydrochloric acid, diluted with an equal bulk of hot water; when it is at least mainly dissolved add 10 c.c. 1·20 nitric acid. Cool the solution, add 3 grams of citric acid, two grams of ammonium sulphate, and as much dilute ammonium hydrate as will make the solution slightly but distinctly alkaline (about 80 c.c. of binormal strength). Add 2 c.c. of a two per cent. potassium iodide solution, and as much silver nitrate as forms an obvious turbidity. Run in potassium cyanide from a burette until the turbidity just disappears.

Alkaline citrate solutions of iron are very dark in colour, and small variations in the turbidity are not easy to follow in the ordinary manner. The difficulty is greatly lessened by performing the operation in the shade and arranging a strong beam of light to cross the liquid. So long as the solution is turbid the path of the light is very distinct; as soon as the turbidity disappears the beam of light is hardly visible, except as it falls on small air bubbles caused by the shaking. A suitable beam of light is provided by enclosing an electric lamp in a box fitted with a condensing lens.

The chief drawback to this process lies in the fact that when chromium is present the silver iodide turbidity disappears when considerably less potassium cyanide has been added than is required to form the double cyanide with the nickel present; but it recurs again and again. This recurring turbidity not only delays the process, but also leaves the operator somewhat undecided as to when the final point has really been reached.

In works' practice, a standard nickel steel is often weighed off at the same time as the samples, so that if the same amount of silver nitrate is used in each test, the value of the cyanide solution in terms of nickel is obtained without a standardisation.

GRAVIMETRIC ESTIMATION IN STEEL.

I. **Without Separation of the Iron.**—Dissolve 1 gram in 10 c.c. of hydrochloric acid, oxidize the iron with 2 c.c. of nitric acid, boil for half a minute, dilute, and filter if necessary. Dilute the filtrate to about 300 c.c., add 2 grams of tartaric acid, heat the solution to about 50° C., and add the dimethyl glyoxime reagent. Make the mixture faintly but distinctly ammoniacal, ascertain that the precipitation is complete by the addition of more reagent, and digest the mixture at the same temperature for 15 to 30 minutes. Filter, and wash with water containing a little ammonium nitrate. Finish as previously described, by weighing the red compound after drying, or as oxide after ignition.

II. **With Separation of the Iron.**—The above precipitation with dimethyl glyoxime can be applied directly to the filtrate from a basic acetate separation of the iron, the addition of tartaric acid being omitted.

Alternatively the nickel may be precipitated, after the addition of acetic acid and ammonium acetate, by hydrogen sulphide and the precipitate finally ignited to NiO as previously described.

ESTIMATION IN SPECIAL STEELS.

Most of the elements associated with nickel in special steels are without influence upon the determination of nickel by the above methods.

Tungsten is eliminated as tungstic oxide by evaporation of the original solution and filtration before proceeding with the estimation for nickel. If iron is removed by the basic acetate process, chromium, molybdenum and vanadium are precipitated with it, and the only elements in the filtrate which may interfere with the cyanometric assay are copper, manganese and cobalt. The cases of the first two have been dealt with previously; cobalt is treated in the succeeding section. All three are without influence upon the dimethyl glyoxime precipitation.

If the iron is held in solution by means of tartaric or citric acid, the glyoxime precipitation is again quite satisfactory in all cases, but the cyanometric determination is impossible in the presence of cobalt.

COBALT (Co = 59·0).

Cobalt is an important constituent of certain high-speed steels, which usually contain also larger amounts of chromium, and smaller quantities of nickel and molybdenum. The following, *e.g.*, is the composition of a tool steel of this description; carbon, 1·48; silicon, 0·72; manganese, 0·31; chromium, 13·32; cobalt, 3·27; molybdenum, 0·56; nickel, 0·74; sulphur, 0·06; phosphorus, 0·038.

Separation from Iron.—The general methods of separating nickel from iron are equally applicable to the case of cobalt, and there does not appear to be a satisfactory method of a special nature.

Separation from Nickel.—The analytical reactions of nickel and cobalt resemble each other very closely, except in respect of the fact that cobalt forms a number of stable compounds in which the element functions in a trivalent capacity. Several methods of separating nickel and cobalt have been based upon this property. Thus the old (1847) potassium nitrite method effects the separation by precipitating the cobalt as a yellow crystalline potassium cobalti-nitrite, $Co(NO_2)_3 \cdot 3KNO_2$, from acetic acid solution, the double nitrite of nickel and potassium, which is a nickelous salt, being soluble under the conditions.

Similarly, cobalt forms a stable cobalticyanide with potassium, which is not so readily decomposed as the nickelo-cyanide. Liebig's two methods of separating the metals are based upon this fact. In one of these,[1] an excess of pure potassium cyanide is added to a neutral solution of the two metals, then an excess of pure potassium hydrate. On adding bromine or bromine water, with constant stirring, until no further precipitation occurs, the nickel is obtained as the black nickelic hydrate, and the undecomposed cobalticyanide passes into the filtrate. The second, known as the mercuric oxide method, also effects the decomposition of potassium nickelo-cyanide by the addition of an emulsion of mercuric oxide in water, the excess of which is filtered off along with the precipitate of nickelous hydrate.

$$K_2Ni(CN)_4 + 2HgO + 2H_2O \rightarrow Ni(OH)_2 + 2Hg(CN)_2 + 2KOH.$$

A more modern method than the above is that of Ilinsky and Knorre,[2] in which the cobalt is again precipitated as an -ic compound, $Co[C_{10}H_6O(NO)]_3$, with nitroso-β-naphthol. The method is particularly suitable for the estimation of small amounts of cobalt associated with large quantities of nickel. This, and the glyoxime precipitation of nickel, are the two processes most frequently used at the present time for the separation of nickel and cobalt. The latter is suited to mixtures of the two elements in any proportion, provided that a sufficiently large excess of the reagent is used in a separation from large amounts of cobalt.

All the above methods provide a filtrate which, unfortunately, is not directly available for the determination of the contained element. For technical purposes, therefore, the solution containing both metals is generally divided into two portions, which are either assayed separately for each metal, or the metals are precipitated together from one portion, and one of them determined in the other.

Gravimetric Determination.—Several excellent methods of determining cobalt gravimetrically depend upon a precipitation in the form of a compound convertible by ignition to an oxide. The hydrates, the sulphate, sulphide, and the nitroso-β-naphthol compounds are cases in point, and three of these are readily obtainable in an insoluble form.

A goodly number of statements in the older (and also some modern) literature might be cited, to the effect that the ignited residue consists of a mixture of CoO and Co_3O_4 in varying proportions. Formerly, therefore, the uncertainty which existed on the matter, led to the practice of finishing the determination by reducing the product of the ignition to metallic cobalt by means of a current of hydrogen.

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[1] *Ann. d. Chem. u. Ph.*, 65. 244.

[2] *Ber.*, 18. 669.

The necessity for this procedure does not exist when the temperature of ignition is under control, and can be maintained at a fairly uniform degree. Local overheating of the mass, which might occur by igniting over a blowpipe flame, is eliminated by the modern practice of ignition in a muffle furnace, and either the one oxide or the other can be secured at will. Cobaltous oxide, CoO, is obtained only at temperatures exceeding 900° C., hence the usual practice is to ignite at a lower and more readily attainable temperature, and weigh the resulting Co_3O_4.

Gorgeu [1] finds that Co_3O_4 at a bright red heat gradually loses oxygen and is converted into CoO, the decomposition being perfectly continuous. Conversely, when the monoxide is heated in presence of air, it absorbs oxygen up to a dull red heat, with formation of Co_3O_4. By measuring the temperature at which the dissociation pressure of Co_3O_4 equals that of the atmosphere, Foote and Smith [2] fix the temperature of decomposition at 905° C. On the other hand, it is stated [3] that the transition point cannot be determined, because regions of solid solution of one oxide in the other exist, and a temperature of 869° C. is given as that above which the region of cobaltous oxide occurs.

Experiments conducted by the author in 1916 are of some interest in this connection; the following is a brief summary of them:

(1) A sample of oxide, obtained by ignition to constant weight of the pure metal at a temperature of about 850° C., was placed in a boat and heated in a porcelain tube. A platinum and platinum-rhodium thermo-couple, which had been carefully calibrated, was inserted in the oxide, and an inverse-rate heating curve recorded as the tube was carefully heated up. The average steady rate of rise of temperature between 830° and 910° was 13 seconds per degree; at the latter temperature the rate increased and attained a maximum of 40 seconds per degree at 920°, beyond which it fell and assumed the normal rate of 13 seconds per degree.

(2) Ten grams of Co_3O_4 were heated in a platinum crucible with a thermo-couple inserted, and a time-temperature curve obtained by means of an automatic recorder. A clearly marked point was obtained at 923°.

(3) A weighed sample of cobaltous oxide, CoO, was heated for a definite period of time at a particular temperature or through a particular range of temperature, and then re-weighed after cooling rapidly in air. The following results were obtained.

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[1] *Compt. Rend.*, 100. 175.

[2] *Journ. Am. Ch. Soc.*, 30. 1344 (1908).

[3] *Chem. Zentr.*, 1912, ii. 1525.

Weight of CoO taken = 1·0118 grams.
After heating for 30 minutes at 500°-550° = 1·0222 grams.
Do. 550°-600° = 1·0350 „
Do. 600°(± 5°) = 1·0580 „
Do. 650° „ = 1·0714 „
Do. 700° „ = 1·0801 „
Do. 750° „ = 1·0833 „
Do. 800° „ = 1·0838 „
Do. 850° „ = 1·0838 „

The ratio of 1·0838 to 1·0118 is almost exactly that of Co_3O_4 to 3CoO. The oxide was finally heated to a temperature of 950°, which was maintained for half an hour, the capsule then removed, quickly cooled and weighed. The weight of the product was 1·0120 grams.

Irrespective of the discrepancy between the author's observations and those of Foote and Smith, of the transition temperature of Co_3O_4 to CoO, it is evident from the above results that a range of temperature of 150 degrees (750°-900°) is available for the ignition of a suitable cobalt compound to Co_3O_4. Variations of temperature not greater than 20 degrees from a mean of, say, 800° are conditions easy to secure in a muffle burning ordinary coal gas.

Precipitation as Hydroxide.—Cobalt is quantitatively precipitated as a cobaltous hydrate by means of a caustic alkali alone, and as a cobaltic compound when an oxidant such as chlorine, bromine, or hydrogen peroxide is also present. The objections to these forms of precipitation, stated in the case of nickel, obviously apply to cobalt.

Precipitation as Sulphide.—The method of precipitating nickel from acetic acid solutions containing also ammonium acetate serves equally well for cobalt. It is perhaps more important than in the case of nickel, that the solution after saturation with hydrogen sulphide, be heated before filtration; otherwise traces of cobalt remain in solution. (Long standing in the cold results in the decomposition and re-solution of very considerable amounts of the sulphide.) The precipitate is collected on paper pulp, washed as in the case of nickel, and ignited at 800°-850° C. to constant weight. The residue is nearly pure Co_3O_4, which contains 73·44 per cent. of cobalt.

Ignition of Cobaltous Sulphate.—Salts of cobalt are converted to sulphate, by evaporation with a slight excess of sulphuric acid, without the troublesome frothing that is associated with the determination of the alkali metals in this way. The ordinary method of estimating the metal as sulphate, is to heat the dried residue very cautiously in order to expel the excess of sulphuric acid, and discontinue the heating when the pink surface of the mass just begins to blacken round the circumference. The blackening is due to the formation of Co_3O_4, and it is by no means easy to prevent this and be assured at the same time of the complete expulsion of the excess of sulphuric acid. More consistent results are obtained by igniting the residue to Co_3O_4 and weighing in that form, though they are not absolutely accurate. The complete decomposition of cobalt sulphate cannot be accomplished at temperatures below 900° C. In about 30 evaporations and ignitions, with amounts of cobalt ranging from ·036 grams to 10 times as much, the author found the residues invariably to contain traces of sulphate after constant weight had been obtained. The amount was very small, and for practical purposes negligible in the estimation of large quantities of cobalt.

Ignition to CoO at a temperature of 950° was found to eliminate the last traces of sulphur.

Precipitation with Nitroso-β-naphthol.—The reagent is made by dissolving 2 grams of the solid in 75 c.c. of glacial acetic acid and diluting the solution with an equal volume of water. A sufficient excess is provided by the use of 1·5 c.c. per milligram of cobalt.

The precipitation is made from warm solutions containing about 5 per cent. of free hydrochloric acid, and the mixture is digested for an hour or more before filtering off the very voluminous dark red precipitate. When a separation of cobalt from nickel is being made, the precipitate is washed with 12 per cent. hydrochloric acid until the washings give no reaction for nickel, and finally with water. Precipitate and filter may be ignited together and the residue weighed as Co_3O_4.

Determination as Phosphate.—Cobalt, zinc, manganese, cadmium and beryllium are precipitated from solutions of their salts as double phosphates with ammonium, the conditions being almost the same for each metal; Dakin,[1] Austen,[2] and others make use of the process for determining the metals.

For the estimation of cobalt, the solution is adjusted to a faint degree of acidity, is then heated nearly to boiling point, and treated with a solution of microscomic salt in amount equal to from 10 to 20 times the cobalt present. The absence of salts of potassium from the solution must be assured. A bulky pale violet flocculent precipitate of the normal or acid orthophosphate is formed at first, which is converted after a time into the pink crystalline and dense double phosphate. The change is facilitated by stirring the warm mixture. The resulting precipitate, which has the composition $CoNH_4PO_4 \cdot H_2O$, may be collected

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[1] *Zeit. f. anal. Chem.*, 39. 273 and 784.

[2] *Amer. Journ. Sci.*, 8 (1899).

on a Gooch crucible, washed with water, and dried at 100°-105° C. It may also be collected on paper pulp and ignited to the pyrophosphate, which contains 40·41 per cent. of cobalt. In the latter event, great care is necessary in the earlier stage of the ignition to prevent mechanical loss in the escaping ammonia and water vapour.

The author finds that the above method is not absolutely accurate, because small amounts of cobalt, which, however, rarely exceed one milligram, may generally be recovered from the filtrate. This observation is confirmed by Dufty.[1] The negative error is counterbalanced, and a positive error frequently induced by silica, which is generally to be found in the final residues when phosphate precipitations are conducted in glass or porcelain vessels.

Volumetric Determination.—The cyanometric determination of cobalt by the method which serves so well for nickel is of little or no value. On titrating a solution of cobalt, containing the silver iodide indicator, with potassium cyanide, the ' clearing ' of the solution is quickly followed by a return of the turbidity, and the operation may be repeated quite a number of times with the same result. The obvious cause of this is the atmospheric oxidation of cobalto- to a cobalti-cyanide, and the end of this reaction does not appear to be capable of exact determination. Moore[2] found, *e.g.*, that the reaction which is usually expressed by the equation

$$2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KHO$$

represents an absorption of oxygen less than the actual amount, though M'Culloch[3] based a method for the volumetric determination of cobalt upon it.

Nearly all the other volumetric methods are based upon the production of a hydrated cobaltic oxide, $2CoO + O \rightarrow Co_2O_3$, the amount of oxygen required for the oxidation being measured directly or after a subsequent reduction of the cobaltic oxide with a standardised reducing agent. Thus, Winkler's process[4] was based upon the amount of permanganate required by the following reaction :

$$6CoCl_2 + 5HgO + 2KMnO_4 + H_2O \rightarrow \\ 3Co_2(HO)_6 + 5HgCl_2 + 2KCl + 2MnO_2 \cdot H_2O.$$

Fleischer's method[5] was applied to the estimation of cobalt in the presence of nickel. The solution was heated to boiling with sodium hydrate and sodium hypochlorite, the mixed hydrates filtered out and

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[1] *Journ. I.S.I.*, 1914, ii. 52.

[2] *Chem. News*, 68. 295.

[3] *Chem. News*, 59. 51.

[4] *Zeit. f. anal. Chem.*, 3. 420.

[5] *Journ. f. prakt. Chem.*, 110. 49.

treated with dilute ammonium hydrate in order to reduce the nickelic compound. The cobaltic hydrate, which is not affected by this treatment, was dissolved in a solution of ferrous ammonium sulphate in dilute sulphuric acid, and the excess of iron titrated with permanganate.

In Donath's process,[1] the oxidation is performed with iodine in a sodium hydrate solution, by which nickel is not affected. The cobaltic oxide is filtered out, distilled with hydrochloric acid and the liberated chlorine absorbed in potassium iodide solution.

Reis and Wiggert [2] add an emulsion of zinc oxide, heat to boiling and then add a standard solution of potassium permanganate. When the cobaltic oxide has settled to the bottom of the vessel, the excess permanganate is titrated with ferrous sulphate solution.

Several other processes of a like nature to the above might be cited. The experience of later observers with these methods leads to the conclusion that no one of them possesses the degree of accuracy that was originally claimed for them. Harris,[3] *e.g.*, after a careful examination of the methods quoted above, is of this opinion.

The principal source of error is due to the fact that in most cases the oxidation does not yield exactly Co_2O_3. The author has never been able to produce this substance by the use of a halogen as oxidant, and can confirm Carnot's statement [4] that the oxidation product contains more oxygen than the sesquioxide.

The most reliable oxidant is hydrogen peroxide in alkaline solution, and results which conform with theory can readily be secured by its use. The best procedure is to effect the oxidation in a solution containing an excess of sodium bicarbonate. When hydrogen peroxide is added to such a mixture, a green cobalt compound is obtained, which is more highly oxygenated than the sesquioxide; it has been termed a cobalto-cobaltite. The decomposition of this substance by boiling with sodium hydrate solution leads to the formation of the perfectly definite hydrated sesquioxide. Upon this reaction Metzl [5] has founded a method for the determination of cobalt, which gives excellent results. Nickel is not oxidised during the reaction and does not interfere in any way with the process, the details of which are appended.

The solution of cobalt, containing up to 0·1 gram of the metal in a volume of 100 c.c., is treated successively with 15 c.c. of 10 per cent. hydrogen peroxide, 30 c.c. of sodium bicarbonate solution (50 grams per litre) and 30 c.c. of sodium hydrate solution (100 grams per litre).

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[1] *Ber.*, 1879, 1868.

[2] *Zeit. f. angew. Chem.*, 1890.

[3] *Journ. Amer. Chem. Soc.*, xx. 173

[4] *Chem. News*, 59. 183.

[5] *Zeit. f. anal. Chem.*, 53. 537.

The flask is shaken vigorously until the green precipitate is decomposed, being replaced by the black cobaltic hydrate, and the mixture is then boiled vigorously for 20 to 30 minutes until the excess of hydrogen peroxide is decomposed, water being added from time to time to replace loss by evaporation. The precipitate is then dissolved, without previous filtration, in a solution of potassium iodide in dilute sulphuric acid, and the resulting free iodine titrated with sodium thiosulphate. From the equation

$$Co_2O_3 + 3H_2SO_4 + 2KI \rightarrow 2CoSO_4 + K_2SO_4 + I_2 + 3H_2O$$

it follows that $Co = I = Na_2S_2O_3 \cdot 5H_2O$

and $1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = 0{\cdot}0059 \text{ gram cobalt.}$

Electrolytic Determination.—The conditions described for the determination of nickel by electrolysis apply to cobalt.

ESTIMATION IN STEEL.

Cobalt steels generally contain other special elements, and the estimation of cobalt either involves its separation from these elements as well as from iron, or the provision of the means of obviating their interference with the estimation.

Variations of the number of metals added, as well as of their amounts, make it very difficult to describe a process of general application to the analysis of 'cobalt steels.' The following is a brief outline of the methods which have been found to give consistently good results with this class of material. Modifications of them may be imposed by exceptional cases, but should not present any great difficulty to the trained chemist.

Material, such as the steel of which the analysis is given at the beginning of this section, is not completely decomposed by the ordinary acids or acid mixtures except after a prolonged digestion. The best way is to effect the decomposition in a tall beaker without a lip. The weighed drillings are placed in it, an excess of the acid mixture added, and a well-fitting clock-glass adjusted. The mixture is allowed to digest overnight at a temperature below boiling point, and decomposition is generally found to be complete next morning. If such an arrangement is impossible, the insoluble residue resulting from an acid attack of shorter duration is filtered off, washed, dried, fused with alkaline carbonates, the melt extracted with hydrochloric acid, and the solution thus obtained added to the original filtrate.

2·4 grams of drillings are decomposed with a mixture of 50 c.c. hydrochloric and 15 c.c. nitric acids, the excess of acid removed, and a 'basic acetate' separation of the iron and chromium from the cobalt, nickel and manganese is made as described on p. 9. The filtrate (500 c.c. out of a total volume of 600 c.c.) is divided into two equal portions.

Nickel is determined in one portion by means of the glyoxime precipitation. The addition of tartaric acid should be unnecessary, but is recommended, because the basic acetate separation is more susceptible to incompleteness when large amounts of chromium are present.

The other 250 c.c. are evaporated to a bulk of about 50 c.c., the solution made ammoniacal and any small precipitate filtered out, redissolved in hydrochloric acid, and the precipitation repeated. The combined filtrates may be treated in several ways.

(1) The solution is neutralised with acetic acid, 5 c.c. added in excess, then about 20 c.c. of ammonium acetate, the mixture brought to boiling point, and a rapid current of hydrogen sulphide passed to saturation. The mixture is again heated up to incipient boiling, the mixed sulphides of cobalt and nickel filtered out, washed and ignited as previously described. From the weight of $NiO+Co_3O_4$ thus obtained, the cobalt is calculated by difference.

The filtrate and washings from the sulphides are boiled down to about half their volume, and 'gassed' again to ensure complete removal of cobalt. If no precipitation results, the liquid is boiled until free from hydrogen sulphide, cooled, and the manganese precipitated with bromine and ammonium hydrate.

(2) The solution is acidified with hydrochloric acid, diluted to about 200 c.c., and the cobalt precipitated from it with nitroso-β-naphthol. The precipitate is washed several times with 12 per cent. hydrochloric acid, then with water, and ignited to Co_3O_4.

(3) When small quantities only of nickel are present, the cobalt may be determined by precipitation as cobalt ammonium phosphate without serious error. The small amount of manganese in the steel, which is precipitated with the cobalt compound, counterbalances the loss of cobalt by imperfect precipitation, and its removal is unnecessary for technical purposes.

(4) Cobalt may be determined by the volumetric process of Metzl, previously described, but a correction should be made for the manganese present, which is otherwise registered as cobalt.

Notes.—Tungsten is separated in the customary manner as WO_3. Vanadium and molybdenum are precipitated with the iron in a basic acetate separation.

Chromium is determined by the Vignal method; a decomposition overnight with a mixture of 42 c.c. water, 8 c.c. sulphuric acid and 5 c.c. nitric acid may be necessary. Manganese can be determined on the solution obtained in the same way by precipitating the iron and chromium, with an emulsion of zinc oxide, and applying the bismuthate process to the filtrate. (See p. 6.)

TUNGSTEN (W = 184·0).

Separation from Iron.—All the methods employed for the determination of tungsten in steel and its alloys with iron involve its separation from the iron, which is generally made by the application of one or other of two methods. Each of these is based upon the fact that the most stable oxide of tungsten is an acid, WO_3, readily forming tungstates, for example, with basic oxides. The lower oxides of tungsten are of little importance to the analytical chemist; they, and solutions of their salts, are unstable, readily taking up oxygen. The oxidised solutions can then either be hydrolysed to tungstic oxide on the one hand or treated with the salt of a base which forms an insoluble tungstate, on the other.

(1) From a solution containing tungsten and ferric iron, and necessarily also an excess of a strong acid, hydrolysis of the tungsten compound to WO_3 is at once brought about by simple dilution or by evaporation of the excess of acid. Tungstic oxide separates quantitatively from chloride solutions if the amount of hydrochloric does not exceed 20 per cent. by volume of the concentrated acid, s.g. 1·2.

(2) The tungstates of the alkali metals, which are numerous, are all soluble in water or excess of alkali, and thus provide a means of separating the element from iron. This separation may take the form of a fusion of the mixed oxides with carbonate of sodium (or potassium), with or without the addition of an oxidant, followed by an extraction with water. The residue is ferric oxide, and the filtrate from it an alkaline solution of sodium tungstate. Fusion is unnecessary when the tungsten in the mixture is largely in excess of the iron; in this case a preliminary roasting in the muffle, followed by an extraction with sodium hydroxide solution, suffices. A wet separation, based upon the same principle, is equally satisfactory when applied to a simple mixture of ferric iron and a soluble tungstate. By delivering such a solution in drops into an excess of a hot and agitated solution of sodium hydroxide, as described under the estimation of molybdenum in steel (*q.v.*), the whole of the tungsten passes into the filtrate from the ferric hydroxide.

This separation is not quantitative, however, when applied to a solution obtained from a tungsten steel opened out by means of hydrochloric and nitric acids; the percentage of tungsten found is generally low to the extent of from 0·1 to 0·3.

A third and particular method of separation is applied to the determination of tungsten in steels, and depends upon the selective solvent action on them of a solution of cuprammonium chloride, such as is used in the separation of the carbon from them (*q.v.*).

Besides carbon, tungsten, and silicon, the residue, after decomposition of the steel with the double copper compound, contains sulphur as sulphide of manganese or iron, chromium associated with considerable amounts of iron, titanium (if present at all), and all the phosphorus if the copper solution used is quite neutral.

The small amounts of sulphur and phosphorus in the steel do not seriously affect the tungsten estimation if the result is arrived at by difference, after ignition, elimination of the silica with hydrofluoric acid, fusion of the residue with sodium carbonate, and weighing of the small amounts of ferric oxide, etc., left after aqueous extraction. Such a procedure, in fact, gives very accurate results with pure carbon-tungsten steels, but when chromium is present the amount of iron oxide to be filtered off after the sodium carbonate fusion may be comparatively large, and considerable amounts of chromium pass into solution along with the tungsten when the melt is extracted with water.

It may occasionally happen that the tungstic oxide obtained by difference in the above manner from a chrome-tungsten steel is less than the amount of impurities associated with it, and herein lies the weakness of the process for general purposes.

By decomposing chrome-tungsten steels with copper solutions which contain an increasing amount of hydrochloric acid, the amount of impurity found in the ignited carbonaceous residue becomes less and less. By using solutions which contain one-third their volume of strong hydrochloric acid, the ignited residue contains only very small amounts of either ferric or chromic oxides, and yet holds all the tungsten. Details are given below.

When steels containing molybdenum as well as tungsten are treated in this way, the former metal may go wholly into solution on continued digestion, but this is not invariably the case. When the tungsten amounts to about a fraction of one per cent., the treatment at boiling point with solutions containing one-third their volume of strong hydrochloric acid makes the results slightly low. In such cases treatment of the steel with cuprammonium chloride and ten per cent. of acid is preferable.

Part of the silicon passes into solution, and cannot therefore be estimated by noting the loss in weight on treating the ignited residue with hydrofluoric acid.

Gravimetric Determination of Tungsten.—Solutions of lead, barium, cadmium and mercury precipitate tungsten quantitatively from neutral solutions of tungstates, or from solutions containing a small amount of acetic acid. Indefiniteness of composition of the precipitates obtained in the first three cases makes it necessary to determine the tungsten in them by further analysis, so that these methods of precipitation are used chiefly as a means of extracting tungsten from solutions such as, *e.g.*, the aqueous extract of a fusion with alkaline carbonates. Mercurous tungstate cannot be weighed directly for the same reason, but as it yields a residue of tungstic oxide on ignition, it forms an invaluable medium by which to determine tungsten. The process is described on p. 19.

Precipitation from solutions of tungstates, followed by an ignition to the oxide, can also be made by means of benzidine; the method was fully worked out by v. Knorre.[1] Benzidine, $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$, is a weak di-acid base, characterised by the formation of a sparingly soluble sulphate $C_{12}H_8(NH_2)_2 \cdot H_2SO_4$. The corresponding tungstate is precipitated in the cold by means of a solution of benzidine hydrochloride as a white, amorphous, flocculent precipitate, which settles and filters slowly and passes through a filter on washing with pure water. From boiling solutions, however, the precipitate is much more compact and can be readily filtered, but as it is slightly soluble in hot solution it is necessary to make the mixture cold before filtration is begun. This inconvenience is overcome, however, by making the precipitation in the cold in the presence of a small quantity of sulphuric acid or an alkaline sulphate, whereby a mixture of the crystalline sulphate and the amorphous tungstate is precipitated, and may be filtered after allowing to stand for 5 minutes only. It is washed with water containing a small quantity of the precipitant, and ignited in the moist condition, leaving a residue of WO_3.

This process is best adapted for the analysis of tungsten ores (*q.v.*), rather than steels and alloys from which the iron has not been separated previously. This is due to the facts that benzidine is oxidised by ferric compounds (necessitating a precipitation from ferrous solutions only), and that low results are obtained from solutions containing free acid other than a small amount of sulphuric. The presence of such weak acids as tartaric and citric *e.g.*, is not tolerable.

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[1] *Ber.*, 38. 783 (1905).

The reagent is prepared by dissolving 14 grams of benzidine hydrochloride in 500 c.c. of water containing 3 c.c. of hydrochloric acid.

Most frequently tungsten is precipitated and weighed as the oxide WO_3, which separates more or less completely by evaporation of solutions which have been acidified with hydrochloric acid. The separation is incomplete, even after repeated evaporations, from solutions containing salts of the alkali metals, on account of the formation of an acid tungstate most difficult of decomposition

$$Na_2WO_4+3WO_3 \rightarrow Na_2W_4O_{13}.$$

The process should not be used therefore in the assay of tungsten ores or other materials, which have been opened out with the usual fusion mixtures.

The separation, however, is complete from solutions containing iron and other steel-making metals, such solutions as are obtained by decomposition with hydrochloric acid. Evaporation of them yields WO_3, contaminated with silica, a small quantity of iron, and chromium if present. It is often recommended that the hydrochloric acid solution of the steel or alloy be evaporated to low bulk a second or third time with acid before dilution and filtration. This treatment is intended to complete the precipitation of the small amount of tungstic oxide supposed to be left in solution after one evaporation. That it is quite unnecessary follows from the fact that WO_3, unless it has been ignited at a red heat, is appreciably soluble in hydrochloric acid, so that after any number of evaporations, the final ' take-up ' with acid always carries into solution much more tungstic oxide than was supposed to be left unprecipitated after the first evaporation. As a matter of fact, tungstic oxide, as previously stated, is insoluble in dilute hydrochloric acid if the concentration does not exceed 20 per cent. by volume of the strong acid.

Volumetric Determination of Tungsten.—The determination of tungsten by volumetric methods is seldom practised in steel-works ; the methods proposed are few. One of them consists in the isolation of pure tungstic oxide, followed by its solution in a measured excess of standard alkali and titration of the excess acidimetrically ; the volumetric operations in this process are obviously superfluous. The method of von der Pfordten[1] is based upon the reduction in strong acid solution of tungsten hexachloride to the tetrachloride by means of nascent hydrogen.

$$WCl_6+Zn+2HCl \rightarrow WCl_4+ZnCl_2+2HCl.$$

The reduction is conducted in an atmosphere of carbon dioxide for an

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[1] *Ber.*, 1883, p. 508.

obvious reason. The reduced compound is then titrated, after the addition of a large amount of manganese sulphate, by means of permanganate. The method of titration is modified by Knecht and Hibbert,[1] who use ferric alum instead of permanganate, with or without a thiocyanate as indicator. In the latter case the complete discharge of the blue colour, which displaces the original brown colour of the tetrachloride solution soon after the titration begins, marks the end of the reaction. The method possesses the advantage of direct application to solutions containing ferric iron, and can therefore be used in the analysis of steel.

GRAVIMETRIC ESTIMATION IN STEEL.

(1) **Rapid Acid Process.**—To 2 grams of drillings contained in a covered beaker add 50 c.c. of concentrated hydrochloric acid, heat to incipient boiling and then remove the beaker from the middle to the corner of the hot plate. Next add a few drops only of nitric acid, and wait until the vigorous action which is induced, subsides. The addition of the nitric acid results in the momentary formation of brown ferric compounds which are quickly reduced again with the production of the unstable dark green compounds which ferrous solutions form with nitric oxide. When this takes place repeat the treatment with nitric acid until it ceases to recur. In this way the whole of the iron is oxidised with the production of a perfect solution of it and the tungsten, and with the use of very little more nitric acid than is required for the oxidation of the iron only. [The use of too much nitric acid is often accompanied by a separation of tungstic oxide at this stage of the process, and associated with it a larger amount of impurity in the form of ferric oxide.] Next evaporate the liquid as quickly as possible until tungstic oxide begins to separate, and afterwards more slowly until a pasty or almost dry condition is reached. Add then a mixture of 40 c.c. of water with 10 c.c. hydrochloric acid, boil, and set aside for at least 15 minutes. Filter through paper pulp, wash with 5 per cent. hydrochloric acid, dry, and ignite in a weighed platinum dish. Remove the silica with hydrofluoric acid alone on the hot plate, ignite again and weigh; the loss in weight gives almost but not quite all the silica present in the original steel. Cover the residue with about twice its weight of dry sodium carbonate and place the dish in the hottest part of the muffle for 5 minutes. When the fused mass is cold, extract with hot water and filter. Ignite the washed residue in the same dish; it is ferric oxide and weighs usually 2 or 3 milligrams only.

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[1] *Analyst*, 1911, p. 96.

Tungstic oxide contains 79·3 per cent. of tungsten. The results obtained by the above process err on the low side to the maximum extent of 0·05 per cent. This amount may safely be added, as a correction, to the percentage of tungsten found, though in the case of steels carrying from 10 to 20 per cent. of tungsten, the deficiency is not of very serious moment.

(2) **Estimation of Tungsten and Silicon together by the Acid Process.**—The above process does not provide for an accurate determination of silicon. Most of it is separated along with the tungstic oxide, and as the exact percentage is in many cases of little moment, it is quite a common practice to add to the amount found by treatment of the residue with hydrofluoric acid a correction empirically established for each class of steel.

If an accurate determination of silicon is wanted, evaporate the original solution to dryness, bake for 10 to 15 minutes, allow to cool, take up with hydrochloric acid, evaporate nearly to dryness again and finish as above.

Or, open out the drillings with about 50 c.c. of nitric acid s.g. 1·20, evaporate to dryness and bake, take up with 30 c.c. hydrochloric acid and again evaporate to dryness. Dissolve in the same acid again, evaporate nearly to dryness and finish as above.

(3) **Copper-ammonium Chloride Process.**—To 5 grams of drillings and 50 grams of cuprammonium chloride crystals add 100 c.c. of water previously mixed with 50 c.c. of hydrochloric acid. Digest the mixture with occasional shaking or stirring until the whole of the precipitated copper passes into solution. Filter, wash with 10 per cent. hydrochloric acid, dry and ignite, Treat the impure residue as above for the removal of silica and ferric oxide.

ESTIMATION IN SPECIAL STEELS.

High-speed steels, with 10 to 20 per cent. of tungsten, almost always contain several units per cent. of chromium, frequently also molybdenum and vanadium in smaller proportion, and less frequently cobalt.

Cobalt passes entirely into the first filtrate in the acid processes and is removed with the ferric oxide in the third method.

Vanadium is not to be found in the tungstic oxide obtained in the first method, though the rich colour of the oxide would appear to point to the contrary. Nevertheless the sensitive colour reaction with hydrogen peroxide, when applied to a solution suitably prepared from the residue, does not reveal the presence of vanadium. The copper-ammonium chloride process is not recommended for steels containing vanadium. This element is left as carbide in the insoluble residue and becomes vanadic pentoxide on ignition. Silica must therefore be removed with the precautions mentioned on p. 20. Fusion afterwards with sodium carbonate and extraction with water, carry sodium vanadate into the filtrate along with tungstate and molybdate.

Small amounts of chromium accompany the tungstic oxide obtained in the first methods, and often also in the third ; its presence is at once revealed by the pale yellow colour of the filtrate from the aqueous extract of the fusion with sodium carbonate. It is determined by acidifying the filtrate with sulphuric acid, and a titration with dilute standard solutions of ferrous ammonium sulphate and potassium permanganate. The amount found is calculated as Cr_2O_3 and subtracted from the original weight of the impure tungstic oxide.

$$1 \text{ c.c. } \frac{N}{50} KMnO_4 = 0{\cdot}000506 \text{ gm. } Cr_2O_3.$$

Molybdenum passes entirely into the filtrate from the tungstic oxide in the acid process and can be determined by one or other of the methods described for it. Results such as the following, found and quoted years ago, have been many times since obtained from steels by the author.

Percentage Present.		Percentage Found.	
Molybdenum.	Tungsten.	Molybdenum.	Tungsten.
2·56	4·50	2·54	4·51
5·67	4·50	5·70	4·51
1·41	4·38	1·40	4·38

Molybdenum is left in quantity in the carbide residue from the attack with copper ammonium chloride. The determination of it in the extract of the sodium carbonate fusion is somewhat complicated and tedious and is not recommended.

To summarise briefly :—Proceed as in method (1) up to the ignition and weighing of the impure WO_3, treat with hydrofluoric acid to remove silica, ignite and weigh again, fuse with sodium carbonate, filter off, ignite and weigh the Fe_2O_3, and deduct this from the previous weight, If the filtrate is yellow, acidify with sulphuric acid, add slight excess of ferrous ammonium sulphate and titrate with permanganate. Deduct the weight of Cr_2O_3 thus found.

MOLYBDENUM (Mo = 96).

Molybdenum forms a series of oxides, the lower members of which have weak basic properties, and thus give rise to true salts of the metal. Very little is known of these salts except the halides, but all are readily oxidised, as are also the bases from which they are derived. The product of the oxidation is molybdic acid, $MoO_3 \cdot Aq$, and the analytical reactions of molybdenum which are most serviceable to the chemist are therefore those of an acidic oxide.

Molybdic oxide MoO_3 is a white solid which turns yellow when heated, melting at redness to a dark yellow liquid and subliming at a higher temperature to tiny, colourless, rhombic plates. The substance is only very slightly soluble in water—the solution reddens litmus.

The normal molybdates of the type X_2MoO_4 are unstable, and readily form polymolybdates containing as much as ten molecules of MoO_3. Ammonium molybdate crystals, *e.g.*, have the composition

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O.$$

MoO_3 also unites with other acidic oxides forming complex compounds, of which phospho-molybdic acid is a notable example. The number of these is very considerable and includes compounds with the oxides of arsenic, vanadium, antimony, tin and silicon.

Towards strong acids MoO_3 functions as a base; thus it combines with hydrogen chloride to form a compound, important because of its volatility at comparatively low temperatures, of the composition $MoO_3 \cdot 2HCl$, and with sulphuric acid forming $MoO_3 \cdot SO_3$.

Separation from Iron.—It is evident from the above that a separation of iron from molybdenum can be made by the ordinary fusion methods, whereby a soluble molybdate of sodium or potassium is obtained. The separation on these lines can also be made in the wet way, though not always so perfectly.

When an alkali is added to an acidified mixture of ferric chloride and molybdic acid, a point is reached at which an insoluble basic ferric molybdate is formed, and no perfect separation of the two metals is possible until sufficient alkali has been added to decompose this compound. Similar compounds are formed by chromic, tungstic and vanadic oxides.

For the separation from small amounts of iron, the excess of alkali required is not large, provided the right kind is used. Large amounts of iron, as in the analysis of steel, require correspondingly larger excesses of alkali, but the addition of increasing amounts improves the separation only very slightly after a certain approximation has been reached, and the aeration of the precipitated flocks of ferric hydrate, by using a mixture of sodium hydrate and carbonate, does not make for material improvement. The figures in the subjoined table are weights of molybdenum recovered in separations from a mixture of one decigram of it with two decigrams of iron.

Excess of 2N alkali.	Ammonium Hydrate.	Sodium Carbonate.	Sodium Hydrate.
0 c.c.	0·0329	—	—
10 c.c.	·0732	0·0936	0·1000
30 c.c.	·0849	·0997	·1002
50 c.c.	·0890	·0998	·1003

The best form of conducting the separation is to run the faintly acid mixture of iron and molybdenum in rapid drops or a thin stream into a sufficient excess of sodium hydrate. Details are given below under the estimation of molybdenum in steel.

Only one other method of separating iron and molybdenum is of much importance; it is the precipitation of the metal as sulphide. On passing a current of hydrogen sulphide through an acid solution of molybdic acid, a black sulphide MoS_3 is precipitated. The compound is soluble in an alkaline sulphide, forming a red sulpho-salt, from which acids re-precipitate the molybdenum sulphide as in the case of arsenic antimony, etc.

Separation from Tungsten.—Volatilisation of molybdic oxide at a red heat serves to separate it from tungstic oxide, though the separation is not always perfect.

Of greater value for this purpose is the reaction previously referred to, viz., the formation of a volatile compound with hydrogen chloride. By passing a current of the dry gas over a mixture of the two oxides, or of their sodium salts, contained in a boat, volatilisation of $MoO_3 \cdot 2HCl$ begins at 200° C. and is completed at about 270° C. The compound forms a white sublimate in the cool portion of the tube, leaving WO_3 (or a mixture of it with sodium chloride) in the boat.

A separation by means of hydrogen sulphide is made by 'gassing' the solution of tungstic and molybdic acids containing a considerable amount of tartaric and some sulphuric acid, whereby molybdenum sulphide is precipitated. The tartaric acid in the filtrate is decomposed by repeated evaporation with nitric acid. The method is due to Rose.

The separation most frequently practised is based upon the difference in the solubilities of the two undried oxides in mineral acids. Desi[1] uses dilute sulphuric acid in which MoO_3 is soluble. This method was investigated fully by Ruegenberg and Smith,[2] who employ warm acid of s.g. 1·38. Other observers have not found the process entirely satisfactory. For all practical purposes the separation by means of dilute hydrochloric acid (20 per cent.) is by far the best, see p. 135.

Gravimetric Determination.—(*a*) *Precipitation as a Molybdate.* Molybdic acid can be precipitated by a number of metallic salts, of which, however, lead and mercury only are in general use. The mercury(ous) precipitation is described at some length on p. 19.

Lead molybdate, when precipitated from a solution of a molybdate by means of lead acetate, separates in the form of a colloidal white compound which settles slowly, is very slow of filtration, and difficult to retain completely even on a close-grained paper. Quite different is the compound when formed in the presence of considerable amounts of dissolved sodium or ammonium salts; it settles well, filters rapidly and is readily washed.

The solution is first adjusted to slight acidity by the addition of hydrochloric acid or ammonium hydrate as required. If, as the result of this operation, several grams of alkaline chloride have been generated in the solution, the precipitation is completed by adding to the boiling mixture an excess of lead acetate and more than sufficient ammonium acetate to decompose the excess of hydrochloric acid. The precipitate is collected on paper pulp, washed with hot water, and ignited along with the filter.

$$PbMoO_4 \times 0{\cdot}2616 = \text{Molybdenum.}$$

When a previous separation of the molybdenum from iron has been made by means of sodium hydrate, the acidification generates sufficient sodium chloride in the solution; this obviously applies also in the case of a previous fusion with mixed carbonates. In other cases the addition of 2 or 3 grams of ammonium chloride should be made before precipitating with the lead salt.

The above process is one of the most stable to be found in analytical chemistry. It is not affected by comparatively large excesses of free acetic acid or of lead acetate. The filter need not be ignited apart from the precipitate, which may be heated to a temperature much higher than is necessary to destroy the paper, without change.

From faintly acetic acid solution lead molybdate may be precipitated and washed practically free from impurity in the presence of copper, cobalt, nickel, manganese, zinc, magnesium and mercuric salts. To

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[1] *Journ. Chem. Soc.*, 74. ii. 221.

[2] *Journ. Amer. C. S.*, 22. 772.

this list may also be added barium, strontium, calcium, uranium, cadmium and aluminium by a slight modification of the precipitation. An excess of hydrochloric acid is first added and then the lead acetate, and any precipitate which may form is then taken into solution by adding more acid. The mixture is then heated to boiling, and ammonium acetate added as before.

When large amounts of molybdenum are present, it is advisable to re-dissolve the ignited lead molybdate in hydrochloric acid, and re-precipitate it.

If a precipitate is contaminated with ferric or chromic oxides, it may be dissolved in a strong solution of sodium hydrate, and re-formed after filtration.

(*b*) *Precipitation as Sulphide.* Molybdenum sulphide is precipitated best from solutions containing about 5 per cent. of free sulphuric acid. Large amounts of molybdenum are difficult to separate completely; the filtrate from an apparently complete precipitation yields further quantities of sulphide on 'gassing,' and several repetitions of the treatment are necessary in most cases. Small quantities do not present much difficulty, particularly if the gassed mixture is heated on the water bath in a closed vessel, and therefore under pressure.

The solution containing not more than 0·1 gram of molybdenum in a bulk of 200 c.c. is treated with 10 c.c. of sulphuric acid, transferred to a pressure bottle and saturated in the cold with hydrogen sulphide. The bottle is tightly closed and heated for an hour in the boiling water bath, allowed to cool, and the contents emptied out into a beaker. The black sulphide MoS_3 is collected either on asbestos in a weighed Gooch crucible or on paper pulp, and washed with cold 2 per cent. sulphuric acid which has been saturated with hydrogen sulphide. A final washing with alcohol, though not necessary, facilitates the drying. The ignition is conducted at a low red heat. In the case of a filtration through a Gooch crucible, the latter is placed inside a larger crucible, from which it is isolated by means of a ring cut out of a sheet of asbestos. Paper pulp filters are transferred to a crucible and ignited along with the precipitate. In both cases the ignition is conducted until sulphur dioxide ceases to come off, when a crystalline residue, yellow when hot and white when cold, is obtained. It is MoO_3, and contains 66·66 per cent. of molybdenum.

When the precipitation with hydrogen sulphide is made from solutions containing much iron, as in the analysis of steel, the final product usually contains a trace of ferric oxide, and consequently needs further treatment (*vide infra*).

Volumetric Determination.—The most important volumetric process for the determination of molybdenum is based upon the reduction of molybdic acid in sulphuric acid solution by means of zinc. The process, which has been described at length on p. 14, is more suited to the analysis of molybdenum metal and ferro-molybdenum than to the estimation of molybdenum in steel. (See also volumetric determination of phosphorus, p. 56.)

Of other volumetric processes, the titration of a solution of a molybdate containing some acetic acid with a standard solution of lead acetate is accurate. The process is improved by filtering off the precipitated lead molybdate before finishing the titration, the end point of which is found by means of tannin, which yields a yellow colour with a soluble molybdate. The converse process is of some value in the analysis of alloys and ores of lead.

Molybdic acid may be estimated by distillation of a soluble molybdate with hydrochloric acid and potassium iodide. The iodine liberated according to the following reaction is absorbed and titrated by the usual method.

$$2MoO_3 + 4HI \rightarrow 2MoO_2I + I_2 + 2H_2O.$$

The method is described by Friedheim and Euler,[1] and a modified form of it by Gooch and Fairbanks.[2]

ESTIMATION IN STEEL.

Method I.—Dissolve 2 grams of the steel in 20 c.c. hydrochloric acid, oxidise with 5 c.c. of nitric acid and expel nitrous fumes. Add a solution of sodium hydrate until the excess of free acid is neutralised, taking care not to produce a red solution (dissolved hydrate) or a precipitate (basic molybdate). Pass the solution, if necessary, through a small pulp filter and place the latter in a beaker containing about 160 c.c. of 2N sodium hydrate solution. Break up the filter, heat the soda solution to boiling point, and run the assay solution in rapid drops from a tap funnel into the alkali, constantly stirring the mixture during the operation. Make up to 500 c.c., filter off 250 c.c., acidify with hydrochloric acid, boil, add an excess of 4 per cent. lead acetate, 20 c.c. of ammonium acetate, heat to boiling, allow to settle, filter, etc.

If the weight of lead molybdate obtained shews more than 2 per cent. of molybdenum in the steel, redissolve the ignited precipitate in 20 c.c. of hydrochloric acid, add 2 drops of nitric acid, and then dilute ammonium hydrate until a white turbidity is obtained. Clear with a few drops of

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[1] *Ber.*, 28. 2066.

[2] *Amer. Journ. Sci.* [4], ii. 156.

hydrochloric acid, add a few drops only of lead acetate solution, and finally 20 c.c. of ammonium acetate. Collect the precipitate as before and ignite.

Notes.—The above process is of fairly general application. Manganese, nickel, cobalt, aluminium and the ordinary elements of steel are without influence upon the process, being either precipitated with the iron, or eliminated subsequently. Traces of chromium in the form of sodium chromate may pass into the alkaline filtrate, being formed by oxidation in the hot alkaline solution by manganese peroxide ; this is quite common with highly manganiferous steels. The subsequent acidification of the filtrate, however, leads to a reduction of the chromate, and the addition of a few drops of sulphurous acid completes the reduction.

Tungstic and vanadic acids pass into the filtrate to a large extent, and as they are precipitated as lead salts under the conditions specified, vitiate the results. Tungsten is removed, and estimated at the same time, by evaporation of the original solution to a paste and extraction of the molybdic acid with 20 per cent. hydrochloric acid. Vanadium is not so easily disposed of, and the method is not recommended for steels containing this element unless modified in the manner described under the estimation of vanadium in high speed steels on p. 152, *q.v.*

Method II.—Decompose two grams of drillings as in the above method and evaporate the solution to a paste. In the absence of tungsten, take up the residue in 2 per cent. sulphuric acid, filter off any silica, and determine the molybdenum in the filtrate by means of the hydrogen sulphide precipitation.

The ignited residue, after weighing, is mixed with four times its weight of dry sodium carbonate and the mixture brought to fusion. The small residue of ferric oxide left on boiling out with water is collected, washed, ignited and weighed. The amount is deducted from the weight of the original impure MoO_3. Alternatively the aqueous extract of the fusion is acidified and the molybdenum determined in the solution *via* a lead acetate precipitation.

When tungsten is present, the pasty residue from the evaporation of the original solution is taken up in 50 c.c. of dilute hydrochloric acid (1 to 4) and the WO_3 filtered off. The filtrate is treated with sodium hydrate solution until free acid is neutralised, the mixture heated to boiling, and a brisk current of hydrogen sulphide passed through it. When sulphur, resulting from the reduction of ferric chloride, begins to separate, sufficient sulphuric acid is added to comply with the conditions, and the estimation finished as above.

Notes.—The author finds that for the amounts of molybdenum usually present in steel, digestion of the gassed mixture under pressure is unnecessary. Complete precipitation of the molybdenum is secured by passing hydrogen sulphide through a solution initially at its boiling point, and until it is nearly cold; the operation need not exceed 30 minutes. It is probable that the precipitation of the molybdenum sulphide is facilitated by the copious separation of sulphur which occurs.

The method is applicable to steels containing vanadium, which passes into the filtrate from the molybdenum sulphide.

VANADIUM (V = 51·0).

Vanadium is extensively used at the present time in the manufacture of special steels. Of these there are various kinds, but the two principal varieties are (1) a material rarely containing more than 0·25 per cent. of vanadium associated usually with much larger amounts of nickel and chromium, and (2) an alloy steel containing 1 per cent. or more of vanadium, together with as much as 15 to 20 per cent. of tungsten, 3 per cent. of chromium, and often also small percentages of molybdenum. The former is made up into machinery parts and the latter into high-speed cutting tools, etc.

The literature of analytical chemistry is particularly rich in processes for the determination of vanadium. The extraordinary chemical activity of the element, manifested in the great number of compounds to which it gives rise, accounts in a large measure for the numerous investigations in this field of research. The first systematic investigation was undertaken by Berzelius in 1830-1, and his published work, the outcome of his experiments with a few grams only of raw material, deservedly ranks as a classic.

An excellent bibliography of the literature of vanadium, from the time of its discovery as a definite new element in 1804, down to 1905, was compiled by Prandtl and published by Voss in 1906. Several excellent monographs on the analytical chemistry of vanadium are also available, such, *e.g.*, as that of Holverscheit (Diss. Berlin, 1890), v. Klecki (Voss, Hamburg, 1894), and Hensen (Deterre, Aachen, 1909).

Since the publication of "The Analysis of Steel-Works Materials" in 1902, at a time when the influence of vanadium on the properties of steel had attracted comparatively little attention, many chemists have been called upon to develop or elaborate methods for the analysis of vanadium alloys and steels. The work of a number of American chemists in this field is particularly commendable; some of it is published by the Bureau of Standards in the form of separate pamphlets.

The above references to the literature are given because it is obviously impossible to produce in a work of this nature more than a very few of the published processes, to the exclusion of many others of merit.

Vanadium forms five oxides, analogous in composition to the oxides of nitrogen. The pentoxide V_2O_5 is a weak acid and gives rise to ortho-, pyro-, and meta vanadates. Most of the gravimetric methods for the determination of vanadium are based upon the precipitation of a metallic vanadate from solutions of vanadic acid or a salt of it. The vanadates vary in colour from white to a deep yellow or brown, the colour of the pentoxide.

Vanadic acid or a vanadate in acid solution is easily reduced by quite a number of reagents to one or other of the lower states of oxidation, and a large number of volumetric processes for the determination of the element is the result. The most stable condition corresponds to quadrivalent vanadium and the reduction is thus expressible by $V_2O_5 \rightarrow V_2O_4 + O$. In the earlier literature this was regarded as a conversion of vanadic to hypovanadic acid. It is referred to now as a reduction from vanadic acid to a vanadyl salt, and, in the case, *e.g.*, of a reduction with sulphur dioxide, the reaction is expressed by the following equation:

$$2H_3VO_4 + H_2SO_4 + SO_2 \rightarrow 2VOSO_4 + 4H_2O.$$

From the point of view of the analytical chemist, the change may be aptly described as a reduction from a vanadylic to vanadylous salt, thus:

$$(VO)_2O_3 \rightarrow 2(VO)O + O$$
$$(VO)_2(SO_4)_3 + H_2S \rightarrow 2(VO)SO_4 + H_2SO_4 + S.$$

Similarly, the evaporation of vanadic oxide with concentrated hydrochloric acid, the basic reaction of Campagne's process,[1] may be regarded as a reduction of vanadylic to vanadylous chloride.

$$V_2O_5 + 6HCl \rightarrow 2VOCl_3 + 3H_2O$$
$$2VOCl_3 \rightarrow 2VOCl_2 + Cl_2.$$

Vanadylous salts in solution have a rich blue colour, difficult to distinguish from that of a solution of copper nitrate.

The less stable and lower states of oxidation, V_2O_3 and VO, can also be secured by wet reactions, and several excellent volumetric processes are based upon such reductions.

Vanadium yields a large number of coloured compounds with a variety of reagents; they have been utilised for the detection and estimation of the element. The blue colour of vanadyl salts, the dark

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[1] *Ber.*, 36. 3166 (1903).

reddish brown solution obtained by passing hydrogen sulphide into a strongly alkaline solution of a vanadate, the formation of aniline black, and the colour reactions with di- and tri-hydroxybenzenes, are cases in point. The most important of such reactions is the formation of a characteristic reddish brown colour on adding hydrogen peroxide to an acid solution of a vanadate. The colour is that of a very unstable per-vanadic acid, HVO_4, or of one of its salts. Some of these salts have been isolated and described by Pissarjewsky.[1] The reaction is extremely sensitive, and furnishes a valuable method for the colorimetric determination of vanadium.

Separation from Iron.—Vanadium is separated from iron by fusion with alkaline carbonates together with an oxidant, a soluble vanadate being thus obtained. This separation is useful in the analysis of vanadium ores and ferro-vanadium.

The wet processes of separation are not so satisfactory. With the exception of the ether separation, which is perfect, there appears to be no other entirely free from error when it is applied to the analysis of ferro-alloys. Thus, vanadic acid is precipitated with the iron in the basic acetate process and also in the barium carbonate separation, etc. Ammonium hydrate also precipitates vanadium with the iron, though it may be dissolved out again, partially or completely, by means of an excess of ammonium phosphate. This reaction is utilised by Bettendorf [2] for the separation from aluminium also.

Much better results are obtained by the use of a caustic alkali. On adding a partially neutralised solution of ferric iron and vanadic acid to an excess of hot sodium hydrate, in the manner described for the estimation of molybdenum in steel, the vanadium is found entirely in the alkaline filtrate. When the process is applied to the analysis of steel, however, the separation is not complete. This is probably due to the formation of a stable manganese vanadate, which is not easily decomposed by the excess of soda. A repetition of the precipitation is therefore necessary, and is successful when the manganese content of the steel is low. Such is generally the case in high-speed steels, and as the amount of vanadium in these steels is relatively large, a reliable process for the joint estimation of molybdenum and vanadium is furnished (*vide infra*).

Gravimetric Determination.—Vanadic acid is quantitatively precipitated from its solutions by salts of ammonium, barium, lead, mercury, manganese and uranium. All these methods have been investigated by a number of workers, with varying results.

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[1] *Zeit. phys. Chem.*, 43. 173 (1903).

[2] *Pogg. Ann.*, 160. 126 (1877).

The precipitation with a salt of barium from a feebly ammoniacal solution, with a salt of uranium from weak acetic acid solutions containing ammonium acetate, and with a salt of manganese from feebly ammoniacal solutions containing an excess of ammonium chloride, were all claimed by Carnot[1] to yield a definite pyrovanadate. Later investigators do not confirm this observation, and the processes, though useful as a means of removing vanadic acid quantitatively from solution, are not directly applicable to the determination of the element. The manganese precipitation is useful as a means of separating vanadic and molybdic acids.

Precipitation with a salt of lead from solutions containing acetic acid was employed by Berzelius, Roscoe, Classen, Holverscheit, and many others. The precipitate is very variable in composition, being influenced considerably by the acidity of the solution, the excess of precipitant, the pressure of foreign soluble salts, and the nature of the precipitant. Lead nitrate, for instance, when added to a solution of vanadic acid or ammonium metavanadate, yields an amorphous precipitate, which is converted by boiling into a dense, crystalline and definite pyrovanadate.

$$2NH_4VO_3+2Pb(NO_3)_2+H_2O \rightarrow Pb_2V_2O_7+2NH_4NO_3+2HNO_3.$$

The precipitation is unfortunately not quite complete because of the formation of nitric acid by the above reaction, and such devices as the addition of ammonium acetate to the mixture invariably result in the formation of a basic compound. Similarly, a hot saturated solution of lead chloride yields dense, crystalline precipitates approximating in weight to, and sometimes exceeding that of, the ortho-vanadate. The precipitates contain chlorine after being washed well, and the filtrates contain traces of vanadium.

Lead acetate, the usual precipitant, yields a yellow substance which becomes much paler in colour on boiling, and contains the whole of the vanadium even in the presence of comparatively large amounts of acetic acid. In the absence of ammonium acetate, it is possible, though not always easy, to secure the definite crystalline pyrovanadate, by using a small excess of lead acetate and a comparatively large excess of acetic acid. The conditions which generally obtain in practice are the same as for molybdenum, the precipitation being made from acetic acid solutions containing soluble salts of sodium and some ammonium acetate. The weight of the dried and ignited precipitate corresponds approximately to the formula $2Pb_2V_2O_7 \cdot PbO$, but varies from this according to excess of precipitant, time of boiling and volume of solution. The author has

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[1] *Compt. Rendu.*, 104. 1803 (1887).

never succeeded in obtaining the definite ortho-vanadate, $Pb_3(VO_4)_2$, in any one of scores of lead precipitations of vanadic acid.

From the above it is evident that a determination of vanadium involves a further analysis of the lead vanadate precipitate.

Precipitation of vanadic acid with a mercurous salt is of direct application to the estimation of the element, and is described on p. 19.

The separation in the form of ammonium metavanadate was one of the earliest methods employed, and has been examined by nearly all subsequent investigators. The following conditions, recommended by Gooch and Gilbert,[1] lead to exact results. The ammoniacal solution is treated with a cold saturated solution of ammonium chloride and the mixture evaporated until, if allowed to cool, solid ammonium chloride would separate. Ammonium hydrate is added from time to time during the evaporation, to maintain alkalinity and keep the solution colourless. If, on cooling, the separation of ammonium chloride is excessive, some of it is dissolved by the careful addition of ammonium hydrate. After standing for a day, the white metavanadate is filtered off, washed with saturated ammonium chloride, dried, and carefully ignited to V_2O_5.

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O.$$

An interesting gravimetric process of an entirely different nature is based upon the reduction of vanadic acid by means of oxalic acid, thus:

$$V_2O_5 + H_2C_2O_4 \rightarrow V_2O_4 + H_2O + 2CO_2.$$

The vanadate is treated with equal parts of a cold saturated solution of oxalic acid and 10 per cent. sulphuric acid. The mixture is warmed gently at first and afterwards raised to boiling, the carbon dioxide evolved being collected in a weighed potash bulb. The method is easy of execution and gives good results.

Volumetric Determination.—The titration of vanadyl sulphate, obtained by reduction of vanadic acid, with a standard solution of potassium permanganate is the most frequently practised of all methods for the estimation of vanadium. The results are very exact, provided sufficient care is taken to remove the excess of reducing agent. The substances employed for the reduction are hydrogen sulphide, sulphur dioxide, hydrochloric acid, and oxalic acid. The first of these quickly reduces warm solutions of vanadates in sulphuric acid solution, the excess of hydrogen sulphide is readily expelled by boiling, and the free sulphur which separates is without influence on the titration. Sulphur

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[1] *Amer. Journ. Sci.*, 14 (1902), 205.

dioxide or sulphurous acid is equally good, but the last traces are not so easy to remove by simple boiling. A current of carbon dioxide materially assists in their complete removal. Reduction with hydrochloric acid, which is obtained by evaporating two or three times with the reagent, must be followed by a further evaporation to fumes with sulphuric acid in order to convert the vanadylous chloride to sulphate before titrating. The reduction with oxalic acid is done by heating in a large flask with an excess (30 c.c.) of concentrated sulphuric acid, and 0·2 gram of oxalic acid per 0·1 gram of vanadium. The heating is continued for 10 minutes after the appearance of sulphur trioxide, in order thoroughly to decompose the excess of oxalic acid, the solution allowed to cool, diluted to about 300 c.c., and titrated.

Titrations of vanadyl sulphate are made in hot solution at a temperature of 70°-80° C. The end point of the reaction is well marked under these circumstances, though the pink colour which defines it disappears as the titrated liquid cools. When the titration is performed upon cold solutions, the end of the reaction is not reached until a pink colour is obtained which persists for at least one minute after it is first formed. From either of the following equations, expressive of the reaction,

$$10VOSO_4+2KMnO_4+8H_2SO_4 \rightarrow 5(VO)_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$$

$$10VOSO_4+2KMnO_4+8H_2SO_4+22H_2O \rightarrow 10H_3VO_4+15H_2SO_4+K_2SO_4+2MnSO_4$$

it follows that $2KMnO_4=5(O)=10V$

and 1 c.c. $\frac{N}{10}$ permanganate = 0·0051 gram vanadium.

An important volumetric method, based also upon the reduction from the V_2O_5 to the V_2O_4 condition, is that of Lindemann.[1] The reducing agent is ferrous ammonium sulphate, and in the original form of the process a standard solution of this reagent is delivered into the vanadium solution containing free sulphuric acid. The end of the reaction is determined by a spot test with potassium ferricyanide. Modern practice consists usually in the addition of an excess of the reducing agent, followed by a back titration of it with a standard solution of potassium permanganate or bichromate until a drop of the reaction mixture no longer produces a blue colour immediately upon mixing it with the indicator. A variation of this procedure is to add the ferricyanide to the reacting mixture, thus creating an internal indicator. From the equation $V_2O_5+2FeO \rightarrow V_2O_4+Fe_2O_3$ it follows that 56 parts of iron are equivalent to 51 parts of vanadium.

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[1] *Zeit. f. anal. Chem.*, 23. 542 (1884).

The above process serves admirably for the determination of comparatively large amounts of vanadium and is therefore very useful in the assay of ferro-vanadium alloys. In the case of steels containing a very small percentage of vanadium, however, the process is not so trustworthy. Particularly is this the case when a previous separation of the iron and vanadium has not been made. The cause of this is a reduction of the ferricyanide to ferrocyanide, which latter reacts with the ferric iron to produce Prussian blue. Hence, in the back titration referred to above, the operation is at an end when a colour reaction is not obtained *immediately* upon mixing.

Reductions to a lower state of oxidation than V_2O_4 are few in number. The most important is the reduction by means of ' nascent ' hydrogen from V_2O_5 to V_2O_2, and is described on p. 14.

The iodometric determination of vanadium is a process of considerable importance. Vanadic acid and nearly all vanadates, soluble and insoluble, are decomposed by boiling with hydrochloric or hydrobromic acid, thus :

$$V_2O_5 + 2HBr \rightarrow V_2O_4 + Br_2 + H_2O.$$

The liberated halogen is absorbed in a solution of potassium iodide and the free iodine formed titrated with sodium thiosulphate. In practice, the vanadate is boiled with an excess of hydrochloric acid and a crystal or two of potassium bromide until bromine is completely expelled and the solution in the distillation flask assumes the characteristic blue colour of vanadyl chloride.

The process constitutes a valuable means of estimating vanadium in the indefinitely constituted precipitates obtained by means of salts of barium, lead, etc., referred to under the gravimetric determination.

Of minor importance is the iodometric method based upon the reaction $V_2O_5 + 4HI \rightarrow V_2O_3 + 2I_2 + 2H_2O$, which is materially assisted by adding a small quantity of syrupy phosphoric acid to the reacting mixture.

Colorimetric Determination.—Small amounts of vanadium are most conveniently estimated by a ' colour test,' based upon the reaction between hydrogen peroxide and a vanadate. As in the estimation of carbon in steel, the test consists in matching the colour with that yielded by a standard solution containing a known amount of vanadium.

The reddish brown colour is intensified by strong acids, is partially bleached by an excess of peroxide, and is developed very slowly from solutions containing other than pentavalent vanadium. The colour is masked to some extent by ferric salts, which should therefore be eliminated as far as possible. Solutions containing small amounts of ferric chloride, however, may be decolorised by the addition of hydrofluoric acid before adding the peroxide. This procedure also eliminates the possible interference of titanium, solutions of which, in the absence of hydrofluoric acid, yield a characteristic yellow colour with hydrogen peroxide. Molybdenum should not be present in the solution, as molybdates also yield a yellow colour with peroxide. Finally, the green colour of nickel and chromium salts renders it necessary either to remove these metals from the solution, or to prepare a standard containing approximately the same amounts of them as in the sample.

VOLUMETRIC ESTIMATION IN STEEL.

I. Two grams of drillings are decomposed by means of dilute sulphuric acid and the iron oxidised with nitric acid exactly as described for the determination of chromium on p. 111. When tungsten is present, the mixture is digested until the separated tungstic oxide is quite yellow before diluting and oxidising the chromium and vanadium with permanganate. Boiling should be maintained for at least 10 minutes after a precipitate of manganic hydrate is obtained, in order to ensure the complete oxidation of the vanadium. The mixture is filtered through freshly-ignited asbestos and the residue washed with water containing a little sulphuric acid. Filtrate and washings, measuring about 300 c.c., are titrated, when cold, in either of the following ways :

(1) An approximately decinormal ferrous ammonium sulphate solution is added until a clear green solution is obtained and the excess titrated with decinormal permanganate ; a pink colour, persisting for a minute, marks the end point of the reaction. Uncertainty respecting the end point is allayed by a further addition of a few drops of the iron solution, followed by the permanganate ; this operation may be repeated as often as necessary. The difference between the final burette readings, is a measure of the chromium present, and, if both solutions are exactly decinormal, each cubic centimetre of the difference represents 0·001736 gram of chromium.

To the titrated solution ferrous solution is again added in order to reduce the vanadic acid, an excess being indicated by a spot test with potassium ferricyanide. The excess is titrated with permanganate, added a little at a time with a test after each addition. When a large drop of the solution no longer produces a blue colour immediately upon mixing with the indicator, the titration is finished. The difference between the second pair of burette readings represents the vanadium, and each cubic centimetre $\left(\frac{N}{10}\right)$ registers 0·0051 gram vanadium.

(2) The titration for chromium is conducted as in (1) and several c.c. of the ferricyanide indicator then added to the solution. The ferrous ammonium sulphate solution is then run in carefully until the change of colour, indicative of the complete reduction of the vanadic acid, is obtained.

Notes.—The above modification of the Vignal chromium process is due to Johnson.[1] It is extensively practised on account of its rapidity and ease of execution, and also because it provides a determination of the chromium, which is an almost invariable constituent of vanadium steels. The results are in general slightly low.

As in the case of non-vanadiferous chromium steels, so also here a 'blank' determination is essential to accuracy. The determination is made upon a plain carbon steel to which known amounts of chromium and vanadium are added in the form of standard solutions, or preferably upon a 'standard' steel of approximately the same composition as the material under assay.

As a two-gram sample of steel containing about 0·25 per cent. of vanadium involves a consumption of only 1 c.c. of decinormal ferrous solution for the reduction of the 5 milligrams of vanadium present, it is advisable to use $\frac{N}{20}$ solutions in the second part of the titration. Greater dilution than this makes the determination of the end point, which is at best not easy, too uncertain.

II. The following method is recommended for the determination of vanadium and molybdenum (if present) in high-speed steels:

Decompose one gram of drillings with hydrochloric and nitric acids, evaporate to a paste, add 50 c.c. of dilute hydrochloric acid (1 acid to 4 water), boil, filter off tungstic oxide and silica, and wash with 5 per cent. hydrochloric acid. (The residue serves for the determination of tungsten.) Concentrate the filtrate and washings to about 20 c.c., neutralise the excess of acid with sodium hydrate, and run the hot solution from a tap funnel into about 80 c.c. of hot binormal sodium hydrate solution, with constant stirring of the latter. Filter off the ferric hydrate, which contains some vanadium but no molybdenum, and wash two or three times with water. Set filtrate and washings aside, redissolve the precipitate in hot 50 per cent. hydrochloric acid and repeat the precipitation, finally washing thoroughly with hot water. Mix the two filtrates, bring to boiling, acidify with hydrochloric acid, boil for 2 minutes and cool to laboratory temperature. Add a solution of potassium permanganate to oxidise the vanadium, an excess (20 c.c.) of 4 per

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[1] *Chemical Analysis of Special Steels, etc.*

cent. lead acetate, and 30 c.c. of ammonium acetate. Heat the mixture to incipient boiling, and allow to stand in a warm place for 20 minutes. Collect the precipitate of lead molybdate and basic vanadate on paper pulp, wash with hot water containing a few drops of acetic acid, dry and ignite at a low temperature until the filter is 'ashed.' Transfer the residue to a beaker, dissolve by warming with hydrochloric acid, add 5 c.c. of concentrated sulphuric acid, and evaporate to copious fumes of sulphur trioxide. Cool, dilute to 20 c.c., with water, filter off the lead sulphate, and wash with cold water.

The solution containing the vanadium and molybdenum and free sulphuric acid is then treated exactly as described on p. 17.

Notes.—The author has practised the above method for a number of years, and has found it extremely useful and reliable in the analysis of vanadium high-speed steels. Though lengthy, it provides a means of determining tungsten, molybdenum and vanadium in one and the same sample.

COLORIMETRIC ESTIMATION IN STEEL.

Of steels containing not more than 0·25 per cent. of vanadium, two grams are dissolved in 20 c.c. of nitric acid (1·20), the solution evaporated to dryness, baked for a few minutes, and the residue dissolved in hydrochloric acid. If tungsten is present, which is not usually the case with this class of material, it is removed in the customary manner. The solution is diluted to about 200 c.c., and treated exactly as described on p. 48 for the separation of phosphoric acid from iron. After the expulsion of the excess of sulphur dioxide left from the second reduction, 0·1 gram of iron is added in the form of a solution of ferric chloride, 20 c.c. of ammonium acetate added and the mixture boiled. The basic acetate precipitate incorporates the whole of the vanadium. It is filtered off as rapidly as possible, and without washing, is redissolved in hot dilute hydrochloric acid. Besides vanadium (and phosphorus) the solution may contain chromium, nickel, and manganese, though much of the last two passes into the original filtrate.

The solution is evaporated just to dryness, 40 c.c. of concentrated nitric acid and about 3 grams of potassium chlorate added, and the mixture boiled vigorously for 5 minutes in order to oxidise the chromium to chromate. Without filtering off any manganese dioxide which may separate, the liquid is diluted to about 200 c.c. with water, the solution brought to boiling and an excess of ammonium hydrate added. The precipitate is filtered off, washed, redissolved in hydrochloric acid and the iron again precipitated with an excess of ammonium hydrate.

The second precipitation eliminates manganese and all but traces of chromium and nickel. The precipitate is washed, again dissolved in acid and the solution evaporated just to dryness.

The residue is moistened with 2 c.c. of hydrochloric acid, dissolved in 20 c.c. of water and transferred to a Nessler cylinder. Ten to twenty drops of hydrofluoric acid solution are added to decolorise the liquid and 2 c.c. of 3 per cent. (10 vols.) hydrogen peroxide. After a few minutes the colour is fully developed. In the meantime a solution of ferric chloride (0·1 gram iron) containing 2 c.c. of hydrochloric acid is similarly treated, and a standard vanadium solution added from a burette until the colours are 'matched.'

The standard solution of vanadium is prepared by dissolving pure ammonium metavanadate in water and is standardised by reducing with sulphur dioxide and titration with permanganate. A solution containing 0·0005 gram vanadium per cubic centimetre is suitable.

Notes.—The operations of removing chromium and nickel, and of preparing the test solution, are substantially those recommended by M'Cabe[1] in an excellent paper on the colorimetric determination of vanadium. The 'ether' method of separating most of the iron from vanadium is employed by him instead of the acetate process described above, and takes the following form.

Two grams of steel are dissolved in hydrochloric acid, the iron oxidised with nitric acid, and the solution evaporated to 10 c.c. It is then transferred to a separating funnel with small quantities of 50 per cent. hydrochloric acid (total final volume 20 c.c.), and shaken with 50 c.c. of ether. The lower layer, and 1½ c.c. of the upper, are then run off, yielding all the vanadium with about 0·1 gram of iron. This is sufficient to incorporate the whole of the vanadium as a basic vanadate when an excess of ammonium hydrate is added.

In the 'acetate' separation, the vanadium exists in the solution as a vanadyl salt, and is precipitated completely with the iron on the addition of ammonium acetate.

ESTIMATION IN PIG IRONS.

The estimation of vanadium in pig irons is rarely called for. The small amount occasionally present is left in the insoluble residue of graphite and silica when the iron is decomposed with hydrochloric acid. By igniting the residue to burn out the graphite, and treating the remainder with hydrofluoric and nitric acids, the vanadium, with a little iron, is left, and a colorimetric estimation may be directly applied.

[1] *Chemical Engineer*, xiii. No. 6, and *Chem. News*, 104. 194 *et seq.*

TITANIUM ($Ti=48{\cdot}1$).

In the form of an alloy with iron, small quantities of titanium are added to steel before or during the casting operations for the purpose of eliminating impurities and producing sounder ingots. The resulting metal is nevertheless practically free from titanium, though steel is occasionally met with containing several hundredths per cent. of the element.

The stable compounds of titanium correspond to the oxide TiO_2, which functions both as acid and as base. Thus by combination with water it yields ortho- and meta-titanic acids, whilst with strong acids it yields salts such as $TiCl_4$ and $Ti(SO_4)_3$.

Orthotitanic acid is precipitated quantitatively from titanic solutions by weak bases such as ammonium hydrate or phenylhydrazine; it is readily soluble in dilute mineral acids. Metatitanic acid, which is soluble only in strong acids, is precipitated from titanic solutions after dilution and boiling. The precipitation takes place even from solutions containing some free acid initially, and it is not difficult to adjust the conditions so as to secure a quantitative precipitation of the titanium. The readiness with which solutions of titanic salts may be hydrolysed is, in fact, their most important property, and furnishes a means not only of determining titanium, but also of separating it from other elements.

Both the titanic acids yield the oxide TiO_2 on ignition. The latter is not appreciably attacked by strong acids, particularly after long ignition at a high temperature; it dissolves, however, in hydrofluoric acid, yielding a volatile fluoride, TiF_4.

The titanous salts are derivatives of the sesquioxide Ti_2O_3. They are very unstable and readily take up oxygen. The oxide itself dissolves in sulphuric acid, yielding a violet solution; it is of little or no interest to the steel-works' chemist.

Separation from Iron.—Of the general methods for separating ferric iron from other metals, those which depend upon the hydrolysis of the iron salt are obviously impossible; titanium is precipitated entirely with the iron, *e.g.*, in the barium carbonate and basic acetate processes. On the other hand, it is easy to effect the hydrolysis of the titanium salt and thus obtain a perfect separation from iron when the latter exists in the solution as a ferrous salt. This is the method generally practised when large amounts of iron are to be separated.

The solution, if acid, is neutralised with sodium carbonate up to the formation of a turbidity, the latter dissolved in a few drops of sulphuric acid, and the solution then saturated in the cold with hydrogen sulphide. After adding 5 to 10 grams of sodium acetate, the liquid is brought to boiling, filtered whilst hot, and the precipitate of metatitanic acid, washed with water containing some hydrogen sulphide, and ignited.

Another way of effecting the separation is to neutralise as before, clear with acid, add an aqueous solution of about 10 grams of sodium thiosulphate, and boil for 15 minutes or more. The precipitate of metatitanic acid and free sulphur is washed with 3 per cent. acetic acid, and ignited to TiO_2.

Each of these precipitations should be made from a comparatively large volume of solution, 200-300 c.c., in the case of a separation from several grams of iron. In both cases the resulting titanic oxide is seldom obtained perfectly free from iron, and the separation must be repeated. If the ignited oxide is not perfectly white, therefore, it is fused with potassium pyrosulphate and the aqueous extract of the fusion treated as before but at much smaller dilution.

For the separation of smaller amounts of iron, the precipitation of the latter as sulphide is very useful. To retain titanium (and aluminium) in solution, tartaric acid equal to at least three times the weight of the iron and titanium together, is added, and hydrogen sulphide passed through the solution to saturation. Ammonium hydrate is then added until the liquid is distinctly alkaline to litmus, and the mixture gassed further. The ferrous sulphide is filtered off and washed with very dilute and colourless ammonium sulphide. Titanium may be precipitated from the filtrate, without destroying the ammonium tartrate, by means of cupferron.

Of the few other methods that may be applied to the separation of iron and titanium, the ' ether separation ' is the most satisfactory of the wet processes. In the dry way, the separation of the mixed oxides is effected by fusion with sodium peroxide. On extraction with water, Walton [1] finds that titanium passes completely into solution as sodium per-titanate, and determines it by acidifying with sulphuric acid, adding 5 per cent. in excess, and applying the colorimetric method described below.

The small amounts of titanium occasionally found in steel are left in the carbonaceous residue when the material is opened out with a neutral solution of copper potassium chloride. Titanium, along with silicon may also be removed as chloride by passing a current of chlorine over the heated drillings. Neither of these methods appears to be practised.

Separation from Aluminium.—The complete analysis of ferrous alloys,

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[1] *Journ. Amer. Chem. Soc.,* 29. 481.

iron ores, and refractory materials almost generally involves a separation of titanium from aluminium. Prior to the introduction of cupferron as a precipitant of titanium, the method generally worked was the second of the two following, both of which are due to Gooch.

The first depends upon the fact that titanium is completely precipitated whilst aluminium remains in solution when an orthophosphate is added to a solution of the mixed salts containing an excess of formic acid. An excess of microcosmic salt and formic acid, together with sufficient ammonium formate to decompose any mineral acid present, are added to the solution, and the mixture boiled. The precipitate is filtered out, washed, dried, and fused with 10 times its weight of sodium carbonate for 15 minutes. After extracting with water, the residue is fused again with carbonate, the melt dissolved up in sulphuric acid, and the titanium precipitated by adding ammonium hydrate and an excess of acetic acid to the boiling solution.

The second method [1] involves much manipulation, viz. : the addition to the solution of sufficient acetic acid to make from 7 to 11 per cent. by volume of the glacial acid, together with sufficient sodium acetate to 'fix' the stronger acids present, and then boiling, filtering, washing with 7 per cent. acetic acid, fusing the ignited residue with sodium carbonate, dissolving in sulphuric acid, pouring into water, neutralising with ammoniun hydrate, re-dissolving the precipitate in sulphuric acid, and precipitating finally by boiling with acetic acid and sodium acetate as before. The whole process, according to this description, appears to be long and tedious, but the individual operations are not of themselves difficult.

The best method for separating titanium from aluminium consists in the precipitation of the former from strongly acid solutions by means of cupferron. It is described more fully below, in connection with the gravimetric determination of titanium.

Gravimetric Determination.—Titanium is determined gravimetrically as the oxide TiO_2. For this purpose, the precipitation is made from pure solutions (*a*) by means of ammonium hydrate, (*b*) by boiling the slightly acid solution of the sulphate. From solutions containing other elements, as, *e.g.*, aluminium, the titanium is precipitated by means of acetic acid and sodium acetate, or by a solution of cupferron.

Cupferron, so called because it precipitates copper and iron quantitatively from their solutions, is the ammonium salt of nitrosophenyhydroxylamine; its molecular formula may be written thus:— $O : N(C_6H_5) : N \cdot O(NH_4)$. It also precipitates titanium quantitatively,

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[1] Gooch, *Chem. News*, 52. 55, 68.

and, as in the case of copper or iron, from solutions that are comparatively strongly acid. The titanium salt of cupferron is pale yellow in colour, and has the composition $Ti(O:N \cdot C_6H_5:NO)_4$.

Cupferron is soluble in water, and the reagent takes the form of a 6 per cent. solution, freshly made for each determination. The aqueous solution does not keep well, being liable to oxidation; ammoniacal solutions of cupferron are much more stable and acids promote decomposition. The reagent is particularly valuable as a means of determining titanium and of separating small quantities of it from larger amounts of aluminium and other metals. Originally recommended by Baudisch,[1] it has since been employed by a number of observers.[2] The method of procedure is as follows.

To the cold acid solution, diluted to 300-400 c.c., the reagent is added slowly whilst stirring continuously. When the yellow compound has settled, more of the reagent is added in order to ascertain the completeness or otherwise of the precipitation. Incompleteness is indicated by a yellow turbidity or further precipitate, but a white precipitate, which is the free base, nitrosophenyl hydroxylamine, indicates an excess. The precipitate is collected on paper pulp, washed well with normal hydrochloric acid, and ignited in a platinum crucible, cautiously at first until the organic matter is destroyed. It is finally ignited strongly in the muffle to constant weight and the residue weighed as TiO_2 containing 60·05 per cent. of titanium.

Zirconium interferes with this process as well as with the Gooch method of separating titanium and aluminium. In the one case, the zirconium is precipitated quantitatively by cupferron, and in the other the titanium is incompletely precipitated.

Volumetric Determination.—The only volumetric process for the determination of titanium depends upon the reduction of the acid titanic solution with zinc, and titration of the resulting titanous salt with potassium permanganate. The best form of procedure is to add a known excess of ferric sulphate to the solution immediately after the reduction, and titrate the ferrous sulphate formed by the re-oxidation of the titanous compound.

The solution to be assayed, containing about 10 per cent. of sulphuric acid, is placed in a flask provided with a plug carrying a Bunsen valve and also a stoppered funnel. An excess of pure zinc is introduced, the

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[1] *Chem. Ztg.*, 33. 1298.

[2] Nissenson, *Zeit. angew. Chem.*, 23. 969; Biltz and Hodtke, *Zeit. anal. Chem.*, 66. 426; Belucci and Grassi, *Analyst*, 36. 520; Thornton, *Amer. Journ. Sci.*, 37. 173, 407.

mixture warmed until all the metal is dissolved, the liquid cooled off, and an excess of a standard solution of ferric sulphate then run in from the funnel. The solution, after diluting largely, is then titrated with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0{\cdot}00481 \text{ g. titanium.}$$

Colorimetric Determination.—Small quantities of titanium are accurately and most conveniently determined colorimetrically. The intensity of the red colour produced when a solution of thymol, *e.g.*, is added to an acid solution of titanic sulphate is proportional to the amount of titanium present. Lenher and Crawford[1] recommend the reagent, which is more sensitive in its indications than hydrogen peroxide. They use a 1 per cent. solution, made by dissolving thymol in a little glacial acetic acid containing 10 per cent. of alcohol, and pouring the resulting solution into sulphuric acid. The operations are substantially those obtaining in the more generally practised hydrogen peroxide process.

Hydrogen peroxide induces a yellow colour when added to acid solutions of titanium, due to the formation of per-titanic acid, the anhydride of which is TiO_3. Upon this reaction, which is extremely sensitive, is based the colorimetric determination of titanium when present in amounts varying from 0·5 to 5 milligrams—larger amounts produce too intense a colour for accurate comparison with a standard.

The colour is destroyed by fluorides, which must therefore be absent. Metals which yield coloured products with hydrogen peroxide must obviously also be excluded; they are molybdenum, vanadium, and chromium. The solution to be tested should contain about 5 per cent. of sulphuric acid, which converts any metatitanic acid possibly present into the ortho compound—the latter alone produces the colour reaction. When the solution is initially coloured yellow by the presence of a ferric salt, a small amount of phosphoric acid may be added. As, however, this substance exerts a slight bleaching action on the pertitanic acid an equal amount should be added to the standard solution used for the purpose of comparison. The same remark applies to excesses of potassium sulphate introduced, *e.g.*, by a pyrosulphate fusion.

The hydrogen peroxide may be used in the form of a 30 per cent. solution, of which about 2 c.c. are required for an assay—proportionately larger amounts of a weaker solution may be used, and an excess is of no moment. The reagent may also be prepared as wanted by dissolving sodium peroxide or potassium percarbonate in dilute sulphuric acid.

[1] *Chem. News*, 107. 152.

The standard titanium solution is prepared by fusing 0·4162 gram of pure titanic oxide at a low temperature with about 8 grams of acid potassium sulphate until the oxide dissolves. The cooled melt is dissolved by warming with 5 per cent. sulphuric acid, and the solution made up to 250 c.c. Each c.c. contains 0·001 gram titanium; more dilute solutions are made from it as required.

A standard solution is also made, and more readily, by dissolving a carefully assayed carbon-free ferro-titanium alloy in dilute nitric acid, or in sulphuric acid (1 : 3) and oxidising the iron with the least possible amount of nitric acid.

ESTIMATION IN STEEL.

(1) The colorimetric process may be conveniently worked as an adjunct to the bismuthate manganese estimation; the operation is carried out as follows: After completing the manganese estimation discharge the faint pink colour with a drop of ferrous sulphate, transfer the solution to a beaker, and stand it on a white slab by the side of a similar beaker containing a similar iron solution, but no titanium. If the carbonaceous matter was thoroughly destroyed in each case both solutions should have only a faint green tinge. Add hydrogen peroxide to each; the standard remains unaltered, but the sample becomes yellow if titanium is present. Then run as much of a prepared solution of titanium into the standard as is needed to match the colour of the sample, and from the amount used calculate the percentage in the steel being assayed. It is easily possible in this way to distinguish 0·005 per cent. titanium, and to estimate from this amount up to one per cent. with great accuracy. Metals which form coloured solutions, such as nickel, copper, or chromium, would interfere if some allowance were not made for them.

(2) This method is more suitable to the determination of titanium when molybdenum and vanadium are present in the steel, since they are removed in the process.

Dissolve five grams of the steel in 30 c.c. hydrochloric acid. If any considerable residue is apparent, then filter, ignite, treat with mixed hydrofluoric and sulphuric acids to remove silica, fuse with sodium carbonate, dissolve in hydrochloric acid to a clear solution, and add to the main filtrate. If, however, the hydrofluoric solution is quite clear, that may be at once added to the main filtrate after evaporating to sulphuric anhydride fumes. When the insoluble residue is very small, dilute, as soon as the steel is dissolved, to about 200 c.c., add ammonium hydrate until a precipitate forms, which disappears lazily or is just permanent, clear the solution with hydrochloric acid, add ten grams of sodium thiosulphate, and boil for fifteen minutes. Filter, wash by decantation with very dilute (2 to 3 per cent.) hot acetic acid, collect on a pulp filter, and ignite to oxide. Fuse the residue with sodium carbonate, extract with water, filter and fuse the residue once more with potassium bisulphate, completing the estimation colorimetrically.

ESTIMATION IN PIG IRONS.

When pig iron is decomposed with hydrochloric acid of spec. grav. 1·1, all the titanium present remains in the insoluble residue. The latter is collected, washed, ignited in a platinum crucible, the residue treated with hydrofluoric and sulphuric acids and the solution evaporated almost to dryness to expel hydrofluoric acid completely. The residue is fused with bisulphate, the melt dissolved up in 5 per cent. sulphuric acid, and the titanium determined colorimetrically.

When pig iron is dissolved in nitric acid s.g. 1·20, all the titanium passes into solution, so that after filtering off graphite and silica, the procedure is the same as in the first method given above for steels.

URANIUM ($U = 238{\cdot}5$).

The salts of uranium are derivatives of the oxides UO_2 and UO_3. The green uranous salts are of the normal type, and are readily oxidised to the yellow and more stable uranyl salts, which contain the radicle UO_2, thus:

$$UO_2 + 2H_2SO_4 \rightarrow U(SO_4)_2 + 2H_2O$$

uranous sulphate.

$$(UO_2)O + H_2SO_4 \rightarrow UO_2 \cdot SO_4 + H_2O$$

uranyl sulphate.

In an acidic function, the higher oxide UO_3 also gives rise to the so-called uranates, which are analogous in composition to the dichromates. Ammonium and sodium hydrate precipitate, *e.g.*, $(NH_4)_2U_2O_7$ and $Na_2U_2O_7$ respectively when added to solutions of uranyl salts.

Each of the above oxides is converted by heating into a uranoso-uranic oxide, $U_3O_8(2UO_3 \cdot UO_2)$, which occurs in nature as pitchblende. This compound also results from the ignition of ammonium uranate.

Very unstable peruranates, obtained by the interaction of hydrogen peroxide and uranyl salts, have been described by Fairley,[1] Pissarjewsky,[2]

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[1] *Trans. Chem. Soc.*, 31. 127. [2] *Zeit. anorg. Chem.*, 24. 108.

and others. They are yellow in alkaline solution and are occasionally utilised for the detection and colorimetric estimation of uranium.

Separation from Iron.—Uranium may be separated from ferric iron by the 'ether method,' and also by the 'basic acetate' process. Brearley[1] has shewn that in the latter case an exact separation is obtained when, after 'neutralising' the solution, one or two per cent. of its volume of acetic acid is added, and no more ammonium acetate used than is necessary to precipitate the iron completely,

No separation of ferric iron from uranium is possible by means of ammonium hydrate, which precipitates both, and quantitatively. The caustic alkalies also precipitate uranium, but not from dilute solutions containing hydrogen peroxide, and they can therefore be utilised for the separation of comparatively small amounts of iron and uranium.

Ammonium carbonate, however, when added in excess, forms a soluble ammonium uranyl carbonate and a perfect separation can be obtained by the use of this reagent. Sodium carbonate and bicarbonate give equally good results. Large amounts of iron should be separated from small amounts of uranium by running their mixed solution slowly into the solution of the alkaline carbonate, stirring constantly during the operation. Traces of iron may escape precipitation, and are conveniently removed from the filtrate by the addition of a few drops of ammonium sulphide. Appended are three results obtained in this way.

	Fe present.	U present.	U found.
Ammon. carb.	2·0 gram.	0·0621 gram.	0·0623 gram.
Sod. carb. -	2·0 ,,	0·0621 ,,	0·0622 ,,
Sod. bicarb. -	2·0 ,,	0·0621 ,,	0·0619 ,,

From solutions of ferrous iron, uranium is separated by precipitating it as uranyl phosphate almost exactly as in the separation of aluminium or chromium from iron. The process is applicable to mixtures of the two metals in any proportions, and is described below.

Gravimetric Determination.—Uranium is generally determined gravimetrically as oxide or phosphate. In the former case it is either precipitated as ammonium uranate or as brown uranyl sulphide UO_2S.

(1) Precipitation with ammonium hydrate is conducted in the usual way of adding a slight excess of the reagent to a hot solution of the uranyl salt, digesting for some time and allowing the precipitate to settle. The yellow compound is filtered, washed with water containing

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[1] *Analytical Chemistry of Uranium* (Longmans, Green & Co.).

a little ammonium nitrate (2 per cent. solution), and finally once with water. It is then dried, and ignited to uranoso-uranic oxide.

$$U_3O_8 \times 0{\cdot}8482 = U.$$

The results are not absolutely accurate, though sufficiently so for practical purposes. According to the temperature of ignition, the colour of the residue varies from dark green (with yellowish or brown patches) to black. The latter results from high temperature ignitions, and is associated with slight loss of weight. It has accordingly been recommended that the residue be re-ignited in a current of hydrogen and converted into uranous oxide, UO_2.

(2) The last procedure is generally followed when uranium is precipitated as sulphide. When care is taken to ensure the absence of carbonates from the ammonium sulphide used as the precipitant, the results obtained are very accurate. The necessity for this precaution is obvious.

(3) Uranium is precipitated quantitatively from neutral solutions of uranyl salts, or from solutions containing free acetic acid, by a soluble phosphate. The precipitate is uranyl hydrogen phosphate, UO_2HPO_4, and is more easily filtrable and washable when obtained with ammonium dihydrogen phosphate instead of the corresponding sodium salt. On ignition at a low temperature and out of contact with organic matter, a yellow residue of pyrophosphate, $(UO_2)_2P_2O_7$, is obtained. At higher temperatures, or when ignited along with a paper filter, some reduction takes place and a pale green residue is obtained, which may be re-oxidised to the pyrophosphate by moistening with nitric acid and re-igniting.

The best procedure is substantially that described for the determination of aluminium as phosphate. Thus, to the boiling uranyl solution is added microcosmic salt in amount about ten times that of the uranium present and the solution is then adjusted to faint acidity. If acid in the first instance, ammonium hydrate is added until a faint precipitate is obtained, and then nitric acid in drops until the solution is just cleared again. On adding a solution of several grams of sodium thiosulphate, and boiling for about ten minutes, the uranyl phosphate is completely precipitated and readily settles to the bottom of the vessel along with co-precipitated sulphur. The precipitate is washed by decantation, collected, dried and ignited along with the filter in a porcelain crucible. The pale green residue obtained contains 68·55 per cent. of uranium. It is not so hygroscopic as the yellow pyrophosphate, into which, as stated above, it is easily converted. The pyrophosphate contains 66·71 per cent. of uranium.

Brearley finds that this process is in no way affected by the presence of moderate excesses of acetic acid or by large amounts of ammonium and sodium salts. Salts of potassium, however, are difficult to remove from the precipitate by washing, and a re-precipitation becomes necessary in exceptional cases. As in the case of aluminium phosphate precipitations a large excess of microcosmic salt is necessary in order to obtain a residue of definite composition ; too small an excess, though sufficient to produce a quantitative precipitation, yields a basic compound.

Volumetric Determination.—Standard solutions of a uranyl salt are employed in the volumetric determination of phosphoric acid, with a spot test indicator of potassium ferrocyanide. The converse process is not extensively practised as a method for the determination of uranium, though it is useful in the estimation of large amounts of the element.

The most important volumetric method depends upon the reduction of uranyl to uranous salt in sulphuric acid solution by means of zinc or aluminium. Using zinc, warm solutions of uranyl sulphate are quickly reduced to a lower state of oxidation (characterised by a brown colour) than that of the uranous salt. If the reduced solution be kept warm, oxidation quickly sets in by exposure to the atmosphere, a fact to which is probably attributable the belief that uranous salts are very unstable. Cold uranous solutions are not sensibly oxidised to any appreciable extent, however, by exposure to or aspiration of air for as much as 10 to 20 minutes. The application of the Jones' reductor to the determination of uranium is based upon these observations ; the process is described on p. 16.

A simpler method, employed by the author and Clark,[1] takes the following form, and occupies no more than 30 minutes.

The solution of uranyl sulphate, containing from 2 to 5 per cent. by volume of sulphuric acid, is poured into a flask containing 50 grams of pure amalgamated zinc (20 to 30 mesh), and the mixture is heated until a dark brown colour is developed. The flask is then cooled off rapidly under the water tap, and the solution strained off from the zinc by pouring through a small pulp filter. After washing the zinc with cold water, by decantation, air is aspirated through the filtrate for a minute, and the clear green solution is then titrated with standard permanganate. On account of the high atomic weight of uranium, a semi-decinormal solution is quite strong enough.

$$1\text{ c.c. }\frac{N}{20}\,KMnO_4 = 0{\cdot}00596\text{ gram uranium.}$$

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[1] *Chem. News*, 103. 146.

A blank determination should be made on the reagents; the amount should not exceed 0·2 c.c. of permanganate.

Electrolytic Determination.—Hydrated uranous oxide separates at the cathode when a solution of a uranyl salt containing free acetic acid is electrolysed. The deposit is tenacious and may be ignited to U_3O_8, in which form it is weighed. Wherry and Smith[1] employed a rotating anode, a current density of 3 to 4 ampères, and an E.M.F. of 12-14 volts. Two decigrams of uranium were deposited under these conditions in from 15 to 30 minutes.

ESTIMATION IN STEEL.

Five to ten grams of drillings are decomposed with hydrochloric acid and the solution filtered, if necessary, after dilution. Any insoluble residue is collected, washed, ignited, the residue dissolved in a few c.c. of acid, and the solution added to the original filtrate.

The liquid, measuring about 350 c.c., is heated nearly to boiling, excess of microcosmic salt added, and then dilute ammonium hydrate until a turbidity or small precipitate persists. The solution is then cleared with a few drops of acid, 10 grams of sodium thiosulphate and 20 c.c. of acetic acid added, and the mixture boiled for 10-15 minutes. The precipitate is allowed to settle, filtered off as quickly as possible, and washed with water containing a few c.c. per litre of acetic acid and ammonium acetate.

In the absence of aluminium, the small quantity of iron which accompanies the uranyl phosphate may be eliminated by dissolving the precipitate from the filter, leaving the sulphur, and re-precipitating the uranium from the solution. Alternatively, the acid solution is treated with sodium peroxide (added until the iron is precipitated and the solution is strongly alkaline) and then with several grams each of sodium and ammonium carbonate. The precipitated ferric hydrate is removed and the uranium precipitated from the filtrate as before. The latter process separates chromium, if present, as chromic acid.

Aluminium, generally present in steel, accompanies the uranium throughout the whole of the above operations, and is finally weighed as the orthophosphate. Its separation from uranium is not easy, and may not be worth the time and trouble spent upon it, particularly when the amount present is known, as is often the case.

Brearley obtained good results by dissolving the mixed phosphates of aluminium and uranium in nitric acid, adding dilute ammonium

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[1] *Journ. Amer. Chem. Soc.*, 29. 806.

hydrate until the excess of nitric acid is nearly neutralised, and pouring the clear solution into a large excess of ammonium carbonate, stirring the while. On filtering at once, traces of aluminium remained in solution, and traces of uranium in the precipitate. The separation was improved by allowing the mixture to stand in a warm place for an hour or two before filtering.

For the determination of the uranium only in a residue of the mixed phosphates of aluminium and uranium, the volumetric process is much easier and more accurate. The ignited phosphates are dissolved in hydrochloric acid, with the addition of a few c.c. of nitric acid if necessary, the solution treated with a few c.c. of sulphuric acid, evaporated and fumed strongly. The residue of sulphates is then dissolved up, the acidity of the solution adjusted, and the uranium determined by reduction with zinc and titration with permanganate as described previously.

Small amounts of uranium, associated with aluminium, may be estimated colorimetrically by matching the colour obtained on adding a mixture of potassium carbonate and sodium peroxide with that yielded similarly by a standard solution of a uranyl salt.

ZIRCONIUM ($Zr = 90 \cdot 6$).

Zirconium is added to steel in small amounts in the form of its alloy with iron, and apparently with results similar to those produced by ferro-titanium. Small though the amount definitely known to be added may be, it is sufficiently large not to escape detection and estimation in the ingot, if present, yet zirconium steels, so called, apparently contain no trace of the element. This statement is made with diffidence, as the steels which have come under the author's notice are very few in number, being of comparatively recent production.

The stable salts of zirconium correspond to the oxide ZrO_2. A hydrated peroxide, stated by some observers to be $Zr_2O_5 \cdot 4H_2O$, and by others to be ZrO_3xH_2O, is obtained as a white precipitate when perhydrol (30 per cent. hydrogen peroxide) is added to a concentrated neutral or slightly acid solution of the sulphate of the normal base, but no stable perzirconates have been isolated.

Separation from Iron.—With the exception of the hydrochloric acid-ether process. the general methods of separating ferric iron from other elements are not applicable to the case of zirconium. The reactions of the latter metal closely follow those of aluminium and ferric iron, and the separation of zirconium from these in the wet way often necessitates very careful manipulation. Most of them furnish at the same time a direct means of estimating the zirconium, and are therefore considered below in that connection.

Determination of Zirconium.—Practically all the methods of determining zirconium are gravimetric.

(1) Zirconium is thrown out of solution quantitatively by ammonium hydrate as $Zr(HO)_4$, closely resembling aluminium hydrate. The precipitate is readily soluble in dilute mineral acids. Ignition of it yields the oxide ZrO_2, which contains 73·90 per cent. of zirconium. The ignited oxide is not readily attacked by acids, weak or strong, with the exception of hydrofluoric acid. When treated with a mixture of sulphuric and hydrofluoric acids in order to eliminate any silica possibly present with the zirconia, loss of zirconium may result. To prevent this Wedekind[1] uses a large excess of both acids, viz., 20 times the amount of zirconia present of sulphuric, and 45 times its weight of hydrofluoric acid.

Several dry methods are available for the analysis of a residue of the mixed oxides of iron and zirconium. For instance, a mixture of ferric oxide and zirconia obtained by an ammonium hydrate precipitation is ignited in a current of hydrogen by Gutbier and Hüller,[2] and its composition calculated from the loss of weight due to the reduction of the iron oxide. (A mixture of ferric oxide and alumina is treated similarly.)

A much better dry method of separating ferric oxide and zirconia is that of Havens and Way,[3] who show that by passing a current of dry hydrogen chloride over ferric oxide, complete volatilisation as the chloride takes place only at 450°-500° C., but by mixing a small amount of chlorine with the acid gas, the same result is obtained at 200°-300° C. In this way, a perfect separation of ferric oxide can be made from the oxides of aluminium, chromium, beryllium and zirconium, all of which remain undecomposed. The mixture of gases is made by allowing sulphuric acid to drop into a warm mixture of strong hydrochloric acid, common salt and a small amount of manganese dioxide. The gases are admitted directly into a tube carrying the boat with its charge of the oxides. The ferric chloride is collected in water.

(2) The formation of an insoluble hydrated peroxide has been utilised for the determination of zirconium and for its separation from iron, aluminium, titanium and other metals. The best results are obtained from the sulphate solution, which may contain a little free acid sufficient to retain iron and aluminium in solution ; chloride and nitrate solutions

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[1] *Ber.*, 44. 1753. [2] *Zeit. f. anorg. Ch.*, 32. 92, 95. [3] *Amer. Journ. Sci.*, 7. 217

are not so satisfactory. The solution, concentrated to low bulk, is treated with a very large excess of 30 per cent. hydrogen peroxide, the mixture shaken well and then allowed to stand for some time before filtering off the precipitate. The latter is then collected, washed and ignited to ZrO_2.

Bailey[1] recommends the method as suitable for the separations referred to above. Later observers do not consider the process to be very satisfactory, low results being the general experience of most. In one case, the author obtained from a zirconium earth containing 83 per cent. of ZrO_2 almost exactly 80 per cent. only.

(3) An excellent method of precipitating zirconium from its solutions and separating it at the same time from iron, is the 'thiosulphate method.' The solution, if acid, is nearly neutralised, and if the iron exists in the ferric condition, a few crystals of sodium thiosulphate are added and the mixture allowed to stand until the iron is reduced. Five grams more of sodium thiosulphate are then added and the mixture boiled for a long time until sulphur dioxide is expelled. The precipitate is collected, washed well and ignited to ZrO_2. Aluminium, if present, is precipitated completely as the hydroxide.

(4) From the point of view of the steel-works' chemist, the most satisfactory method for the determination of zirconium takes the form of a precipitation from the chloride solution by means of sulphurous acid. When a large excess of this reagent is added to a dilute solution of zirconium chloride at its boiling point, and the mixture maintained in vigorous ebullition for a few minutes, the zirconium is completely extracted from the solution in the form of a white precipitate which can be filtered and washed quickly, and ignited to the oxide. Baskerville[2] found that the precipitation is complete from chloride solutions only, hence when sulphates or nitrates are present, it is necessary to precipitate the zirconium from them as hydrate, and dissolve the washed precipitate in hydrochloric acid. Mixtures of zirconium with iron, and of zirconium with aluminium, were successfully assayed by this process.

As it is obviously of importance to know whether a mixture of all three, and particularly one which contains a very large amount of iron, can be analysed in this way, the author and F. W. Gray carried out the following tests.

(*a*) Three grams of Swedish bar iron were dissolved in hydrochloric acid, and to the solution, zirconium and aluminium were added in the form of a solution of their chlorides representing respectively 0·054 gram

[1] *Journ. Chem. Soc.*, 1886, 149. [2] *Journ. Amer. Chem. Soc.*, 16. 475 (1894).

of ZrO_2 and 0·055 gram of Al_2O_3. The mixture was evaporated to a pasty condition so as to eliminate the excess of acid, diluted to 250 c.c. with boiling water, and 25 c.c. of a saturated solution of sulphur dioxide, freshly prepared, added. After boiling for 10 minutes, the precipitate was collected, washed with hot water containing some sulphur dioxide, dried, and ignited. The residue was nearly white, but obviously contained a trace of iron, as expected. Three separate experiments yielded 0·0550, 0·0552 and 0·0555 gram of ZrO_2. Aluminium was determined in the filtrate by a phosphate precipitation and with good results. The residues of ZrO_2 were not assayed for the small quantity of iron present in them.

(*b*) Three grams of a steel containing 0·6 per cent. of chromium, 3·75 per cent. of nickel, and 0·55 per cent. of manganese, were dissolved, the same amounts as before of zirconium and aluminium added and the solution evaporated. Silica was removed after dilution, and the filtrate treated as in (*a*). The amounts of ZrO_2 obtained in the first two trials were respectively 0·053 and 0·054 gram. A third experiment yielded 0·0114 instead of 0·0110 gram added.

The important point in the process is the correct adjustment of the acidity so that there is sufficient acid present to prevent hydrolytic separation of iron and aluminium before adding sulphurous acid, and not too much to prevent the precipitation of zirconium; hence the evaporation of the solution to low bulk. The evaporation may be dispensed with by neutralising the excess of acid with ammonium hydrate, only that if a turbidity is reached in so doing, it is found that an unexpectedly large amount of acid is required to clear the solution again. In such a case, ammonium hydrate is again added a drop at a time, with vigorous stirring throughout, until it is judged that a further addition would produce a turbidity. By operating in this way it is not difficult to detect and determine as little as 2 milligrams in a solution containing several grams of iron as chloride.

Titanium cannot be separated from zirconium by this process.

Of the remaining methods of separating zirconium from iron, the precipitation of the former by phenylhydrazine and of the latter as ferrous sulphide are the most important. The second of these may be well done as follows.

To the solution ammonium hydrate is added until it is nearly neutral and then an excess of a solution of the mixed tartrate and oxalate of ammonium. An excess is indicated by the dissolving to a clear solution of the precipitate which forms at first. The mixture is then heated to boiling, and a slight excess of ammonium sulphide added. After digesting for some time, the ferrous sulphide (which may contain a little aluminium) is filtered off, leaving the zirconium completely in the filtrate.

Separation from Aluminium.—The second and fourth of the preceding methods are applicable to the zirconium-aluminium separation, though, as indicated above, one of them is not an unqualified success. Others of a special kind are the precipitation of the zirconium with (*a*) sodium iodate, (*b*) cupferron.

(*a*) Davis [1] originally investigated the 'iodate process,' which takes the following form. The solution is treated with sodium carbonate until a faint turbidity is obtained, and the mixture shaken thoroughly. The turbidity is then just removed by the careful addition of hydrochloric acid, and an excess of a solution of sodium iodate then added. The mixture is heated for 15 minutes, and allowed to stand for 12 hours after which the precipitate is filtered off, washed with hot water, dissolved in hydrochloric acid, and the zirconium finally precipitated as hydrate. Aluminium is recovered from the original filtrate also by precipitation with ammonium hydrate.

(*b*) Cupferron precipitates zirconium quantitatively under the conditions described for titanium and a valuable method of separating the element from aluminium is thus secured. The precipitate is creamy-white in colour, can be filtered and washed (normal hydrochloric acid) fairly rapidly, and yields a snow-white residue of the oxide on ignition.

Separation from Titanium.—With the exception of the 'perhydrol precipitation' of zirconium, the processes previously described fail to separate titanium, which is precipitated throughout with the zirconium. Fortunately, the amount of titanium in the materials which the works-chemist is called upon to examine is small enough to permit of a colorimetric determination of it, for which purpose the ignited ZrO_2 is fused with acid potassium or sodium sulphate (the latter preferably), and the melt extracted with 5 per cent. sulphuric acid.

The separation of the two metals may be effected by precipitating the zirconium as phosphate, which compound may be generated in solutions of acidity sufficiently great to retain aluminium in solution. Thus a solution of the sulphates containing 1 per cent. of free sulphuric acid is treated with 10-volume hydrogen peroxide, and an excess of sodium or ammonium phosphate then added. After allowing the mixture to stand from 1 to 24 hours accordingly as comparatively large or very small amounts of zirconium are present, the precipitation is complete. The ignited residue ultimately obtained contains 51·8 per cent. of ZrO_2.

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[1] *Journ. Amer. Chem. Soc.*, 11. 26 (1889).

It may be necessary to add a little hydrogen peroxide during the operation of precipitation or afterwards, to retain titanium in its peroxidised condition; otherwise, some of it is precipitated. The yellow colour of pertitanic acid is a guarantee of the correct conditions.

Dittrich and Freund[1] separate zirconium and titanium by neutralising the solution of the mixed nitrates with sodium carbonate, and adding it in drops to a 20 per cent. solution of ammonium salicylate. After boiling the mixture for some time, the precipitate of zirconium salicylate is filtered off, washed with a hot solution of the precipitant and ignited to ZrO_2. Titanium is precipitated from the boiling filtrate with ammonium hydrate.

ESTIMATION IN STEEL.

Either of the two following processes may be applied to the determination of zirconium in steel.

(1) Dissolve 4 grams of the drillings in 50 c.c. of hydrochloric acid, filter off silica and carbonaceous matter and ignite them. Fuse the residue with a little acid potassium sulphate, dissolve out and precipitate with a slight excess of ammonium hydrate. Filter, wash, dissolve in a few cubic centimetres of hot dilute hydrochloric acid and add the solution to the original filtrate from the siliceous residue.

The solution is then treated exactly as described in the preceding section under 4 (*a*). The few steels examined by the author in this way were found to be free from zirconium, though the correct conditions were secured in all cases, as shewn by the fact that one milligram of zirconium added as chloride to the solution which had remained perfectly clear after boiling for 10 minutes with sulphurous acid, was precipitated. A similar result was obtained by the following modification of Johnson's method.

(2) Dissolve 4 grams in 100 c.c. of 20 per cent. sulphuric acid, filter and reserve the filtrate until the insoluble residue has been treated as in (1). Dilute the mixed solutions to 250-300 c.c.; add dilute ammonium hydrate (1 : 1) with constant stirring until a slight precipitate is formed. Continue the addition, drop by drop, until the precipitate just begins to assume a blackish tint, and finish by adding 10 drops more. The precipitate so obtained, containing comparatively little iron and all the zirconium, is filtered through a large paper, washed, and re-dissolved in hydrochloric acid. The resulting solution is then treated as described above.

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[1] *Zeit. f. anorg. Chem.* 56. 244 (1907).

MINOR CONSTITUENTS OF STEEL.

In addition to the elements already dealt with steel may contain small amounts of others not often looked for. A brief account of methods for determining some of them is appended.

Nitrogen.—The determination of nitrogen is based upon the fact that when steel is dissolved in dilute hydrochloric acid, the nitrogen, existing in the steel as nitride, is converted into ammonium chloride. By distilling the solution with an excess of a caustic alkali, the nitrogen is then liberated in the form of ammonia, the amount of which is conveniently determined by the Nessler reagent.

A distillation apparatus similar to the one shewn in Fig. 12 is required, the flask having a capacity of at least 750 cubic centimetres. Into this, 10 grams of pure sodium hydrate and 300 c.c. of distilled water are placed and the solution boiled until a sample of the distillate proves to be ammonia-free. A few fragments of freshly ignited fire-clay prevent violent bumping during the operation. In the meantime 1 gram of the steel is dissolved in 20 c.c. of 50 per cent. hydrochloric acid, and the solution of ferrous chloride transferred to the flask by means of the tap funnel. The distillation is then continued until ammonia is no longer detected in the condensed liquid. The amount of it is determined by matching the colour obtained when 2 c.c. of the Nessler reagent are added to the distillate with that produced by a standard solution of ammonium chloride in an equal volume of ammonia-free water.

The results obtained are subject to a deduction for the amount of nitrogen introduced by the reagents. The blank determination is conducted by boiling 10 grams of soda dissolved in 300 c.c. of water as before until ammonia is expelled, then adding the residue of ferrous hydrate from a previous determination and continuing the distillation until no more ammonia is expelled. The amount found is due to the nitrite contained in the alkali and 300 c.c. of water. The acid used, 20 c.c., is next added and the distillation repeated, thus giving the nitrogen existing as ammonia and nitrite in the acid. The boiling is finally continued nearly to dryness and the last portions of the distillate tested for ammonia ; if found, the acid or alkali used contained nitrate.

The blank should not be large from sodium hydrate made from the metal. For special purposes the alkali may be purified by dissolving 150 grams in 250 c.c. of water and digesting for a day in contact with a zinc-copper couple.

A stock solution of the Nessler reagent is made by dissolving 25 grams potassium iodide in about 100 c.c. of water and adding to all but a few cubic centimetres of it a saturated solution of mercuric chloride until a permanent precipitate is obtained. The remainder of the iodide solution or as much of it as is necessary is then added until the precipitate thins out to a turbidity. To the mixture a cold solution of 60 grams of caustic potash in 60 c.c. of water is added, and finally more mercuric chloride until a small permanent yellow precipitate is obtained. The mixture is diluted to 400 c.c. and allowed to stand for some time before bottling.

A standard solution of ammonia is made by dissolving 0·0382 gram of ammonium chloride in a litre of water ; 1 c.c. of this solution contains 0·01 milligram of nitrogen.

Oxygen.—Slag can occur in steel in small amounts only and then but locally, hence it is by no means easy to secure a representative sample. Oxygen is a constituent of mild steels in which it exists in the form of ferrous oxide or as oxides of manganese, aluminium, etc.

It is often claimed that the determination of oxygen is as important as that of phosphorus and sulphur, but it is by no means certain that the process generally used, due to Ledebur, approaches the methods for sulphur and phosphorus in point of accuracy. It consists of an ignition of the finely divided material in a current of hydrogen, and as oxides of manganese, aluminium and silicon are not reduced, the water obtained represents only the occluded oxygen and that of ferrous oxide.

The hydrogen, generated from zinc and hydrochloric acid, is purified and dried in the usual manner, and any trace of oxygen then removed from it before admission to the tube containing the drillings by passing it over heated palladiumised asbestos, the water thus formed being absorbed in phosphorus pentoxide. The fine drillings, of which about 20 grams are taken, are dried in a desiccator before being charged into the tube. The latter is heated to 850°-900° C. and the temperature maintained whilst several litres of hydrogen are passed, after which it is allowed to cool before cutting off the current. The water formed is absorbed in phosphorus pentoxide and weighed. It is very important that a blank determination should be conducted at frequent intervals, and that the drillings should be scrupulously clean and thoroughly dry.

Other methods have been suggested such as (1) heating the sample in a stream of dry chlorine, (2) dissolving in bromine or iodine at a low temperature, and (3) dissolving in copper sodium chloride solution.

Tin.—This metal is occasionally met with in steel, having been introduced during smelting in the form of tin-plate scrap. By dissolving a large weight of the drillings in hydrochloric acid and gassing the solution with hydrogen sulphide, the tin is precipitated along with copper and arsenic. After filtering and washing the residue with water and dilute hydrochloric acid until free from iron, the sulphide of tin (and arsenic) is dissolved from the paper by means of warm yellow ammonium sulphide. From the solution stannic sulphide is re-precipitated on acidifying with hydrochloric acid and passing hydrogen sulphide again for a few minutes. Without sensible error it may then be collected, dried, and roasted to oxide.

Boron.—A method for the determination of boron will be found under the analysis of ferro-boron in Part III. Steels containing boron, except in mere traces, have not come under the author's observation.

PART III. THE ANALYSIS OF STEEL-MAKING ALLOYS.

MANGANESE ALLOYS.

SPIEGEL AND FERRO-MANGANESE.

Carbon.

THESE alloys are decomposed by acid solutions of copper ammonium chloride. Direct combustion of the metal, without admixture with a flux, is applicable to spiegels. Ferro-manganese is more difficult to decarbonise completely, because the material frits to a hard mass, which is liable to enclose particles of the incompletely burnt alloy. Red lead is reduced to beads of metal by the carbon of the alloy, which frequently exceeds 6 per cent., and low results may accrue in consequence again of enclosed particles. Zinc oxide is not open to such objection, and is, moreover, free from a 'blank.'

Sulphur.

Digest 5 grams of the alloy with 50 c.c. of nitric acid until it is decomposed, evaporate to dryness, dissolve in 30 c.c. of hydrochloric acid, take to dryness, re-dissolve in few c.c. of hydrochloric acid, dilute, boil, filter off silica, and precipitate with barium chloride.

Phosphorus and Silicon.

Weigh off 1 gram of the alloy, moisten with water and decompose with 30 c.c. of nitric acid. Evaporate nearly to dryness, add 20 c.c. of hydrochloric acid, evaporate to dryness and bake. Dissolve again in 10 c.c. of hydrochloric acid, dilute, filter off and determine the silica. Evaporate the filtrate and washings from the silica precipitate to about 20 c.c., add 10 c.c. of nitric acid, neutralise with ammonium hydrate, re-dissolve the precipitate in nitric acid, add 3 or 4 c.c. in excess, and precipitate with the ammonium molybdate reagent, finishing as lead molybdate.

Manganese.

All the processes, described under the analysis of steel, are applicable, with slight modifications, to the alloys of iron with manganese.

In making a basic acetate separation of the iron, corrections for the volume of precipitate and fall of temperature during filtration are necessary. A further correction, in filtering off 500 c.c. from a total of 1000 c.c., of about 2 c.c. for loss by evaporation, should be introduced in the assay of the richer alloy. If the Volhard volumetric process is to be applied to the filtrate, the neutralisation of the original solution and precipitation of the iron should be made with sodium carbonate and acetate respectively, instead of with the corresponding ammonium salts. This modification is not imposed by the gravimetric process of precipitating the manganese from the filtrate with bromine and ammonium hydrate.

Bismuthate Process.—Digest 1·1 grams of spiegel or 0·275 gram of ferro-manganese with 50 c.c. of nitric acid, s.g. 1·42, until solution is complete. (In the assay for manganese of highly siliceous alloys—silico-spiegel and silico-manganese—the decomposition is assisted materially by the occasional addition of a few drops of hydrofluoric acid.) Add bismuthate to the hot solution until the carbonaceous matter is completely oxidised and a precipitate of manganic oxide persists after boiling for two or three minutes. Dissolve the precipitate by adding sulphurous acid or ferrous sulphate solution, cool, and dilute to a measured volume (100 c.c.) in a graduated flask. Mix 25 c.c. of the solution with 30 c.c. of 1·20 nitric acid, add 2 grams of bismuthate, shake well, dilute with an equal volume of water, filter and wash by decantation with 3 per cent. nitric acid. Titrate with decinormal ferrous solution and permanganate.

The filter invariably holds a little manganese, which is, however, negligible in the assay of these alloys, even after the washings are colourless. If the oxidation with bismuthate is not made in strongly acid solutions such as obtain in the operations described, the results are low on account of the formation of manganese dioxide.

Chlorate Process.—Decompose 0·25 gram of the alloy with 30 c.c. of nitric acid and 2 c.c. of hydrochloric acid. Add 0·5 gram of Swedish bar iron or electrolytic iron, digest until the metal dissolves completely, add an equal volume of water, 40 c.c. of nitric acid, 3 grams of potassium chlorate, and boil gently for 10 minutes after manganese dioxide begins to precipitate. Repeat the treatment with acid and chlorate twice, boiling for the same length of time, collect the precipitate, wash, and finish as described under the analysis of steel.

Copper and Titanium.

Small quantities of copper are usually present in these alloys. An estimation, seldom required. can be made by the method described for steel.

Ferro-manganese contains very small amounts of titanium almost invariably, but in this case also an estimation is rarely called for. Digestion in the cold with dilute nitric acid over a period of 24 hours leaves the titanium in the carbonaceous residue, and its amount may be determined by fusion with potassium pyrosulphate followed by the peroxide colorimetric test.

SILICON ALLOYS.

LOW GRADE FERRO-SILICON AND SILICO-SPIEGEL.

Total Carbon.

The powdered alloys are scarcely attacked at all by cold, and only partially by hot copper solutions.

They are easily and completely decarbonised by ignition in a stream of oxygen either with or without such oxidising agents as copper oxide and lead chromate. It is better to dispense with these reagents when possible, because there is then no blank determination to be done; and no metallic beads, (with the attendant possibility of occlusion of some unattacked material,) are formed. As there is no actual fusion, the same boat is available time after time. The ferro-silicon after ignition is powdery or is easily crumbled; silico-spiegel is fritted into a single piece.

Graphite.

The carbon in ferro-silicon exists chiefly as graphite, the combined carbon amounting to a few tenths per cent. only.

	"Lonsdale."	"Ayresome."	"Mostyn."
Combined carbon -	0·20	0·15	0·19
Graphite - - - -	1·39	1·39	1·62
Silicon - - - -	12·32	13·28	12·08

The graphite is determined as follows, combined carbon being obtained by difference. Two or three grams of the powdered alloy are covered with 70-100 c.c. of 1·20 nitric acid and the liquid heated nearly to boiling. The reaction with ferro-silicon is very slight, but on adding next a few drops of hydrofluoric acid the reaction becomes very vigorous, and is maintained by adding from time to time further small quantities of hydrofluoric acid until particles of graphite only are to be seen. The action should not be hurried, but time allowed for the flocks of the nitrated (combined) carbon compound to dissolve before any considerable excess of hydrofluoric acid is added. The decomposition can be effected in the same glass flask time after time without damaging the vessel. This is an advantage, as it allows the course of the reaction to be observed and the complete decomposition of the alloy to be readily determined. The residue is filtered through asbestos, washed with water, then with boiling sodium hydrate (2N), then once with dilute hydrochloric acid, and finally with water until the washings give no reaction with silver nitrate solution. The residue is then burnt in a current of oxygen in the usual way.

The total carbon of silico-spiegels is generally greater than that of ferro-silicon and there is more combined carbon. As before, the graphite is estimated after decomposing the sample with nitric and hydrofluoric acids, and the combined carbon obtained by difference.

Combined carbon	1·41	1·89	1·61	1·31	0·51
Graphite -	0·77	0·34	0·94	0·60	1·22
Silicon - -	—	10·53	10·95	12·13	13·34
Manganese - -	—	19·85	18·14	18·25	20·20

Silicon.

The chief difficulty in the analysis of these alloys for practical purposes lies in the decomposition of the sample. Boiling with brominised hydrochloric acid, aqua regia, or hydrochloric and sulphuric acids, are the common methods of attacking the sample in the wet way. It was thought at one time that these alloys could not be thoroughly decomposed in any of these ways so easily and with the convenience which attends fusion with acid potassium sulphate, sodium carbonate with nitre, or sodium peroxide. This opinion was mainly based on certain observations which were explained by Hogg.

The misconception that ferro-silicon and silico-spiegel cannot be completely decomposed by aqua regia, for instance, has arisen from two causes. In the first place, if the alloy be not finely powdered, the particles become coated with silica, and further decomposition is thereby stopped; and secondly, even if the alloy is sufficiently finely divided, the evaporation to dryness and gentle heating followed by treatment with hydrochloric acid always gives a silica contaminated with oxide of iron. The most obvious inference is that the alloy is only partially decomposed; this, however, is not so. According to Hogg, the peculiar physical condition of the silica is the cause of its taking up and firmly retaining some ferric oxide. To reduce this source of contamination to a minimum, the separated silica should be filtered off after dissolving, the filtrate being then evaporated to dryness to recover the small quantity in solution.

Hogg finds, and the conclusion is supported by much independent testimony, that the silica which passes into solution is much greater with low than with high percentage alloys. For alloys containing 10 to 15 per cent. of silicon, he finds the soluble portion to be between 0·1 and 0·3 per cent., and this amount he does not recover, adding by way of correction 0·2 per cent. to the amount obtained by filtering off immediately after decomposition. A large number of test analyses enables the author to confirm Hogg's conclusions in every particular except the minor one referred to in the following account of the process.

Grind as much of the sieved sample as is needed for the assay in an agate mortar, weigh off two grams, add 50 c.c. concentrated hydrochloric acid and 10 to 20 c.c. nitric acid. Boil to decomposition, which is complete in about 15 minutes, add about twice the volume of water and filter *at once*; wash with cold dilute hydrochloric acid, ignite and weigh. The silica is invariably white, and the residue after treatment with hydrofluoric acid will be found not to exceed two or three milligrams. To the result obtained add only 0·1 per cent. as a correction for the soluble silica.

The amount of silica which dissolves is increased by boiling the solution after diluting. After dilution and allowing to stand on a hot plate for two hours, 20 to 30 milligrams of silica were found dissolved so that the correction of 0·1 per cent. applies only to the conditions stated. The silica as weighed is in a very fine state of division, and it is also very hygroscopic. Hillebrand (*Chemical News*, lxxxiii. 136) states that blasting for nearly half an hour is necessary to expel all the moisture from silica, and it is then not hygroscopic.

Manganese.

The manganese in ferro-silicon may be so small that it can be determined colorimetrically. The manganese in silico-spiegel (as well as that in ferro-silicon) may be determined by making an acetate separation of the iron in the filtrate from the silica and estimating as Mn_3O_4; or titrating the manganous acetate solution with permanganate according to the process described on p. 78. The manganese in either alloy may also be assayed by the bismuthate process if it is first got into solution by weighing off 1·1 grams of the powdered sample and adding 50 c.c. nitric acid (1·20) and 2 or 3 c.c. of hydrofluoric acid. After filtering off the graphite, the procedure for ferro-silicons is the same as that for pig-irons, and for silico-spiegels the same as that for manganese alloys. No interference with the process is exerted by the presence of the hydrofluoric acid. Needlessly large amounts of this acid, however, cause the final permanganate tint to be readily converted into manganic oxide through the agency of the manganous fluoride in solution.

Sulphur.

This element can be estimated gravimetrically as in steels, using 2·5 grams of the sample.

Phosphorus.

The process used for steel cannot be directly applied to the estimation of phosphorus in these alloys, because they are not decomposed by 1·20 nitric acid. By decomposing them with aqua regia and evaporating so as to dehydrate the silica and eliminate hydrochloric acid, a portion of the phosphorus always remains with the silica. This may constitute a source of very serious error when highly phosphoric material is being assayed; *e.g.* of the 0·20 per cent. of phosphorus in a certain silico-spiegel, 0·063 per cent. was found with the ignited silica. An obvious means of minimising, if not actually eliminating, this error, is to filter as soon as the sample is decomposed, as in the estimation of silicon, and use the evaporated filtrate for estimating the phosphorus.

These alloys being readily decomposed by mixtures of nitric and hydrofluoric acids, a removal of the silica with excess of the latter, would at once allay all fear of loss of phosphorus, but the precipitation of phosphorus as ammonium phospho-molybdate is by no means insensible to the presence of hydrofluoric acid. Very small amounts of this acid retard the precipitation, and large amounts prevent it altogether. By preparing identical solutions of the same steel which contained 0·064 per cent. of phosphorus, and adding 1·7, 3·4, and 5·1 c.c. of hydrofluoric acid just before adding the molybdate reagent, the first was found to precipitate almost at once, but the second and third showed no signs of a precipitate for some time. After standing, however, for two hours at about 60° C., the filtered precipitates were converted to lead molybdate and were found to correspond to 0·060, 0·063, and 0·061 per cent. of phosphorus.

Along with the usual amount of nitric acid, a ferro-silicon or silico-spiegel can be easily decomposed by using no more than 4 c.c. of hydrofluoric acid for two grams of the sample; the small quantities of this acid left unused by the silicon are nearly all expelled by the subsequent boilings, so that a series of tests in which silica was added to the above-mentioned steel dissolved in nitro-hydrofluoric acid showed no signs, when the phosphorus was precipitated, of lagging, and the completion of the estimations yielded 0·065, 0·063, 0·064, and 0·066 per cent. instead of the 0·064 of phosphorus actually present. Under these circumstances it is evident that the following process can be conveniently applied.

To two grams of the powdered alloy add 45 c.c. 1·20 nitric acid, and 25 to 30 drops of hydrofluoric acid. When, without the application of heat, the reaction subsides, add another 25 to 30 drops; the small portion of alloy then undecomposed dissolves on boiling. After complete decomposition add permanganate, clear the manganic oxide precipitate with a solution of ferrous sulphate, filter off the graphite, add 6 or 8 c.c. ammonium hydrate, precipitate with the molybdate reagent, and weigh finally as lead molybdate according to the more detailed instructions given for steels.

Commercial hydrofluoric acid may contain small amounts of phosphoric acid. It is estimated (and allowed for) by evaporating 100 or 200 drops of the acid with sulphuric acid in a platinum dish until fumes of sulphur trioxide are given off, transferring to a glass vessel, oxidising with permanganate, clearing with ferrous sulphate, adding ammonia to precipitation of iron, re-dissolving in nitric acid, precipitating with the molybdate reagent, and finishing as usual.

HIGH-GRADE FERRO-SILICON.

Rich ferro-silicon alloys are quite different materials from the old 10-15 per cent. alloys. With rise of silicon content the alloys become less susceptible to the attack of acids and correspondingly more to the attack of alkalies, whilst some alloys cannot be opened out at all satisfactorily in the wet way.

Carbon.

The carbon exists for the greater part as graphite unless the alloy contains much manganese. In addition, a portion of it may also be present combined with the silicon in the form of carborundum, SiC. As this substance is not decomposed by simple ignition, it is necessary to repeat the combustion with the addition of copper oxide or lead chromate. As an alternative, one or other, or a mixture of both these reagents, may be used in the first instance. Red lead may also be used except in the case of alloys of very high silicon content (80 per cent.), when the reaction may become too violent.

Silicon.

The method of decomposing the alloy for the purpose of estimating silicon depends upon its silicon content.

I. **Silicon 20-30 per cent.**—To 0·5 gram of the finely-ground alloy 50 c.c. of hydrochloric and 1 c.c. of nitric acid are added. The beaker is allowed to stand for some time in a warm place, taking care that the liquid is not allowed to boil. Nitric acid is then added, not more than 2 or 3 drops at a time until the alloy is apparently all decomposed, when the whole mixture will have assumed a yellow colour. The liquid is then evaporated to dryness, the residue baked, dissolved up again in a little hydrochloric acid and the silica collected and determined in the usual manner by volatilisation with hydrofluoric and sulphuric acids. (It must not be forgotten that, for exactness, the filtrate must be taken to dryness and baked again in order to recover the small amount of silica which it invariably contains.)

The residue left after treatment with hydrofluoric acid may contain silicon carbide and a little ferric oxide, the latter resulting from a small amount of alloy not decomposed by the initial attack. It is digested in the platinum crucible for half an hour or so with an excess of hydrochloric acid, the liquid filtered after dilution, and the undecomposed silicon carbide, SiC, which is green in colour, collected and weighed. The loss of weight due to this treatment is the ferric oxide from the originally undecomposed portion of the alloy. The amount of silicon which it represents is found empirically to constitute about 30 per cent. of its weight, and this correction is added to the amount previously found: it frequently represents as much as 0·5 per cent. of silicon.

II. **Silicon 35-60 per cent.**—0·5 gram of the 'floured' alloy is fused with 8 grams of sodium peroxide in a nickel crucible, the melt extracted with water, transferred to a large porcelain dish, and the metallic oxides dissolved in hydrochloric acid. The solution is taken to dryness, the residue baked gently, re-dissolved and the silica filtered off. The filtrate is made strongly alkaline with ammonium hydrate and, without boiling, the ferric oxide containing the remainder of the silica is collected on a large filter paper and washed with hot water. The paper is opened out and the precipitate rinsed from it into the porcelain dish, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue baked, re-dissolved, the silica collected as before, and its weight added to the major portion.

III. **Silicon 80 per cent.**—0·5 gram of the alloy is digested in a nickel vessel with a solution of 5 or 6 grams of pure sodium hydrate in 50-60 c.c. of water until action ceases. The mixture is evaporated to dryness, the residue dissolved up again in water, boiled and transferred to a porcelain dish. The major portion of the silica is then collected as in II. by acidifying, evaporating, baking gently, etc. The silica thus obtained contains silicon carbide and a small quantity of undecomposed alloy, and it is examined for these, and the correction applied, as described under I. The filtrate from the siliceous residue is made strongly alkaline with ammonium hydrate, the precipitate filtered off, washed, re-dissolved and the solution taken to dryness as in II. in order to collect the remainder of the silica.

Phosphorus.

Phosphorus is conveniently determined on the filtrate from the silicon determination. For this purpose the filtrate is evaporated to a small volume (30 c.c.), treated with 10-15 c.c. of nitric acid and ammonium hydrate added until a precipitate is obtained. This is dissolved in a few drops of nitric acid and the molybdate reagent then added.

Alternatively, the alloy (2 grams) is opened out by adding it a little at a time to a mixture of hydrofluoric and nitric acids contained in a platinum dish. When decomposition is complete, a little sulphuric acid is added, the mixture evaporated to expel excess of hydrofluoric acid, 1·20 nitric acid added and the estimation completed in the usual manner.

Sulphur.

Of the 20-30 per cent. alloy, 1 gram, very finely divided, is digested with a mixture of 50 c.c. hydrochloric and 10 c.c. nitric acid. The silica is removed in the usual way and sulphur determined on the filtrate by precipitating with barium chloride. The richer alloys are opened out by fusion with a mixture of sodium carbonate and potassium nitrate.

Manganese, Aluminium, Calcium, etc.

The 20-30 per cent. alloy is decomposed as for the determination of sulphur, the silica removed and the filtrate from it taken for the estimation of manganese and aluminium. Thus, a basic acetate precipitation of the iron and aluminium is made and the manganese determined in the filtrate by precipitation with bromine and ammonium hydrate. The precipitate containing the iron and aluminium is dissolved in hydrochloric acid and the aluminium precipitated from the solution and determined as phosphate.

The richer alloys frequently contain calcium and sometimes also magnesium, in addition to aluminium and titanium.

These elements may be estimated by opening out as in the estimation of silicon, and making use only of the filtrate. In order, however, to avoid this lengthy preliminary operation, and because large amounts of material can be more readily dealt with, it is better to proceed as follows with the richer of the high-grade alloys. Decompose two grams of the alloy with nitro-hydrofluoric acid, add a few drops of sulphuric acid to prevent volatilisation of aluminium during the subsequent ignition, evaporate to dryness and ignite. Digest with hydrochloric acid, fuse any insoluble residue with sodium carbonate, and after extracting with hydrochloric acid, add to the main solution. This solution now corresponds in all respects to that of an iron ore, and contains iron, aluminium, manganese, calcium, and magnesium. Titanium, if present, is also in this solution. Add a small excess of ammonium hydrate, filter off iron and aluminium hydrates, and estimate the calcium by precipitation as oxalate and ignition to oxide; or to sulphate after treatment with sulphuric acid. The magnesium is determined in the usual manner in the filtrate as pyrophosphate. If the alloy contains manganese, this element must be removed with bromine and ammonia before the estimation of the alkaline earths. If required, the manganese can be estimated after precipitating the iron and aluminium in the first instance with ammonium acetate instead of the hydrate.

The precipitate is dissolved again and aluminium precipitated from the solution as phosphate.

The determination of the amount of titanium in the aluminum precipitate is made colorimetrically or by a precipitation with cupferron.

SILICO-MANGANESE.

The analysis of this alloy does not differ essentially from that of a 20-30 per cent. ferro-silicon, except in respect of the determination of manganese, which metal amounts to about 50 per cent. of the alloy. For the determination, 0·25 gram, finely ground, is decomposed in the first instance by means of 30 c.c. of nitric acid and 10 to 20 drops of hydrofluoric acid.

CARBORUNDUM.

Silicon carbide, SiC, is an intensely hard substance, and therefore most difficult to pulverise, even in an agate mortar. It cannot be opened out by any of the ordinary acids or any mixture of them, and is, moreover, exceedingly refractory towards the ordinary fusion reagents. Of these, the most efficacious are the caustic alkalies. Commercial varieties of carborundum contain from 60 to 63 per cent. of silicon, 30 to 35 per cent. of carbon and from 2 to 4 per cent. of iron and aluminium.

CHROMIUM ALLOYS.

FERRO-CHROMIUM.

Carbon.

Alloys of iron and chromium are decarbonised with difficulty by heating them alone in a current of oxygen. A flux of some kind is necessary; the most satisfactory are the oxides of lead and bismuth.

A high temperature is the main factor in the complete oxidation of ferro-chromium by the direct combustion method.

Silicon.

One gram of the 'floured' alloy is fused in a nickel crucible, in the manner described below for the determination of chromium, with 10 grams of sodium peroxide. The crucible, whilst still warm, is placed in a 10-inch porcelain dish, the cover glass placed in position, and a stream of hot water projected underneath the cover into the crucible. The reaction which sets in is quite safe, but develops sufficient heat to decompose the excess of peroxide and obviate the necessity of further boiling. The crucible is then rinsed, removed, and the oxides of iron, manganese and nickel dissolved in hydrochloric acid. To the clear yellow solution ammonium hydrate is added in excess and the resulting precipitate at once collected on a large paper and washed with hot water. It contains the whole of the silicon of the alloy. The filter paper is opened out and the precipitate rinsed from it into the porcelain dish, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue baked, and the silica collected and determined in the customary manner. The ignited residue is quite white and does not require treatment with hydrofluoric acid. There is usually no necessity for a blank determination of silicon on the reagent and apparatus.

Manganese.

For an exact determination of manganese in ferro-chromium, it is not advisable to decompose the alloy in a nickel crucible with sodium peroxide, since manganese is introduced into the assay from the vessel, and the amount of it is not necessarily the same as in a blank determination conducted on the same quantity of the reagent and under the same conditions as those obtaining in the estimation.

The alloy (1·1 grams) is intimately mixed in a fine state of division with 10 times its weight of the following mixture :—

Magnesium oxide, - - - - -	200 parts.
Sodium carbonate, - - - - -	50 ,,
Potassium carbonate, - - - - -	50 ,,

The mixture is heated at bright redness in the muffle in a shallow platinum dish for an hour, the dish removed, the contents mixed again with a glass rod, and the roasting continued for an hour more. The mass is boiled out with water and the solid matter allowed to settle. The clear yellow liquid is decanted through an asbestos filter, the oxides again boiled with water containing a little sodium carbonate, and the liquid again decanted after allowing to stand. The treatment is repeated until the filtrate is colourless, whereupon the filter is returned to the beaker containing the main residue. The latter is then dissolved in 30 c.c. of nitric acid (1·20), with the assistance of some hydrogen peroxide or sulphurous acid to reduce and dissolve the peroxide of manganese. After cooling the solution and without removing the asbestos, sodium bismuthate is added and the estimation of manganese completed.

Sulphur and Phosphorus.

Fuse 0·5 gram of the alloy with 5 grams of sodium peroxide, extract with water, boil, and dissolve to a clear solution with hydrochloric acid. Add ammonium hydrate in slight excess, filter and wash. Determine sulphur in the filtrate by acidifying with hydrochloric acid and precipitating with barium chloride. The ignited barium sulphate may contain a small amount of chromic oxide, which will be detected by the colour. For exact purposes, a second fusion of the residue followed by the customary operations, must then be undertaken. The ammonium hydrate precipitate contains the phosphorus as ferric phosphate and some chromium as basic ferric chromate. It is dissolved in dilute nitric acid, a few drops of sulphurous acid added to reduce the chromic acid, and ammonium hydrate until just alkaline. The precipitate is just taken into solution with nitric acid, a few drops added in excess, and the phosphoric acid precipitated with the molybdate reagent.

A blank determination of the amount of sulphur and phosphorus in 5 grams of peroxide fused in the nickel crucible, is necessary.

Aluminium.

Fuse the alloy with sodium peroxide, extract with water, boil for a minute or two and make up to a definite volume after cooling. Filter off a fraction through a dry paper, acidify with nitric acid, adding a few drops further in excess, add a solution of ammonium phosphate (2 grams), and make the mixture alkaline with ammonium hydrate. Digest for some time, collect, wash and ignite the precipitate of aluminium phosphate, which is usually perfectly white and pure.

Iron.

Fuse 0·5 gram of the alloy with 5 grams of sodium peroxide and boil out with water. Rinse out the crucible with water containing a few drops of hydrochloric acid and add 30 to 40 c.c. of acid to the aqueous extract in order to dissolve the metallic oxides. To the solution add several grams of ammonium chloride, and precipitate the iron with ammonium hydrate. Filter, wash several times. re-dissolve in acid and re-precipitate. Wash thoroughly, dissolve in hydrochloric acid, add stannous chloride solution until the mixture is decolorised, precipitate the excess of tin by adding a few drops of mercuric chloride solution, and titrate the ferrous chloride with potassium dichromate.

Chromium.

The chief constituent of this alloy is invariably determined volumetrically, after its conversion to a chromate by direct oxidation of the alloy. The oxidation is most frequently made by fusion with sodium peroxide; occasionally also by roasting with the 'tribasic fusion mixture' referred to above in connection with the determination of manganese.

Peroxide Method.—Mix 0·3 gram of the finely-divided alloy with 4 grams of sodium peroxide in a nickel crucible, and heat gently over a bunsen flame until the mixture begins to soften and then glows spontaneously. Holding the uncovered crucible by the tongs. keep the liquid contents in constant rotation for 3 minutes, and at a dull red heat. Allow to cool, place the crucible in a beaker of about a litre in capacity and add hot water sufficient to cover the crucible. When the effervescence ceases, remove and rinse the crucible thoroughly. Dilute the mixture to about 400 c.c. and boil for a few minutes in order thoroughly to decompose the excess of sodium peroxide. Next add 50 per cent. hydrochloric acid, a little at a time, until the oxides dissolve, yielding a clear rich orange-coloured solution. Boil, add 7 or 8 c.c. of potassium permanganate (*circa* 25 grams per litre), continue the boiling for 5 minutes longer, and add dilute hydrochloric acid (1 to 3) until the precipitate of manganese dioxide is dissolved. Continue the boiling after the addition of a few fragments of ignited firebrick to prevent violent bumping, until chlorine is completely expelled. Dilute largely, cool, and determine the chromium by adding an excess of ferrous solution and titrating back with a standard solution of potassium dichromate.

A solution containing 8·487 grams of the pure solid per litre registers, per c.c. of it, 1 per cent. of chromium on 0·3 gram of the alloy. An approximately equivalent solution of ferrous ammonium sulphate in 20 per cent. sulphuric acid contains 22·7 grams of the crystals.

Tribasic Method.—This is conducted as previously described. The dish containing the sintered mass is placed in a capacious beaker, about 300 c.c. of water and 30 c.c. of concentrated sulphuric acid added and the mixture heated until complete solution is obtained. The titration is the same as above.

Note.—By dissolving the metallic oxides in acid after the fusion by either of the above methods, there can be no uncertainty respecting the completeness of the oxidation. Tiny gritty particles remaining after boiling with acid shew incomplete fusion or oxidation, and a fresh assay must be undertaken on more finely ground material. Occasionally unoxidised particles may actually dissolve in the acid ; hence the addition of a small amount of potassium permanganate in order to complete the oxidation, as recommended in the peroxide method.

METALLIC CHROMIUM.

Carbon.

One gram of the metal is ignited in oxygen with 6 grams of red lead. As the carbon amounts to a few tenths per cent. only, and the material is very refractory, the boat and contents are inserted directly into the combustion tube, fully heated. This procedure is not safe with high-carbon ferro-chromiums on account of the violent action which ensues.

Silicon.

This element may be determined as in steels by dissolving in hydrochloric acid, evaporating to dryness, etc.; it is necessary to treat the ignited residue with hydrofluoric acid.

Iron, Manganese and Phosphorus.

These elements are determined as in ferro-chromium.

Sulphur.

As chromium metal is soluble in hydrochloric acid, an evolution method of some kind is applied, even in laboratories where it is not regularly practised in the analysis of steel. The simple apparatus shewn in Fig. 13 answers quite well for occasional estimations.

One or two grams of the finely-crushed sample are weighed into the first flask, 30 c.c. of hydrochloric acid mixed with 30 c.c. of hot water added, the stopper quickly replaced and the solution boiled until the alloy is dissolved. The second flask contains a solution of lead acetate, acidified with acetic, and the beaker a similar solution to indicate imperfect absorption in the first.

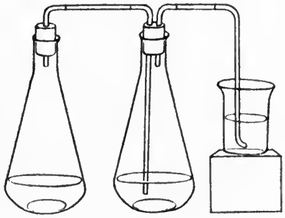

FIG. 13.

When hydrogen sulphide is completely expelled, the precipitated lead sulphide is collected on a small pulp filter, washed with hot water, and precipitate and filter digested with dilute nitric acid, s.g. 1·20. The pulp is strained off by means of a filter plate, the solution of lead nitrate nearly neutralised with ammonium hydrate, and the remaining acid decomposed by the addition of an excess of ammonium acetate. Then two or three grams of ammonium chloride are added, and the lead precipitated with ammonium molybdate, and weighed as $PbMoO_4$. The weight obtained multiplied by 0·0872 gives the equivalent amount of sulphur, calculated from the relations $H_2S = PbS = PbMoO_4$.

Chromium.

Boil half a gram of the alloy with 100 c.c. of dilute sulphuric acid (1 to 3). When decomposition is almost complete, add a solution of potassium permanganate sufficient in amount to oxidise most of the chromium to chromic acid without producing a precipitate of manganese dioxide. In this way the remaining particles of carbide are completely decomposed. Cool, and make up to 250 c.c. Measure off two separate portions of 100 c.c. each, dilute to 300 c.c., heat to boiling, and complete the oxidation of the chromium by the further addition of permanganate as described under the estimation of chromium in steels. The determination is finished by either of the usual volumetric processes.

If, as in Stead's process, the manganese peroxide is dissolved in hydrochloric acid, it is necessary to dilute the mixture very largely in order to eliminate the possibility of reduction of the chromate, thus:—

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 7Cl_2.$$

For this reason also, the chlorine resulting from the decomposition of the MnO_2 precipitate must be boiled off quickly: this is well done by holding and shaking the flask in a free flame.

ALUMINIUM ALLOYS

FERRO-ALUMINIUM.

Carbon.

The alloy is decomposed with the acid solution of cuprammonium chloride, and the carbonaceous residue burnt to carbon dioxide in the usual manner. The carbon exists largely in the form of graphite.

Silicon.

See estimation of sulphur; also estimation of silicon in metallic aluminium.

Manganese.

Decompose with nitric acid (1·20) together with a few drops of hydrofluoric acid, if necessary, and apply the bismuthate process as for steels.

Sulphur.

The gravimetric process as described for steels is directly applicable to these alloys. Silicon may be determined on the insoluble residue left after evaporating the original solution to dryness, and baking.

Phosphorus.

This element is determined as in pig-iron.

Aluminium.

A portion of the filtrate from the silica is taken for the determination of aluminium, or a separate sample may be dissolved in hydrochloric acid. In either case the solution should contain about one decigram of aluminium : more than this only necessitates, however, the use of larger amounts of sodium phosphate in the following procedure.

To the acid solution add two grams of sodium phosphate, when dissolved, add dilute ammonium hydrate until a small but permanent precipitate is formed, then clear with hydrochloric acid, adding about 2 c.c. in excess. Heat to boiling, dilute to about 300 c.c. with hot water, add a crystal or two of sodium thiosulphate to reduce the iron and then an excess of about 10 grams of the same reagent, followed by 20 c.c. of acetic acid. Boil for 15 minutes, filter, wash by decantation with hot water containing a trace of ammonium phosphate, dry, and ignite. Re-dissolve the ignited precipitate in hydrochloric acid, filter if necessary, and re-precipitate as before after adding one gram of sodium phosphate.

Note.—It has previously been stated (p. 104) that a large excess of sodium phosphate is necessary to ensure the formation of a precipitate of definite composition. The following results show that in the presence of the theoretical amount of phosphoric acid the precipitate is not the normal phosphate but a basic compound which, nevertheless, contains the whole of the aluminium present. The original solution contained one decigram of aluminium, and the first precipitation was made after neutralising with ammonium hydrate, re-dissolving the precipitate in acid and adding an excess of 3 c.c.

(i.)	First precipitation : $AlPO_4$ obtained - -	0·4480 grams.
(ii.)	Re-dissolved (i.), and re-precipitated exactly as before, adding one gram of sodium phosphate - - - - - - - -	0·4490 ,,
(iii.)	Re-precipitated (ii.) without adding phosphate	0·4220 ,,
(iv.)	Re-precipitated (iii.) as in (ii.) - - -	0·4485 ,,

METALLIC ALUMINIUM.

Carbon.

The metal is decomposed with cuprammonium chloride solution, and the carbonaceous residue collected and burnt. The sample (2·727 grams), should consist of small lumps or of very coarse borings on account of the vigour with which aluminium is attacked by the reagent.

Silicon and Sulphur.

Two grams of the metal are dissolved in 50 c.c. of a mixture of equal volumes of hydrochloric and nitric acids, the solution evaporated to dryness, and the residue baked gently. After cooling, the residue is dissolved in 40 c.c. of 50 per cent. hydrochloric acid, the siliceous residue filtered out, washed and ignited.

Sulphur is determined in the filtrate by precipitating with barium chloride, after adjusting to an acidity of about 5 per cent. by volume.

The ignited residue of impure silica is fused with sodium carbonate, the melt extracted with water, evaporated to dryness with hydrochloric acid and the silica collected and weighed. In this way the total silicon in the metal is found, and for purposes of steel making, more detailed information is seldom required.

Aluminium metal may contain, however, free or graphitic, as well as combined silicon, the respective amounts of which are approximately obtained by further treatment of the silica obtained as above. Thus, the loss of weight obtained by treatment with hydrofluoric and sulphuric acid represents the combined silicon, whilst a further treatment of the residue, which is now much darker in colour, with a mixture of hydrofluoric and nitric acid, eliminates and determines the graphitic silicon.

Graphitic silicon may be separately determined also by decomposing the metal with a mixture of hydrofluoric and hydrochloric acids, which leaves the graphitic silicon only in the insoluble residue.

Manganese.

This element is determined as in ferro-aluminium.

Iron.

Two grams of the metal are dissolved in 50 c.c. of a mixture of equal volumes of hydrochloric and nitric acids, the solution evaporated to dryness, and the residue taken up in 40 c.c. of 50 per cent. hydrochloric acid. A solution of 5 per cent. sodium hydrate is added, with stirring, until the precipitate aluminium hydrate re-dissolves, and the mixture is then allowed to stand for several hours or overnight. The ferric hydrate is collected, washed, re-dissolved in hydrochloric acid, and re-precipitated with ammonium hydrate. The iron is then determined volumetrically or by direct ignition to oxide.

Phosphorus.

Two grams are opened out and the solution treated exactly as for the determination of iron. To the acid extract of the residue, 10 c.c. of nitric acid are added and ammonium hydrate until a precipitate just begins to form. The solution is cleared, if necessary, with a few drops of nitric acid, and the phosphorus precipitated with ammonium molybdate.

Copper.

Five grams of the metal are dissolved in hydrochloric acid, the insoluble residue filtered off, washed, ignited, and treated with hydrofluoric, nitric and sulphuric acids. After the excess of the more volatile acids has been expelled by evaporation, the residue is boiled out with water and the solution added to the original filtrate. From the mixed solutions the copper is precipitated with hydrogen sulphide or sodium thiosulphate, the precipitated copper sulphide collected, ignited to oxide, and the copper determined either gravimetrically or volumetrically as in steels.

Magnesium.

Two grams of the metal are decomposed by a 5 per cent. solution of 15 grams of sodium hydrate, the liquid digested for half an hour and the insoluble residue filtered off, washed, and dissolved from the filter with dilute nitric acid. This solution is made alkaline with ammonium hydrate, the resulting ferric hydrate filtered out, and the magnesium precipitated from the filtrate and determined as pyrophosphate.

Aluminium.

Aluminium metal generally contains little more than one per cent. of foreign elements, so that the chief constituent is more correctly estimated by difference than by a direct determination as phosphate or in any other way.

The metal, moreover, may contain small amounts of oxide mechanically involved or in solid solution, and there does not appear to be a reliable process for the exact determination of either.

NICKEL AND COBALT ALLOYS.

FERRO-NICKEL.

The analysis of ferro-nickel is conducted as for steel. Thus carbon is determined by direct combustion, manganese by the bismuthate process, sulphur gravimetrically, phosphorus by any of the ordinary methods, and silicon by decomposing the alloy with the nitric-sulphuric acid mixture, etc.

Similarly, nickel is determined cyanometrically in a measured fraction of the filtrate from a basic acetate precipitation of the iron,

METALLIC NICKEL.

As in the case of ferro-nickel, the determination of silicon, manganese, sulphur and phosphorus is made by the methods applied to steel.

Iron.

Iron is determined by dissolving one gram of the metal in 20 c.c. nitric acid (1·20), and evaporating with 5 c.c. of sulphuric acid to thick fumes. The mass is dissolved in water and the iron precipitated with dilute ammonium hydrate. The ferric hydrate is dissolved in hot dilute sulphuric acid and a second precipitation of the iron made. The ferric hydrate is again dissolved in hydrochloric acid and the iron determined in the solution colorimetrically, or volumetrically after reduction with stannous chloride.

Nickel.

On account of the high degree of purity of commercial nickel, the difference between the sum of the percentages of the above elements and 100, may fairly be taken to represent the nickel. The possible errors incidental to the following methods of determining the nickel are greater than that calculated by difference.

(1) The combined filtrates from the ammonium hydrate precipitations of the iron are made up to a definite volume and one-tenth of the solution taken for a cyanometric assay. A silver nitrate solution containing 11·577 grams of the solid per litre, and a potassium cyanide solution containing about 9 grams per litre are used. Each cubic centimetre of the silver solution represents 2 milligrams of nickel.

(2) One-fifth of the filtrates from the iron precipitation is electrolysed, after adding 20-30 c.c. of ammonium hydrate and diluting to 150 c.c. Three hours, at a current density of 1 ampère and an electrode potential of about 3 volts, suffice for a complete deposition of the nickel.

(3) A separate sample of the metal weighing 0·2 gram, is dissolved, and the iron removed as above. The same weight of pure electrolytic nickel is treated similarly and a cyanometric assay of each solution then conducted with a strong solution of potassium cyanide and the usual silver iodide indicator.

METALLIC COBALT.

The determinations of the impurities in metallic cobalt are the same as for metallic nickel. Similarly, the percentage of cobalt is perhaps best obtained by difference, after making allowance for the small amount of nickel which is almost invariably to be found in commercial cobalt.

Nickel.

The metal is opened out as for the determination of iron in metallic nickel, and the ammoniacal filtrates from the ferric hydrate taken for the estimation of nickel. From this solution the nickel is precipitated with dimethylglyoxime, the precipitate is dissolved in hydrochloric acid and the nickel again precipitated and determined.

Cobalt.

A measured portion of the combined filtrates from the iron precipitations is electrolysed under the conditions specified for nickel. From the weight of deposit obtained the amount of nickel found as above is then deducted.

Several other methods for the direct determination of cobalt may be employed, and can easily be devised after a perusal of the section on the determination of cobalt in steel, *q.v.*

TUNGSTEN ALLOYS.

FERRO-TUNGSTEN.

Carbon.

If the alloy contains at least 50 per cent. of tungsten and not more than 2 or 3 per cent. of chromium, the carbon may be determined by simple ignition in oxygen, and poorer alloys may be similarly decarbonised at higher temperatures than ordinarily reached with a gas furnace. Very exact results are obtained from all grades of the alloy by mixing them with red lead.

Manganese.

Tungsten powders and most of the ferro-alloys contain only such an amount of manganese as is incidental to the process of manufacture, and this is usually less than 0·5 per cent. Manganese may be determined in a number of ways, of which the following yield excellent results.

(1) To one gram of the powdered alloy contained in a deep platinum dish add 10 c.c. of hydrofluoric acid, and 5 c.c. of nitric acid, a few drops at a time. Digest until the metal is dissolved, leaving a clear solution or carbonaceous matter only. Pour the solution into a mixture of 10 c.c. nitric and 2 c.c. sulphuric acid with 40 c.c. of water, add 3 grams of red lead, boil for a few minutes, repeat the addition of red lead, boil,

add quickly 200 c.c. of cold water, and filter through asbestos. Determine the permanganic acid in the filtrate volumetrically with standard ferrous sulphate and permanganate solutions.

(2) The above process requires modification if the oxidation is made with sodium bismuthate. Neither tungsten nor hydrofluoric acid separately interferes with the ordinary bismuthate process for estimating manganese, but when they are present together, the results are very erratic.

Accordingly, the solution obtained by decomposing the alloy with nitric and hydrofluoric acids should be evaporated to fumes of sulphur trioxide after adding a few c.c. of sulphuric acid. A few drops of sulphurous acid are then added in order to dissolve any manganic oxide which is apt to separate with the tungstic oxide, then an excess of 1·20 nitric acid, the mixture made up to a definite volume, and a fraction of the filtrate taken for the determination of the manganese. The amount of free sulphuric acid in the solution after adding the nitric acid should not exceed that of a normal solution.

(3) Manganese, and with it also the tungsten, iron and calcium, may be determined on one sample. A method is described below under the determination of tungsten (Method 2).

Phosphorus.

(1) To 2 grams of the powdered alloy add 10 c.c. of nitric acid and then hydrofluoric acid, a little at a time, until decomposition is complete. Add 5 c.c. of sulphuric acid and evaporate to a paste, take up in 30 c.c. of 1·20 nitric acid, boil and filter. To the filtrate add ammonium hydrate until the solution becomes red but not turbid, then 30 c.c. of the molybdate reagent and finish as usual.

The hydrofluoric acid should be tested for phosphorus and the amount of it, if present, allowed for.

The above process is not quite accurate, because the tungstic oxide residue contains more or less phosphorus, and for exact purposes should be examined as described under the determination of phosphorus in tungsten steels on p. 63. To obviate the difficulty, Gray and Smith[1] employ the following excellent method for the determination of phosphorus in ferro-tungstens, tungsten powders, and tungsten ores.

(2) Fuse 2 grams of the alloy at a low red heat with 10 grams of equal parts sodium carbonate and potassium nitrate, dissolve the melt in water and filter, washing with water containing a little ammonium nitrate. Ignite the residue in the original crucible and set aside for a time. To the filtrate add hydrochloric acid and bromine until a rich

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[1] *Chem. News,* 118. 258.

red mixture is obtained, then dilute ammonium hydrate until the tungstic oxide is just taken into solution, then a further excess of 0·880 solution equal to about one-fifth of the volume of the mixture. Precipitate the phosphorus with magnesia mixture, let stand overnight, and filter. Dissolve the precipitate in hydrochloric acid and to the solution add the insoluble residue obtained as above after extracting the original fusion with water. Add more acid if necessary to effect solution, evaporate to dryness, take up in dilute hydrochloric acid, dilute and pass sulphuretted hydrogen. Filter, evaporate the filtrate to low bulk, add 10 c.c. nitric acid, ammonium hydrate until a precipitate forms, just dissolve in nitric acid, add 3 c.c. in excess, and precipitate with ammonium molybdate.

Sulphur and Silicon..

Fuse 1 gram of the alloy at a low red heat—a spirit lamp serves well for the purpose—with 6 grams of potassium nitrate. Extract with water, add 40-50 c.c. of hydrochloric acid, evaporate to dryness, and bake for half an hour. Take up with hydrochloric acid, dilute and filter. Precipitate with barium chloride, and finish as usual. The barium sulphate should not be allowed more than 12 hours for complete precipitation, or it may contain tungstic oxide. If for any reason the filtration has been delayed too long, the filter, after being washed free from ferric chloride, is washed two or three times with dilute ammonium hydrate, and finally with water.

Silicon may be determined upon the tungstic oxide residue obtained above, by igniting and treating the ignited residue with hydrofluoric acid. An approximate determination is obtained also by treating the oxide resulting from the original roasting of the alloy with hydrofluoric and a few drops of sulphuric acid.

Tungsten.

It is not desirable always to use one and the same method for the estimation of tungsten in ferro-tungsten alloys, since variations of tungsten between 20 and 90 per cent. produce variations in the behaviour of the material towards a specific reagent. It is often necessary, moreover, to determine other constitutents on one sample. Several processes are accordingly described below.

(1) The alloy is roasted well and fused with sodium carbonate as described in method (2) for the determination of phosphorus. The mass is boiled out with water for 20 minutes, a few fragments of filter paper being added in order to decompose sodium manganate, and the oxides

of iron and manganese filtered off and washed with water containing a little sodium carbonate. The filtrate is carefully neutralised with dilute nitric acid and the tungsten precipitated with mercurous nitrate and mercuric oxide emulsion as described on p. 19. The ignited residue is examined for silica, ferric oxide, and chromic oxide, the amounts of which are determined (and deducted) as described under the estimation of tungsten in steel.

(If the mercurous nitrate solution is freshly made by adding hot water to the crystals, there is usually left undissolved sufficient basic nitrate to correct the faint acidity of the solution obtained after the addition of nitric acid to the aqueous extract of the fusion. The addition of mercuric oxide emulsion is then unnecessary. Some chemists prepare a stock solution of mercurous nitrate by dissolving 56 grams of the solid in a litre of water containing about 40 c.c. of 1·20 nitric acid. The solution is kept in a stoppered bottle containing also some metallic mercury. This reagent must obviously be supplemented by the mercuric oxide emulsion in order to obtain a complete precipitation of tungstic acid. The emulsion is made by precipitating a hot solution of mercuric chloride with potassium hydrate, allowing to settle, and washing by decantation with hot water until the washings are no longer alkaline to litmus. The yellow oxide is kept in a stoppered bottle in distilled water, and the mixture well shaken for use.)

The method may be used for alloys of all grades of richness. In the case of low grade alloys, the residual ferric oxide should be examined for tungsten. This is done by igniting at a low temperature to burn the filter, dissolving the residue in hydrochloric acid and evaporating to low bulk. On diluting with water, any tungstic oxide present is recovered by filtration and ignition.

(2) The following method provides for the determination of tungsten, silicon, manganese, iron, and lime on one sample.

Digest 1 gram of the sample, finely ground in the agate mortar after it has passed a sieve of 90 meshes per inch, with 100 c.c. of hydrochloric acid and 10 c.c. of nitric acid. (The time required for complete decomposition varies with the tungsten contents of the alloy; continued digestion for a period of 48 hours may be necessary with the more refractory alloys. The decomposition is conveniently carried out in a tall unlipped beaker, covered with a glass, and at a temperature below the boiling point of the acid mixture. There is thus very small loss of acid strength throughout the decomposition.) Evaporate to a paste, take up in dilute hydrochloric acid (1 to 4), boil and filter off tungstic oxide and silica. Determine these as usual. Precipitate the iron from the filtrate by making a basic acetate separation, and determine the iron if necessary by re-dissolving the precipitate in hydrochloric acid, reducing with stannous chloride, and titrating with potassium bichromate. Remove the manganese in the filtrate from the iron precipitate by means of hydrogen sulphide after making alkaline, re-dissolve the manganese sulphide in dilute nitric acid and determine the manganese by the bismuthate method. Precipitate the lime in the filtrate from the sulphide precipitation, after expelling the excess of dissolved gas and filtering from any sulphur which separates, by means of ammonium oxalate, and finish by igniting to oxide.

(3) Cover one or two grams of the powdered alloy in a tared platinum dish with hydrofluoric acid and add strong nitric acid, a little at a time, keeping the basin covered as much as possible. When further addition of nitric acid causes no energetic attack of the metal, as may happen with highly chromiferous alloys when a considerable portion is undecomposed, then add 10 to 15 c.c. strong sulphuric acid and allow to digest until decomposition is complete.

The solution may now be treated in a rapid or a slow way. If the result is required without delay, wash the platinum cover and arrange the basin on a sheet of perforated asbestos millboard over a lighted bunsen with a rose burner, so that after a time it would boil briskly if left to itself. Then rotate the basin with one hand, and with the other direct a continually shifting stream of air on to the surface of the liquid so as to prevent the loss which would otherwise occur through the bursting of bubbles. This operation must be continued with increasing vigilance until dense fumes of sulphuric anhydride are given off and the precipitated tungstic oxide, at first white, becomes yellow. When this point is reached—*i.e.* in five or ten minutes—cool the basin in water, add dilute hydrochloric acid (1 to 5), and boil so as to bring all the iron, (and if present in considerable amounts) manganese, and chromium into solution.

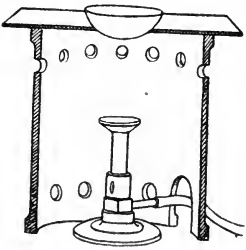
FIG. 14.

The slower, but more pleasant means of reaching the same stage, is to arrange a basin over a bunsen burner, in some such fashion as is suggested by the sketch (Fig. 14) that it may be left evaporating over night. A trial is needed to show the size of flame to be provided, in order completely to expel the hydrofluoric and nitric acids by the following morning, without causing too great an evaporation of the sulphuric acid. In this way the tungstic oxide separates on the surface and falls to the bottom of the basin in flakes, which are very easily filtered and washed.

After the evaporation, the dish is covered on the inside by a film of tungstic oxide of rainbow hues, which cannot be removed by rubbing. This film frequently weighs from ten to fifteen milligrams, so that it can by no means be disregarded. But if the platinum dish is tared before weighing the powder into it, the film need not be removed, as the dish is not in the least attacked by the operation.[1] Collect the precipitate then on a pulp filter, wash well, and return to the dish and ignite. There is, of course, no silica with the tungstic oxide; there may be, however, and generally is, a little ferric oxide, which is determined by fusion with sodium carbonate, etc., and deducted.

Chromium.

This element may be incidentally present in ferro-tungstens, but it is often purposely added in large amounts to such alloys, which are sold for the manufacture of self-hard steels. The determination of chromium is easily made by fusing the finely-divided alloy with sodium peroxide, lixiviating with water, diluting to a measured volume, and filtering off a fraction of the liquid. The filtrate is boiled well to decompose any excess of peroxide, acidified with sulphuric acid, and titrated with ferrous ammonium sulphate and potassium permanganate. Tungstic oxide, which may separate out on acidification, need not be filtered off.

Tin.

Rich alloys are opened out with nitric and hydrofluoric acids as described in Method 3 for the determination of tungsten; low grade alloys are decomposed by means of hydrochloric acid and bromine or potassium chlorate. The tungstic oxide obtained in either case from 2 or 3 grams of the alloy is filtered off and the tin determined in the filtrate. This may be done by precipitating it as sulphide and either converting to oxide or re-dissolving, reducing with antimony, and titrating with standard iodine solution. The latter method may be applied directly to the solution without separating the tin and iron. To do this, add hydrochloric acid in amount sufficient to constitute about one-third of the total volume of the solution, and then about one gram of antimony which has been prepared by grinding the fused metal in an agate mortar until the powder is free from glistening

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[1] The acids used must be free from chlorides.

particles. Boil vigorously for about two minutes, cool off rapidly under the water tap whilst a brisk current of carbon dioxide is passed through the solution, add a piece of white marble, and titrate as quickly as possible with standard iodine solution.

TUNGSTEN POWDER.

A complete analysis of commercial tungsten powder is a matter of considerable difficulty, and for technical purposes is never made.

The assay for tungsten of the high-grade powders used for steel-making can be made rapidly by the following process. The results are not accurate, but do not vary more than 0·5 per cent. from the correct percentage. The error is most commonly a positive one.

Weigh three grams of the powder and spread it in a thin layer over the bottom of a shallow platinum dish. Heat in the muffle at a low temperature at first, and later at a full red heat to constant weight. The colour of the oxidised sample is yellow in the case of powders of high quality—a green colour is indicative of the presence of sodium tungstate. When completely oxidised, allow to cool, moisten the mass with hydrofluoric acid, evaporate, ignite strongly, and weigh. Add water to half fill the basin and about 5 grams of pure sodium hydrate, heat to boiling and transfer to a beaker. Boil until a brown precipitate only remains undissolved, dilute to about 300 c.c., and allow the precipitate to settle. Filter through pulp, clean the dish with hydrochloric acid, precipitate the small quantity of iron in the solution thus obtained with ammonium hydrate, and collect the ferric hydrate on the same filter. Wash well, ignite and weigh. Dissolve the ignited precipitate in 10 c.c. of hydrochloric acid, boil until tungstic oxide begins to separate, add 40 c.c. of hot water, boil, and filter off the tungstic oxide. Deduct the weight obtained from the weight of the residue previously found. The difference, subtracted from the weight of the roasted sample after treatment with hydrofluoric acid, gives the weight of oxide equivalent to the total tungsten in the powder. Thus :—

Weight of dish, - - - - - - - -	22·9400......(1)
Ditto + 3 grams powder after HF treatment, -	26·4823......(2)
Residue insoluble in caustic soda, -	0·0703......(3)
Oxide from hydrochloric acid solution, -	0·0400......(4)
(3) – (4), - - - - - - - -	0·0303......(5)

$$\begin{array}{rl} (2)-(1) & = 3{\cdot}5423 \\ (5) & = \underline{0{\cdot}0303} \end{array}$$

$$3{\cdot}5120 \times \frac{{\cdot}7931}{3} = 92{\cdot}8 \text{ per cent. tungsten.}$$

COMPLETE ANALYSIS.

Carbon.

Ignition in a stream of oxygen yields all the carbon as carbon dioxide. It varies from traces up to several units per cent., and in the latter cases consists principally of free carbon.

Manganese.

Manganese is best determined in the insoluble residue of metallic oxides left after roasting the powder, fusing with sodium carbonate, and boiling out the melt with water. The oxides are collected, washed with water containing a little sodium carbonate, ignited, dissolved in hydrochloric acid, the solution taken to fumes with sulphuric acid, the residue dissolved in dilute nitric acid, and the bismuthate method applied.

Phosphorus and Sulphur.

As in ferro-tungsten alloys.

Water.

When lime is present in a tungsten powder, there is always water also, which is not expelled by heating at 100° C. It may be determined by heating to redness in a stream of dry air, and absorbing in a weighed calcium chloride tube. An approximate method, due to Richards, consists in heating the powder in a closed tube drawn out at one part so as to drive the water beyond the constriction. The tube is then broken at the narrow part, weighed, dried and weighed again.

Sodium Tungstate.

Three grams of the powder are boiled with 100 c.c. of water containing a little ammonium nitrate, the solution poured off through a pulp filter and the treatment repeated upon the residue. The combined filtrates are then adjusted to faintest acidity with nitric acid and the tungstic acid precipitated with mercurous nitrate. The weight of WO_3 obtained after ignition, multiplied by 1·267, gives the weight of sodium tungstate (of the formula Na_2WO_4) in the sample. It is probable that Na_2WO_4 does not correctly represent the soluble sodium tungstate in tungsten powders; ordinary sodium tungstate crystals have the composition, $Na_{10}W_{12}O_{41} \cdot 28H_2O$. The value obtained above is therefore reliable only when the results are expressed in terms of WO_3.

Tungstic Oxide.

In addition to sodium tungstate, tungsten powders may contain oxide, existing as WO_3 or in a less oxygenated form. The lower oxides are betrayed by the blue colour obtained by boiling powders containing them with water. There does not appear to be a reliable method for the determination of the exact amount of these substances, and the following process takes account of tungstic oxide only, lower oxides which may be affected by it being calculated as WO_3.

Three grams of powder are digested for a few minutes with 30 c.c. of hydrochloric acid, the mixture being agitated at frequent intervals. The liquid is strained off through a pulp filter and evaporated, with the aqueous washings of the filter, to low bulk. The tungstic oxide which separates out is collected and weighed. The residue is boiled for 10 minutes with 50 c.c. of 2N sodium hydrate solution, the liquid filtered off and the sodium tungstate in it determined by a ‘ mercury precipitation.’ From the sum of the weights of tungstic oxide obtained by these two extractions, the amount found by an aqueous extraction (as described above for the determination of sodium tungstate) is deducted, and the difference taken as ‘ tungstic oxide.’

The above process cannot be claimed to be exact, though the belief that metallic tungsten is considerably attacked by dilute caustic alkali rests upon questionable evidence. A powder, *e.g.*, was boiled four times successively with 2N sodium hydrate after the above treatment, and the solutions contained respectively 0·006, 0·0043, 0·0034 and 0·0028 grams of tungstic oxide. These additional amounts, representing percentages of 0·20, 0·14, 0·11 and 0·09 may be due to the action of the alkali on the metal, or upon oxides not previously removed, or more probably to both causes.

Tungsten.

The total tungsten is determined by the methods described for ferro-tungsten, of which the first and third are much better than the second, because it is difficult to effect complete decomposition of the powder with a mixture of hydrochloric and nitric acids. The author prefers Method 3, though the first provides a means of determining the following constituents.

Silica, Alumina, Iron, and Lime.

Roast 0·5 gram of the powder in the muffle to constant weight, and treat the residue with hydrofluoric and sulphuric acids in order to determine the silica. The value found needs correction when the powder contains lime, which will obviously be weighed as calcium sulphate. Fuse with sodium carbonate, extract with water, filter, wash with water containing a little sodium carbonate, and pass a current of carbon dioxide through the filtrate. Filter off the precipitate of aluminium hydrate (or basic carbonate), dissolve it in acid and add the solution to that obtained by dissolving the ferric oxide residue similarly. Precipitate iron and aluminium with ammonium hydrate, filter, re-dissolve and re-precipitate. Determine the metals by the customary methods, and also the calcium in the combined filtrates. Calculate the calcium found to calcium sulphate in order to correct the silica determination.

Tungsten is determined in the alkaline filtrate from the iron, etc., by the mercurous nitrate method.

Tungsten Bronzes.

Tungsten powders almost invariably contain small quantities of crystalline bodies of a purple, red and sometimes a yellow colour. They are known as tungsten bronzes and consist of acid tungstates of sodium—the purple red compound is $Na_2W_3O_9$ and the brownish red $Na_4W_5O_{15}$. Potassium and lithium bronzes are also known.

The red crystals are exposed by boiling a tungsten powder with sodium hydrate solution, and may be partially separated by this treatment of that part of a powder which is retained on a 60-mesh sieve. After boiling with sodium hydrate, the residue is washed well and then digested for a short time with a mixture of nitric and hydrofluoric acids, which speedily dissolves all the metallic tungsten and also some of the bronze crystals. The latter are then washed and boiled once more with sodium hydrate. They consist of cubes and tetrahedra, with a specific gravity of about 7·3.

The above furnishes only an approximate separation from the metallic tungsten of a tungsten powder, and there does not appear to be a satisfactory method of effecting a complete separation. An approximate measurement of the amount of bronze in a tungsten powder is furnished by the following treatment.

Dissolve 2·5 grams of the powder in a large platinum dish with nitric and hydrofluoric acids, and evaporate slowly, after adding sulphuric acid, in order to decompose the bronze completely. After fuming, extract as for a determination of total tungsten, filter, add to the filtrate ammonium hydrate and a little ammonium oxalate and filter off iron, aluminium and calcium precipitates. Evaporate the filtrate to dryness, expel ammonium salts, and weigh the residual sodium sulphate. From the amount of alkali thus determined deduct the equivalent of the soluble sodium tungstate and calculate the remainder to tungsten bronze. The purple red $Na_2W_3O_9$ contains 6·20 per cent. and the brown $Na_4W_5O_{15}$, 7·35 per cent. of sodium.

Tin.

Determine as in high-grade ferro-tungsten.

Specific Gravity.

A knowledge of the specific gravity of a tungsten powder is a useful piece of information, because of the large difference between the density of the metal and the associated impurities. Tons of powder were at one time bought at a price determined by the following rough test. A narrow graduated tube was filled with water to a mark, the powder added and the mixture well shaken. The level having been read, a calculation of the specific gravity was made, or, more often, the volume compared with that of a good standard sample similarly treated.

The specific gravity is readily obtained by the ordinary method used for powdered solids. A 25 c.c. specific gravity bottle is filled with distilled water, the temperature noted, and the bottle weighed. Five grams of the powder are introduced into the emptied bottle, water added, boiled for a minute or two, and the mixture cooled to the original temperature. After filling up with water, the weight is again obtained. The following is a typical result obtained in this way:

Weight of metal in air, - - - -	5·0000	grams.
Weight of bottle full of water, - - -	46·2454	,,
Weight of bottle containing powder and water,	50·9230	,,

From these figures, the weight of water equal in volume to that of the tungsten powder is

$$51{\cdot}2454 - 50{\cdot}9230 = 0{\cdot}3224 \text{ grams.}$$

and

$$\text{spec. grav.} = 5 \div 0{\cdot}3224 = 15{\cdot}45.$$

MOLYBDENUM ALLOYS.

FERRO-MOLYBDENUM.

Alloys of iron and molybdenum which are used in modern steel-works' practice contain 80 per cent. and upwards of molybdenum. As they are readily decomposed by the ordinary acids or acid mixtures, the determinations of the minor constituents are similar to those employed in the analysis of steel.

Carbon.

Mix the powdered alloy with red lead and burn in a current of oxygen.

Silicon.

Determine silicon exactly as in steel.

Manganese.

If manganese is estimated by precipitation with bromine and ammonium hydrate after making an acetate separation of the iron, the results are accurate. Unless a large excess of ammonium acetate is used in precipitating the iron, nearly all the molybdenum is in the precipitate. The chlorate process yields low results, which are improved, however, by using larger amounts of potassium chlorate for oxidising. The bismuthate process is not suitable for the determination of manganese in molybdenum steels and alloys.

Sulphur.

The gravimetric estimation of sulphur is accurate if the barium chloride is added to a solution containing more free acid than usual, in order to prevent contamination of the barium sulphate with molybdate. The evolution processes, *i.e.*, the dissolution of the metal in hydrochloric acid and passage of the evolved hydrogen sulphide through absorbents, appears also to be uninfluenced by the presence of molybdenum. Low results might be expected on account of the possible precipitation of molybdenum sulphide in the evolution flask, but this does not seem to be so when strong acid is used for the decomposition.

Phosphorus.

The yellow ammonium phospho-molybdate precipitate is frequently contaminated with molybdic acid, and the determination as lead molybdate or by a volumetric process cannot therefore be applied without some modification of the ordinary procedure. The simplest way is to filter off the yellow precipitate, wash, dissolve in ammonium hydrate, acidify with nitric acid, and make a second precipitation.

Iron and Aluminium.

Precipitated from solutions containing molybdenum by means of ammonium hydrate, ferric and aluminium hydrates always contain more or less molybdenum, and cannot therefore be filtered off and weighed. Neither can the iron be determined by dissolving the alloy, even when the latter contains little or no carbon, in hydrochloric acid, and titrating the ferrous chloride, because molybdenum then exists in the solution as a salt of the sesquioxide. For this reason also, ferric solutions containing molybdenum should not be reduced with stannous chloride or metallic zinc. The amount of molybdenum reduced by sulphur dioxide, however, is very small or nil when the solution contains sufficient free acid, and the ferrous salt may be accurately titrated by means of dichromate or permanganate. The determination of both metals in the same solution is described on p. 18, and is referred to again below.

To determine aluminium, the precipitate obtained with ammonium hydrate should be dissolved in a little brominised hydrochloric acid, the excess of bromine expelled, and the molybdenum precipitated from the diluted solution as sulphide. The filtrate is boiled, a few drops of nitric acid added, and the iron and aluminium re-precipitated, and determined by the usual methods.

Molybdenum.

(1) Decompose 0·5 gram of the alloy with hydrochloric and nitric acids, add 10 c.c. of sulphuric acid and evaporate to fumes. Dilute, boil to dissolve all but silica and filter. Make up the filtrate to 500 c.c. and take 200 c.c. for the determination of iron and molybdenum. Add to the solution 50 c.c. of saturated sulphurous acid, warm for a few minutes, and then vigorously boil the liquid until the excess of sulphur dioxide is removed. If the solution is blue, there has been a slight reduction of the molybdic acid due to too little free sulphuric acid, but the estimation may be carried on. Cool somewhat, and titrate with decinormal permanganate, noting carefully the amount required to discharge the blue colour. This should not exceed 0·2 c.c. The amount is deducted from the final reading and the difference determines the iron. The titrated solution is then passed through the Jones reductor, as described on p. 15, into ferric alum and a second titration made.

The above method provides an excellent means of valuing an alloy for steel-making purposes, and, indeed, is all that is necessary in the analysis of modern high-grade alloys which are almost carbonless, and contain no elements which are reducible by sulphur dioxide or nascent hydrogen.

(2) Decompose 0·5 gram of the alloy with hydrochloric and nitric acids and run the hot solution from a tap funnel into an excess of hot sodium hydrate. Make up to a definite volume and filter off a portion.

Determine the molybdenum by precipitation as molybdate of lead as described on p. 142; a repetition of the precipitation is necessary.

(3) Decompose the alloy as in (1), and remove the silica. Take a portion of the filtrate representing 0·1 gram of the alloy, add ammonium hydrate in excess and pass a current of hydrogen sulphide to saturation. Digest until the ferrous sulphide (and aluminium hydrate) flocks out, filter, and wash the precipitate with water containing some ammonium sulphide. To the filtrate containing ammonium sulpho-molybdate add dilute sulphuric acid, stirring continuously. Digest at boiling point until hydrogen sulphide is completely expelled, collect the sulphide of molybdenum and finish as described on p. 143.

The precipitation of molybdenum in this manner is usually complete. An incomplete precipitation is betrayed by a blue colour in the filtrate, which should be 'gassed' again.

MOLYBDENUM POWDER.

Carbon.

Determine by direct combustion, using red lead.

Molybdenum.

For the estimation of the chief element the powder may be mixed with sodium carbonate and potassium nitrate, placed in a platinum crucible under a layer of sodium carbonate, and heated over the blowpipe flame until decomposed. The bottom only of the crucible should be heated to redness, so as to prevent loss of molybdic oxide by volatilisation. The mass is extracted with water, and the molybdenum determined in a portion of the filtrate from the insoluble oxides by precipitation as lead molybdate.

Alternatively, the powder may be decomposed with aqua regia, any insoluble residue being collected, dried, fused with sodium carbonate and a small quantity of sodium peroxide, and the aqueous extract of the fusion added to the main solution. The mixture is evaporated to dryness and silica removed, also tungsten if present. The filtrate from the silica is made up to a definite volume and portions taken for the estimation of molybdenum, iron, aluminium, sulphur, etc. A double precipitation with ammonium hydrate is sufficient to separate the small amounts of iron and aluminium from the molybdenum.

Oxygen.

The best molybdenum powders are dark grey in colour and anhydrous: black varieties often contain combined water. Besides the metal itself, molybdenum powders may contain more or less oxide. The oxides of molybdenum known for certainty are Mo_2O_3, MoO_2, and MoO_3. The blue colour of partially reduced molybdenum solutions is usually attributed to the formation of Mo_3O_8, though this oxide has apparently not been isolated. By simply shaking a sample of an inferior molybdenum powder with water, the solution is coloured blue, but there is no simple method for identifying all the other oxides. The amount of MoO_3 may be approximately determined by boiling the powder with sodium hydrate solution, in which the metal and the oxides Mo_2O_3 and MoO_2 are practically insoluble. The metal itself and the oxide MoO_2 reduce ammoniacal silver solutions quantitatively, and from the weight of silver obtained, the amount of oxide could be calculated in a mixture of it with the metal.

From the above it appears that a complete analysis of a molybdenum powder is invested with very great difficulties ; in works' practice it is not attempted. Fortunately, modern powders are of a high degree of purity, and, moreover, may be replaced in the manufacture of molybdenum steels by the high-grade ferro-molybdenum alloys.

VANADIUM ALLOYS.

FERRO-VANADIUM.

Vanadium is used in steel-making in the form of an alloy with iron containing from 35 to 40 per cent. of vanadium—poorer or richer alloys are comparatively uncommon. Ferro-vanadium should be examined for copper, aluminium and arsenic, in addition to the usual constituents of ferro-alloys.

Carbon.

This element is generally determined by direct ignition of the alloy in a current of oxygen. The alloy is also readily decomposed by a solution of cuprammonium chloride, a portion of the vanadium remaining with the carbonaceous residue.

Silicon and Sulphur.

These elements are estimated in the same sample after decomposition with aqua regia. The solution from which the precipitation as barium sulphate is made should be more acid than usual, in order to prevent the precipitation of vanadium as barium vanadate.

Manganese.

The bismuthate process as worked for steels gives good results, but particular care must be taken to oxidise completely the carbonaceous matter in the hot initial solution, so that the slow oxidation of vanadyl sulphate and not the unoxidised carbon is accountable for the permanganate used in the titration of the cold solution.

The gravimetric estimation of manganese as oxide after a basic acetate separation of the iron is somewhat troublesome. There is considerable uncertainty in the 'neutralisation,' owing to the formation of a basic ferric vanadate of a light brown colour, which may not contain the whole of the iron. When a pronounced precipitate rather than a turbidity is formed, the solution should be heated to boiling point, and the precipitation of the iron made with as little ammonium acetate as possible. To accomplish this, the precipitate obtained by the addition of a few drops of acetate should be allowed to settle, and the supernatant liquid examined. If the solution is still coloured, more acetate is added, the mixture boiled and again allowed to stand. The operations are repeated if necessary until the precipitation is apparently complete. In this way nearly all the vanadium is precipitated as a basic ferric vanadate instead of passing into the filtrate.

Note.—Conversely the separation of iron and vanadium by repeated acetate precipitations depends upon the addition of *large* amounts of acetate, so as to bring about the formation of basic acetates of iron in preference to basic vanadates. Under the best conditions the separation is unsatisfactory.

Aluminium and Copper.

Pour 60 c.c. of hot sulphuric acid (1 to 5) over two grams of the powdered alloy contained in a flask, and keep at boiling point, with a small exit for steam, until the sample is decomposed. Filter off and wash the residue. The filtrate may contain a little copper, together with practically all the iron and aluminium, and some of the vanadium. (The lower the carbon content of the alloy, the more the vanadium passes into solution.) Pass hydrogen sulphide through the diluted solution, collect any precipitated copper sulphide and reserve it. Boil off the excess of hydrogen sulphide from the filtrate, add sodium phosphate and then dilute ammonium hydrate until a precipitate just forms. Clear the solution with hydrochloric acid, dilute largely, add 10 grams of sodium thiosulphate, 20 c.c. of acetic acid, and then boil, filter, and wash as in the estimation of aluminium in steel. Dissolve the ignited phosphate of aluminium, which contains iron and vanadium, in hydrochloric acid, and re-precipitate it, thus removing iron. To eliminate vanadium, dissolve the residue once more in acid, and to the solution, which is coloured if much vanadium is present, add one gram of sodium phosphate and sodium peroxide until the reddish brown colour of pervanadic acid is fully developed. Make alkaline with ammonium hydrate, boil, allow to settle, filter and wash the precipitate of aluminium phosphate. Set the filter and precipitate to digest in dilute hydrochloric acid, and in the meantime acidify the filtrate strongly and boil to decompose the pervanadic acid and excess of hydrogen peroxide. Make alkaline with ammonium hydrate and boil again. If no precipitate is obtained, reject the solution. If a precipitate does form, collect and wash it, pour over it the hydrochloric acid solution of the main precipitate and wash thoroughly. Finally, re-precipitate the aluminium by means of sodium phosphate and thiosulphate. The ignited precipitate should now be quite white, and contain not more than a trace of vanadium.

The residue which was left on opening out the alloy with sulphuric acid contains most of the copper and some vanadium. It is ignited, the residue dissolved in hydrochloric acid, silica filtered out, and the filtrate 'gassed' with hydrogen sulphide. The copper sulphide is collected on the filter previously used for the same purpose, and the determination of the copper made as described for steels on p. 95.

Arsenic.

Samples of ferro-vanadium containing arsenic are occasionally encountered. The presence of this element is often revealed in the determination of vanadium by the second method described below.

For the determination of arsenic, the alloy is opened out with nitric acid, the solution evaporated to dryness and the residue baked. After dissolving up in cold hydrochloric acid, the solution is saturated with hydrogen sulphide, and the sulphides of arsenic and copper, together with free sulphur and silica, filtered off and washed. Arsenic sulphide is dissolved out of the mixture by digesting with sodium sulphide, re-precipitated, and the determination made volumetrically as described on p. 97.

Phosphorus.

Johnson's method for the determination of phosphorus in vanadium steels, described on p. 65, is applicable to ferro-vanadiums after a preliminary separation of most of the vanadium. For this purpose, 0·5 gram of the alloy is decomposed in a porcelain dish with a mixture of equal volumes of hydrochloric and nitric acids, the solution digested for an hour, 100 c.c. of nitric acid added and the mixture taken to dryness. The residue is baked on the hot plate for some time and finally heated in the muffle for five minutes at about 750° C. The residue is dissolved in hydrochloric acid, the solution evaporated to 10 c.c., 50 c.c. of nitric acid added, the liquid again evaporated to 10 c.c., and a further 10 c.c. of nitric acid added. The vanadium pentoxide which separates out is then filtered through asbestos and washed well with a mixture of 200 c.c. nitric acid, 100 c.c. water, and 20 grams of ferric nitrate. The filtrate is concentrated to 10 c.c. and vanadium pentoxide again filtered out. The filtrate is again evaporated to 10 c.c., 40 c.c. of nitric acid added, the liquid heated to boiling and the phosphorus precipitated with the feebly alkaline solution of ammonium molybdate.

Ferric nitrate for the washing mixture is made by dissolving Swedish bar iron in hydrochloric acid and evaporating twice with nitric acid to a syrup.

Vanadium.

1. **Without Separation of Iron.**—The determination of small amounts of vanadium, as in the analysis of steel, for example, by adding an excess of standardised ferrous sulphate to the solution containing the vanadium as vanadic acid and titrating with permanganate until a fleeting pink tinge appears, is not sufficiently accurate in the present case. The flash of colour marks the point at which the excess of ferrous iron has been oxidised whilst the vanadyl sulphate still remains unattacked, and it is obviously more transient when large amounts of vanadium are present in the solution. On the other hand, the determination of vanadium by adding ferrous sulphate until a spot test with ferricyanide gives a blue colour, or by adding an excess of the ferrous salt and titrating back with permanganate or dichromate, or by measuring the amount of permanganate necessary to the formation of a permanent pink tinge from the point at which ferricyanide gives no blue colour, is sufficiently accurate in any one of these modifications of Lindemann's process.

Dissolve, therefore, 0·5 gram of the powdered alloy in 20 c.c. of dilute sulphuric acid (1 to 5) with the addition of a little nitric acid to complete the decomposition and oxidise the iron, and also a little permanganate to oxidise carbonaceous matter. After boiling, dissolve the precipitate of manganic oxide with a few drops of ferrous sulphate solution, and cool. To the cold solution add permanganate in drops so as to make certain that the vanadium is fully oxidised; *if* the pink colour disappears add more permanganate until it persists. Now run in standardised ferrous ammonium sulphate solution from a burette until a spot test with ferricyanide gives an immediate blue colour.

$$1 \text{ c.c. } \frac{N}{10} \text{ solution} = 0{\cdot}0051 \text{ gram vanadium.}$$

Confirm the determination by adding a few c.c. of the ferrous solution to the titrated solution, and again titrate with permanganate until the spot test with ferricyanide yields no blue colour immediately upon being taken; read the burettes again. Lastly run in permanganate until a permanent pink colour is formed, and note the amount required.

2. **With Previous Separation of Iron.**—Mix 0·5 gram of the finely ground alloy with 10 grams sodium carbonate and a few decigrams of permanganate. Fuse the mixture thoroughly over a powerful burner or by heating to bright redness in the muffle for half an hour. Extract with water, filter off the oxides of iron and manganese and wash with water containing a little sodium carbonate. Reserve the filter and residue. Acidify the filtrate with dilute sulphuric acid, adding a few cubic centimetres in excess, reduce the vanadic acid by means of 20-25 c.c. of sulphurous acid, boil off the excess of sulphur dioxide, and titrate at 70° C. with decinormal permanganate.

Confirm the result by passing the titrated solution through the Jones reductor into ferric alum as described on p. 15, and again titrating at 70° C. (The end point is 'sharpened' considerably by the addition to the solution of a few cubic centimetres of syrupy phosphoric acid.) After deducting the small blank incidental to the process (about 0·2 c.c.), the amount of permanganate used should be three times that recorded in the first titration.

This result is always obtained from the best quality alloys, which need not then be examined for such impurity as arsenic. When this element is present in more than traces, the first permanganate reading is obviously too high. The second reduction eliminates the arsenic from the solution in the form of the gaseous hydride, and the error induced becomes serious. Fortunately the occurrence of arsenic in ferro-vanadium is rare.

The insoluble residue from the aqueous extract of the fusion always contains a small quantity of vanadium, representing a few tenths per cent. It is ignited, the residue dissolved in hydrochloric acid and the solution taken to fumes with sulphuric acid. The amount of vanadium is then determined colorimetrically by the peroxide test, and the solution may afterwards be utilised for the determination of iron.

Iron.

The solution is boiled to expel excess of hydrogen peroxide, neutralised, reduced with sulphur dioxide and titrated with permanganate, a deduction being made from the burette reading of the small amount due to the vanadium previously found.

Rapid Evaluation of Ferro-Vanadium.

Vanadium, iron, and silicon constitute as much as, or more than 99 per cent. of the best quality alloys, which are invariably of very low carbon content. The three elements mentioned may be determined rapidly and conveniently on one sample by the following operations.

Decompose 0·25 gram of the alloy with 10 c.c. of nitric acid (1·20), add 3 c.c. of sulphuric acid, and evaporate to copious fumes of sulphur trioxide. Extract with hot water, filter off the silica, wash, dry and ignite. If the ignited residue is discoloured, determine the silica in it by volatilisation with hydrofluoric and nitric acids, as described on p. 20. A small residue, red in colour, and weighing not more than one or two milligrams, may be left; it is vanadium pentoxide.

The filtrate from the silica is assayed for iron and vanadium by reducing first with sulphurous acid and afterwards with nascent hydrogen exactly as described on p. 18.

FERRO-TITANIUM.

Ferro-titanium is used principally as an agent for the removal of nitrogen and oxygen from steel, for which purpose it is added to the molten metal. The finished steel rarely contains more than traces of the element.

Carbon.

Many of the alloys contain little or no carbon at all. Those which do are easily decarbonised, with or without mixing with red lead, by direct combustion in oxygen.

Manganese.

Decompose the alloy with nitric acid (1·20) with the addition, if necessary, of a few drops of hydrofluoric acid. Determine the manganese in the solution by the bismuthate process.

Sulphur.

As the alloy is usually soluble in hydrochloric or sulphuric acid, sulphur may be determined by one or other of the evolution methods described for steels, unless, as in some cases, the alloy contains copper also. For the gravimetric determination, ferro-titanium may be decomposed with potassium chlorate and hydrochloric acid. After boiling off excess of chlorine, the solution is diluted and made faintly alkaline with ammonium hydrate, the precipitate filtered out and washed, and the filtrate, after acidification, treated with barium chloride. The precipitate contains the iron, titanium, aluminium, and phosphorus, and may be used for the estimation of one or more of these elements.

Copper.

As much as 5 or 6 per cent. of copper is found in some varieties of the commercial alloy. Decomposition with hydrochloric or sulphuric acid and separation of the copper as sulphide leads readily to an iodometric determination of the element, after separating the small amount of iron which accompanies the copper sulphide.

Titanium, Silicon, and Iron.

One of the readiest means of opening out the alloy for the determination of any one of these constituents is by fusion with acid potassium sulphate. Ten grams of the salt are fused in a large platinum crucible, the melt allowed to solidify, and half a gram of the powdered alloy sprinkled over the surface. The mixture is then heated over a bunsen flame and stirred well with a stout platinum wire until no gritty particles can be felt. The wire is left to cool with the fused mass so that on adding water the whole melt may be lifted by it from the crucible. About 10 c.c. of sulphuric acid are added and the mixture heated until nothing but siliceous flakes remain undissolved. The silica is filtered off and determined by loss on treatment with hydrofluoric acid, any residue being then warmed with more sulphuric acid and the liquid added to the main solution. The latter is made up to a definite volume and fractions taken for the subsequent determinations.

Iron is determined in one portion, after reduction with sulphur dioxide, by titrating with permanganate.

The remainder, or portion of it, is neutralised, made slightly acid again, and the titanium precipitated by means of sodium sulphite or thiosulphate. The titanic oxide obtained after ignition of the precipitate may contain aluminium, which is separated and estimated as described on p. 158.

The alloy may also be opened out with a mixture of nitric and hydrochloric acid and the solution evaporated to fumes after adding 10 to 15 c.c. of sulphuric acid. After cooling, a few cubic centimetres of hydrochloric and 100 c.c. of water are added, and the mixture boiled. Silica is filtered out and determined, and the filtrate treated as above with the substitution of potassium dichromate for permanganate in titrating the iron.

Phosphorus.

One gram of the alloy is fused with a mixture of sodium carbonate and potassium nitrate, the melt extracted with hot water and the solution filtered. The filtrate is acidified and tested for aluminium by adding ammonium hydrate until a precipitate is just obtained so as to decide whether it is advisable to make the aluminium-titanium separation mentioned above. In any event, the mixture is made acid again, a solution of ferric nitrate obtained by dissolving 0·1 gram of bar iron in dilute nitric acid added, and then ammonium hydrate to alkalinity. The precipitate is collected, washed, re-dissolved in nitric acid, ammonium hydrate added until the solution becomes red, and the phosphorus precipitated with the molybdate reagent.

FERRO-URANIUM.

The analysis of ferro-uranium alloys is not invested with difficulties, since the material is readily decomposed by mineral acids or mixtures of them.

Carbon.

Ignition of the finely-powdered alloy, mixed with red lead, in a current of oxygen completely decarbonises these alloys.

Silicon.

A mixture of nitric and sulphuric acids opens out the alloy readily. Alloys rich in carbon do not, however, yield a residue of pure silica, and volatilisation with hydrofluoric acid is necessary.

Manganese, Sulphur, and Phosphorus.

Manganese is determined by opening out with a mixture of nitric and sulphuric acids and applying the bismuthate process to the solution. For the determination of sulphur, the ordinary gravimetric process is suitable, except for the fact that the siliceous residue, left after evaporating the original solution to dryness and baking the residue, may contain a little sulphur. After volatilisation with hydrofluoric acid, therefore, the residue is dissolved in a few drops of hydrochloric acid and the solution added to the main bulk before precipitating with barium chloride. Phosphorus is determined by opening out with aqua regia, evaporating to dryness and baking, taking up with 1·20 nitric acid and a little hydrochloric. The siliceous residue is filtered off and treated as in the determination of sulphur, any residue dissolved and added to the main solution. The latter is then treated with ammonium hydrate until a permanent precipitate is obtained, which is then dissolved in a few c.c. of nitric acid, and the phosphoric acid precipitated and determined as usual.

Uranium and Iron.

Uranium may be determined by any one of the methods indicated in Part II. For example, a basic acetate separation of the iron, conducted on the filtrate from a silicon determination, provides a filtrate suitable for the estimation of the uranium as phosphate. Similarly, the iron may be removed by running the nearly neutralised solution into an excess of sodium carbonate and the uranium determined in the same way.

Finally, the fact that uranyl sulphate is not reduced by sulphurous acid, and is very readily reduced by zinc in acid solutions, renders the determination of iron and uranium on one and the same sample very easy. This, together with a determination of the carbon and silicon contents of the alloy, generally constitute all that is required for practical purposes.

ZIRCONIUM ALLOYS.

In point of their zirconium content, the alloys of this metal with iron and aluminium vary greatly. They may contain as little as 20 or as much as 70 per cent. of zirconium. They usually contain little or no carbon, less than 1 per cent. of manganese, but the silicon and aluminium contents are high, as will be seen from the following typical analysis:—Zirconium, 59·26, Iron 4·02, Aluminium 25·20, Silicon 10·91, Manganese 0·52.

The best methods of opening out these alloys are by way of a fusion. Sodium hydrate, sodium peroxide, and potassium nitrate are not so satisfactory as sodium carbonate alone, or a mixture of it with potassium nitrate. By far the best method of decomposition is a fusion with acid potassium fluoride, though the determination of silicon in then obviously impossible.

Silicon.

Fuse 0·5 gram of the finely divided alloy for 30 minutes with sodium carbonate, boil out with water, and filter off ferric oxide and basic carbonate of zirconium, washing with water containing some sodium carbonate. Determine silica in the filtrate by the ordinary process.

Zirconium, Aluminium and Iron.

The following method was found by the author and F. W. Gray to give excellent results.

0·25-0·5 gram of the alloy is placed on the top of 2 grams of acid potassium fluoride contained in a platinum dish or capacious crucible. The dish is placed in front of the muffle until water is expelled from the fluoride and then just inside for 15 minutes in order to roast the alloy. By holding the crucible in a bunsen flame without movement of it, the alloy quietly passes into solution; it is not necessary to use the blowpipe. The melt is extracted with hydrochloric acid and water, and when solution is complete, 10 c.c. of sulphuric acid are added, the mixture evaporated and fumed strongly. The residue is dissolved in water and the bases thrown out of solution with ammonium hydrate. The precipitate is collected, washed well and dissolved in hydrochloric acid. The solution is heated to boiling point and ammonium hydrate added until a small precipitate is obtained, the precipitate re-dissolved in acid, and ammonium hydrate again added a drop at a time whilst stirring the solution vigorously; the addition being stopped just short of turbidity. An excess of freshly made sulphurous acid is added, the mixture boiled for 5-10 minutes and the precipitate filtered off, washed and ignited to ZrO_2.

The filtrate is assayed for iron and aluminium by the customary methods. A simple procedure is to expel the excess of sulphur dioxide, divide the solution into two portions, and precipitate both metals from each portion by ammonium hydrate, weighing the ignited oxides together in one case and re-dissolving them in the other, finishing by a determination of the iron after reduction with stannous chloride. The aluminium is obtained in this way by difference, though a direct determination, by way of checking the result, is desirable, and may readily be made upon a separate portion of the original filtrate.

FERRO-BORON.

Alloys of iron with boron are not of much industrial importance, though a goodly number of experimental steels have been made, from time to time, from the alloys. It would appear that results have not justified expectations—the author has seldom been called upon to attempt the assay of a steel for boron. The element has not been included, therefore, in the section of this book dealing with the analysis of steel.

The determination of boron is made gravimetrically by precipitation as manganese borate from a 50 per cent. alcoholic solution, by Smith[1] and also by Carnielli.[2]

A volumetric method of estimating boric acid is much more useful in the analysis of ferro-boron, because the element is readily separated from iron in the form of the volatile methyl ester of boric acid, and boric acid may be determined by titration with a standard alkali. If sodium hydrate is added to an aqueous solution of boric acid containing phenolphthalein, a pink colour is obtained before all the boric acid is neutralised, so that free boric acid cannot be accurately titrated alone. By introducing a neutral polyatomic alcohol such as glycerol or mannitol, however, the hydrolysis of the sodium borate formed by the neutralisation is held up, and a sharp end reaction is secured, provided that the solutions are free from carbonate.

Upon the principles outlined above Raulin[3] bases an excellent method for the determination of boron in ferro-boron alloys. The alloy is ground as finely as possible and 0·4 gram of it (10-15 per cent. boron) is placed in a distillation flask provided with a reflux condenser and separating funnel. The end of the condenser is connected to a tube which dips into a conical flask charged with 20-25 c.c. of a 2 per cent. solution of sodium hydrate, The alloy is decomposed by heating it with 4 c.c. of 66 per cent. sulphuric acid, the mixture being gradually heated over a spirit lamp until sulphur trioxide appears. The flask is then allowed to cool with the tap of the separating funnel open to prevent a sucking back of the sodium hydrate solution. When cold the mixture is treated with 20 c.c. of pure methyl alcohol and the distillation of the methyl borate conducted over a bath of boiling water. Five further distillations, using 15 c.c. of alcohol each time, are necessary to effect a complete separation.

The flask containing the distillate is heated on the water bath to expel the alcohol and the solution afterwards boiled for a short time over a free flame. A few drops of methyl orange are added, the solution carefully neutralised with hydrochloric acid run in from a burette, and 0·5 c.c. added in excess. The solution is boiled for a minute or two,

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[1] *Chem. News*, 46. 286.

[2] *Journ. Chem. Soc.* 80. ii. 690.

[3] *Moniteur Scient.*, July, 1911, 434.

cooled, and sodium hydrate solution run in until a yellow colour is obtained. About 25 to 30 c.c. of the solution prepared as described below should be required. Then 60 c.c. of a mixture of 2 vols. of 30 per cent. glycerine with 1 vol. of 95 per cent. alcohol are added and a few drops of phenol-phthalein, the mixture is shaken and the titration completed by adding the alkali until a violet colour is produced.

The sodium hydrate solution is prepared by dissolving 15 grams of the solid in water, boiling the solution for about an hour with lime, allowing to stand out of contact with air, filtering, and making up to 1000 c.c. with freshly boiled water. One c.c. of this solution is equivalent approximately to 0·004 grams of boron. The solution is standardised by dissolving a weighed amount of pure boric acid, equivalent to the amount of boron calculated from the assay, in 25 c.c. of water, adding 60 c.c. of the alcoholic glycerol mixture and titrating with the soda, with phenol-phthalein as indicator. The strength of the soda solution is calculated from the following:

$$2NaHO \rightarrow B_2O_3 \rightarrow 2H_3BO_3.$$

80 parts of sodium hydrate are equivalent to 22 parts of boron in the form of boric acid, which contains almost exactly 17 per cent. of the element.

Other Constituents.

Carbon is determined by combustion of the alloy, mixed with bismuth trioxide, in a current of oxygen at a temperature of about 1000° C.

For the estimation of the metals, the alloy is decomposed by adding nitric acid to it a drop at a time until effervescence is at an end, when several c.c. in excess are added and the mixture boiled. After diluting, the insoluble residue is filtered off, washed, dried and ignited, and the residue fused with a mixture of sodium carbonate and potassium nitrate. The aqueous extract of the fusion is added to the original filtrate and the solution analysed by the usual methods for silica, iron and aluminium (basic acetate precipitation), manganese, calcium and magnesium.

Sulphur and phosphorus are determined on separate samples of the alloy, opened out with nitric acid.

PART IV. THE ANALYSIS OF ORES.

IRON ORES.

THE ores of iron are ferric oxide (hydrated and anhydrous), ferrous oxide and carbonate, and mixtures of these with varying amounts of impurities. The chief impurities are compounds of silicon, manganese, sulphur, phosphorus, aluminium, calcium, magnesium, titanium, hydrogen, and carbon. Rarer impurities are barium, nickel, zinc, chromium, molybdenum, arsenic, copper, lead, and the alkali metals. There are frequently present also traces of such rare elements as niobium, indium, gallium, etc., which may be detected spectroscopically, but are difficult of estimation or even of detection by ordinary chemical analysis.

When a constituent of an ore may be estimated singly and directly, it is generally advisable to do so. In this way a special determination can be made for any particular purpose, and in a complete examination the errors of analysis are more likely to be detected than when the estimations involve a series of separations.

Decomposition of Ores.

All commercial ores leave a residue of more or less impure silica when heated with hydrochloric acid. When the residue is obviously impure, and particularly if it contains considerable iron, it must be opened out before proceeding with the analysis. This may be done by fusing it with sodium carbonate or bisulphate, or sometimes by treating it with hydrofluoric and sulphuric acids. The resulting solution, after extraction, is then mixed with the original hydrochloric acid solution. In some cases the insoluble residue is reported as ‘crude silica,’ and in others it is analysed and stated separately.

Crystalline ferric oxide—*i.e.* specular ore—though easily crushed to small laminae, is not easily ground so finely as to be quite soluble in acids. The glistening of small plates is apparent when a moderate amount of patience has been exhausted in grinding enough of the ore for a complete analysis. These ores may often be opened up as follows in a much more satisfactory manner than by fusion.

Pass the ore through a sieve of at least 90 meshes to the inch. Boil a weighed amount with strong hydrochloric acid and then dilute with some soft ashless paper which has been shaken to a pulp in water. Pour this mixture on to a pulp filter with constant agitation, and wash. The filter, which is now uniformly grey owing to the thorough dissemination of the small crystals, is transferred to a crucible, dried, and then charred at the mouth of the muffle. The crystalline ferric oxide is reduced by the glowing mass of carbonised paper, and again re-oxidised when the paper is burned off and the crucible more strongly heated. Everything now passes into solution on heating with hydrochloric acid except a little silica.

From 12 to 14 c.c. concentrated hydrochloric acid will readily dissolve a gram of ore; half that amount should be taken for each additional gram.

The following descriptions may be taken to apply to all kinds of ore after they have been suitably dissolved. They are abbreviated because so many of the operations are similar to those used in analysing metals.

Moisture.

As consignments of ore may pick up considerable moisture en route from rain and snow storms, they should be brought to a definite hygroscopic state, in order that results may be comparable, whether an exact determination of the moisture is required or not. To make the operation quantitative break the ore to pea-sized pieces and weigh off twenty to fifty grams, heat for several hours at 105° C., and re-weigh.

After grinding and passing through a sixty or ninety-mesh sieve the ore should be kept in a stoppered bottle.

Total Iron.

If the ore contains carbonaceous matter one gram of it is roasted in the muffle before being heated with hydrochloric acid.

With familiar ores the siliceous residue may be neglected when apparently free from iron; but otherwise they should be fused or treated with hydrofluoric and sulphuric acids, and the extract of the fusion (or the acid solution as the case may be), assayed for iron. The decomposition of hematite ores with hydrochloric acid is often facilitated by the addition of a gram or so of stannous chloride.

The determination of the iron is made volumetrically by titrating with potassium dichromate after reducing to the ferrous state with sulphurous acid or stannous chloride. The latter reagent is most frequently used, especially where large numbers of samples have to be disposed of quickly.

Ferrous Oxide.

This constituent can be satisfactorily determined only when the ore is free from higher oxides of manganese and organic matter. The former would evolve chlorine with hydrochloric acid, and so cause the results to be low; the latter, by reacting with the bichromate or permanganate used, would make the results too high. It is sometimes possible in the presence of organic matter to estimate the ferrous oxide approximately, after dissolving as usual and cooling, if the organic matter is removed before titrating. Sometimes also a similarly questionable result may be obtained by titrating the iron existing in the ferric state with stannous chloride and iodine; the ferrous oxide being then found by difference after determining the total iron. The presence of pyrites would of course interfere with an accurate estimation.

The direct estimation is made as follows:

Place one gram of the ore and a little sodium carbonate in a flask provided with a rubber bung and bunsen valve attachment. Add 20 c.c. of hot hydrochloric acid, insert the bung quickly, and digest until the ore is decomposed. Cool, dilute and titrate with potassium bichromate.

$$1 \text{ c.c. } \frac{N}{10} K_2Cr_2O_7 = 0{\cdot}00718 \text{ gram FeO.}$$

The ferrous oxide in insoluble residues is assayed separately as in refractory materials.

Silica, Alumina, and Titanic Oxide.

Decompose from three to five grams of the well-ground ore with hydrochloric acid and boil to dryness. ‘Take up’ in hydrochloric acid and collect, ignite, and weigh the silica. If the silica is tolerably pure, determine its amount by volatilisation with hydrofluoric acid, and add the ignited residue after dissolving (*via* fusion if necessary) to the filtrate.

Alumina is precipitated from the ferric solution by adding two or three grams of sodium phosphate, adjusting the acidity, reducing the iron to the ferrous state with thiosulphate, precipitating aluminium phosphate with an excess of the same salt, and completing the estimation as in steel or ferro-aluminium, Any titanic oxide existing in the ore will be found with the aluminium phosphate in a form closely approximating to $TiO_2 \cdot P_2O_5$, and according to its amount it can be estimated colorimetrically or gravimetrically.

If titanic oxide only is to be determined, the hydrochloric acid solution of the ore is evaporated with sulphuric acid to strong fumes, together with the solution obtained by digesting the siliceous residue with hydrofluoric and sulphuric acids. After dissolving up in water, the titanic acid is determined colorimetrically. A gravimetric estimation of titanium can be made by the following modification of Thornton's[1] process.

The ore (0·6 gram) is opened out as just described, the mass of sulphates dissolved out in water and about 4 grams of tartaric acid dissolved in the solution. Ammonium hydrate is added until the solution is nearly neutral, a few c.c. of dilute sulphuric acid introduced, and the liquid gassed with hydrogen sulphide in order to reduce the iron. Ammonium hydrate is then added to alkalinity, and the precipitation of the iron as sulphide completed by passing more hydrogen sulphide. The precipitate and solution are made up to a definite volume (300 c.c.) with water containing colourless ammonium sulphide, and 250 c.c. of the liquid filtered off through a dry paper. The remaining operations consist in the acidification of the solution with 50 per cent. sulphuric acid, expulsion of hydrogen sulphide, and precipitation of the titanium with cupferron.

Titaniferous iron ores are with difficulty soluble in acids and the gravimetric determination of titanium is made after opening out with potassium pyrosulphate. Ten grams of acid potassium sulphate are heated in a platinum crucible over a small flame, until effervescence ceases, when one gram of the finely ground ore is added. The fusion is continued at a dull red heat until the whole melt appears to be homogeneous and fumes of sulphur trioxide, indicative of the decomposition of the pyrosulphate into normal sulphate, appear. When cold, the mass is loosened from the walls of the crucible by external pressure, emptied into a beaker and the crucible well rinsed out with water. A few crystals of sodium sulphite are then added, and the mixture allowed to stand overnight. To the filtrate from the insoluble residue, about one-sixth of its volume of acetic acid and a solution of 20 grams of sodium acetate are added, and the mixture boiled for a minute. The precipitate contains the titanium and aluminium; it is filtered off, washed, and ignited. The separation of the aluminium and titanium is made by fusing with sodium carbonate and extraction with water. Insoluble

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[1] *Amer. Journ. Science*, 37, 407.

sodium titanate, Na_2TiO_3, remains. It is fused with pyrosulphate and the precipitation as metatitanic acid repeated in the manner described above.

The separation of the aluminium and titanium can obviously be made also by fusing with pyrosulphate, and precipitating the titanium with cupferron.

Manganese.

Some ores go completely into solution on digesting in a platinum crucible with a mixture of hydrofluoric and nitric acids, and the bismuthate process can then be applied at once after diluting and boiling; but this mode of attack often fails or is troublesome.

The following is a more general process: Dissolve one gram of the ore in hydrochloric acid, add a little hydrofluoric acid if the siliceous residue is considerable, then 10 c.c. sulphuric acid, and evaporate until the solution fumes strongly, so as completely to expel chlorides. Transfer from the porcelain dish to a flask, dilute with an equal volume of water, add 30 c.c. 1·20 nitric acid, and if everything is dissolved, cool add an excess of bismuthate, and finish as usual.

$$1 \text{ c.c. } \frac{N}{10} \text{ } KMnO_4 = 0{\cdot}00142 \text{ gram } MnO.$$

Sulphur.

This element may exist as sulphide (pyrites, galena) or sulphate (gypsum, barytes).

Five to ten grams of an ordinary ore are digested with nitro-hydrochloric acid, and the soluble portion, after evaporation, treated as though it were from a steel. To examine the insoluble portion, fuse with sodium carbonate, extract the melt with water, filter, or filter a fraction only if the residue is considerable, acidify, evaporate to dryness or not, to remove silica, according as the solution remains clear or becomes turbid, and finally precipitate with barium chloride and weigh the sulphate. Detailed instructions for the estimation of sulphur in ores containing barium are given on p. 235.

Phosphorus.

In dealing with unknown samples, by far the most important consideration in relation to the determination of phosphorus is whether they contain or do not contain titanic oxide. It is well, therefore, to postpone this determination until that of the alumina has been done and the presence or absence of titanium ascertained.

(*a*) If titanium is present, two grams of the ore are dissolved in hydrochloric acid, silica eliminated from the residue with hydrofluoric and sulphuric acids, the two solutions mixed, the iron reduced, alum added, and the phosphorus precipitated as basic aluminium phosphate and titano-phosphate. The remaining operations are described on p. 216.

(*b*) If titanium is absent, two grams of the ore are dissolved in hydrochloric acid, the solution evaporated nearly to dryness, 50 c.c. of 1·20 nitric acid added, the liquid brought to boiling and a strong solution of potassium permanganate added a little at a time until a permanent precipitate of manganic oxide is obtained. As much hydrochloric acid as possible should be removed by evaporation in the first instance, provided that the nitric acid added afterwards creates a clear solution; the excess of hydrochloric acid is thus quickly used up by the permanganate added. The manganic oxide is dissolved by adding a few drops of sulphurous acid, the solution filtered from separated silica, which is washed with as little water as possible, and the filtrate treated with dilute ammonia until it becomes dark red in colour without the formation of a precipitate. The phosphoric acid is then precipitated from the solution by the ammonium molybdate reagent, and the determination completed in the usual manner.

Small amounts of phosphorus which may remain in the insoluble residue are recovered by treating it with hydrofluoric and sulphuric acids, evaporating to low bulk, diluting with 1·20 nitric acid, and precipitating with the molybdate reagent.

Carbon Dioxide.

The amount of this constituent may be very considerable, but its influence in works' operations is relatively small, and consequently the almost universal mode of determining it is by loss when the ore is treated with acid. Any of the more perfected and elaborate pieces of apparatus figured in trade catalogues may be used, but a simple form, such as Parnell's, Fresenius and Wills', or the one shown in Fig. 15, meets most requirements.

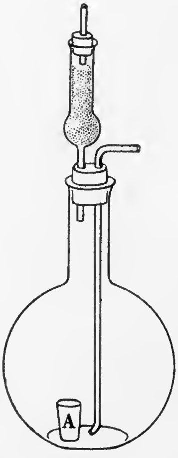

FIG. 15.

From one to two grams of the ore are weighed into the small tube *A*, which is made by cutting down a test tube and flattening the bottom. About 20 c.c. dilute sulphuric acid are added to the flask and the small tube arranged so that no acid can touch the ore. The complete apparatus is then weighed. The ore and acid may be brought into contact, and the liberation of carbon dioxide controlled somewhat by gently tapping and shaking the flask. When all action has ceased the mixture is warmed, but by no means boiled, and a stream of dry air aspirated through the solution and the upright calcium chloride tube so as to drive out carbon dioxide, but no moisture. The flask is allowed to stand, having its entrance and exit closed with rubber caps, until it is quite cold, then re-weighed, and the loss calculated to percentage.

A direct estimation can be made by attaching a weighed potash bulb to the calcium chloride tube so as to absorb the evolved carbon dioxide.

Water and Organic Matter.

If an ore is free from carbon dioxide and ferrous oxide, it is generally sufficiently accurate to express these constituents as " Loss on Ignition." The limited practice of making an analysis add up to a hundred per cent. by calling the difference water and organic matter is less commendable.

Both constituents may be estimated together or separately, as in manganese ores on p. 235; in the latter case a weighed calcium chloride tube is inserted between the combustion tube and the potash bulb.

Lime and Magnesia.

Three grams of the ore are dissolved in an excess of hydrochloric acid. If the residue is small and not likely to contain either of the bases under assay, the acid solution is neutralised with ammonium hydrate and carbonate without filtering. The solution is then diluted to about 250 c.c., and the iron precipitated with a few c.c. of ammonium acetate and acetic acid. The mixture is heated to boiling, made up to about 305 c.c., and 200 c.c. filtered at once through a dry fluted paper. If large amounts of manganese are present, or nickel, or copper, the filtrate is made alkaline with ammonium hydrate, and gassed with hydrogen sulphide. If, however, a small amount only of manganese is present, its removal by means of bromine and ammonium hydrate will cause no appreciable loss either of lime or magnesia.

Lime and magnesia are determined by the customary methods after concentrating the filtrate from the preceding operations to low bulk. An excessive accumulation of ammonium chloride in the solution, preventing the concentration to a sufficiently small volume for the purpose of precipitating magnesium, is conveniently disposed of by the addition of nitric acid before or during the process of evaporation.

Chromium.

Two grams of the ore are fused with sodium carbonate with free access of air in a platinum dish, or with sodium peroxide in a nickel crucible, and the fused mass extracted with water. A yellow filtrate indicates chromium. Its amount may be estimated colorimetrically by comparison with standard solutions of sodium chromate or by acidifying the filtrate with sulphuric acid, and titrating with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \, KMnO_4 = 0{\cdot}00254 \text{ gram } Cr_2O_3.$$

If more than one or two tenths per cent. are present the ore is dissolved in hydrochloric acid and any insoluble residue also dissolved after fusion. The solution is then evaporated with sulphuric acid and treated as that of a steel.

Vanadium.

Vanadium is detected by dissolving the ore in hydrochloric acid, evaporating to as small a bulk as possible, diluting, and adding hydrofluoric acid in drops until the solution is decolorised, or nearly so. The addition of hydrogen peroxide to the solution produces in five minutes the reddish brown colour characteristic of the presence of vanadium.

The amount of vanadium is also best determined in all ores, other than the richly vanadiferous ores used in the manufacture of ferrovanadium, colorimetrically, after separating most of the iron as described for the determination of small quantities of this element in steel.

Copper, Zinc, Nickel, Cobalt.

These constituents are present in British iron ores in negligible amounts only. To determine whether any or all the oxides are worth consideration, dissolve five grams of the ore in hydrochloric acid, and make an acetate separation. It is well to aim at making the neutralisation so nicely that the ferric oxychloride is decomposed by boiling without adding any acetate, so that the filtrate may contain practically all the copper as well as the manganese, nickel, cobalt, and zinc.

Make the filtrate slightly ammoniacal, add 3 or 4 c.c. acetic acid and a few c.c. ammonium acetate, and pass hydrogen sulphide. The manganese only remains in solution. If the volume of the precipitate warrants a further examination dissolve it in nitric acid, evaporate to dryness, take up in hydrochloric acid, precipitate copper with hydrogen sulphide, and estimate its amount in the usual way.

Add sodium carbonate to the concentrated filtrate until a faint precipitate appears, clear with a drop of hydrochloric acid, and pass hydrogen sulphide. Any zinc sulphide precipitated is washed with hydrogen sulphide water, and either ignited to oxide or transformed into phosphate. In the former event a re-ignition with the addition of powdered ammonium carbonate is necessary, in order completely to expel sulphur trioxide.

The filtrate containing nickel and cobalt is acidified, hydrogen sulphide expelled by boiling, the nickel determined by precipitation with dimethyl glyoxime from one portion of the solution, and the cobalt from the other by means of nitroso-β-naphthol.

When the approximate amounts of these rarely occurring oxides have been determined as above, their more exact determination is made upon 10 grams of the ore, which is dissolved, the iron reduced to the ferrous state and the solution gassed with hydrogen sulphide. The precipitate of copper sulphide is collected and ignited, or re-dissolved for an iodometric assay of the copper. The filtrate is boiled well, the iron oxidised with nitric acid and then precipitated by the basic acetate process. The filtrate is made up to a definite volume and the nickel and cobalt determined separately in measured portions of it by the methods previously indicated.

Zinc.

A direct determination of zinc can be made by precipitating it as sulphide from solutions containing free formic acid sufficient in amount to retain the iron in solution. Five to ten grams of the ore are dissolved in hydrochloric acid and the solution evaporated to fumes after the addition of sulphuric acid. The insoluble residue after dilution is filtered out, the filtrate diluted largely (400 c.c.), and gassed with hydrogen sulphide. Copper sulphide, if present, is filtered off, and the excess of mineral acid decomposed by adding ammonium formate in excess, after which 15 c.c. of formic acid s.g. 1·15 are added. Zinc sulphide is precipitated. The mixture is digested for some time, more hydrogen sulphide being passed through it if large amounts of zinc appear to be present, and the precipitate is then collected and washed. If it is white, it may then be roasted carefully and weighed as oxide. If not so pure, it is re-dissolved in hydrochloric acid, the solution made alkaline, then acid again with formic acid, and the zinc re-precipitated with hydrogen sulphide.

Arsenic.

Arsenic is determined by decomposing the ore with hydrochloric acid and distilling off the volatile trichloride. The apparatus is shewn in Fig. 12; the following details will be found useful.

Five grams of the ore and 10 grams of ferric chloride are placed in the distillation flask and a mixture of 50 c.c. of hydrochloric acid with 30 c.c. of water added. The mixture is distilled until 'bumping' sets in, when 18 c.c. of acid and 12 c.c. of water are added, and the distillation continued. A further addition of acid and water is made and the distillation repeated until the mixture 'bumps.' The distillate is made just alkaline with ammonia, then just acid with hydrochloric acid, 10 grams of sodium bicarbonate added and the liquid titrated with iodine.

Alkalis.

Dissolve three grams of the ore in hydrochloric and a few drops of nitric acid and filter. The insoluble residue may contain the greater portion of the alkalis. After ignition, therefore, decompose it with hydrofluoric acid, and only rather more sulphuric acid than is needed to leave all the non-volatile constituents as sulphates after the excess of hydrofluoric acid has been evaporated off. Boil the residue with water, or dilute hydrochloric acid if thought to be necessary, and add to the filtered ferric solution. Neutralise the bulk of the acid, add a small excess of barium chloride, and filter off the precipitated barium sulphate. Heat the filtrate thus obtained nearly to boiling, add an excess of ammonium carbonate, make up to 305 c.c., and preserve 200 c.c. of the clear filtrate.

The preceding operations should have eliminated practically all the iron, aluminium, manganese, barium, calcium, magnesium, and phosphorus. In order to detect any remaining, evaporate the filtered 200 c.c. to dryness, heat gently, extract the residue with hot water, and filter off any insoluble portion.

The clear filtrate is acidified with hydrochloric acid, re-evaporated to dryness, ignited to low redness to drive off any ammonium salts, and weighed as a mixture of sodium and potassium chlorides. The weight of the combined or separate alkaline oxides is obtained as on p. 250.

If the siliceous residue was very small or completely volatilised after ignition, then the main solution only need be dealt with.

CHIEF CONSTITUENTS ON ONE SAMPLE.

When an abundant supply of ore is available the practice of estimating as many constituents as possible on the same sample is not a good one. But the care and exactness required to account for the full weight taken, as well as obtain accurate individual figures, makes it a good exercise for students; and occasions do sometimes arise in the analysis of both minerals and metals which require the work to be done on as small a sample as possible.

Dissolve one and a quarter grams of the ore in hydrochloric acid. If the amount of material for analysis is small, this should be done in a closed vessel, so that the amount of carbon dioxide may be determined; otherwise "Loss on Ignition" is determined before the sample is treated with acid. Add one or two c.c. nitric acid and evaporate the solution to dryness, but do not bake. 'Take up' in hydrochloric acid, collect the silica, and volatilise it with hydrofluoric acid. Return any alumina etc. which had accompanied the silica to the main filtrate.

Neutralise the ferric solution and precipitate with a small amount of ammonium acetate. Collect the basic ferric acetate on a plain filter fitted to a ribbed funnel, and wash it three or four times with hot water containing a drop or two of the precipitant. Transfer as much of the precipitate as possible to the original beaker by means of a spatula, and dissolve the rest from the paper by dropping warm concentrated hydrochloric acid on to it, and washing with cold water.

Re-precipitate the dissolved ferric acetate with ammonium hydrate, collect on the previously-used paper, wash, dry, ignite apart from the paper, and weigh as $Fe_2O_3+Al_2O_3+P_2O_5$. Dissolve in hydrochloric acid, estimate and allow for the small amount of insoluble silica, reduce a fraction of the solution with sulphurous acid and titrate. The remaining fraction is used for a direct estimation of alumina by means of sodium phosphate and thiosulphate in case greater accuracy, or a confirmation of the indirect result deduced from the ferric oxide determination, is required.

The ammoniacal filtrate may be mixed with the acetate filtrate or thrown away according to the amounts of lime and magnesia expected. After evaporating to a suitable bulk the manganese is precipitated with bromine and a small excess of ammonium hydrate, avoiding contact of the solution and atmosphere as much as possible. Collect the manganic hydrate and ignite to mangano-manganic oxide, or estimate in any other convenient way.

The filtrate is then precipitated with ammonium oxalate, in order to estimate lime, and the subsequent filtrate used for the estimation of magnesia after expulsion of ammonium salts. By avoiding the use of fixed alkalis it is possible to estimate alkaline oxides in the filtrate from the magnesia precipitate.

The remaining constituents must be estimated on separate samples.

MANGANESE ORES.

The black oxide of manganese, which, before the introduction of ferro-manganese alloys, was largely used in Sheffield by manufacturers of crucible steel on account of its alleged cleansing and strengthening effects is the most important ore of manganese. Its analysis is typical of the rest. Mineralogically, the black oxide may be pyrolusite, psilomelane, or a mixture of the two, and a complete analysis involves the determination of: manganese dioxide and monoxide, ferric oxide, alumina, baryta, lime, silica, sulphuric, phosphoric and arsenic acids, water and organic matter. Seldom is an analysis of the ore required from the steel-works' chemist at the present time, and a return of the total manganese contents and crude silica, together with the relative freedom of the ore from sulphur and phosphorus, meet all requirements.

GENERAL ANALYSIS.

Digest one gram of the ore with 20 c.c. concentrated hydrochloric acid until only a siliceous residue is undissolved. Evaporate nearly to dryness, add 3 or 4 c.c. hydrochloric acid, dilute to about 150 c.c., add a drop or two of sulphuric acid, and allow the solution to stand overnight.

The residue is collected, washed with very dilute hydrochloric acid, and ignited. Besides silica it may contain barium sulphate, alumina, lime, etc. Fuse therefore with sodium carbonate, evaporate with hydrochloric acid, 'take up' with more hydrochloric and a drop or two of sulphuric acid, and after standing in a warm place for an hour or so, collect and weigh the mixture of silica and barium sulphate. The silica is volatilised with hydrofluoric and a drop of sulphuric acid, and its percentage calculated from the loss; the residue is barium sulphate, which is calculated to oxide. The filtrate is precipitated with ammonium hydrate, and the ignited residue (alumina) and the new filtrate (if it contains lime) added in their respective places in the analysis of the main portion.

Add five or six grams ammonium chloride and an excess of ammonium hydrate to the main filtrate to precipitate iron and aluminium, but not manganese or calcium. The small amount of manganese possibly carried down may be neglected unless it is being estimated on the same sample, and then it must be recovered by a re-precipitation. If a large amount of iron is present the ammonium chloride is omitted, and an acetate separation made as in an iron ore.

Dissolve the ferric and aluminic hydrates, together with the alumina recovered from the siliceous residue, in hydrochloric acid, and estimate the alumina by boiling with sodium phosphate and thiosulphate. Boil the filtrate with nitric acid, remove the liberated sulphur by filtration, precipitate the iron with dilute ammonium hydrate (as phosphate), and estimate it volumetrically in the usual way. Any titanic oxide in the ore will be found partly with the silica and barium sulphate residue, but mostly with the precipitated aluminium phosphate, and on treating the latter with hydrochloric acid it will not dissolve to a clear solution as it does when pure.

The solution containing the manganese is diluted to at least half a litre, precipitated with bromine and *a small excess* of ammonium hydrate, boiled and filtered through a fluted paper. The manganic hydrate is washed with three per cent. nitric acid, the washings neutralised, the small amount of manganese they may contain re-precipitated and added to the bulk, and the whole ignited at the highest attainable muffle temperature before weighing as manganoso-manganic oxide. The calcium is precipitated as oxalate from the combined filtrates after evaporating to about 150 c.c.

Estimated in the above manner the manganese is somewhat too high and the lime too low, on account of the imperfect separation of the two whenever the former is precipitated as hydrated dioxide from neutral or alkaline solutions. A more accurate result is obtained by heating the solution to boiling, making strongly alkaline with ammonium hydrate, and passing a rapid stream of washed sulphuretted hydrogen gas until the manganese is completely precipitated, then filtering rapidly through a fluted paper and measuring the volume of filtrate and residue respectively, so as to avoid washing. The filtrate is evaporated, traces of manganese which have escaped precipitation as sulphide thrown out with bromine and ammonium hydrate, and the calcium precipitated as usual.

The remaining constituents are more conveniently determined on separate samples.

Total Manganese.

The volumetric determination is made as follows: Dissolve one gram in hydrochloric acid, add two or three c.c. hydrofluoric acid to break up silicates, and evaporate with 10 c.c. sulphuric acid to strong fumes: then dilute and filter.

At this point hydrogen peroxide may be added to test for titanic oxide, which, if present, can be at once colorimetrically estimated.

Dilute the solution to 200 c.c., measure out 25 c.c., add 20 c.c. 1·42 nitric acid, and make the bismuthate estimation as in manganese alloys (p. 176).

Peroxide of Manganese.

The respective amounts of manganese existing as dioxide and monoxide, although the information is of little value to the steel maker, must necessarily be determined in order to make a statement of a complete analysis.

From five to six decigrams of 'pure' iron are dissolved in about 70 c.c. dilute sulphuric acid (1 to 3). When the last trace of iron has disappeared half a gram of ore ground as finely as possible in an agate mortar is weighed into a diminutive porcelain crucible, and slid, crucible and all, into the boiling acid ferrous solution. The flask is stoppered, except for a steam exit, and the solution kept boiling until the ore is completely decomposed, which, with very hard varieties, if properly ground, ought not to require more than fifteen minutes. The solution is then cooled, diluted, and titrated with permanganate or bichromate. The amount of peroxide can be calculated from the permanganate value of the ferrous sulphate actually oxidised. From the equation

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O,$$

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = 0{\cdot}00435 \text{ gram } MnO_2.$$

Any ferrous oxide existing in the ore would introduce a negative error when the amount of peroxide is estimated in this way. If the ore is to be used for bleaching purposes, *i.e.*, the production of chlorine, this error in the valuation is desirable, because it corresponds exactly with the available oxygen lost in practice. But from a strictly analytical point of view an absolute process would be preferable. There is a disposition to ignore the separate estimation of the small amounts of ferrous oxide as well as the error it introduces, and from a steel-works' standpoint there is certainly no harm in doing so.

Water and Organic Matter.

These constituents are determined by heating two grams of the ore in a tube between plugs of recently ignited asbestos, and carrying the water and carbon dioxide formed, by means of a current of dried air, into a weighed potash bulb.

The combustion tube need not be more elaborate than a six or eight-inch piece of hard glass tubing (half-inch diameter) drawn out at one end to fit close up to the potash bulb with a rubber joint, and fastened to an air-drying tube at the other by means of a perforated stopper made from thick-walled rubber tubing. The combustion tube, after starting the aspirator, is heated with a bunsen burner.

Sulphur.

To estimate the total sulphuric acid, digest two grams of the ore with hydrochloric acid, fuse the siliceous residue with sodium carbonate, extract the melt with water, and filter. The barium is left on the filter as carbonate; its associated sulphuric acid is in solution. Mix the two filtrates: if any silica is precipitated, then make freely acid, evaporate to dryness, and remove it; but if the solution remains clear, adjust the acidity with ammonium hydrate so that only a small excess of acid is present and add barium chloride. If any co-precipitation of the dissolved silica is feared, the ignited barium sulphate may be treated with hydrofluoric and a drop of sulphuric acid and re-weighed.

The sulphuric acid in combination with barium may sometimes be estimated separately by boiling a suitable portion of the ore with hydrochloric acid, evaporating to low bulk, diluting, and allowing to stand a few hours. The collected residue is ignited, the silica removed by hydrofluoric and sulphuric acids, the residue fused, dissolved in hydrochloric acid, and the solution, which contains all the barium, precipitated with an excess of sulphuric acid. The correctness of the result involves the assumption that no other compound of barium—*e.g.* the carbonate—is present, as well as no soluble sulphate which would obviously generate barium sulphate during the hydrochloric acid treatment of the ore.

Phosphorus.

Dissolve two grams in hydrochloric acid, filter off the siliceous residue and decompose it with hydrofluoric and sulphuric acids. If the ore contains titanic oxide, then separate the phosphorus from the manganous solution as basic aluminium phosphate, fuse the precipitate obtained along with the residue from the silica volatilisation, and proceed further as with titanic irons on p. 62.

But if no titanic oxide is present, then after volatilising the silica and heating to strong fumes, add the sulphuric solution to that containing the manganese, collect the phosphorus as a basic ferric compound, redissolve the precipitate in nitric acid, and estimate the phosphorus *via* phospho-molybdate and lead molybdate in the usual way.

Arsenic.

Manganese ores are seldom free from arsenic, the amount of which may be determined by volatilising it as the trichloride, absorbing the vapours in water, and titrating the arsenious acid resulting from the hydrolysis of the halide compound.

TUNGSTEN ORES.

WOLFRAMITE.

This mineral is a tungstate of iron and manganese, the composition varying greatly in respect of the percentages of ferrous and manganous oxides. In commercial samples the former varies from 10 to 20 per cent., and the latter from 4 to 14. The tungstic oxide usually lies between 70 and 75 per cent. Tin is not infrequently a constituent of the ore.

Tungstic, Ferrous, and Manganous Oxides.

Fuse one gram of the agate-ground material with three or four times its weight of sodium carbonate. Extract the cooled melt with water, add a little sodium peroxide to decompose manganates, and filter off the insoluble oxides of iron and manganese.

Acidify the alkaline filtrate with dilute nitric acid, and then make very faintly alkaline with dilute ammonium hydrate. If aluminium hydrate separates on digestion, filter it off, dissolve it again in hydrochloric acid and evaporate the solution so as to recover traces of tungstic oxide. If no separation of aluminium hydrate occurs, or after removing it in the other event, adjust the solution to very faint acidity and determine the tungstic oxide by the mercurous nitrate precipitation.

The filter holding the insoluble residue from the aqueous extract of the original fusion is 'ashed,' the residue dissolved in hydrochloric acid and the solution, after adding 10 c.c. of sulphuric acid, evaporated to fumes. Traces of tungstic oxide are occasionally found by this treatment, and are recovered by diluting and boiling until the sulphates of iron and manganese are dissolved.

The filtrate is made up to 200 c.c., 50 c.c. of it mixed with 20 c.c. of nitric acid, and the solution assayed for manganese by the bismuthate process.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0{\cdot}00142 \text{ gram MnO.}$$

Another portion of the filtrate is reduced with sulphurous acid and the iron determined by titration with potassium permanganate.

Tin.

Tin occurs in wolfram concentrates principally in the form of cassiterite, which is not decomposed by acids and acid mixtures; in some varieties of wolfram soluble stannine also occurs. The total amount of tin permissible in the manufacture of ferro-tungsten alloys does not exceed one per cent. The following method of estimating the tin, though lengthy, requires little attention during the preliminary stages, and gives excellent results.

One gram of the finely-ground ore, contained in a tall unlipped beaker, is treated with 60 c.c. of hydrochloric acid, the mixture digested with occasional stirring for about an hour, and a few crystals of potassium chlorate then added. The digestion is continued for 24 hours, during which the beaker is kept covered (except when stirring), and the temperature well below boiling point, so as to maintain the volume and strength of the acid as much as possible. Decomposition should be as complete as possible in this time, and the mixture is then evaporated to a paste, taken up with dilute hydrochloric acid (1 to 4), the tungstic oxide and undecomposed tinstone filtered out, and the filtrate set aside for a time. The precipitate is washed from the paper back into the beaker, digested for half an hour with 30 c.c. of ammonium hydrate, and the undissolved tinstone strained off. The filtrate is received in a tared platinum dish, the solution evaporated to dryness, and the residue carefully ignited to tungstic oxide and weighed as such.

The filter is ashed, the residue fused with sodium peroxide in an iron crucible, the melt extracted with water, the solution acidified with hydrochloric acid and added to the original filtrate which was set aside. Tin is precipitated from the solution with hydrogen sulphide, and the stannic sulphide collected and washed. If it is considered desirable on inspection, the sulphide is then dissolved away from the filter with a warm solution of sodium sulphide, the filtrate acidified freely with hydrochloric acid and the re-precipitated sulphide taken into solution by adding a crystal or two of potassium chlorate. If the treatment with sodium sulphide is not deemed necessary, the precipitate is dissolved at once in hydrochloric acid with the addition of a little potassium chlorate or bromine. In either case, the excess of halogen is removed, the stannic chloride reduced by means of powdered antimony, and the liquid titrated with a standardised solution of iodine.

The determination of tin in high-grade wolfram ores is made the subject of an excellent paper by Powell (*Journ. Soc. Chem. Ind. Trans.*, 37. 285).

SCHEELITE.

Samples of commercial scheelite can be opened out by fusion with alkalis or alkaline carbonates or by solution in mixtures of acids, of which hydrofluoric is one. In the latter case the silica cannot be determined, but the procedure does not cause any tungstic oxide to be volatilised, as heating in the dry way with ammonium fluoride is said to.

The analysis is much simplified if care be taken at the outset to open out with hydrochloric acid alone. This can be done by heating one gram of the sample which has been finely crushed, but not necessarily agate-ground, with 60 to 70 c.c. hydrochloric acid—at a temperature quite below boiling point. Some little time is required to effect complete decomposition. After stirring, the undissolved portion is white, in a minute or two it becomes yellow. On repeatedly stirring, the coatings of tungstic oxide dissolve until finally nothing or only a siliceous residue remains. Any attempt to hurry the decomposition by boiling weakens the acid, causes a portion of the dissolved tungstic oxide to precipitate, and retards the operation, as well as prevents its course being clearly observed.

Evaporate the solution nearly to dryness, boil with dilute hydrochloric acid (1 to 5), filter, wash, and ignite in a tared platinum dish. The increased weight is due to silica and tungstic oxide.

The silica is estimated by volatilising with hydrofluoric acid. The residue is pure tungsten trioxide, or contains not more than two or three milligrams of impurities. The small amounts of ferric oxide it may contain are allowed for after fusing with sodium carbonate, etc.

The filtrate is precipitated with ammonium hydrate, and the ferric hydrate dealt with as usual. The calcium is precipitated as oxalate and weighed as oxide or sulphate. The following volumetric process for the estimation of calcium gives excellent results :

Precipitate the calcium with oxalate as usual, and collect on a small asbestos filter. After thorough washing with faintly ammoniacal water, return the filter and its contents to the flask in which the precipitation was made, and digest with hot dilute sulphuric acid (1 to 6) until it is completely decomposed. The solution is then diluted with about its own bulk of water, heated to 70° C., and titrated with permanganate.

The trade complaints sometimes made of the low results obtained when scheelite is opened out with acids and tungstic oxide recovered by evaporation, when compared with those obtained by alkaline fusion and precipitation as mercurous tungstate may be due :

1. To the evaporated residue being so strongly baked that some calcium tungstate is re-formed ; or to the common practice of using strong hydrochloric acid in re-dissolving the residue so that some tungstic oxide also is re-dissolved, and not again completely precipitated on diluting.

2. To the presence of molybdic oxide in the mineral. By the acid process this would not be estimated ; but by the fusion process it would be precipitated along with the tungsten, and only partially driven off during the subsequent ignition.

Traube (who instances tin, fluorine, chlorine, cerium, didymium, lanthanum, magnesium, and copper as having been at various times observed in scheelite) examined ten samples of the mineral from different localities, and in every case found molybdic oxide varying from traces, to 8·23 per cent.

The acid process is to be preferred always because it provides for the detection and estimation of molybdenum, and it also permits a complete analysis to be made in a simple manner.

CHROMIUM ORE.

CHROMITE.

This material is used for the production of chromium alloys, in the manufacture of chrome bricks, and for the lining or beds of certain furnaces. The ore varies greatly in composition, which, however, generally falls within the following limits : chromic oxide, 40 to 60 per cent. ; ferrous oxide, 16 to 35 ; alumina, 2 to 20 ; magnesia, 5 to 18. It is by no means safe to assume that samples taken from the same locality will have practically the same composition.

Chromic Oxide.

This constituent is estimated by titrating the chromic acid, resulting from a fusion of the ore with sodium peroxide, with ferrous ammonium sulphate and potassium bichromate or permanganate. For the fusion, the sample need only be ground to a powder which will pass a sieve of 60 meshes per inch.

$$1 \text{ c.c. } \frac{N}{10} K_2Cr_2O_7 = 0{\cdot}00253 \text{ gram } Cr_2O_3.$$

Iron, Alumina, Magnesia, Lime, Chromium.

These constituents may be conveniently estimated on one sample in the following manner: Open out one gram of the ore with sodium peroxide. Dissolve the melt in water, boil for a few minutes to destroy any undecomposed sodium peroxide, and allow the insoluble oxides of iron, magnesium, calcium, nickel, and (if present) manganese to settle. The solution contains the chromium, aluminium, practically all the silica, and possibly also traces of calcium and magnesium. Pour the clear liquid through a pulp filter and wash the residue by decantation, using 60 to 80 c.c. of water at a time until the washings are perfectly colourless.

Digest the filter with hydrochloric acid so as to dissolve the oxides which have passed on to it. Strain off the paper with a small filter plate, allow the acid solution to run into the beaker containing the bulk of the oxides, and add as much acid more as will dissolve everything to a clear solution and leave an excess of about 10 c.c.

The iron is then precipitated with ammonium hydrate, re-precipitated, and the ferric hydrate finally dissolved in hydrochloric or sulphuric acid, reduced to the ferrous state, and titrated.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 \text{ or } K_2Cr_2O_7 = 0{\cdot}00718 \text{ gram FeO.}$$

Although the total iron is generally calculated to ferrous, a portion possibly exists as ferric oxide.

The combined filtrates are made, not faintly as usual, but decidedly ammoniacal, and the calcium precipitated as oxalate. If the collected calcium oxalate is green it must be re-dissolved in strong hydrochloric acid and re-precipitated. It is also necessary to bear in mind the precautions given on p. 253 if much magnesia is present.

If it is thought desirable to concentrate the filtrate from the calcium oxalate it must be kept ammoniacal during the evaporation, otherwise a compound of nickel is precipitated and much bumping ensues. The magnesium is finally precipitated with microcosmic salt in the usual way. The ignited pyro-phosphate should contain little or no trace of nickel.

Aluminium may be separated from the alkaline chromic liquor in a variety of ways. One of the least troublesome, if circumstances permit.

is to arrange a gas generator so that a steady stream of carbon dioxide may pass through the solution all night. On the following morning the precipitated basic carbonate is collected, washed, and ignited to alumina. In very exact analysis the basic carbonate may be dissolved in hydrochloric acid and re-precipitated with ammonium hydrate so as to eliminate any calcium or magnesium which have originally passed into solution.

But if only a small amount of alumina is present, or if the analysis must be completed without delay, then, after adding a faint excess of hydrochloric acid, add sodium phosphate, and as much ammonium acetate as is needed to decompose the free hydrochloric acid. Filter off the precipitated aluminium phosphate, wash until free from chromic acid, ignite, and weigh.

The filtrate is acidified, halved, and chromium estimated as before with ferrous sulphate and bichromate.

MISCELLANEOUS ORES.

It is seldom that the steel-works' chemist is called upon to make analysis of the ores of such metals as vanadium, molybdenum, nickel, cobalt, etc.; instead, the ferro-alloys of these metals engage his attention. The methods for the analysis of these alloys, with modifications that will readily suggest themselves, may be applied to the ores. Most of the latter contain metals of the second group, which are therefore separable by means of hydrogen sulphide from dilute hydrochloric or sulphuric acid solutions. Many of them are sulphides decomposable by acid mixtures or by fusion with sodium peroxide; the latter procedure paves the way to a direct determination of the sulphur contents of the ore by precipitation as barium sulphate.

PART V. THE ANALYSIS OF REFRACTORY MATERIALS.

THE refractory materials which the steel-works' chemist is called upon to examine are roughly divisible into three groups, according to their silica contents. ' Acid ' refractories include gannister and silica bricks (95-99 per cent. of SiO_2), and firebricks, fireclay, etc. (*circa* 50 per cent.). ' Neutral ' materials include bauxite, which consists largely of the oxides of iron and aluminium, with much combined water and 10 per cent. or less of silica. The representatives of both groups are more or less imperfectly decomposed by the ordinary wet reagents, and are generally opened out by way of a fusion. Dolomite (calcined) and magnesia bricks belong to the ' basic ' group, and may be decomposed in the ' wet ' way.

An ordinary complete analysis usually consists of the determination of total silica, iron oxide, alumina, lime, magnesia, the alkalis, and water. The first of these items is made up of free silica and the combined silica of included minerals ; the separate amounts of these are difficult to estimate and are not usually recorded.

The reagents that have been used in the preliminary fusion of a refractory material by various operators are numerous. In the majority of cases they are sodium and potassium compounds and mixtures of them, and include the hydroxides, the acid sulphates and their decomposition products the pyrosulphates, and more particularly, the carbonates of these metals.

Mixtures of sodium with potassium carbonate have a lower fusion point than those of the single salts. Potassium carbonate melts at about 885°, the sodium salt at 810°, and a mixture of the two in molecular proportions below 700°. There is no particular advantage in using the more fusible mixture, because it is easy to reach and maintain the temperature required to melt either of the single salts, and it is necessary to do so in many cases before decomposition of the refractory material can be effected. As the salts of sodium, in the majority of cases, are more easily removed by the subsequent operations of extraction and washing, it is the general practice to open out siliceous bodies with sodium carbonate.

This substance can be purchased in an almost pure form, and with the separate amounts of the contained impurities also supplied by dealers. Less pure varieties should always be assayed for the amount of silica, alumina, ferric oxide, sulphate, etc., which they may contain.

ACID MATERIALS.

Gannister, Silica Brick, Sand, Fireclay, Moulding Composition, etc.

GENERAL ANALYSIS: AFTER FUSION.

One gram of the finely-ground sample is shaken with 6 grams of sodium carbonate in a stoppered weighing bottle, the mixture emptied into a platinum dish or large crucible containing a layer of 1 gram of the carbonate, and one gram more then added as a cover. The dish with lid in position is heated for a quarter of an hour at low redness over a bunsen flame and then transferred to a muffle furnace where it may be left for 15-20 minutes. A perfect fusion is thus obtained with little or no projection of the contents upon the cover of the dish.

Silica.—The cooled melt is dissolved from the dish with water (100-200 c.c.) and the solution transferred to a larger dish, preferably of platinum. When such a vessel is not available, a flat-bottomed porcelain dish forms a good substitute. An excess of hydrochloric acid (20-30 c.c.), is added through a hole in the glass cover, and when effervescence is at an end, the mixture is evaporated to dryness, and the dry mass heated gently until hydrochloric acid is expelled. The temperature should not exceed 120° when magnesia is present in considerable amounts, since above this point magnesium silicate, soluble in hydrochloric acid, is re-formed. In the absence of much magnesium the temperature may reach 250° or more without loss of silica on extracting with acid, though it is not necessary or advisable to exceed 120°. The dried mass is next moistened with about 5 c.c. of hydrochloric acid, 50 c.c. or so of water added, and the mixture warmed to dissolve all but silica. The latter is filtered off, washed by decantation at first and finally on the filter with water until free from chlorides, and dried.

The filtrate and washings are taken to dryness again in the same dish, the residue baked, and the silica in it—about 1 per cent. of the total—collected and ignited with the main mass. Great care should be taken in transferring the last particles of silica from the dish to the filter—they cling somewhat tenaciously, and are not so readily seen on the sides of a porcelain vessel.

Traces of silica still remain in solution, as may be proved by a third evaporation ; but the amount is very small, and for technical purposes two evaporations suffice.

The ignition should be made at as high a temperature as possible to drive off the water completely and make the silica non-hygroscopic. The time and trouble needed to do this thoroughly cause it to be often left undone. It is necessary then to make two weighings. The first is too high, on account of the water absorbed during the operation, but it enables the rider to be fixed at what is probably the correct weight. The second weighing is then made, after cooling in an air-tight and otherwise good desiccator, by transferring quickly to the balance pan, releasing the beam, and making any needed correction in the former weight from the swing of the pointer on the indicator.

A weighing made in the usual manner may be as much as a centigram too high. Ninety-five centigrams of silica left all night in a closed balance case gained eight per cent. A large number of works' analyses, although not scientifically precise, are very near the truth on account of this latter error and that due to incomplete insolubility of the silica after one evaporation balancing each other.

The silica obtained as above may contain traces of ferric oxide, alumina, titanic oxide and phosphoric acid. It is moistened with water and a drop or two of sulphuric acid, and dissolved by adding hydrofluoric acid cautiously and in large excess. The solution is evaporated to dryness and finally ignited strongly, the silica being calculated from the loss in weight. The small residue left in the crucible is dissolved by digesting it with hydrochloric acid, or it is fused with a little sodium carbonate, etc., and the resulting solution added to the original filtrate.

Alumina and Ferric Oxide.—To the filtrate from the silica determination a gram or so of ammonium chloride is added, and the solution heated to boiling. Dilute ammonium hydrate is then added slowly until a slight excess is present, the precipitated hydroxides of iron and aluminium filtered off at once and washed with hot water containing a little ammonium nitrate.

When lime and magnesia are present only in small amounts and their separation from iron and aluminium is made in the presence of considerable ammonium chloride, without undue delay in the filtration, it is generally unnecessary to repeat the precipitation in order to recover doubtful traces of the former oxides. It may be advisable when either pair of elements is present in large amounts, and it certainly is when large amounts of both pairs are being handled. The precipitate is dissolved in that case from the filter with hot 50 per cent. hydrochloric acid, the hydroxides re-precipitated as above, and ignited to oxides, the weight of which is then taken.

The method of determining the amount of each depends upon the total weight of the two, and also upon their relative proportions.

Silica bricks and gannister contain only about 2 per cent. *in toto*, and it suffices to digest the ignited oxides for some time with hydrochloric acid in order to dissolve out the ferric oxide, and then estimate the amount colorimetrically with thiocyanate. In that case, the alumina is taken by difference.

A more satisfactory procedure, and a necessary one in the case of materials containing much alumina, as, *e.g.*, fireclay, is to decompose the ignited oxides by fusion with potassium pyrosulphate. The necessity arises because of the difficulty with which strongly ignited ferric oxide and alumina dissolve in hydrochloric acid. An extract of the pyrosulphate fusion with 5 per cent. sulphuric acid provides a solution suitable for the colorimetric estimation of titanic and ferric oxides, the alumina again being obtained by difference. The same solution on evaporating to sulphur trioxide fumes and diluting, may also yield a milligram or two of silica which, for very exact purposes, should be removed before applying the colorimetric tests, and its weight added to that of the main portion.

Larger amounts of iron may be estimated by one of the volumetric processes, and aluminium in a separate portion of the solution by precipitation as phosphate.

Lime and Magnesia.—The filtrate from the ammonium hydrate precipitation is concentrated to a bulk of 150 c.c. or thereabouts, made slightly ammoniacal, and an excess of ammonium oxalate added. The mixture is boiled for a few minutes, allowed to cool for 2 or 3 hours, and the calcium oxalate filtered off, washed with water containing a little ammonium hydrate and oxalate, and ignited to oxide in the hottest part of the muffle. By way of a check upon the determination, the residue is treated with a few drops of sulphuric acid, the excess removed, and the resulting calcium sulphate weighed.

$$CaSO_4 \times 0{\cdot}412 = CaO.$$

Calcium oxalate precipitated under the conditions which obtain is difficult to rid completely of the sodium salts present, and it is liable to contain also traces of magnesium. It is advisable therefore to make two precipitations, the second one from the solution obtained by dissolving the oxalate of calcium from the filter with warm and very dilute nitric acid.

The filtrate from the ammonium oxalate precipitation is concentrated to as small a volume as possible, about one-third of its volume of ammonium hydrate added, and then an excess of a solution of ammonium phosphate or microcosmic salt. The mixture is allowed to stand for 12 hours, the precipitate then filtered off and washed with 2 per cent. ammonium hydrate. It is then dissolved from the filter with dilute nitric acid and a re-precipitation made by adding a small amount of the microcosmic salt, and whilst stirring throughout, the full excess of ammonium hydrate gradually. In this way the crystalline ammonium magnesium phosphate is obtained. The precipitate is allowed to stand as before, is then collected, washed, and finally ignited to the pyrophosphate.

$$Mg_2P_2O_7 \times 0{\cdot}362 = MgO.$$

ALTERNATIVE PROCESS TO FUSION.

The difficulties of making a direct determination of silica and the contamination with sodium salts of precipitates, which at best are not easily washed, has led to the following method of analysing highly siliceous materials such as gannister; the process is not of much value in the case of fireclay and similar material.

One or two grams of the substance are treated in a tared platinum crucible with hydrofluoric acid and sufficient sulphuric acid to 'fix' titanium and aluminium as sulphates and leave an excess. The mixture is allowed to stand in a warm situation overnight, and is then evaporated to dryness and the residue ignited and weighed. Hydrofluoric, a drop or two of sulphuric, and 2 or 3 c.c. of hydrochloric acid are then added, the mixture slowly evaporated to dryness, and the residue ignited and weighed. By this treatment all the silica is eliminated.

A muffle is not generally hot enough completely to drive sulphuric acid out of combination with alumina and titanic oxide, so that the amount of silica is not accurately measured by the loss in weight, unless an excess of ammonium carbonate is added to the nearly dried residue, and the crucible strongly ignited to constant weight over a powerful blast lamp. The residue, which consists of ferric oxide, alumina, lime, and magnesia, is dissolved (by means of fusion if necessary) in hydrochloric acid, and the solution analysed as before.

Titanic Oxide.

The determination of titanic oxide (which is almost invariably present in small amounts in clays), is made colorimetrically on the ammonium hydrate precipitate obtained in either of the general processes described above.

Ferrous Oxide.

The ferrous iron in refractory materials as well as in the siliceous residues of iron ores is always determined by some modification of one of the following processes :

(*a*) Fusion with mixed alkaline carbonates or acid potassium sulphate.

(*b*) Digestion with acid in sealed tubes at elevated temperatures.

(*c*) Treatment with hydrofluoric and a stronger acid, or with a mineral acid and some normal fluoride.

In each case the operation must be performed, in an atmosphere of carbon dioxide or purified coal gas, on very finely powdered material. The last process is most used and is said to give the most accurate results, although obviously the presence of organic matter, or pyrites, or metallic particles will vitiate the results in any case.

The following is essentially Willbur and Whittlesey's mode of carrying out the process originally suggested by Avery: Mix the powdered sample intimately with from one to one and a half times its weight of fluorspar or cryolite (free from iron) in a platinum crucible, cover with hydrochloric acid, and heat in an atmosphere of carbon dioxide or coal gas washed by caustic potash, until the materials are all dissolved. The time required for this will vary with the degree of fineness and the nature of the material, but the operation needs very little attention if carried out in some such arrangement as is shown in Fig. 16. This apparatus consists of a bell jar standing in a shallow leaden dish, which is kept supplied with water so as to make an air-tight joint. The tube *A* is for the entrance of the neutral atmosphere and *B* for its exit. When decomposition is complete the cooled solution is diluted and titrated with bichromate.

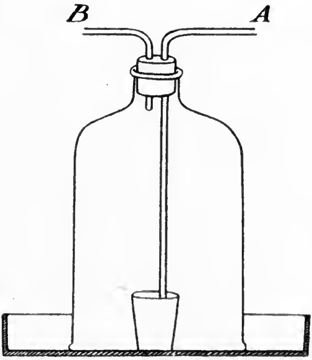

FIG. 16.

Hydrofluoric and sulphuric acids may be used instead of hydrochloric acid and fluorspar, but if much calcium is present the attack is retarded by the formation of calcium sulphate.

Alkalis.

Only two methods designed especially for the estimation of alkalis in insoluble siliceous bodies are practised to any considerable extent; they are (1) the Lawrence Smith process,[1] dating to 1871, in which decomposition of the material is effected by heating with a mixture of calcium carbonate with ammonium chloride: (2) the much older method of opening out with a mixture of sulphuric and hydrofluoric acids, recommended by Berzelius.[2] Other methods of decomposition, such as a fusion with the oxides or basic salts of bismuth and lead, have been used for the general analysis (alkalies included) of siliceous materials; they are not practised at the present time. The general applicability of the first method indicated above renders unnecessary a description of the others.

Lawrence Smith Process.—Specially purified calcium carbonate and ammonium chloride are required for this method. The latter should leave no residue on ignition. Pure calcium carbonate can be prepared, if necessary, from calcite or white marble by dissolving in hydrochloric acid, adding a little slaked lime to precipitate traces of iron, aluminium and phosphoric acid, and then precipitating the hot diluted filtrate with ammonium carbonate.

One gram of the finely-ground refractory material is mixed intimately with 1 gram of ammonium chloride and from 7 to 8 grams of calcium carbonate. The mixture is transferred to a capacious platinum crucible containing a bottom layer of calcium carbonate, and is finally covered with more carbonate, of which 9 grams in all are used.

The crucible is heated very gently at first until the ammonium chloride is nearly all volatilised, and the temperature then raised to that of a fair but not bright red heat, which is maintained for an hour. The heating is conducted over a bunsen burner, the crucible being placed at such a height that its upper empty portion is out of the flame. Too high a temperature is the cause of many a spoiled assay.

The sintered mass is loosened from the crucible by digesting with water, and then washed into a porcelain dish. More water is added and the mixture kept warm for half an hour, large particles or small lumps being broken up during the digestion by grinding with a glass pestle at intervals. The liquid is decanted through a filter, the residue washed several times by decantation with hot water, transferred to the filter, and washed further until the washings yield an opalescence only when tested with silver nitrate solution. The completeness of the decomposition of the

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[1] *Amer. Journ. Sci.*, 50. 269 (1871), and *Chem. News*, 23. 222 *et seq.* (1871)

[2] *Pogg. Ann.*, 1. 169 (1824).

material is then ascertained by treating the residue with hydrochloric acid. It should dissolve completely, leaving no trace of the undecomposed substance.

Calcium is next removed from the filtrate by adding ammonium hydrate, an excess of ammonium carbonate, heating the mixture for a minute or two, and filtering. The precipitate of calcium carbonate so obtained always contains a small amount of ‘ alkali ’ even after being well washed, so it is dissolved in acid, and a second precipitation made in the same manner. The mixed filtrates are then evaporated to dryness in a dish, and the ammonium salts volatilised by moving a free flame carefully over the under surface of the vessel. Traces of calcium still remain in the residue, and are removed by dissolving in water and adding ammonium hydrate and a small quantity of ammonium oxalate. The mixture is allowed to stand for 12 hours to effect complete separation of the calcium oxalate, which is then filtered off and washed, filtrate and washings being received in a weighed platinum dish. The solution is evaporated to dryness and the residue ignited gently. It is next moistened with a drop or two of hydrochloric acid, and the evaporation and ignition repeated. The final residue is a mixture of potassium and sodium chlorides, the weight of which is then recorded. It is a fairly safe precaution to add to this weight, 2 per cent. of it as a correction for ‘ alkalis ’ left in the insoluble residue after lixiviation with water of the original fusion. This amount is the average constant blank, when the process is executed as described.

The separate amounts of the two constituents of the residue are determined by one or other of the following processes.

(1) An indirect method, subject to the possible and frequently large errors incidental to all such processes, consists in the determination of the total chlorine content of the residue, and a calculation of the amounts of sodium and potassium oxides from the result. Chlorine is determined by dissolving the residue in water, and titrating with a standard solution of silver nitrate, with the usual potassium chromate indicator.

If x and y represent the amounts of potassium chloride and sodium chloride respectively in the residue of weight w, and the weight of chlorine found is w_2, then

$$x+y=w_1.$$
$$0{\cdot}4756x+0{\cdot}6047y=w_2.$$

The values of x and y found by solving these equations are converted into the equivalent amounts of oxide thus :—

$$x\times 0{\cdot}6317=\text{amt. of } K_2O.$$
$$y\times 0{\cdot}5303=\quad \text{do.}\quad Na_2O.$$

(2) The potassium chloride in the residue is found by precipitating with a solution of hydrochloroplatinic acid, and the sodium chloride taken by difference.

The residue of mixed chlorides is dissolved in water and treated with an excess of the reagent, which is conveniently made to contain 0·1 gram of platinum per c.c. The excess need only be a few tenths of a c.c. more than the theoretical amount, which is calculated usually on the assumption that the whole of the chloride residue is constituted of the sodium salt.

The mixture is evaporated to a syrup over the water bath and then allowed to cool. The residue is treated with a few c.c. of 80 to 90 per cent. alcohol, the mixture stirred, allowed to stand for a minute, and the supernatant liquid poured off through a weighed Gooch crucible. The treatment with alcohol is repeated several times until the washings are quite colourless; the precipitate is then transferred to the filter, washed twice more, and dried at 130° C. to constant weight.

$$K_2PtCl_6 \times 0{\cdot}3068 = KCl.$$
$$K_2PtCl_6 \times 0{\cdot}1941 = K_2O.$$

Sodium choride is obtained by difference, and the equivalent amount of oxide calculated therefrom.

(3) The potassium is determined by the ' perchlorate method,' which depends upon the insolubility of potassium perchlorate and the solubility of the corresponding sodium compound, in 97 per cent. alcohol.

The mixed chlorides are dissolved in a few c.c. of hot water and the solution treated with two or three times as much perchloric acid as is necessary theoretically to form the perchlorates of both metals. The reagent is usually a 20 per cent. solution of spec. grav. 1·125. The mixture is evaporated until copious fumes of perchloric acid appear, and the syrup then dissolved in hot water. A few drops more of the reagent are added, and the mixture fumed again. After cooling thoroughly, 20 c.c. of 97 per cent. alcohol are added, and the mixture stirred. The liquid is decanted from the potassium perchlorate, the latter washed by decantation with more alcohol, transferred to a weighed Gooch crucible, dried at 120°-130°, and weighed.

$$KClO_4 \times 0{\cdot}5381 = KCl.$$
$$KClO_4 \times 0{\cdot}3406 = K_2O.$$

Water and Organic Matter.

These constituents, and any small amount of carbon dioxide are generally expressed as ' Loss on Ignition ' with sufficient exactness for works' purposes. But when the item is a large one—*e.g.* in fireclays—its components may be shown separately.

Hygroscopic Water is determined by heating from ten to twenty grams of the clay in a shallow tared platinum dish at 100° C. for two or three hours, and then further until a weighing made after an additional hour's heating does not differ materially from the previous one. Any required crushing or grinding of the clay should be done prior to this determination if the further analysis is being made on the dried portion, because it readily absorbs water from the atmosphere.

Combined Water and Organic Matter are determined by heating two grams of the material in a dried tube of refractory glass as in manganese ores (p. 235). The tube should contain an inch or so of copper oxide and a plug of asbestos to prevent the escape from the tube of carbon monoxide and any fine dust. The combustion is continued until the water deposited in the cooler part of the tube is swept completely into the weighed tube containing calcium chloride or sulphuric acid. By that time all organic matter will have passed as carbon dioxide into the weighed potash bulb arranged next in the train. From the increased weight of the separate absorbers the percentages of combined (or plastic) water and organic matter are calculated.

The combined water and organic matter are frequently obtained and shown together by merely igniting one or two grams of the dried clay. The result thus obtained diverges from the truth according as small or large amounts of ferrous oxide are present.

NEUTRAL MATERIALS.

Bauxite.

Hygroscopic and combined water are determined as in fireclays. The sample is then opened out by fusion with sodium carbonate. The silica is obtained by evaporating with acid; it always contains a little titanic oxide, which is left wholly in the residue after the former is volatilised with hydrofluoric acid. The iron is determined volumetrically in a portion of the filtrate and the alumina—as phosphate—in another portion. This aluminium phosphate contains all the titanic oxide, except that found with the silica.

According to Deville, who examined samples from various localities, bauxite may contain alumina in both the crystallised (corundum) and amorphous state, and also more or less carbonate of calcium and phosphoric and vanadic acids.

Chrome Bricks.

These are analysed by the processes given for chromite on p. 239.

Black Lead.

Black lead for foundry use, or plumbago pots are very rarely submitted to any chemical examination beyond determining 'Loss on Ignition.' An actual determination of the carbon is nearly always less than the figure thus obtained, on account of the presence of water or some other volatile constituent. The ash may be examined by processes already described. The following is an analysis of black lead used for steel-foundry purposes:

Loss on ignition, 59·24; Silica, 21·40; Ferric Oxide, 8·05; Alumina, 9·56; Manganous Oxide, 0·28; Lime, 0·70; Magnesia, 0·56—Total, 99·79.

BASIC MATERIALS.

Lime or Magnesia Bricks, Dolomite, Limestone, etc.

With this class of material the possibility of error is perhaps greatest in those cases where a little lime has to be separated from much magnesia. The analysis of a magnesite brick will therefore be described, and the obvious modifications required to fit the processes to the analysis of dolomite, etc., left to the discretion of the reader.

Silica.

Weigh one gram of the powdered brick into a small beaker, moisten with water, add 20 c.c. hydrochloric acid, and boil vigorously until a colourless residue of impure silica only is left. Evaporate to dryness, take up with hydrochloric acid, and filter. The ignited silica is volatilised with hydrofluoric acid and any small residue dissolved and added to the main filtrate.

Alumina and Ferric Oxide.

In order that no appreciable amount either of calcium or magnesium may be incorporated by the aluminium and ferric hydrate precipitate, it is necessary to add, or generate, one or two grams of ammonium chloride. Even with this precaution the alkaline earths are precipitated if the solution is kept boiling for some time. As soon therefore as the hot solution, to which ammonium hydrate has been added in slight excess, begins to boil, it is removed from the burner and filtered as quickly, and as much out of contact with the air, as possible. When these particulars are attended to there seems to be no need to dissolve and re-precipitate the small amounts of ferric and aluminium hydrates, though such an operation would not occupy much time.

Lime.

The filtrate is diluted to 700 or 800 c.c., 8 or 10 grams more of ammonium chloride added, and a solution of ammonium oxalate containing as much of the solid as is equivalent to the combined weights of the lime and magnesia. The hot solution, which must not be boiled, is allowed to cool thoroughly with occasional stirring, and the calcium oxalate precipitate then filtered off. The large dilution recommended is necessary in order to retain magnesia in solution, though it could probably be diminished somewhat if the lime were precipitated from the cold solution. The large excess of ammonium oxalate is necessary to counteract the solvent action of magnesium chloride on calcium oxalate: ammonium chloride exerts no appreciable solvent action.

Notwithstanding these precautions some magnesia is invariably precipitated along with the lime. After filtering the cold solution, the precipitate is re-dissolved in hydrochloric acid, and re-precipitated from a faintly ammoniacal solution in the same way as before, except that less dilution and less ammonium chloride are needed completely to prevent the precipitation of the remaining magnesia. The second precipitate is filtered off in due course and estimated either as oxide or sulphate in the usual manner.

Magnesia.

The combined filtrates are acidified and evaporated to 500 c.c., or some other convenient volume. From 100 to 200 c.c. of this solution is measured into a flask along with one-third its volume of ammonium hydrate, and an excess of a saturated solution of sodium ammonium phosphate is added in drops from a burette to the vigorously shaken liquid. A very tolerable result is obtainable by filtering off the precipitated ammonium magnesium phosphate after shaking the closed flask for about five minutes. but it is customary to allow at least several hours for the magnesia to settle out.

Collect the precipitated phosphate on a pulp filter and clean out the flask with separate portions of the clear filtrate. Then wash with strongly ammoniacal water, using a little at a time by preference, until the washings give a scarcely perceptible opalescence when an excess of nitric acid and silver nitrate are added.

The somewhat bulky precipitate is dried at the mouth of the muffle and the paper ignited from it at as low a temperature as possible. When the precipitate is nearly white, and not before, the dish may be pushed well into the muffle, strongly ignited, and then weighed. Any lumps in the perfectly white precipitate should be broken in order to make sure that they contain no undecarbonised paper, as they are apt to when the ignition is pushed too quickly. It is as well also to dissolve the precipitate in hydrochloric acid, and note that small black particles or other insoluble matter are absent.

Manganous Oxide.

The determination of manganous oxide in dolomite or limestone is simple by a colorimetric process.

Phosphoric Acid.

Five to ten grams of the material are digested with hydrochloric acid and the solution filtered. The ignited siliceous residue is treated with hydrofluoric acid, and any remaining portion dissolved (or fused and extracted) and added to the main solution. If there is not sufficient iron and aluminium present to combine with the phosphoric acid, a little ferric chloride is added, and then ammonium hydrate in slight excess. The precipitate containing the phosphoric acid in combination with iron and aluminium is collected, washed, and dissolved in nitric acid. From this solution it is precipitated with the ammonium molybdate reagent, and the estimation completed as usual.

ZIRCONIA.

The refractory material known commercially as 'zirkite' is of considerable importance to the steel metallurgist because of its very high fusion point, small co-efficient of expansion, and low thermal conductivity.

The principal constituent is zirconium oxide, the remainder being silica, ferric oxide, alumina, titanic oxide, combined water, and a small quantity of manganous oxide. Two varieties of the ore occur, one known as 'favas' by the Brazilian miners, containing from 90 to 93 per cent. of ZrO_2, the other, and specifically lighter, 80 to 86 per cent.; a typical analysis of each kind is appended.

ZrO_2	92·84	83·12
SiO_2	2·12	9·43
Fe_2O_3	2·67	4·42
Al_2O_3	0·56	0·74
TiO_2	0·92	0·81
MnO	trace	0·23
Loss on ignition	0·62	0·93

The analysis of these rich zirconium earths is simple if the determination of silica is omitted ; when this determination is attempted, tedious and many operations are necessary. The ore is not appreciably attacked by the ordinary acids, and is very imperfectly ' broken up ' by fusion with the caustic alkalis or sodium peroxide. Sodium carbonate and acid sodium sulphate yield better results, but a single fusion does not suffice.

The best method of attack is a fusion with acid potassium fluoride, which obviously makes a direct determination of silica impossible.

One gram of the finely-ground substance, contained in a large platinum crucible, is moistened with a drop or two of sulphuric acid in order to prevent loss of titanium during the fusion, and about 6 grams of acid potassium fluoride added. The crucible is heated very cautiously over a small flame until water is completely expelled and a dry mass obtained. The temperature is then raised so as to melt the salt, and is maintained until the material is decomposed ; complete decomposition is evidenced by a clear melt, entirely devoid of particles of apparently solid matter. The entire operation may be controlled (and observed) by gripping the crucible with a pair of tongs and keeping the fluid contents in motion throughout ; not more than 10 minutes are occupied in the process of decomposition. On cooling, a white porcelain-like mass is obtained, to which 10 c.c. of sulphuric acid are added, and the mixture then ' fumed ' copiously. The residue, after cooling, is boiled out with water and the clear solution of sulphates made up to a definite volume with water. Measured fractions of this may be taken for the subsequent estimations, which have already been described.

Thus, *e.g.*, titanium may be determined at once on a portion by the colorimetric method, and the finished assay utilised for the determination of the small amount of manganese, also colorimetrically. The preliminary operations are, the evaporation to fumes of sulphur trioxide, extraction with dilute nitric acid, and an oxidation to permanganic acid with sodium bismuthate or ammonium persulphate.

For the determination of zirconia (also alumina and ferric oxide), another portion of the solution is treated with a slight excess of ammonium hydrate, the precipitated hydroxides filtered off, converted to chlorides, and the zirconium determined by precipitation with sulphurous acid as described on p. 218. Titanium oxide in the ignited zirconia must be allowed for.

A study of that section of Part II. in which is described the analytical chemistry of zirconium, will suggest further means of dealing with the solution of sulphates obtained as above.

By precipitating from another portion with ammonium hydrate, and igniting the washed precipitate, the total weight of the metallic oxides is obtained. As practically the only remaining constituent of these zirconium ores is silica, a direct determination of the latter, for technical purposes, then becomes almost unnecessary. In view of the number of operations entailed by the determination, it is indeed very probable that the calculated difference value is the more exact.

A direct determination of silica involves at least two fusions of the finely-floured material with sodium carbonate or acid sodium sulphate, preferably the latter. Three or four grams of the salt are converted into the pyrosulphate by heating in a platinum crucible until the liquid mass is quiescent, whereupon the weighed sample (0·5 gram) is introduced a little at a time, each portion being thoroughly diffused throughout the melt before adding the next, and the whole mixture heated finally for half an hour over the blast. The mass is extracted with hot water in large quantity, filtered, and the insoluble residue collected, the filter ashed, and the residue again fused as above. The residue left after the second lixiviation is almost pure ZrO_2. The combined filtrates are taken to dryness, the residue taken up with hydrochloric acid and water, filtered off, washed thoroughly with hot water, ignited, weighed, and the silica determined by volatilisation with hydrofluoric and sulphuric acids.

PART VI. ANALYSIS OF SLAGS.

When slag is run into thin pieces and cooled quickly, it is practically homogeneous; there is therefore no difficulty in taking a fair sample. The rapid cooling has often also the effect of converting an otherwise insoluble into a soluble slag. Very large masses of slag which are cooled slowly are not usually homogeneous; indeed, the interior of such masses may be porous and may also, particularly in the case of basic slags, be lined with more or less perfect crystals.[1]

It is unnecessary to give full instructions for the analysis of slags, which are treated on similar lines to those adopted for ores and refractory materials.

BLAST FURNACE SLAG.

An experienced eye may deduce something of the chemical composition of a slag by careful observation of its physical characters during the working of a furnace. The differences in colour are the most obvious: violet, yellow, black, and blue slags being said to correspond respectively with the presence of notable amounts of manganous oxide, manganous sulphide, ferrous oxide, and the oxides of aluminium and zinc, or a sulphide of sodium. The statement that furnaces making grey iron yield a light-coloured, and those making white iron a dark-coloured slag, is not universally true; indeed, white iron is regularly produced with a very grey limy cinder. Dark-coloured slags often indicate slipping or cold working.

Silica.

One gram of the finely-ground slag, freed magnetically from metallic shots, is placed in a wide beaker or porcelain dish, 25 c.c. of water added and the liquid brought to boiling. On adding hydrochloric acid, about 30 c.c. in all, at such a rate that the boiling is not interrupted, decomposition is effected without any possibility of undissolved particles

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[1] Stead and Ridsdale, *Journ. I. and S. I.*, 1889, i. 222.

becoming coated with gelatinous silica. The liquid is boiled briskly to low bulk, a few drops of nitric acid added and the heating continued until hydrochloric acid is completely expelled. The residue is taken up with hydrochloric acid and water, and the silica filtered off and weighed.

The product may not be quite pure, but as a single evaporation does not recover the whole of the silica, the error is balanced to some extent and the results are sufficiently accurate for works' purposes. When a slag contains notable amounts of barium sulphate or titanic oxide, it may be necessary to make a further examination of the ignited silica.

If aluminous ores are being smelted and fluxed with magnesian limestone, it is never safe to omit treatment of the silica with hydrofluoric acid, because spinel (magnesium aluminate) to the extent of two or three per cent. may be present (Shimer). If a further examination of the residue is needed, it should be fused with potassium bisulphate, as sodium carbonate fails to decompose it.

Silica determinations within 0·25 per cent. of the truth are quickly obtained by operating upon a smaller quantity of the sample in the following manner:—

Decompose 0·5 gram with water and hydrochloric acid in a porcelain dish, evaporate to dryness, grind the residue, bake for 20 minutes at about 180° C., take up in acid and water, filter, etc. Ignite at a high temperature.

The loss of silica is again almost balanced by the impurities in the residue, representing usually from 0·5 to 0·75 per cent.

Ferrous Oxide and Alumina.

The filtrate from the silica determination may be used for these determinations. A gram or two of ammonium chloride is added and the hydrates of the metals precipitated with dilute ammonium hydrate. The precipitate may be collected, washed, dried, ignited to oxides and weighed, or re-dissolved in acid without washing, and the aluminium determined by a double precipitation as phosphate after adding several grams of sodium phosphate to the acid solution.

The filtrate from the aluminium precipitations is oxidised with nitric acid, and the iron determined in the solution volumetrically. Alternatively a separate determination of ferrous oxide is made by boiling 2 grams of the slag in a flask provided with a bunsen valve attachment in hydrochloric acid, and titrating the resulting solution of ferrous chloride (without filtration of separated silica) with a weak solution of potassium dichromate.

Lime and Magnesia.

0·6 gram of the slag is opened out as above, the silica filtered off, a few drops of nitric acid added to peroxidise the iron, and a basic acetate precipitation of iron and aluminium made. From five-sixths of the total volume of solution and precipitate, obtained by filtration through a dry paper, calcium is precipitated as oxalate without removing manganese. It is not easy to convert a large mass of calcium oxalate to oxide by ignition, and the determination is best made gravimetrically by weighing as sulphate, or volumetrically by titration with permanganate as in the following alternative method to the above.

To 0·5 gram of the sample add 30 c.c. of boiling water and 10 c.c. of nitric acid, and gradually dilute to about 150 c.c. with hot water. Add a small quantity of ferric nitrate and then dilute ammonium hydrate (1 : 1) very carefully until the solution visibly darkens, but does not become turbid. Then add a solution of 3 grams of ammonium oxalate in boiling water, boil the mixture, filter off the calcium oxalate and wash it. Rinse the precipitate back into the beaker and dissolve it in 10 c.c. of sulphuric acid diluted with 100 c.c. of water, a portion of the mixture being used to dissolve the last traces of precipitate from the filter. Heat the solution to 70° C. and titrate with potassium permanganate (5·643 grams per litre). The time required for the process does not exceed half an hour, and the results are accurate to within 0·25 per cent.

1 c.c. permanganate = 1 per cent. CaO.

Magnesia is determined as phosphate in the filtrate from an oxalate precipitation of the lime, the latter being preceded by the removal of silica and iron and aluminium as hydrates. For accuracy, it is necessary to make a double precipitation of the magnesium.

Manganous Oxide.

Boil one gram of the powdered slag with 40 c.c. of water, and then add 20 c.c. of nitric acid. When the sample is decomposed, dilute if necessary, cool, and determine the manganese in the solution by the bismuthate process.

Sulphur.

Sulphur may be determined gravimetrically by the aqua regia process used for steels, or more simply and with equally good results by the following method.

To one gram of the powdered slag contained in a small flask add 20 c.c. of water, 2 c.c. of bromine, and 15 c.c. of hydrochloric acid. Warm gently until the sample is decomposed, dilute with 40 c.c. of water and filter into a beaker. Dilute the filtrate with an equal volume of water and add dilute ammonium hydrate until the aluminium hydrate which forms disappears only slowly on stirring. Precipitate the sulphuric acid from the solution with barium chloride, and finish as usual.

As the sulphur exists almost entirely as calcium sulphide it may be estimated volumetrically with sufficient accuracy for all practical purposes. Weigh from a quarter to one gram of the slag into the flask (p. 74) along with half a gram or so of sulphur-free iron or steel or zinc, moisten the powder with water, heat and add 20 c.c. hydrochloric acid. The evolved sulphuretted hydrogen is absorbed in zinc acetate, titrated with iodine, and calculated to sulphur.

In tabulated analyses the sulphur may be expressed as calcium sulphide or as calcium and sulphur separately ; but it is not uncommon to express sulphur as such, and all the calcium as oxide.

Phosphoric Acid.

The amount of phosphorus is generally very small and rarely estimated. The sample is decomposed with nitric acid and a few drops of hydrofluoric acid, the mixture filtered and the phosphoric acid precipitated from the filtrate with the ammonium molybdate reagent. A larger excess of free nitric acid than usual should be present in the solution.

Alkalis.

Alkalis are determined as in fire-clays, the potash by precipitation as perchlorate, and soda by difference.

Titanic Oxide.

This is a frequent constituent of slags, but it has no metallurgical significance. It is determined by boiling the slag with nitric acid, cooling, and filtering. The filtrate contains most of the titanium. The undissolved portion is added to it after igniting, fusing with sodium carbonate, and digesting with sulphuric acid. The total is estimated colorimetrically.

The crystals of cyano-nitride of titanium, commonly observed in blast-furnace 'bears,' may be separated from the slag, according to Reinhardt, by treating the mixture successively with hydrofluoric, hydrofluoric and sulphuric, and sulphuric and chromic acids. The titanium is estimated by fusing with potassium bisulphate, digesting with acidulated water, and precipitating with a small excess of ammonium hydrate, followed by a small excess of acetic acid. The formula of the crystals approximates to $Ti_5(CN)_4$.

TAP CINDER.

Puddler's tap cinder may be regarded as a ferrous silicate in which are dissolved various amounts of ferrous and ferric oxides. As the slag or cinder is quite decomposed by hydrochloric acid the analysis is very simple.

Silica, Ferrous and Ferric Oxides, Alumina, Lime and Magnesia.

Dissolve one and a half grams in the same way as blast-furnace slag, evaporate, collect the silica, and estimate it. Precipitate the iron and aluminium in the filtrate with ammonium acetate, make the solution up to 300, and filter off 200 c.c. for the estimation of lime and magnesia in the usual way after separating manganese with bromine and ammonium hydrate, or as sulphide.

The residue is dissolved in acid, and one-third of the solution used for the estimation of total iron. The remaining two-thirds is treated like a ferro-aluminium. The precipitate obtained is rarely pure aluminium phosphate; it will contain any chromic or titanic oxides present in the slag as well as traces of vanadic oxide. Chromic and titanic oxide may be determined from this precipitate: the former by titrating the chromic acid after fusing with sodium carbonate or by matching its colour with sodium chromate solutions, and the latter by the hydrogen peroxide test. These determinations are rarely called for.

Sulphur.

Sulphur is determined gravimetrically by the aqua regia process. It exists partly as ferrous sulphide.

Manganous Oxide and Vanadic Oxide.

Manganous oxide is determined as in blast-furnace slags. A little hydrofluoric acid is nearly always needed to complete the decomposition. The presence of a few tenths per cent. of vanadic oxide may be observed during the titration by the rapid disappearance of the permanganate tint first formed, and its amount may be roughly estimated during the same operation. The peroxide colour estimation can be made only when titanium is absent, and hydrofluoric acid has either not been used or has been completely expelled. The separate estimation of titanic and vanadic oxides is made as in iron ores.

Ferrous Oxide.

Dissolve half a gram of the very finely ground slag in hydrochloric acid, and titrate with bichromate. The result is likely to be too high on account of the interference of small particles of iron and ferrous sulphide. The former cannot be removed magnetically, because the cinder itself is more or less magnetic. The ferric iron is represented as usual by the difference between the volume of bichromate needed to titrate the iron existing as ferrous oxide, and the volume needed for the total iron after converting to ferrous oxide.

Phosphoric Acid

Dissolve half a gram of the slag with nitric and hydrofluoric acids, boil off most of the latter, and dilute to 100 c.c. To 25 c.c. (·25 gram) add 12 to 14 c.c. ammonia, and just clear the solution with nitric acid; then add at least twice the usual amount of nitro-molybdate reagent and transform the precipitated phospho-molybdate to the lead salt for weighing.

ACID SIEMENS' SLAG.

These slags are generally insoluble in hydrochloric acid. Fuse one and a quarter grams with two or three grams sodium carbonate, evaporate the dissolved melt with hydrochloric acid, and collect the silica exactly as in a Refractory (p. 244). Precipitate the filtrate with ammonium acetate, and estimate the total iron, alumina, lime, and magnesia as in former slags. The separated hydrate or sulphide of manganese may be ignited and weighed, or prepared in ways previously described for the bismuthate estimation.

Manganous Oxide.

A direct determination of manganous oxide is made by dissolving 0·5 gram of the slag in hydrofluoric and hydrochloric acids, evaporating with sulphuric acid to fumes, adding nitric acid and oxidising with bismuthate, etc., as usual. A mixture of hydrofluoric and nitric acids will sometimes dissolve very finely powdered slags, and thus dispense with the sulphuric acid evaporation, but it is not to be generally depended upon.

Sulphur.

Two grams of the slag are fused with sodium carbonate, the acidified solution of the melt evaporated, silica removed, and barium choride added to the filtrate after neutralising most of the free acid with ammonium hydrate.

Phosphoric Acid.

Decompose 2 grams with hydrochloric and hydrofluoric acids, evaporate nearly to dryness, transfer to a glass vessel, boil with nitric acid and permanganate, and finish as for an iron ore.

BASIC SIEMENS' SLAG.

Silica.

Dissolve one and a half grams in hydrochloric acid, evaporate with a little nitric acid, and estimate the collected silica. It should be treated with hydrofluoric and sulphuric acids in order that a small dark-coloured residue, which probably contains chromic oxide, may be fused, dissolved in acid, and added to the following solution :

Oxides of Iron and Aluminium.

Neutralise the solution until a slight turbidity forms, add 2 or 3 c.c. acetic acid, and when boiling as much ammonium acetate only as is needed to complete the precipitation of the basic phosphates of iron and aluminium. It is desirable, if not essential, for the completeness of the subsequent separations that all the phosphoric acid should be precipitated ; a little ferric chloride should therefore be added if it is feared that a sufficient amount of the basic oxides is not present to effect this. The collected precipitate is re-dissolved and the total iron and alumina determined as in tap cinder. The precipitated aluminium phosphate contains also chromic, titanic, and vanadic oxides, which may be separated by fusing with sodium carbonate, extracting the melt with water and filtering. Chromic, vanadic, and aluminic oxides are in the filtrate ; the residue contains titanic and traces of manganic and ferric oxides.

Lime and Magnesia.

These are determined in a fraction of the filtrate as in blast furnace slag. The manganese is previously separated as sulphide : if with bromine and ammonium hydrate, two precipitations are necessary.

Manganous Oxide and Sulphur.

These are determined as in tap cinder.

Phosphoric Acid.

As in tap cinder. The phosphorus is conveniently precipitated from a portion of the solution intended for the estimation of manganous oxide.

If the sample contains 10 to 20 per cent. of phosphoric acid, a decigram is as much as can conveniently be handled when the yellow precipitate is to be re-dissolved and the determination made by weighing as lead molybdate. If the final precipitation takes the form of ammonium magnesium phosphate, much larger amounts can be used.

MILL SCALE: ELECTRIC FURNACE SLAGS.

Mill scale may be analysed exactly as a pure magnetic iron ore. The sum of the percentages of ferrous and ferric oxides in scales from different irons and plain carbon steels is seldom less than 98 and frequently exceeds 99. The ratio of iron to oxygen varies between the limits represented by the formulæ Fe_7O_8 and Fe_4O_5. The other constituents consist of small quantities of manganous oxide, silica and phosphoric acid, sulphur being almost entirely absent in most cases.

The extraordinary variety of the steels which are produced in modern electric furnaces makes a classification of the associated slags extremely difficult, the broad classification into soluble and insoluble slags being perhaps the only possible one. Precise instructions for their analysis are out of the question, nor are they necessary. The main constituents are determined by such methods as have already been described; slags from furnaces making alloy steels demand the application of methods for the determination of the special elements that may be involved, and suitable modifications of the processes for the determination of the invariable constituents.

PART VII. THE ANALYSIS OF FUEL.

I. SOLID FUELS.

COAL AND COKE.

The chemical analysis of coal for technical purposes always involves the determination of moisture, ash, volatile matter, and fixed carbon, the whole constituting what is known as a proximate analysis. The impurities sulphur and phosphorus are frequently included, but the ultimate analysis for carbon, hydrogen, oxygen, and nitrogen is rarely called for.

Of primary importance is the matter of sampling, not by any means easy in the case of a material such as coal, which is a mixture of several substances of unequal specific gravities. Errors much greater than those of actual analysis are frequently attributable to imperfect sampling.

The final laboratory sample is obtained, after the various quartering operations, by passing the material through a sieve of 60 meshes to the inch. It should be kept in a wide stoppered bottle of sufficient capacity to permit intimate mixing of the contents by shaking at each weighing out of a sample for analysis. In order to eliminate errors due to slow oxidation of the finely divided material, the analysis should be made as soon as possible after the receipt of the sample.

Moisture.

The recognised method of determining moisture, by which term is meant hygroscopic water, consists in heating one gram of the sample in a platinum crucible for an hour at 105° C., whereby, it is assumed, the loosely retained water is expelled.

Drying to constant weight at 105° C. or at a higher temperature is an impossible operation. The heating not only eliminates water, but promotes oxidation of the coal and also expels small but not negligible amounts of gaseous decomposition products. The nett alteration in weight due to these causes may be plus or minus, dependent upon the temperature, state of division and nature of the coal. It frequently happens, *e.g.*, that the weight gradually falls under the heating down to a minimum, and then begins to rise again.

The percentage of moisture actually recorded may thus be in excess or below that of the true amount, and the results have therefore only a relative value. The extent of the error, however, when the operation is conducted at the temperature and for the time specified, is very small, and when material of approximately the same composition is being regularly handled, slight differences in the amount of hygroscopic water are readily detected.

Ash.

Two or three grams of the coal or coke are heated in a platinum dish in the muffle until all organic matter is burnt out; the residue is weighed and the amount reported as ash.

The heating should be conducted gently at first until the volatile matter is expelled, especially in the case of caking coals, so as to prevent the formation of a hard coke difficult to decarbonise. The ignition is usually complete when no black particles are discernible in the ash, but it is not safe to accept this indication. The dish, after weighing, is again placed in the muffle for about half an hour, cooled and re-weighed, and the treatment is repeated if necessary until the difference between two consecutive weighings is less than one milligram from a two-gram sample.

The ash is obviously not the original mineral matter of the coal, but the result of its ignition in air. Sulphur existing as sulphide (pyrites), *e.g.*, is oxidised, carbonates are converted into oxides, and clayey material loses combined water.

Volatile Matter and Fixed Carbon.

The method in general use for the determination of volatile matter and fixed carbon or coke is that recommended by the American Chemical Society,[1] which is described as follows.

" Place one gram of fresh, undried, powdered coal in a platinum crucible, wieghing 20 to 30 grams, and having a tightly fitting cover. Heat over the full flame of a bunsen burner for 7 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 fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the

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[1] *Journ. Amer. Chem. Soc.*, xxi. p. 1122.

under surface should remain covered with carbon. To find the 'Volatile Combustible Matter' subtract the percentage of moisture from the loss found here."

The above conditions are realised by the use of a powerful Meker burner, the free flame of which need not necessarily reach 20 cm., protected from draughts by means of a sheet iron chimney. A triangle made from nichrome wire, which is largely used as the resistance winding of electrically heated combustion furnaces, may conveniently be substituted for the platinum article.

Fuels such as lignite and peat, containing a high percentage of volatile matter, should be heated very gently for a few minutes before subjecting them to the full heat of the burner, in order to avoid possible mechanical loss which might otherwise occur. Coke, on the other hand, does not generate sufficient volatile matter to expel all the air at once from the crucible, and there is then a loss of fixed carbon due to oxidation. For very exact work, the determination of volatile matter in such materials is made by ignition at a cherry red heat in a current of nitrogen. A less accurate modification of the standard process consists in the introduction along with the sample of coke of a small weighed amount of coal, yielding sufficient combustible matter to create a non-oxidising atmosphere in the crucible and a pre-determined weight of residual coke which is, of course, deducted from the total final weight.

As one gram only of material is treated in the above method, the residue of coke left from a coal is obviously insufficient to enable the chemist to pronounce an opinion respecting its mechanical properties. From 20 to 30 grams of coal should be 'coked' for this purpose. The sample, roughly powdered and weighed to the nearest centigram, is charged into a fire-clay crucible such as is used in the dry assay of metalliferous ores. The rim of the crucible, and also the lid, are previously ground on a flat surface so as to ensure good surface contact. The crucible, with its charge of coal and lid in position, is placed in a hot muffle, the mouth of which is then partially closed, and allowed to remain until the flame issuing between rim and cover just dies down. It is then removed, allowed to cool, the coke turned out, and weighed.

Sulphur.

Sulphur exists in coal in three different forms: as sulphide (iron pyrites), as sulphate, and as an organic compound. The total amount only is usually determined for technical purposes.

The non-oxidised sulphur is first converted into sulphite and sulphate by roasting the sample with lime or magnesia mixed with carbonates of sodium and potassium. Sulphites are further oxidised to sulphates by a wet oxidant, and the total sulphate determined by means of a barium chloride precipitation.

The 'Eschka mixture' used for the dry oxidation consists of one part of anhydrous sodium carbonate mixed with two parts of light calcined magnesia. This is the mixture generally used, but an equally good one, and one which has usually a smaller sulphur blank, is compounded of eight parts of pure lime and one part each of the anhydrous carbonates of sodium and potassium.

Three grams of the latter mixture are shaken with one gram of the coal or coke in a stoppered bottle, the whole transferred to a capacious platinum crucible, and one gram more of the mixture then added to form a cover. The crucible is then transferred to the muffle and heated, cautiously at first, until the fuel appears to be completely burned, as ascertained by occasional stirring with a platinum rod. The contents of the crucible are then emptied into a beaker, about 70 c.c. of water and a few drops of bromine added, and finally a small excess of hydrochloric acid. On boiling, complete solution usually results; traces of insoluble matter may be removed by filtration. The sulphur is precipitated with a solution of barium chloride and the determination completed in the usual manner. The amount of sulphur introduced by the reagent mixture must be determined and allowed for by a blank experiment conducted exactly as in the assay. Determinations of sulphur and ash must not be executed at the same time in the muffle, as the lime used in the former absorbs sulphur dioxide generated in the latter. The usual recommendations in the case of the Eschka mixture are as follows. Two-thirds of two grams of the mixture are intimately mixed with one gram of the finely divided fuel in a large platinum crucible, and the whole covered with the remaining one third. The crucible is placed in an inclined position and heated very cautiously by allowing the tip of an alcohol flame just to reach the crucible near the surface of the mixture. The coal gradually burns throughout its mass without yielding smoke, and combustion is complete in about an hour. Coke may be heated more strongly than coal at the beginning, and the temperature in both cases may be increased considerably towards the end without loss of sulphur. The remaining operations are substantially the same as described above.

In laboratories where the calorific value of a fuel is regularly determined by means of the bomb calorimeter the determination of the total sulphur is easily made on the washings from the vessel. In these the sulphur exists as sulphuric acid which, after filtration from the ash and slight acidification with hydrochloric acid, may at once be precipitated and weighed as barium sulphate.

Phosphorus.

The whole of the phosphorus in coal or coke remains in the ash, and may vary in amount from traces up to three per cent.

For its determination five to ten grams of the fuel are ashed in a platinum crucible, and the residue treated with about five c.c. of hydrochloric acid, ten c.c. of hydrofluoric acid and a few drops of sulphuric acid. The mixture is evaporated to fumes, and dissolved in about twenty c.c. of nitric acid, specific gravity 1·20, in which a decigram or so of pure bar iron has been previously dissolved. The solution is transferred to a small flask, dilute ammonium hydrate added until the free acid is seen to be neutralised by the reddening of the solution, and fifty cubic centimetres of molybdate reagent added. The determination is completed by one or other of the methods described on p. 58, *et seq.*

ANALYSIS OF THE ASH.

An analysis of the ash from a fuel involves the determination of silica, lime, magnesia, ferric oxide and alumina, and is conducted as for refractory materials, *q.v.* In addition, phosphorus and sulphur, the former of which has already been dealt with, are usually reported. The sulphur is determined by fusion with sodium carbonate, extraction with water and precipitation with barium chloride from the acidified filtrate. The proportion of the total sulphur found in the ash is obviously dependent upon the relative proportion of ‘ sulphide ’ and ‘ sulphate ’ sulphur in the fuel.

ULTIMATE ANALYSIS.

Carbon and Hydrogen.

Carbon and hydrogen are determined simultaneously by burning coal contained in a boat in a purified stream of air or oxygen, the resulting carbon dioxide and water produced being absorbed and weighed.

A long glass tube is required for the purpose, and is heated in a combustion furnace burning gas. For six inches of its length the tube is loosely packed with granulated copper oxide, freshly ignited ; this part of the tube should be wrapped with asbestos cloth. The tube is freed from moisture before introducing the fuel by heating it to dull redness whilst several litres of dried air are slowly passed through it until the weight of a calcium chloride attachment tube remains constant.

The burners under the empty portion of the tube are then turned out and this part of the tube allowed to cool. In the meantime the exit end of the tube is joined up to the calcium chloride tube, this in turn to the potash bulbs with calcium chloride prolong, and the last to an aspirator. The usual train for drying and purifying the air or oxygen is placed in front of the combustion tube.

When the empty part of the tube has become cold, one-fifth of a gram of the coal or coke, previously mixed with two or three grams of perfectly dry lead chromate, are transferred to a boat and the latter inserted in position in the tube. Air or oxygen is then slowly aspirated and the boat cautiously heated up by lighting the burners one at a time, finishing with those immediately underneath it. Great care is necessary at first to prevent escape of hydrocarbons which may not be completely oxidised by the red hot column of copper oxide. Later the temperature may be increased up to that of redness.

When the combustion appears to be complete and all traces of moisture have been driven out of the tube, the absorption tubes are removed, allowed to cool, and weighed separately.

The increase of weight of the calcium chloride tube, less that due to hygroscopic water in the fuel, multiplied by 0·1111 gives the amount of hydrogen in the sample taken. The increase in the weight of the potash bulbs multiplied by 0·2727 gives the amount of carbon in the sample taken.

Nitrogen.

The Kjeldahl method is usually employed for the determination of nitrogen in coal. It consists in the conversion of the nitrogen into ammonium sulphate by heating the coal with concentrated sulphuric acid in the presence also of a little mercury. Potassium sulphate is generally added also, in order to raise the boiling point of the mixture and promote solution of the fuel. The mercury in the solution is then precipitated as sulphide, and the mixture treated with an excess of sodium hydrate. The liberated ammonia is boiled off and absorbed in a standard solution of an acid, the excess of which is determined by titration with a standard alkali.

One gram of the coal is weighed out into a round-bottomed flask of about 250 c.c. capacity, a small globule of clean mercury weighing not more than a gram introduced, and then about 25 c.c. of concentrated sulphuric acid. The mixture is then heated just to boiling over a small flame, and maintained thus for about twenty minutes, after which about 10 grams of potassium sulphate are added. The boiling is continued until the coal is all dissolved yielding a nearly colourless solution. This result is obtained in an hour and a half, or less. The mixture is allowed to cool and is then washed into a large conical flask of 600 to 700 c.c. capacity. The mercury in solution is precipitated by adding 25 to 30 c.c. of a solution of potassium sulphide (40 grams per litre), and a few small fragments of ignited fire brick introduced in order to prevent bumping in the subsequent operations. An excess of sodium hydrate solution is next added (about 90 grams in 150 c.c. of water), and the flask connected up by means of a delivery tube to a similar one containing a measured volume (25 c.c.) of decinormal sulphuric acid, kept cool by immersion of the flask in a dish of water. The end of the delivery tube is arranged so as nearly to touch the surface of the acid before the distillation is commenced. This last operation is conducted as briskly as possible until about one half of the liquid has been boiled off, whereupon the distillate is titrated with decinormal sodium hydrate solution using methyl orange or cochineal as indicator. Each c.c. of decinormal sulphuric acid neutralised by the ammonia distilled over represents 0·0014 grams of nitrogen.

Oxygen.

Oxygen is not determined directly. As in the analysis of pure organic compounds, the element is determined by ‘ difference,’ which in this case introduces errors other than those of manipulation. The percentage difference is obtained by subtracting from one hundred the sum of the determined percentage of carbon, hydrogen, nitrogen, sulphur and ash. As already pointed out, the figure obtained in an ash determination is calculated from the weight of the product of the complete ignition of the fuel. This product may contain oxygen in the form of ferric oxide resulting from the oxidation of pyrites in the coal, and be deficient in oxygen to the extent of the carbon dioxide evolved by the decomposition of carbonates. The calculated figure is thus only approximately accurate.

In this connection the following recommendation is made by the Committee on Coal Analysis of the American Chemical Society[1]:

“ The method to be used in calculating the oxygen of the coal presents, perhaps, the question of the greatest difficulty. If we could be sure that all of the sulphur is present in the form of pyrites, and that this is converted into ferric oxide in the ash, the oxygen should be found by subtracting from one hundred the sum of carbon, hydrogen, nitrogen, ash, and five-eighths of the sulphur. This is probably the safest rule

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[1] *Journal of American Chemical Society*, xxi. 1129.

which can be given for general use, and especially for coals high in sulphur. The operator should, however, satisfy himself as to whether the ash is practically free from sulphates, and, if possible, whether the sulphur is mainly in the form of pyrites. If necessary, the rule should be modified, in particular cases, accordingly."

II. GAS ANALYSIS.

The complete analysis of blast furnace gas or producer gas for open hearth furnaces may involve a determination of carbon dioxide, oxygen, nitrogen, methane, hydrogen, carbon monoxide, and occasionally ethylene and other unsaturated hydrocarbons.

Of these the carbon dioxide, oxygen, carbon monoxide and ethylene may each be determined by direct absorption of them with suitable reagents. When these gases have been removed the residue, consisting of hydrogen, methane and nitrogen, can be exploded with a measured excess of oxygen or, better still, burnt without explosion. From the contraction in volume which results, the amount of oxygen used and the carbon dioxide formed, the respective amounts of methane and hydrogen can be calculated, the nitrogen being finally taken by difference. Carbon monoxide may also be estimated by combustion along with the methane and hydrogen, but the preliminary direct absorption of it in a solution of cuprous chloride is preferable.

Sampling the Gas for Analysis.

The collection of a sample of the gas for analysis is usually done by inserting into the flue or stack a tube through which the gas issues, or is aspirated, into the gas burette or sampling bottle. So long as the gases are at a comparatively low temperature, glass or flexible lead tubing is quite satisfactory, but for hot gases iron, porcelain, or even quartz tubes may be used and, if necessary, be water-cooled. Long pieces of rubber tubing which are not only porous but may absorb certain gases, should not be inserted in the sampling arrangement. A gaseous mixture flowing through a pipe may vary in composition from the surfaces of the pipe to the centre, and where very accurate analyses are required for special purposes, the sampling tube may be inserted right across the gas main from side to side and have a fine longitudinal slit or a series of holes over the entire length inserted in the pipe.

A simple form of sampling bottle sufficient for most technical purposes consists of a vessel *A*, Fig. 17, connected to a reservoir *B*. The former is closed at the top by a bung through which passes a glass T-piece having a stop-cock at each extremity. Near the bottom of *A* are two other taps, *G* and *D*, the latter being connected by flexible tubing to the reservoir *B*. By raising *B*, *A* can be filled with the confining liquid. The best of all liquids is mercury in which most gases have a negligible solubility; but less costly liquids are generally employed. These are usually water saturated with the gas being sampled, strong brine, or still better, a solution of equal volumes of glycerol and water. The taps *C* and *F* are opened, connection made with the gas flue or main, and the air swept out of the T-piece by the gas. The tap *F* is then closed, *D* opened and the reservoir *B* lowered, whereby the gas is drawn into *A*.

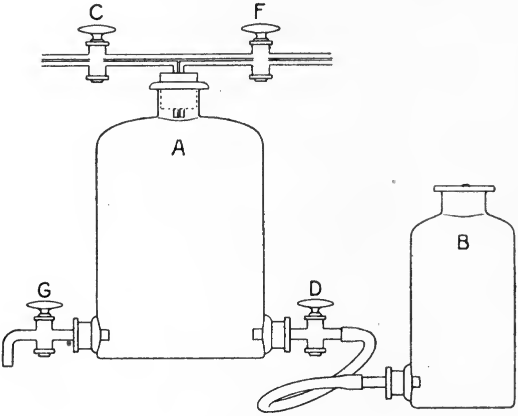

FIG. 17.

When an average sample is required over a specified period of time, this may be obtained by filling *A*, closing *F* and *D*, and then slowly drawing in the gas by allowing the liquid to run out at a pre-determined rate from *G*.

Hempel's Apparatus.

A definite volume, usually about 50 c.c., of the gas to be analysed is drawn into the graduated burette *A*, Fig. 18, closed at the top by a stop-cock and connected at its lower end by pressure tubing to the pressure tube *B*. By raising or lowering the latter, the levels of the liquid in the two tubes are brought into coincidence and the volume of gas taken for analysis is then read off. The constituents carbon dioxide, oxygen, ethylene, and carbon monoxide are removed one by one by absorption in a suitable reagent enclosed in a pipette. The double pipette is shewn in the figure connected up to the graduated burette by means of capillary glass tubing and thick-walled rubber joinings. The single pipette is shewn separately in Fig. 19.

Carbon dioxide is absorbed by means of a 33 per cent. solution of stick caustic potash in a single pipette. In carrying out the absorption, the whole of the lower bulb and the capillary tube are first filled with the liquid before connecting up with the burette *A*. By raising *B* the gas is forced completely over into the pipette in which it is allowed to remain for two or three minutes, the sides of the bulb being wetted from time to time by shaking the pipette. On the completion of the absorption, the gas is transferred back again to the burette, the liquid levels in *A* and *B* equalised, and the volume of the residual gas read off. It is advisable to allow a constant interval of say, half a minute to elapse

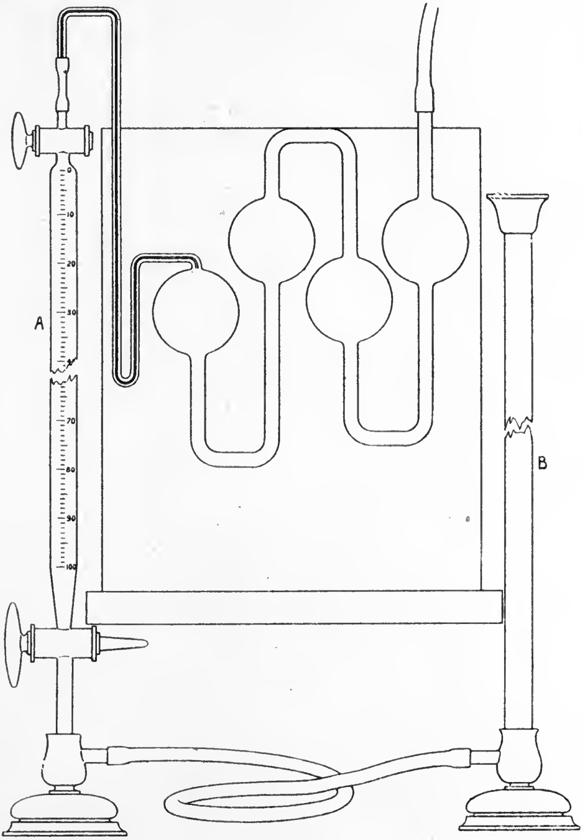

FIG. 18.

before each such reading is taken in order to minimise errors due to the draining down of the liquid from the sides of the burette. In ordinary technical work of this character, it is generally assumed that the temperature and atmospheric pressure do not alter during the course of one analysis, and no note is taken of either. When the analysis is carried out over mercury, however, it may be worth while to note the temperature and pressure at each volume reading and where necessary apply a correction.

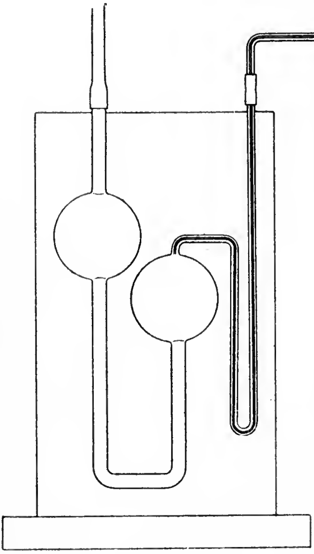

FIG. 19.

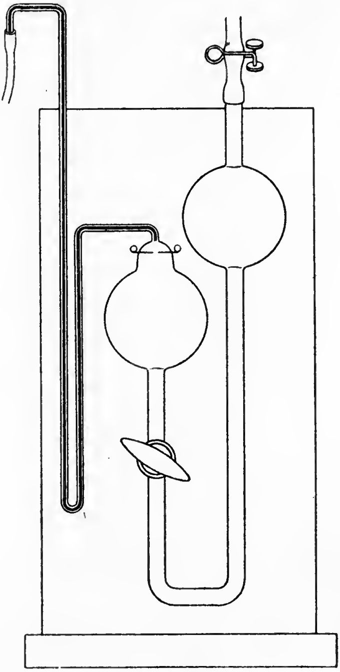

FIG. 20.

Oxygen is absorbed in an alkaline solution of pyrogallol enclosed in a pipette of the double form. This pattern is made use of in the case of solutions which are rapidly attacked by atmospheric oxygen, which is cut off from the absorbing solution by charging the extra bulbs with water. A suitable solution for the absorption of oxygen is made by dissolving 5 grams of pyrogallol in 15 c.c. of water and adding 120 grams of caustic potash in 80 c.c. of water.

Carbon monoxide is similarly absorbed in a double pipette by a solution containing 30 grams of cuprous chloride in 50 c.c. of water and 150 c.c. of hydrochloric acid. It is advisable frequently to renew this solution and also to maintain two pipettes, one to remove the bulk of the carbon monoxide from the gas, and the other, filled with a slightly used solution, to take out the last traces.

Carbon monoxide can be also determined by explosion with oxygen, but in the majority of cases direct absorption is preferable.

When it is necessary to make a separate estimation of the unsaturated hydrocarbons, these are absorbed by means of bromine dissolved in a 10 per cent. solution of potassium bromide. Such a solution has a smaller vapour pressure than an aqueous solution of bromine. The removal of these constituents is carried out after the absorption of carbon dioxide.

The residue of gas after the foregoing absorptions have been effected consists of hydrogen, nitrogen and saturated hydrocarbons, the chief constituent of the last being methane. They are determined by an explosion with a known excess of oxygen in a special pipette, Fig. 20, fitted with platinum electrodes across which a spark is passed from an induction coil. For an analysis of 50 c.c. of producer gas an addition of 10 or 12 c.c. of 'cylinder oxygen' (which has been previously assayed), is made to the gas residue in the burette. The mixture is passed into the explosion pipette filled with water, the pinch-cocks screwed up, and the glass stop-cock partly closed. The electrodes are joined up to the secondary terminals of the induction coil, of which the primary terminals are connected with an accumulator cell, and a spark is passed. The residual gas mixture is then transferred to the burette and from that into the 'potash pipette' in order to absorb the carbon dioxide resulting from the combustion of the methane. The total contraction is next measured and finally the excess of oxygen in the manner described above. It is advisable to measure the amount of gas remaining after the explosion and also the subsequent absorption of the carbon dioxide, since, under the high pressure momentarily induced by the explosion, the water may dissolve an appreciable amount of carbon dioxide, which would introduce a considerable error into the calculations were the volume of the carbon dioxide produced used as a known quantity.

In the complete combustion of methane according to the reaction

$$\underset{\text{2 vols.}}{CH_4} + \underset{\text{4 vols.}}{2(O_2)} = \underset{\text{—}}{CO_2} + \underset{\text{—}}{2H_2O}$$

there is a total measured contraction of 6 volumes for every 2 volumes of methane, *i.e.*, the contraction due to the explosion plus that due to the absorption of the carbon dioxide formed is equal to 3 times the volume of methane originally present. Also, the volume of oxygen used in the explosion is twice that of the methane present.

In the combustion of the hydrogen

$$\underset{\text{4 vols.}}{2H_2} + \underset{\text{2 vols.}}{O_2} = \underset{—}{2H_2O}$$

there is a contraction equal to $1\frac{1}{2}$ times the volume of the hydrogen present, and the volume of oxygen used is half that of the hydrogen.

Hence if C is the total contraction and [O] is the oxygen used up,

$$C = 3[CH_4] + \tfrac{3}{2}[H],$$
$$[O] = 2[CH_4] + \tfrac{1}{2}[H],$$

from which

$$[CH_4] = [O] - \tfrac{1}{3}C,$$
$$[H] = \tfrac{4}{3}C - 2[O].$$

The nitrogen is found by difference, account being taken of the amount introduced with the oxygen. The following result of an analysis of producer gas will illustrate the necessary readings and calculations.

Volume of gas taken for analysis - - - -	52·8 c.c.
,, after absorption in KOH - - - -	50·2 ,,
,, ,, ,, pyrogallol - - -	50·0 ,,
,, ,, ,, cuprous chloride -	38·6 ,,
,, ,, addition of oxygen containing 95 per cent. O_2 and 5 per cent. N_2 - -	49·8 ,,
,, ,, explosion and absorption in KOH -	30·6 ,,
,, ,, second absorption in pyrogallol -	30·1 ,,

Volume of $CO_2 = 52·8 - 50·2 =$ 2·6 c.c. - - - 5·0 per cent.
,, $O_2 = 50·2 - 50·0 =$ 0·2 c.c. - - - 0·4 ,,
,, $CO = 50·0 - 38·6 = 11·4$ c.c. - - - 21·6 ,,
Volume of oxygen added = ·95(49·8 − 38·6) = 10·6 c.c.
,, nitrogen ,, = ·05(49·8 − 38·6) = 0·6 ,,
Total contraction = 49·8 − 30·6 = 19·2 ,,
Volume of excess oxygen = 30·6 − 30·1 = 0·5 ,,
,, oxygen used up = 10·6 − 0·5 = 10·1 ,,

Volume of $CH_4 = 10·1 - \frac{1}{3}(19·2) =$ 3·7 c.c. - 7·0 per cent.
,, $H_2 = \frac{4}{3}(19·2) - 2(10·1) =$ 5·4 c.c. - 10·0 per cent.
,, $N_2 = 30·1 - 0·6 =$ 29·5 c.c. - 55·8 per cent.

The Bone-Wheeler Apparatus.

As an example of an apparatus suitable for exact analyses, and particularly for the determination of small amounts of methane, as well as for detecting small differences in composition, the apparatus designed by Bone and Wheeler, and described in the *Journ. Soc. Chem. Ind.*, 1908, Jan. 15, p. 10, also in Vol. II. of "An Investigation of the

Coals of Canada, etc." (Ottawa: Government Printing Bureau) may be cited. The following description is taken from the sources mentioned, as also the accompanying Figure 21.

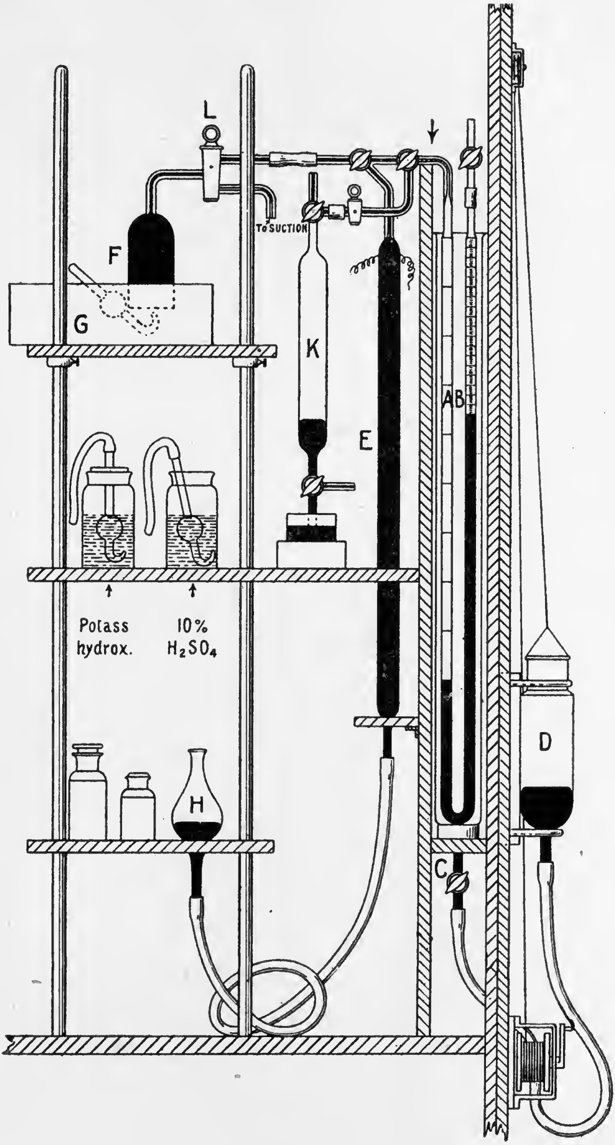

FIG. 21.

"The apparatus consists essentially of three parts, viz. :—(1) a water-jacketed combination of measuring and pressure tubes, *A* and *B*, communicating through the glass tap, *C*, with the mercury reservoir, *D*; (2) an absorption or laboratory vessel, *F*, standing over mercury in a mahogany trough, *G*; (3) an explosion tube, *E*, fitted with firing wires, and connected with a separate mercury reservoir, *H*. All the connections between *A*, *E*, and *F* are of capillary bore throughout, with suitable glass taps wherever necessary. The figure also shews how connection is made between the measuring tube, *A*, and the special "sampling tube," *K*, whenever the latter is employed for the introduction of the sample under examination. The sample may also be introduced into the apparatus from an ordinary test-tube, under the wide open end of the absorption vessel, *F*, which has been previously filled with mercury. Before commencing an analysis, the whole of the apparatus, including all the connections between *A*, *E* and *F*, is completely filled with mercury, and, needless to say, the whole of the subsequent operations are conducted over mercury."

"The principle of measurement at constant volume is adopted. For this purpose the gas is brought to a certain 'constant volume' mark in the measuring tube, *A* (by suitable manipulation of the mercury reservoir, *D*, and the tap, *C*), and its pressure read off on the pressure tube, *B*. There are a series of such constant volume marks on *A*, each coinciding with a 100 mm. mark on the pressure tube, *B* (*i.e.*, with 0, 100, 200, etc., mm.), so that the actual pressure of the gas is given by 0, 100, or 200, etc., according to the particular constant volume mark selected for the analysis. The tubes *A* and *B* are made in one piece, which is surrounded by a water-jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube with alkalis, and it is obvious that the wetting of *A* and *B* with the same liquid eliminates the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing, a device which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in *B* is inadvertently allowed to run up the tube with unusual velocity. The tap in question also allows of the vacuum being easily made in *B* whenever necessary. The advantages of this mode of measurement over the more usual method of determining the volume under atmospheric pressure are twofold, viz. (1) it allows the use of smaller volumes of gas for an analysis—thus from 5 to 10 c.c. can be made to have a pressure of 100 mm., according to the particular volume mark selected, and this pressure can easily be read off to within 0·2 mm. without employing a telescope, and (2) the measurements are, of course, independent of the barometric pressure and at the same time are unaffected by tension of aqueous vapour.

The length of the pressure tube, *B* (about 700 mm.), amply provides for the proper dilution of the 'explosive mixture' in an explosion analysis. If the apparatus is required for the analysis of such diluted gases as producer gas or blast-furnace gas only, the length of the pressure tube need not exceed 400 mm., in which case the lengths of the measuring tube, *A*, and the explosion tube, *E*, could be correspondingly diminished, with consequent reduction of the total height of the apparatus above the working bench. But such a reduced apparatus would be unsuitable for the analysis of richer gases.

The arrangements for the various 'absorptions' are of the simplest. Instead of using a number of large absorption vessels each containing a particular reagent which is used unchanged many times over in successive analyses, all the absorptions are carried out over mercury in the one absorption vessel, *F*, in each case with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use.

To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid 'in situ' between each successive reagent, the wide (open) end of the vessel is immersed under the mercury in the trough, *G*, whilst the top terminates in a capillary three-way tap, *L*. One of the parallel branches of this tap communicates, through a stout rubber joint, with the measuring vessel, *A*, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel to serve as a trap for either the mercury or the reagent which is being discarded after use. The insertion of a tap between the pump and the bottle obviates the continuous exhaustion of the latter, a single exhaustion at the outset of an analysis being all that is required. From 2 to 10 c.c. of the particular reagent to be used are introduced into the absorption vessel (previously filled with mercury), by means of a suitable pipette, from below the surface of the mercury in the trough. Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the tap, *L*, leading to the above-mentioned exhausted bottle; the same device allows of the complete withdrawal of the reagent after use, without taking down the absorption vessel, and also of the rinsing out of the latter ‘in situ’ with water, or dilute sulphuric acid, before the next reagent is used.

The reagents used for absorption are:—(1) A 33 per cent. solution of caustic potash for removal of carbon dioxide. (2) Pyrogallol for absorption of oxygen; this is made by dissolving 1 part of the solid in 4 parts of water. About 2 c.c. of this solution are introduced and then three or four times this amount of the potash solution used for carbon dioxide absorptions. (3) A solution of bromine in 10 per cent. potassium bromide for absorbing ethylene. This reagent attacks the mercury, so that not more than five minutes, which are ample, should be allowed for the absorption, after which the vessel is rinsed first with potash solution and afterwards with dilute sulphuric acid. The residual gases are also, before measurement, again brought into the laboratory vessel and washed with potash in order to remove traces of bromine vapour. (4) Cuprous chloride for the absorption of carbon monoxide. The ammoniacal solution of this reagent is generally used in preference to the solution in hydrochloric acid. It can be made by passing ammonia gas into a mixture of about 70 grams of cuprous chloride and 15 grams of ammonium chloride suspended in 300 c.c. of water, out of contact with air. When the liquid after shaking smells faintly of ammonia, 20 grams more of the copper salt are added, and the liquid preserved in a stoppered bottle. Such a solution has a very small vapour tension of ammonia. Two treatments of the gas with this solution are necessary for the complete removal of carbon monoxide.

In order to obtain perfect combustion of the hydrogen and methane remaining after the absorptions, it is necessary to use a large excess of oxygen; too small an amount leads to the formation of oxides of nitrogen and nitric acid when the mixture is fired. The minimum amount to be added is found by calculating first the volume required theoretically for the combustion of the methane and hydrogen estimated to be present. The calculated combined volume of the ‘explosive mixture’ (*i.e.*, the sum of the oxygen and the combustibles) is then doubled to find the minimum excess of oxygen. Thus, supposing 100 mm. of gas remain after the absorption, of which, say 30 mm. are combustible, and assuming these to consist of equal volumes of methane and hydrogen, the former would require theoretically 30, and the latter 7·5 mm. of oxygen, giving a total volume of $30 + 37{\cdot}5 = 67{\cdot}5$ mm. of ‘explosive mixture.’ The minimum volume of oxygen to be added is therefore

$$37{\cdot}5 + (2 \times 67{\cdot}5) = 172{\cdot}5 \text{ mm.}$$

The total contraction due to the explosion, consisting of twice the volume of the methane present plus one and a half times that of the hydrogen, is measured after the explosion, and lastly the carbon dioxide resulting from the combustion of the methane, the respective volumes of which are identical.

An example of the readings and calculations is appended.

Producer Gas.

Vacuum reading	0·0 mm.
Initial reading	120·0 „
Gas taken	120·0 „
After absorption in KOH	113·8 „
„ „ pyrogallol	113·2 „
„ „ bromine	113·0 „
„ „ cuprous chloride	87·4 „
„ adding oxygen	268·3 „
„ explosion	233·5 „
„ absorption in KOH	225·1 „

Carbon Dioxide	120·0 – 113·8 = 6·2	5·2 per cent.
Oxygen	113·8 – 113·2 = 0·6	0·5 „
Ethlyene	113·2 – 113·0 = 0·2	0·2 „
Carbon Monoxide	113·0 – 87·4 = 25·6	21·3 „
Methane	233·5 – 225·1 = 8·4	7·0 „

Total contraction due to explosion = 34·8.
Contraction due to combustion of methane = 16·8.
Contraction „ „ hydrogen = 18·0.

Hydrogen = $\frac{2}{3}$ × 18·0	= 12·0	10·0 „
Nitrogen by difference		55·8 „

PART VIII. THE ANALYSIS OF BOILER WATER, SCALES, ETC.

THE analysis of boiler water, for technical purposes, primarily involves a determination of the mineral matter capable of forming a deposit on the boiler plates. The principal scale-forming ingredients of water are salts of calcium and magnesium. Stillman has, however, pointed out the importance of the determination of the alkali metals although of course their salts cannot be considered as scale-formers. This arises from the fact that if the water does not contain sufficient chlorine to 'fix' these metals as chlorides, the excess of sodium or potassium will be in union with the sulphate radicle, an equivalent diminution in the amount of scale-forming calcium sulphate resulting.

Water supplied to boilers does not usually contain any substance likely to attack the plates whilst it remains in solution ; free acid must of course be neutralised, and neutral metallic salts in general have little action on steel at working temperatures and pressures, with the exception of the readily hydrolysable magnesium chloride.

THE COMPLETE ANALYSIS OF BOILER WATER.

Total Solids.—A measured volume (a litre will generally provide sufficient solid residue for its complete analysis) of the sample is evaporated to dryness over the water bath in a weighed platinum dish. The residue is dried to constant weight at 105°-110° C.

The readiness with which magnesium chloride decomposes, and the difficulty with which the complete expulsion of water of crystallisation from calcium sulphate and chloride is effected, make the results of this estimation unreliable when these substances are present in large amounts. As the dried residue is nearly always very hygroscopic, Mason recommends the evaporation of the sample in a weighed flask of about 100 c.c. capacity. The flask is provided with a stop-cock instead of the usual glass stopper, the latter, after cooling, being sometimes difficult to dislodge.

Organic Matter and Carbon Dioxide.—The 'total-solids residue' is gently ignited over a bunsen flame, finishing at a red heat. The loss of weight represents organic matter and carbon dioxide.

Some analysts prefer to determine the carbon dioxide separately by first re-carbonating the residue obtained on ignition, so as to obtain the total 'fixed' solids, and then decomposing a portion of this new residue with acid, the evolved carbon dioxide being estimated by means of one of the many forms of apparatus for this purpose.

Iron, Alumina, Lime, Magnesia, Silica, etc.—The 'total-solids' residue is exhausted with a mixture of equal parts of hydrochloric acid and water, and the solution filtered into a graduated flask.

A portion of the filtrate, after making up to the mark, is precipitated with ammonium hydrate, the ferric and aluminium hydrates filtered off, ignited, and weighed together. In the filtrate from these, the calcium is precipitated as oxalate and weighed as lime. The filtrate from the calcium oxalate is transferred to a weighed dish and evaporated to dryness with a slight excess of sulphuric acid. Ignition to constant weight gives sulphates of magnesium, potassium, and sodium. The mass is extracted with water, and the magnesium precipitated from half the solution and weighed as pyrophosphate. In the other half the potassium is determined as potassium platinic chloride, and the sodium obtained finally by difference.

The other portion of the filtrate is precipitated with barium chloride, and the resulting barium sulphate estimated as usual.

The residue, after ignition, may contain silica, ferric oxide, alumina, and possibly calcium sulphate. It is fused with sodium carbonate, extracted as usual with hydrochloric acid, evaporated to dryness, baked, and the silica determined as usual. The filtrate is examined for iron, aluminium, and calcium, and the amounts found added to those already found in the original filtrate.

Chlorine.—This is determined in a fresh sample of the water by means of a standard silver nitrate solution, using potassium chromate as an indicator.

TABULATION OF THE RESULTS.

It is customary to unite the anions and kathions by calculation according to the following scheme:

(*a*) The 'chlorion' is combined with the sodium, and if in excess, with potassium, magnesium, and calcium, in the order named.

(*b*) The 'sulphation' is combined with any alkali left uncombined by the chlorine, and then with calcium and magnesium.

(*c*) The carbon dioxide, after the combinations (*a*) and (*b*) have been made, is finally linked with calcium and magnesium.

RAPID SCHEMES FOR THE ANALYSIS OF BOILER WATER.

A rapid approximate analysis of boiler water will often be found sufficient for most purposes, and there are several such schemes.

For example, the solid residue obtained by evaporation of a measured volume of the water may be extracted with a mixture of equal parts of alcohol and water, and, without further analysis, the residue may be regarded as 'scale-forming material.' Again, after weighing the total solid residue, this may be re-carbonated, ignited, and weighed, thus yielding the total mineral matter, and by difference the organic matter. Extraction of the residue with water then yields by difference the total scale-formers of which, if necessary, a systematic analysis may be made. The second of these schemes would evidently be grossly inaccurate if, after ignition, the solubility of calcium sulphate in distilled water were appreciable. The fact that it is not has been amply proved by Main.

As the most important and dangerous constituents of boiler water are salts of magnesium and calcium, a rapid scheme for their determination is of value, more particularly as such a determination would yield information sufficient to make possible their almost complete removal from the feed water by precipitation. With a view to this, Kalmann's method for the technical analysis of boiler water consists in the determination of

(1) *Combined Carbon Dioxide*—by titration with decinormal acid ;

(2) *Calcium*—by precipitation as oxalate without previous removal of silica, iron, and aluminium ;

(3) *Magnesium*—as pyrophosphate in the filtrate from the calcium.

For the same reason, a brief description of a method for the determination of the 'hardness' of water is appended. More detailed instructions will be found in books dealing with water analysis.

HARDNESS OF WATER.

The determination of calcium and magnesium carbonates (temporary hardness) is done by titrating with a standard solution of sulphuric acid. The sulphates of these two metals (permanent hardness) are then determined by adding excess of standard sodium carbonate, boiling for about half-an-hour to precipitate the carbonates, and titrating the excess of alkali. If magnesium sulphate is present, the solution must be evaporated to dryness and the titration performed on an aqueous extract of the residue.

Results are usually expressed in parts of calcium carbonate per 100,000 of the water.

Temporary Hardness.—500 c.c. of the water are titrated with decinormal sulphuric acid, using methyl orange as an indicator.

$$1 \text{ c.c. } \frac{N}{10} H_2SO_4 = 0{\cdot}005 \text{ gram } CaCO_3.$$

Permanent Hardness.—250 c.c. of the water are boiled for half-an-hour (or, if magnesium sulphate is present, are evaporated to dryness) with 50 c.c. decinormal sodium carbonate. After filtering (or extracting with freshly boiled distilled water) and making up to 250 c.c., the excess of sodium carbonate is determined on a fraction by means of the standard acid.

BOILER SCALES.

The analysis of a boiler scale presents no difficulty. Many scales may be opened out with hydrochloric acid, leaving a small siliceous residue, which may be weighed as silica. If not readily attacked by acids, the ordinary fusion mixture may be used and the analysis conducted as for a refractory material (*q.v.*).

The results of the analysis should not be taken as a basis for judging the character of the water. The same figures are seldom yielded by two samples of scale taken from different parts of the same boiler, whilst their composition is necessarily influenced to some extent by the means adopted for preventing their formation.

When calcium sulphate is the predominating constituent, the scale is usually very hard, and often possesses a distinctly vitreous appearance. When first deposited this substance is probably hydrated, but contact with the hot plates removes the water of crystallisation, and bakes the anhydrous salt into a hard coherent mass.

When the chief constituent of a boiler scale is calcium carbonate, the scale is not so hard as in the case of sulphate. The hardness, however, is very variable, and would appear to be influenced considerably by the minor constituents.

Magnesia scales, which do not present any marked physical character, may consist of oxide, hydrate, or carbonate. Contact with the hot plates may result in removal of carbon dioxide from the carbonate, and this action may be followed by a partial or complete dehydration of the hydrate. It seems to be generally agreed that magnesium hydrate is an extremely common constituent of boiler scales formed from magnesian waters. A determination of the combined water in a boiler scale should accordingly not be forgotten.

The presence of zinc in boiler scales need occasion no alarm, as alkaline solutions of this metal are frequently used as anti-incrusting agents.

Prevention of Scale Formation.

A very large number of substances has been used for the prevention of scale formation. Exclusive of the innumerable compositions that have been placed on the market from time to time, such substances as tannic acid, caustic soda, ammonium chloride, etc., have been used.

The best and most scientific treatment of the boiler water, however, consists in the precipitation of the calcium and magnesium salts outside the boiler. It is beyond the scope of this work to deal with the many mechanical contrivances for the rapid deposition and filtration of the precipitated materials from the feed water before its admission to the boiler, but the determination of the necessary amounts of the precipitants used is of importance.

Dr. Clark was apparently the first to recommend the addition of lime in quantity sufficient to precipitate the combined carbon dioxide, but this evidently does not account for the sulphates of calcium and magnesium. Since that time, 1841, this subject has engaged the attention of many workers, and the general result of their labours has been the adoption of sodium carbonate, slaked lime, and caustic soda as precipitants. The addition to these, or to a mixture of them, of a small quantity of alum to facilitate the deposition of organic matter, suffices to reduce the quantity of scale-forming material to a minimum.

The following treatment of this matter is substantially an account of Kalmann's paper on Bérenger and Stingl's method of softening water. The paper is excellently abstracted in the *Journ. Soc. Chem. Ind.*, 1890, 1065.

The magnesium and calcium salts are classified into three groups:

I. *Calcium Salts other than Bicarbonate.*—These are precipitated with sodium carbonate, one molecule of which is required for every molecule of such calcium salt.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4. \quad\ldots\ldots\ldots\ldots (a)$$

II. *Bicarbonate of Calcium and Magnesium.*—These are removed by calcium or sodium hydrate, separately or together.

$$\left.\begin{aligned} Ca(HCO_3)_2 + Ca(OH)_2 &= 2CaCO_3 + 2H_2O \\ Ca(HCO_3)_2 + 2NaHO &= CaCO_3 + Na_2CO_3 + 2H_2O \\ Mg(HCO_3)_2 + 2Ca(OH)_2 &= 2CaCO_3 + Mg(OH)_2 + 2H_2O \\ Mg(HCO_3)_2 + 4NaHO &= 2Na_2CO_3 + Mg(OH)_2 + 2H_2O \end{aligned}\right\} \ldots\ldots\ldots (b)$$

III. *Magnesium Salts other than Bicarbonate.*—These are removed by caustic soda.

$$MgSO_4 + 2NaHO = Mg(HO)_2 + Na_2SO_4. \qquad \text{(c)}$$

It is evident from the (*b*) equations that one molecule of calcium bicarbonate requires one molecule of lime or two molecules of caustic soda, whilst double these quantities are necessary for the complete precipitation of one molecule of the magnesium compound. This latter fact is due to the solubility of normal magnesium carbonate, so that the precipitation is effected as hydrate.

It will be further noticed from an inspection of the second and fourth of the (*b*) equations that the use of sodium hydrate results in the formation of an equivalent amount of carbonate of sodium. This amount may actually be less than, just equal to, or greater than the amount required for precipitating the calcium salts of Class I. Accordingly there are three cases to be considered :

(1) When there is less sodium carbonate formed than is required for the precipitation of Class I. compounds, the softening of the water is accomplished by a mixture of caustic soda and carbonate of soda.

(2) When the sodium carbonate formed is just sufficient to precipitate Class I., sodium hydrate only is required.

(3) When the sodium carbonate formed is more than necessary, a portion of the caustic soda is replaced by lime, and the softening reagents will then be sodium and calcium hydrates.

The determination of the amounts of precipitants necessary will follow from the results of Kalmann's rapid analysis of the water, made as specified previously (p. 285).

The method of calculation is appended :

Let x = amount of sod. carb. chemically equiv. to the cal. carb.
y = do. do. do. mag. carb.
z = do. do. do. other cal. salts.
w = do. do. do. other mag. salts.

Then, having determined the combined carbon dioxide, let its sodium carbonate equivalent be called a. Thus

$$x + y = a. \qquad (1)$$

If b and c represent respectively the sodium carbonate equivalents of the total calcium and the total hardness

$$x + z = b. \qquad (2)$$

$$x + y + z + w = c. \qquad (3)$$

The sodium carbonate represented by z and w must be wholly or partly causticised, and from (1) and (3) this amount

$$z + w = c - a. \qquad (4)$$

Now, when sodium hydrate is used for precipitating the carbonates, it has been shown that an amount of sodium carbonate is formed equal to $x+2y$. Of this amount z parts are required for the Class I. compounds, so that we have the three cases mentioned above according to whether $x+2y$ is less than, equal to, or greater than z, that is, according to whether $x+2y-z$ is negative, zero, or positive.

Now from (1) and (2) $x+2y-z=2a-b$.

We have therefore

(A) $2a-b=-m$. For softening, use m parts of sodium carbonate, and $c-a-m$ parts of sodium hydrate.

(B) $2a-b=0$. Use $c-a$ parts of sodium hydrate.

(C) $2a-b=+m$. Use $c-a$ parts of sodium hydrate and the equivalent in lime of m parts of sodium carbonate.

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