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INDUSTRIAL INORGANIC ANALYSIS

INDUSTRIAL INORGANIC ANALYSIS

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PREFACE

THE ADVANCES in chemical and allied industries, with corresponding specialization in analytical chemistry in works practice, have led in recent years to the publication of a number of reference books on special fields of analysis.

To serve the laboratories of the mining and metallurgical industries there are several excellent books on the analysis of iron and steel, and others like the A.S.T.M. *Methods of Chemical Analysis of Metals*. These all necessarily omit many elements which must be considered in a general inorganic laboratory. Other references, although comprehensive, merely compile a number of methods and leave the selection of a procedure largely to the reader.

Over a period of years the writer has accumulated a series of notes on analytical procedures, briefly outlining the theory, the separations necessary in a complex sample, frequently giving certain hints in manipulative technique which are extremely useful, and assessing the value of the method for universal or specialized work.

In presenting the results of our experience in book form we hope they will be of some assistance to the younger analytical chemists not only in the mining and metallurgical field but in all inorganic chemical industries.

While this volume is written primarily for the industrial analytical chemist, we believe it may also serve to acquaint the university student at the senior or graduate level with the technique and viewpoint of the industrial laboratory. It has been the writer's experience that new men often take a long time to become accustomed to procedures suitable for analysing many samples in

a day. They are not assisted in a true understanding of their work by the usual company laboratory manual, which merely gives detailed instructions for the products handled, with no discussion of theory or interfering elements.

As a result, too many chemists tend to perform their work mechanically, and when confronted with an unknown sample appear unable to quickly choose the most suitable analytical procedures. It is hoped that the comments and suggestions which accompany the description of methods in this book will aid the analyst in both theory and practice.

It is necessary in a volume of this kind to draw heavily on the work of others, not only from publications but from unpublished data. In all cases every endeavour has been made to give proper credit in the text to individuals and corporations.

To enable improvements to be effected in a future revision of this book, the author would be very glad to receive suggestions and comments from readers.

January, 1953 R. S. YOUNG

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ALUMINIUM

SINCE aluminium is not only the most abundant element, next to oxygen and silicon, on the earth's surface, but also is one of the most important engineering metals, its determination is of very frequent occurrence in nearly all metallurgical industries. The analysis of aluminium is required in rocks, soils, ores, refractories, metals and alloys, and percentages may vary over a wide range from a few tenths in rocks to nearly 100 per cent. for aluminium metal.

Qualitative tests for the determination of aluminium and other elements are not given here, since excellent reference works devoted to qualitative chemical analysis are available. Examples of these are McAlpine and Soule, *Qualitative Chemical Analysis*,[16] and Treadwell and Hall, *Analytical Chemistry*, Vol. 1: "Qualitative Analysis."[22] For work on micro-chemistry the reader is referred to Emich and Schneider[11] and Benedetti-Pichler,[6] while for chemical microscopy the recommended text is the standard work of Chamot and Mason.[9]

The accurate determination of aluminium in a complex product is one of the most difficult in an analytical laboratory. It is nearly always determined gravimetrically in the ammonia precipitate after prior removal of silica and metals of Group 2. A great many other elements are also precipitated by ammonia and separations from these must usually be made. In a few cases where only aluminium, iron, and titanium are known to be present, the mixed oxides are weighed, iron and titanium determined volumetrically and colorimetrically, respectively, and aluminium thereby obtained by difference. Aluminium hydroxide precipitates at *p*H 4–7·5, points approximately indicated by the colour change of

methyl red. Appreciable re-solution of aluminium hydroxide and consequent loss occurs in more alkaline solutions. For this reason it is difficult to remove elements like Co, Zn, Ni, Cu, etc. from aluminium by repeated hydroxide separations. In addition to the difficulty of separating these elements, based on *p*H changes, aluminium hydroxide has a greater tendency than iron to adsorb or occlude Cu, Ni, etc.

In metallurgical laboratories aluminium is usually determined in one of the following ways:

1. As Al_2O_3 from mixed oxides after ammonium hydroxide precipitation. This is used where the quantities of other constituents, apart from iron, are quite small, and the mixed oxide R_2O_3 represents essentially $Fe_2O_3 + Al_2O_3$. Iron is determined volumetrically and Al_2O_3 by difference. If titanium is present it is usually determined colorimetrically and subtracted from the total mixed oxides.
2. As $AlPO_4$. This depends on the principle that aluminium can be determined in the presence of iron by reducing the latter to the ferrous state with sodium thiosulphate and precipitating aluminium as phosphate in dilute acetic acid solution.
3. Colorimetrically, based on the fact that aluminium gives a red colour with a dyestuff commonly called aluminon.
4. By difference. This is used for aluminium metal and high aluminium alloys. The usual impurities or alloy elements are Si, Cu, Fe, Ti, Zn, Mg, Pb, Cr, Sn. The rapid methods for control purposes and accurate umpire procedure for the determination of these elements in the above classes of material are given in complete detail by the Aluminum Company of America,[1] the British Aluminium Company,[7] and the Association of Light Alloy Refiners,[10] and need not be considered here.

GENERAL PROCEDURES

Aluminium is generally determined in metallurgical products on a sample taken for aluminium, calcium, and magnesium. Frequently silica also is determined on this same portion. It is

often convenient to remember that aluminium and its alloys can be dissolved by hot 20% NaOH solution. This separates aluminium at once from iron, one of its commonest interfering elements. As a general rule, weigh out 0·5–2 gm. sample and decompose with 10 ml. HCl, 10 ml. HNO_3, and 10 ml 1 : 1 H_2SO_4. For high sulphide materials add a few millilitres of bromine prior to acid treatment. Take to strong fumes of H_2SO_4. If silica is not desired on this sample, and the material is a slag or silicate, a few ml. HF should be added with the preceding acids initially to effect complete decomposition.

Take up in 5 ml. HCl and 100 ml. hot water. Boil, filter, and wash thoroughly with hot water. Scour the beaker well with a rubber policeman. Place the paper in a platinum crucible, dry, ignite, add approximately 5 gm. sodium carbonate and fuse the residue. When cool, add the contents of the crucible to the filtrate and evaporate to dryness on the edge of the hotplate on asbestos, using Fisher Speedyvap watch glasses. Moisten twice with HCl to dehydrate the silica and take to complete dryness each time. Take up in 5 ml. HCl, 100 ml. hot water, and boil. Filter and wash thoroughly, scrubbing out the beaker with a rubber policeman. For accurate work, this filtrate will have to be evaporated to dryness again, dehydrated as before, and the small quantity of remaining silica recovered and added to the first precipitate.

Pass H_2S into the filtrate from the silica separations containing Cu, Fe, Al, Ca, etc. to remove Group 2, i.e. As, Sb, Bi, Cu, Cd, Sn, etc. Filter and wash thoroughly with acidulated hydrogen sulphide water. Boil the filtrate to remove all hydrogen sulphide, add a few ml. hydrogen peroxide to oxidize the iron, and again boil the solution to eliminate H_2O_2. Add a few drops of methyl red, and ammonium hydroxide cautiously until the colour of the solution changes to a distinct yellow. If much iron is present, the colour can be seen by adding just enough ammonium hydroxide to precipitate the iron and allowing the latter to settle after a short boil, whereupon the indicator can be easily seen in the supernatant liquid.

Boil for a minute or two and filter on Whatman No. 541 paper, washing thoroughly with hot 2% ammonium chloride. Reserve the filtrate for calcium and magnesium. Transfer the

precipitate to the original beaker, dissolve off the filter paper with HCl, adding a little more HCl if necessary to effect complete solution. Since the removal of aluminium hydroxide from filter paper by extraction with acid is difficult, for work of the highest accuracy the thoroughly washed paper should be macerated before the final filtration. Re-precipitate the aluminium with ammonium hydroxide as before, using methyl red. Filter, using a little paper pulp, and wash thoroughly with hot 2% ammonium chloride. Scrub the beaker thoroughly with a policeman, since small quantities of aluminium hydroxide are often tenaciously retained on glassware.

The aluminium in the form of hydroxide has now been separated from members of preceding and succeeding groups, but it may, of course, be contaminated by one or more of the following elements: Be, Fe, Ti, Cr, Th, V, Zr, U, In, Ce, Ga, Nb, Ta, Tl, and traces of Ni, Co, Mn, and Zn.

The procedure from this point depends on the presence of other elements and on the speed and accuracy demanded for the analysis.

1. Weighing as oxide

If, as is often the case, the sample contains only iron and traces of other elements, precipitate by ammonium hydroxide. The aluminium may be determined by subtracting the iron, calculated as Fe_2O_3, from the weight of the combined oxides. In this case the precipitate of aluminium hydroxide is placed in a platinum crucible, dried, charred, ignited, cooled and weighed rapidly as Al_2O_3. If iron has not been determined on a separate sample, it may be analysed on this portion by getting it into solution in acids and determining volumetrically by dichromate.

If the ammonia precipitate contains considerable quantities of other elements, then further separations must be carried out to isolate the aluminium:

(*a*) Precipitation with sodium hydroxide will separate aluminium from Fe, Ti, Zr, Cr, U, Co, and Mn, which are insoluble in this reagent. Beryllium and vanadium accompany aluminium.

(*b*) Cupferron will separate aluminium together with Cr, Mn, and Ni, from Fe, Ti, Zr, V, Nb, and Ta.

(*c*) Aluminium, together with Be, Ti, U, V, and Zr, is not precipitated by H_2S in ammoniacal tartrate solution and can thus be separated from Fe, Mn, Ni, Co, and Zn.[20]

(*d*) Electrolysis with a mercury cathode in dilute sulphuric acid will separate aluminium together with Be, Ti, Zr, and V from Fe, Ni, Co, Cr, Mn, and Zn, which are deposited. Designs of mercury cathodes are described by several workers.[17, 18]

(*e*) Aluminium is precipitated by 8-hydroxyquinoline and separated from phosphates, fluorides, and borates in ammoniacal solution; from V, Mo, Ti, Nb, Ta, in ammoniacal solution containing hydrogen peroxide; and from beryllium in an acetic acid solution.

(*f*) Chromium can also be separated by oxidation in sodium hydroxide, acidifying with HNO_3, and precipitating aluminium with ammonium hydroxide, or by oxidizing chromium with perchloric acid, cooling, diluting, and precipitating aluminium with ammonium hydroxide.

(*g*) Phosphorus can be removed by fusing with sodium carbonate and extracting the melt with ammonium carbonate. On filtration, iron and aluminium are removed as precipitates while sodium phosphate passes into solution.

(*h*) Uranium is separated from aluminium by treatment with $(NH_4)_2CO_3$, uranium remaining in solution.

(*i*) Aluminium, together with Co, Ni, Be, Cr, Mn, Ti, Zr can be separated from iron by an ether separation. Details are given in the section on Cobalt.

(*j*) Aluminium, together with Fe, etc., can be separated from Co, Ni, and Mn by a zinc oxide separation.[23]

(*k*) For aluminium in presence of considerable quantities of vanadium, a method used at Rhodesia Broken Hill Development Company is to separate the latter as barium vanadate by adding a slight excess of barium chloride. The excess of the latter is then removed by adding a few drops of H_2SO_4. The procedure is as follows: To the acid solution add sodium hydroxide, then sufficient 35% barium chloride solution to precipitate all vanadium as barium vanadate. Boil well,

filter, and wash. Make the filtrate just acid with H_2SO_4, using methyl orange. Add a little pulp, boil, allow to settle, filter off barium sulphate and wash well with hot water. The aluminium is in the filtrate and may be determined by any standard method.

When separating aluminium and iron with ammonium hydroxide it is often useful to remember that the following are usually not precipitated, assuming an excess of ammonia and ammonium salts are present: Ag, Cu, Mo, Cd, Pt, Ni, Co, Zn, Tl(ous), V(ate), Mn, Ca, Sr, Ba, Mg, W. The following elements are precipitated by ammonia under these conditions: Hg, Pb, Sn, Bi, Sb(ous), Au, Rh, Os, Fe, Al, Cr, Ti, U, Be, Zr, Th, Ce, In, Ga, Tl(ic), V (vanadyl), Nb, Ta. The above lists must, of course, be used with caution, for often the presence of other elements in certain ratios alters the precipitating action of ammonia.

An excellent presentation of separations for aluminium and other elements is given by Lundell and Hoffman.[15] Other procedures are given by standard reference works in the agricultural,[4] metals and alloys,[5, 23] mineral,[12] and general analytical fields.[20]

In all cases ignition of the purified aluminium hydroxide precipitate to Al_2O_3 should take place at 1200° C. to constant weight. Since ignited Al_2O_3 absorbs moisture readily, care should be taken to transfer the residue to a good desiccator and weigh reasonably quickly.

If it is necessary to determine traces of other elements in the final precipitate of Al_2O_3, the latter may be brought into solution by treatment with H_2SO_4 and HF in a platinum dish, or the calcined alumina can be decomposed by fusion with $KHSO_4$ in a platinum crucible.

The reactions involved are as follows:

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

$$Al_2O_3 \times 0{\cdot}5292 = Al$$

2. Weighing as phosphate

Aluminium is frequently determined in the presence of iron by precipitation as $AlPO_4$. After some practice, an analyst can

secure fairly good results on routine work with this method but the details must be very carefully watched. The procedure to the point of obtaining the combined hydroxide is identical with that used for the determination wherein the aluminium is weighed finally as oxide. The combined hydroxides, after washing thoroughly with 2% ammonium chloride, are transferred to the original beaker and all traces removed from the paper by washing with HCl. If necessary, add a little more HCl and boil to effect complete solution, being careful to get all traces of hydroxides from the sides of the beaker into solution.

Cool, add at least a fivefold excess of $(NH_4)_2HPO_4$ and carefully neutralize with ammonium hydroxide from a burette until a slight permanent precipitate, which does not dissolve on vigorous stirring, is formed. Just re-dissolve this precipitate with 1·5 ml. concentrated HCl added from a burette. Make the volume to 400–600 ml. and add 25 ml. of a 40% solution of sodium thiosulphate. Bring to a boil on asbestos on the hotplate. Add 7 ml. acetic acid and continue boiling for 45 minutes. It is preferable to use 2-litre beakers for the final stages of this determination to minimize the danger of loss through bumping.

Filter quickly while hot through Whatman No. 40 paper, using paper pulp and ribbed funnels. Wash thoroughly with hot 5% ammonium nitrate, and scrub out the beaker completely with a policeman. Place the paper and precipitate in a weighed porcelain crucible, dry, ignite at about 1000° C., and weigh as $AlPO_4$.

The reactions involved are as follows:

$$2FeCl_3 + 2Na_2S_2O_3 \rightarrow 2FeCl_2 + Na_2S_4O_6 + 2NaCl$$

$$2HCl + Na_2S_2O_3 \rightarrow 2NaCl + SO_2 + S + H_2O$$

$$AlCl_3 + (NH_4)_2HPO_4 \rightarrow AlPO_4 + 2NH_4Cl + HCl$$

$$AlPO_4 \times 0{\cdot}4180 = Al_2O_3$$

$$\times 0{\cdot}2212 = Al$$

3. Colorimetric procedure

For the determination of very small quantities of aluminium the colorimetric method using aluminon is employed.[8, 13, 19, 21] Aluminon, the ammonium salt of aurin tricarboxylic acid, is a dye which forms with aluminium a bright red lake,

$$(C_6H_3OH\ COONH_4)_2{:}C{:}C_6H_3COONH_4{:}O,$$

The lake is obtained by adding a solution of ammonium carbonate in dilute ammonium hydroxide to a solution containing the dye and free acetic acid. If the quantity of aluminium is less than 0·1 mg. in 50 ml. of solution, a clear faint pink to a deep red colour is obtained; with larger quantities, the red lake precipitates out. Iron and beryllium are the chief interfering elements.

The procedure is as follows:

To the solution add 5 ml. HCl, 5 ml. acetic acid, and 5 ml. 0·2% aqueous solution of aurin tricarboxylic acid. Then add ammonia which has been saturated with ammonium carbonate until the mixture is alkaline to litmus. Make the solution acid with the addition of 5 ml. acetic acid, allow to stand 10 minutes, and again neutralize with the ammonium carbonate mixture adding 5 ml. excess. Cool and compare the colours produced with standards similarly prepared.

SPECIAL PROCEDURES

1. Magnesium-base alloys

Aluminium is best separated in magnesium-base alloys by precipitating it with ammonium benzoate, which separates aluminium from most divalent metals, dissolving the precipitate in ammoniacal tartrate and reprecipitating with 8-hydroxyquinoline in dilute acetic acid solution. The 8-hydroxyquinoline precipitation of aluminium may be represented:

$$Al(C_2H_3O_2)_3 + 3H(C_9H_6NO) \rightarrow Al(C_9H_6NO)_3 + 3HC_2H_3O_2$$

2. Pigments

The determination of metallic aluminium in aluminium pigments is described by Light and Russell.[14]

3. Steels

The determination of aluminium in steel is given in a publication of the Aluminum Research Laboratories[3] and in the Methods of the U.S. Steel Corporation.[23]

4. Aluminium ores

The analysis of aluminium ore materials is given in full in a publication of the Aluminum Research Laboratories.[2]

For assistance in any special problem in aluminium analyses, the chemist is advised to contact Aluminum Research Laboratories, New Kensington, Pa., or Kingston, Ont., Canada, or the British Aluminium Co., Ltd., Salisbury House, London Wall, London, E.C.2.

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ANTIMONY

ANTIMONY is found in small quantities in many minerals, ores, smelter and refinery products, and it is an important constituent in a number of non-ferrous alloys. This element is nearly always determined volumetrically and its analysis does not usually present serious difficulties.[1, 2, 4] The chief point to bear in mind is the volatility of $SbCl_3$ and consequent low results. Antimony trichloride commences to volatilize from HCl solutions at as low a temperature as 100° C., and decomposition of material should be carried out with mixtures of HCl, HNO_3, and H_2SO_4, at as low a temperature as possible, or with bromine or nitrochlorate present as oxidizing agents, followed if necessary by fusion of the insoluble matter in Na_2CO_3 or NaOH. Antimony pentachloride boils at 140° C. and care should also be taken to avoid losses from overheating this compound.

GENERAL PROCEDURE

Weigh out 0·5 to 5 gm. sample, depending on the antimony content, and bring into solution with 10 ml. HCl and 10 ml. HNO_3, heating at a low temperature. If necessary, add a few drops of HF to decompose the silicates, add 10 ml. 1 : 1 H_2SO_4 and take to strong fumes of the latter. Cool, add hot water, and filter off silica and lead sulphate. If any appreciable quantity of the latter is present it will occlude a little antimony, and for accurate work it is necessary to dilute, dissolve in HCl, warm and filter.

To the HCl or H_2SO_4 solution add about 75 ml. of 1 : 1 HCl and pass in a rapid stream of H_2S for a few minutes. Arsenic will be precipitated from the strongly acid solution, whereas antimony

and all other members of the H_2S group will remain in solution. Filter and wash well with 1:1 HCl. Dilute the filtrate with double its volume of warm water and saturate with H_2S. Antimony sulphide and other members of the group are then precipitated from Fe, V, Mn, Cr, and other elements which consume permanganate. Filter and wash thoroughly with 1:2 HCl. Place the paper and precipitate in the original beaker and add 15 ml. 20% NaOH and 10 gm. Na_2S crystals. Dilute to 100 ml. and warm on the steam bath for one hour. Filter and wash. Antimony and tin are in the filtrate free from Cu, Bi, Cd, Pb, etc. Boil out all H_2S on the hot plate.

Acidify the filtrate with H_2SO_4 and take to fumes. Cool and get all antimony into the trivalent condition by treating with sulphurous acid in hot 1:2 H_2SO_4 and boiling until all SO_2 is expelled. Adjust the acid concentration to 10 ml. HCl and 10 ml. of H_2SO_4 per 100 ml. Cool to around 10° C. and titrate with standard $KMnO_4$ solution until a faint pink tint persists for 5 seconds upon stirring.

1 ml. of 0·00855 normal $KMnO_4$ (0·27 gm. per litre) = 0·0005 gm. Sb

$$5Sb_2(SO_4)_3 + 4KMnO_4 + 24H_2O \rightarrow 10H_3SbO_4 + 4MnSO_4 + 9H_2SO_4 + 2K_2SO_4$$

The same solution can be used afterwards for the determination of tin by the iodimetric method.

If arsenic is required on the sample, it can be determined by the usual volatilization of $AsCl_3$, and antimony determined in the residual liquid in the flask. In this case ferrous sulphate or hydrazine sulphate should be used instead of cuprous chloride as a reducing agent to avoid the introduction of large quantities of copper which would require laborious removal from a small quantity of antimony. After volatilization of arsenic, the contents of the flask are transferred to a beaker, diluted with water until a concentration of 10 per cent. HCl is attained, and hydrogen sulphide passed in until all antimony and other Group 2 metals are precipitated. Antimony is then removed, with tin if present, by solution in sodium hydroxide and sodium sulphide, and the determination is completed as given above.

After removal of arsenic by distillation at a temperature of

about 108° C. the antimony can be distilled by adding $ZnCl_2$ and HCl, raising the temperature to about 200° C., and evaporating to a low volume. Titrate with $KMnO_4$ or $KBrO_3$.

Small amounts of selenium and tellurium do not interfere with the $KBrO_3$ titration, but larger quantities should be removed with SO_2.

$$KBrO_3 + 3SbCl_3 + 6HCl \rightarrow 3SbCl_5 + KBr + 3H_2O$$

The end point is determined by the disappearance of the colour of methyl orange indicator, caused by the action of free bromine liberated.

$$KBrO_3 + 5KBr + 6HCl \rightarrow 6KCl + 3H_20 + 3Br_2$$

SPECIAL PROCEDURES

1. Antimonial lead

Antimony in antimonial lead is separated from the lead by fuming with H_2SO_4, filtering, dissolving the $PbSO_4$ in dilute HCl or HNO_3 and re-fuming, re-filtering, and recovering the occluded antimony.

2. Blister and refined copper

When antimony is to be determined in blister or refined copper, it is collected together with As, Bi, Pb, Se, and Te, with a ferric hydroxide precipitate by neutralizing a nitric acid solution of copper containing a ferric salt, with NH_4OH, filtering off the ferric hydroxide, dissolving in HCl and reprecipitating to get rid of most of the copper.[5] Arsenic may be removed with H_2S in strong HCl solution or by volatilizing and collecting for iodimetric titration if its determination is required. Precipitate selenium and tellurium with SO_2 in strong and dilute HCl solution respectively, keeping the temperature as low as possible to avoid loss of antimony as $SbCl_3$. Boil out all SO_2 from the combined filtrates of the selenium and tellurium determination and treat with sodium hydroxide and sodium sulphide to separate the antimony from the insoluble sulphides of Bi, Cu, Cd, Pb, etc. Carry on the procedure from this point and titrate the antimony with $KMnO_4$.

Alternatively, antimony can be distilled, after the low-temperature distillation of arsenic and subsequent removal of Se+Te by precipitation with SO_2, and the distillate titrated with $KMnO_4$ or $KBrO_3$. A very large sample must be taken for these determinations, 50–500 gm. of copper usually being required. A series of samples may be combined after the ferric hydroxide precipitation.

3. Copper-base alloys

A colorimetric determination of antimony in copper-base alloys is described by Holler.[3]

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ARSENIC

ARSENIC is widely distributed in nature, and ranges from high percentages in arsenical ores to the very low percentages occurring as impurities in finished metallurgical products.

When determining arsenic it must be kept in mind that volatilization of arsenious chloride occurs readily in hydrochloric acid solution, and the solution treatment therefore must be an oxidizing one. Arsenic can be determined in nearly all classes of material by distillation as arsenious chloride from a hydrochloric acid solution. If the temperature of the vapour is kept below 108° C. the only interfering element in this procedure is germanium.[2]

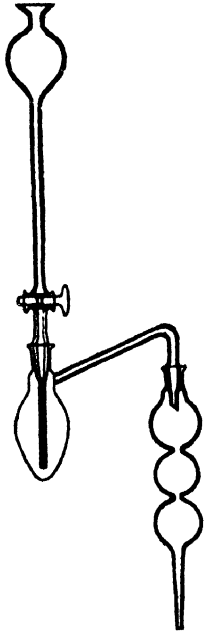
It is sometimes useful to remember that arsenic may be eliminated from a solution by repeated boiling down to a low volume with HCl in the presence of $Na_2S_2O_3$.

GENERAL PROCEDURE

The sample is brought into solution with bromine and HNO_3, or nitrochlorate mixture, followed if necessary by aqua regia. Any insoluble material is fused with Na_2CO_3. Ten ml. 1:1 sulphuric acid are added to the solution and the sample taken to strong fumes of H_2SO_4 to eliminate all nitric acid. About 150–250 ml. HCl are added and the sample gently warmed to effect solution. The solution is transferred to a 500 or 1000 ml. flask fitted with a thermometer and an outlet tube attached to a vertical condenser, the lower end of which dips into a beaker or small flask filled with cold water and kept cool with ice-cold water. If the

quantities of arsenic are large and there is a possibility of incomplete absorption special precautions to overcome this are necessary. An efficient absorption system consisting of a stoppered flask with a guard tube, and the end of the condenser outlet tube drawn to a point to give small bubbles passing through the absorbent, are illustrations of refinements which may be necessary. Use sulphur-free rubber stoppers.

An all-glass apparatus termed the Knorr arsenic distillation apparatus, illustrated in Fig. 1, eliminates the possibility of a little sulphur sometimes present in rubber stoppers and tubing interfering with the final iodimetric titration. It is very handy when a large number of arsenic determinations are carried out, though for low arsenics where a large sample is necessary the small distilling flask of this equipment is a drawback. A few pieces of silica brick in the distillation flask will prevent bumping.



Courtesy E. Machlett and Son

FIG. 1. Knorr arsenic distillation apparatus

To reduce the arsenic to the arsenious condition, a choice may be made of several reducing agents, ferrous sulphate, cuprous chloride, or hydrazine sulphate being commonly used. About 15–30 gm. Cu_2Cl_2 or $FeSO_4$ are added and distillation carried on until 100–150 ml. of distillate have been collected. Where any appreciable quantity of arsenic is present, a further 50–100 ml. HCl are added and distillation continued to a low volume.

Remove the flask and save the contents for the determination of antimony or any other element desired. Wash down the condenser and add a few drops of methyl orange to the distillate in the beaker or flask. Add NH_4OH until the indicator turns yellow, then add HCl until it just turns red. Cool in ice water and add 5–10 gm. $NaHCO_3$. Add 10 ml. starch solution and titrate with a standard iodine solution to a deep blue. Subtract the blank obtained by carrying through a distillation on acid and reagents and titrating with iodine solution.

1 ml. 0·1N. iodine solution = 0·00375 gm. As

$$2\,AsCl_3 + 6H_2O \rightarrow 2H_3AsO_3 + 6HCl$$

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2HI$$

$$NaHCO_3 + HI \rightarrow NaI + H_2O + CO_2$$

$$As_2O_3 + 2H_2O + 2I_2 \rightarrow As_2O_5 + 4HI$$

Alternative procedure for isolation of arsenic

Another method for the isolation of arsenic is precipitation with H_2S in strong HCl solution. After prior separation of arsenic with other members of Group 2 by H_2S in 5% HCl solution from Fe, Al, and other members of the succeeding groups, As, Sb, and Sn are separated from the copper by solution in 15 ml. 20% NaOH solution and 10 gm. Na_2S crystals in 50 ml. hot water. Warm on the steam bath, filter, and wash. As, Sb, and Sn are in the filtrate, free from Cu, Bi, etc.

Boil out all H_2S on the hot plate, and acidify strongly with HCl until the solution is approximately 9N., i.e. 75% HCl. Precipitate the arsenic, free of Sb and Sn, by passing in a rapid stream of H_2S at room temperature and allowing to stand an hour or more. Filter off on a Gooch crucible and wash well with 1:1 HCl and finally with hot water. The precipitate of As_2S_3 may then be dried at 105° C. and weighed. The weight may be checked if impurities are suspected by dissolving the sulphide through the filter with hot dilute NH_4OH, washing, drying, and reweighing.

If arsenic is obtained as sulphide, free from other substances, it may be dissolved in NaOH, acidified with H_2SO_4 in the presence of $KHSO_4$ and a little tartaric acid or filter paper, and fumed to strong fumes of SO_3. Take up in water and proceed with titration, adding NH_4OH, HCl, $NaHCO_3$ in the usual manner.

Arsenic is precipitated very much more readily with H_2S if it is first reduced with SO_2 in H_2SO_4 solution. Boil out all SO_2, add HCl, and gas with H_2S. A clean precipitate is quickly obtained.

Arsenic in blister copper

For the separation of small amounts of arsenic from materials such as blister copper, it is usually collected in a ferric hydroxide precipitate by adding 0·2 gm. of ferric salt for every 10 mg. of As.

Other elements such as Sb, Se, Te, Bi, etc., will also be precipitated, but they do not interfere with the determination of arsenic by the distillation method, under the conditions outlined.[4]

Determination of small quantities of arsenic

Very small quantities of arsenic, less than 0·1 mg., are best determined by volatilizing as arsine, AsH_3, and comparing the colour produced on strips of paper impregnated with mercuric chloride with standard stains similarly prepared.[1, 3] The equipment required consists of sensitized mercuric chloride paper and a Gutzeit apparatus, both obtainable from any chemical dealer.



Courtesy Fisher Scientific Co.

FIG. 2. Gutzeit apparatus for small quantities of arsenic

Folded dry lead acetate paper is placed in the lowest tube of the apparatus in Fig. 2 to remove H_2S from the arsine and is renewed in each test. In the tube above, glass wool moistened with lead acetate solution is packed to remove the last traces of H_2S and to moisten the arsine.

In the upper constricted tube of the apparatus is carefully placed the sensitized mercuric chloride paper.

The following reagents are required:

(*a*) Ferric alum solution. 8·4 gm. ferric ammonium alum are dissolved in water containing 1 gm. NaCl and 2 ml. H_2SO_4, and diluted to 100 ml. 2 ml. of this solution contain approximately 0·1 gm. Fe_2O_3.

(*b*) Lead acetate solution. Dissolve 1 gm. lead acetate in water, add enough acetic acid to clear the solution, and dilute to 100 ml.

(*c*) Zinc. Treat one-third to one-sixth inch mesh arsenic-free zinc with HCl until the surface is clean, wash with water.

(*d*) Stannous chloride. Dissolve 8 gm. stannous chloride in 9·5 ml. of water containing 0·5 ml. HCl.

(*e*) Lead acetate paper. Soak qualitative filter paper in the lead acetate solution, dry, and cut into strips $7 \times 0{\cdot}5$ cm.

(*f*) Standard stains. A set of standard stained papers ranging from 0·001–0·05 mg. As_2O_3 can be prepared by volatilizing known amounts of arsenic in the manner below. The stains can be protected from the deleterious action of moisture and light by dipping in molten paraffin and placing in a well-stoppered test tube in the dark.

The sample is prepared in the usual way by boiling with HNO_3, removing the latter with H_2SO_4, and reducing the arsenic to the trivalent state by ferrous sulphate. Hg, Pt, Pd, Ag, Ni, Co, and large amounts of Cu are undesirable and should be separated prior to the test. If more than 0·1 mg. antimony is present the arsenic should be separated by distillation in a Knorr or similar apparatus prior to the Gutzeit test.

Place 50 ml. of the arsenic solution, prepared as above, 3 ml. H_2SO_4, 2 ml. ferric alum solution, and 0·5 ml. of stannous chloride solution in the bottle of the apparatus. Place the lead acetate paper and glass wool saturated with lead acetate solution in their respective tubes, and connect with the upper tube containing the strip of sensitized paper. Add 35 gm. of the As-free zinc shot to the solution in the bottle and insert the stopper carrying the tubes. Shake gently and allow to stand in a bath at 25° C. for one hour. Remove the test paper and compare with standards.

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BARIUM

EXCEPT in a few special industries the determination of barium is not a frequent analytical procedure in the metallurgical field. Its determination does not entail serious difficulties, the chief interfering elements being calcium and strontium.[2, 4] If H_2SO_4 is present barium will be found with SiO_2 and $PbSO_4$, and if there is not enough iron or aluminium to take care of phosphates or arsenates barium may be found in the ammonia precipitate.

Barium may be easily separated from nearly all other elements by precipitation of the latter with H_2S in acid and in ammoniacal solutions. In practice it is frequently possible to fuse the sample directly, or the residue after acid treatment, with sodium carbonate, forming the insoluble carbonates of barium, and calcium and strontium if present. These are filtered, dissolved in HCl and precipitated with H_2SO_4. If barium is the only alkaline earth present it is weighed as $BaSO_4$. If SiO_2 is present it should be removed by dehydration in HCl and filtration prior to the precipitation of barium as $BaSO_4$. An alternative is to treat the $BaSO_4$ precipitate contaminated with SiO_2, with HF and a few drops of H_2SO_4, and take to dryness to remove SiO_2. If lead is present as $PbSO_4$ it may be removed from $BaSO_4$ with a hot concentrated solution of ammonium acetate.

If calcium and strontium are present it is necessary to separate barium as barium chromate. This method depends on the fact that barium is precipitated from solutions slightly acid with acetic acid by an excess of ammonium chromate, whereas strontium and calcium remain in solution. Osborn reports an excellent method for separating barium from calcium, based on the fact that $CaSO_4$ is soluble in a dilute mixture of $HClO_4$ and H_2SO_4, whereas $BaSO_4$ is precipitated.[3]

GENERAL PROCEDURE

The procedure given below may be shortened accordingly if interfering elements are absent. Weigh 1 gm. sample and decompose with 10 ml. HNO_3, 10 ml. HCl, a few ml. HF, 10 ml. 1:1 H_2SO_4, and take to strong fumes of the latter. Cool, add a little hot water, boil, and filter. Barium, together with Ca, Sr, and Pb if present, will be on the filter paper. If lead is present, wash the precipitate thoroughly with a hot concentrated solution of ammonium acetate and finally with hot water. If barium alone is present it may be weighed directly as $BaSO_4$ after removing lead with ammonium acetate.

$$BaSO_4 \times 0{\cdot}5885 = Ba$$

If calcium and strontium are present, the precipitate of alkaline earth sulphates is ignited, cooled, mixed with 8 gm. Na_2CO_3, and fused. The fusion is leached out with hot water, filtered, and the precipitate washed thoroughly with hot 0·2% Na_2CO_3 solution. The carbonates are dissolved from the paper with hot dilute HNO_3, and the paper washed thoroughly with hot water. Cool the solution, neutralize with NH_4OH, and make just acid with dilute HNO_3. Add 10 ml. of 30% ammonium acetate solution. Heat to boiling and while stirring add 20 ml. of 10% ammonium dichromate solution. Allow to stand on a warm plate for 3 hours, filter the supernatant liquid and wash by decantation with dilute ammonium acetate solution.

Dissolve the precipitate on the paper with warm dilute HNO_3 and wash the paper. Add more acid if necessary till all is dissolved and then dilute NH_4OH slowly and with stirring until the precipitate forming again no longer dissolves. Add 10 ml. of 30% ammonium acetate, bring the liquid to boiling while swirling. Let stand on a warm plate 2 hours, filter, and wash with 0·2% ammonium acetate solution. Dry, ignite, and weigh as $BaCrO_4$.

$$(NH_4)_2Cr_2O_7 + 2Ba(NO_3)_2 + H_2O \rightarrow 2BaCrO_4 + 2NH_4NO_3 + 2HNO_3$$

$$BaCrO_4 \times 0{\cdot}5422 = Ba$$

Beyer and Rieman[1] studied the conditions for the separation of

barium from strontium, using a double precipitation of barium chromate.

If SiO_2 is present and is not eliminated with HF it may be dehydrated with HCl and removed by filtration prior to the precipitation of the alkaline earths, and Pb if present, with H_2SO_4. If the sample is not completely decomposed by acid treatment, the residue may be fused with about 8 gm. Na_2CO_3 and the resulting $BaCO_3$ dissolved in HCl.

When it is necessary to separate phosphates from barium, add $(NH_4)_2CO_3$ to the HCl solution until a slight permanent turbidity is obtained, and just clear the solution with a few drops of HCl. Now add ferric chloride drop by drop until the solution above the yellowish white precipitate becomes brownish in colour. Dilute the solution to about 400 ml., bring to boiling, filter, and wash the residue with water containing ammonium acetate. The filtrate contains the alkaline earths, free from phosphorus.

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BERYLLIUM

ALTHOUGH beryllium is a comparatively rare element, it occurs occasionally in rocks and minerals, and in recent years has become of considerable importance in the metallurgical field as an alloying element with copper. It is also used as a moderator in the atomic pile.

Beryllium closely resembles aluminium in its chemical properties, and indeed the chief difficulty in its analysis lies in a complete separation from aluminium. Various methods are employed to separate beryllium from other members of the same Group, Fe, Al, Ti, Ni, Co, Zn, Mn, Cr, V, and Zr, when these are present in the sample.[3, 5, 6] A sodium hydroxide separation will give Be, Al, V, P, in the filtrate free of Fe, Ti, Cr. Beryllium can be separated as insoluble BeO from P and V by fusion with Na_2CO_3 and extraction of the melt with water; sodium phosphate and sodium vanadate go into solution. Aluminium can be separated from beryllium by precipitating the former with 8-hydroxyquinoline, or by passing HCl gas into a cold solution of the chlorides in equal parts of HCl and ether. Beryllium can be separated from iron by an ether extraction.[7]

GENERAL PROCEDURES

1. Ores

For ores weigh out a 1–5 gm. sample depending on the beryllium content, and fuse with 2–10 gm. Na_2CO_3. Take such a weight of sample that the final weight of BeO is not more than 0·25 gm.; otherwise the usual 35 ml. platinum crucible will not contain the voluminous $Be(OH)_2$ precipitate easily, and in any case the

washing of such a large quantity of colloidal material is very difficult. Osborn[4] has shown that the only reliable ratio is 2 parts Na_2CO_3 to 1 part of beryl, and 30 minutes fusion is convenient for temperatures of 800° to 1200° C. If the material contains substances which would damage a platinum crucible by direct fusion, treat first with 10 ml. HNO_3, 10 ml. HCl, 10 ml. 1:1 H_2SO_4 and take to fumes of the latter. Dilute, filter, wash, and fuse the insoluble residue with Na_2CO_3. Dissolve in HCl and take to dryness twice to dehydrate silica, moistening both times with HCl in the usual manner. Take up in sufficient HCl to dissolve all Al, Fe, Be, etc., and filter off silica, washing thoroughly with hot water.

Beryllium oxide is not attacked by molten sodium carbonate or by dilute acids. Treatment with aqua regia and H_2SO_4 to fumes of the latter is necessary to effect solution of beryllia, BeO.

Adjust the acidity of the filtrate to approximately 5 ml. HCl per 100 ml. solution and pass in H_2S to remove all Group 2 metals. Filter and wash thoroughly with hot acidulated H_2S water and finally with a little hot water. Boil the filtrate to remove all H_2S, add a little H_2O_2 to oxidize iron, and again boil.

If phosphorus is present it is recommended to remove this with ammonium molybdate after the initial separation with ammonium hydroxide.[1] Dissolve the hydroxides in a minimum of dilute nitric acid and wash the paper free from acid with hot water. Dilute the solution to 200 ml. and bring the total nitric acid content to 20 ml. Add 25 gm. of ammonium nitrate and heat in an Erlenmeyer flask to 40–50° C. Add 100 ml. of the molybdate reagent, stopper, and shake vigorously for 5-10 minutes. Allow the solution to stand overnight, filter and wash moderately with 5% ammonium nitrate. Evaporate the filtrate from above to fumes of sulphuric acid and remove Group 2 elements with H_2S.

The molybdate reagent is prepared as follows:

Mix 118 gm. of the 85% molybdic acid with 400 ml. water, add 80 ml. of ammonium hydroxide and filter when solution is complete. Prepare a second solution containing 400 ml. of nitric acid and 600 ml. of water. Vigorously agitate the latter by means of a current of air and add the molybdate solution very slowly through a tube dipping under the solution. When all has been added, continue the current of air for 1–2 hours. Let stand, filter, and store in a glass-stoppered bottle.

In the presence of chromium the solution is boiled with silver nitrate and ammonium persulphate to oxidize chromium to chromate. An excess of HCl is added to precipitate silver and the latter filtered off. The filtrate is then treated with NH_4OH, filtered, and washed. Chromium is in the filtrate, while beryllium with aluminium, etc., are in the precipitate.

If large quantities of aluminium are present, a separation using HCl gas and ether is advisable prior to final precipitation of Al, Fe, and Ti with 8-hydroxyquinoline. Evaporate until the solution begins to crystallize, wash down the sides of the beaker, cool, add an equal volume of ether, pass dry HCl through the cold solution until the two phases are completely miscible, and continue a slow stream of HCl for another hour. Filter through a Gooch crucible and wash well with a solution of equal parts HCl and ether, saturated with HCl gas. Dissolve the aluminium chloride from the filter with a small quantity of hot water and reprecipitate with HCl as before. Combine the two filtrates and evaporate to a small volume.

To the filtrate add 2 drops of methyl red and neutralize with NH_4OH. Boil and filter, washing several times with hot, slightly ammoniacal 1% NH_4Cl. Dissolve the precipitate with hot 1:1 HCl and reprecipitate, filter, and wash as before. Dissolve this precipitate in hot 1:1 HCl and wash the paper thoroughly. Neutralize with NH_4OH, using methyl red, and make just acid with HCl. Heat the solution to 60° C. and add an excess of 8-hydroxyquinoline. The latter is prepared by triturating 5 gm. of the solid reagent with 10 ml. of glacial acetic acid and then adding to 200 ml. of hot water. 1 ml. of this solution of 8-hydroxyquinoline will precipitate 0·0029 gm. Al_2O_3, and approximately equal quantities of ferric and titanium oxides.

Add 2N. ammonium acetate until Fe, Al, Zn, and Zr are precipitated, and add 25 ml. excess. An excess of 8-hydroxyquinoline is indicated by a yellow colour in the supernatant liquid after the precipitate has settled. Filter and wash well with cold water. Beryllium is in the filtrate free from other substances precipitable by NH_4OH. If vanadium is present in the sample it will be in the filtrate with beryllium after the 8-hydroxyquinoline separation and may be removed with cupferron.

If vanadium is present, dilute the cooled acid solution to 200 ml.

and then add permanganate to a slight pink. Cool the solution to 10° C. and add a cold 6% solution of cupferron while stirring, until no further precipitation takes place. Stir in a little paper pulp, and filter, using light suction. Wash with cold 10% sulphuric acid containing 1·5 gm. of cupferron per litre. Discard the precipitate.

The filtrate from above is evaporated to 50 ml., 25 ml. of nitric acid are added and the solution slowly evaporated to fumes of sulphuric acid. The solution is treated with more nitric acid until all organic matter has been destroyed.

Heat the filtrate to 60° C. and add NH_4OH until alkaline to methyl red, then add 2 ml. excess. $BeSO_4 + 2NH_4OH \rightarrow Be(OH)_2 + (NH_4)_2SO_4$. Boil for a minute or two and filter through Whatman No. 541 paper, using paper pulp. Wash thoroughly with hot 2% ammonium nitrate. Small quantities of the precipitate usually adhere tenaciously to the sides of the beaker and if thorough scrubbing will not remove it, dissolve in a little HNO_3 and reprecipitate with NH_4OH.

Place paper and precipitate in a platinum crucible, dry, ignite cautiously, and finally at 1000° C. for an hour. Cover, cool, weigh quickly as BeO. $BeO \times 0{\cdot}3603 = Be$.

2. Beryllium-copper alloys

Beryllium-copper alloys are analysed by first determining copper electrolytically and then beryllium on the remaining solution. If iron is present an aliquot representing 0·5–1·0 gm. sample is taken, a few drops of HF and 5 ml. H_2SO_4 added, and the solution taken to fumes of SO_3. It is cooled, diluted, oxidized with a little bromine water, and made just ammoniacal, using phenolphthalein. The solution is boiled, filtered, washed with hot 1% NH_4Cl, dried, ignited, and weighed as combined oxides of beryllium and iron.

From an iron determination calculate the quantity of Fe_2O_3 present in the precipitate and deduct this from the total weight. The net weight represents BeO.

If aluminium is present in these alloys the above procedure is followed to the point where the combined hydroxides are obtained. Dissolve the precipitate in 1:1 HCl and re-precipitate with NH_4OH, washing thoroughly with hot 1% NH_4Cl. Dissolve in 1:1 HCl and neutralize with NH_4OH, using methyl red as

indicator. Then add HCl dropwise until the solution is just acid. Heat to 60° C., add an excess of 8-hydroxyquinoline and carry on the precipitation of aluminium as outlined above, determining beryllium in the filtrate by precipitation as the hydroxide. If much iron or aluminium is present, repeat the precipitation with 8-hydroxyquinoline, combining the filtrates for the beryllium determination.

Colorimetric determination

Very small quantities of beryllium may be determined colorimetrically by quinalizarin, 8-oxyanthraquinone, or curcumin.[2, 4, 6] None of these can be used directly but in a few cases the presence of interfering elements may be easily overcome. Details may be found in the references cited.

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BISMUTH

ALTHOUGH bismuth is not an abundant element, small quantities are found in many ores of lead, copper, cobalt, arsenic, nickel, molybdenum, tin, silver, and vanadium. It is a constitutent of many low-melting alloys and its determination is of frequent occurrence in many metallurgical industries.

Bismuth is commonly determined as Bi_2O_3, as BiOCl, or colorimetrically depending on whether it occurs in high, intermediate, or low percentages respectively.[1, 3] Since bismuth deposits on both cathode and anode it must be removed prior to electrolysis of copper or lead. Bismuth is separated from As, Sb, Sn, Se, Te by digestion in ammonium sulphide. Bismuth sulphide remains insoluble, together with sulphides of Hg, Pb, Cu, Cd. Mercury sulphide is insoluble in dilute HNO_3 and may be separated in this manner, while Cu and Cd may be separated from bismuth by precipitating the latter as oxychloride, or as carbonate by adding a slight excess of $(NH_4)_2CO_3$ to the solution nearly neutralized by ammonia.

The separation of bismuth from lead is probably the commonest and most important manipulation in bismuth analysis. In technical work lead is often separated as $PbSO_4$, but a little bismuth is always occluded, and for accurate analyses it is necessary to dissolve in ammonium acetate, add H_2SO_4, take to fumes and again filter off $PbSO_4$.

GENERAL PROCEDURES

1. Determination as Bi_2O_3

Weigh 0·5–1·0 gm. sample, add 25 ml. H_2O and 10 ml. HNO_3. If the material is a sulphide add a few drops of bromine before

addition of nitric acid. Take to dryness on the hot plate, add 5 ml. HCl, 10 ml. 1:1 H_2SO_4, and take to strong fumes of SO_3. Cool, dilute with 50 ml. water, add 3 gm. tartaric acid, boil, filter, and wash well with 2% H_2SO_4.

Allow to stand an hour and refilter if necessary to remove any lead which may have gone through the first filtration. Pass in H_2S and filter off sulphides of Bi, Cu, Cd, Sb, As, Se, Te, etc., washing thoroughly with acidulated H_2S water.

Leach the sulphides with a 10% K_2S solution saturated with H_2S to remove As, Sb, Sn, Se, Te. Dissolve the remaining sulphides of Bi, Cu, and Cd in HNO_3 and bromine water, and boil off the latter. Make the solution slightly alkaline with NH_4OH and add 1 gm. ammonium carbonate. Boil 5 minutes, add 1 ml. NH_4OH and 1 gm. ammonium carbonate. Boil 5 minutes, add 1 ml. NH_4OH, and filter off the basic carbonate on a tared Gooch. Ignite, cool and weigh as Bi_2O_3.

$$2Bi(OH)_2NO_3 + (NH_4)_2CO_3 \rightarrow Bi_2O_3.CO_2.H_2O + 2NH_4NO_3 + H_2O$$

$$Bi_2O_3 \times 0{\cdot}8970 = Bi$$

2. Determination as BiOCl

Take a sufficient weight of sample to insure that the quantity of bismuth present does not greatly exceed 10 mg. Bring into solution with HNO_3, HCl, and HF if necessary. Moisten twice with HCl and dehydrate SiO_2. Take up in HCl, filter off SiO_2 and silver. Adjust the acidity to approximately 5% and pass in H_2S to precipitate all Group 2 metals.

Digest the sulphides with $(NH_4)_2S$ and filter off As, Sb, Sn, Se, Te, Mo, from Bi and other sulphides of the group. Dissolve the latter in hot dilute HNO_3 and add sufficient NH_4OH to neutralize most of the acid. Cautiously add to the solution, now diluted to about 300 ml., NH_4OH drop by drop until all the acid has been neutralized and a faint opalescence appears. Now add 1–3 ml. of 1:4 HCl, stir the mixture and allow the BiOCl to settle an hour on the steam bath. One ml. concentrated HCl is sufficient to completely precipitate 1 gram of bismuth. Filter the solution hot through a weighed Gooch crucible, wash by decantation twice with

hot water, and wash into the Gooch. Dry at 105° C. and weigh as BiOCl.

$$BiCl_3 + H_2O \rightarrow 2HCl + BiOCl$$

$$BiOCl \times 0{\cdot}8024 = Bi$$

Although moderate amounts of copper and cadmium do not interfere, it may be necessary in some cases to precipitate bismuth as carbonate by adding dilute NH_4OH cautiously until a faint turbidity is obtained and then an excess of $(NH_4)_2CO_3$. Heat the solution to boiling, filter, wash, dissolve in HCl or HNO_3, and determine the bismuth as BiOCl according to the procedure outlined above.[8] If iron is present it acts as a collector of bismuth in the ammonium-hydroxide-carbonate separation. It is advisable to add a little iron where this element is absent or very low.

3. Colorimetric determination of Bi

This determination is applicable to small quantities of bismuth occurring in ores, concentrates, blister copper, and similar products. It depends on the yellow colour of bismuth iodide, formed when KI is added to a bismuth salt.

For a bismuth content of 0·005–0·02% use 2 gm. For higher or lower concentrations adjust the weight of sample accordingly so that not more than 0·5 mg. bismuth is present in the solutions to be compared colorimetrically. Add 25 ml. nitric acid-potassium chlorate mixture, consisting of a saturated solution of potassium chlorate in nitric acid, i.e. about 100 gm. $KClO_3$ per litre. Add a few drops of HF if necessary, and 20 ml. 1:1 H_2SO_4. Take to strong fumes of SO_3. Cool, dilute to 50 ml. with water and add 10 ml. HNO_3. Boil, filter off the insoluble portion, and wash well with hot water. For blister copper it is, of course, merely necessary to dissolve in HNO_3 and boil out all nitrous fumes.

Make the solution ammoniacal and add 15 ml. NH_4OH in excess. Add 5 ml. saturated $(NH_4)_2CO_3$ solution, boil 15 minutes, and allow to stand warm for at least an hour. Filter and wash once with ammonia wash solution which contains 30 ml. NH_4OH, 1 gm. NH_4NO_3, and 15 ml. saturated $(NH_4)_2CO_3$ solution per litre.

In this determination be sure to avoid water washes, which might form BiOCl to be retained on the filter paper, or which also

might give appreciable solution of other bismuth compounds, leading to a significant error for small quantities of this element.

Dissolve the precipitate back into the original beaker with hot 1:1 HCl. Neutralize with NH_4OH, acidify, and adjust acidity to 1 ml. HCl in 100 ml. solution. If the copper content is low, add a little copper solution to help collect the bismuth in the next operation. Gas with H_2S for 15 minutes and allow to stand for 2 hours. Filter and wash twice with hot H_2S water.

Place paper and precipitate in original beaker, add 50 ml. nitric acid-potassium chlorate solution, 10 ml. 1:1 H_2SO_4 and take to strong fumes, if necessary adding HNO_3 to oxidize paper while fuming. Cool, dilute to 150 ml., add 10 ml. of 10 g.p.l. ferric nitrate solution containing 10 gm. ferric nitrate and 10 ml. HNO_3 per litre. Add 10 ml. HNO_3, and boil.

Cool, make ammoniacal, add 15 ml. NH_4OH in excess and 5 ml. saturated $(NH_4)_2CO_3$ solution. Boil 15 minutes and allow to stand warm one hour. Filter and wash ten times with hot ammonia wash solution to remove all copper. Dissolve the precipitate on the paper with hot H_2SO_4 solution containing 133 ml. H_2SO_4 per litre, using not more than 15 ml. Wash with hot water.

Add 1 gm. KI and destroy the liberated iodine by careful addition of 1 g.p.l. SO_2. The colour of bismuth iodide is not destroyed. Transfer to a Nessler tube and dilute to 100 ml. Match the colour of the sample by the addition of a standard solution of bismuth sulphate containing 0·0001 gm. Bi per ml. to a blank of water, 2 ml. H_2SO_4, 1 gm. KI, the same quantity of iron as in the determination, and a few drops of SO_2 solution. Alternatively, compare the colour obtained with that of permanent standards in a Lovibond Nesslerizer or Hellige Comparator, or read the value from a graph prepared with known quantities in a photoelectric colorimeter. A solution containing 0·1115 gm. Bi_2O_3 + 20 ml. HNO_3 in 1 litre contains 0·0001 gm. Bi per ml., or 0·1 gm. Bi + 10 ml. H_2SO_4 in 1 litre may be used.

The equations for these reactions may be represented:

$$Bi_2(SO_4)_3 + 6KI \rightarrow 2BiI_3 + 3K_2SO_4$$

Excess reagent dissolves the precipitated BiI_3, forming the yellow complex ion: $BiI_3 + KI \rightarrow KBiI_4$. Copper and iron interfere; the

former is removed with NH_4OH in the ferric hydroxide collection of bismuth, and iron can be removed by H_2S precipitation or a small quantity may be left in if reduced by SO_2 to the ferrous state.

$$2FeCl_3 + 2KI \rightarrow 2FeCl_2 + 2KCl + I_2$$
$$I_2 + 2H_2O + SO_2 \rightarrow H_2SO_4 + 2HI$$

It may be necessary to remove traces of selenium or tellurium which have been carried along with bismuth and are precipitated on addition of SO_2. A filtration through a double Whatman No. 42 paper immediately preceding the colour comparison can be employed if necessary to remove these.

SPECIAL PROCEDURES

Bismuth in refined copper or other refined metals as a routine determination is usually determined spectrographically.[2, 5, 6]

Small quantities of bismuth may also be determined in mine and smelter products by dithizone.[4, 7]

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BORON

ALTHOUGH BORON is not a common constituent of metallurgical products, it occurs in some ores and minerals, soils, fluxes, ceramic and paint materials, certain steels, abrasives, buffers for electroplating, etc., and its analysis may be occasionally required in any industrial laboratory.

Since boric acid may be lost if digestions are carried out at too high a temperature in open beakers, the methods of decomposition must be carefully controlled. As Pyrex ware contains boron it is essential to carry along careful blanks during all operations. Quartz flasks and beakers should be substituted for glass in work of high accuracy. When alkali or alkaline earth borates are acidified, treated with methyl alcohol, and boiled, all the boron is volatilized as methyl borate. This serves to separate boron from nearly all other elements. The ester, methyl borate, is caught and saponified in alkaline solution, the alcohol expelled, and the boric acid titrated with a standard solution of NaOH. Boric acid cannot be titrated directly with NaOH, since indicators have not yet been found to give a sharp colour change at the neutralization point, *p*H 11. If a polyhydric alcohol such as mannitol is added, however, compounds of stronger acid properties are formed and the titration can be made with phenolphthalein.[1, 2, 3]

GENERAL PROCEDURE

Weigh 0·5–5 gm. sample, depending on the boron content, into a beaker, add 1:1 HCl, cover, and heat gently on a water bath until solution is complete. If the material is not soluble in HCl, fuse directly or fuse the insoluble residue with 6 parts Na_2CO_3,

decompose the melt carefully with HCl, but do not boil, since boric acid might be lost with the steam. Pour the solution into a flask *B*, which should have a capacity of 250 or 500 ml. Add about 1 gm. anhydrous $CaCl_2$ for each ml. of solution, running it through a paper funnel to keep the neck of the flask clean. Connect it with the rest of the apparatus shown in Fig. 3. Flask *A* of 500 ml. capacity contains methanol, having a safety tube containing a little mercury, and a capillary boiling tube 3 mm. in bore, the latter closed at 1 cm. from the lower end. Flask *D*, a 250 ml. Erlenmeyer, should contain 10 ml. of 0·5N. NaOH, and be provided

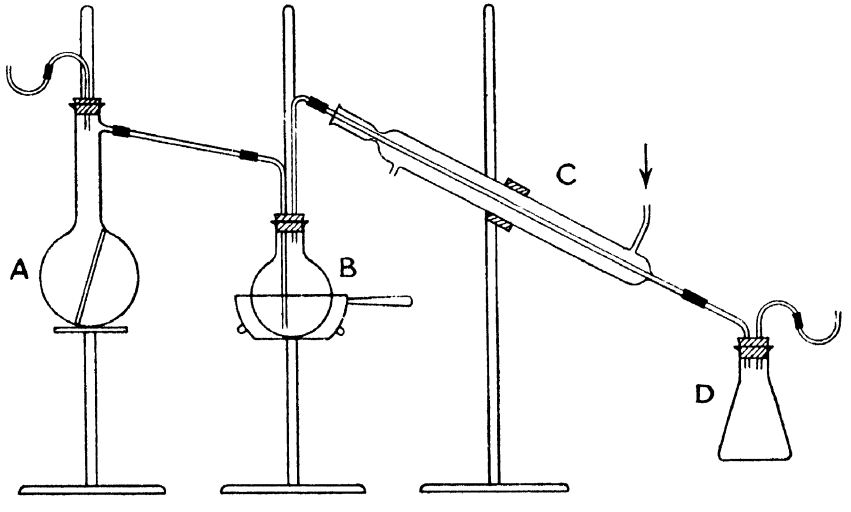


FIG. 3. Distilling apparatus for boron

with a U-tube as a water trap, to prevent escape of methyl borate. It is connected to flask *B* through the condenser *C*.

The decomposition flask *B* of 500 ml. is not heated until about 25 ml. of alcohol has condensed in it. After that the water bath is heated by a small flame or hot plate, and the flask kept hot enough to prevent further condensation of alcohol. The distillation should not be rapid enough to allow methyl borate to escape from the system.

When a distillate of about 100 ml. has collected, the receiver is exchanged for a fresh one and the collection of a second distillate is continued. The contents of the trap tube are added to the first receiver and a preliminary titration is made as follows: Add a drop

of *p*-nitrophenol solution and run in the standard NaOH until the indicator shows that the free mineral acid is neutralized. Then add 1 ml. phenolphthalein and continue the titration until the colour of the indicator begins to appear. The end point will not be sharp, but the alkali used between the two end points indicates approximately the amount of boric acid in the distillate. If the mineral is likely to contain more than 3–4% B_2O_3 use 0·5N. NaOH, the object being to keep the distillate as free from water as possible and thus facilitate the dehydration later on.

After completing the titration add to the distillate twice as much NaOH as was used between the two end points, transfer the distillate to the second distilling apparatus, and boil off the alcohol. The addition of an excess of NaOH prevents the loss of boron by converting unstable $NaBO_2$ to stable Na_3BO_3.

In the meantime the second distillate of 100 ml. will have collected. Unless the alcohol contained water or insufficient $CaCl_2$ was used, the second distillate will contain the remainder of the boron. Stop the distillation before removing the receiver, treat the second distillate like the first and add it to the latter. The distillation can be considered complete if less than 1 ml. of 0·1N. NaOH were required for titrating the second distillate.

When the alcohol has been boiled off on the steam bath, remove the liquid to a casserole, rinsing the flask once or twice with water, and heat with rotation over a hotplate or small direct flame until the last of the alcohol has been boiled out.

Return the solution to the flask and carefully add 1 : 1 HCl from a dropping bulb until the colour of both indicators is just discharged. Put in the boiling tube, heat the flask on the steam bath for a minute or two, then attach to the filter pump and boil under reduced pressure until the liquid is nearly cold and only an occasional bubble appears. When all CO_2 is thereby removed, break the vacuum, cool under the tap, and proceed to the final titration.

Neutralize the excess HCl by adding 0·5N. NaOH carefully until the yellow of *p*-nitrophenol just appears. Adjust to acid reaction with 0·1N. HCl and then to the appearance of a faint yellow colour with 0·1N. NaOH. The solution is now exactly neutral as the indicator itself shows this colour in a neutral solution.

Add 1 gm. of mannitol, read the burette, and continue titrating with 0·1N. NaOH to the end point for phenolpthalein. Add another gram of mannitol and if this causes a disappearance of the red colour add more NaOH until it reappears. The first red colour that is permanent in the presence of mannitol is the end point of the titration. About 0·6 gm. mannitol for each 10 ml. of solution will give the smallest titration error and sharpest end point.

The blank is determined using the reagents and procedure outlined above.

$$1 \text{ ml. } 0{\cdot}1\text{N. NaOH} = 0{\cdot}00348 \text{ gm. } B_2O_3$$
$$= 0{\cdot}00108 \text{ gm. B}$$

p-nitrophenol indicator. A saturated water solution.

phenolphthalein indicator. One gram per litre in ethyl alcohol.

The equations representing the steps in this analysis are:

volatilization: $H_3BO_3 + 3CH_3OH \rightarrow B(OCH_3)_3 + 3H_2O$

saponification: $B(OCH_3)_3 + 3NaOH \rightarrow Na_3BO_3 + 3CH_3OH$

neutralization: $Na_3BO_3 + 3HCl \rightarrow H_3BO_3 + 3NaCl$

titration:

$$H_3BO_3 + \begin{matrix} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} + 3NaOH \rightarrow \begin{matrix} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} + Na_3BO_3 + 3H_2O$$

SPECIAL PROCEDURES

1. Sampling and analysis of boron trifluoride is discussed by Swinehart, Bumblis, and Flisik.[4]

2. The analysis of boron carbide is given by Scott and Furman.[3] After fusion with Na_2CO_3 in a platinum crucible the procedure is essentially that described above.

3. The determination of small amounts of boron in steel has been worked out by T. R. Cunningham of Union Carbide Research Laboratories, and is reproduced here. This is given in full

not only because of the increasing importance of boron in steel, but to furnish a procedure which analytical chemists may find useful as a guide for low quantities of boron in many materials.

This determination is based on the distillation of methyl borate from a phosphoric acid solution, and finished by the curcumin colorimetric method in an electrophotometer.

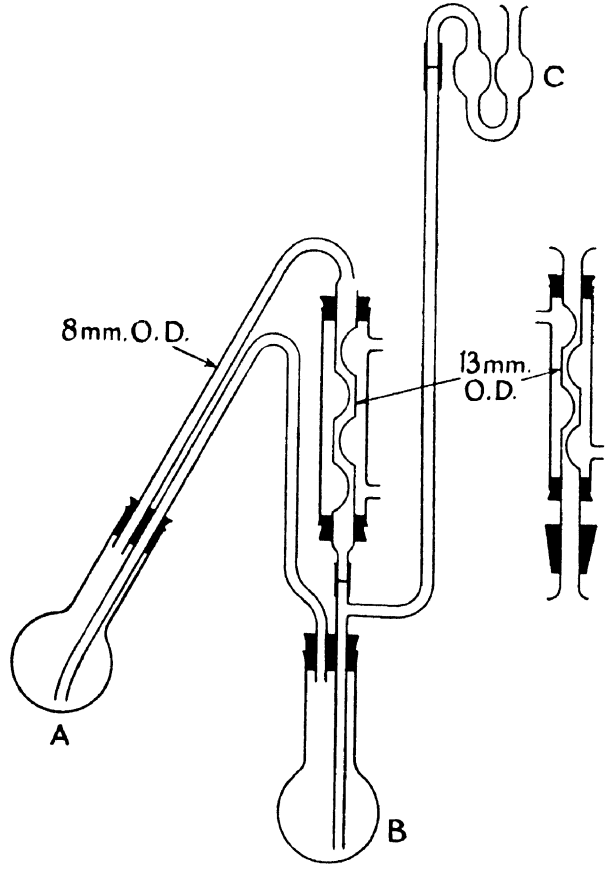


FIG. 4. Apparatus for determination of boron in steel

Apparatus. Flasks *A* and *B* in Fig. 4 are 100 ml. quartz flasks. The remainder of the apparatus is made of Corning glass No. 728, with the exception of the condenser jacket. The core of the auxiliary condenser is also made of Corning glass No. 728, and is flanged at the bottom so as to fit closely to the neck of the 100 ml. quartz flask.

Casseroles. New 300 ml. porcelain casseroles are used for the evaporation and colour reactions.

The water bath is automatically controlled to hold the temperature at 55° C. ± 3°. The casserole should be immersed at least ¾ in. in the water.

Corning glass No. 728 is considered to be boron-free glass in this method; however, the manufacturer's specifications show it to contain a maximum of 0·04% B_2O_3, and this should be borne in mind.

Reagents used

All reagents should be stored in boron-free containers.

HCl (1:9). Mix 10 ml. of conc. HCl and 90 ml. of cold, freshly distilled water.

$Ca(OH)_2$, 0·2N Suspension. Prepare by igniting c.p. $CaCO_3$ in a platinum dish first at a temperature of 500–600° C. and finally at 900–1000° C. for at least 30 minutes; then cool, grind in an agate mortar, transfer 5·6 gm. to a 1000 ml. volumetric flask, dilute to the mark with cold, freshly distilled water, and mix thoroughly. Mix thoroughly each time before drawing off a portion for use.

Curcumin Solution (0·025%). Dissolve 0·100 gm. of curcumin in 400 ml. of 95% ethyl alcohol, filter, and store in a brown bottle. This solution showed no change after standing for 2 weeks, but should not be kept longer than 4 weeks. One or two points of the concentration-absorption curve should be checked after each preparation of new reagent.

Phosphoric Acid (85%). Mallinckrodt's "Analytical Reagent" phosphoric acid was found to have the lowest blank.

Oxalic Acid (10%). Dissolve 50 gm. of c.p. oxalic acid in 450 ml. of c.p. acetone, and filter. This reagent is stable for at least 2 weeks.

Potassium Permanganate. C.p. $KMnO_4$.

Methyl Alcohol. Analytical grade methyl alcohol that has been redistilled from NaOH or KOH in boron-free apparatus.

Procedure. Wash the auxiliary condenser with water and H_3PO_4 before using, to insure the complete removal of all methyl alcohol from the previous run. Transfer 0·500 gm. of steel turnings containing up to 0·002% boron to a 100 ml. quartz flask

and connect with the auxiliary condenser. Add 10 ml. of H_3PO_4 through the condenser and heat the flask gently until the reaction ceases. Cool to room temperature, disconnect the condenser, and add 0·05 gm. of solid $KMnO_4$ and 5 drops of water to the flask. Again connect with the condenser and boil the solution until all of the $KMnO_4$ has been decomposed. Cool to room temperature, and pour 25 ml. of methyl alcohol through the condenser. Disconnect the flask *A* and insert as shown on Fig. 4.

Add 5 ml. of the 0·2N. $Ca(OH)_2$ suspension and 25 ml. of methyl alcohol to flask *B* and insert in the apparatus. Add a sufficient amount, 0·2 to 0·3 ml., of the 0·2N. $Ca(OH)_2$ suspension to trap *C* to form a liquid seal. Place flasks *A* and *B* in beakers containing hot water and heat to boiling; continue the distillation for from 30 minutes to 1 hour. Remove the hot water beakers and transfer the solutions in flask *B* and trap *C* to a 300 ml. porcelain casserole and rinse well with water. Next rinse flask *B* and trap *C* with 2 drops of 1:9 HCl, add to the casserole, and again rinse with a little water. Evaporate the solution to dryness on a steam bath and cool to room temperature.

Take the residue up in 1 ml. of 1:9 HCl, add 5 ml. of the 10% oxalic acid solution and mix by twirling. Next add 2 ml. of the curcumin solution, mix well, evaporate to dryness on a water bath held at $55° \pm 3°$ C., and then bake for 30 ± 5 minutes. Take the residue up in 25 ml. of acetone, filter through a 1bG4 frit crucible, and wash with an additional 25 ml. of the acetone, using from 3 to 5 ml. portions for each washing. Transfer the solution to a 100 ml. volumetric flask and dilute to the mark with cold, freshly distilled water. The colour intensity is best measured in a photoelectric colorimeter, using a green filter having a transmission maximum 525–540 mμ. The colour change is from yellowish-green to deep rose, depending on the amount of boron present.

Carry a blank on the reagents used through all steps of the method. In the absence of iron the $KMnO_4$ is not reduced, but this does not affect the distillation. Subtract the amount of boron obtained on the blank determination from the amount found in the steel, and multiply the remainder by 100 and divide by the weight of sample taken to obtain the per cent. soluble boron.

Prepare the colour absorption-concentration curve by evaporating various amounts of a standard boric acid solution containing

from 0 to 0·01 mg. B with 5 ml. of the 0·2N $Ca(OH)_2$ suspension, and carry through all steps of the colour formation. This will give low values for distilled samples with errors ranging from 0% at 0·003 mg. to 10% at 0·01 mg. boron. A more accurate curve is obtained by distilling steel samples to which known amounts of boron have been added. Such samples are prepared by adding definite amounts of boric acid to 5 ml. of 0·2N. $Ca(OH)_2$ suspension in a 100 ml. quartz flask and evaporating to dryness. One-half gm. of a boron-free steel is added to the flask which is connected to the auxiliary condenser; add 10 ml. of phosphoric acid through the condenser and complete the determination as previously described.

To obtain the acid-soluble boron, dilute the solution in flask *A*, after the distillation, to 90 ml. with water containing 10 ml. of HCl. Filter on a 9 cm. Whatman No. 42 paper or its equivalent containing a little ashless paper pulp, and wash out the flask thoroughly; then wash the paper and any residue first at least 20 times with hot 2% HCl and finally from 12 to 15 times with cold water to remove most of the free acid. Transfer the paper to a 15 to 20 ml. platinum crucible, add 5 ml. of the 0·2N. $Ca(OH)_2$ suspension, and evaporate to dryness. When dry, ignite at 600–700° C., until the carbon is removed. Then add 1 gm. of Na_2CO_3, and fuse the residue, finally tilting and heating the crucible so that the fusion is collected in a ball. Cool and remove the greater part of the fused mass by exerting a little pressure on the crucible wall. Transfer to a 100 ml. quartz flask and connect with the auxiliary condenser. Remove the remainder of the fusion from the crucible by washing with 10 ml. of H_3PO_4 in approximately three portions, adding each portion to the flask through the condenser. Heat to obtain a complete solution, cool to room temperature, add 25 ml. of methyl alcohol through the condenser, and then disconnect the flask *A* and insert as shown in Fig. 4. Complete the determination as previously described. Run a blank on all the reagents used, make the proper correction, multiply the remainder by 100 and divide by the weight of sample taken to obtain the per cent. acid-insoluble boron. Combine the soluble and acid-insoluble boron to obtain the total boron in the sample.

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CADMIUM

THE PRINCIPAL occurrence of cadmium is in zinc ores, where small quantities are nearly always found. It concentrates in certain stages of zinc production, where it is obtained as a by-product for use in various alloys, paints, plating, amalgams, atomic piles, etc.

The best method for cadmium is a gravimetric one, weighing as $CdSO_4$.[3] This necessitates the separation of cadmium from all other elements. The most important separation is that from zinc, its commonest associated metal. Cadmium may be separated from copper by electrolysing the latter in the presence of 2–3 ml. HNO_3 and H_2SO_4 per 100 ml.[4]

GENERAL PROCEDURE

Weigh out 0·5–25 gm., depending on the cadmium content, dissolve in HCl, HNO_3, add 25 ml. 1:1 H_2SO_4 and take to strong fumes of the latter. Cool, add water, boil, filter, and wash. Dilute to approximately 300 ml. and pass in H_2S for about 30 minutes. After the iron has been reduced, add NH_4OH cautiously until a heavy precipitation of ZnS occurs, keeping the solution sufficiently acid so that no iron precipitates. Allow the precipitate to settle, filter, and wash with cold water.

Dissolve the sulphides on the paper with 1:2 HCl, catching the solution in a clean beaker. After all ZnS has been dissolved wash the paper three more times with 1:2 HCl. This strength of acid will dissolve the cadmium and zinc but not As, Cu, Hg, Sb. If bismuth or tin are present they must be removed with ammonium sulphide for tin, and NH_4OH for bismuth, prior to the final precipitation of cadmium.

Add 15 ml. 1:1 H_2SO_4 and evaporate to fumes. Cool, dilute to 200 ml., and pass in H_2S as before. Filter off the precipitated CdS, redissolve as previously, and make a third precipitation if necessary. The filtrates may be tested for zinc by a few drops of 10% solution of potassium ferrocyanide. The filtrate from the final precipitation should show only a faint turbidity.

Dissolve the final precipitate of CdS in HCl, add 10 ml. 1:1 H_2SO_4, and take to strong fumes of the latter in a beaker. Cool, add water, transfer to a weighed platinum crucible or dish, and evaporate carefully to dryness. Place in a muffle and slowly raise the temperature to approximately 500° C. Cool, dissolve the residue in a little water, carefully evaporate, and again heat. Cool, weigh, and repeat the operation until a constant weight is obtained.

$$CdSO_4 \times 0{\cdot}5392 = Cd$$

SPECIAL PROCEDURES

1. Thompson[5] gives a promising determination of cadmium using brucine sulphate-potassium iodide mixture to precipitate cadmium from zinc-cadmium mixtures.

2. Young and Barker[6] reported a useful rapid plant test for small quantities of cadmium in zinc electrolyte, based on the use of β-naphthoquinoline.

3. Barker, Cahill, and Young[1] isolate most of the cadmium from zinc by precipitation of the former with zinc dust, thus eliminating the practical difficulty of filtering large quantities of zinc sulphide. This procedure is as follows:

To 1000 ml. of sample or less, add sufficient H_2SO_4 to acidify to 0·2–0·5 gm./litre acid. Add 1–2 gm. −325 mesh zinc dust and agitate carefully at around 110 r.p.m. for 1 hour, keeping the temperature at approximately 50° C.

Filter by suction through a 7 cm. Whatman No. 42 filter paper, and wash the precipitate 5 times with warm water. Transfer the paper and precipitate to a 400 ml. beaker containing 15 ml. HCl and rinse the funnel and original precipitation beaker with 35% HCl, adding the rinsings to the main solution. Boil until solution is effected and filter, washing 5 times with hot water.

Neutralize the filtrate with ammonia and reacidify so that the

solution contains 5 ml. HCl per 150 ml. of solution. Cool to room temperature and pass in H_2S for 30 minutes, adding water or dilute ammonia to the solution if necessary to ensure precipitation of cadmium together with a fair amount of zinc. Filter and wash 5 times with warm water. Dissolve the zinc and cadmium sulphides through the paper into the original beaker with hot 10% HCl and wash the paper well with hot water. Add 10 ml. 1:1 H_2SO_4 to the solution and fume to dryness. Cool, add 30–40 ml. water and 8 ml. 1:1 H_2SO_4 to the beaker, together with a little paper pulp. Warm or boil to effect solution and cool. Filter through a small Whatman No. 40 paper into a 100 ml. measuring cylinder and wash until a volume of 90 ml. is obtained. Transfer to a 250 ml. beaker, wash the cylinder with a further 10 ml. of water, and add to the main solution, giving a total volume of 100 ml. Pass in H_2S for 30 minutes. If the cadmium is slow in coming down, add water in 5 ml. portions until precipitation commences.

After 30 minutes filter at once by suction through a weighed sintered glass crucible, and wash 5 times with warm water. Dry for 1 hour at 110° C. Cool and weigh as CdS. $CdS \times 0{\cdot}778 = Cd$.

4. Copeland and Griffith[2] give the polarographic procedure for cadmium in zinc used by the New Jersey Zinc Co., for about 0·001% Cd.

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CALCIUM

CALCIUM is a common element in all types of metallurgical and industrial analyses. It occurs in minerals, ores, slags, waters, fluxes, fertilizers; in building materials such as lime, cement, plaster; and even in alloys.

Calcium is nearly always determined volumetrically by titration with potassium permanganate, after separation of the H_2S and $(NH_4)_2S$ groups and precipitation of calcium as oxalate.[1, 2, 3, 4] In industrial analyses, Al, Ca, and Mg are generally determined on the same sample. The usual methods for the decomposition of samples may be followed, but it must always be borne in mind that calcium sulphate is fairly insoluble in water and may be lost with silica if the sample is taken to fumes of SO_3 and then filtered in dilute H_2SO_4 solution. If phosphates are present they must be removed as iron or aluminium phosphates with NH_4OH. Acid-insoluble calcium compounds such as $CaSO_4$ must be fused with Na_2CO_3 and then taken up in acid. Calcium in CaF_2 may be determined by removing fluorine during the initial decomposition of the sample. It may be necessary in this case to add a little SiO_2 and take to fumes of SO_3.

GENERAL PROCEDURE

To a 0·5–5 gm. sample, depending on the calcium content, add sufficient HCl and HNO_3, and boil to effect solution. For sulphide ores add a little bromine solution and allow to stand for 10 minutes before addition of HNO_3. For slags or refractory products add a few drops of HF, after HNO_3 and HCl. If a residue remains, add 10 ml. 1:1 H_2SO_4 and evaporate to dryness.

Take up in 10 ml. HCl, 50 ml. water, and boil. Filter and wash well with hot water. Place paper and precipitate in platinum crucible, dry, ignite, fuse residue with Na_2CO_3, and add contents of crucible to the filtrate. Evaporate filtrate to dryness twice, moistening with HCl both times to dehydrate silica, take up in 10 ml. HCl, 75 ml. hot water, boil, filter off silica, and wash thoroughly with hot water.

Adjust acidity to 5–10% HCl and gas out all members of Group 2 with H_2S. Filter and wash thoroughly. Make the filtrate ammoniacal and pass in a little more H_2S. Filter off all the sulphides of Group 3, washing well. Boil thoroughly to remove all H_2S. The solution now contains only Ca, Ba, Sr, Mg, and the alkalies.

If, as frequently happens, iron and aluminium are virtually the only members of Group 3 present, it is preferable to precipitate these with NH_4OH rather than with ammonium sulphide. If nickel and cobalt are present as well, they will pass through into the filtrate with Ca and Mg, but the oxalates of Ni and Co are soluble in a large excess of NH_4OH and NH_4Cl, and do not interfere in the calcium determination unless present in considerable quantities. In this case remove Ni and Co by electrolysis in ammoniacal solution after removal of Fe and Al, prior to precipitation of calcium as oxalate. Large amounts of Ni and Co tend to give a co-precipitation of these elements with calcium oxalate.

Since significant quantities of barium and strontium are rarely encountered in most analyses, calcium can usually be precipitated directly as the oxalate in faintly ammoniacal solution. If appreciable quantities of barium and strontium are present with calcium in the sample it is necessary to convert the alkaline earths to nitrates, expel all moisture by heating, and extract calcium nitrate by a mixture of equal parts anhydrous ether and absolute alcohol. The nitrates of barium and strontium are nearly insoluble in this mixture.

Heat the solution to boiling, and to the faintly ammoniacal solution add 10 ml. of saturated ammonium oxalate solution. Saturated $(NH_4)_2C_2O_4$ solution contains about 5 gm. in 100 ml. at room temperature, or 0·5 gm. in 10 ml., sufficient to precipitate approximately 0·2 gm. CaO, or 20% CaO on a 1 gm. sample.

Boil a few minutes and allow to stand several hours, preferably overnight. Filter through single-fold Whatman No. 40 paper and wash thoroughly with hot 0·1% ammonium oxalate solution, and finally with hot water. It is necessary to remove all traces of ammonium oxalate from the filter paper and the precipitate with thorough washing, otherwise it will consume $KMnO_4$ in the final titration. Retain the filtrate for magnesium.

Transfer the bulk of the precipitate, by washing, from the funnel to the original beaker and then place the latter under the funnel. Pour 50 ml. of hot 25% H_2SO_4 through the paper in several washes, and then wash thoroughly with hot water. Heat the filtrate to about 60° C. and titrate immediately with standard $KMnO_4$ to the first permanent pink. Now add the filter paper containing the last traces of the precipitate of calcium oxalate to the titrated solution, together with a final washing of the funnel, and complete the titration to the first permanent pink.

If a large precipitate of calcium oxalate is obtained it is advisable to re-dissolve in dilute HCl, and reprecipitate with NH_4OH and ammonium oxalate to free the precipitate of occluded salts. This second precipitation is necessary for very accurate work, since magnesium oxalate is readily occluded by calcium oxalate.

The above procedure may be considerably shortened if no silica or few members of preceding groups are present in the calcium-bearing material. In many cases fusion with Na_2CO_3, solution in HCl, oxidation with H_2O_2, and removal of iron and aluminium with NH_4OH, will give a filtrate in which calcium can be precipitated at once as the oxalate.

$$(NH_4)_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 + 2NH_4Cl$$

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow$$
$$5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

1 ml. 0·1N. $KMnO_4$ = 0·002804 gm. CaO
= 0·002004 gm. Ca

A solution of $KMnO_4$ containing 2·85 gm. per litre has a value of 1 ml. = 0·0025 gm. CaO, and is often used in technical work.

SPECIAL PROCEDURES

1. Available lime

There are two methods used to obtain the amount of "available lime" in quicklime and hydrated lime.

(*a*) Place 1 gm. of material in a 500 ml. flask, add 30 gm. sugar and 300 ml. water, and shake vigorously until the sugar has dissolved. Make up to 500 ml. and shake at 10-minute intervals for 1–2 hours. Allow the insoluble material to settle, filter part of the solution, and withdraw 50 ml. of this for titration. Add 2 drops phenolphthalein and titrate with 0·1N. oxalic acid, to the disappearance of the pink colour.

1 ml. 0·1N. oxalic acid = 0·0028 gm. CaO

0·1N. oxalic acid, 6·303 gm. $H_2C_2O_4.2H_2O$ in 1 litre of water.

This determination is based on the fact that calcium in the form of CaO forms a water-soluble saccharate, $C_{12}H_{22}O_{11}.CaO.2H_2O$, while compounds such as $CaCO_3$, CaF_2, etc., do not form calcium saccharate.

(*b*) Weigh 1·402 gm. sample into a 400 ml. beaker, add 200 ml. hot water, and boil for 3 minutes. Cool, add 2 drops of phenolphthalein and titrate with 1·0N. HCl. When the pink colour disappears in streaks, reduce the rate of acid addition until the colour fades throughout the solution for 1–2 seconds. Note the reading and ignore the return of colour. Repeat the experiment, substituting for the 400 ml. beaker a 1 litre graduated flask carrying a one-hole stopper fitted with a short glass tube drawn out to a point. Cool, and add dropwise with vigorous stirring about 4·5 ml. less acid than before. Call this number of ml. used "A". Grind up any small lumps with a glass rod flattened at one end, dilute to the mark with freshly boiled distilled water, close the flask with a solid stopper, mix thoroughly for 4–5 minutes and let settle for half an hour.

Pipette off a 200 ml. portion, add phenolphthalein and titrate slowly with 0·5N. HCl until the solution remains colourless on standing 1 minute. Call this additional number of ml. "B". Then the percentage of available CaO = 2A + 5B.

(*c*) "Available lime" may also be measured by doing a total calcium, and determining CO_2 by evolution with the aid of a

Schroedter apparatus or by absorbing in a Geissler bulb or similar equipment, as described in the section on Carbon. In the absence of sulphates or silicates of calcium this will give an indication of CaO and $CaCO_3$. It is commonly used in determining quality of lime for metallurgical industries.

2. Calcium sulphate

The determination of calcium sulphate in sulphide ores has been described by Young and Hall.[5]

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CARBON

CARBON may be encountered in the analytical laboratory of a metallurgical industry as carbonate in minerals and ores, as carbon in iron and steel or non-ferrous alloys, in coals, gases, organic compounds, graphite, amorphous carbon, or industrial diamond.

GENERAL PROCEDURES

1. Determination of carbon in carbonates

(*a*) There are several methods of determining carbon in these products. One is by the loss of weight of a carbonate when treated with a known weight of acid. This is used for approximate determinations and may be carried out in a form of apparatus such as Schroedter's alkalimeter, illustrated in Fig. 5.

Place 1 gm. of the sample in the bottom of the flask, and H_2SO_4 and HCl in the left and right hand bulbs respectively. Weigh the apparatus. Open stopper *B* and allow the HCl to flow on the carbonate, then close the stopper. The gas liberated flows through H_2SO_4 which absorbs the moisture. After the vigorous action has ceased, place the apparatus on a hot plate and boil the solution for 3 minutes. Aspirate CO_2-free air, purified by passing through soda lime, through the solution to expel the last traces of CO_2 by applying gentle suction at *A* and opening *B*. Weigh the apparatus again and take the loss of weight as the CO_2 of the sample. If sulphides are present, a little acidified $CuSO_4$ or similar solution should be used in place of H_2SO_4.

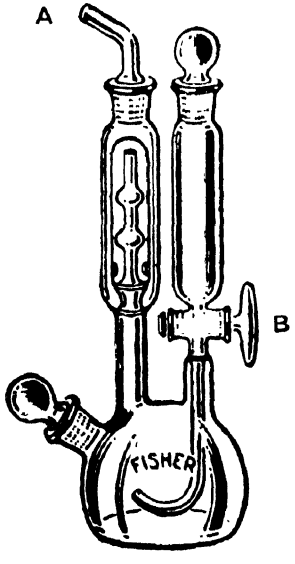
(*b*) A more accurate procedure for the determination of carbon in carbonaceous materials, e.g. carbon dioxide in lime, is to

decompose the sample with HCl and absorb the CO_2 evolved in ascarite in a standard train quite similar to that described below for carbon in iron and steel.

Weigh 1–5 gm. into a decomposition flask, add HCl, and, when all initial effervescence has ceased, heat gently. A scrubbing unit of calcium chloride and ascarite is placed ahead of the decomposition flask to remove CO_2 from the stream of air which is slowly aspirated through the train.

Scrubbers containing $H_2SO_4 + Cr_2O_3$ or MnO_2, $CaCl_2$, and P_2O_5 to remove sulphur compounds, water vapour, and hydrochloric acid are inserted between the decomposition flask and the absorption bulb. A final $CaCl_2$ tube after the absorption bulb prevents water vapour getting into the latter from the aspirator.

The increase in weight of the absorption bulb gives the CO_2 evolved from the carbonate sample.



Courtesy Fisher Scientific Co.

FIG. 5. Schroedter alkalimeter

(*c*) The determination of carbonate in materials decomposed by hot, very dilute HCl may also be effected by the apparatus shown as Fig. 6 on page 52. CO_2 is evolved and is absorbed in an excess of $Ba(OH)_2$, giving a precipitate of $BaCO_3$.[6] On titration with dilute HCl, using phenolphthalein indicator, none of the $BaCO_3$ is decomposed until all the excess $Ba(OH)_2$ has been neutralized, indicated by the change from pink to colourless. The procedure is given as follows:

Add a weighed amount of sample to flask *A* together with about 50 ml. freshly boiled distilled water. Immediately replace stopper of flask *A*. Run into flask *B* a known volume of standard barium hydroxide solution and a few drops of phenolphthalein indicator. Re-stopper the flask immediately. Close screw clip *y* and evacuate the apparatus to about half an atmosphere. Close screw clip *x* and cautiously loosen screw clip *y*, to admit a slow stream of CO_2-free air to bubble through the water in *A*. Admit

the charge of hydrochloric acid from *T* and heat the water bath to boiling. Air charged with carbon dioxide then passes from flask *A*, via the splash head and length of tubing, into *B*. The strength of HCl used for decomposition should not exceed 1·0N., or about 10% by volume. Under these conditions the quantity of HCl passing into the absorption flask is negligible. At intervals shake flask *B* to ensure absorption of CO_2. When atmospheric pressure is restored in the apparatus, remove the stopper in flask *B* and titrate the excess barium hydroxide with standard acid. If correct

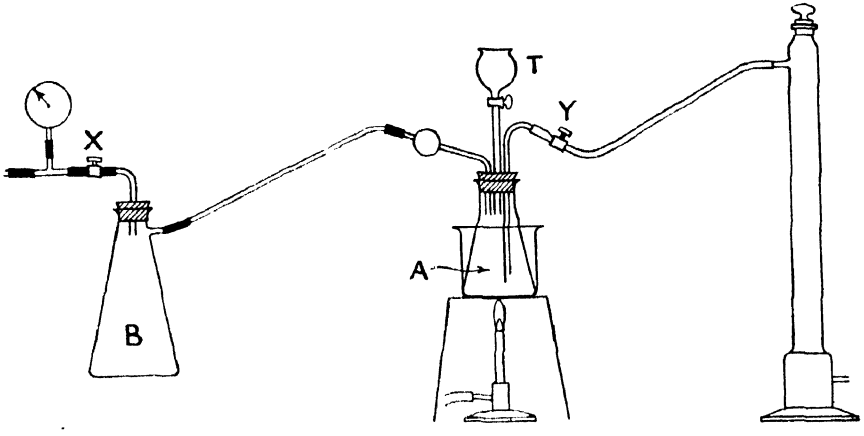


FIG. 6. Equipment for determination of carbonate in solid materials

adjustments have been made the restoration of atmospheric pressure should require about 15–20 minutes.

Reagents

Barium hydroxide 0·2N. = 15·8 gm. $Ba(OH)_2.8H_2O$ per 500 ml.

1 ml. of 0·2N. hydrochloric acid = 1 ml. of 0·2N. $Ba(OH)_2$ = 0·0044 gm. CO_2.

2. Determination of carbon in irons and steels

(*a*) The standard method for determining carbon in non-carbonaceous materials is by direct combustion, passing a stream of purified oxygen over the heated sample, absorbing and weighing the CO_2 evolved. A great many types of combustion trains are employed and for further details reference should be made to

books on iron and steel analysis, where the development of this determination has reached a high stage of speed and accuracy.[2, 3, 5, 7, 9, 10]

A satisfactory train which will allow the determination of CO_2 in any type of iron or steel is illustrated as Fig. 7. The apparatus consists of the following parts.

1. Mercury valve.
2. Bottle containing concentrated H_2SO_4.
3. Tower containing $CaCl_2$.
4. Tower with stick NaOH.
5. Electric furnace with combustion tube.
6. Bottle with 5% $KMnO_4$.
7. Tower with MnO_2.
8. Bottle with concentrated H_2SO_4.
9. Tower with P_2O_5, or preferably anhydrone.
10. Weighed absorption bulb with ascarite and anhydrone.
11. H_2SO_4 guard tube and gauge.

The train can, of course, be simplified where the oxygen is very pure, and the steels do not contain high sulphur, selenium, etc. The absorption bulb may be any of the standard types: Fleming-Martin, Miller, Stetser-Norton, Nesbitt, etc. Ascarite and similar soda-asbestos mixtures are now supplied with self-indicating granules, giving the degree of exhaustion of the absorbent.

In all combustion trains where gases must be dried it is advisable to remove the bulk of the moisture with stick KOH, concentrated H_2SO_4, or similar desiccants, and reserve the expensive anhydrone for the last 2–3% of moisture where its great efficiency can be utilized to best advantage.

Spread 1–3 gm. of the drillings or millings sized between 14 and 60 mesh in a

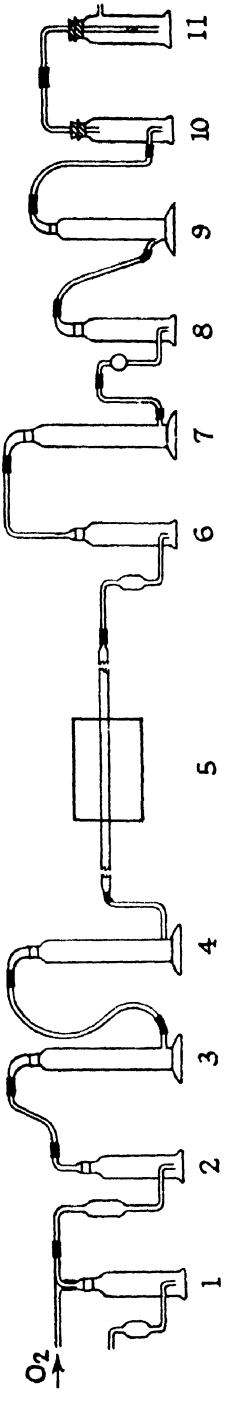


FIG. 7. Apparatus for determination of carbon by direct combustion in any iron or steel

groove of the RR Alundum in a boat, and insert the latter carefully into the combustion tube in the furnace. The temperature of the latter should be 1050–1100° C., except for certain high alloy steels where a temperature of 1200° or higher is necessary even with the presence of an accelerator.

As soon as the boat has been pushed into position in the hottest part of the tube, close the latter and turn on the oxygen slowly until the flow is 300 ml. per minute. When the sample has burned, in 1–2 minutes, reduce the flow of oxygen to 150 ml. per minute for 5–7 minutes to sweep out the CO_2.

Close the oxygen valve, disconnect the CO_2 absorption bulb, place it in the balance case for 5 minutes, open momentarily, and weigh. Weighing is best done by using a similar bulb as a counterpoise. Remove the boat from the tube and examine. If the drillings are not thoroughly fused in a solid pig it indicates incomplete combustion and the determination must be repeated, using a higher temperature or an accelerator. A blank run must be made on all carbon determinations to obtain a proper correction. The blank should be less than 0·0005 gm.

The best accelerator is 0·5 gm. of 20–40 mesh tin added to the sample in the boat. When tin is employed it is necessary to increase the flow of oxygen during combustion. For high alloy steels a temperature of 1250° C., if necessary with tin as an accelerator, is employed.

$$CO_2 \times 0{\cdot}2729 = C$$

(*b*) In recent years the measurement of the volume of CO_2 evolved when a steel sample is burned in oxygen has replaced the gravimetric procedure in most steelworks laboratories. Sulphur compounds are removed by MnO_2, and CO_2 is absorbed by KOH. The difference in volume of gases before and after absorption in KOH is the quantity of CO_2 evolved and consequently proportional to the carbon present in the steel. Equipment is listed by all leading chemical supply houses.

SPECIAL PROCEDURES

1. Graphite in cast iron is determined by dissolving 1–3 gm. sample in 50 ml. HNO_3 on the steam bath. Add a few drops of

HF to facilitate filtration of any separated silicic acid. Filter through ignited asbestos on a small Gooch crucible which will fit in the combustion tube of the CO_2 apparatus. Wash thoroughly with hot water, then with hot 12% KOH, hot water, 5% HCl, and finally with hot water. Dry at a temperature not exceeding 150° C. and determine the graphite by direct combustion at approximately 900° C. in the apparatus used for the determination of total carbon. The combustion tube must be closed immediately after inserting the sample.

Methods for the evaluation of industrial and activated carbon are given in the books of Hassler[4] and Mantell.[8]

2. The determination of carbon in organic materials may also be carried out by wet combustion. Oxidation is effected by chromic and sulphuric acids, and the evolved CO_2 may be measured gravimetrically or by absorption in $Ba(OH)_2$ and back titration of the excess hydroxide with standard HCl.[1]

3. The determination of the diamond content of grinding wheels, impregnated tools and other industrial products where diamonds are found in matrices of metal, ceramic, plastic, or cemented carbide is given by Young, Simpson, and Benfield.[11]

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CHLORINE

CHLORINE occurs in minerals, waters, ores, and many industrial products. It may be determined gravimetrically as AgCl, or volumetrically in two ways.[3, 4] In the volumetric method of Volhard the chloride is precipitated by a slight excess of a standard solution of $AgNO_3$ and the excess determined, after filtration, by titrating with thiocyanate. In Mohr's volumetric procedure, which is of restricted application to waters and neutral solutions, the chloride is titrated with silver nitrate containing potassium chromate as indicator. Very small quantities of chlorine are determined in waterworks practice by a colorimetric procedure, using *o*-tolidine.

Most substances containing chlorine can be decomposed by treatment with HNO_3. The use of H_2SO_4 should be avoided for fear of driving off HCl. For chlorides of Ag, Pb, and Hg it is necessary to fuse or digest with Na_2CO_3 or NaOH. If bromine or iodine is present it is necessary to separate them as follows: Iodine may be expelled by addition of 3 gm. sodium nitrite and 3 ml. of 1 : 1 H_2SO_4 to each 0·25 gm. of iodine in a volume of about 700 ml., and boiling the latter for 45 minutes. Chlorine and bromine remain in the flask. Bromine may be removed by neutralizing the solution remaining, after the expulsion of iodine given above, with NaOH and evaporating to about 50 ml. Cool, add about 65 ml. excess 1 : 2 acetic acid. Add 1·5 gm. $KMnO_4$ and pass a slow current of steam into the flask until all bromine has been expelled.

GENERAL PROCEDURES

1. Gravimetric method

Weigh out 0·5–5 gm. sample, depending on the chlorine content, to give approximately 0·1 gm. chlorine, decompose with HNO_3, and fuse any insoluble portion with Na_2CO_3. Dilute to approximately 200 ml., adjust the concentration of HNO_3 to about 2 ml. and add with stirring a 5% $AgNO_3$ solution until the precipitate coagulates and no more is formed. If silicic acid separates out, remove it with ammonia, making a reprecipitation if necessary to free the precipitate of occluded chloride. Then make the solution acid with HNO_3 and add $AgNO_3$ as usual. One ml. of 5% $AgNO_3$ will precipitate approximately 0·01 gm. Cl. Heat the solution to boiling, allow the precipitate to settle, and add a few more drops of $AgNO_3$ to be sure all chloride has been precipitated. Avoid a large excess of $AgNO_3$.

$$AgNO_3 + HCl \rightarrow AgCl + HNO_3$$

Set the beaker aside in the dark for several hours or preferably overnight. Filter through a weighed Gooch crucible previously washed with HNO_3 and dried in the oven. Wash by decantation with a solution containing 0·05 gm. $AgNO_3$ per litre, transfer to the crucible, wash with 1% HNO_3 to remove all $AgNO_3$ and finally several times with hot water.

Dry at 130–150° C. for an hour, cool in a desiccator, and weigh.

$$AgCl \times 0{\cdot}2474 = Cl$$

2. Volumetric method by precipitation with silver nitrate and titration with thiocyanate

In this method an alkali thiocyanate combines with silver in an acid solution and the excess of the thiocyanate reacts with an added ferric salt to form the reddish-brown ferric thiocyanate marking the end point of the reaction. In practice an excess of $AgNO_3$ is added to the nitric acid solution containing the chloride, AgCl is filtered off, and the excess of silver is titrated with thiocyanate in the presence of the ferric salt.

The sample is decomposed as outlined under the gravimetric method and the solution is made acid with HNO_3 to the extent of about 5 ml. excess for 150 ml. A measured excess of 0·1N. $AgNO_3$ is now added and the precipitated AgCl filtered off and washed thoroughly to free it of $AgNO_3$. The combined filtrate and washings are titrated with standard 0·1N. KCNS or NH_4CNS, using 5 ml. of a saturated solution of ferric ammonium alum as indicator. A permanent reddish-brown colour, best seen against a white base, marks the end point of the reaction. From this titration the quantity of $AgNO_3$ which reacted with the chlorine can be obtained.

$$NH_4CNS + AgNO_3 \rightarrow AgCNS + NH_4NO_3$$

$$3NH_4CNS + NH_4.Fe(SO_4)_2.12H_2O \rightarrow Fe(CNS)_3 + 2(NH_4)_2SO_4 + 12H_2O$$

1 ml. 0·1N. $AgNO_3 = 0{\cdot}003546$ gm. Cl

In routine work it is advisable to have 1 ml. of thiocyanate = 1 ml. of silver nitrate. Approximately 8 gm. NH_4CNS or 10 gm. KCNS, and 17·1 gm. $AgNO_3$ per litre gives a 0·1N. solution. The latter can be standardized against 0·1N. NaCl, which contains 5·846 gm. NaCl per litre.

3. Volumetric method by titration with silver nitrate in neutral solution containing potassium chromate

In this method silver combines with chlorine in presence of a chromate preferentially, since as long as any soluble chloride is present the silver chromate formed initially is decomposed, $Ag_2CrO_4 + 2NaCl \rightarrow 2AgCl + Na_2CrO_4$. When all the chlorine has combined with silver, an excess of K_2CrO_4 at once forms the red Ag_2CrO_4, which indicates the end point of the reaction. Since this procedure must be carried out in a neutral solution, its application is chiefly confined to water-soluble chlorides, brines, waters, etc.[1]

To the neutral solution in a porcelain casserole add 2–3 drops of a saturated solution of potassium chromate and then the 0·1N. $AgNO_3$ solution slowly with vigorous stirring. When a permanent red tint is obtained record the volume of $AgNO_3$, and add an

equivalent solution of NaCl carefully until the red colour is just destroyed. Deduct this from the volume of $AgNO_3$ used.

$$1 \text{ ml. } 0{\cdot}1\text{N. } AgNO_3 = 0{\cdot}003546 \text{ gm. Cl}$$

In this and the previous volumetric method, free chlorine and free HCl are neutralized by ammonium hydroxide and boiled to convert them to chlorides.

Cyanides and chlorides are usually not separated from each other because the combined chloride and cyanide can be determined by Volhard's method, and then the cyanide in a second sample by titration with standard silver nitrate, as described in the section on cyanogen.

4. Colorimetric determination

Very small quantities of free chlorine in waterworks practice are determined by *o*-tolidine, the latter acquiring a yellow colour in the presence of this element.[2] Comparison is made with coloured discs ranging from 0·1–1 p.p.m. chlorine. Owing to the widespread occurrence of small quantities of chlorides, it is necessary to run careful blanks when determining chlorine.

Preparation of the *o*-tolidine solution may be facilitated by the following procedure:

Weigh out 1 gm. *o*-tolidine, transfer to a mortar, and add 5 ml. of 1:5 HCl prepared by adding 100 ml. of concentrated HCl to 400 ml. of water. Grind to a thin paste and add 150–200 ml. of water. The *o*-tolidine goes into solution at once. Transfer to a litre flask and make up to 505 ml. with water. Make up to the mark by adding the balance, 495 ml., of the 1:5 HCl.

Mix 1 ml. of the *o*-tolidine solution with 100 ml. of the filtered water in a 100 ml. Nessler tube. Allow to stand 5 minutes or until maximum development of colour is attained. Match against coloured disc standards in a Nesslerizer or similar instrument. The following substances interfere and their presence must be considered in evaluating results: nitrites, ferric compounds, manganic compounds, chlorates, and organic colouring matter.

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CHROMIUM

CHROMIUM is a common element in metallurgical laboratories, as it occurs widely in ores, irons and steels, alloys, electroplating solutions, pigments, etc. Chromium is nearly always determined volumetrically by oxidation to chromate and subsequent reduction by an excess of ferrous sulphate, finally titrating the excess of the latter with $KMnO_4$.[3, 4]

GENERAL PROCEDURES

1. Ores

For ores and similar materials fuse 1 gm. of the finely ground sample with 8 gm. sodium peroxide in an Armco iron crucible, transfer to a beaker and treat with 200 ml. warm water. When the melt has dissolved, remove the crucible, washing thoroughly, boil, filter through asbestos and wash well.

$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$
$$NaFeO_2 + 2H_2O \rightarrow NaOH + Fe(OH)_3$$

To the filtrate add 60 ml. 1:1 H_2SO_4 and 5 ml. HNO_3. Boil, add a 25% solution of $AgNO_3$ in amount equal to 0·01 gm. of the salt for each 0·01 gm. of chromium present. Heat to boiling and add 2–4 gm. of ammonium persulphate to oxidize the chromium completely. Boil for 10 minutes and if permanganic acid or oxides of manganese are present add 10 ml. of a 10% NaCl solution and resume boiling for 5 minutes after the manganese compounds are reduced, to ensure that all chlorine has been expelled.

Cool the solution to room temperature, add 3 ml. H_3PO_4, and a measured excess of 0·1N. ferrous ammonium sulphate. Titrate

with 0·1N. $KMnO_4$ with vigorous stirring to the first faint permanent darkening of the clear green colour.

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$$

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

1 ml. of 0·1N. ferrous ammonium sulphate $= \frac{Cr}{3} = 0{\cdot}001734$ gm. Cr

The ferrous ammonium sulphate solution is prepared by dissolving 39·2 gm. in 1 litre of water containing 20 ml. 1:1 H_2SO_4, and standardizing against 0·1N. $KMnO_4$. A 0·1N. $KMnO_4$ solution is made by dissolving 3·2 gm. $KMnO_4$ in water, diluting to 1 litre, and standardizing against sodium oxalate. A 0·1N. $Na_2C_2O_4$ solution contains 6·7002 gm. per litre.

By this procedure chromium is separated from nearly all common elements except Al, As, Mo, W, V, and the presence of these does not interfere with the titration. Vanadium, arsenic, etc., are reduced by ferrous sulphate but are again oxidized with the consumption of an equivalent amount of permanganate. Chromium may be separated from uranium by oxidizing completely with HNO_3 and $NaClO_3$, adding NH_4OH, and filtering. Chromium is in the filtrate.

2. Irons and steels

For irons and steels the sample can be dissolved in acids and taken to fumes of H_2SO_4 or $HClO_4$.[1, 5] In the latter case the sample is cooled rapidly in cold water, diluted with cold water, boiled, cooled, a few drops of $AgNO_3$ added, and titrated directly with ferrous ammonium sulphate and $KMnO_4$ in the usual manner. For very low chromiums the iron can be separated with ether, as described in the section on Cobalt.

It must be realized when decomposing samples for chromium with perchloric acid that the presence of HF simultaneously will lead to partial volatilization of chromium, and indeed all the chromium can be removed by repeated fuming with a mixture of perchloric and hydrofluoric acids.

For accurate work the visual titration must be corrected for dilution effect and colour interference. This is done most

conveniently for occasional analyses by boiling the solution, which has just been titrated, for 10 minutes to destroy the slight excess of permanganate, cooling to room temperature, and then titrating with $KMnO_4$ to the colour that was originally taken as the end point.

The solution after the titration of chromium can be used for the determination of vanadium.

The titration of chromium may be done potentiometrically, in which case a direct titration with a standard ferrous ammonium sulphate solution is used. Chromium may be titrated in this manner without separating iron. Vanadium is also reduced by ferrous sulphate and is counted as chromium.

3. Colorimetric procedure for small quantities of chromium

(*a*) If potentiometric titration apparatus is not available, very small quantities of chromium, in the absence of uranium, can be determined colorimetrically by comparing the colour obtained after filtration of the solution resulting from a Na_2O_2 fusion with standards of K_2CrO_4 or $K_2Cr_2O_7$ in similar alkaline solutions. A solution containing 0·283 gm. $K_2Cr_2O_7$ in 1 litre has a value of 1 ml. = 0·0001 gm. Cr.

(*b*) Chromium may be determined in ferrous alloys with the Spekker photoelectric absorptiometer[2] or similar photoelectric colorimetric equipment.

A good procedure has been recently described for very low chromium contents in biological material.[6]

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COBALT

COBALT is found associated in minerals and ores with copper, nickel, arsenic, iron, and sulphur. It is an important constituent of many high speed steels, magnets, cemented carbides, and alloys. Cobalt is also used as a catalyst, for electroplating, in the glass, ceramic, and paint industries, and as a minor but essential element in livestock licks and feedstuffs, and pasture fertilizers.

Cobalt may be determined by weighing as the oxide Co_3O_4, as the metal after electrolysis, by titration with cyanide, potentiometrically, or colorimetrically. In certain cases it may be determined spectrographically or polarographically. The chief separations of cobalt are from members of previous groups by removal of the latter with hydrogen sulphide in acid solution, from iron by a zinc oxide or phosphate separation or ether extraction, and from nickel by precipitation of cobalt with α-nitroso β-naphthol or separation of nickel with dimethylglyoxime.

In certain alloys or high speed steels, chromium, vanadium, and tungsten are frequently associated with cobalt. These can be eliminated with a zinc oxide separation from an acid solution oxidized with nitric acid, in the absence of copper and molybdenum. Tungsten can be removed by filtering off tungstic oxide in the initial decomposition with HNO_3. Chromium may be removed as chromyl chloride by several additions of HCl to a perchloric acid solution of the alloy. Other methods of separation may be employed, such as precipitation with sodium hydroxide in the presence of sodium peroxide to throw chromium and vanadium into the filtrate, and solution of the material in perchloric acid, fuming and filtering off the precipitated tungstic oxide. In cemented carbides, cobalt may be determined after tungsten,

molybdenum, and the bulk of tantalum and niobium have been removed by a double precipitation with KOH and filtration, followed by a cupferron separation.[4]

Cobalt is very tenaciously retained by the hydroxides of iron and aluminium, and it is nearly impossible to separate cobalt completely from large quantities of iron and aluminium even by repeated ammonia precipitations. A large excess of ammonia and ammonium salts will minimize the retention of cobalt in an iron hydroxide precipitate.[13] This is undoubtedly the principal reason for the greater adsorption of cobalt by aluminium than by iron. Pouring the iron-cobalt solution into ammonia also appears to minimize the adsorption of cobalt by ferric hydroxide.

GENERAL PROCEDURES

The following procedures are applicable to nearly all classes of material, and in the absence of interfering elements may be shortened accordingly.

1. Gravimetric determination as Co_3O_4 after precipitation with α-nitroso β-naphthol

A. *Separation of iron with zinc oxide.* Weigh out 0·5–10 gm. depending on the cobalt content of the sample, and take into solution with 10–25 ml. HNO_3, 10–25 ml. HCl, 10 ml. 1:1 H_2SO_4, and a few drops of HF if necessary. For high sulphide products initial treatment with a little bromine or potassium chlorate is advisable to avoid the inclusion of undissolved particles in a bead of sulphur. Certain high-cobalt alloys, such as Stellites, are best decomposed by prolonged treatment with perchloric acid. Evaporate to strong fumes of SO_3, cool, dilute with water, and boil. Adjust the acidity to 5–10% H_2SO_4, and gas out all Group 2 metals with H_2S. Filter off the precipitated sulphides and silica, and wash thoroughly with acidulated H_2S water.

Boil the filtrate for 15 minutes to remove all H_2S, oxidize the iron with H_2O_2, and boil to remove the excess of peroxide. Nearly neutralize with Na_2CO_3 solution and boil to remove all CO_2. Add a suspension of zinc oxide until the precipitate assumes the colour of coffee containing cream. Boil and filter, washing 3–4 times with hot water. Transfer the precipitate back

to the original beaker, just dissolve with HCl, and reprecipitate with zinc oxide emulsion. Filter through the original filter paper and wash thoroughly 7–8 times with hot water. The filtrate will contain only Co, Ni, Mn, and a few other elements not affecting the α-nitroso β-naphthol precipitation. A turbidity in the filtrate caused by colloidal zinc oxide may be disregarded, as subsequent acid treatment dissolves this. For very accurate work on small quantities of cobalt in the presence of large amounts of iron, aluminium, etc., a third precipitation may be necessary.

Add 20 ml. HCl in a volume of 500 ml. to dissolve the colloidal zinc oxide, and hold the nickel in solution, heat to boiling, and cautiously add sufficient α-nitroso β-naphthol in 1:1 acetic acid to precipitate all the cobalt. Use 0·5 gm. α-nitroso β-naphthol for each 0·01 gm. Co. Allow the brick-red precipitate of cobalti-nitroso β-naphthol to boil several minutes, remove from hot plate, and allow to stand in a warm place several hours.

Filter on a Whatman No. 42 paper, using pulp, wash several times with hot water, then 10 times with hot 5% HCl, and finally with hot water until free of chlorides. Place paper and precipitate in a weighed porcelain crucible, dry, ignite carefully in a muffle at a temperature not exceeding 850° C. Cool in a desiccator and weigh as Co_3O_4.

$$Co_3O_4 \times 0{\cdot}7342 = Co$$

For routine work the precipitate may be ignited in a fireclay crucible or annealing cup and brushed on to the balance pan.

It is sometimes recommended to add a suspension of ZnO to the sample in a flask, shake, allow to settle, and withdraw an aliquot portion of the supernatant liquid for the cobalt determination. Our results have indicated that this practice is not satisfactory for accurate work.[23]

The zinc oxide separation may be expressed thus:

$$ZnO + H_2O \rightarrow Zn(OH)_2$$
$$3Zn(OH)_2 + 2FeCl_3 \rightarrow 2Fe(OH)_3 + 3ZnCl_2$$
$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
$$2HCl + ZnO \rightarrow ZnCl_2 + H_2O$$
$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$$
$$H_2SO_4 + ZnO \rightarrow ZnSO_4 + H_2O$$

The α-nitroso β-naphthol precipitation is represented thus:

$$3C_{10}H_6(NO)OH + CoCl_3 \rightarrow \{C_{10}H_6(NO)O\}_3Co + 3HCl$$

Hydrochloric acid must be present at this precipitation to keep in solution the nickel and uranium compounds formed with α-nitroso β-naphthol. Uranium is precipitated with α-nitroso β-naphthol in the presence of acetic acid, but if HCl is present uranium remains in solution.

If the final residue of Co_3O_4 is contaminated with nickel, or if it is very bulky, it may be dissolved in HCl and cobalt reprecipitated with α-nitroso β-naphthol. A better procedure, especially if iron contamination is suspected, is to transfer the cobalt oxide to a beaker, dissolve in acids, take to fumes of SO_3, and electrolyse as described below under 2.

B. *Separation of iron with sodium phosphate.* The zinc oxide separation of iron for cobalt determinations has several drawbacks. Two precipitations, and for very accurate work three precipitations, are necessary to liberate cobalt completely from the iron precipitate. It can only be used in conjunction with subsequent precipitation of cobalt with α-nitroso β-naphthol, and this procedure is not suitable for large quantities of cobalt, which are best determined electrolytically.

When iron is precipitated as ferric phosphate from a solution containing cobalt there is remarkably little occlusion of cobalt.[23] For all routine work, one precipitation, even in the presence of large quantities of iron, is sufficient. A filtrate is obtained upon which cobalt may be determined directly by electrolysis.

Decompose the sample with acids or by fusion, as described under A, evaporate to fumes of SO_3, and remove copper and other Group 2 elements with H_2S in 5–10% HCl or H_2SO_4 solution. Boil out H_2S, add sufficient H_2O_2 to oxidize the iron present, and again boil until H_2O_2 is removed.

Add sufficient trisodium phosphate solution to precipitate all the iron, plus 5 ml. excess solution. Ten ml. of the phosphate solution given below will precipitate 0·05 gm. Fe. If aluminium and other elements precipitated by phosphate are present, additional phosphate solution must, of course, be added. To reduce the bulk of solution, for samples high in Fe, Al, etc., use a more concentrated sodium phosphate solution. Then add

NH_4OH carefully from a dispensing burette with vigorous stirring until purple cobaltous phosphate is formed. If the sample is low in cobalt it may be difficult to see the cobaltous phosphate, and a piece of red litmus should be used as indicator. When the litmus turns blue a *p*H of approximately 5·6 has been reached, and this is sufficient to ensure that cobaltous phosphate has been precipitated at *p*H 5·3.

The cobaltous phosphate is now dissolved by the addition of exactly 10 ml. of glacial acetic acid, with vigorous stirring. This will be found to give a *p*H of 3–3·5. Oxidize the solution by adding 5–20 ml. H_2O_2 and stir thoroughly. The iron is now precipitated as a white creamy precipitate of ferric phosphate.

$$2Na_3PO_4.12H_2O + Fe_2(SO_4)_3 \rightarrow 2FePO_4 + 3Na_2SO_4 + 24H_2O$$

Bring the sample to the boil on the hot plate, stirring occasionally to prevent bumping if a heavy iron precipitate is present. Filter through a Whatman No. 531 or 541 paper on a fluted funnel, using paper pulp. If a heavy precipitate of ferric phosphate is present, filter through a Buchner funnel. Wash the precipitate 8–10 times with hot acetic acid wash solution.

Proceed directly with the determination of cobalt by precipitation with α-nitroso β-naphthol, or add 10 ml. 1:1 H_2SO_4, 40 ml. NH_4OH, and electrolyse immediately.

Reagents

Trisodium phosphate solution: Dissolve 34·05 gm. of $Na_3PO_4.12H_2O$ in 1 litre of water. Ten ml. will precipitate 0·05 gm. Fe.

Acetic acid wash solution: 25 ml. of glacial acetic acid in 1 litre of water.

This method of first raising and then lowering the *p*H of the solution has been found to give the best separation of cobalt from iron. All the iron is precipitated and none of the cobalt is retained by one precipitation of the iron.

If a large excess of phosphate has been added and the cobalt is to be determined electrolytically, some of the cobalt will be precipitated as the phosphate on the addition of ammonia

immediately before electrolysis. Keep the quantity of added phosphate to a minimum.

By the use of dilute acetic acid as wash solution there is no danger of precipitating cobalt phosphate in the pores of the ferric phosphate precipitate, and the latter may be washed entirely free of cobalt.

Aluminium phosphate will be precipitated at *p*H 3·5 and will be removed with the ferric phosphate. Manganese, calcium, nickel, and magnesium are not precipitated and will be found in the cobalt solution. The only one of these elements which may interfere in the subsequent determination of cobalt is calcium in the electrolytic procedure if a large excess of phosphate is present. In this case when ammonia is added calcium phosphate is precipitated and may occlude cobalt. If large quantities of calcium are present they may be precipitated as the oxalate in acetic acid after the phosphate separation.

Uranium, titanium, and zirconium are removed by the phosphate separation; chromium and vanadium divide. In the presence of the latter a preliminary sodium hydroxide separation may be made.

C. *Separation of iron with ether.* Iron may be satisfactorily removed in cobalt determinations by means of an ether separation. This is particularly suitable for low cobalt steels or slags, since several 10 gm. portions may be combined after the ether extraction. Iron must be in the ferric state. Concentration of iron should not be over 1 gm. in 10 ml., and preferably in 20 ml. For each 20 ml. of solution at least 30 ml. ether should be used. With a little practice the chemist will find an ether separation very useful for removing iron, not only for cobalt work, but in many other determinations.

After the sample has been completely decomposed by acid treatment with HNO_3 and fumed to dryness with H_2SO_4, HCl is added and this is evaporated carefully to syrupy consistency. Transfer the contents of the beaker to a 250 or 500 ml. separatory funnel, rinsing out the beaker thoroughly with HCl of s.g. 1·10 and finally several times with ether. Add more ether to bring the concentration up to 30 ml. per gm. of iron in 20 ml. HCl of s.g. 1·10. Hydrochloric acid of s.g. 1·10 is made by mixing 526 ml. concentrated HCl with 474 ml. water.

Shake the funnel vigorously under the cold water tap, allow to settle and draw off the lower layer into a 400 ml. beaker. This contains the cobalt together with Cu, Ni, Mn, etc., while the upper layer contains nearly all the iron. Extract the upper and lower layers again with ether and HCl of s.g. 1·10 to make a complete separation.

It is usually advisable to let the separatory funnel stand for a few minutes after drawing off the lower layer, to collect the small quantities of acid remaining after the initial shake and withdrawal. Swirling the funnel will help to collect the last droplets of acid from the upper ether layer.

The upper layer in the separatory funnel, containing ferric chloride and ether, can be drawn off and placed in a Winchester. Add water and shake. The ferric chloride goes into the lower aqueous layer while ether remains on top. This lower layer can be removed by siphoning and is discarded, giving an excellent recovery of ether.

The partition coefficient of iron is approximately 50. With 1 gm. of iron the first ether extraction removes all but 0·02 gm. A second extraction removes all but 0·5 mg.

Place the beaker containing cobalt and other elements on the edge of the hot plate on asbestos until all ether has been driven off. Add 5 ml. HNO_3, 10 ml. 1:1 H_2SO_4, and take to fumes of SO_3. Cool, take up in water, adjust acidity to approximately 5–10% H_2SO_4 and gas out all preceding group elements with H_2S.

Remove H_2S by boiling, oxidize with H_2O_2, and if chromium and vanadium are absent, add 4 ml. HCl for each 100 ml. of solution and proceed directly with the α-nitroso β-naphthol precipitation. If chromium and vanadium are present, remove with NaOH-Na_2O_2 separation, or with zinc oxide.

2. Electrolytic determination of cobalt

A. *Electrolysis in ammoniacal solution following treatment with* H_2SO_4. For medium or large quantities of cobalt the electrolytic determination is the most satisfactory procedure. Depending on the nature of the sample, electrolysis may be preceded by separation of iron with zinc oxide or ether and precipitation of cobalt by α-nitroso β-naphthol, or separation of iron with phosphate. Cobalt may even be electrolysed in the presence of iron.

Dilute the sample, which has been fumed with H_2SO_4, with water, add 5 ml. 1:1 H_2SO_4, neutralize with NH_4OH and add 40 ml. excess. If the sample was fumed to dryness add more 1:1 H_2SO_4 or ammonium sulphate to ensure the presence of the latter after making ammoniacal. Electrolyse overnight on a stationary cabinet at 0·5–1 ampere or on a rotating electrolytic apparatus at 2 amperes for 1 hour. Unlike the electrolytic copper determination, it is difficult to tell by dilution when deposition of cobalt is complete owing to the similarity in appearance between cobalt and platinum in the cloudy ammoniacal solution. The solution may be tested for complete deposition by withdrawing a few drops with a pipette on to a spot plate and testing with potassium thiocarbonate, phenylthiohydantoic acid, nitroso-R-salt, or ammonium sulphide, by the usual spot tests for these reagents.

Wash the cathode, taking particular care to wash off any particles of ferric hydroxide which may be adhering to the meshes of the cathode if a little iron were present during the electrolysis. Rinse in alcohol, dry on a hot plate or in a blast of warm air from a hair-drier, and weigh the previously tared cathode.

If nickel was suspected in the original sample and the cobalt was not separated by α-nitroso β-naphthol, place the cathode in a 300 ml. Berzelius beaker, add 50 ml. HNO_3 and dissolve off the plating by placing on the edge of a hot plate for 10 minutes, making sure that all parts of the cathode come in contact with the hot acid. Remove the cathode, washing thoroughly into the beaker, and test the solution for nickel in the usual manner with dimethylglyoxime. Subtract the nickel content, if any, from the weight of the cobalt deposit obtained on the cathode.

For routine work cobalt may be deposited electrolytically in the presence of iron. The following procedure is used by the laboratories of the Union Minière du Haut Katanga for high-cobalt iron products like alloys going 40% Co, 45% Fe. Remove copper with H_2S in dilute H_2SO_4, boil to remove all H_2S, add H_2O_2 and evaporate to a low volume. Alternatively, copper may be removed electrolytically in acid solution. Cool, make ammoniacal, and add 30 ml. excess NH_4OH. Electrolyse the solution containing suspended ferric hydroxide in a tall 600 ml. beaker for 45 minutes on a rotating apparatus at 2 amperes. Lower the beaker from the cathode, washing the latter, just dissolve

the ferric hydroxide with H_2SO_4 and reprecipitate with NH_4OH, adding 30 ml. excess. Continue the electrolysis for 30 minutes longer, lower the beaker, dissolve the $Fe(OH)_3$ and reprecipitate as before to set free any occluded cobalt. Continue the electrolysis a further 30 minutes. This should result in complete deposition of cobalt, indicated by a negative test for this element when a small portion of the solution is withdrawn with a pipette, filtered, and tested on the spot plate with ammonium sulphide, phenylthiohydantoic acid, or nitroso-R-salt.

Since a little iron is occluded with the deposited cobalt on the cathode it is necessary in accurate work to dissolve the plating in HNO_3, take to fumes of H_2SO_4, make ammoniacal, and re-electrolyse. The second electrolysis at 2 amperes requires only about an hour or less with rotating anodes.

The procedure of dissolving the cobalt deposit in HNO_3 and eliminating the latter by evaporating to fumes of H_2SO_4 may be shortened by dissolving the plating in HCl, neutralizing with NH_4OH and re-electrolysing. An excess of 60 ml. NH_4OH and 15 ml. of a saturated SO_2 solution are added, and electrolysis is carried out at 2 amperes and 10 volts. The deposited cobalt should be a light grey colour.

B. *Electrolysis following removal of iron with phosphate.* Large quantities of cobalt are readily determined electrolytically following removal of iron with phosphate.[23] In the presence of nickel the combined cobalt + nickel may be determined electrolytically and nickel or cobalt subsequently determined on the dissolved plating by dimethylglyoxime or α-nitroso β-naphthol, respectively. Alternatively, cobalt may be separated with α-nitroso β-naphthol after removal of iron with phosphate, and finally determined electrolytically.

Evaporate the filtrate from the phosphate separation of iron to low volume, add 10 ml. 1:1 H_2SO_4, 5 gm. borax and carefully add NH_4OH to neutralization, followed by 30–40 ml. excess. Electrolyse on a rotating cabinet with a current of 3 amperes and 6 volts. Do not prolong the electrolysis after all the cobalt is deposited, particularly in the presence of manganese, or a black cathode deposit will be obtained and results will be high. If a large excess of ammonia is present, and the electrolysis is not unduly prolonged after spot tests with potassium thiocarbonate,

phenylthiohydantoic acid, or nitroso-R-salt indicate deposition is completed, excellent results will be obtained.

The addition of borax to the electrolysing solution is optional, many chemists preferring an ammonium sulphate-ammonia medium only.

Spot tests for completion of cobalt electrolysis

1. *Ammonium sulphide.* The addition of a few drops of ammonium sulphide precipitates black cobalt sulphide. A number of other Group 3 elements, of course, also give dark-coloured sulphides under these conditions.

2. *Potassium thiocarbonate*, K_2CS_3. This is prepared by saturating one half of a solution of 5% KOH with H_2S, adding the other half, and heating moderately with 1/25 of its volume of carbon disulphide. The dark red liquid is decanted from the undissolved carbon disulphide and kept in a well-closed flask. Cobalt in ammoniacal solution gives a yellow colour with little, and brown or black with much, cobalt.

3. *Phenylthiohydantoic acid*, $C_9H_{10}O_2NS$. A few drops of a solution of 1 gm. phenylthiohydantoic acid in 100 ml. ethyl alcohol added to an ammoniacal cobalt solution gives a pink colour.

4. *Nitroso-R-salt*, $C_{10}H_4OH.NO(SO_3Na)_2$. To a few drops of the cobalt solution add several drops 50% sodium acetate, acidify with HNO_3, and add several drops of a 0·5% solution of nitroso-R-salt in water. A permanent red colour indicates the presence of cobalt.

A method has been published in which nickel and cobalt are separated by electrolysis by depositing cobalt on the anode as Co_2O_3.[20] A diaphragm revolving electrode was used as cathode. About 0·04 gm. Co could be deposited on this anode successfully, together with 1 gm. of nickel on the cathode. The deposited cobaltic oxide contains a little nickel and must be dissolved and re-deposited. The solution must be well buffered at *p*H 5, and a high temperature is desirable for best deposits. This procedure is not suitable for routine work.

In all cobalt electrolytic work it must be kept in mind that cobalt and nickel, unlike copper, are not easily dissolved off a platinum cathode in cold nitric acid. Following cobalt electro-

lysis, cathodes should be vigorously boiled five minutes in nitric acid, washed, and if necessary burned over a hot bunsen flame before re-use.

3. Volumetric determination with potassium cyanide

In the absence of nickel, cobalt may be determined by cyanide titration in a manner similar to this familiar procedure for nickel.

Potassium cyanide reacts with cobaltic sulphate to give a complex cobalt cyanide. The end point of the reaction is determined by an indirect indicator, silver iodide, which gives a turbidity to the solution until a slight excess of potassium cyanide is present. Silver iodide is formed *in situ* by the action of $AgNO_3$ on KI.

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

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

$$10KCN + Co_2(SO_4)_3 \rightarrow 2\{2KCN.Co(CN)_3\} + 3K_2SO_4$$

The end point of the reaction is indicated by the disappearance of the cloudy precipitate of silver iodide. Since it is generally easier to detect the appearance of a turbidity than its disappearance, a slight excess of KCN is added and a back titration with $AgNO_3$ carried out until a faint opalesence is again formed.

Decompose the sample with 10 ml. HNO_3, 10 ml. HCl, a few drops of HF if necessary, in the usual manner, add 10 ml. 1:1 H_2SO_4 and fume strongly to dehydrate silica. Dissolve in water, gas out copper and other Group 2 elements with H_2S, and filter off the precipitated sulphides, silica, etc. Boil out all H_2S, and oxidize thoroughly by adding 10 ml. HNO_3, 1–2 gm. potassium chlorate, and boiling gently for 15–20 minutes. Cool in a water bath, add NH_4OH just to the neutral point, and add 10–20 ml. of ammonium citrate-sulphate buffer solution for each 0·1 gm. of iron present. Place a piece of litmus paper against the side of the beaker and carefully add NH_4OH until the litmus turns blue. Add exactly 2 ml. more NH_4OH and boil gently for 2–5 minutes.

Cool in a water bath, add 5 ml. of 10% KI and 2–3 ml. of standard $AgNO_3$ solution from a burette. Add standard KCN solution from a burette with constant stirring until the cloudiness produced by silver iodide disappears. Finally add standard $AgNO_3$ solution drop by drop with constant stirring, over a black

background, until a persistent cloudiness is again produced. The total number of ml. of standard $AgNO_3$ solution used is then subtracted from the number of ml. of standard KCN to give the percentage of cobalt.

$$10KCN + Co_2(SO_4)_3 \rightarrow 2\{2KCN.Co(CN)_3\} + 3K_2SO_4$$

1 gm. Co = 5·5234 gm. KCN

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

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

130·22 gm. KCN = 169·89 gm. $AgNO_3$

1 gm. Co = 7·2060 gm. $AgNO_3$

Standardize the cyanide solution against the silver nitrate, and in addition titrate the cyanide against a solution containing a known amount of cobalt. One gram of $CoSO_4.7H_2O$ contains 0·2097 gm. cobalt, and a 25 ml. aliquot from a litre of solution containing one gram of this salt gives a convenient quantity for titration against dilute KCN. Check the solution of $CoSO_4.7H_2O$ electrolytically. It is useful to have two standard KCN solutions, one for low cobalts, with a value approximating 1 ml. = 0·001 gm. Co, and another for high cobalts possessing a titre of 1 ml. = 0·005 gm. Co.

These solutions are made up to contain 5·6 gm. KCN + 1 gm. KOH per litre, and 28 gm. KCN and 5 gm. KOH per litre, respectively. They are standardized against silver nitrate solutions containing 7·2060 gm. $AgNO_3$ and 36·0300 gm. $AgNO_3$ per litre, respectively. Standardization should be carried out at least once a week.

After the addition of silver nitrate to the samples, keep them out of direct sunlight, as the latter has a tendency to reduce AgI to metallic silver and give erratic results.

The ammonium citrate-sulphate solution has the following composition:

Citric acid	200 gm.
Ammonium sulphate	270 gm.
Ammonia	200 ml.
Water to make	1000 ml.

With the exception of copper, which is removed with H_2S, and, of course, nickel, very few elements interfere with the cyanide titration of cobalt.[6]

4. Colorimetric determination of cobalt

A. *Ammonium Thiocyanate.* Cobalt forms a complex with ammonium thiocyanate which can be extracted with amyl alcohol and ether, and the blue cobaltothiocyanate colour measured in a colorimeter.[24]

$$CoCl_2 + 4NH_4CNS \rightarrow (NH_4)_2\{Co(CNS)_4\} + 2NH_4Cl$$

Decompose the sample with 10 ml. HNO_3 and 10 ml. HCl, adding a few drops of bromine initially for sulphide ores, or HF for silicate materials if necessary. For high iron material use HNO_3 and $KClO_3$. Evaporate the sample to dryness but do not bake. Traces of HNO_3 have no effect on the formation of the thiocyanate complex.

Dissolve the samples in approximately 25 ml. of water, and add exactly 1 ml. HCl for every 50 ml. of subsequent dilution of the sample. Boil, cool, and wash out into appropriate measuring cylinders or calibrated flasks. The amount of dilution of the samples depends on the amount of cobalt present and can be read off from the table below.

TABLE 1

Weights and Dilutions of Samples According to Percentage Cobalt Present

% Co in sample	Wt. of sample taken for analysis gm.	Dilution ml.	Aliquot taken for analysis ml.	Factor for % Co
0·01 to 0·20	2·0	50	5	0·5
0·16 to 0·80	0·5	50	5	2
0·80 to 3·20	0·5	200	5	8

(*a*) *Cobalt samples with less than* 36 *mg. iron.* Measure out 5 ml. of sodium thiosulphate solution, 3 ml. of sodium phosphate solution, and 10 ml. of ammonium thiocyanate solution. Add with vigorous agitation 5 ml. of solution of the sample The *p*H is now 3·5–4·0 and the concentration of NH_4CNS is 26 per cent.

Add 10 ml. of the amyl alcohol-ether mixture and shake the whole thoroughly again. Transfer to a separatory funnel, run off the lower aqueous layer, and discard. Transfer the solution of the cobalt complex to a test tube or a 1 cm. absorptiometer cell. For visual comparison match the intensity of colour of the test solution with the standard copper sulphate solutions. The comparison may be carried out in a La Motte comparator for hydrogen ion determinations with a source of artificial light, or the tubes may simply be held against a white background out of direct sunlight. It will be found possible to take a reading half-way between any two of the standards if the colour of the test solution lies between them.

In the photoelectric comparison, absorption of the test solution is compared with an amyl alcohol-ether blank. The amount of cobalt present in the test solution is then read off from the calibration curve.

By either means of comparison the amount in milligrams of cobalt present in the extract is obtained and the percentage of cobalt in the sample is given by multiplying by the appropriate factor shown in the last column of Table I.

(*b*) *Cobalt samples with more than* 36 *mg. iron.* Carry out the analysis of these samples in exactly the same way as for those under (*a*), but in this case add initially 2 ml. of ammonium acetate solution. The *p*H is still 3·5–4·0 and the concentration of NH_4CNS is 24 per cent. Unless iron is known to be absent it is preferable in all cases to add 2 ml. ammonium acetate as a routine procedure. Copper does not interfere with the production of the blue colour of the cobalt complex even when present to the extent of 60 per cent. Iron if present in amount greater than about 36 mg. will interfere unless ammonium acetate is used. Vanadium forms a blue complex which is extracted with the amyl alcohol-ether solution. If, however, ammonium acetate and a few drops of tartaric acid are added to the reagents this blue complex is not formed, and vanadium will not interfere. The following do not give coloured complexes which are soluble in amyl alcohol-ether: Cr, Mn, Ni, Ti, Mo, U. Other common elements such as Al, Si, Mg, Ca, P, Bi, As, Pb, and the alkalies are without effect.

This rapid procedure is very satisfactory for a range of 0·02–0·50 mg. cobalt or 0·01–4% Co.

Reagents

Ammonium thiocyanate: Dissolve 600 gm. of NH_4CNS in 1 litre of water.

Sodium phosphate: Dissolve 83·3 gm. of $Na_3PO_4.12H_2O$ in 1 litre of water.

Sodium thiosulphate: Dissolve 200 gm. of $Na_2S_2O_3.5H_2O$ in 1 litre of water.

Ammonium acetate: Dissolve 700 gm. of $NH_4C_2H_3O_2$ in 1 litre of water.

Tartaric acid: Dissolve 50 gm. of $C_4H_6O_6$ in 1 litre of water.

Amyl alcohol-ether: Mix 3 parts by volume of amyl alcohol with 1 part of ethyl ether.

For visual comparison, solutions of copper sulphate may be used as permanent standards since the blue colour of the copper sulphate solution matches almost identically the blue of the cobalt complex. A solution of copper sulphate in water containing 8 gm. $CuSO_4.5H_2O$ per litre will match an extract containing 0·02 mg. Co per 10 ml. For photoelectric comparison, of course, a calibration curve for the absorptiometer, giving drum reading against mg. cobalt, is drawn up once, using extracts of standard solutions, and values of future unknowns are read off directly from this curve. Photoelectric comparison is more satisfactory for this and similar colour matching.

B. *Nitroso-R-salt*, $C_{10}H_4OH.NO(SO_3Na)_2$. This determination is based on the fact that the coloured complexes formed by most of the common elements with nitroso-R-salt, except cobalt, are destroyed by nitric acid. The full development of the colour with cobalt is attained in the presence of sodium acetate, and such variables as quantity of nitric acid and of nitroso-R-salt, time of boiling, etc., have an influence on the development of colour.[26]

The colour comparisons are conveniently done in a photoelectric instrument such as a Spekker photoelectric absorptiometer. A calibration curve is drawn, plotting drum readings against concentrations of cobalt. To 0, 1, 2, etc., up to 11 ml. of standard cobalt sulphate solutions are added 2 ml. Spekker acid, 10 ml. nitroso-R-salt solution, and 10 ml. sodium acetate solution. A blank is made by adding 2 ml. Spekker acid and 10 ml. sodium

acetate solution but omitting the nitroso-R-salt. The blank and standard solutions are brought to a boil on the hot plate. Five ml. HNO_3 are added and the solutions are boiled for at least 1 minute and not more than 2 minutes. The standards and blank are then cooled and diluted to 100 ml. with water.

The absorption of the standards is measured on the Spekker photoelectric absorptiometer using 1 cm. cells and Hilger No. 6 blue filters. The blank is set at 1·0 and the differences obtained are plotted against the weights of cobalt taken.

Procedure. For samples containing 0·01–0·20% cobalt use a 0·25 gm. sample. With higher grade materials take a 0·5 gm. sample and after decomposition dilute to volume and take a suitable aliquot containing 0·01–0·5 mg. cobalt for analysis. For very low concentrations of cobalt, as in refined metals, larger aliquots representing 1–20 gm. may be taken. The maximum quantity of cobalt permissible in a sample is 0·5 mg., as above this concentration the solution no longer appears to follow Beer's law exactly.

Decompose with HNO_3, HCl, and bromine, add 5–7·5 ml. 1:1 H_2SO_4 and take to strong fumes. Some products will require the use of HF for complete decomposition. Care should be taken in the addition of reagents as an excessive concentration of salts in the final solution will increase the absorption.

Cool, dilute to about 30 ml., add 2 ml. HCl, and boil to solution of soluble salts. Pass a brisk current of hydrogen sulphide through the solution for 10 minutes and filter through a Whatman No. 40 paper, washing well with acidulated H_2S water. Boil off H_2S, add 5 ml. HNO_3 and take to fumes of SO_3.

Alternatively, remove copper by electrolysis. For products like blister or refined copper, determine cobalt on the solution obtained after the electrolysis of copper. Evaporate this solution to fumes of SO_3 and continue heating until only a small amount of H_2SO_4 remains.

Cool, dilute to about 25 ml. with water, and boil to solution of salts. Cool, carefully neutralize with 20% NaOH to a point where the solution becomes a deep wine red. Should there be little or no iron present, add 2 drops phenolphthalein and take to the first faint pink. Immediately add 2 ml. Spekker acid, followed by 10 ml. nitroso-R-salt solution and 10 ml. sodium

acetate solution. Bring to a vigorous boil, add 5 ml. HNO_3, and then boil for at least 1 minute and not more than 2 minutes. Cool and dilute with water to 100 ml.

At the same time carry out a blank exactly as was done in calibrating the graph. The absorption of the sample is measured in the same manner as were the standards, with the blank setting at 1·0. The drum reading obtained for the sample is subtracted from 1·0 and this difference is measured off on the calibration graph to obtain the weight of cobalt present.

Copper must be removed, and with it, if H_2S is used, all Group 2 elements will be eliminated. Manganese over 10%, nickel over 3%, and chromium above 5% must be removed prior to the colour comparison. The following are without effect on the determination, even in quantities over 100 times that of the cobalt: Fe, Al, Zn, Ti, Th, U, Zr, W, Ba, Sr, Ca, Mg. By increasing the sodium acetate, and nitric acid additions, and paying strict attention to times of boiling, it has been shown by Hall and Young[7] that small quantities of copper need not be removed for this procedure.

With the following procedure, 0·1–0·5 mg. Co can be determined in the presence of 10–12 mg. Cu without separation of the latter. For a mill feed running 3% Cu and 0·13% Co weigh out 0·25 gm. sample. Dissolve in HNO_3 and HCl, and add HF and Br if necessary. Add 5 ml. of Spekker acid, take to fuming on the hot plate and fume strongly for about 5 minutes. Cool, take up in 20 ml. water, and boil the sample for several minutes.

Add 30 ml. sodium acetate solution and 10 ml. of nitroso-R-salt solution to the sample. Bring to the boil and boil for exactly one minute.

Add 10 ml. of HNO_3 to the boiling sample and if all the flocculent precipitate does not dissolve, add 2–5 ml. more HNO_3. Continue the boiling for another minute, remove from hot plate, cool, make up to 100 ml. in measuring cylinder. Mix well and filter the sample through dry paper into a dry Erlenmeyer flask. Only 50 ml. need be filtered.

Measure the absorption of this solution against distilled water as for standard cobalt solution.

Unless the samples are boiled thoroughly before the addition of HNO_3 all the colour of the cobalt complex will not develop and

results will be low. Prolonging the boiling beyond one minute does not result in any further development of colour. The subsequent boiling after the addition of the acid is not so important and need not be watched so carefully, but the samples should not be boiled for a prolonged period.

In this procedure the samples are not filtered until after they have been coloured up. Residual insoluble matter has no effect on the production of the cobalt colour. This method shortens the time required for analysis.

Ten ml. of nitroso-R-salt solution are only sufficient to form the cobalt complex with about 0·6 mg. Co.

With 5 ml. of Spekker acid added originally to a 0·25 gm. sample it is not necessary for routine work to neutralize with sodium hydroxide and add 2 ml. Spekker acid. Fuming the samples strongly will give an acid concentration of 1–4 ml. acid which has no effect on the final results. Samples fumed to complete dryness and those having 4 ml. Spekker acid gave the same cobalt figure under the above condition.

Reagents

Cobalt sulphate: Dissolve 0·2385 gm. $CoSO_4.7H_2O$ in water and make up to 1 litre. 1 ml. = 0·05 mg. Co.

Nitroso-R-salt: Dissolve 1 gm. in water and make up to 500 ml.

Spekker Acid: Mix 150 ml. H_3PO_4 and 150 ml. H_2SO_4, and make up to 1 litre.

Sodium acetate: Dissolve 500 gm. $NaC_2H_3O_2.3H_2O$ in water and make up to 1 litre.

5. Potentiometric determination of cobalt

A very satisfactory procedure for cobalt on a wide range of products is a potentiometric one, based on the oxidation of cobalt in ammoniacal solution by potassium ferricyanide.[6] In the cold and in the presence of ammonium citrate practically the only common element which interferes is manganese, and this can be removed by a nitro-chlorate separation. The potentiometric procedure is applicable in the presence of large quantities of copper, nickel, and iron, the three commonest interfering elements in other methods for cobalt.

The details given below apply to most non-ferrous mining and metallurgical products, and can be modified slightly for irons and steels or other samples.[1] It is an excellent procedure for cobalt in cemented carbides.[4, 21]

Reagents

Ammonium citrate solution: Dissolve 200 gm. citric acid in water and add slowly 270 ml. of ammonia. Cool and make up to 1 litre. Tartaric acid may be used in place of citric acid if desired.

Cobalt nitrate solution: Weigh out 5·00 gm. of AnalaR cobalt nitrate, dissolve in water, and make up to 1 litre. Standardize the solution by determining the cobalt electrolytically. One ml. of this solution should contain 1 mg. Co.

Potassium ferricyanide solution: Weigh out 11 gm. of potassium ferricyanide, dissolve in water, and make up to 1 litre. This solution must be kept in a brown bottle since it decomposes if exposed to light.

Standardization of the potassium ferricyanide solution

Measure carefully 10 ml. of potassium ferricyanide solution from a standard burette or pipette into a 600 ml. beaker. Add 20 ml. of ammonium citrate, 80 ml. ammonia, and make up to 400–500 ml. with water. Place the beaker in position on the Cambridge potentiometric titration apparatus or a similar instrument and switch on the current and stirrer. Unclamp the galvanometer and turn the centre switch to normal. By altering the coarse and fine adjustments the light beam is brought either to the middle of the scale or to the left-hand side. Run in standard cobalt nitrate solution from a burette until a large and permanent deflection is given on the galvanometer scale. The end point is very sensitive and will be given on the addition of a drop of cobalt nitrate. The setting on the galvanometer for the titration of the standard must be retained for the titration of the samples. Ten ml. of potassium ferricyanide should be equivalent to 20 ml. of cobalt nitrate, or 1 ml. of potassium ferricyanide equals 2 mg. Co.

Procedure. Decompose the sample with HNO_3, HCl, and Br or HF if necessary. When all the sample is in solution boil

thoroughly to drive off nitrous fumes, but it is not necessary to evaporate to low bulk. If the samples cannot be decomposed without the addition of H_2SO_4, add 10–25 ml. of 1:1 H_2SO_4 and evaporate to fumes.

If manganese is present evaporate the mixed acid solution nearly to dryness. Add 40–50 ml. HNO_3 and carefully add several successive small portions of sodium chlorate, boiling gently after each addition. Dilute slightly and filter off the MnO_2 through a Whatman No. 42 paper, or through asbestos on a Gooch crucible.

The insoluble matter other than MnO_2 need not be filtered off, but if large quantities are present it is a good practice to do so. Cool the samples and titrate carefully with ammonia until the iron just begins to precipitate. Redissolve the iron by the addition of a drop or two of 1:1 HNO_3. Cool the samples again thoroughly.

Measure out carefully from a standard burette or pipette into a 600 ml. beaker sufficient excess potassium ferricyanide solution to give a back titration of 10–15 ml. of cobalt nitrate solution. Add 10–20 ml. ammonium citrate for every 0·1 gm. iron present in the sample, followed by 80 ml. ammonia. Pour the sample very slowly with constant stirring into the beaker containing potassium ferricyanide, etc. There must be no heating effect produced at this point, and if the sample has been almost neutralized and cooled beforehand no heat will be developed.

Place the beaker containing the sample on the potentiometer and switch on the current and stirrer. Set the instrument in the same way as directed under standardization of the potassium ferricyanide. Back titrate the excess potassium ferricyanide with standard cobalt nitrate solution until the end point is shown by a large and permanent deflection of the galvanometer beam.

If chromium and vanadium are present the samples should be decomposed with HNO_3 and HCl, and then taken to strong fumes of a low volume of perchloric acid. The sample is then poured directly into the beaker containing excess ferricyanide, ammonium citrate, and 80 ml. ammonia, without preliminary neutralization. Vanadium is in the vanadate state and does not interfere with the titration.

Quantities of cobalt up to 100–150 mg. in complex materials can be accurately and rapidly determined in this manner. The

following are without interference: Hg(ic), Pb, Fe, Ni, Cu, Bi, Cd, As(ic), Sb, Sn(ic), Se, Te, Mo, Cr(ate), Be, Al, Zn, Ti, W, U, V(ate), Zr.

Spectrographic and polarographic determination of cobalt

Spectrographic procedures for cobalt have been reported by Gallaher[5] and Standen,[16] and polarographic determinations by Maasen,[12] Thanheiser and Maasen,[18, 19] Kolthoff and Langer,[9] Kolthoff and Lingane,[10] Lingane and Kerlinger,[11] Jones,[8] and Stromberg and Zelyanskaya.[17] Gallaher[5] has described a method for the spectrographic determination of beryllium and cobalt in copper alloys. Up to 2% Be and 0·5% Co can be obtained from the lines Cu 1 3247·5Å, Be 1 3321·3Å, and Co 1 3453 5Å. Standen[16] has reported the most sensitive cobalt lines for qualititative work are 2424·930 and 2521·363Å, the limit of detection being approximately 0·001% in a zinc matrix. A useful table is presented showing the concentration of other elements which may interfere with identification of traces of elements sought. Table 2 below is extracted from this source.

TABLE 2

Interfering Elements in Spectrographic Determination of Cobalt

Cobalt line Å	Concentration of elements which may interfere with traces of cobalt sought Concentration expressed in per cent in zinc matrix										
	Bi	*Ce*	*In*	*Ir*	*Li*	*Mo*	*Nb*	*Ti*	*V*	*W*	*Zr*
3405·120	10	10	—	—	—	1	—	10	10	—	0·1
2521·363	—	—	1	—	—	—	1	—	—	0·1	—
2424·930	—	—	—	1	10	—	—	—	—	—	—

SPECIAL PROCEDURES

1. Oxide cobalt

It is often necessary in the mining and metallurgical industries to differentiate oxidized cobalt from sulphide cobalt. The

following procedure is applicable to ores and concentrator products.[25] It is based on the selective solvent action of dilute H_2SO_4 or HCl, in the presence of HF and the reducing agent sulphurous acid, on oxidized cobalt minerals.

Depending upon the quantity of oxide cobalt present in the material and on the analytical method used for cobalt, select a weight of −200 mesh sample that will enable an accurate determination of cobalt to be made on the leached portion. For instance, in a mill feed or tail running 0·02% oxide cobalt, at least 25 gm. must be taken for the initial sample if cobalt is to be precipitated by α-nitroso β-naphthol and weighed as oxide or determined electrolytically. If the colorimetric nitroso-R-salt procedure is employed on the same sample a weight of 0·25 gm. will suffice.

The ratio of leach solution to sample may vary quite widely, depending on the quantity of oxide cobalt present and on the other constituents of the ore. In general, add 15–25 ml. of 10% by volume HCl saturated with SO_2, or of 5% by volume H_2SO_4 saturated with SO_2, to each gram of material in a stoppered Erlenmeyer flask or covered beaker. When the initial effervesence and attack has subsided, add 0·1–0·3 ml. HF per gram of sample. For large samples these quantities of HF can be reduced proportionally.

Shake the flask or beaker for 10–15 seconds every 10 minutes for an hour, allow to stand an hour, and again agitate briefly at intervals of 10 minutes for the third hour. A useful timer for controlling such intermittent mechanical shaking has been described.[28] Filter the sample through a Whatman No. 40 paper, using pulp, and wash thoroughly with hot water. To the filtrate add 10 ml. 1:1 H_2SO_4, if necessary, boil out SO_2, and evaporate to fumes of SO_3. Cool, dilute, boil to solution of salts, and remove copper and other Group 2 metals with H_2S.

Filter off copper and other sulphides and wash well with acidulated H_2S water. Boil out H_2S from the filtrate, and proceed with the determination of cobalt by any standard method. For gravimetric or electrolytic procedures iron may be separated by zinc oxide, ether, or sodium phosphate, and the cobalt precipitated with α-nitroso β-naphthol and weighed as oxide or deposited electrolytically. If the nitroso-R-salt method is employed, the filtrate after oxidation of the iron with HNO_3 is taken to fumes of

SO_3 before proceeding with development of the colour in the usual manner.

2. Metallic cobalt

The following procedure, based on the report of Smirnov and Mishin,[15] has given good results on Rhokana products when taken in conjunction with microscopic studies of metallic cobalt in mattes, slags, etc.

To 2 gm. of −200 mesh slag add 50 ml. of 7% mercuric chloride solution. Boil 1 minute, filter through Whatman No. 42 paper and wash thoroughly with hot water. The following reaction occurs: $HgCl_2 + Co \rightarrow CoCl_2 + Hg$. Metallic cobalt passes into the filtrate as the chloride and can be determined by any suitable procedure.

The following, if present in metallic form, will be extracted along with the cobalt: Mn, Cr, Fe, Ni, Bi, Cu. Cobaltosic oxide, Co_3O_4, is insoluble in the mercuric chloride solution, and cobaltic oxide, Co_2O_3, is only soluble to the extent of 0·1–0·3%. Cobaltous oxide, however, appears to be slightly soluble. The extent of its solubility is difficult to determine as it is invariably mixed with Co_3O_4 and Co_2O_3. Cobalt sulphide and cobalt silicate are apparently insoluble in the mercuric chloride solution.

When determining cobalt on the filtrate it is necessary to keep in mind the following facts: The α-nitroso β-naphthol and ammonium thiocyanate procedures can be applied directly, electrolytic or nitroso-R-salt methods must be preceded by elimination of mercury with H_2S. By using an excess of NH_4Cl the potentiometric procedure is directly applicable.

3. Other procedures

A number of other procedures for the determination of cobalt have been proposed and doubtless give good results in certain cases. They will be briefly cited here, but the author has not had sufficient experience with some of them to justify recommending. The other procedures described in detail in this chapter have been used successfully for many years by the writer or his associates.

(*a*) Schoeller determines substantial quantities of cobalt by weighing as pyrophosphate obtained by ignition of cobalt ammonium phosphate. Since the solubility of the latter increases

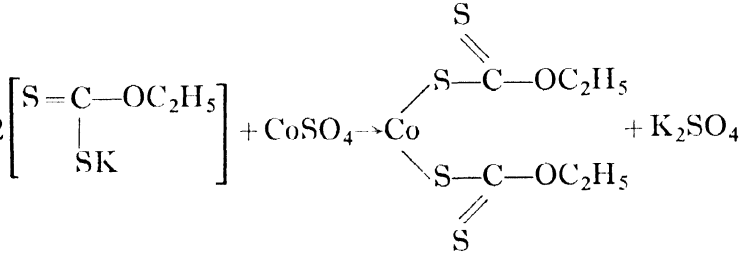
with ammonia concentration, complete precipitation requires a delicate adjustment. Schoeller[14] adds a slight excess of ammonia and recovers the remaining trace of cobalt from the filtrate as sulphide. The major cobalt fraction is weighed as $Co_2P_2O_7$ and the minor fraction as Co_3O_4. The procedure has obvious drawbacks for large numbers of routine determinations.

(*b*) Cobalt may be precipitated as potassium cobaltinitrite, $2K_3Co(NO_2)_6.3H_2O$, by adding a hot solution of potassium nitrite to an acetic acid solution of cobalt and allowing to stand overnight. So many substances interfere, however, such as oxidizing agents, free mineral acids, Group 2 elements, appreciable quantities of Fe, Al, Cr, alkaline earths, and ammonium salts that for most materials cobalt and nickel must be isolated by electrolysis before carrying on with the potassium cobaltinitrite procedure. The details are outlined in Scott and Furman's *Standard Methods of Chemical Analysis*.

(*c*) Fairchild[3] prefers to weigh cobalt as sulphate at 550-600° C.

(*d*) Ellis and Thompson[2] determine cobalt in biological materials with nitrosocresol.

(*e*) Cobalt may be separated, together with copper and silver, from a number of other elements by potassium or sodium ethyl xanthate in ammoniacal solution, keeping the iron in solution by tartrate.



Results with this separation at the Central Laboratory, Nkana, and the Diamond Research Laboratory, Johannesburg, have not been promising for accurate analyses.[22]

(*f*) Differentiation of cobalt oxides is determined by Murex Ltd., of Rainham, England, in the following manner.

Place 1 gm. of the finely-ground sample in a 250 ml. Erlenmeyer flask with 20 ml. water and shake well until all particles are

thoroughly wetted. Add 30 ml. glacial acetic acid and attach to the flask a reflux condenser. Boil gently for one hour. Pour the contents of the flask on to a tared sintered glass crucible, and wash well with hot water. Dry to constant weight in the oven at 105° C.

Cobaltous oxide, CoO, is soluble in acetic acid under these conditions, whereas the higher oxides Co_2O_3 and Co_3O_4 are insoluble.

Cobalt sulphide is virtually insoluble in dilute acetic acid under these conditions, and consequently cobaltous oxide can be separated from the sulphide by this procedure.[27]

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COPPER

COPPER is one of the most widely used industrial metals and in either the pure or alloyed forms is one of the commonest elements determined in most metallurgical laboratories. It may be encountered in quantities varying from traces in many minerals to nearly 100% in refined copper, and the number and amounts of associated elements are very varied. Owing to its great importance, the analysis of copper has been developed both in speed and accuracy to a very high degree.

Copper may be best determined in three ways: electrolytically, by weighing the metal deposited on the cathode upon electrolysis; volumetrically, by titration of iodine liberated when KI is added to a solution of cupric salt; or for very small quantities colorimetrically using sodium diethyldithiocarbamate or dithizone.

Although in many products copper can be determined electrolytically or volumetrically in the presence of numerous other elements, in other cases it is necessary to separate copper or remove interfering elements. Copper may be separated from succeeding groups by precipitation with H_2S in 5–10% by volume HCl or H_2SO_4. Silver may be removed from solutions containing copper as insoluble AgCl and lead as insoluble $PbSO_4$. Mercury is very rarely associated with copper but may be removed as the insoluble mercurous form in HCl solution. The following elements, in addition to Ag, Pb, and Hg which can be separated by decomposition in HCl or H_2SO_4, also accompany copper in the H_2S precipitation in acid solution: As, Sb, Sn, Bi, Cd, Se, Te, Mo, Au and the platinum metals. A large part of any As, Se, and Te present can be removed by boiling vigorously with HCl prior to any oxidation with HNO_3, Br, etc., or after the addition of a

reducing agent, such as sodium thiosulphate or ferrous sulphate. Selenium and tellurium can be separated by passing in SO_2 to HCl solutions containing copper.

Sn, As, and Sb can be separated from copper by volatilizing the former with hydrobromic acid-bromine mixture. Details are given by Sherman.[18] As, Sb, and Sn can also be separated from Cu by digestion of the sulphides in Na_2S_2 or $(NH_4)_2S$, in which copper sulphide is insoluble. Copper can be separated from molybdenum by electrolysis, if a re-deposition is made, as a little molybdenum is deposited the first time with copper, or by boiling in dilute H_2SO_4 solution with sheet aluminium. The latter separation, however, is not satisfactory for the long iodide method when Cu and Mo are present together.[21]

As, Sb, Bi, Se, Te can be collected and removed from a copper solution by a ferric hydroxide precipitate. This is one of the best methods of collecting and removing small quantities of these elements from an impure copper sample, and is particularly useful in obtaining a solution which will give a bright adherent copper deposit on electrolysis.[20]

Gold and the platinum metals are rarely encountered in quantities exceeding a few ounces per ton in copper-containing products, except in refinery slimes and similar material.[20] For the latter, copper may usually be isolated by treatment with HCl in the absence of oxidizing agents, leaving gold and the platinum metals unattacked. HCl is generally better than HNO_3 for unknown material, owing to the solubility of platinum and palladium, when alloyed with silver, in HNO_3.

GENERAL PROCEDURES

Decomposition of ores, mattes, slags, alloys, etc.

Weigh out 0·5–5 gm. sample, depending on the copper content, add 10–25 ml. HCl and boil for a few minutes to remove As, etc. Add 10 ml. HNO_3 and 10 ml. 1:1 H_2SO_4 and boil vigorously. Unless any acid-insoluble residue at this stage is known to be copper-free, add a few drops of HF to decompose silicates and bring the entire sample into solution. Take to strong fumes of SO_3, cool, dilute with hot water, boil, filter, and wash thoroughly with

hot water. The filtrate may be used directly for determination of copper by electrolysis or the short iodide method, or copper may be separated by H_2S precipitation prior to titration or electrolysis.

The above procedure may be modified according to the ease of decomposition of the sample or to the presence of other elements in the product. Slags often require considerable HF, or fusion of the acid-insoluble residue with Na_2CO_3. Many ores and minerals require only an attack with HNO_3 to get all the copper into solution. High sulphide products are usually treated with a few drops of bromine or potassium chlorate solution prior to the addition of HNO_3. This oxidizes the sulphide to the sulphate form and prevents the occlusion of particles of undecomposed material in the ball of sulphur which usually forms in the absence of these oxidizing agents.

An excellent method of decomposing converter mattes and slags and similar products containing refractory oxides, silicates, etc., is by direct fusion with sodium or potassium bisulphate in a pear-shaped Pyrex "copper" flask. The fusions are made over a battery of gas burners or electric heaters, and, if necessary, they are finally individually heated strongly for a few minutes over a blast burner. The melt is allowed to solidify in a thin layer around the sides of the flask by swirling the latter after withdrawing from the flame. After cooling, about 75 ml. of warm water and 5 ml. 1:1 H_2SO_4 are added, the flask placed on the hot plate, and the sample brought into solution. The solution is filtered into a beaker and is ready for direct determination of copper by electrolysis or for its separation with H_2S.

Blister and refined copper are dissolved in sulphuric and nitric acids, the nitrous fumes boiled out, and the solution made up to 1 litre in a volumetric flask. Usually 10-gram samples are taken and dissolved in a solution of 75 ml. water, 50 ml. 1:1 H_2SO_4, and 25 ml. HNO_3. If any insoluble residue, which contains copper, remains, it may be filtered off, ignited, fused with bisulphate, and added to the filtrate. If appreciable quantities of silver are present in the blister, the addition of just sufficient NaCl to precipitate the silver as AgCl is necessary. An aliquot of 1 gm. is usually taken from the 10 gm. portion of blister, and copper of course determined by electrolysis. Aliquots for refined copper are usually 2 or 5 gm.

For high copper alloys like brasses and bronzes where the electrolytic procedure is indicated, but the presence of tin and small quantities of arsenic and antimony necessitates their removal, the following procedure will give good results. Dissolve 2 gm. in 25 ml. 1:1 HNO_3, add 50 ml. water and allow to stand on a steam bath for an hour. Filter off the metastannic acid through Whatman No. 42 paper, using pulp, and washing with hot 1% HNO_3. Reserve the filtrate and washings, and treat the precipitate as follows to recover the occluded copper. Transfer the filter paper and contents to the original beaker, add 15 ml. 1:1 H_2SO_4 and 25 ml. HNO_3. Heat until all organic matter is decomposed, transfer the digested solution to a 400 ml. beaker and dilute to 250 ml. Add 25% NaOH solution until the tin hydroxide has dissolved. Add 20 ml. of 25% Na_2S solution and digest on the steam bath for several hours until the supernatant liquid is clear. Cool, filter through Whatman No. 42 paper and wash the precipitate with 2% Na_2S solution. The residue contains the sulphides of copper and lead, together with any bismuth and cadmium if present. Dissolve the residue in a little HNO_3 and add to the original filtrate obtained by decomposition of the sample in HNO_3. If it is desired to determine Cu and Pb simultaneously by electrodeposition on cathode and anode, respectively, electrolyse in HNO_3 solution containing 10–12 ml. HNO_3 in a volume of 150 ml. If copper alone is desired, or the quantity of lead is unsuitable for an electrolytic determination, add 10 ml. 1:1 H_2SO_4 to the combined HNO_3 solutions, and evaporate to fumes of SO_3. Filter off $PbSO_4$ and electrolyse the copper.

An alternative procedure for removing tin, arsenic, and antimony prior to determination of copper by electrolysis is to volatilize them by boiling with hydrobromic acid. Decompose the sample with HNO_3, add 10–15 ml. $HClO_4$ and heat to copious white fumes. Cool, wash down the cover and sides of the beaker, and add 15–25 ml. of 48% HBr. Heat to strong fumes of perchloric acid, and if the solution is not clear add a further 15–25 ml. HBr and evaporate again to near dryness. Tin, arsenic, and antimony will be volatilized. Take up in 1:1 HNO_3 and carry on with the electrolysis of copper.

When the sample has been decomposed, and all copper is in the

filtrate with sulphuric as the only acid present, the determination can be carried out in several ways.

1. Electrolytic determination

The electrolytic determination has the advantage that it is applicable to products ranging from traces to 100% copper. One weighing gives directly the quantity of copper, and personal factors are reduced to a minimum. Since large quantities may be taken, very accurate results on high copper materials or heterogeneous products may be obtained. Electrolysis may be carried out rapidly with rotating anodes, mechanical or electromagnetic stirring, or it may be done overnight with a stationary electrolytic apparatus. Commercial types of electrolytic equipment include the Braun, Slomin, Baird and Tatlock, etc. Rabbitts[15] describes a useful type of electrolytic analyser, which has several desirable features.

On the other hand, small quantities of substances such as As, Sb, Bi, Se, Te deposit on the cathode and not only contaminate the copper but often produce a dark, loosely adherent coating which easily flakes off the cathode in removing from the apparatus and weighing.

Bismuth below 0·01 gm. will be deposited on the cathode to give a dark but adherent coating with copper. Experiments at Rhokana Corporation show complete recovery of 0·1 gm. copper + 0·01 gm. bismuth on the cathode. Larger quantities of bismuth adversely affect the plating characteristics of the deposit.

Interference from antimony in copper electrolyses can be illustrated from the following table:

Sb present gm.	Wt. Cu gm.	
nil	0·1000	
0·0005	0·1001	0·1001
0·001	0·1003	0·1003
0·01	0·1034	0·1028
0·02	0·1064	0·1058

Above these quantities the physical character of the deposit was

affected, a dark coloured and loosely adherent deposit of copper being observed.

Arsenic in the standard sulphuric-nitric acid electrolyte for copper gave the following results with 0·0989 gm. Cu:

As present gm.	Cu found gm.
0·0005	0·0992
0·001	0·0992
0·0100	0·0993
0·0200	0·1001

Above these quantities the physical character of the deposit was affected; the cathode had a dark colour and a deposit of copper fell off on washing. It is evident that small quantities of arsenic are not as deleterious as equivalent quantities of antimony. If a dark-looking copper deposit, due to small quantities of arsenic, is obtained, a re-deposition from a nitric-sulphuric solution will give an arsenic-free copper deposit.

The effect of selenium and tellurium on copper electrolysis is shown on page 97, wherein varying quantities of these elements were added to 0·4990 gm. copper, and the standard sulphuric-nitric electrolyte employed.

Selenium, up to a quantity about 0·5% of the copper present, will largely plate out with the copper in an adherent form, but above this amount will give rise to pronounced darkening and non-adherence on the cathode. Tellurium present to an extent of only 0·1% of the copper will cause a darkening of the cathode deposit, but its deposition is nearly quantitative in quantities up to about 1% of the copper. Above this, the cathode deposit becomes very black and non-adherent.

Norwitz[12] has reported that if selenium and tellurium are oxidized to the sexivalent state with $KMnO_4$ in a nitric acid solution of copper, the latter can be electrolysed quantitatively free of Se and Te. We have been unable to obtain consistent results with this procedure, most of the values being outside the range of precision required in an electrolytic copper determination.

Se added gm.	Wt. cathode deposit gm.	Character of deposit
nil	0·4990	
	0·4990	
0·0005	0·4992	
	0·4992	Similar to pure copper
0·0025	0·5016	Faint darkening, but adherent.
	0·5016	
0·0050	0·5044	Pronounced darkening, non-adherent.
	0·5036	
Te added		
nil	0·4991	
	0·4990	
0·0005	0·4995	Faint darkening, but adherent.
	0·4996	
0·0025	0·5013	Slight darkening, but adherent.
	0·5015	
0·0050	0·5035	Slight darkening, but adherent.
	0·5035	
0·0500	0·5466	Very dark; non-adherent.
	0·5434	

These elements, however, can be removed from a copper solution in a ferric hydroxide precipitate.[20] To the sulphuric or nitric acid solution of copper add a little ferric sulphate or ferric nitrate, unless sufficient iron is already present in the solution to collect all the As, etc. Iron should be present to the extent of 10–30 times the impurities present. Add a few drops of HNO_3 unless already present, or a few ml. of H_2O_2, and boil to oxidize the iron. Precipitate the iron with the addition of NH_4OH and add a slight excess. Boil, filter on Whatman No. 531 paper and wash several times with hot water. Transfer the ferric hydroxide precipitate back to the original beaker, dissolve in 1:1 H_2SO_4, and reprecipitate with NH_4OH, adding an excess. Boil, filter, wash thoroughly with hot water. The filtrate contains all the copper, free from As, Sb, Bi, Se, Te. Make acid with 1:1 H_2SO_4, adding 5–10 ml. excess, add 1–2 ml. HNO_3, and electrolyse.

Molybdenum, when present in appreciable quantities, is deposited to a slight extent with copper. The deposition is not proportional to the amount of molybdenum present. The

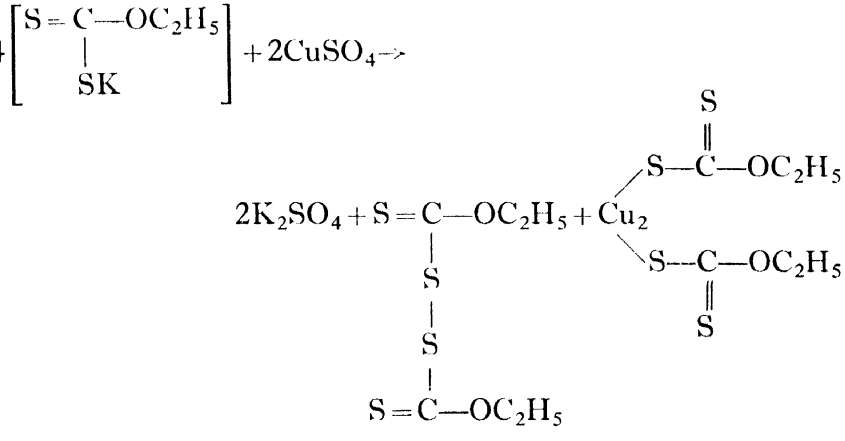
following results obtained by the writer are illustrative of the behaviour of this element in copper electrolysis using a standard sulphuric-nitric acid electrolyte.

Mo present gm.	Cu found gm.	Remarks
Nil	0·1092	
0·0151	0·1090	Faint darkening of cathode,
	0·1092	but no effect on weight.
0·1518	0·1184	Cathode slightly dark,
	0·1168	deposition a little slower than in absence of Mo.
0·4554	0·1194	,,
	0·1190	,,
0·9108	0·1170	,,
	0·1202	,,

All the copper is deposited in the form of an adherent but off-colour layer on the cathode. A re-plating under the same conditions results in deposition of the copper free from molybdenum even though the latter is present in large excess.

When small quantities of copper in the presence of large amounts of iron are to be determined electrolytically it is advisable to make a prior separation of the copper with H_2S. Otherwise great difficulty is usually encountered in the deposition of copper, or an initial deposition is followed by solution of the copper off the cathode. This is particularly noticeable when an excess of HNO_3 is present in the plating solution, and is ascribed to the solvent action of ferric nitrate on copper. For products of this nature the copper may be removed as CuS with a stream of H_2S, or the sample may be boiled with $Na_2S_2O_3$ in sulphuric acid solution, filtered, washed, dried, ignited, dissolved in HNO_3 and transferred to an electrolytic beaker.[19]

Another procedure for isolating copper from substances which interfere with its electrolytic determination is to add potassium or sodium ethyl xanthate in ammoniacal solution, holding up iron with tartrate.[3] Copper, with Co and Ag, is precipitated free from As, Sb, Bi, Se, Te. A second xanthate solution, or preferably one ammoniacal separation, may be necessary where large quantities of interfering elements are present.



di-xanthogen. cuprous xanthate.

In a rotating electrolytic apparatus 45 minutes at 1 ampere and 2–2·5 volts is usually sufficient for complete deposition of copper in ores, concentrates, mattes, slags, etc. The universal test for completeness of deposition is to dilute the solution and determine whether any further copper is plated on the stem of the cathode after several minutes. A more delicate test employs a spot reagent like sodium diethyl dithiocarbamate on a drop or two of the solution. The latter test is less serviceable, as traces of copper are always present in the electrolyte even after the completion of electrolysis. They should not, however, exceed 0·1 mg. in a well-conducted electrolysis, i.e. within the accuracy of routine weighing on the ordinary analytical balance.

If the electrolysed solution is required for the analysis of other elements the beaker is lowered below the cathode and the latter washed simultaneously from a wash bottle, catching all the washings in the beaker below. The cathode is then dipped in three beakers of alcohol.

If the electrolysed solution is not required, the washing may be carried out as given above, or the original beaker of solution may be quickly replaced by a beaker of distilled water, the cathode released from its support and lowered into the beaker, and then rinsed successively in four or five beakers of water, finally in two or three beakers of alcohol.

The cathodes may be dried in several ways after dipping in alcohol; igniting the alcohol with the flame of a small alcohol

lamp, allowing the cathode to dry on a small hot plate, or exposing it to a blast of warm air from a hair drier. If the cathode is ignited in a flame it is essential to keep the cathode moving or else local overheating and oxidation may occur. For the same reason the cathodes must not be kept on a hot plate any longer than is necessary to drive off the alcohol and leave them perfectly dry.

If a cathode remains dark after boiling in HNO_3 it is nearly always due to carbon. Ignite the cathode over a burner for a minute and the original colour will be restored.

Refined copper and similar samples are usually electrolysed overnight on a stationary cabinet at 0·5–1·0 amperes and 2–2·5 volts. The slow plating at a low amperage in the cold reduces any tendency for co-deposition of traces of other metals, and is used for work of the highest accuracy.

2. Volumetric determination with iodide-thiosulphate

This method is used extensively on ores, slags, flue dusts, and similar products where elements such as As, Sb, Sn, Cd, Bi, Se, Te, etc., which would contaminate an electrolytic copper deposit may be present. Very few elements interfere with the potassium iodide method. The procedure depends on the fact that potassium iodide liberates iodine when treated with cupric salts, and the liberated iodine is titrated with sodium thiosulphate.[5, 10, 17]

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

or

$$2Cu(C_2H_3O_2)_2 + 4KI \rightarrow Cu_2I_2 + 4KC_2H_3O_2 + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Two volumetric methods employing potassium iodide are used in metallurgical practice, generally termed long iodide and short iodide methods. In the latter the copper is not separated as CuS by H_2S, since the chief reason for this separation is the interference of iron in the final titration, and it is prevented in the short iodide method by the addition of potassium or sodium fluoride to repress the ionization of iron. The short iodide method is rapid and quite satisfactory for ores and most routine metallurgical products where the copper content is not over 15 per cent. and the amounts of other substances such as iron present are not excessive. If chromium is present the sample is not

treated with H_2SO_4 but all HNO_3 is eliminated by evaporating twice with HCl. Vanadium is about the only common element which interferes with the short iodide method, and in its presence the copper should be separated as CuS by the long iodide method.

(*a*) *Long iodide method*

In this the copper is separated by one of the procedures outlined below, and arsenic and antimony oxidized by the addition of bromine water. About the only elements present which then interfere are selenium and molybdenum. The former can be removed by prior separation with SO_2 in strong HCl solution, by separation with a ferric hydroxide precipitate, or by evaporating several times to dryness with HCl prior to any oxidizing treatment. Careful ignition of the CuS will eliminate selenium, which volatilizes at about 690° C., without fusing any CuO to the glaze of the porcelain crucible which occurs at about 900° C. Tellurium, of course, cannot be driven off in this manner. Molybdenum can be separated by treatment with NaOH or $NaOH + H_2S$ and filtering, when copper goes to the precipitate and molybdenum to the filtrate.

Though not recorded in reference books, it is useful to note that gold, platinum, and palladium in quantities up to 10 per cent. of the copper present have no significant effect on the long iodide titration.[20]

Copper may be separated as CuS by treatment with H_2S, as Cu_2S with $Na_2S_2O_3$, or as metallic copper by aluminium sheet.

I. Where a large number of copper determinations are carried out the most convenient source of H_2S is a large cylinder of the gas, now available everywhere commercially. An acid concentration of 5–10% HCl or H_2SO_4 and a vigorous stream of H_2S are necessary for complete precipitation of copper. It is essential to remove the CuS which often adheres to the glass tube leading the H_2S into the beaker, and add it to the sample. The precipitated CuS should be thoroughly washed with acidulated H_2S water, placed in a porcelain crucible, dried, ignited to CuO, dissolved in 1:1 HNO_3, and transferred to a small flask or beaker. If the muffle temperature is too low all the carbon will not be burnt off and it will interfere with the subsequent titration; if too high the

copper oxide will be fused into the porcelain crucible. A temperature of 600–700° C. is satisfactory.

II. Another convenient method of separating copper as sulphide is by the addition of a concentrated $Na_2S_2O_3$ solution to a boiling sulphuric acid solution of the copper sample. The H_2S generated under these conditions gradually precipitates the copper as Cu_2S, after about 10 minutes boiling, in a form which is easily filtered and washed.

$$2CuSO_4 + 2Na_2S_2O_3 + 2H_2O \rightarrow Cu_2S + 2Na_2SO_4 + 2H_2SO_4 + S$$

Cuprous sulphide is less easily oxidized by the air than cupric sulphide obtained by precipitation with H_2S, and may be washed with water. Copper sulphide obtained by sodium thiosulphate precipitation is much more granular and easily washed, dried, and ignited than that obtained by H_2S precipitation. Where the filtrate is discarded it is preferable to use $Na_2S_2O_3$. This method has the advantage that the disagreeable handling of H_2S is eliminated and the whole procedure can be carried out on a laboratory hot plate in an ordinary hood. The principal disadvantage of this method is the difficulty of removing the excess sulphur from the filtrate, if the latter is required for further determinations. Unlike free H_2S, which is easily removed by boiling, $Na_2S_2O_3$ requires long boiling, repeated treatment with HNO_3, and filtration of the precipitated sulphur.

The precipitate of Cu_2S from the thiosulphate precipitation is washed, dried, ignited to oxide, and dissolved in HNO_3 as in the previous procedure using H_2S. While only about 1 ml. of a 50% sodium thiosulphate solution is theoretically required to precipitate 0·1 gm. copper, in practice it is necessary to add a large excess to reduce ferric salts and precipitate other Group 2 elements. Add 5–20 ml. of a 50% solution of $Na_2S_2O_3.5H_2O$ per sample, depending on the copper, iron, and other metals present.

III. A third method for the separation of copper from iron is by boiling with an aluminium sheet in 5–10% H_2SO_4 solution until all the copper has been reduced to the metallic state. Boiling should be continued until the copper detaches itself from the aluminium sheet. The solution is filtered, washed, and the precipitated copper dissolved off the filter paper and the aluminium sheet with dilute HNO_3 into the original beaker. The

filter paper is thoroughly washed with successive small portions of hot water, and the filtrate is then ready for the following steps of the long iodide procedure.

It should be mentioned here that, contrary to the recommendations of many reference books, the separation of copper from molybdenum by means of aluminium is not satisfactory for a subsequent long iodide determination of copper.[21] Separation of copper by sodium thiosulphate or zinc is likewise subject to later interference by molybdenum. If these separations are practised, the short iodide procedure, in which molybdenum does not interfere, should be employed.

The copper, whether from H_2S, thiosulphate, or aluminium precipitation, is now in the form of a small volume of copper nitrate solution. The solution is boiled for several minutes to eliminate nitrous fumes. If arsenic and antimony are present, about 5 ml. of bromine water are added and the solution again boiled. Ammonium hydroxide is now added until a slight excess is present. The solution is boiled to remove the excess NH_4OH. Acetic acid is added until the dark blue colour of the copper-ammonia complex has disappeared, and then 5 ml. excess is added. The sample is boiled for a minute or two. The sides of the flask are washed down, the solution is cooled in a water trough, and 5 ml. of 80% KI solution added. An adjustable level water trough, such as described by Young and Rolling[23] is very convenient for this work. The sample is titrated with standard $Na_2S_2O_3$ until the dark brown colour turns to a straw yellow, then 5 ml. of 0·5% starch solution are added and titration continued from blue to the yellowish-white end point.

Molybdenum interferes in the iodimetric determination of copper unless the short iodide procedure is used. The ordinary long iodide procedure for copper is quite useless in the presence of even small quantities of molybdenum, giving variable results or a returning end point. In addition, ignition of sulphides of molybdenum and copper, even at a low temperature, leads to fusion with the glaze of porcelain crucibles.

(*b*) *Short iodide method*

In this procedure copper is not separated from iron, but the interference of the latter is prevented by adding a fluoride to the

solution.[8, 9] Very few elements interfere. Vanadium interferes, and appreciable quantities of selenium and tellurium lead to a slow release of iodine in the solution after the titration appears to be complete. This is due to the liberation of iodine from KI by selenic and telluric acids or copper salts of these acids, and may be minimized by having only a very slight excess of acetic acid present at the endpoint.

It has already been mentioned that molybdenum does not interfere in the short iodide procedure. Apparently the addition of fluoride produces a complex in which hexavalent molybdenum is undissociated.

$$Mo(SO_4)_3 + 6NaF \rightarrow MoF_6 + 3Na_2SO_4$$
$$MoF_6 + NaF \rightarrow \text{complex salt}$$
$$Na\ Mo\ F_7?$$

Some work should be done to determine the nature of this complex.

The following results indicate the non-interference of even large quantities of molybdenum when the short iodide method is employed.

2 gm. Nchanga tails Mo added	Cu present 0·0226 gm. Cu found	
gm.	gm.	%
nil	0·0226	1·13
	0·0226	1·13
0·0151	0·0226	1·13
	0·0228	1·14
0·1518	0·0228	1·14
0·1518	0·0226	1·13
0·4554	0·0226	1·13
	0·0226	1·13
0·9108	0·0224	1·12
	0·0224	1·12

Decomposition of the sample may be effected in the usual manner outlined previously. For many materials such as mine and mill samples the following method is rapid and satisfactory:

Weigh 0·5–2 gm. sample into a 300 ml. Phillips beaker, add a

few drops of 1:1 bromine-acetic acid mixture, about 10 ml. nitric acid-potassium chlorate mixture containing 100 gm. $KClO_3$ per litre of nitric acid, and allow to stand for 5 minutes. Place on hot plate, take to dryness, and bake a few minutes. Cool, add 1–2 ml. HNO_3, wash down sides of beaker and cover glass with hot water.

Boil and filter into 300 ml. Erlenmeyer flask, and wash 6 times with hot water. Add a small excess of NH_4OH and at once re-acidify with acetic acid, adding about 5 ml. excess, and boil. If manganese is present the following precautions are necessary for the short iodide procedure.[14]

1. Some free sulphuric acid should be present. If the samples have been fumed dry, add a little sulphuric acid prior to the neutralization with ammonia.
2. Avoid a large excess of ammonia. Add acetic acid immediately after the ammonia neutralization, in order to dissolve any manganous hydroxide inadvertently formed, before it becomes oxidized to higher oxides of manganese.
3. The solution should never be boiled after the addition of ammonia unless it has been re-acidified with acetic acid.

Remove from hot plate and add 1–3 gm. sodium fluoride depending on the iron content of the sample, wash down sides of Erlenmeyer, and place in cooling tray. Sodium, potassium, and ammonium fluoride form a complex in which iron exists in an undissociated state as ferric fluoride. The reaction may be represented thus:

$$12NaF + Fe_2(SO_4)_3 \rightarrow 2Na_3FeF_6 + 3Na_2SO_4$$

Titrate in the usual manner using KI, starch, and standard $Na_2S_2O_3$. A larger excess of KI is necessary with the short iodide method; otherwise the titration is similar to the previous procedure.

In industrial laboratories the standard $Na_2S_2O_3$ solution is frequently made by dissolving 195 gm. $Na_2S_2O_3.5H_2O$ and approximately 25 gm. NaOH in water and keeping in about 4 litres of solution for at least a week to stabilize. Then make up to 20 litres ready for use. 1 ml. of this $Na_2S_2O_3$ should be approximately equivalent to 0·0025 gm. Cu, or 0·25% on a 1 gm. sample. The solution should be standardized against 0·05 gm. freshly cleaned highest purity copper foil by dissolving the latter in 1:1

HNO_3 and treating exactly as in the procedure described above. The standard $Na_2S_2O_3$ should be checked at weekly intervals.

3. Colorimetric method

For very small quantities of copper the following colorimetric methods will give good results.[1, 6, 13, 16]

A. *Sodium diethyldithiocarbamate*, $(C_2H_5)_2N{-}C(=S){-}S{-}Na$

The reagent is used in the form of a 0·1% solution in water. This gives a distinct golden brown colour with 0·1 p.p.m. copper in solution, while with 1 p.p.m. the solution becomes turbid and a very dark brown colour develops. In the absence of Fe, Co, Al, Sb, Bi, Sn, Pb, Zn and Hg, the colour may be compared directly with standards similarly prepared.

If these elements are present, dissolve 2 gm. citric acid in about 50 ml. of the solution containing not more than 0·1 gm. of iron which must be in the ferric condition, and 0·1 mg. of copper. Make alkaline with NH_4OH, dilute to 70 ml., add 10 ml. of the reagent solution and extract immediately by shaking with four successive quantities of 2·5 ml. of carbon tetrachloride. If nickel is present add dimethylglyoxime and filter before extracting copper diethyldithiocarbamate with CCl_4. If the final extract contains more than a trace of colour, continue the extractions.

The combined extracts are then compared with standards similarly prepared either visually in a colorimeter or Nessler tubes, or by means of a photoelectric colorimeter. By this procedure copper up to 8% can be determined in aluminium alloys containing the following percentages of other elements: Fe 2, Mn 2, Ni 4, Cr 2, Zn 11, Mg 10, Pb 2, Sn 5, Ti 2, Bi 2.

A standard copper solution made by dissolving 0·0393 gm. $CuSO_4.5H_2O$ in 1 litre of water contains 0·01 mg. Cu per ml.

If large quantities of mercury are present this procedure is not satisfactory, and a colorimetric method based on the blue colour of the copper-ammonia complex should be employed. Mercury can be kept in solution by the addition of an excess of ammonia and ammonium citrate. At Rhokana this procedure has been used successfully with the Hilger photoelectric absorptiometer for a

sample containing over 3 gm. Hg to 1 mg. Cu.[4] The method has many applications for copper in the presence of other elements which are troublesome to remove, such as selenium and tellurium in refinery slimes.

Mehlig[11] discusses the colorimetric determination of copper with ammonia, and gives a list of interfering anions and cations.

B. *Dithizone*, $C_6H_5.N:N.C.S.NH.NH.C_6H_5$

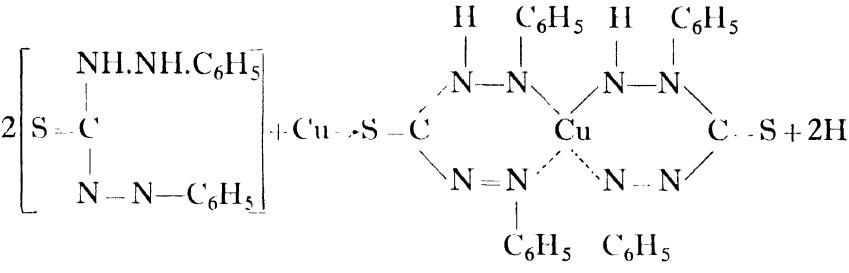
A rapid method for determining small amounts of copper in tailings or similar products uses an extraction with successive additions of diphenylthiocarbazone (dithizone). Weigh out 1 gm. tailing into a tall lipless 400 ml. beaker, add a few crystals of $KClO_3$ and 10 ml. 1:1 HNO_3. A few additional crystals of $KClO_3$ may be necessary to clear up any free sulphur floating on the surface. Add about 25 ml. additional HNO_3 at intervals to avoid frothing and boil several minutes to eliminate all free chlorine.

Add distilled water to a 250 ml. mark on the 400 ml. beaker, and stir vigorously. Pipette out 2 ml. and place in a 75 ml. separatory funnel containing several ml. of 2% hydroxylamine hydrochloride solution. Add to the funnel 0·5 ml. of standard dithizone solution from a 10 ml. burette, and shake the separatory funnel vigorously until the lower green dithizone layer turns red, showing that the dithizone has reacted completely with the copper. This lower layer is then drawn off and another addition of dithizone is made. Successive additions of standard dithizone solution are made in decreasing amounts, shaken up until they turn red and then drawn off until finally the green dithizone solution remains green after shaking, showing that all the copper has been extracted. The number of ml. of standard dithizone solution which are turned from green to red is then an accurate measure of the amount of copper originally present.

A solution containing 0·225 gm. dithizone per litre of CCl_4 gives a convenient value of 1 ml. = 0·02 mg. Cu. The dithizone solution is standardized against copper sulphate or a known tailing sample in the manner described above, and is covered in a 500 ml. separatory funnel with dilute H_2SO_3. This stock solution should be kept out of the light.

If the end point is inadvertently overstepped add a measured

quantity of the tailing solution to the separatory funnel and continue titrating in the usual manner. Only Bi, Hg, Au, Ag, Pd and Tl react with dithizone in oxidized acid solution to form dithizonates. Since these usually occur only in traces in industrial work they do not often affect the dithizone determination of copper.



Extraction of small quantities of many metals from a sample by means of dithizone is an excellent procedure, particularly when determining impurities in refined metals. In an oxidized solution, metals react with dithizone as follows:

In acid solution: Bi, Cu, Au, Hg, Pd, Ag, Tl.
In neutral solution: In.
In basic solution: Cd, Co, Pb, Mn, Ni, Zn.

C. *Tetraethylenepentamine*

It has been found at Nkana that the colorimetric procedure of Crumpler[2] offers some advantages for determining small quantities of copper in the presence of high concentrations of selenium and tellurium, since the latter do not interfere in this method. The ammonia-ammonium citrate method, however, is of wider application for this purpose.[4]

D. Hoste[7] has recently proposed 2.2 diquinolyl as a specific reagent for copper.

SPECIAL PROCEDURES

1. Volumetric determination with cyanide

For rapid works control on copper sulphate solutions in concentrators, electroplating, or leaching plants the cyanide titration for copper may be employed.

$$2Cu(NH_3)_4SO_4.H_2O + 7KCN \rightarrow$$
$$K_3NH_4Cu_2(CN)_6 + NH_4CNO + 2K_2SO_4 + 6NH_3 + H_2O$$

The temperature, volume of solution, excess of ammonia, and rapidity of titration should be the same in the determination as in the standardization. While this method is far less accurate than the iodide volumetric procedures, there may be conditions where its simplicity and rapidity sanction its use for plant operators. The following procedure is typical for this class of work.

Secure a representative sample of the clear copper sulphate solution by withdrawing several portions from a tank or pipeline into a beaker, stir, and pipette out 10 ml. into a clean 400 ml. beaker. If the solution contains suspended matter, filter before pipetting off the 10-ml. portion. Add about 150 ml. distilled water to the 400 ml. beaker.

Add concentrated ammonium hydroxide, with stirring, to the solution until a blue colour forms. Now add 10 ml. additional ammonium hydroxide. Set the beaker in a pan of cold water for several minutes. Bring the volume of solution to 200 ml. or half of the capacity of the beaker, if necessary, with distilled water.

Titrate carefully with the solution of potassium cyanide, stirring vigorously, until the blue colour disappears. A KCN solution made by dissolving 50 gm. KCN in 1 litre is of such a strength that 1 ml. = roughly 0·01 gm. Cu, giving a convenient burette titration of about 100 ml. on a 10 ml. sample pipetted from a saturated $CuSO_4$ solution. Since the KCN solution gradually grows weaker it should be standardized at weekly intervals by treating a convenient volume of a standard copper sulphate solution with ammonia, cooling, diluting to volume, and titrating in the regular manner. A copper sulphate solution containing 3·9278 gm. $CuSO_4.5H_2O$ per 100 ml. serves as a convenient standard for checking the value of the KCN solution. One ml. of this copper sulphate solution contains 0·01 gm. Cu.

While the method as outlined above is simple and rapid, it is necessary to observe the following points if a reasonable degree of accuracy is desired:

1. Temperature of the solution affects the titration. The beaker of ammoniacal copper solution should be titrated in the

cold and at approximately the same temperature as the standardization was carried out.

2. The ammonia concentration should be constant. An excess of 10 ml. NH_4OH added after the development of the blue colour should be used for both analysis and standardization.

3. The volume of solution should be the same. A final volume of 200 ml., or the half-way mark on a 400 ml. beaker, is a good one. Add only distilled water to make up the volume to this level.

4. Silver, nickel, cobalt, zinc, and cadmium interfere, but their presence in more than traces is unlikely in solutions where this cyanide procedure would be considered satisfactory.

2. Oxide copper

In many parts of the world copper occurs as oxide and sulphide, and it is necessary to distinguish between the two forms. This determination is based on the fact that dilute H_2SO_4 saturated with SO_2 dissolves oxidized forms of copper but does not attack sulphides. An exception to this is the oxide mineral cuprite, Cu_2O, which liberates only approximately half of its copper in the dilute acid leaching solution. Where appreciable quantities of cuprite are present, therefore, this method gives a low figure for oxide copper.[22]

Weigh 0·5–2 gm. of −100 mesh sample into a 250 ml. Pyrex "copper" flask or Erlenmeyer, add 30 ml. of 5% by volume H_2SO_4 saturated with SO_2, cover, and let stand for one hour, swirling occasionally. Filter into a 400 ml. beaker and wash 6 times with hot water. The filtrate contains all the malachite, azurite, tenorite, chrysocolla, and half the cuprite. Sulphides and native copper are unattacked and remain on the precipitate. Boil off excess SO_2 from the filtrate, precipitate copper with 20% $Na_2S_2O_3$ solution, and proceed with the usual long iodide method.

If preferred, the short iodide method may be used by filtering into a 300 ml. Phillips flask, washing, boiling, adding 1 ml. HNO_3, and taking down to fumes. Add 1–2 ml. HNO_3, wash down sides and cover and boil to solution. Add a slight excess of NH_4OH, boil off excess, and make slightly acid with acetic acid. Add 1–3 gm. of sodium fluoride, boil, cool, and proceed with the usual KI-$Na_2S_2O_3$ titration. If manganese is present the precautions

mentioned on page 105 must be observed, or else the long iodide method used.

If large quantities of copper are in the oxide leach solution it is often preferable to determine copper electrolytically. After filtering and washing thoroughly with hot water, the filtrate is boiled to expel SO_2, 5 ml. HNO_3 are added, and the solution electrolysed on the rotating electrolytic apparatus in the usual manner.

The determination of chrysocolla in copper ores has been described by Young and Simpson.[24]

For information on special problems in the analysis of copper products the chemist is advised to contact the Copper Development Association, Grand Buildings, Trafalgar Square, London, W.C.2. The British Standards Institution in 1951 published as B.S. 1800 a useful booklet entitled "Methods for the Analysis of Raw Copper."

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CYANOGEN

OWING to the wide use of cyanides in mining and metallurgical operations for gold extraction, flotation of ores, heat treatment of metals, electroplating, etc., the determination of these compounds is often required in many inorganic laboratories.

Methods are given below for free cyanide, total cyanide, total cyanogen, and very small quantities of total cyanide in industrial waters.

Where sulphides are present in the solution used for the determination of cyanides, they must be removed with lead carbonate or barium nitrate, and cyanides determined on the filtered solution.

1. Free cyanide

Free cyanide is a term used to indicate the equivalent, in terms of KCN, of all the cyanogen present as simple cyanides of the alkalies and the alkaline earth metals, such as K, Na, NH_4, Ca, and Ba cyanides.[2] It does not include cyanogen present in the form of double cyanides.

Weigh out a sample or measure sufficient filtered solution so that the content of KCN or its equivalent is not more than 0·2 gm. Add a few drops of a 5% solution of potassium iodide. Titrate with standard $AgNO_3$ solution over a black background with constant stirring to the first appearance of a permanent yellow turbidity or opalescence.

1 ml. 0·1N. $AgNO_3 = 0{\cdot}01302$ gm. KCN

Where many determinations are made it is advisable to have a silver nitrate solution containing 6·524 gm. $AgNO_3$ per litre, in which case 1 ml. $AgNO_3 = 0{\cdot}005$ gm. KCN. To convert to

sodium cyanide multiply the KCN value by 0·753. For instance, a solution of 8·664 gm. $AgNO_3$ per litre will have a value of 1 ml. = 0·005 gm. NaCN.

The reactions are:

$$AgNO_3 + 2KCN \rightarrow KAg(CN)_2 + KNO_3$$
$$KAg(CN)_2 + AgNO_3 \rightarrow 2AgCN + KNO_3$$

The end point of the reaction can be determined by the formation of insoluble AgCN when the excess $AgNO_3$ reacts with the soluble $KAg(CN)_2$, but the addition of KI renders the end point sharper due to the great insolubility of AgI.

$$AgNO_3 + KI \rightarrow KNO_3 + AgI$$

Most commercial cyanides and cyanogen compounds are water-soluble. If the sample is an insoluble cyanide, place in a distilling flask, add 200 ml. 1:4 H_2SO_4, and distil about 150 ml. into a 4% NaOH solution in a receiver. Determine the cyanide in the distillate by standard methods.[3, 5, 7]

2. Total cyanide

Total cyanide is a term used to indicate, in terms of KCN, all of the cyanogen existing in the form of simple cyanides, HCN, and the double cyanides of zinc.

Measure out a suitable quantity of sample or cyanide solution and add 10 ml. of sodium hydroxide-potassium iodide solution. The latter consists of 4 gm. NaOH and 1 gm. KI per 100 ml. of water. Titrate as above for free cyanide with standard $AgNO_3$ solution.

3. Small quantities of cyanide (0–15 p.p.m.)

The determination of cyanide in industrial waters and similar materials, where the amount present is very low, is best done colorimetrically after separation by distillation. Guaiac paper, dipped into 0·25% $CuSO_4$ solution for one minute and then immersed in a cyanide solution gives a blue colour.

The range of this method is from zero to 15 p.p.m. of sodium or potassium cyanide. The cyanide content of concentrator waters cannot be determined directly because interfering compounds

such as xanthate and thiocyanate are present. By distillation, however, HCN can be separated and determined colorimetrically.

Measure 250 ml. of the filtered sample into a 500 ml. distilling flask and add 1 gm. cuprous chloride dissolved in 5 ml. HCl. Shake and add 50 ml. 4N. H_2SO_4. Connect the flask to a condenser set vertically and distil, receiving the distillate in a small bottle containing 25 ml. of 0·5% NaOH solution. A 20-minute distillation will usually suffice.

Dilute the distillate to 250 ml. and place 5 ml. of the well-mixed solution on a small watch-glass. Add a drop of B.D.H. universal indicator and then add 1:40 HCl to bring the *p*H to 7–7·5, a yellowish green colour. Dip a strip of the guaiac paper into 0·25% $CuSO_4$ solution for 1 minute and then immerse for 10 minutes in the solution to be tested.

Meanwhile treat similar strips of guaiac paper with $CuSO_4$ solution and place in standard solutions of NaCN or KCN of strengths covering the range being tested. Remove all papers after 10 minutes in cyanide and wash to stop further development of colour. Estimate the cyanide content of the unknown by comparing with colour of standards. Since the colours of the strips are not permanent, comparisons must be made promptly. It is necessary to do a blank distillation and colour test because NaOH frequently contains a trace of cyanide.

Reagents

Guaiac paper. Make a 4% alcoholic solution of powdered gum guaiac. Saturate a 15 cm. No. 42 Whatman filter paper with this solution, support on a glass rod and dry in a dark place. Cut into strips of uniform size, discarding the outer portions of the paper. Keep in a stoppered tube in a dark place.

Standard NaCN solution. Weigh 1 gm. of NaCN and make up to 1 litre. Measure out 100 ml. of this thoroughly-mixed solution and dilute to 1 litre, equivalent to 100 p.p.m. Measure 1, 2, 3, ml. of the latter solution and dilute to 100 ml. to obtain solutions of 1, 2, 3, parts per million. These latter standards must be made fresh every four hours, but the stronger solutions need not be renewed so frequently.

Other methods for determining small amounts of cyanide are described by Fasken.[4] In one, KCNS formed by treating HCN

or an alkali cyanide with $(NH_4)_2S_2$, after distillation of the cyanide, is measured by comparison against a series of standards by adding ferric chloride to the latter and to the unknown.

$$KCN + (NH_4)_2S_2 \rightarrow KCNS + (NH_4)_2S$$
$$3KCNS + FeCl_3 \rightarrow Fe(CNS)_3 + 3KCl$$

Yellow ammonium sulphide converts cyanide to thiocyanate in slightly alkaline solution. The thiocyanate reacts quantitatively with ferric ion to form coloured ferric thiocyanate. The cyanide concentration should be between 0·05 mg. and 2·0 mg. in 50 ml. of distillate or from 0·1 to 4·0 p.p.m. in the original water. Full details for this quantitative procedure are given in *Standard Methods for the Examination of Water and Sewage*.[1]

For concentrations of cyanide less than 0·1 p.p.m. the oxidation of phenolphthalin to phenolphthalein in presence of cyanide and a cupric salt, giving a red colour, is employed.

In these procedures sulphides should be removed before distilling, by the addition of lead acetate and filtering off the lead sulphide. If free halogens are present they should be removed by silver nitrate before the phenolphthalein test.

The same method is used in the detection of cyanides in underground waters in the gold mines of South Africa,[6] but the exact procedure and details of precautions necessary are not given in this reference.

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FLUORINE

THE DETERMINATION of fluorine is occasionally required in many industrial laboratories. Fluorine occurs in some minerals and ores, fertilizers, fluxes, wood preservatives, etc., and its accurate determination in the presence of interfering elements requires considerable experience and close attention to details of procedure. The role of uranium hexafluoride in atomic energy processes has led to further developments in the analysis of fluorine, which are reviewed in Rodden's book.[9]

Fluorine may be lost as gaseous SiF_4 or HF during decomposition with acids, and as insoluble CaF_2 when the solution is made ammoniacal for the separation of iron and aluminium. In the presence of fluorine, therefore, both SiO_2 and Ca may be lost unless special precautions are taken.

The determination of SiO_2 and fluorine when these occur in the same sample is carried out as follows. After fusion with sodium and potassium carbonates as detailed below, the mass is digested for an hour with 200 ml. hot water and washed thoroughly with the latter. The insoluble residue, consisting chiefly of $CaCO_3$, is discarded. To the filtrate are added about 10 gm. $(NH_4)_2CO_3$, the solution is boiled for 5 minutes and allowed to stand several hours. The precipitate of silicic acid is filtered off, washed with $(NH_4)_2CO_3$ solution, and retained for SiO_2. Since a small amount of silica passes into the filtrate it must be recovered and added to the main precipitate. This is done by evaporating the solution on the water bath almost to dryness, taking up in a little water, then neutralizing the ammonium carbonate with HCl, using phenolphthalein. Upon boiling, the pink colour is restored; the solution is then cooled and acid added to discharge the colour.

This is repeated until finally the addition of 1–2 ml. of 2N. HCl is sufficient to discharge the colour. About 5 ml. of an ammoniacal zinc oxide solution is added and the mixture boiled to the complete expulsion of ammonia. The precipitate of zinc silicate and zinc oxide is filtered and washed with water. This precipitate is added to the main silica portion, and SiO_2 determined in the usual manner by acid dehydration. The fluoride is determined in the filtrate by precipitation as CaF_2, PbFCl, or by the volumetric method.

Where calcium is required in a fluorine-containing material, it is necessary to eliminate the fluorine during the decomposition of the sample by repeated evaporation with acids, preferably with the addition of silica if the material does not contain the latter. Fluorspar analysis is discussed by several workers.[5, 11]

GENERAL PROCEDURES

1. Determination of fluorine gravimetrically

A. *As calcium fluoride.* Fuse 0·5–2 gm. of material with ten times its weight of sodium and potassium carbonates, and digest the mass for an hour with 200 ml. hot water. Break up all lumps and boil for 10 minutes. Filter and wash the residue of calcium carbonate as outlined in the preceding section, neutralize the solution containing the fluorine with HCl, and then just bring to the basic side with Na_2CO_3.

To the faintly basic solution add 1 ml. of 2N. Na_2CO_3 and sufficient $CaCl_2$ solution to precipitate completely the fluoride and the excess of carbonate. When no more precipitate forms, add 2–3 ml. $CaCl_2$ solution in excess. Allow the precipitate to settle, filter, and wash with hot water. Test the filtrate with additional $CaCl_2$ solution.

The combined precipitate of calcium fluoride and carbonate is dried and transferred to a platinum dish; the ash of the filter, burned separately, is added and the material ignited. After cooling, an excess of dilute acetic acid is added and the mixture evaporated to dryness on the water bath. The lime is converted to calcium acetate, while the fluoride remains unaffected. The residue is taken up with a little water, filtered, and washed with small portions of hot water, by which procedure calcium acetate is

removed while calcium fluoride remains on the filter. The residue is dried, separated from the filter, and ignited. This, together with the ash of the filter, is weighed as CaF_2.

$$CaF_2 \times 0{\cdot}4867 = F$$

To confirm the result, the residue is treated with a slight excess of H_2SO_4 and taken to fumes in a platinum dish. The adhering acid is removed as usual by heating with $(NH_4)_2CO_3$, and the ignited residue weighed as $CaSO_4$.

$$CaSO_4 \times 0{\cdot}5735 = CaF_2$$
$$\times 0{\cdot}2791 = F$$
$$Na_2CO_3 + CaF_2 \rightarrow CaCO_3 + 2NaF$$
$$(NH_4)_2CO_3 + SiO_2 + H_2O \rightarrow H_2SiO_3 + CO_2 + 2NH_3 + H_2O$$
$$2NaF + CaCl_2 \rightarrow CaF_2 + 2NaCl$$
$$CaO + 2HC_2H_3O_2 \rightarrow Ca(C_2H_3O_2)_2 + H_2O$$

B. *As lead chlorofluoride.* Workers in the Manhattan Project found no difference in accuracy between the calcium fluoride and lead chlorofluoride gravimetric procedures,[9] but the latter was more rapid and convenient for many routine determinations. The details of the lead chlorofluoride method may be found in several standard references.[6, 9] Fuse the sample with sodium carbonate, cool, dissolve in water, and filter. Boil the precipitate with 50 ml. of 2% Na_2CO_3, filter and add this filtrate to the previous one.

Add a solution of 1 gm. zinc oxide in 20 ml. of 10% HNO_3. Boil, filter, and wash well with hot water. Add three drops of methyl red to the filtrate, nearly neutralize with HNO_3, and evaporate to a volume of about 200 ml., keeping the solution alkaline throughout the evaporation. Cool, add dilute HNO_3 until a faint pink colour develops.

Add 1 gm. zinc oxide that has been dissolved in NH_4OH with the aid of a little ammonium carbonate, and boil until the odour of ammonia can no longer be detected. This usually requires concentration to about 50 ml. Dilute to 100 ml. with hot water, allow to settle, and filter. Wash the residue with cold water.

The filtrate is now free of substances which interfere in the lead chlorofluoride precipitation. Add a few drops of bromophenol blue indicator to the solution, 3 ml. of a 10% solution of sodium

chloride, and dilute to 250 ml. Add dilute HNO_3 until the colour changes to yellow and then add dilute NaOH until the colour just changes to blue. Add 2 ml. of 1:1 HCl, 5 gm. lead nitrate and heat on the steam bath. Stir until the lead nitrate has dissolved, and add 5 gm. sodium acetate. Stir, and allow to remain on the steam bath 30 minutes with occasional stirring. Allow to stand at room temperature overnight and filter through a weighed Gooch crucible. Wash the precipitate in the beaker and in the crucible once with cold water, 5 times with a saturated solution of lead chlorofluoride, and once with cold water. Dry the crucible and contents at 120° C. for one hour, cool, and weigh. $PbFCl \times 0{\cdot}0726 = F$.

If desired, the precipitate can be filtered on a Whatman No. 42 paper, dissolved in dilute HNO_3, and titrated for chlorine by Volhard's method. From the amount of chlorine found, the fluorine content of the sample can be determined.

Lead chlorofluoride wash solution. Dissolve 10 gm. lead nitrate in 200 ml. water and pour this solution into 100 ml. of a solution containing 1 gm. sodium fluoride and 2 ml. HCl. Mix thoroughly, let settle, decant the supernatant liquid, and wash the precipitate 5 times by decantation with 200 ml. portions of water. Add 1 litre of water to the precipitate, stir, allow to stand 1 hour, and filter. More wash solution can be prepared as needed by treating the precipitate with fresh portions of water.

$$Pb(NO_3)_2 + HCl + NaF \rightarrow PbFCl + NaNO_3 + HNO_3$$

2. Determination of F volumetrically with thorium nitrate

The reagents required for this determination are as follows:

1. Zirconium nitrate, 1 gm. $Zr(NO_3)_4.5H_2O$ in 250 ml. water.
2. Alizarin red, 1 gm. of sodium alizarin sulphonate in 100 ml. of ethyl alcohol. Filter off the undissolved residue and add 150 ml. of ethyl alcohol to the filtrate. The two solutions are kept in stock and mixed, three parts of solution (1) and two of solution (2) as needed.
3. Thorium nitrate solution, standardized against a known fluoride solution.
4. Standard fluoride, 0·02N. LiF, specially purified NaF, or AnalaR ammonium fluoride.
5. HCl, approximately 1:50.

Determination in soluble fluorides

(*a*) *Absence of interfering elements.* Any ion which forms a precipitate or a non-dissociated salt with fluorine or with thorium interferes with the titration.[4, 8] Consequently if Ba, Ca, Fe, Al, PO_4, etc., are present, the sample must be subjected to the treatment outlined under (*b*) below.

Dissolve a weighed quantity of the fluoride in water and make up to a given volume. Transfer an aliquot of the solution to be analysed to a small Berzelius beaker, add water to make a volume of approximately 20 ml., and 3 drops of the zirconium-alizarin mixture. If necessary, add just enough dilute HCl to destroy the colour. Add an equal volume of neutral ethyl alcohol and titrate over a white surface in a good light with the standard thorium nitrate to a faint permanent re-appearance of colour. The reaction is slow near the end point.

$$Th(NO_3)_4 + 4NaF \rightarrow ThF_4 + 4NaNO_3$$

When titrating with 0·01N. $Th(NO_3)_4$, make a correction for the fluorine which combines with the indicator. Determine this by titrating the number of drops of indicator used in the titration with 0·01N. fluorine solution to the disappearance of the colour.

If the volume of the solution to be titrated is sufficiently small, 4–8 ml., so that the colour can be distinguished, the accuracy of the titration is increased by using only one drop of indicator. If the volume is large it may be necessary to add more than 3 drops. For very accurate results it is necessary to standardize the $Th(NO_3)_4$ in approximately the same volume and with the same number of drops of indicator as the unknown, and titrate the two to the same colour. The end point is not sharp in the presence of a large amount of thorium fluoride; not more than 10 ml. of 0·1N. $Th(NO_3)_4$ should be used for the titration.

(*b*) *Presence of interfering elements.* When interfering elements such as Ca, Ba, Fe, Al, PO_4, etc., are present in the soluble fluoride solution, the fluorine must be separated from the other elements before the titrations can be made. This may be done by volatilizing it as hydrofluosilicic acid by adding perchloric acid, water, and several pieces of glass to the sample in a distillation flask, and distilling. When only a small quantity of fluorine, <10 mg., is present in the sample and the temperature is not allowed to rise

above approximately 125° C., the pieces of glass appear to supply the silica necessary to combine with the fluorine to form H_2SiF_6, and there is no noticeable etching of the flask. If there is more fluorine present or the temperature is allowed to rise higher, SiO_2 is taken from the flask, and etching is noticeable. In either case, however, the fluorine is recovered quantitatively.

Place the sample in a small distillation flask, add a few glass beads or pieces of porous plate, 5 ml. of 60% $HClO_4$, and sufficient water to cause the solution to boil at 110° C. or less. Place the flask on an asbestos mat with an opening large enough so that one-third of the flask is exposed to the heating element or burner. Close with a 2-hole rubber stopper through which passes a thermometer and a capillary tube, both of which extend down into the liquid. Connect a dropping funnel with the capillary tube so that water may be added during the process of distillation and fill this with water. Connect the flask with a water condenser. The distillate may be collected in an open container. Distil until the boiling point of the solution reaches 135° C. Titrate with $Th(NO_3)_4$ as directed in the previous section.

Determination in insoluble fluorides

Water-insoluble fluorides which are decomposed by $HClO_4$ may be analysed by the procedure outlined in (*b*), above. Fluorides which cannot be decomposed by $HClO_4$, such as opal glass, must be fused with Na_2CO_3, and the silica separated with $(NH_4)_2CO_3$ and ZnO, since the presence of large quantities of SiO_2 retards the volatilization of fluorine. The filtrate containing the fluoride either is determined volumetrically directly, or, if interfering elements are present, determined after the distillation procedure described above.[6, 10, 13]

Fuse 0·5–1 gm. sample with 2·5–5 gm. sodium carbonate, leach with hot water, filter, and wash. Transfer the insoluble residue back to the dish in which it was leached by means of a fine jet with about 50 ml. hot water, add sodium carbonate to make approximately a 2% solution, boil a few minutes, filter, and wash thoroughly with hot water. To the combined filtrates which should have a volume of 300 ml., add 0·5 gm. ZnO dissolved in $HClO_4$, boil the alkaline solution for 1 minute, filter, and wash with hot water. Concentrate the filtrate to 200 ml., add a drop of

methyl red, neutralize to a very faint pink with dilute $HClO_4$, add a solution of 0·25 gm. ZnO and 0·5 gm. of $(NH_4)_2CO_3$ dissolved in 0·5 ml. of NH_4OH and 10 ml. of water. Place on steam bath until a clear solution is obtained. Boil the solution until the odour of ammonia has entirely disappeared, concentrate to about 100 ml., filter, and wash with cold water. Concentrate the filtrate to 25 ml. and either transfer directly to the distillation flask for the determination of fluorine, or to a 50 ml. volumetric flask, make up to volume, and take an aliquot for the determination.

SPECIAL PROCEDURES

1. A procedure for the determination of sodium fluosilicate in timber preserving solutions is given by Young and Pinkney.[14] Decomposition of the solution with NaOH and NH_4OH to give insoluble zinc silicate and zinc hydroxide, which are filtered from the soluble sodium fluoride, is followed by addition of $CaCl_2$ to give CaF_2.

2. An analytical method for gaseous fluorine is given by Turnbull *et al.*[12]

3. The determination of fluorine in organic compounds is discussed by Elving and Ligett [3], and Kimball and Tufts.[7]

4. The determination of fluorine in foods and waters is presented in some detail by such authorities as the A.O.A.C.[2] and the Society of Public Analysts.[1] Since this procedure has been found in our experience to be very suitable for the determination of small quantities of fluorine in many inorganic products the modification used at Nchanga Consolidated Copper Mines is given here in detail.

Reagents

1. Zinc oxide, ammonia, ammonium carbonate. 2·5 gm. ZnO are weighed into a beaker and moistened with water. 5·0 ml. of NH_4OH are added and the mixture shaken thoroughly. 5 gm. $(NH_4)_2CO_3$ are added; if necessary heat to complete solution and make up to 100 ml. with water.
2. Silver sulphate. Use reagent grade silver sulphate.
3. Perchloric acid. Concentrated 70%.

4. Alizarin S solution. 0·01% in water.

5. Thorium nitrate. 0·25 gm. of the salt dissolved in water and made up to 1 litre.

6. Standard sodium fluoride. 0·221 gm. NaF dissolved in water and made up to 1 litre. 1 ml. = 0·1 mg. F.

Decomposition

Fuse 0·5 gm. sample with 2·5 gm. AnalaR sodium carbonate. Platinum crucibles used in this operation are carefully cleaned with hot dilute NaOH solution to ensure freedom from fluorine, derived from HF-silica volatilizations. A blank must be carried right through the analysis using similar quantities of all reagents employed in the determination.

Leach the fused mass with hot water, filter and wash. Transfer the insoluble residue to the dish in which it was leached by means of a fine jet of hot water, using about 50 ml. Add Na_2CO_3 to make approximately a 2% solution. Boil a few minutes, filter and wash thoroughly with hot water.

Adjust the combined filtrates to a volume of about 300 ml., add 0·5 gm. ZnO dissolved in dilute perchloric acid, boil the alkaline solution for one minute, filter, and wash with hot water.

Concentrate the filtrates to volumes of 200 ml. Add a drop of methyl red, neutralize to a very faint pink with dilute 1:10 perchloric acid and add 10 ml. of the zinc oxide ammonia reagent, equivalent to 0·25 gm. ZnO. Boil the solution until the odour of NH_3 has entirely disappeared. Continue boiling to concentrate the volume of the solution to 100 ml. Filter and wash with cold water. Concentrate the filtrate to 25 ml. until salts begin to precipitate.

Distillation apparatus

1. As illustrated in Fig. 8, a 3-litre distillation flask for steam generation is fitted with a tap funnel. Between the steam delivery tube and inlet to the 125 ml. distillation flask is a T-piece fitted with a short length of rubber tubing and a screw clip. This clip is adjusted during distillations to permit condensate to drip out, which would otherwise cause serious fluctuations of temperature in the 125 ml. distillation flask.

2. One or more sample distillation flasks of 125 ml. capacity are fitted with two-holed rubber stoppers each carrying a small-bore steam delivery tube reaching to the bottom of the flask, and a 0–200° C. thermometer also to the bottom of the flask. The graduation filler is removed from the thermometer using hot nitric acid-potassium chlorate mixture and a wire brush. During distillation it is difficult to read the thermometer, and a suitable mark is made on the neck of the flask opposite the 135° C. graduation of the thermometer. The distilling flask rests on an asbestos board which has a circular hole into which the bottom of

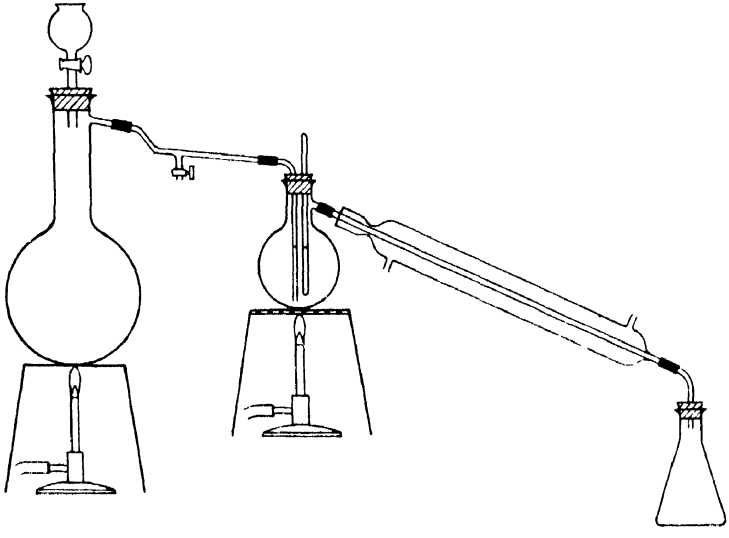


FIG. 8. Apparatus for determination of fluorine

the flask is fitted. It is important that the hole is snug-fitting and that the board is a little below the level of the liquid in the flask. This is to prevent local overheating with a consequent excessive acidity in the distillate.

3. A Liebig's condenser fitted to the delivery arm of the 125 ml. distillation flask.

4. A suitable flask to collect up to 400 ml. distillate.

5. Burners for heating distillation flasks and steam generators. One steam generator will conveniently serve two distillation assemblies.

Procedure

The fluorine content of the sample is distilled over as fluosilicic acid, H_2SiF_6, from a solution of perchloric acid which is maintained at 135° C. Perchloric acid should be handled with care as it may cause severe skin burns. Boiling concentrated perchloric acid will cause violent explosions if it comes into contact with carbonaceous material. However, with care in the distillation, provided the steam supply is maintained and provided the temperature is not permitted to rise above 135° C., there is no danger of an explosion, and rubber stoppers can be used since $HClO_4$ boils at 200° C.

Add a few fragments of crushed Pyrex glass and two or three crystals of silver sulphate to the distillation flask. Enough silver sulphate should be introduced to precipitate all the chloride in the portion of sample being treated. Transfer the sample to the flask using a long-stemmed funnel and a minimum quantity of water. If the volume is now more than 30 ml., concentrate the alkaline solution by boiling in the distillation flask. When the volume is low enough, remove the flame and cool.

Boil the water in the steam generator, which should first have been made alkaline with a pellet of sodium hydroxide. Add 15 ml. perchloric acid to the sample, close the distillation flask, connect up the steam delivery tube to the steam generator, leaving the generator in the meantime open to the atmosphere. Place a flame under the distillation flask and raise the temperature to 130° C. Should the contents of the flask bump before the temperature of 130° is reached, close the top of the steam generator and pass a gentle current of steam through the flask. At 130° C. increase the steam flow and continue heating, bringing the temperature of the flask to 135° C., and maintain at this temperature ± 1° C. by adjusting the burner. Continue distilling until 250–400 ml. distillate has been collected. The blank is distilled exactly as are the samples.

Titration

Thoroughly mix the distillate and measure the volume. Titrate 100 ml. in a Nessler tube with 0·05N. NaOH using methyl orange as indicator until the colour matches that of a similar tube containing distilled water and the same amount of methyl orange.

Take another 100 ml. distillate in a Nessler tube and add sufficient 0·05N. HCl to make the total acidity equal to 5·0 ml. of 0·05N. HCl. This figure is calculated from the previous titration.

Prepare a "control" cylinder containing 100 ml. of distilled water and 5·0 ml. 0·05N. HCl. Add to both test and control cylinders 2 ml. of alizarin S solution.

From a 10 ml. burette add sufficient thorium nitrate solution to the test cylinder to give a slight pink colour compared to the yellow of the control cylinder. Add an exactly similar quantity of thorium nitrate to the control cylinder, which then becomes more pink than the test solution. From a burette add standard sodium fluoride solution to the control cylinder until the tints of test and control cylinders are matched exactly. The volume of standard fluoride solution added corresponds to the amount present in 100 ml. of distillate. Calculate the fluorine content of the whole distillate, subtract the blank and report result as a percentage of the sample.

Determination of fluorine in water

Special reagent: Lime, free of fluorine

Prepare an ammonium carbonate reagent by dissolving 110 gm. of ammonium carbonate and 55 ml. of ammonia in water and diluting to 600 ml. Dissolve 200 gm. of dry calcium chloride in about 600 ml. of warm distilled water. Stir into this solution 20 ml. of the ammonium carbonate reagent, bring the mixture just to boiling point, allow the precipitate to settle for a few minutes and then filter on a Buchner funnel with suction and reject the precipitate. Repeat the precipitation and filtration three times with 20 ml. portions of the ammonium carbonate reagent. Finally treat the clear filtrate from the last precipitation with the remainder of the ammonium carbonate reagent, stir the mixture well and bring it to the boiling point. Allow the precipitate to settle, filter, wash several times with hot water until free from chloride and dry at 100° C. Ignite to oxide in a platinum dish in small quantities of 1–2 gm. as required.

Procedure. To a platinum dish add 1 gm. of fluorine-free lime and 100 ml. of the water under examination. Evaporate to dryness on a water bath and ignite at dull red heat.

The ash is transferred to a 125 ml. distilling flask with about 5 ml. water and rinsed in with 15 ml. perchloric acid. Pyrex glass fragments and Ag_2SO_4 having been added to the flask, the distillation is completed exactly as in the determination of fluorine in ores given above. Calculate fluorine as parts per million.

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GOLD

GOLD is usually determined in metallurgical laboratories by fire assay methods. Occasionally, however, it may be necessary to analyse high-grade materials such as jewellery or refinery products by wet methods. Gold is frequently associated with silver and occasionally with the platinum metals, and its determination may be encountered in ores, concentrates, blister copper, lead bullion, electrolytic refinery slimes, solutions, etc.

GENERAL PROCEDURES

1. Determination of gold by wet method

This procedure is suitable for appreciable quantities of gold, whereas the small amounts occurring in ores, etc., are best determined by fire assay methods. The principle of the wet method is the reduction of a gold chloride solution to metallic gold with SO_2 and oxalic acid. Only Se, Te, Pb, and the alkaline earths must be removed.[4, 6, 7]

Dissolve the sample, containing not more than 1 gm. of gold, in 10 ml. HNO_3, 20 ml. HCl, and a few drops of HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, dilute with water, boil, and filter off SiO_2, $PbSO_4$, $BaSO_4$, etc. If calcium or large quantities of other elements of Groups 3 and 4 are present, gold may be separated at this point by precipitation in 5% H_2SO_4 or HCl with H_2S. Selenium and tellurium if present will accompany the gold but they may be removed later.

Silver, if present, can be separated at this stage, in dilute hydrochloric acid solution, and weighed as AgCl. To each 100 ml. of

5% HCl solution containing not over 0·5 gm. of gold add 25 ml. of a saturated SO_2 solution, and digest on the steam bath for 1 hour. Add 10 ml. more of the SO_2 solution and set aside to cool for another hour. Pour the supernatant liquid through a Whatman No. 40 filter paper, using pulp, and wash the precipitate well by decantation with hot 1% HCl. Examine the filtrate carefully for particles of gold which may have passed through the paper.

Small amounts of the platinum metals, if present, co-precipitate with gold, and a re-precipitation is therefore necessary. Return the filter to the beaker and dissolve the gold in aqua regia, using 8 ml. HCl, 2 ml. HNO_3, and 10 ml. of water for each 0·5 gm. or less of gold. If selenium or tellurium are present, this is a convenient place to remove them by solution in dilute HNO_3 and filtration from the gold before the re-solution of the latter in *aqua regia*.

Filter the *aqua regia* solution from the paper pulp, washing the latter very thoroughly with hot 1% HCl. Evaporate the filtrate to dryness on the steam bath, add 2–3 ml. HCl, evaporate to dryness again, and repeat this operation several times to eliminate all HNO_3. Take up the residue with 3 ml. HCl, 5 drops H_2SO_4, and 75 ml. water for each 0·5 gm. or less of gold. A little metallic gold may have separated but its presence can be disregarded.

For each 75 ml. of this solution add 25 ml. of a saturated solution of oxalic acid and boil for 10 minutes. Test for completeness of precipitation by adding another 5 ml. of oxalic acid solution and boiling for another 5 minutes. Allow the solution to digest on the steam bath for 4 hours. Filter off the gold through a Whatman No. 42 paper, wipe out the inside of the beaker with pieces of filter paper, and make sure all the metal is transferred from the beaker. Ignite cautiously in a tared porcelain crucible and weigh as metallic gold.

It is sometimes useful to remember that gold can be removed from Pt and Pd, as well as from most other metals, by extracting with ether in 5% HCl.

2. Determination of gold by fire assay

Gold in ores, concentrates, blister copper, etc., is usually determined by fire assay, frequently by a combination of wet and dry procedures.[1, 2, 8, 9, 10]

A. *Blister copper, refinery slimes and residues, etc.* Weigh out 1–3 assay tons, depending on the gold content, into 2-litre beakers. Add 20 ml. mercuric nitrate or sulphate solution containing 25 gm. mercury per litre, i.e. approximately 43 gm./litre $Hg(NO_3)_2.H_2O$ or 37 gm. $HgSO_4$, and let stand one hour. The purpose of this is to hasten the solution of the copper by forming a galvanic couple. Add 75 ml. water and 100–150 ml. H_2SO_4. Take down to fumes on the hot plate.

Cool, take up in water, and wash sides and cover of beaker. Bring to boil and add 20 ml. salt solution containing 50 gm. NaCl per litre. Boil for 5 minutes, fill beaker to 1 litre with water, and allow to settle overnight. Add a few more ml. of NaCl to test for completeness of precipitation of silver.

Filter through Whatman No. 40 paper, using paper pulp, and wash with hot water. Clean out beaker well with paper and transfer paper and residue to folded lead foil in a 3-inch scorifier. Burn the paper off carefully in front of the muffle. Add 30 gm. test lead, 1 gm. borax, 0·5 gm. SiO_2, and scorify to half-inch ring, leaving a lead button of about 25 gm.

Pour, clean, hammer, and place in a No. 8 cupel. Cupel at approximately 850–900° C., clean the bead well, flatten out, anneal, and weigh on the assay balance. When silver is determined in this manner it is important to keep the cupellation temperature as low as possible to avoid losses. Fire assayers accustomed to straight gold ores nearly always obtain low results on silver in a mixed gold-silver product, due to cupellation losses. Part the gold-silver bead in a porcelain cup, first with 1:6 HNO_3 and then with 1:1 HNO_3. Wash three times by decantation with hot water, dry, and anneal. Weigh the gold bead. The difference in weights represents the silver.

For complex materials containing large quantities of acid-insoluble metallic compounds it may be necessary to transfer the precipitate of Au, Ag, etc., to a large porcelain crucible, burn off most of the paper at a low heat, mix with fluxes in a large mortar, and transfer to fusion pots. Fuse and pour, transfer the lead button to scorifiers and scorify before cupelling.

In the presence of platinum metals it is advisable to dissolve the gold bead in *aqua regia*, 4 HCl:1 HNO_3, in a covered cup in a warm place. Filter into 100 ml. beaker through a 9 cm. Whatman

No. 40 paper, wash, evaporate carefully to a syrup. Add dilute HCl and evaporate again, repeating this operation twice. Transfer the solution to double lead boats in a 3-inch scorifier and evaporate to dryness at low heat.

Add test lead until the total amount of lead is about 40 gm. Add a sufficient quantity of silver so that there is at least 12 times as much silver as gold + platinum. Scorify to $\frac{1}{2}$ in. rings. Pour and clean the buttons. Cupel on No. 5 Mabor, clean, and part as before, using 1:6 and then 1:1 HNO_3. Wash and transfer the gold to porcelain cups, dry, anneal, and weigh.

B. *Ores, concentrates, etc.* Weigh out 1–10 assay tons of −100 mesh material, depending on the gold content. For very low grade ores where it is necessary to use more than 2 assay tons, a number of separate fusions are made and the lead buttons afterwards combined.

If the sulphur content of the material exceeds 2 per cent. the sample must be roasted. Place the material in a flat fireclay roasting dish and calcine in an open muffle or furnace. When cold, pulverize the calcine in a porcelain mortar, and transfer to the fusion pot or to a 2-litre beaker, depending upon whether a direct fusion or a preliminary acid treatment is to be carried out.

For some concentrates and other materials rich in base metals it is often preferable to separate as much of the latter as possible by acid treatment after roasting. Transfer the calcine to a 2-litre beaker, add 100 ml. water and 100 ml. H_2SO_4. Take to strong fumes, cool, dilute to a litre, boil till all soluble salts are dissolved, cool. Add about 10 ml. of a 50 gm./litre NaCl solution and stir. Add about 50 ml. of a 10 gm./litre lead nitrate solution, stir, and dilute with cold water to about 1800 ml.

Allow to settle overnight and filter through Whatman No. 40 paper, using paper pulp. Wash out the beaker thoroughly, wipe the inside with another filter paper and add this to the precipitate. Transfer the filter paper and contents to a No. 2 assay crucible, combining the contents of several beakers if these have been necessary in the preliminary solution of the sample.

Dry the crucible on a hot plate and burn off the paper at a low temperature in the assay furnace. Remove from the furnace, allow to cool, and mix in the crucible with a suitable flux, depending on the character of the ore, to obtain a lead button of 50–60 gm.

If a direct fusion is employed, of course, the ore is mixed, after calcining if necessary, with flux and melted at once in the assay furnace. Better mixing of the precipitate and flux may be effected by transferring the former to a large porcelain crucible, burning off most of the filter paper at a very low heat, and transferring to a large mortar. Addition of the flux to the mortar, and thorough grinding with a pestle, followed by a rinse with a little dry litharge alone, will give a homogeneous sample to be transferred to the fusion crucible.

When a quiet fusion has been obtained pour into a cast iron mould and allow to cool. Hammer the lead button free of slag. If base metals such as Cu, Ni, Co, Sb are present in the lead button, scorify until these go into the slag and the lead button weighs about 20 gm.

Place the lead cube in a cupel, and cupel at approximately 850–900° C. Remove the cupel from the muffle immediately the operation is complete, and cover with an inverted red-hot cupel. When cool, remove the gold-silver bead from the cupel with forceps. Flatten the bead on the anvil carefully to remove any adhering cupel material, and weigh on the assay balance.

Remove the silver by parting the bead in a small porcelain cup, first with 1:6 HNO_3 and then with 1:1 HNO_3. Wash three times by decantation with hot water, dry, anneal. Weigh the gold bead on the assay balance. The difference in weights represents silver.

If there is not more than three times as much silver as gold in the bead it will not part readily. In this case inquartation must be practised. The gold-silver button after weighing is wrapped with about 10 times its weight of pure silver foil in 4 gm. of sheet lead and then cupelled. The resulting button is flattened and parted, and gold is weighed in the usual way. It is preferable to add the silver before the original cupelling, since inquarted gold tends to be low.

SPECIAL PROCEDURES

1. Gold in a cyanide solution can be determined by the following procedure outlined by Detweiler.[3]

This is an adaptation of Cassel's method and has been used

successfully in the Denver Equipment Laboratory for small quantities of gold in cyanide solutions. It requires only a small amount of equipment and a fair estimation of the gold in the solution can be made in fifteen or twenty minutes.

The amount of solution used depends on the gold content. Twenty-five ml. is a convenient amount, but it should contain at least 0·02 oz. gold per ton. Larger amounts of low grade solutions can be evaporated to a small volume. If lime precipitates on evaporation, add 0·5 gm. of cyanide and filter, wash the paper with a small amount of water and make the volume of the filtrate up to 25 ml.

To the 25 ml. portion add 0·5 gm. of sodium bromate. After the salt has dissolved, add sulphuric acid, a little at a time, shaking between each addition, until the solution is brown and reddish-brown fumes are evolved. Shake until the reaction is complete and add 2 or 3 ml. of acid to make sure. This operation should be carried on in a hood or well-ventilated place since the bromine as well as cyanic acid evolved are very toxic. The solution should be straw coloured at this point.

Add saturated stannous chloride solution a drop at a time with vigorous shaking until the solution and the atmosphere in the flask are colourless. Dilute to exactly 50 ml., and transfer to a 4 oz. square flint glass bottle. A faint pink tint indicates 0·01 - 0·02 oz. gold per ton of solution if a 25 ml. sample was taken; a deeper colour indicates more.

Estimation of the amount of gold is made by comparing the colour with that developed from a solution of known gold content which has been carried through the same process. A convenient method is to use a standard solution of higher gold content, and match the colour by dilution. As an example, assume that the unknown contains approximately 0·02 oz. gold per ton. Use 10 ml. of a standard which contains 0·10 oz. per ton. Dilution to 60 ml. is required to match the unknown. Then the assay is 1/6 of 0·10 or 0·016 oz. per ton. Charts of various dilutions can be made to simplify calculations.

2. Another procedure for gold in cyanide solutions has been described by Schellinger.[5] Heat from 5 to 17 assay tons of solution in a large beaker until nearly boiling. Add 8 gm. granulated test lead, sprinkled evenly over bottom of beaker. Acidify with

10 ml. HCl and boil for 15 minutes. Cool and filter through Whatman No. 4 paper. Wash, return paper to beaker and dry quickly on hot plate. Transfer paper to lead foil together with any lead particles in the beaker. Cupel in the usual way.

3. A useful extractive titrimetric procedure for gold, employing dithizone, has been described for the beads obtained in the assay of precious metals.[11]

In some countries results of gold analyses are expressed in pennyweights (dwt.). One ounce troy = 20 dwt.; 1 dwt. = 0·05 oz.

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IRON

IRON is one of the commonest elements determined in analytical laboratories. It is almost invariably present in base metal ores and hence is found in nearly all metallurgical products. Methods for its determination are well standardized and usually few interfering elements are present to require involved purification.

Iron is nearly always separated with NH_4OH, after prior removal of Group 2 elements with H_2S in acid solution. In this way, iron, together with Al, Ti, Cr, Th, Be, Nb, Ta, V, U, Zr, In, Ga, Tl, Ce, etc., is separated from all other elements. In many cases the only contaminant present in more than traces is aluminium and since it does not interfere in the volumetric determination, iron may be determined directly by dissolving the $Fe(OH)_3$ precipitate in acid, reducing, and titrating with an oxidizing reagent.[2, 5]

In industrial work, iron is usually determined volumetrically by titration with $KMnO_4$ or $K_2Cr_2O_7$. The latter is less subject to interference from small amounts of contaminants, the end point is more readily detectable, and the solution is very stable, hence it is preferred for most work. Either diphenylamine or barium diphenylamine sulphonate may be used as internal indicator.

It must be kept in mind that many substances are occluded in a ferric hydroxide precipitate. In fact the best way of collecting small quantities of As, Sb, Bi, Se, Te, etc. is by means of a ferric hydroxide precipitation. When separating iron from Cu, Ni, Co, and other elements soluble in excess NH_4OH, it is necessary to dissolve the first precipitate of ferric hydroxide in acid and re-

precipitate with NH_4OH to free the iron from the occluded complex ammonia compounds. Cobalt in particular is tenaciously held by $Fe(OH)_3$ and even after repeated precipitations minute traces of cobalt are still retained by the iron. A large excess of NH_4OH minimizes the retention of cobalt and nickel in ferric hydroxide. It may even be necessary with a very heavy iron precipitate to re-precipitate a third time in order to wash out the soluble, but occluded, copper, cobalt, and nickel ammonia complex compounds. The presence of sufficient ammonium salt, such as NH_4Cl, is necessary to ensure precipitation of iron free from Zn, Mn, Ca, Mg.

If it is desired to separate iron from other elements precipitated by NH_4OH or $(NH_4)_2S$ there are several alternatives. On treatment with Na_2O_2 iron is precipitated with Ni, Co, and Mn free of V, Al, P, Cr, U. Electrolysis at a mercury cathode deposits iron, together with Cr, Zn, Ni, Co, while Al, Ti, Zr, P, V, U remain in solution. Cupferron precipitates iron, together with Ti, V, Zr, from solutions containing Al, Be, P, Mn, Cr, Ni, Co, Zn. Precipitation of iron as sulphide in a solution containing ammonium tartrate and ammonium sulphide, together with sulphides of Co, Ni, Zn, separates iron from Al, P, Ti, U, V, Zr. Iron is separated from uranium by $(NH_4)_2CO_3$, uranium remaining soluble in the solution as long as CO_2 is present.

An ether separation will remove iron, together with Ga, Ge, Au, Mo, Tl, and small amounts of Te, As, Sb, Sn, P, Ir, from elements in the iron group as Al, Cr, Co, Ni, Zn, Mn, P, Ti, U, V, Zr.[1] Details of the ether separation are given in the chapter on Cobalt. Though usually employed to remove large quantities of iron when determining other constituents of a sample, an ether separation is sometimes useful for isolating iron prior to its determination. Recently, Wells and Hunter[6] have proposed amyl acetate as a substitute for ether to remove iron in metallurgical analyses. For the separation of Al, Mn, Cu, Ti, Co, Ni, Cr, Ca, and Mg, amyl acetate appears to be nearly as efficient as ether. The boiling point of amyl acetate is higher than that of water, and consequently great care must be exercised when evaporating a sample of these immiscible liquids. It is preferable to separate them and evaporate separately, later combining if necessary.

GENERAL PROCEDURE

Weigh 0·5–2 gm. sample into a 250 ml. beaker, add 10 ml. HNO_3, 10 ml. HCl, and boil. If the material is a slag or similar refractory product add a few drops of HF to decompose the silicates. If the sample is a high sulphide ore or concentrate, add initially the usual few millilitres of bromine, allow to stand a few minutes and add HNO_3, again allowing to stand, before adding HCl. This avoids the formation of a large bead of sulphur, which might occlude particles of undecomposed material. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Take up in hot water, boil, filter off SiO_2 and $PbSO_4$, and wash thoroughly with hot water.

For many substances it may be desirable to fuse directly with Na_2CO_3 or $KHSO_4$, in place of an acid treatment. In many metallurgical industries it is customary to do iron and silica on the same sample. Since the sample usually contains metallic sulphides it is first treated with HNO_3, HCl, and H_2SO_4, evaporated to dryness, taken up in water and HCl, filtered, and the insoluble residue fused in a platinum crucible with five times its weight of Na_2CO_3. The fusion is added to the original filtrate and the solution taken to dryness twice and dehydrated with HCl in the usual manner. The SiO_2 is filtered off, washed, and iron determined in the filtrate by the usual hydroxide precipitation and titration.

It is sometimes useful to remember that iron and sulphur may be determined on the same sample by decomposing as usual for sulphur and determining this as $BaSO_4$, then carrying out an iron on the filtrate. The presence of excess $BaCl_2$ has no effect when the dichromate titration for iron is used.

The HCl or H_2SO_4 solution, obtained by complete decomposition of the material with acids, by fusion, or by a combination of these, is now adjusted to an acidity of 5–10% HCl or H_2SO_4 and Group 2 metals are removed with H_2S. After filtering off the sulphides of Cu, As, Bi, Sb, etc., and washing thoroughly with acidulated H_2S water, the filtrate is boiled for 15 minutes to remove all H_2S, and sufficient H_2O_2 is added to oxidize all iron to the ferric state. Boiling is continued a few minutes to remove the excess of H_2O_2.

The solution is removed from the hot plate, cooled slightly, and NH_4OH cautiously added until all iron is precipitated. If HCl was not initially present, a little NH_4Cl should be added to keep zinc in solution. The beaker is placed on the hot plate and boiled for several minutes to render the ferric hydroxide more readily filterable. With a heavy precipitate of ferric hydroxide great care must be taken in the initial stages of heating to avoid bumping. Frequent or even continuous stirring is sometimes necessary until boiling commences, when no further bumping occurs. The solution is filtered hot through No. 531 or 541 Whatman paper and washed thoroughly with hot water.

If the filtrate is to be used for the determination of Ca, or Mg, and aluminium is present with the iron, care must be taken not to have a large excess of NH_4OH during the precipitation of iron and aluminium. Appreciable solution of $Al(OH)_3$ may then occur and this will contaminate Ca, Mg, etc. Ferric hydroxide is not soluble in excess NH_4OH, and in fact an excess is desirable to minimize co-precipitation of Ni, Co, etc., as well as copper where that element is not removed beforehand by H_2S precipitation.

It is nearly always necessary to remove occluded impurities from the ferric hydroxide precipitate by a second precipitation. The precipitate is transferred by washing to the original beaker, sufficient HCl is added to dissolve the $Fe(OH)_3$, and the iron is again precipitated with NH_4OH. The sample is boiled, filtered, washed thoroughly with hot water, and the precipitate transferred to the original beaker by washing repeatedly with hot dilute HCl and finally with hot water. The sample is boiled, additional HCl being added if necessary to dissolve all $Fe(OH)_3$, and particular care taken that all of the latter on the walls of the beaker is washed down with HCl and hot water.

From this point on one has the choice of two volumetric procedures, both depending on the reduction of iron by means of stannous chloride or a metal such as Pb, Zn, or Al, and subsequent oxidation by titration with a standard solution of an oxidant. When all the ferrous iron has been oxidized to the ferric a sharp colour change occurs, marking the end point of the reaction. Using $KMnO_4$, this solution acts as its own indicator, a slight excess over that required for complete oxidation imparting a pink colour to the solution which persists for 30 seconds. When

$K_2Cr_2O_7$ is employed, the indicator diphenylamine or barium diphenylamine sulphonate added to the solution gives an intense violet-blue colour when all the ferrous iron has been oxidized to ferric. Diphenylamine indicator is used as a 1% solution in H_2SO_4. Barium diphenylamine sulphonate is prepared by dissolving 0·32 gm. in 100 ml. of water containing 1 ml. H_2SO_4. Allow the barium sulphate to settle and decant the solution.

1. Titration of iron with $K_2Cr_2O_7$

When the precipitate of $Fe(OH)_3$ has been dissolved in HCl or H_2SO_4, preferably the former, it is heated nearly to boiling and a solution of stannous chloride carefully added from a burette with constant stirring until the yellow colour of $FeCl_3$ just disappears. The solution is now cooled in running water, and 10 ml. saturated mercuric chloride solution added rapidly. Fifteen ml. of a sulphuric-phosphoric acid mixture containing 150 ml. H_2SO_4 + 150 ml. H_3PO_4 in 1 litre, are now added, 3 drops of diphenylamine, and the solution titrated with standard $K_2Cr_2O_7$ until the green colour of the chromic salt changes to a violet-blue, due to the action of ferric salt on diphenylamine. Nitric acid must be absent for this titration.

With some samples it is preferable to add a final drop of the diphenylamine indicator when the green colour of the solution is fading to the final blue. This results in a very sharp end point.

1 ml. 0·1N. $K_2Cr_2O_7 = 0{\cdot}005585$ gm. Fe

$$1\text{N. } K_2Cr_2O_7 = \frac{K_2Cr_2O_7}{6}$$

0·1N. $K_2Cr_2O_7 = 4{\cdot}9035$ gm. per litre of $K_2Cr_2O_7$.

In industrial work, 4·3908 gm. $K_2Cr_2O_7$ per litre gives a solution having a value of 1 ml. = 0·005 gm. Fe. It may be advisable for low irons to have another standard of 1 ml. = 0·0025 gm. Fe.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$SnCl_2 + 2HgCl_2 \rightarrow 2HgCl + SnCl_4$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightarrow 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O$$

Though it is not necessary to standardize known $K_2Cr_2O_7$ solutions against standard irons, unknown dichromate solutions

and potassium permanganate standards may be checked most conveniently against ferrous ammonium sulphate. This salt is obtainable in a pure state and its high molecular weight gives a favourable iron factor. A weight of 1·0000 gm. $FeSO_4(NH_4)_2SO_4.6H_2O$ is equivalent to 0·1424 gm. Fe, or approximately 25 ml. of 0·1N. $K_2Cr_2O_7$ or $KMnO_4$. The ferrous ammonium sulphate should be carried through all steps of the iron determination.

In the above titration it is preferable to keep the volume of the solution low, not over 100 ml. If more than a drop or two excess stannous chloride has been added a few drops of $KMnO_4$ should be added to restore the yellow colour, and then the latter carefully discharged again with stannous chloride. If more than a drop or two excess stannous chloride is present, on the addition of mercuric chloride, especially if the solution is warm, there is a tendency for the production of a dark grey precipitate of metallic mercury which vitiates results. If the end point with the dichromate titration has been overstepped, a back titration may be made with standard ferrous ammonium sulphate. The phosphoric-sulphuric acid mixture prevents the yellow colour of ferric iron from producing a green at the blue end point. Phosphoric acid is added to lower the oxidation potential of the ferric-ferrous system below the value ordinarily attained in either H_2SO_4 or HCl solutions.

This is the most satisfactory routine method for iron. Scarcely any elements interfere, the only one of the iron group whose prior removal is necessary being vanadium if the latter occurs in quantities exceeding 10% of the iron.

Where appreciable quantities of vanadium are present the best method of separating iron is by treatment with NaOH and filtering, all the iron remaining on the precipitate. If the amount of vanadium is high, a re-precipitation should be carried out to free the iron precipitate of occluded vanadium.

The end point of the $K_2Cr_2O_7$ titration is sharp and stable, and small quantities of contaminants do not interfere, as for instance cobalt does when using $KMnO_4$. Uranium is not reduced by stannous chloride and small quantities do not interfere in the $K_2Cr_2O_7$ determination of iron. Larger amounts mask the end point of reduction and must be removed by $(NH_4)_2CO_3$. Organic

substances do not interfere. The standard $K_2Cr_2O_7$ solution may be made up by weighing out the salt directly and it is very stable, scarcely any change occurring when it is checked at intervals over many years.

The stannous chloride reduction is rapid and very satisfactory, and is recommended for most purposes. Stannous chloride solution may be made by dissolving 80 gm. $SnCl_2.2H_2O$ in 180 ml. HCl on a hot plate and then diluting with 300 ml. water. Place a stick of tin in the bottle to keep the $SnCl_2$ in the reduced state. A weaker $SnCl_2$ solution for the dichromate procedure is given sometimes in texts, as 60 gm. $SnCl_2$ in 600 ml. HCl and 400 ml. water. There is no need for haste when cooling ferrous solutions and titrating, after reduction with stannous chloride, since these are very stable in the air.

Occasionally, it may be preferable for certain products to reduce the iron by means of test lead in 10% HCl solution, or zinc or aluminium in 10% H_2SO_4. In these cases copper is precipitated in the metallic form and removed with the Pb, Zn, or Al. In the absence of other interfering elements, it is possible on some copper products then to boil the 10% H_2SO_4 solution of the sample, which has been taken to fumes of SO_3, with aluminium until colourless, filter off copper, and titrate the reduced iron in the filtrate with $K_2Cr_2O_7$ or $KMnO_4$. Reduction by test lead is preferably carried out in HCl solution, in which case $K_2Cr_2O_7$ is the better titrating solution.

2. Titration of iron with $KMnO_4$

The titration of iron with $KMnO_4$ is most satisfactorily performed in 5% H_2SO_4, but by the addition of a solution known as the Zimmermann-Reinhardt solution it is possible to titrate with $KMnO_4$ in HCl. Since this is often more convenient in industrial laboratories than working with H_2SO_4, or displacing HCl by evaporation with H_2SO_4, it is widely used.

Reduce the iron in HCl solution by stannous chloride, cool, add 10 ml. mercuric chloride, 25 ml. of the Zimmermann-Reinhardt solution, and titrate with $KMnO_4$ to a definite pink tint. The Zimmermann-Reinhardt solution is made by dissolving 200 gm. of $MnSO_4.4H_2O$ in 1 litre of water and adding a cooled mixture of 400 ml. of H_2SO_4, 1200 ml. of water, and 400 ml. of H_3PO_4.

$$5FeCl_2 + KMnO_4 + 8HCl \rightarrow 5FeCl_3 + KCl + MnCl_2 + 4H_2O$$

1 ml. 0·1N. $KMnO_4 = 0{\cdot}005585$ gm. Fe.

$$\text{N } KMnO_4 = \frac{KMnO_4}{5} \qquad 0{\cdot}1\text{N. } KMnO_4 = 3{\cdot}16 \text{ gm./litre.}$$

Since the strength of standard $KMnO_4$ changes and frequent checking is necessary, the solution is seldom made up to an exact titre. If desired, however, 2·83 gm. made up to 1 litre gives a theoretical value of 1 ml. = 0·005 gm. Fe.

As indicated previously, in some industrial products it may be preferable to remove copper and reduce iron simultaneously in 10% H_2SO_4 solution by pieces of sheet aluminium, filter, and titrate the reduced iron directly with $KMnO_4$.

SPECIAL PROCEDURES

1. Determination of ferric and ferrous iron

It is occasionally necessary to determine the form in which iron occurs in materials, and several methods are available for this purpose. If the sample requires a long and involved decomposition and separation procedure, the results are usually only approximate since the original form of the iron may change during the analysis.

A. *Stannous chloride titration of ferric iron.* To the sample in a casserole is added 25 ml. of HCl and an equal volume of water. The solution is quickly heated to boiling and titrated with a standard $SnCl_2$ solution until the colour changes from yellow to colourless.

A solution made by dissolving 2 gm. of stannous chloride crystals in hot concentrated HCl and then diluting to 1 litre has a value of approximately 1 ml. = 0·001 gm. Fe. This solution is standardized against a known standard solution of ferric ammonium alum, 8·6322 gm. of which dissolved in dilute HCl and made up to 1 litre gives a value of approximately 1 ml. = 0·001 gm. Fe. The stannous chloride solution should be kept in a dark bottle to which the titrating burette is attached in such a way that the solution is siphoned out, the air entering the bottle passing through phosphorus or pyrogallic acid to remove oxygen.

Since this gives a measure of ferric iron, oxidizing agents must have been absent in the initial attack of the sample, and exposure to air must be kept at a minimum, to avoid oxidation of ferrous iron. Likewise reducing conditions must be avoided prior to the addition of $SnCl_2$.

B. *Titanous salt titration of ferric iron.* The iron solution, which may contain HCl, H_2SO_4, or HF if boric acid be present in excess, but not HNO_3, is titrated in the cold with a standard solution of titanous sulphate or chloride. Potassium thiocyanate is used as indicator, the end point being the disappearance of the red colour of ferric thiocyanate.

The 0·1N. titanous sulphate solution may be prepared by mixing 100 ml. of a 20% solution with 80 ml. of 1:1 H_2SO_4 and making the volume up to 1 litre with cold water. The standard solution must be kept out of direct sunlight and be carefully protected from the air, since it is easily oxidized. This is best done by an arrangement such as shown in Fig. 9, *A* being a Kipp generator containing marble and HCl for the production of CO_2, *S* being the storage bottle of titanous sulphate or chloride, and *B* the titrating burette. Fill the bottle *S* to the neck with a titanous solution, turn the 3-way stop-cock *F* so that the solution enters the burette *B*, and then turn so that the burette is emptied. Meanwhile admit CO_2 from *A* until all the air is expelled from the system, and then fill burette *B* ready for use.

The solution is standardized in the following manner. Dissolve 1·5 gm. ferrous ammonium sulphate in 100 ml. of 5% H_2SO_4, titrate this with 0·1N. $KMnO_4$ to the usual pink end point and then boil for 10 minutes to expel the slight excess of $KMnO_4$ and oxygen. Cool, add 5 ml. of 10% KCNS, and titrate with the titanous salt solution to the complete disappearance of colour.

$$2TiSO_4 + Fe_2(SO_4)_3 \rightarrow Ti_2(SO_4)_3 + 2FeSO_4$$

$$TiCl_2 + FeCl_3 \rightarrow TiCl_3 + FeCl_2$$

$$3KCNS + FeCl_3 \rightarrow Fe(CNS)_3 + 3KCl$$

Total iron may of course be determined with a titanous solution if all the iron is converted to the ferric form by oxidation with $KClO_3$ in HCl solution and the excess of chlorate removed by evaporation, or by addition of $KMnO_4$ in H_2SO_4 solution to the

appearance of the pink colour. As a general rule, however, total iron is determined by the usual titration with $K_2Cr_2O_7$, titanous solution being used only for special determinations such as that of ferric iron given below under 2.

C. *Determination of ferrous iron with* $K_2Cr_2O_7$. Ferrous iron may be determined in solutions and materials where the decomposition procedures have not been oxidizing, which transforms the

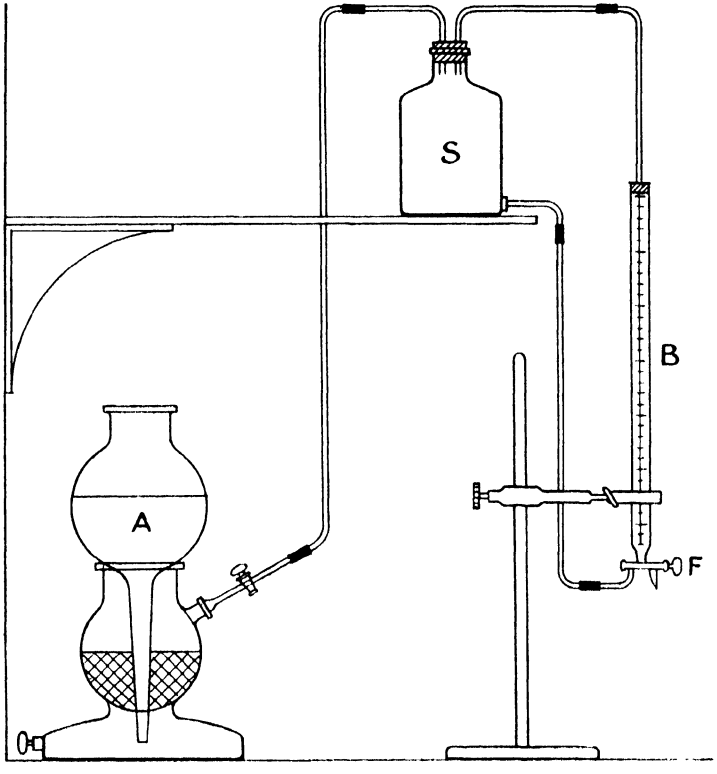


FIG. 9. Apparatus for titrations with titanous salt solutions

iron to the ferric state, or reducing, which changes the original ferric iron to ferrous. It will be appreciated that such conditions are seldom attained in practice, and consequently this method is generally merely a close approximation. In many cases, however, it is sufficiently accurate for industrial purposes, and may be used to check the value for ferrous iron obtained from the figure Total Fe – Ferric Fe = Ferrous Fe.

Add 15 ml. HCl to the sample and bring to a boil. Cover and cool rapidly. Add 3 drops diphenylamine indicator and titrate with standard $K_2Cr_2O_7$ to the appearance of the violet-blue end point.

D. A good procedure for rapidly determining the forms of iron in leaching, refining, or pickling operations utilizes precipitated copper powder as a reducing agent and $K_2Cr_2O_7$ as the titrating solution.[7]

To a 250 ml. beaker add 50 ml. water, 15 ml. of 20% H_2SO_4, and a convenient measured volume of the unknown solution, filtered if not already clear. Titrate ferrous iron with $K_2Cr_2O_7$ using barium diphenylamine sulphonate as internal indicator. One ml. of 0·1N. $K_2Cr_2O_7 = 0{\cdot}01519$ gm. $FeSO_4$.

To the solution after the above titration add a slight excess of copper metal precipitated powder, stir for two minutes, filter and titrate again with standard $K_2Cr_2O_7$. This titration gives the total iron, and the net titre represents ferric iron. One ml. of 0·1N. $K_2Cr_2O_7 = 0{\cdot}01999$ gm. $Fe_2(SO_4)_3$.

2. Determination of magnetite in copper slags

Hawley's method for the determination of magnetite in copper slags is essentially a method for the determination of ferric iron, the magnetite content being calculated from the ferric iron value on the assumption that all the ferric iron present in a slag is combined in the form of magnetite.[4] The procedure takes advantage of the fact that magnetite is acted on very slowly by hot HNO_3 and $NaClO_3$. The sulphides, however, are quickly removed by such action, making a correct determination of ferric iron in the residue possible.

Treat a 0·5–1 gm. sample of −100 mesh material with 20 ml. of a mixture of equal parts HNO_3 and 15% $NaClO_3$, previously heated almost to boiling. The beaker is shaken to prevent sticking of the sample and is boiled for 1 minute, whereupon 100 ml. of cold water is added. The mixture is filtered on a Gooch or Caldwell crucible and washed acid-free. In a covered beaker 7 ml. of water is brought to a boil with 10 ml. of a mixture of 3 parts HCl and 1 part HF. The residue from the Gooch or Caldwell crucible is quickly transferred to the beaker and the cover

replaced. Boiling is continued until the residue has gone into solution and the filter disintegrated.

The hot solution is poured into a porcelain casserole containing enough ice water to bring the temperature down to 20° C., 20 ml. of HCl saturated with H_3BO_3 is added, and the iron is titrated with standard titanous chloride after the addition of 20 ml. of 10% KCNS as indicator. The cooling of the solution before the addition of KCNS is necessary because ferric iron is reduced by KCNS in a hot solution. The end point is usually sharp and easily determined. Occasionally the red colour fades slowly and there is danger of using too much titanous chloride. In these cases it is found best to run in an excess of titanous chloride, and titrate back to a permanent red colour with standard ferric chloride.

The titanous chloride is standardized against standard ferric chloride, duplicating as closely as possible the conditions obtaining in an actual analysis, and is kept under hydrogen or carbon dioxide. The difference between total iron and ferric iron as determined by this method gives ferrous iron. The results obtained by this procedure indicate that magnetite may be determined with a probable accuracy of about 2 per cent., varying with the slag.

3. Determination of small amounts of iron colorimetrically

For the determination of small amounts of iron, as for instance in blister or refined copper, refined lead and zinc, etc., a colorimetric determination using ammonium thiocyanate is generally employed.

It is necessary to remove iron contamination from drillings of copper or other metals with dilute HCl or HNO_3, rinse carefully in distilled water, and dry, before commencing an iron determination. Use a non-ferrous spatula for weighing out NH_4CNS.

Dissolve 10–200 gm. sample in HNO_3 or HCl, or both if necessary, and add NH_4OH cautiously until all basic salts have dissolved. Heat to boiling and allow to stand several hours. Filter through Whatman 531 or 541 paper, and wash several times with hot water. Dissolve the precipitate off the filter paper with HCl, make the filtrate ammoniacal, and again filter off the iron.

Wash thoroughly with hot water until free of Cu, Ni, etc. If necessary, do a third precipitation to remove occluded impurities from the iron hydroxide. Small quantities of copper do not interfere with the ammonium thiocyanate determination of iron. For instance, 0·0008% iron can be determined in zinc oxide in the presence of 0·008% copper. Larger quantities are preferably removed by ammonia.

Dissolve the precipitate off the filter paper with 5 ml. HCl and wash with hot water, keeping the volume below 40 ml. Transfer to a Nessler tube and add 10 ml. NH_4CNS solution made by dissolving 23 gm. in 2500 ml. water. To the comparing Nessler tube add 5 ml. HCl, water, and 10 ml. NH_4CNS solution. Make up to 50 ml. mark and add, drop by drop, standard $Fe_2(SO_4)_3$ solution containing 0·0005 gm. Fe per ml. The iron solution is made by dissolving 0·4474 gm. ferric sulphate, $Fe_2(SO_4)_3$, in 250 ml. water to which a few drops of H_2SO_4 have been added to dissolve basic salts. Alternatively, the ferric thiocyanate colour can be compared with standards in a colorimeter.

Since traces of iron are common in analytical reagents it is necessary to carry through a blank carefully, using the same quantities of reagents, water, etc., as in the unknown sample. It may be necessary to re-distil HNO_3 or HCl if the iron in the sample is very low and large quantities are needed.

4. Differentiation of pyrite and pyrrhotite

McLachlan [3] describes a procedure for the quantitative determination of pyrite and pyrrhotite in Noranda ore and mill products. It is based on the solubility of pyrrhotite and insolubility of pyrite in a hot solution containing 2 parts water to 1 part HCl by volume.

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LEAD

THE DETERMINATION of lead is required in minerals and ores, alloys, paints, insecticides, foodstuffs. Its importance in many metallurgical industries has led to the development of rapid routine methods for the analysis of lead.

The principal separation of lead is based on the insolubility of its sulphate. It may also be separated from members of Group 3 and succeeding groups by H_2S precipitation in dilute HCl solution. When lead is separated as sulphate it may be contaminated with SiO_2, Ba, Ca, Sr, W, Nb and Ta. Lead may be separated from SiO_2 and Ba by extraction with ammonium acetate, and from Ca and Sr by electrolysis in HNO_3 or by precipitation with H_2S in acid solution. After separating lead from silica and barium with an ammonium acetate extraction of the sulphate, it can be precipitated as sulphide by gassing with H_2S. This procedure is often preferable to taking to fumes of sulphuric and destroying ammonium acetate. Tungsten can be separated by digestion in HNO_3 and any co-precipitated lead recovered by solution of the tungstic acid in ammonia and ammonium tartrate and precipitation of the lead by $(NH_4)_2S$. Lead can be separated from Nb and Ta by precipitation with H_2S in an acid solution containing tartaric acid.

GENERAL PROCEDURE

Lead may be determined gravimetrically, electrolytically, or volumetrically, while for very small quantities one of the best methods is by dithizone.

1. Gravimetric determination as $PbSO_4$

Weigh out 0·5–2 gm. of the ore or alloy, dissolve in 10 ml. HNO_3, 10 ml. HCl, and a little HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, add 100 ml. of water for every 0·1 gm. of lead present. Boil, filter through a previously weighed Gooch crucible, wash thoroughly with 3% H_2SO_4 and finally with several small hot water washes, or with 50% alcohol solution to remove the free acid. Dry and ignite at 500° C. Cool and weigh as $PbSO_4$.

$$PbSO_4 \times 0{\cdot}6833 = Pb$$

This procedure is very satisfactory for alloys,[2, 5] but for many ores which contain silica or barium it is necessary to modify it slightly.[13] Instead of filtering through a Gooch crucible at first, filter off the crude $PbSO_4$ on a Whatman No. 42 filter paper, and wash thoroughly with 3% H_2SO_4 as before. Dissolve the $PbSO_4$ off the paper by repeated extraction with strong ammonium acetate solution, leaving the silica and barium on the paper. Evaporate the acetate solution to dryness, take up with water, and add a large excess of H_2SO_4. Alternatively, precipitate lead as sulphide in ammonium acetate by gassing with H_2S, filter, dissolve in HNO_3 and bromine, and precipitate as $PbSO_4$. Boil, filter off the precipitate of $PbSO_4$ on a Gooch crucible and proceed as outlined above.

If calcium is present it will not be completely removed by washing with dilute alcohol, and had better be removed with barium and strontium, by precipitating lead as sulphide in dilute HCl solution. Where HCl has been used in the decomposition of a sample, it is preferable after taking to fumes of SO_3 to cool, wash down the sides of the beaker with a few ml. of water, and again evaporate to fumes of SO_3. This removes the last traces of HCl, the presence of which leads to low results.

2. Electrolytic determination as PbO_2

When an electric current is passed through a solution of lead containing sufficient free HNO_3 all the lead will be deposited on the anode as PbO_2. The method is adapted to a wide variety of substances and can be carried out directly on the sample in the absence of the interfering elements Bi, Sn, Sb, Ag, Mn, Cl, Hg,

As, P, Se, Te, or, if these are present, after a preliminary separation of lead as $PbSO_4$.

Sand-blasted platinum gauze electrodes are preferable for this deposition and 0·1 gm. of lead is about the maximum quantity that can be firmly deposited on such an anode.

Weigh out 0·5–2 gm. sample into a 250 ml. beaker and dissolve in 1:1 HNO_3. If necessary, add HCl, HF, 10 ml. 1:1 H_2SO_4 and take to fumes of SO_3. Most materials will require the decomposition with mixed acids and subsequent separation of lead as $PbSO_4$. If lead has been separated as sulphate it can be brought into a condition for electrolysis by boiling with an excess of NH_4OH and pouring the mixture, with constant stirring, into enough HNO_3 to leave an excess of 10 ml. acid per 100 ml. of solution.

The solution, either prepared directly by dissolving the sample in HNO_3 or separating the lead as $PbSO_4$ and transforming it into nitrate as described above, should contain 10% HNO_3 and not over 0·1 gm. lead. It may be electrolysed overnight at 0·2–0·5 ampere and 2–2·5 volts, or by rapid deposition with a rotating cathode at 1·5–1·7 amperes per 100 sq. cm., the E.M.F. varying between wide limits. Test for completeness of deposition by adding a little water and after 15 minutes observing whether any further deposition occurs on the stem of the anode. Rinse the anode with water, then in alcohol, and dry in an oven at 220° C. for 30 minutes. Cool and weigh as PbO_2. Use the empirical factor 0·8643 instead of the theoretical value 0·8662 for converting PbO_2 to Pb. Remove the deposit of PbO_2 from the anode by dissolving in warm 1:3 HNO_3 containing a little H_2O_2.

3. Volumetric determination by ammonium molybdate

Lead is precipitated from an acetic acid solution by a standard solution of ammonium molybdate, the termination of the reaction being indicated by the yellow colour produced by the excess of reagent when a drop of the mixture comes in contact with a drop of tannin solution used as an outside indicator.[6, 10]

$$Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 \rightarrow PbMoO_4 + 2NH_4C_2H_3O_2$$

Usually lead is separated from nearly all interfering elements by filtration as lead sulphate and subsequent extraction with strong ammonium acetate slightly acidified with acetic acid.

Weigh 0·5–2 gm. sample into a 250 ml. beaker and decompose with 10 ml. HCl, 10 ml. HNO_3, and a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, add water, boil until all basic ferric sulphate is in solution, and filter off the precipitated $PbSO_4$. Wash thoroughly with 3% H_2SO_4 and finally several times with hot water.

Dissolve the $PbSO_4$ with concentrated ammonium acetate solution. A large excess of ammonium acetate must be avoided, since it gives a troublesome transitory end point in the titration. With large precipitates it is most convenient to wash by decantation, retaining as much of the $PbSO_4$ precipitate as possible in the beaker. The lead sulphate is then brought into solution by washing the filter with hot saturated ammonium acetate followed by hot water, receiving the washings in the beaker containing the bulk of the lead precipitate. With precipitates which have not been washed by decantation, transfer the filter paper to the original beaker containing the precipitate, and add saturated ammonium acetate solution. When the precipitate is dissolved, add water and heat nearly to the boiling point. Place the filter paper on the side of the beaker by means of a stirring rod and titrate to the end point, then stir in the filter paper which will require a few more drops of the molybdate solution to give the end point.

To avoid over-running the end point a little of the solution may be kept in reserve and the bulk of the solution titrated rapidly to the brown end point. The reserve solution is now added in portions and the titration continued carefully to the end point.

The indicator is made by dissolving 1 gm. of tannin in 500 ml. of cold water, and adding 5 drops of a saturated mercuric chloride solution. It will then keep for some weeks, whereas without preservative it must be made fresh every day or two.

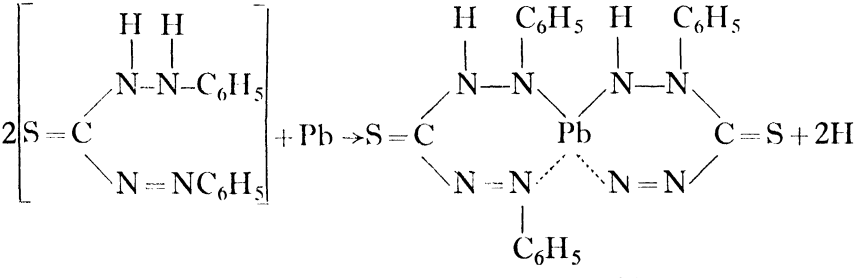
The standard molybdate solution is made by dissolving 4·4 gm. ammonium molybdate in 1 litre of water and standardizing against pure lead foil. After several days the solution becomes stabilized and will stand almost indefinitely with very slight changes in strength. 1 ml. of the above solution = 0·005 gm. Pb.

If barium or a large quantity of SiO_2 is associated with the $PbSO_4$ precipitate, it is necessary to extract the lead by ammonium acetate and filter off the insoluble $BaSO_4$ and SiO_2, washing thoroughly with saturated ammonium acetate.

If calcium is present in appreciable quantities it is best to precipitate lead with H_2S from a solution slightly acid with HCl. Filter and wash thoroughly with hot acidulated H_2S water. Dissolve the precipitate off the filter paper with dilute HNO_3 into the original beaker, wash thoroughly, add 10 ml. 1:1 H_2SO_4 and take to fumes of SO_3. Filter off the precipitated $PbSO_4$ and carry on as outlined above.

4. Determination of small quantities of lead by dithizone

The following method is adapted to the rapid determination of small quantities of bismuth and lead in mine, smelter, or refinery products containing Cu, Ni, Fe, Co, Zn, etc. The method depends on the fact that cyanide ion in alkaline solution inhibits the reaction between dithizone and all metals except stannous tin, thallous thallium, lead, and bismuth.[9, 12]



dithizone lead dithizonate

If tin and thallium are negligible, lead and bismuth can be extracted with dithizone in reduced alkaline solution of KCN. The lead and bismuth are removed from this extract by shaking with 10% HNO_3. Bismuth is titrated out free from lead at a *p*H of 2 with dithizone, after which lead is titrated at *p*H 8. In the absence of bismuth, of course, the following procedure can be simplified by extracting lead at *p*H 8 after rinsing with 2% KCN.

Dissolve 1–10 gm. sample in sufficient HNO_3 to bring all lead and bismuth into solution. Cool, add water and HCl so that the final solution contains 1 vol. H_2O:2 vol. HNO_3:4 vol. HCl. Wash the sample into a 250 ml. separatory funnel with 1:1 HCl, add ether, shake, and withdraw the ether by suction into a short separatory funnel which makes it easy to return any acid solution carried over. Make a second extraction with ether to remove all

the iron. Filter the solution from S and SiO_2, if necessary, and make up to a known volume.

A good procedure for lead in metallic copper, nickel, or cobalt is to collect the lead with $Fe(OH)_3$ and then proceed with the isolation of bismuth and lead in a cyanide solution, titrating with dithizone. This is the method described by Young and Leibowitz.[12]

Pipette out a suitable aliquot, place in a 75 ml. separatory funnel and dilute with water to about 30–40 ml. Add 10 drops 50% citric acid, neutralize with NH_4OH, and add another 10 drops 50% citric acid. Add sufficient KCN to give a clear solution after the first turbid appearance of insoluble cyanides.

Add several drops of B.D.H. universal indicator and carefully add NH_4OH drop by drop to the appearance of a green colour, indicating *p*H 8. Add several ml. of dithizone solution from a burette, shake the separatory funnel vigorously, draw off and retain the red dithizonates of lead and bismuth in a test tube. Continue the additions of dithizone until all the lead and bismuth are extracted, indicated by the lower CCl_4 layer in the separatory funnel remaining green after shaking. A little excess dithizone does no harm and it is not necessary to record the volume of dithizone used in this extraction.

The collected red dithizonates of lead and bismuth are placed in a separatory funnel, rinsing the test tubes thoroughly with CCl_4, and 10 ml. of 2% KCN are added. The funnel is shaken and the upper aqueous layer withdrawn by suction. This rinsing with 2% KCN is repeated to remove the last traces of copper and other metals. About 10–15 ml. of 10% HNO_3 are added to the separatory funnel, the latter shaken vigorously, and the lower green layer drawn off and discarded.

The clear solution containing bismuth and lead is now adjusted to *p*H 2, a pale red, with *meta*-cresol purple. Titrate the bismuth with standard dithizone solution, making the usual shakings and withdrawals, until the lower CCl_4 layer does not turn brown but remains green on shaking, indicating that the dithizone has reacted with all the bismuth. The number of ml. of dithizone used multiplied by the bismuth value of the solution gives the amount of bismuth in the sample.

Now add several drops of B.D.H. universal indicator, 1 ml. of

saturated sodium acetate, a little KCN and adjust the *p*H of the solution in the separatory funnel to 8 with NH_4OH until a grass-green or light blue-green colour results. Titrate the lead with dithizone in the usual manner until the lower CCl_4 layer no longer turns red on shaking, but remains green, indicating that all the lead has reacted with the dithizone.

From the number of ml. of dithizone solution used, and the value of the latter in terms of lead, the quantity of lead in the sample can be obtained.

The dithizone solution is standardized against a known quantity of lead and bismuth in the presence of other interfering elements, using the same procedure. A stock solution of concentrated dithizone is prepared by sprinkling diphenylthiocarbazone powder on a filter paper fitted to a glass funnel and pouring CCl_4 through the funnel. The nearly saturated dithizone is kept in a Pyrex flask covered with a layer of H_2SO_3 and is protected from light and heat. The standardized dithizone solution is prepared by diluting the above concentrated solution with CCl_4 to a concentration of approximately 0·025 mg. dithizone per ml., which is the theoretical equivalent of 0·010 mg. Pb per ml. The dithizone solution is standardized against a lead nitrate solution containing 3·197 gm. $Pb(NO_3)_2$ per litre, or 2 mg. Pb per ml. This stock solution of lead nitrate in 1% HNO_3 may be diluted to 0·01 mg. Pb per ml. as required. The latter dilute solution is not stable for long periods, and should therefore be freshly prepared from the stock solution when needed.

Other procedures for determining small quantities of lead are given by Cantarow and Trumper [3] in their book on lead poisoning, by A.O.A.C.,[1] and by Copeland and Griffith who describe the polarographic determination of lead in zinc.[4]

SPECIAL PROCEDURES

1. Forms of lead

A. *In slags.* A procedure for roughly determining the forms of lead in slag and other metallurgical products has been worked out by Oldright and Miller.[8] While this method, like similar empirical determinations, is not perfect, it does give an approximate idea of the forms of lead and is quite useful in metallurgical

plants, especially if employed in conjunction with microscopic studies. The procedure is as follows:

Place a 0·5–5 gm. of −100 mesh sample in a 250 ml. beaker, add 25 ml. of a saturated solution of ammonium acetate, dilute to 100 ml. and boil for 10 minutes. Filter the solution through an asbestos mat in a Gooch crucible, and wash the residue free from the solvent with hot distilled water. The filtrate contains whatever amount of lead was present as oxide, sulphate, or basic sulphate. The residue contains the lead present as sulphide, silicate, and metal. For slags, treatment with ammonium acetate may be omitted.

Transfer the residue or the weighed sample of slag to a beaker and evaporate until the residue is only slightly moist, then add 10 to 20 ml. of a 10% solution of silver nitrate. Treat for 1 hour in the cold, occasionally stirring with a rod to break up lumps, filter through an asbestos mat in a Gooch crucible, and wash the residue free from silver nitrate. The filtrate contains the lead that was originally present in the metallic form. The residue contains the lead present as sulphide and silicate.

Transfer the residue to a 250 ml. beaker, expel water as before, and add 25 to 50 ml. of a saturated solution of sodium chloride containing 60 grams of ferric chloride, $FeCl_3.6H_2O$, per litre. Treat at 25–28° C. for 12 hours and agitate occasionally. Filter the solution through filter paper and wash the residue once with some of the original solvent, then wash free from soluble chlorides with hot water. The filtrate contains the lead originally present as sulphides. The residue contains the lead present as silicates. The filtrates and residue are then analysed by standard methods to determine the lead content of each. From these data the percentages of the total lead content present originally in the oxidized form and as metallic lead, lead sulphide, and lead silicate may be calculated.

If the material is analysed for oxidized lead compounds, extreme care should be exercised in preparing the sample so that the amount of lead sulphide altered and reported as the oxide will be negligible. In fresh lead blast-furnace slags, where oxidized lead compounds are not present, but only metallic lead, lead sulphide, and lead silicate, any alteration of the sulphide will not affect the results. All alteration products of lead sulphide are soluble in the ferric

chloride brine solution used, so the lead dissolved will be computed as lead sulphide.

In filtering through a Gooch crucible the amount of asbestos used as a mat should be as small as possible to prevent difficulties in the final decomposition of the residue. The lead silicate remains as a residue on the asbestos mat, and all of the solids must be digested together with solvents to dissolve the lead, then fumed with sulphuric acid, etc., the asbestos being carried along with the lead through the final titration with ammonium molybdate.

B. *In ores and concentrator products.* A procedure is given in Low, Weinig, and Schoder[7] for the differentiation of oxide lead from sulphide lead, using the solubility of the former in ammonium acetate. This does not dissolve lead phosphate or vanadates. A better method for complex lead ores is given by Young, Golledge, and Talbot,[11] which depends on the solubility of lead sulphate, carbonate, and oxide in ammonium acetate, and the treatment of the residue consisting of lead sulphide, phosphate, and vanadates with dilute perchloric acid. The lead sulphide is virtually insoluble in this solution whereas the oxidized lead dissolves. The details are as follows:

Weigh out 1 gram of −200 mesh sample into a small stoppered Erlenmeyer flask and add 100 ml. of 60% ammonium acetate solution. Allow to stand at room temperature for 1½ hours, shaking the flask every 10–15 minutes. Filter through a 15 cm. No. 42 Whatman paper and wash by decantation thoroughly with cold water, retaining as much of the residue in the beaker as possible. A small quantity of material will unavoidably pass on to the filter paper, but this should be kept to a minimum. The filtrate contains lead present as sulphate, carbonate, and oxide.

Replace the original flask under the funnel and pour through the paper 100 ml. of cold 10% by volume perchloric acid. Reserve any lead sulphide residue on the paper for addition to final sulphide residue. Stopper the flask and allow to stand at room temperature for 2 hours, shaking the flask for a few seconds every 10–15 minutes. Filter through a 15 cm. No. 42 Whatman filter paper having an 11 cm. No. 42 paper as a cone outside the former, and wash thoroughly with cold 1% perchloric acid. The remaining oxide lead minerals like pyromorphite, descloizite, and

vanadinite are in the filtrate, while lead sulphide remains on the filter paper.

Owing to the tendency for finely-divided lead sulphide to oxidize on exposure to air and moisture, the filtrations should be carried through as rapidly as possible, and prolonged washing should be avoided. The presence of laboratory fumes increases this tendency of lead sulphide to oxidize.

If the lead minerals are very finely disseminated in a siliceous gangue it may be necessary to add a few drops of HF to the sample during both leaches. Small quantities of HF are without effect on lead sulphide; as high as 5% HF by volume dissolves insignificant amounts under the conditions of the above procedure.

The oxide lead in the filtrate from the ammonium acetate and perchloric acid treatments may be combined and lead determined by any suitable procedure. They may also, if desired, be determined separately, thus differentiating between lead present as sulphate or carbonate and lead found as phosphate or the vanadates. The final residue of lead sulphide may be easily dissolved in nitric acid and bromine, and lead determined as usual.

Owing to the time required to decompose the finely-divided mineral particles carried into the filter paper following the perchloric acid treatment, it will be found preferable to determine sulphide lead from the relation: total lead-oxide lead = sulphide lead.

2. A symposium on tetraethyl lead in gasoline, featuring a number of analytical procedures, is given in the October, 1950, issue of *Analytical Chemistry*.

Special problems in the analysis of lead may be submitted by the chemist to the Lead Industries Association, 420 Lexington Avenue, New York 17, N.Y.

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MAGNESIUM

MAGNESIUM is a common constituent of rocks, soils, minerals, and ores; ceramic and refractory materials; lime, cement, plaster, and other building materials. In addition the great importance of magnesium and its alloys in light metal applications makes its analysis a common one in metallurgical laboratories.

Magnesium is almost invariably determined gravimetrically by precipitating as magnesium ammonium phosphate after prior separation of the hydrogen sulphide, ammonium sulphide, and ammonium carbonate groups, and igniting to magnesium pyrophosphate.[2, 3, 4] Usually in industrial laboratories, aluminium, calcium, and magnesium are determined on the same sample by precipitating aluminium with NH_4OH in the presence of NH_4Cl, separating calcium in the filtrate with ammonium oxalate, and finally determining magnesium in the filtrate after filtering off calcium oxalate. If the amount of calcium present is appreciable it is essential to re-precipitate in order to set free any occluded magnesium salts.

For very accurate work it is necessary to dissolve the precipitate of magnesium ammonium phosphate in HCl and re-precipitate to set free occluded alkali salts and provide optimum conditions for the precipitation of $MgNH_4PO_4$ instead of other magnesium phosphates.

GENERAL PROCEDURES

Since magnesium is usually determined with aluminium and calcium on the same sample, or after the removal and determination of all other elements except the alkalies, a detailed description of the removal of interfering elements is not necessary.

Weigh out 0·5–2 gm. sample and decompose with 10 ml. HCl, 10 ml. HNO_3, and a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, dilute with hot water, add 5 ml. HCl and boil. If the sample is insoluble in acid, fuse with Na_2CO_3, dissolve the melt in HCl, and evaporate to dryness twice to dehydrate SiO_2. Take up in 5 ml. HCl and a little water, and boil.

Filter off SiO_2 and wash thoroughly with hot water. Adjust the acidity to approximately 5% HCl and gas out all Group 2 metals with H_2S. Filter off the precipitated sulphides and wash thoroughly with acidulated H_2S water. If metals of Group 3 such as Ni, Co, Cr, Mn, Zn, V, Ti, etc., are present they may be removed by making the filtrate ammoniacal and passing in H_2S for a few minutes longer. Filter off the precipitated sulphides, washing thoroughly with ammoniacal H_2S water. If only iron and aluminium are present it is preferable to remove them with NH_4OH in the presence of NH_4Cl. Care should be taken to avoid a large excess of NH_4OH owing to its solvent action on $Al(OH)_3$. Double precipitations are necessary to free iron and aluminium hydroxides of occluded calcium and magnesium salts. Nickel and cobalt, if present, will pass into the filtrate with the Ca and Mg, but the phosphates of Ni and Co are slightly soluble in NH_4OH and NH_4 salts and do not interfere unless appreciable quantities are present. In the latter case, Ni and Co can be removed by electrolysis in the ammoniacal filtrate after the precipitation of Fe and Al. Where large amounts of iron or aluminium are present it is preferable to separate these with NH_4OH and then eliminate the members of Group 3 which are soluble in ammonia by passing H_2S into the filtrate. In this case the filtrate from the separation of Group 2 sulphides is boiled to remove H_2S, oxidized with H_2O_2, and iron and aluminium precipitated with NH_4OH. After the precipitation and removal of all sulphides with H_2S in acid and ammoniacal solution, the filtrate is boiled to eliminate H_2S and filtered if necessary to remove any separated sulphur.

Calcium is now removed by addition of ammonium oxalate, as described in the section on Calcium. If much calcium is present the precipitate must be dissolved in HCl or HNO_3 and re-precipitated to liberate occluded magnesium. After filtering off the

calcium oxalate and washing thoroughly with hot water, the filtrate containing magnesium and alkali salts in presence of ammonia is ready for the precipitation of magnesium.

The presence of large quantities of ammonium salts interferes with the rapid precipitation of magnesium and with the formation of the desired magnesium ammonium phosphate compound. In nearly all cases, therefore, it is best to evaporate down to a low volume, cautiously add 50–75 ml. HNO_3, and take to dryness. If necessary, add more HNO_3 and evaporate again to get rid of nearly all ammonium salts. Dilute to 200 ml. and add sufficient diammonium phosphate to precipitate all the magnesium and have a five-fold excess. Usually 10–20 ml. of 10–20% ammonium phosphate solution is sufficient. 10 ml. of a 10% solution of $(NH_4)_2HPO_4$ will precipitate about 0·3 gm. of MgO or 30% on a 1 gm. sample. A five-fold excess for 30% MgO on a 1 gm. sample would require 50 ml. of 10% solution. Add NH_4OH until the solution is ammoniacal, and then 10% excess. The solution should be stirred vigorously to promote the formation of the precipitate.

$$(NH_4)_2HPO_4 + Mg(NO_3)_2 + NH_4OH \rightarrow MgNH_4PO_4 + 2NH_4NO_3 + H_2O$$

$$2MgNH_4PO_4 \rightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$

Allow the precipitate to settle 4 hours or preferably overnight. Filter through Whatman No. 40 or 42 paper and wash thoroughly with 5% NH_4OH. Place in weighed porcelain crucible and ignite at 1000° C. to constant weight.

For accurate work dissolve the precipitate off the filter paper with HCl, and re-precipitate with NH_4OH and ammonium phosphate. Allow to settle overnight and filter on Whatman No. 42 paper, washing thoroughly with 5% NH_4OH. Transfer to a platinum crucible, dry and ignite very slowly with free access of air to avoid any reduction of the phosphate with consequent injury to the crucible. Finally ignite for 30 minutes at approximately 1000° C. in the muffle. Cool in a desiccator and weigh as $Mg_2P_2O_7$.

$$Mg_2P_2O_7 \times 0{\cdot}2185 = Mg$$

$$\times 0{\cdot}3623 = MgO$$

SPECIAL PROCEDURES

The analysis of magnesium metal and alloys is fully covered in an excellent publication of the Dow Chemical Company.[1]

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MANGANESE

MANGANESE is widely distributed in ores, steels, alloys, and other metallurgical products. The element is almost invariably determined volumetrically in industrial practice, and usually relatively few interfering elements must be removed. Small quantities of manganese are best determined colorimetrically.

Manganese can be separated from members of the copper group by precipitating the latter in acid solution with H_2S, and it is isolated along with other members of Group 3 by H_2S precipitation in ammoniacal solution. It can be separated from other elements of Group 3 by boiling with HNO_3 and $KClO_3$ or $NaClO_3$, precipitating MnO_2. Manganese is not precipitated by ammonia unless bromine is present, and can thus be separated from Fe, Al, Ti, Cr, Zr, U. Manganese can be removed in the filtrate, together with Ni and Co, from the ZnO precipitate containing Al, Cr, Fe, P, Ti, V, W, Zr, Nb, and Ta. Nickel and cobalt can be separated from Mn by electrolysis in ammoniacal solution. Manganese, together with Fe, Ni, and Co can be precipitated from Al, V, Cr, and U by treatment with Na_2O_2 in alkaline solution.

Manganese can be separated from Fe, Ti, V, and Zr by cupferron, and from Fe by an ether extraction.

It is well to bear in mind that in ordinary nitric-sulphuric acid electrolysis, part of the manganese deposits on the anode as hydrated MnO_2, and part remains in solution. None is deposited on the cathode.

In both volumetric methods it is essential to avoid contamination of the solution with chloride ion prior to the oxidation of the

manganese. If the sample is insoluble in HNO_3, and HCl has been used in its decomposition, it must be taken to strong fumes of H_2SO_4 to eliminate chlorides.

GENERAL PROCEDURES

1. The ammonium persulphate method

This method involves oxidation of manganous salts to permanganate with ammonium persulphate in the presence of silver nitrate, and titration of the permanganic acid with sodium arsenite. The latter is used since ferrous ammonium sulphate would be oxidized by ammonium persulphate, and titration with $KMnO_4$ as in Volhard's method would result in the precipitated MnO_2 going to $HMnO_4$ in presence of persulphate. In the presence of over 0·5% W or 1% Cr, manganese must be separated by a zinc oxide separation, or by a nitro-chlorate separation.[2, 3, 6, 8, 9]

Weigh 0·5–2 gm. sample into a 400 ml. beaker. Add 30 ml. nitric-sulphuric-phosphoric acid mixture and heat gently. Boil until oxides of nitrogen are expelled, and dilute with 100 ml. hot water. If it is necessary to decompose with *aqua regia* and HF, or by a carbonate fusion, eliminate all chlorides by taking to strong fumes of SO_3, add 15 ml. nitric-sulphuric-phosphoric acid mixture, boil to expel nitrous fumes, and take up in 100 ml. hot water as before.

If tungsten or chromium are present in quantities greater than 0·5 and 1% respectively, add a suspension of zinc oxide to precipitate all Fe, Al, W, Cr, etc., boil, filter, wash thoroughly, dissolve in HNO_3, re-precipitate with ZnO, filter and wash well with hot water. The manganese will be in the filtrate, along with any nickel and cobalt present.

Small quantities of manganese are volatilized if a mixture of perchloric and hydrofluoric acids is used to decompose the sample.

Alternatively manganese can be separated by dissolving the sample in HCl and HNO_3, filtering off any yellow residue of tungsten and taking to fumes of $HClO_4$ or H_2SO_4. Add 50 ml. HNO_3 and boil. Carefully add a few crystals of $NaClO_3$ and heat, repeating this operation until about 8 gm. of $NaClO_3$ has

been added. Filter the precipitated MnO_2 through a Gooch containing asbestos previously washed with hot colourless HNO_3. Wash with a little HNO_3 and finally with cold water. Discard the filtrate and washings, replace the receiving vessel with a clean one, and dissolve the MnO_2 by washing the beaker and the filter with 50 ml. of 5% HNO_3 to which 10 ml. of 3% H_2O_2 has been added. Wash the beaker and filter 3 times with water, boil the solution to decompose the peroxide, and reserve for the determination of Mn. The above reaction may be represented:

$$9Mn(NO_3)_2 + 3NaClO_3 + 7H_2O \rightarrow 9MnO_2 + 3NaNO_3 + NOCl + Cl_2 + 14HNO_3$$

To the solution obtained by one of the foregoing methods, free of Cl, Cr, and W, add in succession 5 ml. of 1% $AgNO_3$ and 10 ml. of a 30% solution of ammonium persulphate.

Stir, heat rapidly to boiling, and boil 1 minute after the foam disappears. Cool rapidly in a water trough and titrate immediately with sodium arsenite until the solution assumes a yellowish colour or until one drop produces no further change in the colour of the solution. The reactions are:

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

$$2HMnO_4 + Na_3AsO_3 \rightarrow Na_3AsO_4 + 2MnO_2 + H_2O + O_2$$

$$HMnO_4 + Na_3AsO_3 \rightarrow Na_3AsO_4 + HMnO_3$$

$$MnO_4 + As^{III} \rightarrow As^{V} + Mn^{IV} + Mn^{V}$$

green yellow

Reagents

Nitric-sulphuric-phosphoric acid mixture: add 185 ml. of 1:1 H_2SO_4 to 440 ml. H_2O, then add 125 ml. of H_3PO_4 and 250 ml. HNO_3.

Standard sodium arsenite solution: $NaAsO_2$ or Na_3AsO_3. Prepare a stock solution by dissolving 22 gm. in 1000 ml. water, allow to age 3 weeks, and dilute to 1000 ml. for use as needed. This gives a stable solution. The sodium arsenite is usually standardized against standard steels. The standard is run through all steps of a regular determination, and the arsenite

solution is adjusted for routine work so that 1 ml. = 0·1% Mn on a 0·5 gm. sample, i.e. 0·0005 gm. Mn. If desired, sodium arsenite solution of approximately 1 ml. = 0·0001 gm. Mn can be made by weighing 0·337 gm. As_2O_3 + 1·1 gm. Na_2CO_3 and diluting to 1 litre. A 0·1N. arsenious acid solution contains 4·95 gm. As_2O_3 + 15 gm. Na_2CO_3 per litre.

2. The sodium bismuthate method

This procedure depends on the oxidation of manganese to permanganic acid with sodium bismuthate, its reduction with standard ferrous salt and final titration with standard $KMnO_4$.[2, 3, 6, 8, 9] It can be employed with assurance for a wide range of manganese contents.

In this method chromium and vanadium must be eliminated by a zinc oxide separation. Cobalt must be removed since it is oxidized by the bismuthate and subsequently reduced with the permanganic acid. Large quantities of nickel cause a colour interference at the visual end point. Manganese can be separated from cobalt and nickel by treatment with sodium chlorate and HNO_3 as outlined above. Of the other interfering substances cerium is rarely encountered, and HCl, HF, organic matter, etc., can be eliminated by fuming with H_2SO_4.

If the sample is in nitric acid solution, boil to the expulsion of oxides of nitrogen. Cool, and add a small quantity of sodium bismuthate until a pink colour develops or MnO_2 precipitates. This is done to destroy any organic or reducing substances which may be present in the solution. Boil 2 minutes and add a freshly prepared solution of SO_2 until the solution is clear. Boil until all SO_2 and nitrogen oxides are expelled. Cool to 15° C.

If the sample is in sulphuric acid solution, heat to boiling, add ammonium persulphate first and finally a very small quantity of sodium bismuthate. Then reduce with H_2SO_3, boil and cool as directed above. If the sample is in perchloric acid solution, add HNO_3 to 15%, and reoxidize and reduce as indicated above.

To the cool solution containing 15–20 ml. HNO_3 or 5–10 ml. H_2SO_4 per 100 ml., add an excess of sodium bismuthate at least 25 times as much as the weight of manganese present. Stir vigorously and if all or nearly all the bismuthate added should dissolve, add more immediately. Let the solution stand 1 minute

and add 50 ml. of a 3% HNO_3 solution free of nitrous acid. Filter without delay through a purified asbestos pad in a Gooch crucible. Wash the residue 4–5 times with the 3% HNO_3 solution until the last runnings are colourless, and titrate the filtrate in the following manner. The reaction may be symbolized thus:

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O.$$

If the sample is in H_2SO_4 or HNO_3 solution add 2 ml. of H_3PO_4 to the filtrate and stir. In perchloric acid omit the H_3PO_4. Add from a burette standard ferrous sulphate solution until the pink colour is discharged, and 1–2 ml. excess. Back titrate this excess with standard $KMnO_4$ solution until one drop gives a distinguishable pink end point.

To ascertain the blank due to colour interference, if the solution is coloured boil for 10 minutes. Cool to the same temperature as before and titrate again to the same end point. If this titration requires more of the permanganate than is required to give an end point in a colourless solution, subtract the difference from the ml. of $KMnO_4$ used in the titration. Titrate the blank to the same end point with $KMnO_4$ as a check on reagents used. Then add the same volume of the ferrous sulphate solution as was used in the determination and titrate with $KMnO_4$, noting the ml. of the latter added in both titrations. The difference in the volumes of the $KMnO_4$ used in the two titrations represents the manganese in the sample.

Reagents

3% HNO_3: Boil 40 ml. HNO_3, cool, and bubble air through it for 5 minutes. Dilute to 1000 ml., add 1 gm. sodium bismuthate and allow to settle. Keep in a cool dark place.

Ferrous ammonium sulphate: dissolve 12 gm. $Fe(NH_4)_2.(SO_4)_2.6H_2O$ in a cold solution of 50 ml. H_2SO_4 in 950 ml. H_2O.

$KMnO_4$, 0·03N.: dissolve 1 gm. KOH in 1000 ml. H_2O and add 1 gm. $KMnO_4$. Allow to age one week and filter through a purified asbestos pad. Dissolve 0·1 gm. of standard sodium oxalate in 100 ml. of boiled and cooled 5% H_2SO_4 solution.

Add $KMnO_4$ with constant stirring to a faint pink colour. Heat to 70° C. and titrate with $KMnO_4$, stirring constantly and adding the solution dropwise to a lasting pink end point. Titrate a blank H_2SO_4 solution in the same way and subtract this blank from the ml. $KMnO_4$ solution used to titrate the oxalate. Calculate the manganese value of 1 ml. of $KMnO_4$ solution. A normal solution of sodium oxalate contains 67 gm. per litre.

1 ml. 0·1N. $KMnO_4$ = 0·001099 gm. Mn

1 ml. 0·03N. $KMnO_4$ = 0·0003296 gm. Mn

The standard $KMnO_4$ is titrated against the ferrous ammonium sulphate daily to determine this ratio. The reaction is

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

3. Potentiometric method

A new procedure for manganese has been proposed in recent years, based on the potentiometric titration of manganous ion in neutral pyrophosphate solution.[4] We have found this method very satisfactory on a wide range of metallurgical products and feel justified in recommending its use in general industrial laboratories.

Decompose 0·5–10 gm. sample, depending on the manganese content, with HCl, HNO_3, HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to fumes. If the material decomposes completely in HCl, or HNO_3, treatment with these acids alone is sufficient, but when HNO_3 is employed the sample must be boiled thoroughly to remove oxides of nitrogen. It is a good practice in this case to add a small amount of urea or sulphamic acid to remove the last traces of nitric oxide, since these are titrated by permanganate. It is usually unnecessary to filter but this operation may be required in some cases.

To a 25 or 50 ml. sample of the acidic manganese solution add 150 -300 ml. of saturated sodium pyrophosphate solution. Adjust the *p*H to a value of 6–7 by the addition of either dilute sulphuric acid or sodium hydroxide. This adjustment may be made in colourless solutions with bromthymol blue or chlorophenol red, or in coloured solutions with indicator test papers. Alternatively a glass electrode *p*H meter can be used.

Titrate with 0·08N. $KMnO_4$ solution on a potentiometric assembly, using a bright platinum electrode and a saturated calomel electrode, with a motor-driven stirrer, to the usual end point where the sharp break in the curve appears.

Large amounts of aluminium, cadmium, chromium 3, cobalt 2, copper, iron 3, magnesium, molybdenum 6, nickel, tungsten 6, uranium 6, zinc, chloride, nitrate, perchlorate, and sulphate ions are without significant effect. Vanadium up to about one-fifth of the manganese has little effect, but the interference of larger amounts can be overcome by titrating at *p*H 3–3·5.

Saturated sodium pyrophosphate. Approximately 12 gm. $Na_4P_2O_7.10H_2O$/100ml. water at room temperature. Prepare fresh every two weeks.

0·08 N. $KMnO_4$. Dissolve 3·16 gm. $KMnO_4$ in 1 litre of water. One ml. = 0·004394 gm. Mn.

The reaction may be represented:

$$4Mn^{++} + MnO_4^- + 15H_2P_2O_7^{=} \rightarrow 5Mn(H_2P_2O_7)_3^{\equiv} + 4H_2O$$

$1KMnO_4$ or 158·03 gm. $\rightarrow$ 4Mn or 219·72 gm. Mn

1 litre 0·02M $KMnO_4$ = 4·394 gm. Mn

1 ml. 0·02M $KMnO_4$ = 0·004394 gm. Mn

$$\text{N. } KMnO_4 = \frac{KMnO_4}{4}. \qquad 0{\cdot}08\text{N. } KMnO_4 = \frac{158{\cdot}03}{4} \times 0{\cdot}08$$

$$= 3{\cdot}16 \text{ gm.}$$

SPECIAL PROCEDURES

1. In irons and steels

A good procedure for manganese in irons and steels has been recently published by an authoritative body.[5] The sample is dissolved in dilute sulphuric acid, any other acid solutions necessary for complete solution being removed by fuming after oxidation, and a zinc oxide separation is made. The resultant solution is strongly acidified to prevent interference from cobalt and oxidized with ammonium persulphate. The permanganic acid is titrated using ferrous ammonium sulphate and potassium dichromate, with barium diphenylamine sulphonate as indicator.

2. Colorimetric determination

For very small quantities of manganese the faint pink colour obtained by oxidation with ammonium persulphate, sodium bismuthate, or potassium periodate, may be compared in a colorimeter with standards similarly prepared.[1, 7]

3. Gravimetric procedure

It is only rarely that the analyst will have occasion to do manganese gravimetrically, since the bismuthate procedure can be used for a very wide range of products. The best gravimetric method is precipitation of manganese ammonium phosphate in a slightly ammoniacal solution containing an excess of ammonium salts. Prior separation of manganese from other elements which are precipitated is usually effected by the nitric acid–chlorate procedure.[2, 6]

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MERCURY

MERCURY in ores is found chiefly as cinnabar, HgS, and its determination in an industrial laboratory is rather rare. Nearly all mercury compounds are volatile when heated and this should be borne in mind when decomposing samples containing this element. Mercury can be separated from members of succeeding groups by precipitation of the mercuric salt with H_2S in acid solution. Mercuric sulphide can be separated from sulphides of As, Sb, and Sn by digestion in yellow $(NH_4)_2S$ solution, the latter sulphides dissolving, whereas HgS remains insoluble. Mercury can be separated from Pb, Bi, Cd, and Cu by digestion of sulphides in hot dilute HNO_3 in which HgS is insoluble. A separation from Se and Te can be effected by adding to a cold dilute solution of *aqua regia* containing Hg, Se, and Te, a little chlorine water and phosphorous acid. Mercurous chloride is precipitated after some time while Se and Te remain in solution. Silver can be separated from bivalent mercury by precipitating the former with HCl, decanting, warming the AgCl with a little dilute HNO_3 and again precipitating the silver by the addition of water and a few drops of HCl. The mercury is recovered in the combined filtrates.

GENERAL PROCEDURES

1. Determination of Hg by volatilization and amalgamation

In this method a sample containing not over 0·1 gm. mercury is weighed into the iron or nickel crucible *A*, shown in Fig. 10. Mix 5–10 gm. of iron filings, free from grease and other impurities, with the sample and sprinkle additional filings over the surface. Sulphide ores should be mixed with about twice their weight of a

flux of 4 parts ZnO to 1 part Na_2CO_3, and about 5 times the weight of iron filings added, mixing the whole thoroughly.[3]

Place the crucible with the charge in the clamp, cover it with a weighed piece of gold or silver foil large enough to extend beyond the rim of the crucible. Clamp the assembly of condenser *B*, foil, and crucible together tightly. Start a stream of cold water through the condenser, and heat the crucible gradually with a

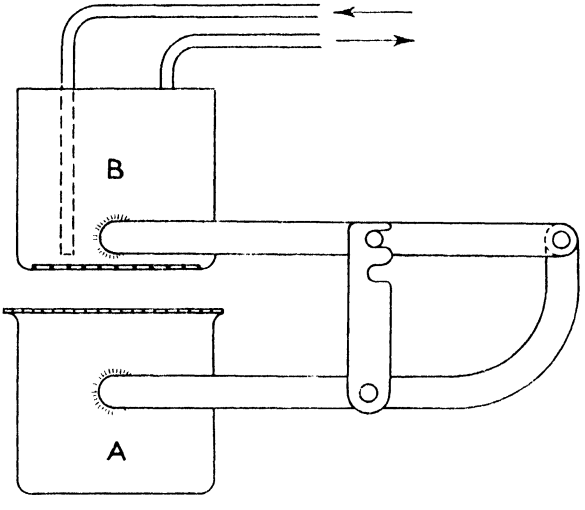


FIG. 10. Apparatus for determination of mercury by volatilization and amalgamation

small flame or electrical element. The metal foil should never become hot, otherwise mercury will be lost.

After heating for 30 minutes let the apparatus cool, allowing the water to continue flowing through the condenser during this period. Remove the foil carefully, wash it with alcohol and allow to dry in the air or over a $CaCl_2$ desiccator. Weigh, the increase in weight being metallic mercury. Ignition of the foil will volatilize the mercury and render the foil available for further amalgamations.

2. Determination of mercury by titration with thiocyanate

Mercuric nitrate forms an insoluble thiocyanate and can be titrated with a standard thiocyanate solution, using a ferric salt as the indicator for the end of the reaction.[2, 4, 6]

$$2NH_4CNS + Hg(NO_3)_2 \rightarrow Hg(CNS)_2 + 2NH_4NO_3$$

HCl or chlorides, and Ag, must be absent, and all the mercury must be in the mercuric state. The method can be used in the presence of Pb, Cu, Bi, Cd, Sn, As, Sb, Tl, Fe, Zn, Mn, Ni, Co.

Prepare a solution of bivalent mercury containing approximately 10 ml. of HNO_3 or 5 ml. H_2SO_4 per 100 ml., and no Cl, Pd, or Ag. Add a 5% $KMnO_4$ solution dropwise with stirring until a red colour of MnO_2 persists for 5 minutes. Destroy the excess by the careful addition of a ferrous sulphate solution. Add 2 ml. of a saturated ferric alum solution for every 100 ml. of sample and titrate with 0·1 or 0·01N. ammonium thiocyanate until a distinct pink persists after vigorous shaking. Since the colour is removed rather slowly as the end point approaches, under-titration must be avoided.

A 0·1N. NH_4CNS solution is made by dissolving 7·4 gm. NH_4CNS in water and diluting to 1 litre. 1 ml. of 0·1N. NH_4CNS = 0·01003 gm. Hg. The thiocyanate is best standardized against a weighed portion of pure dry mercury which has been dissolved in warm 1:1 HNO_3 and carried through the method. The thiocyanate may also be standardized against silver nitrate as described under methods for silver. Forty ml. of a standard silver solution containing 0·01079 gm. Ag per ml. are measured carefully into a beaker and diluted to about 100 ml. Two ml. of ferric alum indicator are added and the solution titrated with the NH_4CNS solution to the appearance of the permanent faint red colour. Ferric alum is made by dissolving enough ferric ammonium sulphate or ferric sulphate to make a saturated solution, and then adding enough pure colourless HNO_3 to clear the solution and produce a pale yellow colour.

SPECIAL PROCEDURES

1. Small quantities of mercury may be determined with dithizone.[1, 5]

2. Mercury vapour detectors are marketed by the General Electric Company to determine 0·004 to 0·37 parts per million by volume with an accuracy of approximately 5%. The toxic limit for continual breathing is 1 mg. of mercury vapour in 10 cubic metres of air.

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MOLYBDENUM

MOLYBDENUM occurs in ores, irons and steels, alloys and reagents, and its determination is frequently required in industrial laboratories. Molybdenum may be separated from succeeding groups by precipitation with H_2S in acid solution. It is isolated from Pb, Cu, Cd, and Bi by digestion of the sulphides in Na_2S and NaOH, in which molybdenum dissolves. Copper may be separated from molybdenum by adding NaOH to a solution of the sulphates, when copper and iron go into the precipitate, molybdenum remaining in the filtrate. Copper may also be separated from molybdenum by precipitation on aluminium, molybdenum not depositing on the latter. Molybdenum may be separated from tungsten by precipitation of MoS_3 in presence of tartaric acid.

Arsenic and antimony may be removed by distillation or by a ferric hydroxide precipitation. Precipitation of trivalent iron with NH_4OH, followed if necessary by solution and re-precipitation, serves to separate the following elements from molybdenum: As, Sb, Sn, Bi, Se, Te, P, as well as Fe, Al, Ti, Cr, U, V, Nb. Copper, nickel and cobalt accompany molybdenum. Molybdenum is partially deposited with copper from a nitric-sulphuric electrolyte but a re-deposition will eliminate it.

It has been demonstrated [8] that only 80–90% of molybdenum is extracted by an ether separation when the element is alone, if other alloying elements are present, or if about 1 gm. of iron is present. With 5 gm. or more iron present the extraction can be increased to 97%.

GENERAL PROCEDURES

1. Determination of molybdenum by α-benzoin oxime, $C_6H_5.CHOH.C:NOH.C_6H_5$.

This method is adapted to the determination of molybdenum in almost all substances and few elements interfere.[1] The following are not precipitated: Se, Te, Ag, Pb, Hg, Bi, Cu, Cd, As, Sb, Sn, Al, Fe, Ti, Zn, Cr^{III}, V^{IV}, Ce, U, Ni, Co, Mn, Zn, Pt metals except Pd.

Decompose a weight of sample, which will give not more than 0·15 gm. molybdenum, with HNO_3, HCl, and HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Filter and wash thoroughly with hot 1% H_2SO_4. To make sure all molybdenum is in the hexavalent state, add sufficient 0·1N. $KMnO_4$ to give a permanent pink colour to the solution. If vanadates or chromates are present, add sufficient freshly prepared H_2SO_3 to reduce them, heat to boiling, and boil to remove all SO_2. Cool the solution to a temperature of 10° C. An adjustable level cooling trough,[9] to which ice can be added, is convenient for this.

Slowly add, with stirring, 10 ml. of a solution of 2 gm. α-benzoin oxime in 100 ml. of alcohol and 5 ml. extra for each 0·01 gm. molybdenum present. Continue to stir the solution, add just enough bromine water to tint the solution a pale yellow and then add a few ml. of the benzoin oxime reagent. Allow the beaker and contents to remain in the cooling bath 10–15 minutes with occasional stirring, add a little paper pulp, and filter through No. 40 Whatman paper. Wash the precipitate with 200 ml. of a cold, freshly prepared solution containing 25–50 ml. of α-benzoin oxime solution and 10 ml. H_2SO_4 per litre. If sufficient reagent has been employed the filtrate will deposit needle-like crystals. $3C_{14}H_{13}O_2N + Mo(SO_4)_3 \rightarrow (C_{14}H_{11}O_2N)_3Mo + 3H_2SO_4$ is the probable reaction period.

Transfer the precipitate and paper to a weighed platinum crucible and cautiously dry. Char, without flaming, and ignite in a muffle at 500–525° C. to constant weight. If the MoO_3 contains no impurities except tungsten it should dissolve completely in warm dilute NH_4OH. Treat the ignited residue with 5 ml. NH_4OH, digest, and filter through a small paper. Wash

well with 1% NH_4OH. Ignite the paper and contents in the original crucible, cool and weigh. The difference in weight represents the MoO_3 present.

If tungsten is present, the ammoniacal filtrate should be treated as follows. Add 5 ml. 1:1 H_2SO_4 and evaporate to fumes of SO_3. Cool, dilute to 25 ml. with water, add 1–2 ml. cinchonine solution containing 125 gm. cinchonine dissolved in 1000 ml. 1:1 HCl. Digest at 80–90° C. overnight. Filter through Whatman No. 40 paper containing a little paper pulp, and wash with cinchonine wash solution containing 30 ml. of the cinchonine solution diluted to 1000 ml. Transfer the paper and contents to a platinum crucible, char the paper, and ignite at 750–850° C. to constant weight. Cool, weigh, and subtract from the weight of MoO_3 obtained previously.

$$MoO_3 \times 0{\cdot}6667 = Mo$$

It is well to remember that molybdenum sulphide when ignited to oxide even at a low temperature in a muffle will fuse with the glaze of porcelain crucibles.

For accurate work in the presence of tungsten the following procedure recommended by the Climax Molybdenum Company should be followed.[2, 3]

Place the weighed sample in a small beaker and add 10 ml. H_2O and 30 ml. of HCl. Heat below boiling until the evolution of hydrogen ceases, which will require from 15 minutes to 1 hour. Tungsten separates as a black powder containing a large amount of carbides. Add nitric acid cautiously to the hot solution, a few drops at a time. When the action is over add 5–10 ml. more and then boil down to 10–15 ml. but not to dryness. The precipitate should be yellow with no trace of dark metallic tungsten. If it is not, add more HCl and a little HNO_3 and continue boiling. Add 50 ml. H_2O, heat for a few minutes and filter off the tungstic acid through a Whatman No. 42 filter paper. Wash with hot 5% HCl until all iron salts are removed, then with hot 1% ammonium nitrate solution to remove the acid. The precipitate very easily becomes colloidal and runs through the filter; it must, therefore, never be washed with pure water.

This precipitate may contain all of the tungsten, but frequently

a little remains in the filtrate as colloidal tungstic acid. In a sulphuric or perchloric acid solution, especially where considerable ferric or alkali salt is present, a very appreciable amount usually remains in solution and cannot be recovered by the usual methods. It is important, therefore, to use only HCl and HNO_3 solutions. Evaporate the filtrate and washings to dryness, take up with a little concentrated HCl, and when the salts have dissolved, dilute, filter, and wash as before. Reserve the filtrate and washings for the Mo determination.

Add the paper to the main precipitate and burn off the carbon in a weighed platinum crucible at a low red heat. The tungstic oxide will contain all of the SiO_2, sometimes chromic oxide, vanadium pentoxide, and MoO_3. If any WO_3 adheres to the beaker, it may be removed by wiping with a piece of ashless filter paper moistened with concentrated NH_4OH, this paper being ignited with the main precipitate.

If a silica determination is not desired, the precipitate need not be weighed. Add 1 ml. HF, 1 drop H_2SO_4, and evaporate very carefully to dryness. Then raise the temperature until no more SO_3 fumes are given off. Heat to 525° C. for 5 minutes, cool, and weigh as the combined $WO_3 + MoO_3 + Fe_2O_3 + Cr_2O_3 + V_2O_5$. Fuse with 1 or 2 gm. Na_2CO_3 in an open crucible for 5 minutes with free access to air to oxidize Cr_2O_3 to sodium chromate. Dissolve in water, filter through a small paper, using a little paper pulp, wash thoroughly and ignite the residue in the same platinum crucible. The difference between the two weights is the weight of $WO_3 + Cr_2O_3. + MoO_3$. If the filtrate is yellow, the chromium is estimated colorimetrically by comparison with a standard solution of potassium bichromate. The V_2O_5 in the tungstic acid precipitate is usually small and except for extreme accuracy is ignored.

The tungstic oxide precipitate is always contaminated with molybdenum if the latter is present in the steel. The filtrate from the sodium carbonate fusion is diluted with water to 250 ml. in a volumetric flask and 50 ml. aliquot portions transferred with a pipette into a separatory funnel. Five ml. H_3PO_4 and 20 ml. $HClO_4$ are added. The coloured molybdenum thiocyanate complex is then formed by the addition of NaCNS and $SnCl_2$, and extracted with butyl acetate as described in the colorimetric

method. Comparison is made with a standard of suitable molybdenum content.

To the reserved filtrate from the tungsten precipitation add 15 ml. H_2SO_4 and evaporate to fumes. Cool, dilute with water and warm until salts are in solution. Cool to 20° C., reduce Cr and V with ferrous sulphate and continue with the precipitation of molybdenum as described under the procedure for molybdenum with tungsten absent.

If it is suspected that some tungsten is still in solution in spite of the precautions taken for its complete removal, it may be recovered as follows:

The ignited and weighed molybdenum precipitate is dissolved in 10 ml. of 10% NH_4OH and any insoluble residue filtered off. To the filtrate add 5 ml. HNO_3 and evaporate to dryness. Take up in 5 ml. HCl and dilute to 25 ml. Add 1 ml. cinchonine solution and digest at room temperature for 1 to 2 hours or preferably overnight, stirring occasionally if a precipitate forms. Filter through a Whatman No. 40 paper containing a little paper pulp and wash with cinchonine wash solution. Return the paper to the crucible and ignite as before at 500–525° C. Cool and weigh. Any tungsten recovered here is deducted from the weight of MoO_3 and added to the weight of WO_3 previously determined. The molybdenum found colorimetrically in the first tungsten precipitate is added to the molybdenum found gravimetrically.

When carefully performed and all necessary corrections have been made, accurate determinations of silicon, tungsten, and molybdenum can be made on one sample.

NOTES

(*a*) Precipitation of molybdenum by alpha benzoin oxime succeeds best in a sulphuric acid solution containing 5–10% by volume. Solutions of 5% by volume HNO_3, HCl, or H_3PO_4 are also satisfactory but the sulphuric acid solution is preferred. Tartaric and hydrofluoric acids must not be present. According to Climax Molybdenum Company, precipitations made from perchloric acid solutions gave somewhat low results.

(*b*) The precipitation must be done in a cold solution to avoid reduction of the hexavalent molybdenum before precipitation is complete.

(*c*) Low results are obtained if the precipitate is not filtered rapidly. Filtration should be completed within 0·5 hour after precipitation.

2. Volumetric method with Jones reductor and $KMnO_4$

In this method molybdenum is reduced by zinc in a Jones reductor and oxidized with a standard $KMnO_4$ solution. The solution must be free of elements like Fe, As, Sb, Ti, V, U, W, etc., which are also reduced by zinc and afterwards oxidized by $KMnO_4$.[4, 5, 6]

Weigh out a sample sufficient to give 0·2–0·3 gm. Mo and decompose with HCl, HNO_3, and HF if necessary. Add 20 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, add hot water, and filter off SiO_2 and $PbSO_4$.

If iron is not present in the sample add sufficient ferric sulphate to provide 10 times as much iron as there is arsenic present. Add NH_4OH and make two $Fe(OH)_3$ precipitations, combining the filtrates which contain nearly all the molybdenum. For very accurate work the small quantity of molybdenum present in the final $Fe(OH)_3$ precipitate may be determined colorimetrically according to the method given below under 3.

Add to the ammoniacal filtrate 2 gm. tartaric acid and saturate the warm solution with H_2S. Filter off the precipitated MoS_3 and wash well with acidulated H_2S water. The MoS_3 is dissolved off the paper with hot HNO_3, H_2SO_4 is added, and the solution is taken to strong fumes of SO_3 to remove all traces of organic matter or HNO_3. Cool, add water, and adjust the acidity to about 5% H_2SO_4. Add a few grams of granulated zinc and heat gently until the molybdenum is reduced. This preliminary reduction in an open beaker serves to decrease the danger of incomplete reduction later in the Jones reductor, and also to precipitate any copper which may be present and would otherwise coat the zinc in the reductor.

Place in the receiving flask of the reductor a 5-fold excess of a standard solution of ferric sulphate. The latter solution is made by dissolving 60 gm. ferric sulphate and 25 ml. H_2SO_4 in water, adding 150 ml. of 85% H_3PO_4, and diluting with water to 1 litre. 1 ml. of this solution is equivalent approximately to 0·01 gm. Mo,

and it is standardized by passing a measured volume through the reductor and titrating with standard $KMnO_4$.

Connect the receiving flask to the reductor and pass the molybdenum solution through it at the rate of 20–30 ml. per minute, receiving the reduced solution beneath the surface of the ferric sulphate solution. The rate of passage of the solution may be regulated by the use of a filter pump attached to the filtering flask used as a receiver. When the funnel which forms the inlet of the reductor is nearly but not entirely empty, 150 ml. of cold water are put through in successive 25 ml. portions, the liquid being drawn down almost to the constriction each time before addition of the next 25 ml. portion. No air is thus drawn through the reductor.

The molybdenum solution is green as it passes through the lower part of the reductor, but on coming in contact with the ferric phosphate it is changed to a bright red due to its immediate partial oxidation, which is accompanied by the reduction of a corresponding amount of the ferric salt to the ferrous condition. The solution in the receiver is immediately titrated with 0·1N. $KMnO_4$ solution to a faint permanent pink.

$$2H_2MoO_4 + 3Zn + 6H_2SO_4 \rightarrow Mo_2(SO_4)_3 + 3ZnSO_4 + 8H_2O$$

$$3Fe_2(SO_4)_3 + Mo_2(SO_4)_3 + 8H_2O \rightarrow 6FeSO_4 + 2H_2MoO_4 + 6H_2SO_4$$

$$5Mo_2(SO_4)_3 + 6KMnO_4 + 16H_2O \rightarrow 10H_2MoO_4 + 6MnSO_4 + 6H_2SO_4 + 3K_2SO_4$$

A blank is always run on the reductor by passing through dilute H_2SO_4 of the same volume and concentration as the molybdenum solution and titrating with $KMnO_4$.

The number of ml. of $KMnO_4$, less the blank, gives a measure of the quantity of molybdenum present. 1 ml. of 0·1N. $KMnO_4$ = 0·0032 gm. Mo.

3. Determination of molybdenum colorimetrically

Transfer the sample containing less than 0·001 gm. Mo to a small flask. Add 10–20 ml. 60% $HClO_4$, boil, and fume until all carbonaceous matter has been destroyed.[7] Cool, add 25 ml. water, and boil several minutes to expel free chlorine.

Add 2 gm. tartaric acid and a slight excess of 10% NaOH.

Heat at 80° C. for a few minutes. Neutralize with 1:1 H_2SO_4 and then for each 8 ml. of solution add an excess of 2 ml. 1:1 H_2SO_4. Cool to room temperature and transfer the solution to a 250 ml. separatory funnel, rinsing out the flask with 10% H_2SO_4. Add 10 ml. of a 5% solution of NaCNS. Shake vigorously for 30 seconds, treat with 5 ml. of the $SnCl_2$ solution and shake well for 1 minute. Cool to room temperature, add 20 ml. of treated butyl acetate or 50 ml. of treated ethyl ether, stopper, and shake well. For statisfactory colour comparisons the concentration of molybdenum should not exceed 0·05 mg. per ml. of solvent.

The stannous chloride reduces the iron to the ferrous state and the molybdenum from the hexavalent to a lower state, possibly a quinquevalent. Sodium thiocyanate then reacts with reduced molybdenum to form a complex sodium molybdenum thiocyanate, perhaps $Na_3Mo(CNS)_6.xH_2O$, which gives an amber to red colour to the ether or butyl acetate layer.

Allow the extract to separate and draw off the lower layer which may be discarded. Transfer the extract to a Nessler tube or colorimeter and compare with a standard similarly carried through all steps of the procedure. On very low molybdenum materials it is preferable to add another portion of NaCNS and $SnCl_2$, mix in the separatory funnel, and again extract. If the extract is turbid it can be filtered through a layer of glass wool. The standard steel may be prepared by adding portions of a standard molybdenum solution to a Mo-free steel, or a standard molybdenum steel may be used.

Solutions

Stannous chloride. Transfer 350 gm. $SnCl_2.2H_2O$ to a 500 ml. Erlenmeyer flask, add 200 ml. of 1:1 HCl, and boil gently until solution is practically complete. Transfer the solution to a 1-litre bottle, dilute to 1000 ml. with freshly boiled water, add a few pieces of metallic tin, and stopper.

Butyl acetate. Saturate technical butyl acetate with NaCNS and $SnCl_2$ by shaking, and keep in a dark bottle.

Standard molybdenum solution. Dissolve 0·5 gm. of pure $Na_2MoO_4.2H_2O$ in 1000 ml. of water containing 5 ml. of H_2SO_4, and standardize by reducing 100 ml. of the solution in a Jones reductor and titrating with $KMnO_4$. Each ml. of the solution

should contain approximately 0·0002 gm. Mo. The standard solution may also be made from a Bureau of Standards sample.

The Climax Molybdenum Company, through its London or New York offices, is always available for suggestions in any special problem of molybdenum analysis.

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NICKEL

NICKEL, owing to its widespread use in metals and alloys, is a very common element in a metallurgical laboratory. As a general rule it may be determined volumetrically with KCN, gravimetrically with dimethylglyoxime, or electrolytically, with only one or two separations. The method employed will depend on the quantity of nickel present and the degree of accuracy desired.

Nickel is separated from members of preceding groups by precipitation of the latter with H_2S in acid solution, and from Ca, Ba, Sr, Mg, Na, K, etc., by precipitation of nickel in $(NH_4)_2S$ solution. All copper must be removed prior to the volumetric or electrolytic determinations, and if more than 2–3% copper is present it is preferable to remove it before a dimethylglyoxime separation of nickel, otherwise several re-precipitations of the nickel dimethylglyoxime are necessary. Cobalt, if present, will be titrated with nickel in the KCN volumetric procedure, and weighed with nickel in the electrolytic method. In the presence of tungsten a turbidity is obtained in nickel determinations, and it is best to filter off any tungstic oxide resulting from the initial decomposition of an alloy with HNO_3, before proceeding with the analysis. Chromium can be separated from nickel by several additions of HCl to a perchloric acid solution of the alloy until brown fumes of chromyl chloride are no longer given off.

GENERAL PROCEDURES

1. Determination of nickel with dimethylglyoxime

This reagent is almost specific for nickel, and is suitable for a wide range of products.[1, 3, 4, 5, 7] The precipitate is very voluminous, so that the method is particularly useful for small

quantities of nickel, i.e. less than 0·05 gm. nickel or 5% on a 1 gm. sample. Larger quantities are difficult to collect and wash on a Gooch crucible, but often it is convenient to precipitate amounts as large as 0·25 gm. nickel with dimethylglyoxime, filter on Whatman No. 40 paper, dissolve off with dilute HNO_3, and re-precipitate once or twice to free occluded salts. The precipitate may then be dissolved in dilute HCl or HNO_3 and titrated with KCN, or it may be taken to fumes with H_2SO_4 to destroy all HNO_3 and organic matter, and electrolysed.

Weigh out an amount of sample containing less than 0·05 gm. nickel and dissolve in 10–20 ml. HNO_3, 10–20 ml. HCl, and a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. If desired, acid-insoluble products such as oxide and silicate slags can be fused directly in Pyrex "copper" flasks with $NaHSO_4$. Sulphide ores or concentrates should be treated with a few drops of bromine or a chlorate prior to addition of HNO_3. Irons or steels can be dissolved in HCl or HNO_3, and $HClO_4$ used in place of H_2SO_4 to dehydrate SiO_2.

Add hot water, boil, and filter off SiO_2, etc., through Whatman No. 40 paper, washing thoroughly with hot water. If copper is the only Group 2 metal it may conveniently be removed and determined by electrolysis after adding 1–2 ml. HNO_3 to the sulphuric acid solution. If other Group 2 elements are present in considerable quantity they should be removed, together with copper, by adjusting the acid concentration of the filtrate to 5–10% H_2SO_4 and passing in H_2S until all are precipitated. Filter and wash well with acidulated H_2S water. Boil the filtrate to expel H_2S and oxidize the solution with H_2O_2, or HNO_3 + $KClO_3$, followed by vigorous boiling, to transform all iron to the ferric state. Small quantities of copper below 2 per cent. do not materially affect the dimethylglyoxime precipitation, but larger amounts necessitate re-precipitations and a better practice is to remove this element, with others of that group, at the start.

To the oxidized solution containing nickel is now added 5–20 ml. of a 25% tartaric or citric acid solution to prevent the precipitation of the hydroxides of Fe, Al, Cr, etc., when the solution is made ammoniacal. It requires about 3 gm. or 12 ml. of a 25% solution of tartaric acid to hold 1 gm. of iron in solution. A further 5–10 ml. of 10% solution of NH_4Cl is added to keep zinc

and manganese in solution. In the absence of these this step can be omitted. The solution is now made faintly ammoniacal with NH_4OH, and if it does not remain perfectly clear, the solution is just reacidified with HCl and additional tartaric acid or NH_4Cl added, followed by ammonia. If a precipitate still forms at this stage it must be removed by filtration through a Whatman 42 paper.

To the clear, faintly ammoniacal solution is added, with stirring, sufficient 1% alcoholic solution of dimethylglyoxime to precipitate all the nickel. Usually 10 ml. of a 1% dimethylglyoxime solution will precipitate completely 0·01 gm. nickel. The solution is now made distinctly ammoniacal and allowed to stand in a warm place for an hour. For very small quantities of nickel it is necessary to allow the samples to stand overnight. Where large quantities of cobalt are present it is better to precipitate nickel in the presence of a sodium or ammonium acetate solution with dimethylglyoxime. After the addition of tartaric acid to hold up iron, make just ammoniacal, then make acid with acetic, add dimethylglyoxime and make ammoniacal. To reduce the salt concentration it is often advisable to electrolyse cobalt and nickel together and determine the latter on the dissolved plating with dimethylglyoxime.

Dimethylglyoxime sodium salt, which is soluble in water to the extent of 20 gm./100 ml., may be used in place of the 1% alcoholic solution if desired. It has obvious advantages where an alcoholic solution is undesirable or where large quantities of nickel must be precipitated.

Filter on a weighed Gooch crucible containing an asbestos mat previously washed with HCl and water. Wash thoroughly with hot water. Small quantities of the scarlet precipitate of nickel dimethylglyoxime sometimes adhere tightly to the side of the beaker and must be removed carefully with a policeman. Dry in an oven for 1–2 hours at 110° C., cool in a desiccator, and weigh.

$$\text{Wt. of nickel dimethylglyoxime} \times 0{\cdot}2031 = \text{Ni}$$

Bismuth is precipitated by dimethylglyoxime in ammoniacal solution, but the presence of tartrate inhibits this precipitation. If bismuth is not removed prior to the precipitation of nickel, tartaric acid must therefore be added even if Fe, Al, etc., are

absent. Palladium is precipitated by dimethylglyoxime in acid or ammoniacal solution, and platinum and gold tend to co-precipitate. On the rare occasions when these elements are present they may be removed with H_2S in acid solution prior to the nickel precipitation.

If more than 2% Cu, Co, or Mn are present it is best to dissolve the first nickel dimethylglyoxime precipitate in dilute HCl or HNO_3, and re-precipitate with NH_4OH. The precipitate should be scarlet, and a dark red colour indicates the presence of co-precipitated impurities.

For very small quantities of nickel in the presence of large amounts of iron it is often desirable to get rid of nearly all the iron with an ether separation before determining nickel with dimethylglyoxime. Details of the ether separation are given later under *Determination of Nickel Electrolytically*. Nickel can be separated from iron and aluminium by precipitation of the latter as hydroxides in ammoniacal solution, but if any appreciable quantity of iron or aluminium is present several re-precipitations are necessary and the bulk of the resulting solutions may be considerable. The dimethylglyoxime precipitation is more rapid and satisfactory after the removal of iron with ether, NH_4OH, ZnO, or phosphate, but in industrial work iron and aluminium are generally held in solution with tartaric or citric acids. A large excess of NH_4OH must be present when separating nickel from iron by several precipitations of $Fe(OH)_3$. This is undoubtedly the main explanation for the greater ease of separation of iron than aluminium.

In the absence of iron or aluminium the mineral acid is neutralized with NH_4OH, acetic acid is added to bring it back well on the acid side, and then NH_4OH added till the solution is ammoniacal. This is for the purpose of having ammonium acetate and acetic acid present if all the NH_4OH were driven off by standing in a warm place overnight. Under these conditions the nickel dimethylglyoxime will not go back into solution as it would do if only mineral acid were present after the disappearance of free NH_4OH. Tartaric or citric acids serve the same purpose. A large excess of NH_4OH is to be avoided, but the solution should be well on the ammoniacal side.

$$NiCl_2 + 2\{HNO:(CH_3)_2C.C(CH_3):NOH\} + 2NH_4OH \rightarrow$$
$$Ni\{ON:(CH_3)2C.C(CH_3):NOH\}_2 + 2NH_4Cl + 2H_2O$$

2. Determination of nickel volumetrically with KCN

This method is an excellent routine procedure for nickel in the absence of cobalt or where the small quantities of the latter are counted as nickel.[1, 3, 4, 5] Copper must be removed prior to the determination. Iron and aluminium are held in solution by citric or tartaric acid. In the hands of an experienced chemist good results are obtained on products ranging from tailings of 0·2% to mattes of 50% nickel. Two concentrations of KCN are commonly employed, one having a strength of 1 ml. = 0·005 gm. Ni, and the other 1 ml. = 0·01 gm. Ni.

Weigh out 0·5–5 gm. depending on the nickel content, and dissolve in 10–20 ml. HNO_3, 10–20 ml. HCl, and a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. If desired, refractory products like oxide or silicate slags can be fused directly in Pyrex "copper" flasks with $NaHSO_4$. Irons or steels may be dissolved in HCl or HNO_3 and the SiO_2 dehydrated by fuming strongly with $HClO_4$. High sulphide products should be digested in the cold with a little bromine or chlorate solution prior to the addition of HNO_3.

Filter off the dehydrated silica and wash thoroughly with hot water. If copper is to be removed by electrolysis in sulphuric acid solution add 1–2 ml. HNO_3 per 100 ml. solution, electrolyse, and place the solutions on the hot plate to boil after adding 1–3 ml. additional HNO_3 and a spoonful of $KClO_3$. If copper is to be removed by H_2S, adjust the acidity to 5–10% H_2SO_4 and gas out all copper. Filter, wash thoroughly with acidulated H_2S water, boil out all H_2S from the filtrate and oxidize with nitrochlorate or H_2O_2 by boiling on the hot plate for 10 minutes.

To the nickel solution, free of copper but containing Fe, Al, etc., add enough citric acid, tartaric acid, ammonium citrate, sodium citrate, or similar substance to hold all the iron and aluminium in solution after making ammoniacal. Where large numbers of nickels are determined volumetrically a sodium citrate solution is made by cautiously mixing 1300 gm. citric acid with 1250 gm. Na_2CO_3 in 5 litres of water. This is equivalent to about 570 gm. sodium citrate per litre, and from 10–60 ml. of this solution is added to the sample, depending on the quantity of iron to be held in solution. Add exactly 5 ml. of a silver nitrate solution

containing 1 gm. per litre, and if a silver chloride turbidity derived from the $KClO_3$ added previously does not form, add a drop of HCl.

Just clear the turbidity by the cautious addition of NH_4OH, stirring constantly, and add 2–4 drops excess. This must be done very carefully since an excess of NH_4OH causes low results. Place in cooling trough[10] and cool below 20° C. Add exactly 5 ml. KI solution, containing 80 gm./litre KI, and titrate carefully with standard KCN to the disappearance of turbidity. This should be done over a black background with vigorous stirring.

A standard solution of KCN is made by weighing out 23 gm. KCN per litre, adding a few sticks of KOH, and titrating against 1 gm. nickel ammonium sulphate which contains 0·1485 gm. Ni. The value of the latter may be checked by electrolysis. A KCN solution having a value of 1 ml. = 0·005 gm. Ni should take 29·70 ml. + 0·20 ml. for blank, or a total of 29·90 ml. KCN for this quantity of nickel ammonium sulphate. The nickel ammonium sulphate should be carried through all the steps of the determination, and a blank should also be run at the same time. The latter usually is in the neighbourhood of 0·20 ml. KCN of this strength.

If desired, a solution of $AgNO_3$ of equivalent strength to the KCN may be used in case the end point has been overrun. A solution of KCN having a value of 1 ml. = 0·005 gm. Ni would be equivalent to $AgNO_3$ solution of 29·29 gm. per litre.

The principle of the KCN method is as follows. Nickel ions react with KCN in slightly ammoniacal solution to form a complex anion $\{Ni(CN)_4\}^{=}$. If the solution of the nickel salt contains a precipitate of AgI produced by adding a known amount of $AgNO_3$ and a few drops of KI solution, the turbidity will not disappear until all the nickel has entered into reaction with the KCN.

$$Ni(NH_3)_6Cl_2 + 4KCN \rightarrow K_2\{Ni(CN)_4\} + 6NH_3 + 2KCl$$
$$AgI + 2KCN \rightarrow K\{Ag(CN)_2\} + KI$$

The standard KCN changes slowly and must be standardized at weekly intervals.

For very low amounts of nickel in the presence of large quantities of iron a preliminary ether separation may be employed, since otherwise a recurring turbidity often appears. For slags containing iron and cobalt a very thorough oxidation by boiling with

HNO_3 and $KClO_3$ must be practised, and sufficient sodium citrate added to turn the brownish colour of the solution to a green.

3. Determination of nickel electrolytically

The electrolytic method for nickel is used for large quantities of this element, giving an accuracy greater than can be obtained by the volumetric procedure.[1, 3, 4, 5, 7] Like the latter, however, it gives nickel + cobalt where cobalt is also present, and the two are then separated by determining nickel with dimethylglyoxime when the quantity of nickel is not too high, or cobalt with α-nitroso β-naphthol or colorimetrically where the amount of cobalt is not too great. In both cases it is advisable to dissolve the first precipitate in acid and re-precipitate to obtain nickel free from cobalt, or vice versa. Where large quantities of both nickel and cobalt occur together in an alloy, it may be convenient to isolate these two by an electrolytic separation, followed by a determination of the cobalt potentiometrically. Nickel is thus obtained by difference.

The electrolysis of nickel is carried out in an ammoniacal solution free of copper and nitrates, containing ammonium sulphate and about 40 ml. excess NH_4OH. Decompose a 0·5–5 gm. sample as before with HNO_3, HCl, and HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. If desired, the sample may be fused directly in a Pyrex "copper" flask with $NaHSO_4$. Remove copper either by electrolysis or gassing with H_2S. If copper is to be determined electrolytically it will be preferable to add 1–3 ml. HNO_3 to the sulphuric acid solution prior to electrolysis, and in this case the solution must afterwards be evaporated to fumes of SO_3 to get rid of HNO_3 before making ammoniacal. If only a small quantity of copper is present, or if it is not to be determined, then electrolysis of copper may be carried out in sulphuric acid solution alone, after which the solution is simply neutralized with NH_4OH, an excess added, and nickel plated out in ammoniacal solution. If copper is removed with H_2S it may conveniently be done in 5–10% H_2SO_4 solution, filtering, and washing thoroughly with acidulated H_2S water. Boil out all H_2S and oxidize by boiling with H_2O_2 to get all iron to the ferric state.

Neutralize with NH_4OH and add 40 ml. excess. In the absence

of Fe, Al, etc., place on the electrolytic apparatus and plate out nickel at 2 amperes and 2–2·5 volts on a rotating cabinet for 45 minutes or until completed, or at 0·3–0·5 amperes overnight with stationary equipment. After the solution has become colourless, test for completeness of deposition by withdrawing a few ml. on a test plate and adding 1 ml. of a solution of potassium thiocarbonate. A pink or red colour indicates the presence of nickel. Potassium thiocarbonate is prepared by saturating one half of a 5% solution of KOH with H_2S, adding the other half, and heating moderately with 1/25th of its volume of CS_2. The dark red liquid is decanted from the undissolved CS_2 and kept in a well-closed flask. This is a more specific test for nickel than $(NH_4)_2S$, although Mn and Zn if in appreciable quantities in the solution will obscure the K_2CS_3 tests. Dimethylglyoxime may also be used as a spot test for the end point of electrolysis.

Remove the cathode, rinsing thoroughly in water and alcohol, and dry on a small hot plate, in a blast of hot air from a hair drier, or by careful ignition of alcohol, and weigh as metallic nickel. If cobalt is present, it must be determined by dissolving the deposit on the cathode carefully in boiling HNO_3 and separating cobalt with α-nitroso β-naphthol, or determining cobalt potentiometrically or colorimetrically. The deposited Ni + Co minus the cobalt present gives nickel. Alternatively, and particularly where the nickel content is less than that of cobalt, nickel may be determined in the dissolved plating with dimethylglyoxime.

Where iron or aluminium is present in the solution prepared for the electrolytic determination of nickel, there are several courses open to the analyst. Nickel can be determined by electrolysis in strongly ammoniacal solution in the presence of iron or aluminium. If large quantities of the latter are present, electrolysis is slow owing to the occlusion of nickel in a voluminous precipitate of iron or aluminium hydroxides. All the nickel can be plated out in time, however, but the deposit must be dissolved in boiling HNO_3, taken to fumes of H_2SO_4, and re-plated, since a little iron is always deposited mechanically.

Wherever possible it is advisable to remove iron or aluminium prior to electrolysis. If small quantities of iron are present, two separations with NH_4OH, using a considerable excess of ammonia, will free the precipitate of nickel. For large quantities of iron,

and particularly for aluminium, which retains nickel tenaciously, three or four precipitations are often necessary. In this method of separation the solution is made strongly ammoniacal, boiled briskly for several minutes, filtered on a Whatman No. 31 or 531 paper and washed several times with hot water. The precipitate is transferred back to the original beaker, dissolved in 1:1 H_2SO_4, re-precipitated with NH_4OH, and again boiled, filtered, and washed. The bulk of the filtrate should be kept as low as possible to avoid tedious evaporation later to a volume suitable for electrolysis. When the filtrate no longer appears pale blue, and in addition another re-precipitation shows absence of nickel by $(NH_4)_2S$ or K_2CS_3 test, separation of nickel from iron and aluminium may be assumed to be complete.

Where iron alone is present with nickel, as in irons and steels, it may be removed prior to electrolysis by an ether separation.[5] When the sample has been completely dissolved in acids and taken to dryness with H_2SO_4, HCl is added and the solution evaporated to a syrupy consistency. The contents of the beaker are transferred to a separatory funnel, rinsing out the beaker several times with HCl of s.g. 1·10 and finally several times with ether. Add more ether to give a concentration of 30 ml. ether per 1 gm. of iron in 20 ml. HCl solution. Shake vigorously under a cold-water tap, allow to settle, and draw off the lower layer containing the Ni, Co, etc., into a 400 ml. beaker. Hydrochloric acid of s.g. 1·10 is made by mixing 526 ml. concentrated HCl with 474 ml. water. For very accurate work a second separation of the traces of nickel present in the upper iron layer must be made. Evaporate the ether cautiously on the edge of the hot plate, add HNO_3 and $KClO_3$, 10 ml. 1:1 H_2SO_4, and take to strong fumes of SO_3. If copper has not been removed previously, separate it by electrolysis or H_2S and carry out the electrolysis of nickel in ammoniacal solution as described above.

A third method of isolating nickel for electrolysis, and in some ways the most accurate, is to precipitate the element in the presence of Fe, Al, etc., with dimethylglyoxime, filter, dissolve the precipitate in hot dilute HNO_3, add 10 ml. 1:1 H_2SO_4, take to fumes of SO_3 and proceed with the electrolysis in ammoniacal solution.[7] This method is naturally only used where a very large precipitate of nickel dimethylglyoxime, which cannot be readily

weighed directly, is formed. Add sufficient dimethylglyoxime to precipitate all the nickel, and follow out directions previously given for this procedure in the presence of Fe, Al, Cr, etc. Allow the precipitate to settle for 30 minutes in a warm place, filter on a large No. 40 Whatman paper and wash 4–5 times with hot water. Test the filtrate with dimethylglyoxime for completeness of precipitation. Transfer the precipitate to the original beaker and dissolve all the nickel dimethylglyoxime off the paper with hot dilute HNO_3, catching it in the beaker containing the precipitate. Add more dilute hot HNO_3, if necessary, to dissolve the precipitate, add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. To destroy all traces of organic matter it may be necessary to add more HNO_3, a little $KClO_3$, and again take to fumes of SO_3. Cool, neutralize with NH_4OH and add 40 ml. excess. Electrolyse nickel as described above. In this case, of course, the deposit of nickel does not contain any cobalt. This is a handy procedure where fairly large concentrations of nickel occur together with considerable quantities of cobalt and iron.

When nickel is plated overnight it is advisable in the morning to add another 10 ml. NH_4OH and increase the amperage from 0·3–0·5 up to 1 ampere for 15 minutes before testing the solution for complete deposition. After taking off the cathodes, the solutions before discarding should be finally tested by adding a few ml. of 1% dimethylglyoxime solution. The solutions should remain colourless or show merely a faint yellow tinge.

The deposit of nickel on a platinum cathode, unlike copper, is not removed by immersion for a few seconds in cold HNO_3. The cathodes should be boiled in HNO_3 for 5–10 minutes after a nickel electrolysis. If a cathode remains dark after this treatment it is due to carbon. Ignite over a gas flame in the oxidizing zone for a few minutes.

SPECIAL PROCEDURES

1. Iron may also be removed from nickel by a precipitation with phosphate as described under Cobalt.[8] For some samples this is superior to the precipitation with NH_4OH as less nickel is adsorbed.

2. A rapid procedure for the determination of very small quantities of nickel which is sometimes useful is that wherein

nickel is isolated with dimethylglyoxime, extracted with chloroform, transferred to a dilute acid layer and finally titrated with standard dithizone.[9]

3. Another procedure for small quantities of nickel in the presence of large quantities of cobalt and iron is described by Hall and Young.[2]

4. For very small quantities of nickel, as in the purification of zinc electrolyte, the nickel glyoxime may be collected by kerosene or amyl alcohol and the pale pink colour viewed. 100 ml. of a solution containing 0·1 mg./litre imparts a pale pink to the kerosene layer. Cobalt does not interfere. This excellent rapid plant control method is described by Young.[6]

5. Small quantities of nickel in cobalt oxide, iron-ores, etc., can be determined polarographically. Fuse 1 gm. sample with 10 gm. $NaHSO_4$ in a Pyrex "copper" flask, dissolve the melt in 2 ml. HCl and a small quantity of water, and transfer to a 100 ml. volumetric flask. Alternatively, bring the sample into solution with HCl and HNO_3, evaporate to dryness, dissolve in 2 ml. HCl and a small quantity of water, add 8 gm. NH_4Cl, and transfer to the 100 ml. flask.

Add 5 ml. pyridine to the flask. The *p*H should now be 5–5·5, and if not the fusion or evaporation periods were not long enough. Add 1 ml. of 1 per cent. gelatin in water, and make the solution to 100 ml. volume. Centrifuge to precipitate iron, if necessary, and transfer a portion of the decanted solution to the polarographic cell. Pass in nitrogen for three minutes and measure the diffusion current for nickel, comparing it with that of a standard.

6. Low concentrations of nickel in ores can be satisfactorily determined by a colorimetric procedure based on the formation of a wine-red complex, nickelic dimethylglyoxime, when alkaline nickel solutions are oxidized and treated with dimethylglyoxime. Dissolve the samples by acid treatment and evaporate to fumes of SO_3, or fuse with $KHSO_4$, add 20 ml. HCl, 75 ml. water, and boil to solution of salts. Transfer to a 500-ml. volumetric flask and make to volume.

Withdraw a suitable 10 or 25 ml. aliquot to contain approximately 0·05 mg. Ni and transfer to a 100 ml. volumetric flask. Add to the flask 5 ml. 20 per cent. tartaric acid solution or enough

to hold iron in solution, sodium hydroxide solution until the acid is neutralized and then 2–3 ml. excess, and cool to room temperature. Add 0·5–1 gm. potassium persulphate, swirl the flask to dissolve nearly all this salt, add 3 ml. dimethylglyoxime solution and allow two minutes for colour development. Make the flask to volume, shake, and determine the transmittance in a spectrophotometer at a wave length of 530 mμ, or in an electrophotometer with a 525 mμ filter, comparing against a series of known solutions in the usual manner.

The International Nickel Company Inc., 67 Wall Street, New York 5, U.S.A., is always willing to assist chemists having a special problem in nickel analysis.

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NIOBIUM AND TANTALUM

NIOBIUM and tantalum are invariably associated together in minerals, and are occasionally encountered in steels and alloys in industrial laboratories. Methods for their determination are rather long and complicated, especially if many other elements are present. Full details are given in the references cited, particularly in the work of Schoeller and Powell.[3] The following procedure is of general application to ores and alloys, but various shortened modifications may be practised in the absence of some interfering elements.[2, 4] In view of the complexity of the operations, it is recommended that a standard sample of known niobium and tantalum content be invariably included with the unknowns.

GENERAL PROCEDURES

A 0·25 gm. sample of mineral is fused with 3 gm. of $KHSO_4$ in a silica crucible. The melt is warmed in the crucible with 15 ml. of 20% tartaric acid solution until detached and transferred to a 250 ml. beaker with 75 ml. of hot water. After addition of 5 ml. of 10% H_2SO_4 the melt is cautiously dissolved by warming and continuous stirring.

The hot solution is treated with H_2S until cold and set aside for several hours to clear with the addition of a little paper pulp. The solution is filtered, the filtrate containing the iron as ferrous salt is heated to boiling in a 600 ml. beaker, stirred, treated with 25–35 ml. HCl and boiled for 3 minutes. The flocculent white

precipitate containing the bulk of the niobic, tantalic, and tungstic acids is mixed with filter pulp, filtered, and washed with 2% HCl or NH_4Cl. If bulky, it is returned to the beaker with the wash-liquor, thoroughly churned up with 100 ml. of liquid and once more gathered on the same paper. The precipitate is ignited wet in a tared silica or porcelain crucible.

The filtrate from the above precipitation containing the minor earth-acid fraction is concentrated to 50 ml. in an 800 ml. beaker, transferred to a 250 ml. beaker and evaporated on the hot plate to a syrupy consistency. It is diluted to 25 ml., saturated with H_2S, and heated with 5 ml. saturated NH_4Cl solution, excess of NH_4OH, and a few ml. of $(NH_4)_2S$. The precipitate consisting of ferrous and manganous sulphides is collected after settling overnight, and washed with $(NH_4)_2S$ solution.

The filtrate from the sulphide precipitation is acidified with HCl and boiled to expel H_2S. It is then treated with 3 gm. ammonium oxalate and an equal bulk of saturated NH_4Cl solution, and approximately neutralized with NH_4OH using litmus paper. The boiling solution is precipitated with 0·5 gm. tannin in aqueous solution added drop by drop during brisk agitation. The precipitate of minor earth fraction and titania is filtered off and washed with hot 2% NH_4Cl, the filtrate being tested for complete precipitation by boiling and neutralization. This is carried out by evaporation to 300–400 ml., addition of another 0·5 gm. tannin followed by N. NH_4OH added drop by drop to the boiling solution until a slight precipitate is produced. If this is dirty-grey (Zr, Th, Al, Be), mauve (Fe), brown (U), or bluish-black (V), and readily soluble upon re-acidification with N. HCl, the titanium precipitation is complete. If, however, the precipitate still shows an orange tint, more N. NH_4OH is added to complete the precipitation of titanium. In this case the second precipitate is collected and added to the former.

The major earth-acid precipitate and the minor earth acid + titania precipitate are combined and weighed as $(Ta,Nb)_2O_5 + TiO_2$. If tungsten is present in the ore, it also is found in this precipitate and must be separated by the magnesia method.

For the separation of tungsten the mixed oxides are fused with 4–6 gm. K_2CO_3 in a platinum crucible over a blast burner till the melt is clear. After cooling it is dissolved in 150 ml. hot water,

heated, stirred, and precipitated drop by drop with 25–40 ml. of a freshly-prepared slightly ammoniacal solution of 4 gm. crystallized magnesium sulphate and 8 gm. NH_4Cl in 100 ml. water. After settling for 10 minutes on the water bath the white flocculent precipitate of magnesium niobate and tantalate is collected and washed thoroughly with 2% NH_4Cl.

If the quantity of tungstic oxide present exceeds 0·02 gm., it is advisable to repeat the separation. The magnesia precipitate is rinsed back and digested with a little dilute HCl. The suspension is boiled and treated with 5 gm. each of NH_4Cl and ammonium acetate, and a solution of 0·5–1 gm. tannin. The precipitate is mixed with paper pulp, filtered, washed with 2% ammonium nitrate solution containing a little tannin, and ignited in a platinum crucible. The ignited oxides are again treated by fusion with K_2CO_3 and precipitation with magnesia mixture, the second magnesia precipitate being converted into oxides by the procedure just described, and weighed as $(Ta,Nb)_2O_5$.

The filtrate or combined filtrate from the magnesia precipitation contains the whole of the tungstic acid and usually a little niobic acid, unless tantalic acid largely predominates in the oxide mixture. It is treated with 10–20 gm. NH_4Cl and the tungstic and niobic oxides recovered by the tannin-cinchonine method. If the tannin precipitate prior to the addition of cinchonine solution is coffee-brown, and yellow after ignition, its niobium content, if any, is very small. If, on the other hand, it is reddish-brown or even reddish, and pale yellow to white after ignition, it is certain to contain niobium.

The magnesia method separates tungstic oxide, not only from the earth acids, but from titania, zirconia, and complex mixtures of all the earths. A very subordinate amount of tungstic oxide occurs in some tantalites, but it is usually absent or negligible.

Titania is determined in a separate portion in the following manner. A 0·1 gm. sample is fused with 2 gm. $KHSO_4$ in a silica crucible, the melt dissolved in 30 ml. of saturated ammonium oxalate solution, the solution transferred to a beaker, diluted to 75 ml. and treated with an equal volume of saturated NH_4Cl. The earth acids and titania are precipitated with 1·5 gm. of tannin and the filtrate tested for complete precipitation as described previously. The ignited tannin precipitate is once more fused

with bisulphate and brought into solution with ammonium oxalate as before. The resultant colourless solution is treated with 25 ml. of 10% H_2SO_4 and H_2O_2, transferred to a graduated 200 ml. flask, and an aliquot portion, 20 or 50 ml., is tested colorimetrically.

The colour of titanic sulphate in the presence of H_2O_2 is best compared when it is of a deep straw yellow tint, corresponding to less than 0·001 gm. of titania per 100 ml. of test solution. It is bleached by HF even in minute quantity and by large amounts of phosphoric acid and potassium sulphate, but the presence of considerable free H_2SO_4 tends to overcome the interference of the latter, which is present from the bisulphate fusion. Uranium, vanadium, molybdenum, and chromates interfere by giving a colour with the peroxide. Iron interferes if present in quantity; the yellow tint is discharged by H_3PO_4 due to the formation of ferric phosphate, but the acid itself has a slight bleaching effect.

The titanium solution is treated with 5 ml. of H_3PO_4, 5 ml. of 6% H_2O_2, 9 ml. of H_2SO_4, and diluted to 100 ml. in a Nessler tube. A standard tube is prepared with the same quantities of reagents as the unknown, including K_2SO_4, and diluted to nearly 100 ml. A solution of titanium sulphate of known strength is slowly added to the standard from a burette until the colours match. The standard is then diluted exactly to the mark and the colours again matched. Standard titanium solution is prepared by fusing 0·1 gm. of pure titania with 3 gm. $KHSO_4$. The melt is dissolved in 100 ml. of N. H_2SO_4 and the solution is diluted to one litre, giving a value of 1 ml. = 0·0001 gm. TiO_2.

Since titania is determined in a separate portion, it need not be eliminated prior to the separation of niobium from tantalum by the tannin method provided the Ta_2O_5:TiO_2 ratio is well over 50. The separation of tantalum from niobium is based on the fact that the tantalic oxide is more readily precipitated by tannin from slightly acid oxalate solution than any other earth in general and niobic oxide in particular. A clear-cut separation cannot be accomplished in a single precipitation, since tantalum cannot be quantitatively precipitated without appreciable co-precipitation of niobium. A process of fractional precipitation has to be adopted. This can be controlled because the colour of the precipitated tantalum-tannin complex is a reliable indicator of its purity.

The pure tantalum complex is light yellow; the niobium complex which is bright vermilion red possesses strong colouring power, hence a small admixture of niobium imparts an orange colour to the tantalum precipitate.

It will be readily understood that titania should be either absent or very subordinate in amount, since it is partly co-precipitated with tantalum before any niobium is precipitated, and its red tannin complex produces a buff to brownish discoloration of the tantalum precipitate, thus masking the colour changes on which the process wholly depends. If, however, the titania present is well below 2% of the tantalic oxide, the interference is not sufficiently marked to vitiate the results, though the tantalum precipitate will always be dark yellow instead of light yellow. In these cases the quantity of titania in the separated oxides is determined colorimetrically. About 75% of the titania passes into the tantalum fraction.

The fractionation process furnishes three products:

1. Niobium-free tantalum fraction (yellow precipitates).
2. Mixed or intermediate fraction (orange to red precipitates).
3. Tantalum-free niobium filtrate.

The second fraction is re-treated, giving another three fractions, the intermediate one of which is again fractioned. The pure tantalum fractions are ignited together, and the niobium filtrates combined. The tannin precipitates are mixed with a little filter-pulp, and washed with hot 2% NH_4Cl. If bulky, they are collected under slight suction.

The mixed pentoxides containing not more than 0·2 gm. Ta_2O_5 are fused with $KHSO_4$ in a silica crucible and the melt is dissolved in a hot solution of 3–4 gm. ammonium oxalate. The hot solution is filtered into a 600 ml. beaker, any small siliceous residue being ignited and its weight deducted. The filtrate, or combined filtrate, is boiled and treated gradually with 10–15 ml. of a freshly prepared 2% solution of tannin. This will cause the formation of a yellow or an orange to red precipitate. The ignited fractions are re-treated by fusing with bisulphate and repeating the precipitation with tannin. The weight of the combined precipitates representing the tantalum fraction must be corrected for any adsorbed salts and traces of lime, and for titania

and silica. The oxide is leached with 2% HCl, collected, ignited strongly, weighed, and fused with bisulphate. The melt is dissolved in ammonium oxalate solution with the addition of dilute H_2SO_4 and a little H_2O_2. The small residue is filtered, washed, ignited, and weighed. The titania in the filtrate is determined colorimetrically. The weights of the siliceous residue and titania subtracted from the weight of the leached precipitate give the net weight of Ta_2O_5.

Since the niobic oxide is a final product it is usually sufficient to take it by difference. If it is necessary to make a direct determination the combined filtrates obtained in the fractionation are boiled and precipitated with more tannin and a slight excess of ammonia. The precipitate is collected under slight suction, washed with 2% NH_4Cl, ignited, and weighed. As in the case of the tantalum fraction, the weight of the ignited precipitate must be corrected for adsorbed salts, lime, silica, titania, and probably traces of ferric oxide.

SPECIAL PROCEDURE

The following procedure is recommended for niobium and tantalum in stainless steels by Cunningham,[1] who has had long experience in this field.

From 2 to 5 gm. of the sample are transferred to a 600 ml. covered beaker and treated with from 25 to 50 ml. of HCl and 10 ml. of HNO_3 at a temperature of approximately 90° C. When all action appears to have ceased 30–60 ml. of $HClO_4$ are introduced and the solution is boiled until dense fumes of $HClO_4$ are freely evolved, and the boiling continued for about 5 minutes longer to insure the complete conversion of the chromium to chromic acid. Two hundred ml. of hot water, 50–100 ml. of H_2SO_3, and 10 ml. of HCl are introduced and the solution is boiled for 5 minutes. Considerable ashless paper pulp is introduced, the contents of the beaker allowed to digest at a temperature of 60–70° C. for 15 minutes, or until the supernatant liquid is clear, and filtered on an 11-cm. paper containing some ashless paper pulp. The beaker is scrubbed with a filter paper moistened with 2% HCl and added to the filter. The paper and precipitates are washed 12–15 times

with hot 2% HCl, and ignited in a 50 ml. platinum dish at a low temperature to burn off the carbon of the filter paper.

Approximately 5 ml. of HF and 10 ml. of 1:1 H_2SO_4 are introduced, the solution is evaporated to dense fumes of sulphur trioxide and the fuming continued until the volume has been reduced to approximately 2·5 ml. to insure the complete expulsion of all HF. Should the precipitate not dissolve after several minutes' heating, approximately 2 ml. of $HClO_4$ are added and the solution is evaporated as described. If the evaporation is allowed to proceed almost to dryness, any separated niobic or tantalic acids may be dissolved by the addition of several ml. of H_2SO_4 and further heating for 1–2 minutes. The contents of the dish are allowed to cool somewhat and transferred to a 400 ml. beaker by means of about 200 ml. of hot 2% HCl. Any adhering precipitate is removed from the dish by means of an 11-cm. filter paper moistened with 2% HCl, and added to the beaker. About 50 ml. of H_2SO_3 is added, and the solution is boiled for 5 minutes. Some ashless paper pulp is introduced, and the solution is digested at a temperature of 60–70° C. for 15 minutes, or until the supernatant liquid is clear, and filtered on an 11-cm. paper containing some ashless paper pulp and washed 10 times with hot 2% HCl. The precipitate is ignited in a 50 ml. platinum dish, first at a low temperature to burn off the carbon of the filter paper, and finally to constant weight at 1000–1050° C., cooled and weighed. For a control analysis, the weight obtained multiplied by 69·9 and divided by the weight of sample taken, will give the approximate percentage of niobium.

To the ignited and weighed precipitate of $Nb_2O_5 + Ta_2O_5$ is added 0·0500 gm. of pure TiO_2, and the mixture is fused with 2–3 gm. of $K_2S_2O_7$. The dish and its contents are permitted to cool somewhat, 5 ml. of H_2SO_4 are introduced and the heating is continued on a hot plate until a clear solution is obtained. The contents of the dish are allowed to cool partially, transferred to a dry 250 ml. beaker and rinsed successively with three 5-ml. portions of H_2SO_4. The dish is further rinsed with 20 ml. of 5% succinic acid containing 1 ml. of 30% H_2O_2, and the rinsings added to the beaker. The solution is stirred thoroughly, diluted to 100 ml. with cold water, heated to 60–70° C., passed through a Jones reductor into a solution of ferric sulphate and titrated with

a standard solution of potassium permanganate. The niobium and titanium are reduced from $Nb_2(SO_4)_5$ and $Ti(SO_4)_2$ to $Nb_2(SO_4)_3$ and $Ti_2(SO_4)_3$, respectively, whereas the tantalum is not affected. The titanium added serves to prevent hydrolysis of the niobium and tantalum in the reductor. The niobous and titanous sulphates immediately react with the ferric sulphate to form $Nb_2(SO_4)_5$ and $Ti(SO_4)_2$, respectively, and a corresponding amount of ferrous sulphate equivalent to the reduced niobium and titanium.

A Jones reductor having a column of 20-mesh zinc 30 in. long is required. The zinc should be amalgamated by treating 800 gm., of very low iron content, with 400 ml. of a 2·5% mercuric chloride solution in an 800 ml. beaker and stirring vigorously for 2 minutes. The solution is decanted off and the zinc washed with water, transferred to the 30-in. reductor and further washed with hot 2·5% H_2SO_4 and water. The reductor, filled with amalgamated zinc as described, is good for about 6 determinations, when it should be emptied and filled with new zinc freshly amalgamated. Immediately before using the reductor it is well to pass through it 200 ml. of almost boiling water in order to pre-heat the column of zinc. The reductor is then connected to a 1000 ml. suction flask with the delivery tube dipping beneath the surface of 25 ml. of ferric sulphate solution. The latter is prepared by dissolving 100 gm. of ferric sulphate in a solution containing 150 ml. of phosphoric acid, 20 ml. of 1:1 H_2SO_4, and 850 ml. of water. The following solutions are passed through the reductor in the order named: 100 ml. of hot 20% H_2SO_4; the niobium solution, also heated to 60–70° C.; 100 ml. of hot 20% H_2SO_4 containing 1 gm. of dissolved succinic acid; and three 50 ml. portions of cold water. At no time is the funnel that forms the reductor inlet permitted to become entirely empty, and the reductor when idle should always be kept full with distilled water to above the top of the zinc.

The solution is cooled to room temperature by addition of several ice cubes prepared from distilled water, transferred to an 800 ml. beaker and titrated with 0·05N. potassium permanganate solution that has been standardized against sodium oxalate from the Bureau of Standards. One ml. of 0·05N. $KMnO_4$ is equivalent to 0·002323 gm. Nb or 0·002395 gm. Ti. A "blank" of the

reagents and reductor is made by fusing a 0·0500 gm. portion of pure TiO_2 with 2–3 gm. of $K_2S_2O_7$, or the same amount used in the analysis, and carrying through the solution of the melt and its passage through the Jones reductor, all as described in the paragraphs above. The solution is cooled to room temperature and titrated with 0·05N. $KMnO_4$. The total volume of standard 0·05N. $KMnO_4$ solution required, less the "blank" (including 0·0500 gm. TiO_2) is multiplied by 0·002323 and divided by the weight of sample taken to give the per cent. niobium. The weight of niobium found is multiplied by 1·43 to give the corresponding weight of Nb_2O_5. The weight of the total oxides of $Nb_2O_5 + Ta_2O_5$ obtained as described on page 204, less the weight of Nb_2O_5 found, gives the weight of Ta_2O_5, which, multiplied by 81·91 and divided by the weight of sample taken, gives the percentage of tantalum in the steel.

The tantalum content of the total oxides obtained on a 10 gm. sample can also be obtained by fusion with 12 times its weight of $K_2S_2O_7$, and the melt, when cool, is dissolved in 10 ml. of hot 2% ammonium oxalate. The solution is treated with 2 ml. of 1:1 H_2SO_4, diluted to 250 ml. with hot water, and heated to boiling. Four drops of 0·25% solution of bromphenol blue, prepared by dissolving 0·25 gm. of the indicator in 7·5 ml. of 0·05N. NaOH and diluting with cold water to 100 ml., are added, followed by 1:2 ammonia drop by drop until the yellow colour just changes to a distinct purple. This corresponds to a *p*H of approximately 4·6. From 25 to 30 ml. of a freshly prepared 1% solution of tannin are added, followed by 10 gm. of ammonium chloride and some ashless paper pulp, and the solution is gently boiled for at least 15 minutes. The hot solution is filtered on an 11 cm. paper containing some ashless paper pulp, and the paper and precipitate washed from 20 to 25 times with a hot 2% solution of ammonium chloride and ignited in platinum at a low temperature to burn off the carbon of the filter paper. The precipitate is treated in platinum with 5 ml. of 1:1 H_2SO_4 and 1 ml. of HF, the solution evaporated to a volume of 2 ml., cooled and transferred to a 250 ml. beaker by means of 150 ml. of cold 2% HCl. Twenty-five ml. of H_2SO_3 and some ashless paper pulp are introduced, the solution boiled for at least 5 minutes, and allowed to stand for 30 minutes or longer at about 70° C. before filtering. The

precipitate is ignited and weighed. A weight of 0·0200 gm. of pure TiO_2 is added, the mixture fused with 12 times its weight of $K_2S_2O_7$ and the melt dissolved as described on page 204. The solution is passed through the reductor and titrated with standard 0·05N. $KMnO_4$, all as described on pages 204–206. A blank on the reductor and TiO_2 is carried through as described and the difference in volume of permanganate between the sample and the "blank" is the volume equivalent to any Nb_2O_5. The weight of Ta_2O_5 ($+Nb_2O_5$) less the Nb_2O_5 found, multiplied by 81·91 and divided by the weight of sample taken, gives the percentage of tantalum.

Note 1. A modification of this method is necessary for steels containing molybdenum, tungsten, and titanium. Both molybdenum and tungsten lead to high niobium results. Titanium, if present in amounts greater than 0·10% leads not only to a badly contaminated niobium precipitate, but also to incomplete precipitation of the niobium.

Note 2. If desired, the ignited and weighed precipitate of $Nb_2O_5 + Ta_2O_5$, obtained as described on pages 203–204, may be fused with $K_2S_2O_7$ without any TiO_2 addition, the melt dissolved as described on page 204, and the solution passed through the reductor, cooled, and titrated, all as described above. A "blank" in this case is run on the reductor by dissolving 2–3 gm. of $K_2S_2O_7$ in 100 ml. of 2% H_2SO_4 containing the same amounts of succinic acid and H_2O_2 that were used in the analysis, and putting the solution through the reductor as described, cooling and titrating. It is very difficult to obtain complete reduction of niobium by means of a Jones reductor unless titanium is added, but if the directions given are closely followed, the reduction is so nearly complete that the error thus introduced is not significant when dealing with the amount of niobium usually found in a sample of steel.

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NITROGEN

EXCEPT in laboratories where the routine examination of foodstuffs, agricultural products, or waters is carried on, the industrial analytical chemist is not often required to carry out a determination of nitrogen. The element is so common, however, that a laboratory in any industry from time to time receives a request for a nitrogen determination, whether it be in a soil, water, fertilizer, vegetable or animal material, dyestuff or similar organic compound, nitrate, ammonia, nitric acid, etc. Nitrogen in gases is usually determined by difference, after removal of all other constituents by absorbents or combustion, and details may be found in standard references on gas analysis.[4, 7, 9]

In explosives and other specialized laboratories where a great many determinations of nitrogen in nitrates, nitrites, or mixed acids are required, a nitrometer is commonly used. This instrument measures the nitric oxide evolved when H_2SO_4 in the presence of mercury acts on a nitrate:

$$2KNO_3 + 4H_2SO_4 + 3Hg \rightarrow K_2SO_4 + 3HgSO_4 + 4H_2O + 2NO$$

Details of the operation of the du Pont nitrometer are given in standard references on gas analysis.

There are three types of nitrogen determination which the ordinary laboratory may encounter:

1. Total nitrogen.
2. Organic and ammoniacal nitrogen.
3. Nitrate nitrogen.

The standard method for determining nitrogen is to oxidize organic substances with H_2SO_4 in the presence of catalysts and convert the nitrogen to ammonia which is held by the acid as

$(NH_4)_2SO_4$. The ammonia is measured by making the solution alkaline with NaOH, heating, and absorbing the evolved NH_3 in standard acid, titrating the excess of the latter with standard alkali.

Total nitrogen includes, as its name implies, all the nitrogen present in the sample. It is necessary to reduce any nitrates present by adding salicylic acid, zinc dust, etc., prior to the above oxidation process.

Organic and ammoniacal nitrogen does not include nitrates, and the sample is simply oxidized by digesting with H_2SO_4 and carrying out the regular Kjeldahl-Gunning-Arnold method given below. This nitrogen determination is of very great importance since protein is calculated from it. For cereal foods such as wheat flour, bread, macaroni, etc., organic and ammoniacal nitrogen $\times$ 5·7 = protein. In calculating protein of milk and its products the factor used is 6·38. For nearly all other organic substances like hay and fodder crops, fruits, nuts, beer and wine, tea, vegetables, meats, etc., organic and ammoniacal nitrogen $\times$ 6·25 = protein.

The determination of nitrate nitrogen is of importance in agricultural and sanitary chemistry in soils, waters, plants, fertilizers, etc., and is usually carried out colorimetrically with phenoldisulphonic acid.[1, 2]

It is sometimes useful to remember that nitrites can be quickly removed from solution by sulphamic acid:

$$HO.SO_2.NH_2 + HNO_2 \rightarrow H_2O + N_2 + H_2SO_4.$$

1. Total nitrogen

Place 0·5–5 gm., according to the nitrogen content of the material to be analysed, in a Kjeldahl digestion flask. Add 30 ml. H_2SO_4 containing 1 gm. commercial salicylic acid. Shake until thoroughly mixed and allow to stand, shaking frequently, for at least 30 minutes, or until complete solution results. Add 5 gm. $Na_2S_2O_3$ and heat the solution for 5 minutes, cool, add 10 gm. K_2SO_4 or anhydrous Na_2SO_4 and heat very gently until foaming ceases.

Digest for a time after the mixture is colourless or nearly so, or until oxidation is complete, which usually requires 2 hours. Cool,

dilute with about 200 ml. water and add a few pieces of granulated zinc, pumice-stone, or carborundum[6] to prevent bumping.

Add sufficient NaOH, usually 60 ml. of 45% solution, to make the solution strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask to the condenser by means of a Kjeldahl connecting bulb, taking care that the tip of the condenser extends below the surface of the standard 0·1N. H_2SO_4 in the receiver. An adapter to give fine bubbles is usually attached on the end of the condenser.

Mix the contents by shaking and distil until all NH_3 has passed over into a measured quantity of the standard acid. The first 100 ml. of the distillate, which is usually caught in a 300 ml. Erlenmeyer flask, generally contains all the NH_3.

Usually 10–50 ml. of standard acid, diluted with distilled water to a volume of 50–75 ml. in the flask, are employed.

By placing 2–3 drops of methyl red indicator in the standard acid at the outset it is easy to see whether more acid is required. If the sample proves to be high in nitrogen and the colour of the distillate changes from red to a pale yellow before the end of the distillation, more standard acid can be added quickly from a pipette without loss of the determination. The ammonia is held in the aqueous solution fairly well until the saturation point is reached.

Titrate the excess acid with 0·1N. NaOH. From the quantity of acid neutralized by NH_3 the nitrogen content of the sample may be calculated.

$$\begin{aligned} 1 \text{ ml. } 0{\cdot}1\text{N. } H_2SO_4 &= 0{\cdot}001703 \text{ gm. } NH_3 \\ &= 0{\cdot}001401 \text{ gm. N} \end{aligned}$$

Test the reagents by a blank determination. Where large numbers of nitrogen determinations are made, the standard acids and alkalies are adjusted to N/14 so that 1 ml. of acid = 0·001 gm. N or 0·10% on a 1 gm. sample.

$$KNO_3 + 4H_2 \rightarrow NH_3 + KOH + 2H_2O$$

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

A useful rack to hold Kjeldahl and other round-bottomed flasks has been recently described.[10]

2. Organic and ammoniacal nitrogen

Place 0·5–5 gm., according to the nitrogen content of the sample to be analysed, in a Kjeldahl flask. Add 15–18 gm. K_2SO_4 or anhydrous Na_2SO_4, 1 gm. $CuSO_4$ plus 0·2 gm. Se, or 0·7 gm. HgO plus 0·2 gm. Se, and 25 ml. of H_2SO_4. Heat the mixture gently until frothing ceases, then boil briskly and continue the digestion for a time after the mixture is colourless or nearly so, or until oxidation is complete. This usually requires 2 hours.

Cool, add about 200 ml. water, a few pieces of pumice-stone or carborundum, and if HgO has been used, add also 50 ml. of 4% K_2S or Na_2S solution. Make strongly alkaline with 60 ml. of 45% NaOH, and complete the determination as outlined above for Total Nitrogen.

3. Nitrate nitrogen

A. *Soils.* Place 100 gm. of air-dried soil, passed through a 20-mesh screen, and 500 ml. water in a suitable container and agitate for 5 minutes. Add 1 gm. CaO or 2 gm. of precipitated $CaCO_3$, agitate thoroughly, allow to stand 10–20 minutes and obtain a clear filtrate. If the filtrate contains less than 6 p.p.m. of Cl proceed as below under (*a*); if it contains more than 6 p.p.m. Cl use the procedure under (*b*). In both cases use 25 ml. or a quantity that will contain not more than 0·1 mg. nitrogen in the form of nitrate.

B. *Waters.* (*a*) For water of low chloride content, <6 p.p.m. To 100 ml. or a quantity that contains less than 0·05 mg. nitrogen as NO_3, add sufficient silver sulphate solution to precipitate all but about 0·5 mg. Cl. The silver sulphate solution is made by dissolving 4·397 gm. of Ag_2SO_4 in 1 litre of water; this gives a solution of 1 ml. = 1 mg. of Cl.

Heat to boiling and allow to settle, or add a little alumina cream or carbon black, filter and wash well with small quantities of hot water. Evaporate the filtrate to dryness in a porcelain dish on a steam bath. When cool, treat with 2 ml. of phenoldisulphonic acid, rubbing with a glass rod to insure intimate contact. Dilute with water and slowly add NH_4OH until the maximum yellow

colour is developed. Filter if necessary, transfer to a colorimeter, and compare with standards in the usual manner.

(*b*) For water of high chloride content, >6 p.p.m. To 100 ml., or a quantity that contains less than 0·1 mg. of nitrogen as NO_3, in a 300 ml. casserole add 2 ml. of the NaOH solution and concentrate by boiling to about 1/3 of the original volume. Transfer to a 100 ml. test-tube and dilute to a volume of about 75 ml. Prepare a blank by placing about 75 ml. of NH_3-free water and 2 ml. of sodium hydroxide solution in a 100 ml. test-tube. Place a strip of aluminium foil in each tube. Close the ends of the test-tubes with rubber stoppers connected by means of bent glass tubes with other test-tubes containing about 50 ml. of NH_3-free water. These latter tubes serve as traps to prevent the escape of NH_3 and at the same time permit the free evolution of hydrogen.

Allow the sample and blank to stand at room temperature for 12 hours or until reduction is complete. Add 2 ml. Nessler's reagent to the traps. If high in NH_3, indicating frothing over of the sample, discard the determination. Disregard the traps if they contain only 0·01–0·02 mg. of nitrogen as NH_3 each. Transfer the sample and blank to distillation flasks, using 250 ml. of NH_3-free water for each; distil into Nessler tubes containing 2 ml. Nessler's reagent until NH_3 ceases to be evolved, and compare with standards as in the determination of free NH_3 (2). Subtract the quantity of nitrogen found in the blank from that found in the sample. Calculate to p.p.m. nitrate nitrogen.

Reagents

Aluminium foil. Pure strips 10 cm. long, weighing about 0·5 gm.

Sodium hydroxide solution. Dissolve 250 gm. NaOH in 1250 ml. water. Add 2 strips of aluminium foil and let stand 12 hours. Concentrate the solution to 1 litre by boiling.

Nessler's reagent. Dissolve 143 gm. NaOH in 950 ml. water and filter through asbestos. Add 50 gm. red HgI_2 to the filtrate and dilute with water to 1 litre. Mix thoroughly, allow to settle, and use the supernatant liquid.

Standard nitrate solution. Dissolve 0·607 gm. $NaNO_3$ in 1 litre of NO_3-free water. Evaporate 50 ml. of this to dryness in a porcelain dish. Cool and add 2 ml. phenoldisulphonic

acid, rubbing to insure intimate contact, and dilute to 500 ml. 1 ml. of this = 0·01 mg. of N as NO_3, and the solution is permanent. Prepare standards for comparison by adding NH_4OH to a measured volume of the standard solution in Nessler tubes or a colorimeter.

Modifications of the above basic procedures for nitrates have been published recently[5, 8] to improve the methods for nitrates when these are carried out on a routine basis.

SPECIAL PROCEDURES

Oxides of nitrogen in air

Occasionally an industrial laboratory is called upon for a determination of oxides of nitrogen in air. A procedure, using the phenoldisulphonic acid reagent, has been published in recent years by the U.S. Bureau of Mines.[3]

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OXYGEN

With the exception of oxygen in gases, which is usually determined by absorption in alkaline pyrogallol in an Orsat apparatus,[6, 10, 11] the determination of this element is rarely encountered in most industrial laboratories. Exceptions to this are the determination of dissolved oxygen in water,[2, 3] and of oxygen in refined copper. The former is discussed in the section on water analysis, and oxygen in refined copper is given below. In this case oxygen is actually determined by difference after the expulsion of H_2S and H_2O when purified hydrogen is passed over heated copper. In the absence of sulphur this method could be used for oxygen in other solids, absorbing the water vapour in suitable absorbents.

Sulphur and oxygen in refined copper

Sulphur and oxygen in refined copper are determined simultaneously by passing purified hydrogen over copper drillings heated in a combustion tube, and catching the resulting H_2S and H_2O in ammoniacal cadmium chloride solution. The sulphur is determined by titration of the sulphide with the standard iodine-thiosulphate procedure, and oxygen is obtained by difference from the loss in weight of the copper drillings after expulsion of oxygen + sulphur.

Commercial hydrogen from a cylinder is purified by passing through the following train:

1. Mercury check valve.
2. Empty trap bottle.
3. 500 ml. of 10% KOH + 15 gm. $KMnO_4$.
4. Empty trap bottle.

5. 400 ml. H_2SO_4.
6. Empty trap bottle.
7. 500 ml. of 80% KOH + 25 gm. pyrogallic acid.
8. Trap bottle with a few sticks of KOH.
9. Drying bottle half full of stick KOH.
10. $CaCl_2$ drying bottle.
11. Drying bottle containing glass wool sprinkled with P_2O_5.
12. Distribution bottle. Two outlet tubes to furnaces.

The copper drillings are screened through a $\frac{3}{32}$in. sieve and the coarse only used for this determination. Fifty gm. are weighed out, placed in a combustion boat, and introduced into the silica tube of the furnace. The hydrogen with any resulting hydrogen sulphide and water vapour, is passed from the combustion tube into sulphur absorption bottles consisting of two Erlenmeyer flasks containing ammoniacal cadmium chloride. An empty bottle is inserted as a trap between the absorption flasks and the combustion tube.

Hydrogen gas is passed through the system for 5 minutes, the current is turned on and the furnace slowly brought up to a temperature of 850° C. This temperature is maintained for 4 hours, the current is turned off, and the furnace allowed to cool. When the combustion tube has cooled nearly to room temperature the hydrogen gas is turned off, the sample transferred to a desiccator, cooled, and weighed. The difference in weight is oxygen and sulphur. During the period of heating and cooling, hydrogen gas is passed through the train at 3–4 bubbles a second.

In the sulphur absorption flask is placed 25 ml. ammoniacal cadmium chloride solution. All the H_2S is invariably caught in the first absorption flask and the second is merely as a safeguard. When the heating is over, the flask is detached, washed down, and 25 ml. HCl added. The flask is cooled, and 10 ml. standard iodine solution added from a burette. The excess iodine is titrated with standard sodium thiosulphate, using starch as indicator. The quantity of sulphur determined is subtracted from the loss in weight of the copper sample to obtain the oxygen.

Short lengths of rubber tubing, glass tubing, and rubber stoppers are used for making all connections. The stoppers on

the ends of the quartz combustion tube are protected by asbestos and water-cooled copper spiral tubing.

The quantity of sample may vary from 10 to 200 gm., but a weight of 50 gm. in a quartz bulb is a convenient size. In this case the whole bulb is weighed. If boats are used the size of the sample may vary depending on the length and diameter of the combustion tube and furnace.

Reagents

Ammoniacal cadmium chloride. Dissolve 12 gm. cadmium chloride in 50 ml. water. Add 70 ml. NH_4OH and dilute to 1 litre with water. Transfer to stock bottle. To 5 ml. NH_4OH add 995 ml. water, and add this solution to the original in the stock bottle.

Sodium thiosulphate solution, 0·01N. Dissolve 2·482 gm. $Na_2S_2O_3.5H_2O$ in water and dilute to 1 litre.

Iodine solution, 0·01N. Dissolve together in the minimum quantity of water 5–7 gm. KI and 1·28 gm. iodine. Dilute to 1 litre. 1 ml. of 0·01N. iodine = 0·0001603 gm. sulphur. Standardize against arsenious acid.

Arsenious acid, 0·01N. Dissolve 0·4946 gm. As_2O_3 in 20 ml. of 20% KOH solution. Neutralize the excess alkali with dilute H_2SO_4 and add 500 ml. of water containing 25 gm. sodium bicarbonate. Dilute to 1 litre.

$$H_2 + Cu_2O \rightarrow H_2O + 2Cu$$

$$H_2 + Cu_2S \rightarrow H_2S + 2Cu$$

$$H_2S + CdCl_2 + 2NH_4OH \rightarrow CdS + 2NH_4Cl + 2H_2O$$

$$CdS + 2HCl \rightarrow H_2S + CdCl_2$$

$$H_2S + I_2 \rightarrow 2HI + S$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$$Na_3AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$$

SPECIAL PROCEDURES

1. Brady [4] describes a procedure for the determination of small amounts of oxygen in gases, based on the fact that sodium anthraquinone β-sulphonate in the reduced state reacts quantitatively

with oxygen. Another helpful method is given by MacHattie and MacConachie.[8]

2. A useful procedure for the removal of oxygen from gas streams has been recently described,[9] utilizing vanadous sulphate made by reducing 0·1 M. vanadyl sulphate with amalgamated zinc.

3. The determination of oxygen in organic compounds is described by Aluise, Hall, Staats, and Becker.[1]

4. Methods for the determination of oxygen in steel are given by Lundell, Hoffman, and Bright[7] and in aluminium by the handbooks of the aluminium companies.[5]

5. Recently, vacuum fusion methods have been used for the determination of oxygen in metals.[12] This depends on the reduction of the oxides by carbon in the molten metal to give carbon monoxide which is converted to carbon dioxide and measured in terms of its pressure exerted in a calibrated volume. The determination of oxygen in non-ferrous metals is usually done in a molten iron bath contained in a graphite crucible. In this way the iron is saturated with carbon. The addition of a metal such as zirconium gives a dilute solution of zirconium in iron. The zirconium oxide can then react with the carbon.

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PHOSPHORUS

PHOSPHORUS occurs in a number of ores and metallurgical products, in soils, fertilizers, plant products and other foodstuffs, and methods for its determination are of importance in most industrial laboratories.

For metallurgical products an oxidizing attack with HNO_3 must be used at first to prevent possible loss of phosphorus as phosphine. Most phosphorus-containing materials yield readily to acid treatment, though for some a fusion with Na_2CO_3 or Na_2O_2 will be necessary. Samples should not be fumed for long at high temperatures with H_2SO_4. The most important separation of phosphorus is based on its precipitation in HNO_3 with ammonium molybdate. Phosphorus can be separated from members of Group 2 by precipitation with H_2S in acid solution, and from Fe, Ni, Co, Ti, Zr, by precipitating the latter with NaOH or by fusion with Na_2CO_3 or Na_2O_2. Small quantities of phosphorus are often conveniently collected from large amounts of Cu, Ni, Zn, Co, etc., in a ferric hydroxide precipitate.

GENERAL PROCEDURES

Phosphorus is almost invariably separated in the presence of a number of other elements by precipitation with ammonium molybdate in HNO_3. It is then determined gravimetrically by solution of the yellow ammonium phosphomolybdate in NH_4OH and re-precipitation of the phosphorus as magnesium ammonium phosphate, or volumetrically by dissolving the ammonium phosphomolybdate in a known excess of standard NaOH and back-titrating with standard HNO_3.[1, 2, 4, 5, 7, 8]

Weigh out 0·5–5 gm., depending on the phosphorus content, and dissolve in HNO_3. If the sample is not soluble in HNO_3, add HCl, and HF if necessary. Evaporate to dryness to remove HCl and HF, moistening several times with HNO_3. Take up in 5–10% HNO_3, boil, filter, and wash thoroughly with hot water. It may be preferable to fuse the material in an iron or nickel crucible with Na_2O_2, or in a platinum crucible with Na_2CO_3, take up the melt in water and filter off the phosphorus from the iron, etc., washing the residue thoroughly with 1% Na_2CO_3 solution. Nearly neutralize the solution with NH_4OH and bring to about 5–10% acid with HNO_3.

To the 100–200 ml. solution heated to about 40–50° C., containing 5–10% HNO_3, 5–15% NH_4NO_3, and about 0·05 gm. phosphorus, add a 15–25 fold excess of ammonium molybdate reagent, i.e. 14 gm. for 0·05 gm. P, stopper, and shake vigorously for 10 minutes. If the amount of phosphorus is small or substances that retard the precipitation, like V, Ti, Zr, As, Si, H_2SO_4, HCl, or organic substances, are present, use a larger excess of the molybdate reagent. In routine analyses allow the precipitate to settle 30 minutes, for very accurate work allow the solution to stand overnight. The following reaction represents the universal method of separating phosphorus as ammonium phosphomolybdate.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow$$
$$(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$

In the presence of vanadium, prior to precipitation, cool the solution to 15° C., add sufficient ferrous sulphate to reduce the vanadium and then a few drops of H_2SO_3. If the solution does not contain iron, at this point add about 1 gm. of iron as ferric nitrate, free from phosphorus, to prevent subsequent reduction of the molybdenum. Add a 20–30 fold excess of cool molybdate reagent and shake for 10 minutes. Allow the solution to stand for at least 30 minutes or overnight, and proceed with filtration as given below.

Having obtained the precipitate of ammonium phosphomolybdate, the analyst has the option of completing the procedure gravimetrically or volumetrically.

1. Gravimetric determination by precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate

Filter the yellow ammonium phosphomolybdate precipitate on a No. 42 Whatman paper and wash well with 5% NH_4NO_3 solution. Dissolve the precipitate in dilute NH_4OH and wash the paper successively with hot water, dilute HCl, and finally again with NH_4OH. Treat the ammoniacal solution with 0·5 gm. citric acid and filter if not clear.

Make the solution slightly acid, cool, add 10 ml. of magnesia mixture and then 1 ml. additional for every 0·01 gm. P_2O_5 that is expected. Add dilute NH_4OH slowly with constant stirring until the solution is alkaline and the white magnesium ammonium phosphate appears. Add a further 10 ml. dilute NH_4OH per 100 ml. of solution, and set aside for 4 hours or overnight.

Filter and wash the precipitate several times with dilute NH_4OH. Dissolve the precipitate in dilute HCl into the original beaker and wash the filter thoroughly with dilute HCl and finally with hot water. Dilute the solution to 100 ml. and add 2 ml. magnesia mixture. Add dilute NH_4OH slowly with constant stirring as before and finally add 10 ml. excess. Allow the solution to stand several hours or preferably overnight.

Filter on Whatman No. 42 paper, and wash with 5% NH_4OH until free from chlorides. Transfer paper and precipitate to a weighed platinum crucible, dry and heat carefully until the paper chars. Burn the carbon at the lowest possible temperature and then ignite at 1000° C. to constant weight. Weigh as $Mg_2P_2O_7$.

$Mg_2P_2O_7 \times 0{\cdot}2783 = P$. The reactions are:

$$H_3PO_4 + MgCl_2 + 3NH_4OH \rightarrow MgNH_4PO_4 + 2NH_4Cl + 3H_2O$$

$$2MgNH_4PO_4 \rightarrow 2NH_3 + H_2O + Mg_2P_2O_7$$

2. Volumetric determination by solution of the ammonium phosphomolybdate precipitate in a standard solution of alkali and titration with acid

This is the most important rapid routine method for phosphorus. The reaction may be represented thus:

$$(NH_4)_3PO_4.12MoO_3 + 23NaOH \rightarrow$$
$$11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O$$

In this procedure the yellow ammonium phosphomolybdate is usually left to settle only about 15 minutes after a 10-minute shaking period, as outlined previously. The precipitate is filtered and washed thoroughly with small portions of 1% KNO_3 until no further acid is present in the washings. The paper and precipitate are returned to the flask and sufficient 0·1N. NaOH is added to decompose the precipitate and to leave about 2 ml. excess. Dilute with 25 ml. water and stir or shake until the precipitate has all dissolved. Dilute to 100 ml. with water, add 3–4 drops of phenolphthalein and titrate to a colourless end point with standard 0·1N. HNO_3 which is exactly equivalent to the alkali solution. The end point may be checked by adding 1 drop of the standard 0·1N. NaOH, which should give a pink colour.

Reagents

Ammonium molybdate solution:

Molybdic acid, 85%	65 gm.
NH_4OH	143 ml.
HNO_3, s.g. 1·20	715 ml.
H_2O	142 ml.

Add the molybdic acid to the water and dissolve by adding the ammonia and stirring. Cool the solution and pour very slowly into the acid, the latter being constantly agitated during the addition. Add 1–2 drops of a 10% solution of ammonium phosphate and allow the solution to stand 12 hours. Decant the clear liquid or filter through an asbestos pad as required for use.

Dilute HNO_3, s.g. 1·20:

HNO_3, s.g. 1·42,	476 ml.
H_2O	524 ml.

Standard NaOH. Dissolve 6·6 gm. of NaOH in 1000 ml. of CO_2-free water, add 1 ml. of a standard $Ba(OH)_2$ solution, dilute to the mark, mix thoroughly and let stand for 24 hours. Titrate against standard acid and check against a standard steel of known phosphorus content. Adjust the volume so that 1 ml. = 0·01% P on 2 gm. sample. A 0·1N. NaOH solution contains 4 gm. NaOH per litre and 1 ml. = 0·000135 gm. P.

The solution should be protected from CO_2 with a trap of ascarite or solid KOH. The standard NaOH may be checked against potassium acid phthalate. One ml. of 0·1N. NaOH = 0·0204 gm. potassium acid phthalate.

Standard HNO_3. Mix 7 ml. of HNO_3 and 1000 ml. of CO_2-free water. Titrate against standard NaOH, using phenolphthalein, and make it equivalent to the NaOH by adding distilled water. A 0·1N. HNO_3 solution contains 6·3 gm. HNO_3 per litre.

Magnesia mixture

Magnesium chloride	100 gm.
Ammonium chloride	200 gm.
Water to make	1000 ml.

Dissolve the salts in 500 ml. of water add a slight excess of NH_4OH, let the solution stand overnight, filter, make just acid with HCl, and dilute to 1 litre.

3. Colorimetric determination of phosphorus

Small quantities of phosphate in boiler waters, soil extracts, and similar materials are determined colorimetrically by the blue colour formed when ammonium phosphomolybdate is reduced with stannous chloride or hydroquinone.[6, 9] For the determination of sodium hexametaphosphate in "threshold treatment" it must be recalled that this compound does not give the ordinary phosphate reactions and must be converted to orthophosphate by boiling for 4 hours in 1% H_2SO_4 solution before applying the colorimetric test.

The procedure for the colorimetric determination of phosphorus is as follows:

To 5 ml. of the filtered boiler water, in a 50 ml. Nessler tube, add the following reagents carefully measured by separate pipettes and in the order given. The water must be brilliantly clear, so that only soluble phosphate is determined. During and after each addition, swirl the sample to mix thoroughly:

1 ml. of sulphuric acid solution

1 ml. of molybdate solution

1 ml. of hydroquinone solution.

Now allow the solution to stand for 5 minutes, so that the olive green colour, which develops when phosphates are present, can develop properly.

During the five minutes necessary for the colour to develop, measure 2 ml. of the carbonate-sulphite solution into a separate Nessler tube. At the end of the five minutes pour the treated solution being tested for phosphate quickly into the 2 ml. of carbonate-sulphite solution, pouring backwards and forwards a few times to ensure thorough mixing.

The blue colour of the phosphate compound quickly develops, and as it is not permanent, its intensity should be measured as soon as possible. For this purpose a standard phosphate solution equivalent to 100 parts per million of PO_4 is used. A range of solutions containing 10, 25, 50, 75, parts of PO_4 is made from the standard solution by dilution. 5 ml. of every one of these solutions are pipetted into a 50 ml. Nessler tube and submitted to the same treatment as the sample. Then the sample solution is matched with one of the standard solutions.

Solutions required

(*a*) *Sulphuric acid solution.* To 200 ml. of water add 65 ml. of sulphuric acid and dilute to 500 ml. with water.

(*b*) *Molybdate solution.* Dissolve without heat 17·5 gm. of ammonium molybdate in about 200 ml. of water. To another 200 ml. of cold water add 10·5 ml. of sulphuric acid. Mix the two solutions and make the volume up to 500 ml. with water. This solution should be stored in the dark.

(*c*) *Hydroquinone solution.* Thoroughly dissolve 5 gm. of pure hydroquinone in 500 ml. of water, and add 0·3 ml. of sulphuric acid. Care must be taken that all the hydroquinone is in solution before adding the acid, otherwise the solution will turn brown and be spoiled.

This solution slowly darkens in colour, but is satisfactory, if kept in the dark, for about three weeks. The slight brown colour is detrimental merely because it makes the comparison more difficult, and not because of deterioration in strength.

(*d*) *Carbonate-sulphite solution.* In 500 ml. of water dissolve 100 gm. of anhydrous sodium carbonate and 24 gm. of anhydrous sodium sulphite, or 45 gm. $Na_2SO_3.7H_2O$.

(*e*) *Phosphate solution.* The standard solution containing 100 parts per million of PO_4 is obtained by dissolving 0·1390 gm. of dibasic ammonium phosphate, $(NH_4)_2HPO_4$, in water and making up to one litre. This solution can now be diluted to any desired strength.

This method may be used as a "limit" test by using two standard solutions of known PO_4 content. Presuming the operator is trying to keep 50 parts per million of PO_4 in the boiler water, suitable strengths would be 30 parts per million and 70 parts per million of PO_4. Five ml. of each would then be treated in exactly the same manner as the sample of boiler water in order to develop the blue colour. It would then be an easy matter to decide whether or not the PO_4 content of the boiler water is within a reasonable range of the desired PO_4 content.

The phosphate concentration in boiler waters containing tannin can be determined by adsorbing the latter with decolorizing charcoal. Under controlled conditions very little adsorption of phosphate occurs. The details are given by Goldman and Love.[3] Two 0·7 gm. portions of decolorizing charcoal such as Norite A or SG 11 are added, one at a time, to a 50 ml. portion of water in a flask. The latter is shaken for a minute, after each addition, and filtered through a dry paper, discarding the first 15 ml.

SPECIAL PROCEDURES

1. An alternative procedure for small quantities of phosphate in water is the following. It differs from the previous method chiefly in using stannous chloride instead of hydroquinone as reducing agent for ammonium phosphomolybdate.

As a means of controlling the feed of sodium hexametaphosphate such as Calgon in the threshold treatment a direct method of determining metaphosphate in very low concentrations would be desirable, but no suitable method for routine field use has been devised. An indirect method has, however, been developed, based upon the fact that hexametaphosphate does not respond to the ordinary colorimetric method used for the determination of orthophosphate and the fact that metaphosphate may be converted quite rapidly into orthophosphate by a process of molecular hydration when boiled in an acid solution.[10]

The test is an adaptation of the Truog and Meyer modification of the Denigès colorimetric procedure. The metaphosphate is determined as the difference between the orthophosphate found in the water as it is sampled and the orthophosphate found in the water after conversion of the metaphosphate to orthophosphate. The comparison of the colour may be carried out either in Nessler tubes or a colorimeter. The colour formed is only stable for a few hours and a fresh standard must be prepared each time the test is run. Differences in phosphate content of 0·05 p.p.m. can be distinguished by eye in the range 0–5 p.p.m.

It must be kept in mind that this procedure measures the total metaphosphate in the solution, i.e. not only the free sodium hexametaphosphate but also that which has formed the soluble sodium calcium metaphosphate.

Preparation of reagents

(1) 4N. *Sulphuric acid.* To prepare approximately 4N. sulphuric acid, add 120 ml. of sulphuric acid to 600 ml. of water. The acid should be added cautiously, and, if possible, the beaker should be immersed in cold water. After the acid has been added, cool the solution and make up to one litre.

(2) *Standard phosphate solution.* Dissolve exactly 0·1335 gm. of KH_2PO_4 in water and make up to one litre. 0·1296 gm. of $(NH_4)_2HPO_4$ may be substituted. One ml. of this solution made up to 100 ml. with water gives a solution having a PO_4 content equivalent to 1 p.p.m. of sodium metaphosphate, $NaPO_3$.

(3) *Ammonium molybdate.* Dissolve 50 gm. of ammonium molybdate in 500 ml. water and make up to one litre with the above 4N. sulphuric acid.

(4) *Stannous chloride.* Add 10 ml. of hydrochloric acid to 90 ml. of water. Dissolve 2·5 gm. of $SnCl_2.2H_2O$ in this solution and filter if a turbidity exists. To minimize oxidation this solution may be kept in a bottle with a stopcock at the bottom and a layer of medicinal paraffin 5 mm. thick floated over the surface.

Procedure

(1) Filter about 450 ml. of the water to be treated through a Whatman No. 42 paper to obtain a perfectly clear sample.

Measure out 100 ml. sample in the graduated cylinder and pour into a 300 ml. Erlenmeyer flask.

(2) From a graduated pipette add 12 ml. of the 4N. sulphuric acid to the flask containing the water to be tested. Heat to boiling and keep hot for 4 hours. This may be done in one of several ways. The flask may be covered with a watch glass and kept on a hot plate just off the boil, or a reflux condenser may be fitted. After 4 hours, cool, transfer the contents of the flask to a 100 ml. graduated cylinder and make up to 100 ml. with distilled water. Return to the flask and add a further 12 ml. of distilled water.

(3) Into a Nessler glass pour 50 ml. of the water from (2) above and pipette in a further 6 ml., making 56 ml. in all.

(4) Into each of six Nessler glasses measure 50 ml. of the filtered, unboiled original sample of water. Add standard phosphate solution as follows from a graduated pipette, nil, 0·5 ml., 1·0 ml., 1·5 ml., 2·0 ml., and 2·5 ml. These are equivalent to 0, 1, 2, 3, 4, and 5 parts of metaphosphate per million. Pipette 6 ml. of 4N. sulphuric acid from a 10 ml. graduated pipette into each Nessler glass and mix.

(5) To all Nessler glasses, seven in all, add 2 ml. of ammonium molybdate solution and mix thoroughly.

(6) Add 4 drops of stannous chloride solution to each Nessler glass, mix thoroughly, allow the colour to develop by standing 5 minutes, and compare.

If the orthophosphate content in the original sample is high, due to colloidal orthophosphate, the colour obtained may be too deep for accurate matching and then dilution is necessary. For example, pipette out 11·2 ml. of the boiled sample from (2) above into a Nessler glass, pipette in 4·8 ml. of the 4N. sulphuric acid and make up to 56 ml. Into each of the six Nessler glasses add by pipette 10 ml. of the original sample, add the orthophosphate as before, make up to 50 ml., add 6 ml. of the 4N. sulphuric acid, and complete the test as before. There is a serious disadvantage in this case as the final figure for the metaphosphate present must be multiplied by 5. The metaphosphate content would be only known approximately. However, if the orthophosphate content is high no other course is available.

Some tannins and their oxidation products give a little colour when no phosphate is present. In such low concentrations as are encountered in threshold treatment, however, there is no interference since the water being tested is also used for the preparation of standards. Tannins may be removed, if necessary, by charcoal as described earlier.

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PLATINUM METALS

THE PLATINUM METALS occur in ores, concentrates, refinery slimes, jewellery, electrical and other scientific instruments, and catalysts. Their determination may be carried out by preliminary fire assay to collect the small quantities occurring in ores, etc., followed by chemical separations.[7] For larger amounts of the platinum metals direct chemical determinations are used. As a general rule, platinum and palladium are the only platinum metals determined, iridium, rhodium, osmium, and ruthenium being rarely encountered in industrial laboratories. Methods for the determination of these four may be found in the works of Schoeller and Powell, Hillebrand and Lundell, Smith, etc., cited below.

GENERAL PROCEDURE

1. Determination of platinum and palladium by wet methods

Dissolve the sample in *aqua regia*, and if any insoluble metal remains, indicating an alloy containing considerable Rh, Ir, or Ru, fuse the residue in a silver, nickel, or iron crucible with 3 parts NaOH + 1 part Na_2O_2 for each part of the insoluble residue.[2, 4, 5] Sperrylite, $PtAs_2$, must be roasted thoroughly before it will dissolve in *aqua regia*.

Evaporate the solution carefully just to a syrup and add HCl, repeating this operation several times to remove all traces of HNO_3. If large amounts of Fe, Ni, Co, etc., are present it is advisable to separate the platinum metals with H_2S in 5% HCl solution.

It has been recently shown by Jackson and Beamish,[3] in a critical study of platinum sulphide precipitation, that precipitation from a solution previously evaporated in the presence of NaCl produces high results. Accurate results can be obtained by not evaporating in the presence of NaCl or by evaporating simultaneously in the presence of NaCl and NH_4Cl.

Filter, wash with acidulated H_2S water, and dissolve the sulphides in *aqua regia*. Repeat the elimination of HNO_3 by several evaporations with HCl. If platinum or palladium is the only Group 2 metal present, the sulphide may be ignited directly to metal in a porcelain crucible.

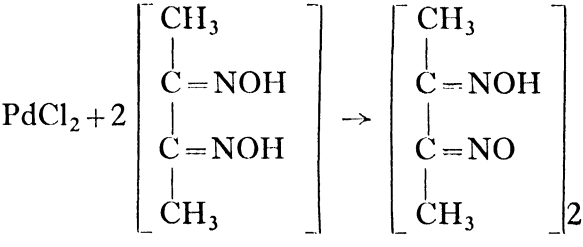
If gold is present it must be separated by treatment with SO_2 and oxalic acid as described under Gold. Remove the oxalic acid by evaporation with *aqua regia*, and remove HNO_3 by several evaporations with HCl.

In the absence of gold and other elements precipitated by H_2S in acid solution, platinum may also be precipitated as metal by formic acid. To the HCl solution containing about 5 ml. HCl and less than 0·5 gm. platinum per 100 ml. solution, add 3 gm. sodium acetate and 1 ml. formic acid. Digest in a warm place for several hours. Filter and wash thoroughly. Add additional sodium acetate and formic acid to the filtrate and digest further to insure complete precipitation. Dry and ignite the paper and precipitate in a porcelain crucible. Weigh as metallic platinum. If palladium is the only platinum metal present, it too may be precipitated by formic acid and weighed as metallic palladium.

If palladium is present with platinum it may be determined by precipitation with dimethylglyoxime in sulphuric or hydrochloric acid solution. To the cold 3% HCl solution containing no Au, Se, or Ni, and not over 0·1 gm. palladium in 200 ml., add a slight excess of a 1% solution of dimethylglyoxime in 2% HCl. Gold and selenium are reduced and precipitated in the metallic state by dimethylglyoxime. 0·1 gm. of palladium requires 0·22 gm. of the solid dimethylglyoxime. The solution is set aside for an hour and the orange-yellow precipitate is collected on a Gooch filter, washed with 1% HCl, and then with hot water.

If re-precipitation is necessary, in the presence of more than traces of platinum indicated by a green colour of the palladium

precipitate, collect the first precipitate on paper and digest with *aqua regia* until the compound is dissolved. Take to a syrup and moisten with HCl once or twice to eliminate most of the HNO_3. Cool, dilute, and re-precipitate palladium with dimethylglyoxime in the cold in the same manner as before. A trace of HNO_3 is not detrimental to the separation of palladium, in fact it tends to prevent the co-precipitation of platinum. Filter on a Gooch crucible and wash as before. Dry at 110° C. to constant weight.



Wt. of precipitate $[(CH_3)_2C_2NOH:NO]_2Pd \times 0{\cdot}3167 = Pd$

The filtrate from the palladium precipitation above may be used for the determination of platinum. Evaporate to a syrupy consistency, adding HCl several times to eliminate all HNO_3. If a large excess of dimethylglyoxime has been added, it will be necessary to destroy all traces of organic matter by adding *aqua regia* and H_2SO_4 and taking to strong fumes of SO_3.

Cool, add 10 ml. water, a few drops of HCl, and about 2 gm. NH_4Cl. Stir well, add 10 ml. of ethyl alcohol and allow to stand overnight. $PtCl_4 + 2NH_4Cl \rightarrow (NH_4)_2PtCl_6$. Filter on a Gooch crucible, washing with dilute NH_4Cl + alcohol. Dry at a temperature not exceeding 100° C., cool in a desiccator, and weigh as $(NH_4)_2PtCl_6$.

$$(NH_4)_2PtCl_6 \times 0{\cdot}4397 = Pt$$

If desired, the precipitate may be ignited slowly in a porcelain crucible to metallic platinum. If appreciable quantities of Pd and Rh, or large quantities of base metals are present, it is advisable to purify the precipitate of ammonium chloroplatinate by re-precipitation. Dissolve in hot *aqua regia*, remove HNO_3 by repeated evaporations with HCl, and precipitate again with NH_4Cl in the same manner as before. Iridium precipitates with platinum on treatment with NH_4Cl.

2. Determination of platinum and palladium by fire assay

Weigh out 1–2 assay tons of −100 mesh material. If the ore is very low grade it may be necessary to combine the lead buttons from a number of fusions. If the sulphur content is over 2 per cent., roast to eliminate sulphur. Mix with a suitable flux, depending on the character of the ore, to obtain a lead button of 50–60 gm. Add sufficient pure silver foil to give a final silver content greater than 10 times the combined precious metals.

Fuse in an assay crucible until a quiet melt is obtained, and pour into a cast iron mould. Hammer the lead button free from slag and scorify until free of Cu, Ni, Co, Sb, etc., and the button has been reduced to the proper size to cupel. Cupel at a temperature of 1000° C.

Place the bead in a 50 ml. beaker, add H_2SO_4 and take to fumes of SO_3. The residue from this parting should contain all Au, Pt, and other members of the platinum group except palladium, while Ag and Pd dissolve. Wash the residue thoroughly by decantation, saving the washings. Transfer the residue finally by washing to a small glazed porcelain cup, dry, ignite, and weigh. This weight represents Au, Pt, Rh, Ir, Os, Ru, but no, or very little, palladium.[1, 6]

The decanted washings from the separation above are cooled, diluted to 100 ml., and palladium precipitated with dimethylglyoxime. Have the solution about 3% acid and use an aqueous 0·1% solution of dimethylglyoxime as precipitant. Filter off the yellow palladium dimethylglyoxime in a micro Gooch crucible, dry at 110° C., and weigh. The palladium found is added to the weight of the previously obtained residue, and the sum reported as platinum metals + gold.

If gold is desired separately, the residue of Au + Pt, etc., is dissolved in *aqua regia*. The solution is evaporated twice just to dryness with HCl to eliminate all HNO_3. The sample is taken up with 1 ml. HCl and water, and the gold precipitated with sodium nitrite or sulphur dioxide. Filter through Whatman No. 40 paper, using pulp, and wash. Wipe out the inside of the beaker with a filter paper and add this to the filter.

Place filter paper and contents in lead foil and add silver to the extent of 3–4 times the weight of the gold. Dry, char the paper,

and scorify in a small scorifier at a temperature of 1000° C. Cupel in a Mabor No. 6 cupel, clean the bead well, flatten, and anneal.

Part in a porcelain cup first with 1:6 HNO_3, then with 1:1 HNO_3. Wash three times by decantation with hot water, dry and anneal. Weigh on the assay balance as metallic gold.

If desired, platinum may be determined on the filtrate from the gold precipitated by $NaNO_2$. Evaporate to a syrupy consistency several times with HCl to eliminate all HNO_3, and precipitate platinum with NH_4Cl as directed in the previous determination.

Palladium may also be separated from gold and silver by parting in HNO_3, the palladium and silver dissolving and the gold remaining as a residue. Palladium may then be determined with dimethylglyoxime, and silver as AgCl.

When determining the platinum metals in blister copper, refinery slimes, or other base metal products it must be kept in mind that Pd, unlike Pt and Au, is dissolved by hot concentrated HNO_3 and boiling concentrated H_2SO_4.[7] The precipitate of Au, Pt, and AgCl formed after adding a chloride to a nitric or sulphuric acid solution of the sample therefore does not contain the palladium. The latter can be recovered by evaporating the filtrate to dryness several times with hydrochloric acid and finally precipitating the palladium with dimethylglyoxime as described above. A little of the palladium may accompany the precipitate of Au, Pt, and AgCl and this should be removed from the final parting operation given above.

3. Determination of platinum and palladium by dithizone

An extractive titrimetric method for platinum and palladium, based on dithizone, has been described recently.[8] This is of particular application to beads obtained in precious metal assay work.

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POTASSIUM AND SODIUM

POTASSIUM AND SODIUM are found in minerals, soils, ores, fertilizers, brines, building materials, glass, refractories, and a variety of important industrial chemicals such as salt, caustic soda, soda ash, etc. Their determination therefore is of common occurrence in industrial laboratories. The other alkalies, Li, Rb, and Cs, are rather rare metals and are very seldom encountered in most laboratories. Procedures for their determination are given in the references of Hillebrand and Lundell, Scott and Furman, and Schoeller and Powell, listed below. Our discussion will be limited to potassium and sodium.

Potassium and sodium are separated from members of preceding groups by precipitation of the latter with H_2S in acid and in ammoniacal solution, by precipitation of the alkaline earths with ammonium carbonate, and of magnesium with ammonium phosphate. Potassium and sodium are consequently found in the final filtrates of a complete analysis. They are usually weighed together as chlorides, the potassium then separated and weighed as the perchlorate or chloroplatinate, and sodium obtained by difference. In the determination of small quantities of sodium and potassium, careful blanks must be carried along with the analysis since traces of these alkalies are common in reagents, glassware, etc.

In industrial chemicals the sodium content is often obtained indirectly, as acid titration for NaOH and Na_2CO_3; sulphur determination for Na_2SO_4 and Na_2S; chlorine for NaCl.

GENERAL PROCEDURES

Potassium and sodium are usually determined in solids by the J. Lawrence Smith decomposition. In this the finely powdered mineral is heated in a special platinum crucible with a mixture of NH_4Cl and $CaCO_3$, whereby the alkali metals are converted to chlorides which can be extracted with water. Generally only Ca and SO_4, if present, dissolve, and since both of these are easily removable, a solution of the alkali chlorides only is readily obtained. Where the material cannot be fused directly in a platinum crucible, it is treated with acids first, filtered, washed, and the residue decomposed with NH_4Cl and $CaCO_3$ in a platinum crucible as described. Other elements are separated from potassium and sodium in the filtrate by H_2S, $(NH_4)_2S$, $(NH_4)_2CO_3$, and $(NH_4)_2HPO_4$ as required, and this filtrate is combined with the aqueous extract formed after fusing the residue with NH_4Cl and $CaCO_3$. Where the alkalies are already in a form soluble in water, of course, the procedures below may be shortened accordingly.

Triturate 0·5–1·0 gm. of the finely powdered mineral with an equal quantity of pure NH_4Cl in an agate mortar over glazed paper, add 3–6 gm. pure $CaCO_3$, and mix intimately with the former. Specially prepared NH_4Cl and $CaCO_3$ reagents for alkali fusions may now be obtained. Transfer the mixture to a platinum crucible, preferably the J. Lawrence Smith alkali crucible furnished by suppliers of platinum ware, rinse the mortar and pestle with 1–2 gm. $CaCO_3$ and add it to the contents of the crucible. The bottom of the crucible should be lined with a little $CaCO_3$ to prevent adhesion of the mass to the crucible after ignition.

Place the covered crucible in a slightly inclined position with the top protected from the heat of the flame. This can be done by setting the crucible in a hole in a cylinder of fireclay or through a hole in a piece of asbestos board clamped at a slight angle. Heat the crucible gradually over a small flame or electric element for about 15 minutes until no more ammonia is evolved, but avoid heating sufficiently to cause the evolution of NH_4Cl. Then raise the temperature gradually until finally the lower $\frac{3}{4}$ of the crucible

is brought to a red heat, and maintain this temperature for one hour. The reactions may be expressed thus:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O + CO_2$$

$$2KAlSi_3O_8 + CaCl_2 + 6CaCO_3 \rightarrow 6CaSiO_3 + Ca(AlO_2)_2 + 2KCl + 6CO_2$$

Allow the crucible to cool and remove the sintered cake by digesting in warm water in a porcelain or platinum dish. Heat the covered dish with 50–75 ml. of water for half an hour, reduce the large particles to a fine powder by rubbing with a pestle in the dish, and decant the clear solution through a filter. Wash the residue 4 times by decantation, transfer to a filter, and wash with hot water until a few ml. of the washings give only a faint turbidity with $AgNO_3$. To make sure the decomposition of the mineral has been complete, treat the residue with HCl. No trace of undecomposed mineral should remain undissolved.

The aqueous extract obtained in the above operation contains the chlorides of calcium and the alkalies, together with a little sulphate if present. To remove the calcium, treat the solution with NH_4OH and $(NH_4)_2CO_3$, heat to boiling, filter, and wash the residue. Dissolve the precipitate in HCl and repeat the precipitation. If any sulphur is present it should be removed by a suitable amount of a 10% $BaCl_2$ solution before the second precipitation of the calcium. The excess of barium is then removed by ammonium carbonate with the second precipitation of calcium.

Evaporate the combined filtrates to dryness, preferably in a large platinum dish, and carefully drive off the ammonium salts by gentle ignition. Dissolve the residue in a little water and precipitate the last traces of calcium by the addition of a few drops of NH_4OH and ammonium oxalate. Allow to stand several hours and filter off any calcium oxalate, washing with 0·1% ammonium oxalate solution.

Evaporate the filtrate to dryness in a weighed platinum dish and gently ignite to remove ammonium salts. Moisten the cooled mass with HCl to transform any carbonate to chloride, and again evaporate to dryness and ignite gently. This evaporation and ignition must be conducted very carefully, first over a steam bath, then in an oven at 110–130° C., and finally over a hotplate. To remove the last traces of ammonium salts the platinum dish may

be heated by waving a free flame back and forth under the vessel. The dish should not be heated to more than faint redness in any one spot and the salt must not be heated higher than the first signs of incipient fusion.

Cool the dish in a desiccator and weigh the combined chlorides, NaCl + KCl. Dissolve in water, and if an insoluble residue remains, filter off, weigh, and deduct from the weight of the chlorides.

POTASSIUM

1. Chloroplatinate method

This method depends on the fact that potassium chloroplatinate is practically insoluble in strong ethyl alcohol whereas the other chloroplatinates are readily soluble.[1, 4, 5] It is applicable in the presence of chlorides of Na, Mg, Ca, Sr. Operations must be carried out in an atmosphere free of ammonia fumes.

$$H_2PtCl_6.H_2O + 2KCl \rightarrow K_2PtCl_6 + 2HCl + 6H_2O$$

Treat the aqueous solution of the alkali chlorides contained in a small glass or porcelain vessel with slightly more than enough chloroplatinic acid to convert all the chlorides present into the corresponding chloroplatinates. The chloroplatinic acid solution is made by dissolving a weighed quantity of platinum foil in *aqua regia* diluted with an equal volume of water. Evaporate the solution nearly to dryness and add a large excess of HCl. Again evaporate nearly to dryness. Repeat the evaporation with HCl 3–4 times to get rid of any nitrogen compounds. Dilute with 1% HCl so that the resulting solution will contain 10% platinum.

Evaporate the solution of alkali chloroplatinates on the steam bath to a syrupy consistency or until solidification occurs on cooling. Flood the cooled residue with a small quantity of 80% ethyl alcohol, grind thoroughly with the flattened end of a stirring rod, and allow to stand 30 minutes. Pour the liquid through a previously weighed filtering crucible. Rub up the residue again with the glass pestle, adding more alcohol, and wash by decantation with small portions of alcohol until the wash liquid becomes colourless. Transfer the precipitate to the crucible and wash several times with alcohol. Dry in an oven for 1 hour at 110° C.,

cool in a desiccator, and weigh as K_2PtCl_6. Calculate the KCl equivalent to the K_2PtCl_6, and subtract this from the mixed KCl + NaCl residue to give the sodium present.

$$K_2PtCl_6 \times 0{\cdot}3067 = KCl$$
$$K_2PtCl_6 \times 0{\cdot}1608 = K$$

2. The perchlorate method

This method depends on the insolubility of $KClO_4$, and the solubility of sodium and other perchlorates in 97% ethyl alcohol.[1, 4, 7] The procedure is applicable in the presence of chlorides and nitrates of Ba, Ca, Mg, and the alkalies. Avoid ammonia fumes, since ammonium perchlorate may be formed and weighed with potassium.

To the neutral or slightly acidified solution add twice as much $HClO_4$ as is required to convert all the bases present into perchlorates, and evaporate on the steam bath, with stirring, to a syrupy consistency. Add a little hot water and continue the evaporation with constant stirring until all the HCl is expelled and heavy fumes of $HClO_4$ are given off. Cool, and stir up the crystallized mass thoroughly with 20 ml. of 97% C_2H_5OH to which 0·2% $HClO_4$ has been added, but do not break up the $KClO_4$ crystals so fine that they pass through the filter. Allow the mixture to settle and decant the alcohol off through a filtering crucible. Repeat the washing once by decantation and then warm to remove the alcohol. Dissolve the residue in hot water, add about 1 ml. $HClO_4$, and evaporate again until fumes of $HClO_4$ are given off. Wash the residue once by decantation and then several times on the filter. Remove the adhering wash liquid by washing with 97% C_2H_5OH, dry in an oven at 110–130° C., and finally heat in a muffle for 15 minutes at 350° C. Cool in a desiccator and weigh as $KClO_4$. Subtract the equivalent weight of KCl from the combined KCl + NaCl residue to give the percentage of sodium:

$$KClO_4 \times 0{\cdot}5381 = KCl$$
$$KClO_4 \times 0{\cdot}2822 = K$$

In these determinations it must be recalled that lithium accompanies sodium, whereas rubidium and cæsium are separated with

potassium. These elements occur so rarely in industrial chemistry, however, that procedures for further separations may be consulted from the references given below.[4, 6, 7, 8]

Where a small amount of sodium occurs in the presence of a large quantity of potassium, or vice versa, it may be advantageous to concentrate one before a final separation is attempted. In this case, concentrate the aqueous solution as far as possible without causing deposition, set the vessel in ice water, and saturate the solution with HCl gas. When the solution is saturated with the gas, wash the delivery tube and the inside of the flask into the solution, and stir to break up any lumps. Filter, using gentle suction. Transfer the precipitate to the filter with ice-cold water saturated with HCl gas, and wash several times with small quantities of this liquid, sucking the filter dry after each application of the wash liquid. When a small quantity of potassium is present in a large amount of sodium, the potassium will be found in the filtrate along with some sodium and salts of other metals originally present. When a small quantity of sodium is present in a large amount of potassium, the sodium will be found in the filtrate along with some potassium.

SODIUM

1. Usually sodium and potassium are weighed together as chlorides, and potassium then determined by the chloroplatinate or perchlorate method. The NaCl is determined by difference.

$$NaCl \times 0{\cdot}3934 = Na$$

2. A direct determination of sodium may be made by removing the platinum from the filtrate obtained in the determination of potassium by the chloroplatinate method, and weighing the sodium as NaCl.

Evaporate the filtrate from the chloroplatinate method on a water bath to remove most of the alcohol. Dilute to 100 ml., add 5 ml. formic acid, and boil until a brown colour indicating initial reduction of platinum is obtained. Add a slight excess of NH_4OH and continue boiling for a few minutes. Allow the sample to stand in a warm place until the platinum has settled. Filter hot and wash free of chloride.

Evaporate the filtrate to dryness on the water bath and ignite gently to remove ammonium salts and organic matter. Dissolve in water, filter into a weighed platinum dish, and determine the sodium as NaCl in the same manner as described above for the mixed chlorides.

3. Sodium may be determined on the filtrate from the perchlorate method by evaporating the alcohol on a hot plate. Cool to room temperature. Add rapidly from a burette with constant stirring 1·5 ml. of *n*-butyl alcohol containing 20% of HCl gas, and then rapidly 7 ml. more to form a 6% HCl solution. Heat to boiling to coagulate the NaCl. Cool, filter on a weighed filtering crucible, and wash 8–10 times with *n*-butyl alcohol containing 7% HCl gas but keeping the wash liquid at a minimum.

Dry the crucible and NaCl in an oven at 250° C. for 1 hour and ignite at a very dull red heat. Cool in a desiccator and weigh as impure NaCl. Wash the precipitate through the filter with hot water, dry, and ignite the crucible and filter again, cool and weigh. The loss in weight represents pure NaCl.

4. *Determination of sodium as sodium zinc uranyl acetate*

This method is applicable to the determination of small quantities of sodium. Moderate amounts of K, NH_4, Mg, Ca, and Ba do not interfere. The solution should preferably be a chloride, though sulphate may be present in the absence of Ca, Ba, and Sr. Phosphates, silicates, and oxalates interfere.

Separate any interfering elements with $(NH_4)_2S$ and $(NH_4)_2CO_3$, and take an aliquot if necessary so that the sample will not contain more than 0·02 gm. sodium and 0·05 gm. potassium. Evaporate the neutral solution thus obtained to a very low volume, and add to the concentrated solution at least 10 ml. of the zinc uranyl acetate reagent for each 1 ml. of the solution. Stir well and allow to stand at 20° C. for 45 minutes, stirring occasionally. Filter through a weighed Gooch crucible, using gentle suction. Wash the precipitate 5–10 times with 2 ml. portions of the zinc uranyl acetate reagent, sucking the filter dry after each addition. Now wash the precipitate 5 times with 2 ml. portions of 95% C_2H_5OH saturated with sodium zinc uranyl acetate at 20° C. Finally wash thoroughly with ether to remove the alcohol, and draw dry air through the filter to remove the ether.

Dry the precipitate at 40° C. for 15 minutes, place in a desiccator for a few minutes, and weigh as sodium zinc uranyl acetate, $NaZn(UO_2)_3.(C_2H_3O_2)_9.6H_2O$.

$$\text{Wt of precipitate} \times 0{\cdot}01495 = \text{Na}$$

Reagents

Zinc uranyl acetate: Solution A. Weigh 77 gm. uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, into a 600 ml. beaker. Add 13·3 ml. acetic acid and 410 ml. water. Heat to 70° C. and stir until solution is complete.

Solution B. Weigh 231 gm. zinc acetate $Zn(C_2H_3O_2)_2.3H_2O$ into a 600 ml. beaker. Add 6·6 ml. acetic acid, 262 ml. water, warm to 70° C. and stir until solution is complete.

Mix solutions A and B at about 70° C. and allow to stand 24 hours. Filter into a clean dry bottle. The reagent is stable but should be filtered before use if not perfectly clear.

Uranyl zinc acetate may now be purchased from chemical supply houses. It requires approximately 6·6 gm. of this reagent to react with 0·1 gm. sodium.

$$3UO_3(C_2H_3O_2)_2.2H_2O + 2Zn(C_2H_3O_2)_2.3H_2O + 2NaCl \rightarrow NaZn(UO_2)_3(C_2H_3O_2)_9.6H_2O + ZnCl_2 + NaC_2H_3O_2.3H_2O + 3H_2O$$

SPECIAL PROCEDURES

Potassium and sodium can be determined for routine purposes by means of flame photometry, measuring the intensity of the lines in a photoelectric instrument made by the Perkin-Elmer Corp., Glenbrook, Conn. The sodium content of aluminium can be quickly determined by measuring light intensities of atomized solutions in a Beckman flame spectrophotometer.[2]

Other types of flame photometers have been described [3] for the rapid determination of sodium and potassium in biological materials.

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SELENIUM AND TELLURIUM

SELENIUM AND TELLURIUM are found in some ores and minerals, flue dusts, refinery slimes, glasses, certain steels and non-ferrous alloys, photoelectric cells, rectifiers, and tellurium lead. The elements are frequently associated together in samples handled in an industrial laboratory, and will be discussed together below. While selenium and tellurium are members of Group 2, precipitation by H_2S in acid solution is not entirely quantitative unless the elements are in the lower state of oxidation and the gassing is prolonged. The outstanding separation for these elements is precipitation with SO_2 in HCl solution. It is often useful to remember that selenium and tellurium can be separated from Cu, Bi, etc., by solution in ammonium sulphide. Selenium and tellurium, like arsenic, can be separated from antimony and tin by gassing with H_2S in 2 parts HCl to 1 part water. In the analysis of selenium and tellurium it is essential to realize that these elements are easily volatilized from strong HCl solutions heated above 100° C. Selenium is appreciably volatile from fuming perchloric acid solutions.

The following directions are designed for a material containing 1–5% selenium or tellurium.[2,3,4] If the product is very low in these elements it will be necessary to greatly increase the size of the sample, or combine a number of 10 gm. samples after removing insoluble matter.[1] For blister copper the selenium and tellurium should be collected from a 100 gm. sample in a ferric hydroxide precipitate formed by adding an iron salt to the copper nitrate solution, making ammoniacal, and filtering off the ferric hydroxide

together with occluded Se, Te, As, Sb, Bi. When bringing concentrates into solution care must be taken that the addition of HNO_3 to large quantities of chlorate in the presence of sulphide does not give a violent reaction.

GENERAL PROCEDURE

Weigh 1–2 gm. into a 400 ml. beaker, add 2–4 gm. potassium chlorate, 10 ml. water, 20–30 ml. HNO_3 and allow to stand 15 minutes in the cold. Place on steam bath and evaporate to dryness. Add 15 ml. 1:1 HCl and again evaporate on the steam bath to dryness.

Take up in 15 ml. HCl, 30 ml. water, and warm on the steam bath until all soluble salts are in solution. Filter off the insoluble matter such as SiO_2, Ag, Pb, etc., on Whatman No. 40 paper and wash well with hot water. When only one of the elements selenium and tellurium is present in a fairly pure solution the following method may of course be modified to proceed directly to the separation of selenium with SO_2 in strong HCl or of tellurium in dilute HCl. Heat the clear filtrate just to boiling, remove from the hot plate, and add HCl equal to $\frac{1}{3}$ the volume of solution present. For reduction with SO_2, selenium and tellurium must be in the quadrivalent state and HNO_3 must be absent. The sexivalent compounds are easily reduced to the quadrivalent state by heating with dilute HCl, $<$6N., at a temperature below 100° C. until chlorine has been expelled. HNO_3 can be eliminated by evaporation with dilute HCl at a temperature below 100° C.

Pass in SO_2 gas from a commercial cylinder at a fairly rapid rate at a temperature of 15–20° C. The red selenium is first precipitated and on continued passage of SO_2 the black tellurium appears. Continue the stream of SO_2 until the precipitate coagulates, remove the beaker, washing down the gas tube, and allow to settle for an hour. Filter through Whatman No. 40 paper and wash several times with cold water. Selenium and tellurium are precipitated free from nearly all interfering elements in HCl solution of 28–40% by volume. Selenium alone is not quantitatively precipitated unless the concentration is over 28% HCl, and tellurium is not precipitated alone quantitatively if the HCl concentration is over 42%. Prolonged passage of SO_2 gas

into solutions of selenium and tellurium is to be avoided. It is often preferable to add a saturated solution of SO_2 and allow to stand.

Place the paper and precipitate in the original beaker, add 15 ml. HNO_3, and break up the paper by means of a pair of glass rods. Heat on the steam bath for 15 minutes or until the precipitate of selenium and tellurium is entirely dissolved. Dilute to 30 ml. with water, filter off the paper pulp, and wash thoroughly with numerous small portions of hot water, keeping the volume as low as possible. Evaporate the filtrate to dryness on the steam bath. This treatment separates selenium and tellurium from any gold which would also be precipitated with SO_2.

Add 100 ml. HCl, wash down the sides of the beaker with hot water, warm on the steam bath for a few minutes, and saturate with SO_2 gas at 15–20° C. The red selenium is precipitated quantitatively, free from tellurium, in HCl of concentrations greater than 90 per cent. Allow the precipitate to settle several hours and filter through a weighed Gooch crucible having a thick mat of asbestos. The asbestos in the crucible should have been washed thoroughly with concentrated HCl, and the crucible heated in the muffle before placing in the drying oven to get the tare weight.

Wash the precipitate several times with HCl, scrubbing the beaker well, and then with cold water until free of chlorides. The filtrate and washings are retained for tellurium. Finally wash several times with alcohol, discarding the alcohol washings. Dry at 110° C. for 1–2 hours and weigh as Se. After weighing, heat the crucible in the muffle at 700° C. to expel the selenium, and reweigh as a check.

Dilute the filtrate and washings to 300 ml. if not already up to that volume, so that the HCl concentration is about 25–30% by volume. Heat just to boiling, pass in SO_2 until well saturated, add 10 ml. of a 15% solution of hydrazine hydrochloride and allow to stand for several hours on a steam bath.

Filter on a weighed Gooch crucible and wash with 1:3 HCl, then with hot water, and finally with alcohol. Wash tellurium rapidly as it oxidizes more readily when moist than does selenium. Dry at 110° C. for 1–2 hours and weigh as tellurium.

Carry through duplicate samples to which known quantities of selenium and tellurium have been added, as a check on possible

losses of these elements in the processes of heating, precipitating, filtering, etc. The double precipitation outlined above will give satisfactory results for selenium and tellurium in nearly all classes of materials.

SPECIAL PROCEDURES

1. For selenium and tellurium in some materials such as glass it will be necessary to decompose in the presence of HF, or for lead slimes to fuse with $Na_2CO_3 + NaNO_3$ in a nickel crucible, filter, and acidify the filtrate with HCl.

2. With anode muds rich in silver chloride the latter may be dissolved in NH_4OH, after prior acid treatment, to set free occluded selenium and tellurium.[5, 6]

In such refinery slimes it is usually advisable to remove silver as chloride, separate Se and Te with SO_2, dissolve in hot dilute HNO_3 to remove gold and occluded platinum metals, and precipitate Se and Te separately as described above. For small quantities of Se and Te it may be preferable to collect these, together with As, Sb, Bi, etc., in a ferric hydroxide precipitate, dissolve in HCl, and gas with SO_2. Where large quantities of lead are present in a slime it is better to remove lead initially with H_2SO_4 before separating Se and Te in HCl with SO_2. In some cases it may be desirable to separate the sulphides of Group 2 from iron, after collection in a ferric hydroxide precipitate and removal of copper with ammonia, by ammonium sulphide treatment. As, Sb, Se, and Te can be thus dissolved away from Bi, Pb, and traces of copper. Finally the Se and Te are isolated by SO_2 in HCl.[5]

3. For tellurium in lead dissolve a large sample, e.g. 100 gm., in 200 ml. H_2O and 100 ml. HNO_3, and add 70 ml. 1:1 H_2SO_4. Cool and filter, washing well with hot water. Retain the precipitate to recover occluded tellurium and reduce the bulk of the filtrate by boiling, finally taking to fumes. Filter and wash. Dissolve the combined precipitate in HCl, heat, and gas with SO_2 in 10–15% HCl solution. Filter, dissolve any tellurium off the paper with hot 1:1 HNO_3 and add to the filtrate above. Evaporate the combined filtrates to dryness. Cool, take up with 20 ml. HCl, dilute to 50 ml. with water, and heat to boiling. Filter, wash, add another 20 ml. HCl, dilute to 150 ml. with water, and heat to

boiling. Gas for 5 minutes with SO_2. Filter through a weighed Gooch crucible, wash with water, dry for one hour at 105° C., cool, and weigh as tellurium.

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SILICON

SILICON is a very abundant and widespread element, and its determination is required on nearly every class of material. It is almost invariably separated as an insoluble precipitate of SiO_2 obtained after dehydration with acids, and can be determined by the loss in weight after treatment with HF. About the only element which interferes seriously in the usual silica analysis is fluorine.[3] For routine work in industrial practice it is frequently customary to determine crude silica on slags, etc., by weighing the insoluble residue after a carbonate fusion and dehydration with acid.

GENERAL PROCEDURE

Weigh out 0·5–5 gm. sample, depending on the silicon content, moisten with a few ml. water, add 10–20 ml. HNO_3, 10–20 ml. HCl, and 10 ml. 1:1 H_2SO_4. Evaporate to strong fumes of H_2SO_4. If sulphides are present a few drops of bromine or KBr-Br mixture should be added prior to the initial addition of acid. If an insoluble residue remains, this must be decomposed by fusion with sodium carbonate, solution in acid, and dehydration. If the sample does not contain sulphides or metals that would injure platinum, it may be decomposed directly by fusing with Na_2CO_3, dissolving the solidified melt in dilute HCl, and evaporating twice to dryness, moistening with HCl both times. Silicon carbide is fused with Na_2CO_3 in a platinum crucible, whereas ferrosilicon is fused with Na_2O_2 in an iron crucible.

Dehydration of the silica, to transfer it into a form amenable to filtration and washing, is effected by fuming strongly for 10–15 minutes with H_2SO_4 or $HClO_4$, or evaporating twice to dryness with HCl and moistening with the latter each time.[1, 8] If silver is

present dehydration should be carried out with H_2SO_4. Materials such as irons and steels are usually treated with H_2SO_4 or $HClO_4$ to dehydrate the SiO_2.[2, 11] It is not necessary to evaporate to dryness, in fact in this case basic ferric sulphate is formed with H_2SO_4 and is difficult to get back into solution.

Perchloric acid is better for dehydrating silicas in iron and steels, since there is no production of sparingly-soluble ferric sulphate. It has been shown recently by an authoritative body[6] that perchloric acid is markedly superior to other dehydrating agents in the analysis of silicon in irons and steels, and in addition perchloric acid is a much better decomposing agent for resistant carbides. Fifty ml. of $HClO_4$ are recommended for a 5 gm. sample.

Perchloric acid is likewise preferred for samples where Pb, Ba, Ca, or Sr are present, as these perchlorates are completely soluble in water, unlike the corresponding sulphates.

Following dehydration, the sample is cooled, 5–10 ml. HCl added unless there is H_2SO_4 or $HClO_4$ present, followed by 50–100 ml. hot water. Boil, filter through a Whatman 40 or 42 paper, with paper pulp, and wash thoroughly with hot 2% HCl and finally with hot water. Scrub the beaker or casserole thoroughly with a rubber policeman to remove all adhering traces of SiO_2. Retain the filtrate and again evaporate this to dryness, moistening twice with HCl. Take up as before with HCl and hot water, boil, and filter off the silica which has escaped dehydration the first time. If H_2SO_4 or $HClO_4$ are used to dehydrate SiO_2, of course, the addition of a small quantity of these to the filtrate is employed instead of HCl. Place the combined papers and precipitate in a platinum crucible, dry, and ignite carefully in a muffle. Care must be taken to avoid loss of the light silica precipitate, and usually it is best to char the moist paper and finally ignite at a bright red heat until all carbonaceous matter is destroyed.

Cool the crucible in a desiccator, weigh, add 10 ml. HF and 2 drops of 1:1 H_2SO_4, place on the edge of the hot plate, and evaporate carefully to dryness. Place in the muffle and gradually increase the temperature to a bright red heat, cool in a desiccator, and reweigh. The difference in weights represents SiO_2:

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

$$SiO_2 \times 0{\cdot}4675 = Si$$

In silica determinations, and in all analyses where a carbonate fusion is made, a great time-saver is a Monel metal plate with depressions into which the molten material is poured, as described by the writer.[12] The melt solidifies very rapidly in the form of a button, and is picked up with platinum-tipped tongs and placed, together with the crucible, in the beaker or casserole in which the solution of the material is to take place. In this way only a thin layer of the solidified melt is left in the platinum crucible, and this very rapidly disintegrates with dilute HCl. The crucible is lifted partly out of the beaker, rinsed, and is immediately ready for another fusion. The button which was placed in the beaker alongside, but not in, the crucible, is soon attacked and dissolved with dilute HCl. If necessary, a few taps with the flattened end of a glass stirring rod will break up the button and increase the rate of solution. The Monel metal plate may conveniently be about 12 in. × 4 in. × ¼ in. with round depressions 1 in. in diameter × $\frac{5}{32}$ in. deep at the centre of the concave surface. There is virtually no attack of the Monel plate, since examples of the latter are known to the writer in perfect condition after hundreds of thousands of carbonate fusions have been poured upon them.

In industrial work the second evaporation is frequently omitted except for very high silicas. If lead, tungsten, barium, or other elements which give a sulphuric acid-insoluble precipitate are known to be absent, treatment with HF may be omitted. In this case the silica precipitate is ignited in a small fireclay crucible, the latter cooled in a desiccator and the contents brushed on to the balance pan. A desiccator plate[13] will be found very useful in routine silica determinations. Dehydration by means of perchloric acid is very useful when Pb, Ba, etc., are present since the perchlorates of the latter are soluble and the insoluble residue represents true SiO_2.

The presence of boron in the residue will cause an error in the silica determination since it will volatilize with the HF treatment. Boron may be separated by volatilization as $B(OCH_3)_3$ with methyl alcohol in HCl before expulsion of SiO_2 with HF.

In the presence of fluorine a 0·5 gm. sample of ore or other product is treated with 15 ml. of 20% $HClO_4$ saturated with boric acid at 50° C. The sample is heated until fumes of $HClO_4$ are given off for 5 minutes, cooled, a few ml. of water added and the

fuming is repeated for 5 minutes. The residue is diluted with 75 ml. water, the solution boiled, and silica and insoluble matter filtered off. The filter paper is washed, first with a dilute $HClO_4$ solution and finally with hot water to remove all free calcium salts. The paper with residue is ignited in a platinum crucible, and the silica volatilized by treatment with HF and determined in the usual manner by the loss of weight. The method is based on the fact that when a silicate containing a fluoride is fused with boric oxide no loss of SiO_2 occurs, since the fluorine is expelled as boron trifluoride, BF_3.

In all silica determinations it is essential to run a blank from time to time, employing the same reagents and glassware as used in the analysis. For all accurate work it is necessary to add to the solution of the reagents approximately as much iron and aluminium as is contained in the sample under analysis. Otherwise very little of the silica that is introduced by glassware, reagents, etc., is carried down as a precipitate, and the blank is lower than it should be.

As a general rule other elements are determined on the filtrate from the silica separation. Iron and silica, or silica, alumina, lime, and magnesia are often done on the same sample. The residue from the HF evaporation of SiO_2 in a platinum crucible may consist of compounds of Al, Mg, etc., so it is retained and fused with $KHSO_4$. The melt is then dissolved in the filtrate from the silica separation.

In these determinations it is advisable to use Speedyvap watch glasses for rapid evaporations. In the absence of a water bath, silica evaporations may be carried out by placing porcelain casseroles on a 600 ml. beaker filled with boiling water on the hot plate. A few pieces of test lead in the bottom of the beaker will prevent bumping.

For taking a silica sample down rapidly to dryness without spitting, as in high iron materials, the use of a quartz radiant heater is recommended. A vitreosil heater is clamped directly above the casserole containing the sample for dehydration. Evaporation from the top minimizes spitting.

SPECIAL PROCEDURES

1. In recent years work has been reported [4, 9] on the rapid determination of silica in works laboratories by the mutual flocculation of gelatin and silicic acid. Dehydration of silica is eliminated and the procedure works satisfactorily on many materials ranging from 0·1 to 40% Si. We have not had success with this procedure on ores, concentrates, and slags though we have had good results on ferrosilicons. It is possible that while it is apparently satisfactory for metals and alloys, including metallic iron, aluminium, and magnesium, the presence of calcium in ore materials may interfere in this method.

2. For rapid routine analyses of slags and similar products the material can usually be fused directly with sodium carbonate in platinum dishes or crucibles, the contents poured on to a Monel metal plate and the solidified button together with the dish or crucible placed in an 800 ml. beaker. A little dilute HCl is now added to dissolve the fusion, the platinum dish rinsed and removed, and the contents of the beaker evaporated rapidly on the hot plate. A large beaker such as an 800 ml. covered with a Fisher Speedyvap watch glass, enables evaporation to proceed quickly. Remove from hot plate, just moisten with HCl, place on hot plate, and evaporate to dryness. Remove, moisten with HCl, and again take to dryness, allowing to bake several minutes. Remove from hot plate, cool, add 5–10 ml. HCl, 50–75 ml. hot water, and boil. Filter and wash. Transfer to fireclay crucibles and ignite in a muffle for 15 minutes at bright red heat. Cool, brush contents on to balance pan and weigh. It may be quite satisfactory for works control to report this crude silica or insoluble as SiO_2, or it may be preferable to convert it by means of a correction factor to true silica. If the slag or other product is fairly constant in composition, it is possible to apply a correction factor to the crude silica obtained in this manner. Since the loss of silica through a single evaporation may tend to be balanced by gains through weighing small quantities of other substances in the final precipitate besides true SiO_2, this correction is generally not large.

3. For determination of free silica in rocks and dusts, a procedure similar to that worked out by Rabson for Witwatersrand

dusts may be employed.[7] The technique for this determination naturally varies with the type of material under examination, and results should be checked by microscopic and X-ray investigations.

In this method the non-mineral matter is first removed. The sample is then ignited to decrease the solubility of the quartz in alkali solution. Potassium pyrosulphate is added and a fusion carried out at low red heat. The silicic acid liberated by the decomposition of the silicates is extracted with sodium hydroxide solution under controlled conditions. The sodium hydroxide treatment is repeated on the residue of quartz after the silicic acid has been removed, and the amount of quartz dissolved is determined colorimetrically. An estimate of the quartz dissolved in the first extraction is obtained by doubling the quartz dissolved in the second extraction.

The residue of quartz is ignited and weighed. Since it is generally contaminated with a small amount of undecomposed silicate, it is evaporated with hydrofluoric acid to determine the undecomposed silicate residue, for which a suitable correction is made. To the weight of quartz thus found is added the amount dissolved in the alkali treatments. The combined silica is determined colorimetrically in the solution from the first sodium hydroxide treatment, the silica due to solution of quartz being deducted.

Talvitie[10] has recently outlined a procedure for the determination of quartz in the presence of silicates, using phosphoric acid.

4. The determination of silicon in organosilicon compounds has been reviewed by McHard, Servais, and Clark.[5]

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SILVER

SILVER is found in minerals, ores, concentrates, smelter and refinery products, jewellery, electroplating solutions, etc. In small quantities it is best determined by fire assay methods, which have already been discussed in the sections on gold and the platinum metals.[3] It is important in fire assay work to keep the cupellation temperature as low as possible to avoid losses of silver. Silver is usually determined gravimetrically by weighing as AgCl in nitric acid solution.[2] Very few elements interfere, about the only common ones being silicon, lead, and mercury. Silica and lead may be separated by dehydrating with H_2SO_4 instead of HCl, whereas elements such as bismuth and antimony which hydrolyse in the dilute acid solution necessary for the complete precipitation of the silver may be separated by repeated solution of the mixed chlorides in NH_4OH and re-precipitation with HCl.[5] Silver chloride is virtually insoluble in dilute HNO_3 containing a small excess of the chloride ion. It is appreciably soluble in strong nitric or hydrochloric acids, and in water.

Silver may be determined in pig lead by precipitation as AgI in HNO_3 and tartaric acid solution.[1] This procedure is not applicable for products like copper refinery slimes containing selenium and tellurium, since selenious acid solutions are reduced by KI with precipitation of selenium. Silver must be first separated as AgCl.

Silver can be separated, together with Cu and Co, from a number of other elements by precipitation with sodium or potassium ethyl xanthate in ammonia, in the presence of tartrate to keep iron in solution.

GENERAL PROCEDURE

1. Gravimetric method as AgCl

Weigh out 0·5–5 gm. sample, depending on the silver content, to obtain a final weight of about 0·2 gm. silver. Decompose with 10–20 ml. HNO_3 and remove SiO_2 and Pb if present by adding 10 ml. 1:1 H_2SO_4 and taking to strong fumes of SO_3. If silver is apt to be initially present as chloride, treat the nitric acid-insoluble portion with NH_4OH separately to liberate occluded substances, and add to the main solution.[5] Silver chloride forms with ammonia the compound $2AgCl.3NH_4OH$ which is soluble in ammonia.[3] If an acid-insoluble residue is present, fuse with sodium carbonate, cool, add water, filter off the insoluble silver carbonate from the soluble NaCl, etc., and dissolve the silver carbonate in HNO_3. In the analysis of silver it must be kept in mind that silver sulphate is only slightly soluble in water, hence sufficient H_2SO_4 and water must be present to keep it in solution during washing, etc.

Bring the solution of approximately 1% HNO_3, containing about 0·2 gm. silver in 400 ml., to 70° C. and add sufficient 10% HCl slowly and with constant stirring to precipitate all the silver. Work out of direct sunlight. Avoid the addition of a large excess, and stir vigorously to coagulate the fine AgCl particles which otherwise tend to pass through the filter. 25 ml. of 10% HCl will precipitate over 1 gm. of silver.

$$AgNO_3 + HCl \rightarrow HNO_3 + AgCl$$

Warm until the precipitate settles and test the supernatant liquid with several drops of HCl to make sure that precipitation is complete. Allow the covered solution to stand in a dark place for several hours or preferably overnight. Pour the supernatant liquid through a weighed Gooch crucible, wash the precipitate by decantation several times with 0·1% HCl and transfer the precipitate to the crucible, washing several times with hot water.

Dry the crucible and contents at 100° C. in an oven for 1–2 hours until constant weight has been obtained. Cool in a desiccator and weigh as AgCl. $AgCl \times 0{\cdot}7526 = Ag$.

When analysing various materials such as refinery slimes for silver by the wet method, it is often desirable to express the final

result in ounces per ton as well as percentages. This can be done by utilizing the relation 100 oz. per ton = 0·3429%. In some countries gold and silver are reported in pennyweights. 20 dwt. = 1 oz. Troy.

The limit of accuracy when determining Ag gravimetrically as AgCl, using the analytical balance sensitive to 0·0001 gm. is of the order of 0·3–0·6 oz./ton when using 10 gm. samples on materials ranging from 1 to 1000 oz./ton. Using a 100 gm. sample the accuracy ranges from complete to 0·06 oz./ton. Table 3 illustrates the accuracy which can be obtained by the gravimetric procedure with samples of varying silver contents. This table indicates that for most materials a sample weight may be selected which will enable a very satisfactory silver determination to be made without recourse to a fire assay procedure.

TABLE 3

Limit of accuracy in determining silver gravimetrically as AgCl

Wt. of sample taken gm.	Silver content oz./ton	Wt. of silver in sample gm.	Possible error oz./ton	Percentage error
1	1	0·00003	—	—
	10	0·0003	4·2	42
	100	0·0034	3·8	3·8
	1000	0·0342	3·0	0·30
	10000	0·3429	2·9	0·029
10	1	0·0003	0·42	42
	10	0·0034	0·38	3·8
	100	0·0342	0·30	0·30
	1000	0·3429	0·29	0·029
	10000	3·429	nil	nil
100	1	0·0034	0·038	3·8
	10	0·0342	0·030	0·30
	100	0·3429	0·029	0·029
	1000	3·429	nil	nil
1000	1	0·0342	0·0030	0·30
	10	0·3429	0·0029	0·029
	100	3·429	nil	nil

2. Volumetric method with NH_4CNS

This method is based on the greater affinity of silver ions than ferric for thiocyanate.[4] When all the silver has been precipitated as thiocyanate, the ferric indicator reacts with the NH_4CNS to produce the characteristic red colour of $Fe(CNS)_3$. The titration is carried out in the cold in a dilute HNO_3 solution, usually 1–10% by volume.

$$AgNO_3 + NH_4CNS \rightarrow NH_4NO_3 + AgCNS$$
$$Fe(NO_3)_3 + 3NH_4CNS \rightarrow 3NH_4NO_3 + Fe(CNS)_3$$

The solution must be free of nitrous fumes, chlorides, sulphates, mercury, palladium, and salts that impart a strong colour to the solution.

Prepare 200 ml. of an approximately 5% HNO_3 solution containing about 0·3 gm. silver and none of the interfering elements listed above. Add 4 ml. ferric alum indicator solution and then HNO_3 drop by drop until the solution becomes practically colourless. Titrate with the standard NH_4CNS solution until a faint pink tint persists after vigorous shaking. As the colour is slowly removed at the end it is essential to guard against under titration.

1 ml. 0·1N. NH_4CNS = 0·016989 gm. $AgNO_3$
= 0·010788 gm. Ag

Dissolve 9 gm. of NH_4CNS in 1 litre of water and standardize against a 0·1N. $AgNO_3$ solution made by weighing 16·989 gm. $AgNO_3$ per litre, or dissolving 10·788 gm. pure silver in HNO_3 and making up to 1 litre. If a number of volumetric determinations for silver are to be made, it is usual to adjust the NH_4CNS solutions so that 1 ml. = 0·005 gm. silver. In this case about 3·7 gm. NH_4CNS per litre are required, and the solution is adjusted by titration against a standard silver solution containing 1·25 gm. pure silver foil dissolved in 10 ml. dilute HNO_3, and diluted to 250 ml. One ml. of this solution contains 0·005 gm. silver.

The solution of ferric alum is made by dissolving enough ferric ammonium sulphate or ferric sulphate to make a saturated solution, and then adding enough boiled HNO_3 to bleach the

brown colour of the solution. The same quantity, 2 ml. per 100 ml. of solution, should be used in all titrations.

SPECIAL PROCEDURES

1. In handling products like refinery slimes where part of the silver may be present as AgCl it may be preferable to separate the HNO_3-soluble fraction from AgCl, SiO_2, etc., and treat the latter with NH_4OH.[5] AgCl dissolves in NH_4OH and may be added to the main portion, leaving Fe, Se, Pb, Bi, etc., on the filter paper. The combined filtrate of Cu, Ag, etc. in HNO_3 solution may be treated with a little HCl to precipitate the silver.

For silver in copper refinery slimes place sample in 600 ml. beaker and add 75 ml. HNO_3 and 5 gm. $KClO_3$.[5] Heat slowly and finally evaporate to 50 ml. Cool, dilute to 450 ml., add 10 ml. HCl and allow to settle 4 hours. Filter through Whatman No. 42 paper and wash well with 2% HNO_3. Dissolve AgCl off the paper with hot 1:1 NH_4OH and wash well. Heat the filtrate, cool, and if any turbidity appears, filter before making acid. Add HNO_3 to about 1%, and precipitate silver by the addition of HCl in the usual manner. This gives silver free of Au, Si, Pb, Se, etc. Avoid boiling ammoniacal solutions of silver salts, since explosive compounds of silver and nitrogen are formed under such conditions.

With heterogeneous materials such as refinery slimes it is often preferable to decompose a large inital sample, made up to volume and withdraw a suitable aliquot. A convenient dispensing pipette for routine aliquoting has been described.[6]

2. Silver is determined in such materials as lead by the following procedure,[1] precipitating as AgI in the presence of tartaric acid to hold up impurities which might otherwise precipitate with KI.

Reagents

(*a*) Potassium iodide solution, 10 gm. per litre. Prepare fresh as required.

(*b*) Nitric-tartaric acid wash solution. Dissolve 20 gm. of chloride-free tartaric acid in 200 ml. of 1:9 HNO_3 and dilute to 1 litre.

Weigh out 100 gm. of the milled sample into an 800 ml. beaker, add 1 gm. of chloride-free tartaric acid, 400 ml. of 1:4 HNO_3 and heat gently to dissolve the sample. When reaction ceases add 10 ml. of HNO_3, continue to heat gently until all metal is dissolved, boil to expel brown fumes, and cool to room temperature. Filter through a Gooch crucible, and discard the precipitate.

It is essential that after this filtration the silver be precipitated and filtered as soon as possible, in order to minimize the possibility of precipitation of any salts of lead.

Dilute the filtrate in a 600 ml. beaker, to 400 ml., and heat to 50° or 60° C. Add slowly, while stirring, 5 ml. of KI solution and digest at 50° C. for 15 minutes, avoiding direct sunlight. Filter through a weighed 15 ml. Gooch crucible.

Transfer the precipitate to the asbestos filter, and wash twice with hot nitric-tartaric acid wash solution. Wash the precipitate six times with hot water by filling the Gooch crucible and draining by suction. Continue washing until the washings show no colour when H_2S is passed into the filtrate. Dry the AgI precipitate at 110° C. to constant weight. $AgI \times 0{\cdot}46 = Ag$.

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SODIUM

See POTASSIUM and SODIUM

SULPHUR

SULPHUR is one of the commonest elements determined in a chemical laboratory. It occurs as sulphides, sulphates, and various other sulphur-containing compounds, and its analysis is required in ores, concentrates, metals and alloys, soils, waters, foodstuffs, agricultural materials, building products, and many industrial articles.

Sulphur is generally determined gravimetrically by precipitation as barium sulphate, but if all the sulphur is in the sulphide form as in irons or steels it may be determined by evolution of H_2S upon treatment with HCl.[6, 9, 10] In the gravimetric analysis of sulphur all sulphide sulphur must be oxidized by bromine or a chlorate prior to addition of HNO_3 and HCl to decompose the sample. The silica in the material is then dehydrated by several evaporations with HCl, filtered off, and $BaCl_2$ added to the filtrate to precipitate sulphur as $BaSO_4$. In industrial work very few, if any, other elements are removed prior to addition of $BaCl_2$, though for very accurate work it is preferable to remove iron or reduce it to the ferrous state. Copper may be removed by electrolysis in HNO_3 solution or during reduction of iron with aluminium. Usually, however, Cu, Ni, Co, Fe, etc., are not removed prior to precipitation of sulphur with $BaCl_2$.

GENERAL PROCEDURES

1. Gravimetric method

Weigh out 0·5–10 gm. sample, depending on the sulphur content, into a 400 ml. beaker and add 10–30 ml. KBr-Br mixture. This mixture is made by dissolving 160 gm. KBr in as small a

quantity of water as possible in a 2 litre beaker, adding 100 ml. bromine under a hood with a good draught, with vigorous stirring, and making up to 1 litre in the beaker.

Allow the sulphur sample to stand 10 minutes in the cold and add 10–25 ml. HNO_3. After 15 minutes place on asbestos at edge of hot plate and take to dryness slowly. If the material is not soluble in HNO_3, add HCl after decomposition with HNO_3 has proceeded for some time. If a portion of the sample is insoluble in *aqua regia* a few drops of HF may be added after decomposition with HNO_3, and then with $HNO_3 + HCl$, has proceeded as far as possible. As a general rule even refractory slags are decomposed almost completely with the bromine, HNO_3, and HCl, and the very small quantity of undecomposed material does not contain sulphur.

The sample is carefully taken to dryness, moistened with HCl, evaporated to dryness, moistened a second time with HCl and again evaporated to dryness. This serves to eliminate HNO_3 and to dehydrate silica. Five ml. HCl are now added, 50–75 ml. of hot water, and the sample is boiled, filtered into a 600 ml. beaker and washed thoroughly with hot water. It may be necessary to use a double Whatman No. 40 or No. 42 filter paper, and even add paper pulp to this, in order to obtain a crystal clear filtrate from highly siliceous ores or slags. For certain types of highly siliceous ores where great difficulty is experienced in obtaining a clear filtrate for the precipitation of sulphur, it is preferable to remove the iron with NH_4OH. This removes all SiO_2 as well and gives a clear filtrate. In this case it is advisable to add $(NH_4)_2CO_3$ as well as NH_4OH to remove traces of Pb or Ba which might otherwise be eventually precipitated along with sulphur. For heavy iron precipitates dissolve and re-precipitate to set free any occluded sulphur.

The filtrate is diluted to 300 ml., boiled for 5 minutes to eliminate all CO_2, and sufficient 10% $BaCl_2$ solution added cautiously to precipitate all the sulphur. Ten ml. of 10% $BaCl_2.2H_2O$ solution will precipitate 0·13 gm. sulphur. The sample is removed from the hot plate and set in a warm place away from all sulphur fumes for two hours or preferably overnight.

The precipitate of $BaSO_4$ is filtered through Whatman No. 40 or 42 paper, using paper pulp. It is washed thoroughly with

hot water, and in case large quantities of Fe, Cu, Ni, Co, Zn, are present, it is preferable to wash several times by decantation with hot 1% HCl prior to the final washing with hot water. The paper and precipitate are transferred to a fireclay crucible, dried, and ignited in a muffle for 30 minutes at a bright red heat. The crucibles are cooled in a desiccator, the contents brushed out on to a balance pan watch glass with a stiff bristle brush, and weighed as $BaSO_4$.

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2HCl$$
$$BaSO_4 \times 0{\cdot}1373 = S$$

In this work, as in routine silica and other gravimetric determinations, a copper or transite tray with holes to accommodate fireclay crucibles or other subjects, is a great convenience.[12] It may be made with a vertical handle lifting in and out of a large desiccator. The latter is then kept in the balance room and only the tray carried from muffle or oven to the desiccator.

In all procedures for sulphur it is essential to carry through a blank on reagents and solutions from time to time.

For very accurate work the precipitate of $BaSO_4$ may be ignited and weighed in a previously weighed platinum crucible.

For sulphur in lead sulphide ores oxidation with Br and HNO_3, followed by evaporation twice with HCl will dehydrate SiO_2. Add Na_2CO_3 solution to transpose Pb and SO_4, boil, filter, and wash. Determine sulphur in the usual manner on the filtrate.

Sulphur in antimony ores, concentrates, or metallic antimony is not easy, owing to the hydrolysis of antimony in the very dilute hydrochloric acid solution required for precipitation of barium sulphate. It is best to remove antimony by heating for an hour in 20% HCl with 5 gm. of ingot iron filings. Sometimes a second treatment is necessary to remove the last of the antimony.

If the sample for sulphur is largely insoluble in acids and contains no substances which would injure a platinum crucible, a direct fusion may be employed. Fuse the finely pulverized material with 5 times its weight of Na_2CO_3 and about 0·5 gm. KNO_3. Extract with water, evaporate to dryness, dehydrate SiO_2 as before with HCl, and obtain a clear filtrate for the precipitation of $BaSO_4$.

This method can be used for sulphur on the sulphates of Ba,

Ca, Sr, and Pb.[7] Fuse with Na_2CO_3 and extract with water. Filter off the insoluble carbonates of Ba, Ca, Sr, and Pb, and wash well with hot dilute Na_2CO_3 solution. The sulphur will be in the filtrate in the form of Na_2SO_4 and can be determined by acidifying with HCl, boiling, and precipitating sulphur with $BaCl_2$ in the usual manner. It is not necessary to fuse the sulphates of Pb, Ca, or Sr. They may be transposed by digesting with a strong solution of Na_2CO_3 saturated with CO_2, keeping the solution at boiling temperature for half an hour. The lead, etc., is precipitated as the water-insoluble carbonate. Filter, wash well, and determine sulphur on the filtrate.[13]

When sulphur is precipitated from a hot solution of fairly small volume in the presence of considerable ferric iron, the $BaSO_4$ precipitate is always slightly contaminated with iron. For work of the highest accuracy it is necessary to remove iron by two ammonia precipitations, using an excess of NH_4OH to minimize the occlusion of sulphuric acid in the ferric hydroxide precipitate. Wash thoroughly with hot water and make the filtrate slightly acid with HCl. Precipitate the sulphur as $BaSO_4$ with $BaCl_2$ solution in the usual manner. The sulphate ion is only adsorbed to a very slight extent by $Fe(OH)_3$ and a single precipitation suffices for nearly all work. The phosphate separation of iron likewise gives very low adsorption of sulphur, but zinc oxide may give very high adsorption.[8]

Instead of removing iron it may be reduced to the ferrous condition, in which state it is less likely to contaminate the $BaSO_4$ precipitate. This is conveniently done by boiling for 5 minutes with a little powdered aluminium until the solution becomes colourless. Filter, wash, and precipitate the sulphur in the filtrate with $BaCl_2$ as usual. Other metals which are precipitated by aluminium, such as copper, will be removed at the same time.

Many materials can be decomposed with $HClO_4$ and taken to fumes of perchloric to drive off HNO_3 and dehydrate SiO_2. Sulphur can then be determined in the filtrate with $BaCl_2$ in the ordinary way.

2. Evolution method

A. *Evolution of S as H_2S by acid treatment.* Sulphur may be determined in iron and steel, in mattes, and certain other metal-

lurgical products where all the sulphur is present as sulphide, by absorbing the H_2S evolved upon treatment with HCl, in a cadmium chloride solution, adding an excess of KIO_3, acidifying and titrating the excess iodine with standard $Na_2S_2O_3$. It is necessary to ascertain by experiment whether all the sulphur in the product is liberated as H_2S by HCl treatment. If so, this evolution method offers a quick procedure for sulphur. The apparatus is illustrated in Fig. 11.

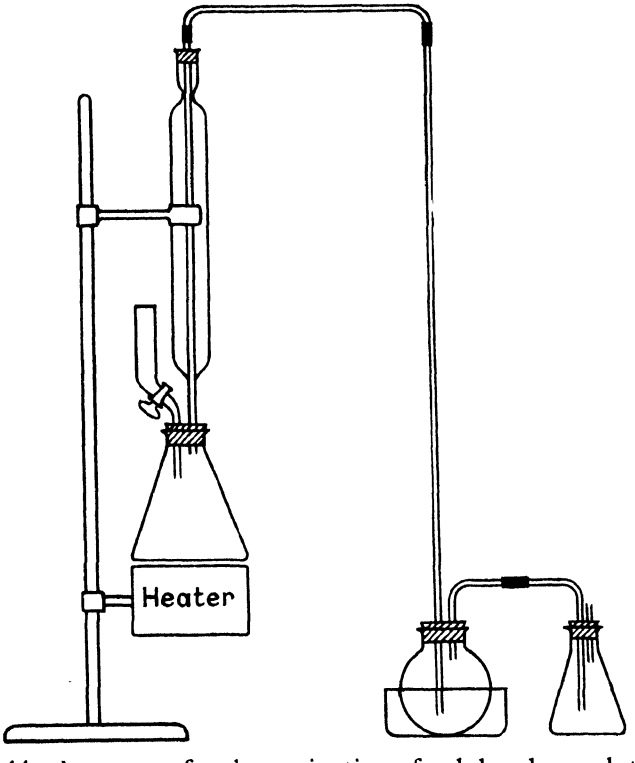


FIG. 11. Apparatus for determination of sulphur by evolution

A 500 ml. wide-mouth Erlenmeyer flask is fitted with a stopper carrying a 250 ml. dropping funnel and a reflux condenser. A glass tube connects the top of the condenser to a litre boiling flask. A 200 ml. Erlenmeyer flask, serving as a trap, is connected to an outlet from the litre flask. An electric heater is used to heat the 500 ml. Erlenmeyer, and the litre flask is placed in a pan of cold water.

The sample of matte or other material is dissolved in 100 ml. HCl admitted to the 500 ml. Erlenmeyer through the dropping funnel. The H_2S evolved is absorbed in 50–100 ml. ammoniacal cadmium chloride solution diluted with water to about 400 ml. in the litre flask. In the 200 ml. Erlenmeyer are placed 50 ml. cadmium chloride solution and 50 ml. water. A quantity of KIO_3.KI solution in excess of that necessary to give sufficient iodine to completely decompose the H_2S formed from the cadmium sulphide is added to the precipitate of cadmium sulphide in the litre flask. The solution is acidified with HCl and the excess iodine back-titrated with standard $Na_2S_2O_3$.

Weigh 0·5–5 gm. sample into the 500 ml. Erlenmeyer flask and add 100 ml. HCl rapidly through the dropping funnel. Close the funnel stopcock and apply heat. When the liquid boils, lower the resistance in the heating coil, and boil quietly for 10 minutes or until the sample is decomposed. Turn off the heat, flush the system with air from a compressed-air line by means of a glass tube in a stopper fitting into the dropping funnel. Remove the absorption flask, washing the fittings into the flask. Add an excess of standard KIO_3.KI solution, usually 10–25 ml., to the flask from a burette. Quickly acidify the solution by adding about 50 ml. HCl, stopper the flask and shake vigorously for several minutes. The simultaneous generation of iodine from KIO_3.KI and H_2S from CdS is essential since it prevents loss of H_2S. Starch solution is added and the excess iodine back-titrated with standard $Na_2S_2O_3$.

$$H_2S + CdCl_2 \rightarrow CdS + 2HCl$$

$$H_2S + I_2 \rightarrow 2HI + S$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

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

Care is necessary in inserting the stopper carrying the reflux condenser and funnel into the 500 ml. Erlenmeyer to secure a gas-tight connection. To avoid acidifying the ammoniacal $CdCl_2$ solution it is advisable to discontinue heating the acid solution as soon as decomposition of the matte is complete.

In the presence of selenium, a part of which is evolved as H_2Se, the above method must be modified by inserting in the apparatus

a flask or tube containing acid zinc-potassium chloride solution which retains the selenium but allows the H_2S to pass through. Insert between the reflux condenser and the flask containing the ammoniacal cadmium chloride, a flask or bottle containing 200 ml. of the acid zinc-potassium chloride solution so that the stream of H_2S must bubble through the latter before reaching the $CdCl_2$.

An all glass apparatus, such as illustrated in A.S.T.M. *Methods of Analysis of Metals*,[1] is preferable for sulphide sulphur work.

Reagents

1. Potassium iodate—potassium iodide solution: KIO_3 5·599 gm. per litre. KI 24·0 gm. per litre. 1 ml. of this solution = 0·0025 gm. S.

Standardize the KIO_3.KI solution against arsenious acid. 25 ml. of 0·1N. As_2O_3 is equivalent to 16·20 ml. of the above iodate solution.

2. Sodium thiosulphate solution: $Na_2S_2O_3$ 39·10 gm. per litre. 1 ml. = 1 ml. of the above KIO_3.KI solution.

3. Ammoniacal cadmium chloride solution: 22·5 gm. $CdCl_2$ dissolved in 1 litre of 1:1 NH_4OH. 50 ml. of this solution will absorb the H_2S from a 0·5 gm. sample containing 35% sulphide sulphur.

4. Acid zinc-potassium chloride solution: mix 10 gm. zinc oxide with water and dissolve with HCl, adding a slight excess only. Add 50 gm. KCl and dilute to 1 litre. Add a solution of KOH until a small portion gives a yellow colour on adding thymol blue indicator, then add dilute HCl until the colour is full red. Any other method of adjusting the acidity of the solution to about *p*H 1 with the same acid and alkali is satisfactory.

B. *Evolution of S as SO_2 by burning in oxygen.* Sulphur has been determined extensively in recent years by volumetric measurements in an absorption apparatus for SO_2 following burning of the sample of iron or steel, etc. in oxygen.[1, 5] In one method the principle is a titration of the residual NaOH in an absorption vessel by H_2SO_4, after passing in SO_2 to a hydrogen peroxide solution of excess NaOH. Though CO_2 is also absorbed by NaOH it is liberated again on acidification, so that sulphur can

be determined in the presence of CO_2. In the other procedure the evolved gases are passed into starch-iodide solution and titrated with standard KIO_3 solution. Carbon dioxide does not affect the titration.

$$SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI$$
$$KIO_3 + 5KI + 6HCl \rightarrow 3I_2 + 6KCl + 3H_2O$$

C. *Evolution of S as H_2S by burning in hydrogen.* The procedure for sulphur in refined copper, wherein sulphur and oxygen are determined together by combustion in a stream of hydrogen, has already been described under Oxygen.

SPECIAL PROCEDURES

Sulphate sulphur

(*a*) *Water-soluble sulphates.* It occasionally happens that "sulphate-sulphur" is required in metallurgical plants. This generally means water-soluble sulphur as distinct from the water-insoluble sulphides of Cu, Ni, Zn, Fe, Co, etc. In this case oxidation of the sample is omitted, and the material is boiled with water for a few minutes, filtered, washed, HCl is added to the filtrate to give about 1 ml. per 100 ml. of solution and $BaCl_2$ is added to precipitate sulphur as $BaSO_4$. If soluble sulphides, such as Na_2S, are present the procedure is altered in the following manner.

If water-soluble and insoluble sulphides and soluble sulphates are all present in the sample, the soluble sulphides may be removed from the aqueous filtrate of the sulphates and sulphides by acidifying strongly with HCl and boiling long enough to expel all H_2S, which is only evolved from the sulphide portion. A small amount of the sulphide will be oxidized during the boiling operation but it can be neglected in industrial work.

(*b*) *Water-insoluble sulphates.* If, however, by a determination of "sulphate-sulphur" is meant calcium sulphate, the best procedure is based on the fact that a dilute ammonium chloride solution will dissolve calcium sulphate but has virtually no effect on sulphides of Cu, Fe, Co, Zn, Pb. For details see a paper by Young and Hall[14] on the determination of calcium sulphate in sulphide ores.

Differentiation of the forms of sulphur

If a soluble sulphide and a sulphate are present together they may be boiled directly with HCl to eliminate H_2S from the sulphide portion, and then the sulphur determined on the solution represents only that from the sulphate. The water-insoluble sulphates of Ca, Sr, Ba, and Pb cannot be determined in this way in the presence of sulphides. In this case the sulphide is determined by evolution, and the sulphate from the equation: total sulphur – sulphide sulphur = sulphate sulphur.

Barium, calcium, and strontium sulphates are soluble in boiling 60% $HClO_4$. On dilution the $BaSO_4$ is precipitated, $CaSO_4$ remains entirely soluble, and $SrSO_4$ comes down only after vigorous stirring.[7]

If a soluble sulphide and sulphate are present together, total sulphur may be determined by adding bromine water and boiling gently prior to any addition of HCl and $BaCl_2$.

If an insoluble sulphide like copper sulphide, and an insoluble sulphate such as calcium sulphate are present together, they may be differentiated by boiling with sodium carbonate to transpose the insoluble sulphate to the water-soluble sodium sulphate, filtering, and determining sulphur in the filtrate. Work at Rhokana Corporation indicates that under these conditions oxidation of copper sulphide is negligible. For instance, boiling the following samples for 15 minutes with 50 ml. of 10% Na_2CO_3 solution gave these results:

TABLE 4

Determination of Sulphur in Copper Sulphide and Calcium Sulphate

Sample	Wt. taken gm.	Total sulphur %	Sulphate present %	Sulphur recovered %
$CaSO_4.2H_2O$	0·2	18·62	18·62	18·62
Copper concentrate	1	23·13		nil
Mill feed	3	1·81		0·17
3 gm. Mill feed +0·2 gm. $CaSO_4.2H_2O$	3·2	2·86	1·32	1·29

Sulphide sulphur in ores and concentrates

(*a*) A modification of the evolution procedure described earlier for sulphide sulphur enables this method to be employed for sulphide sulphur in ores, concentrates, etc. in the presence of sulphate sulphur. Pyrite, however, cannot be determined in this way and in the presence of this mineral the method fails for sulphides of Cu, Zn, etc. The procedure is as follows:

Weigh a 1 gm. sample into a 500 ml. Erlenmeyer flask, and add 1 gm. of lead grain, 5 ml. of 10% $BaCl_2$, 10 ml. of 10% $SnCl_2$ in 1:1 HCl, and 25 ml. of HCl. Connect quickly to the distilling apparatus and boil 15–20 minutes until all the H_2S has been driven over, catching the H_2S in 50 ml. of ammoniacal cadmium chloride solution containing 22·5 gm./litre $CdCl_2$ in 1:1 NH_4OH.

Conduct a current of air through the apparatus while distilling to ensure that all the H_2S is swept through to the cadmium solution.

Filter off the cadmium sulphide and wash three times with warm water. Transfer paper and precipitate to 300 ml. of 5% HCl, add 10 ml. of starch indicator, and titrate at once with N/16 iodine. One ml. of N/16 I = 0·001 gm. S. N/16 iodine contains 7·9313 gm. iodine dissolved in about 20 gm. potassium iodide in a minimum quantity of water and made up to one litre.

The solution should be stirred during the titration with the capillary tube used to conduct the H_2S into the cadmium solution, as some of the CdS adheres tenaciously to the inside of the tube, and is not easily removed.

(*b*) Williamson[11] describes procedures for the evaluation of soluble and insoluble sulphur in a sulphide treatment plant which depend on the solubility of $CaSO_4$ and other sulphates in dilute Na_2CO_3 solution, and the insolubility of sulphide sulphur in this solution.

A 2 gm. sample is weighed into a 250 ml. beaker and digested for 10 minutes with 35 ml. of 1·0N. Na_2CO_3 solution. The sample is filtered and washed four times. The filtrate is discarded and the washed solids are returned to the original beaker. This material is taken to dryness with 25 ml. of HNO_3 containing 1 gm. of $KClO_3$ and baked on a moderate hot plate for 10 minutes. The sample is taken up with 5 ml. of HCl and evaporated twice,

7 ml. of HCl and 35 ml. of H_2O are added and the sample boiled. After cooling, 10 ml. of NH_4OH are added and the excess ammonia expelled by boiling. The precipitate is filtered and washed five times with distilled water. The filtrate is acidified with 3–4 ml. of HCl, heated to boiling, and sulphur precipitated with 20 ml. of 10% $BaCl_2$. The sample is digested for half an hour. The $BaSO_4$ precipitate is washed 5 times with water, ignited, and weighed.

The following determination gives the soluble sulphur and is used on calcines. A 1·373 gm. sample is weighed into a 250 ml. beaker. Add 35 ml. of 1·0N. Na_2CO_3 solution. Boil for 10 minutes. This step is important as sufficient time must be given to take up all soluble sulphates. Filter on No. 1 Whatman paper. Wash 5 times with hot H_2O. Neutralize the filtrate with HCl and add 3 or 4 ml. excess. Heat to boiling and precipitate with $BaCl_2$ as in total sulphur determination.

Sulphur in organic materials

For organic materials such as plant products, a careful fusion with $Na_2CO_3 + Na_2O_2$ in a nickel crucible may be made, or the material may be oxidized with magnesium nitrate solution and slowly ignited.[2] The sample is then taken up in HCl, filtered, and a $BaSO_4$ precipitation made as usual.

Sulphur in coal

Sulphur in coal is usually done on the residue in the bomb after a determination of B.t.u. in a calorimeter. It may also be done by mixing 3 parts Eschka's mixture to 1 part of coal, placing in a crucible in a cold muffle which is raised to 800° C. and kept at that temperature for 1½ hours. Cool, digest with hot water, filter, and determine sulphur on the filtrate. Eschka's mixture consists of 2 parts MgO and 1 part anhydrous Na_2CO_3.

Sulphur in flue gases

The determination of oxides of sulphur in flue gases has been described by Gillham,[5] Flint,[4] and Corbett.[3] It was found that when an 80% isopropyl alcohol : 20% water mixture was used negligible oxidation of SO_2 occurs while the gases are being

sampled and absorbed. By first acidifying the absorbing solution with HCl and then passing O_2-free nitrogen through the liquid, dissolved SO_2 is removed completely without oxidation. This SO_2 is then absorbed in hydrogen peroxide. Sulphuric acid mist is completely removed by the use of a sintered glass filter in conjunction with the absorbing solutions of isopropyl alcohol and water.

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TANTALUM

See NIOBIUM and TANTALUM

TELLURIUM

See SELENIUM and TELLURIUM

THORIUM

BY VIRTUE of its importance in radioactivity and atomic energy developments, thorium may be encountered in many laboratories of mining and metallurgical organizations. The chief separations of thorium are based on the insolubility of its oxalate in acid solution whereas the oxalates of most metals are soluble under these conditions, and the insolubility of thorium iodate in acid solution which serves to separate it from the iodates of rare earths which are soluble in acid. The following general procedure, which combines these two separations, will give good results for thorium in all classes of material. It is based largely on the recommendations of workers associated with the Manhattan Project.[4]

Weigh out a 5 gm. sample, transfer to a silica evaporating dish, and add 8 ml. H_2SO_4. Stir with a glass rod, cover, and heat on a sand bath just below 200° C. for two hours with frequent stirring. Avoid overheating, boiling of H_2SO_4, or spattering. Cool and add 50 ml. ice cold water, with constant stirring. Decant the turbid liquid into a 400 ml. beaker and treat the residue with 3 ml. H_2SO_4 for a further three hours. After cooling the dish and adding cold water as before, wash all the material into the 400 ml. beaker and stir thoroughly to dissolve all soluble salts. Warm the solution to about 40° C. and add 0·5 ml. of a 1% gelatin solution. Filter through Whatman 42 paper, wash thoroughly. Transfer the insoluble residue of silica and undecomposed minerals to a platinum dish and calcine. Mix with about three times its weight of KHF_2, fuse, and stir with a platinum wire. Cool, add 2 ml. H_2SO_4, and fume strongly. Fuse any insoluble residue with Na_2CO_3, leach with water, and make acid with H_2SO_4. Filter off any precipitate and add the H_2SO_4 extracts to the main solution.

To a 600 ml. beaker that contains the clear solution of about 100 ml. from the above acid treatments and fusions, add 50 ml. HNO_3 with stirring. If ceric salts are present, reduce to the cerous state by adding H_2O_2 to the nitric acid solution. Now add slowly to the acid solution, with stirring, an iodate solution containing 16 gm. KIO_3 dissolved in 50 ml. HNO_3 and 30 ml. water. Cover and cool in ice water to room temperature. Filter through Whatman 541 paper to obtain a clear filtrate. Wash the last traces of thorium iodate on to the paper with 30–50 ml. of a wash solution containing 8 gm. KIO_3, 50 ml. HNO_3, and enough water to make 1 litre. Transfer the precipitate back to the original beaker with the wash solution, stir to break up lumps, and refilter through the same paper. Wash the precipitate back into the original beaker with distilled water, heat to nearly the boiling point, and add slowly 30–90 ml. HNO_3 until the solution is clear. Prepare a solution of KIO_3 in boiling water such that 8 gm. KIO_3 is present for every 60 ml. of HNO_3 that is used to dissolve the precipitate. Add this KIO_3 solution to the hot thorium iodate solution with brisk stirring. Cool to room temperature in ice water. Filter the precipitate, wash off the paper and refilter as was done with the first iodate precipitation. Finally wash the precipitate back into the original beaker with water, washing both sides of the paper thoroughly. Retain the paper.

Warm the suspension of thorium iodate, which should have a volume of about 100 ml., to about 40° C. and add 25 ml. HCl. Pass in SO_2 until a clear, faintly yellow solution smelling of SO_2 is produced. Filter through the same Whatman 541 paper that was used before. To remove all iodate left on or in the paper, pass the filtrate through the paper a second time. Wash well with water and retain the filter paper. Make the filtrate alkaline with NH_4OH and allow the white hydroxide to stand one hour. Filter through the same paper used previously and test the filtrate with NH_4OH to be sure that precipitation of thorium was complete. Wash the precipitate with 50–100 ml. of 5% NH_4Cl made ammoniacal with a few drops of NH_4OH. Dissolve the thorium hydroxide off the paper by pouring through the filter a solution of 25 ml. HCl in 100 ml. of water. Refilter the filtrate through the same paper and wash the latter well with hot water.

Heat the filtrate, which should have a volume of about 400 ml.,

to boiling. Add with constant stirring a boiling solution of 25 gm. oxalic acid in 200 ml. water. Stir the thorium oxalate precipitate and allow to settle overnight. Filter through a Whatman No. 42 paper and wash thoroughly with 50 ml. water. Be sure all traces of precipitate have been removed from the sides of the beaker, if necessary wiping with a small piece of filter paper. Place the paper and precipitate in a weighed platinum crucible, char, ignite cautiously, and heat for 2 hours at 900–1000° C. with free access of air. Weigh as ThO_2. $ThO_2 \times 0{\cdot}8788 = Th$.

The reactions in this analysis are as follows:

$$Th(NO_3)_4 + 4KIO_3 \rightarrow 4KNO_3 + Th(IO_3)_4$$
$$Th(IO_3)_4 + 4NH_4OH \rightarrow 4NH_4IO_3 + Th(OH)_4$$
$$Th(OH)_4 + 4HCl \rightarrow ThCl_4 + 4H_2O$$
$$ThCl_4 + 2H_2C_2O_4 \rightarrow 4HCl + Th(C_2O_4)_2$$
$$Th(C_2O_4)_2 + O_2 \rightarrow ThO_2 + 4CO_2$$

SPECIAL PROCEDURES

In the absence of certain interfering elements, many other procedures may be applied. These are described in Rodden's book [4] and other references,[1, 5, 6] or in recent papers of Indian workers.[2, 3, 7]

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TIN

ALTHOUGH tin is not often determined in ores or minerals, apart from actual tin mining operations, it is an important industrial metal and the analysis of tin is of frequent occurrence in most metallurgical laboratories. In tin determinations it must be kept in mind that HCl or *aqua regia* solutions must not be evaporated to dryness, since stannic chloride is appreciably volatile. No volatilization occurs when dilute HCl solutions are boiled in covered beakers, or when HCl-H_2SO_4 solutions are evaporated to fumes of SO_3.

The best method for the determination of tin is oxidation to the quadrivalent state by the addition of a standard iodine solution, after reduction to the divalent form in H_2SO_4 or HCl by such reducing agents as granulated lead, powdered antimony, or strips of aluminium, iron, or nickel.[2, 5]

$$SnCl_4 + 2Pb + 2HCl \rightarrow SnCl_2 + 2PbCl_2 + H_2$$
$$SnCl_2 + I_2 + 2HCl \rightarrow SnCl_4 + 2HI$$

Usually this iodimetric method can be applied without the complete separation of tin from other elements. The principal precautions in this procedure are complete reduction of tin to the stannous form and the prevention of subsequent re-oxidation by air. For the latter it is necessary to keep a non-oxidizing atmosphere by the use of CO_2, usually evolved from $NaHCO_3$.

Tin can be separated from elements other than those of the H_2S group by precipitation with H_2S in 5–10% HCl or H_2SO_4. It can be separated from Cu, Bi, Cd, etc., by precipitation of the latter in alkaline sulphide solution. The separation of tin from copper can be carried out by precipitation with NH_4OH in the

presence of ammonium salts. Selenium and tellurium can be removed from tin samples by SO_2 in strong and weak HCl solutions, followed by boiling out the SO_2 from the filtrates prior to determination of tin. Tin can be separated from arsenic by distillation of the latter as $AsCl_3$, or by precipitation of arsenic with H_2S in strong HCl, and from antimony by precipitation of the antimony on metallic iron. The separation of silicon from tin should be performed by dehydrating with H_2SO_4 or $HClO_4$. Lead is removed by evaporation with H_2SO_4. If molybdenum is present the tin should be reduced with lead, the molybdenum removed with α-benzoin oxime, or the tin removed with a ferric hydroxide precipitation.

For very accurate work it may be necessary to distil over the tin as $SnCl_4$ from a sample such as steel containing Cr, Mo, V, and W which interfere with the titration. Details of this procedure are given in the methods of the U.S. Steel Corporation for tin, cited below.[6] Tungsten in small amounts can be separated by precipitating tin with H_2S in dilute HCl solution containing tartaric acid. If considerable tungsten is present the separation should be done by repeated precipitation with NH_4OH in the presence of ammonium salts, followed by solution of the final precipitate in HCl and tartaric acids and precipitation of the tin by H_2S. It should be kept in mind that tin may be conveniently eliminated by volatilization with Br-HBr mixture. It is sometimes useful to remember that metastannic acid retains copper and antimony but virtually no lead.

GENERAL PROCEDURES

1. Metals and alloys

Decompose 0·5–5 gm. sample with 10 ml. HCl and 10 ml. HNO_3, add 10 ml. 1:1 H_2SO_4 and take to fumes of SO_3. Filter off silica and lead if present, and precipitate tin with H_2S in 5–10% HCl or H_2SO_4 if necessary to remove from Fe, Al, Zn, Ni, Cr, Co, V, etc. Remove copper if present in appreciable quantities with NH_4OH in the presence of ammonium salts. The sample should be finally obtained in a solution containing not more than 0·2 gm. tin, about 10–15 ml. H_2SO_4, and 100 ml. HCl in 300 ml.

solution.[1] Nitrates, tungsten, molybdenum, and vanadium should be absent. Proceed with determination as outlined below.

2. Ores, concentrates, etc.

Weigh 0·5 gm. medium or high grade tin concentrate or 1 gm. low grade into a 50 ml. high form iron or nickel crucible.[3] Add 4 gm. Na_2CO_3, mix thoroughly, and cover with 8 gm. Na_2O_2. Heat the crucible and contents over a small burner or element to expel any water in the flux until the charge starts to melt. Carefully finish the fusion by revolving the crucible round the outer edge of the flame until the mixture melts down quietly. When the contents are in quiet fusion, continue heating with the full heat of the burner or element, while rotating the crucible, for about two minutes.

Let the melt solidify and cool, place the crucible in a 400 ml. beaker, add 60 ml. of cold water, and allow the melt to disintegrate. Remove the crucible from the beaker with a glass rod, rinsing it thoroughly with hot water. Add 50 ml. HCl to the beaker, stirring the solution until all has dissolved, as indicated by the clear green colour of nickel chloride or the brown colour of ferric chloride. Clean the crucible with 50 ml. HCl and add to main solution.

Transfer the solution to a 500 ml. Erlenmeyer flask and dilute to 250 ml. Introduce a nickel strip or foil weighing about 5 gm., boil the solution gently for about 30 minutes until all ferric chloride has been reduced, and small quantities of Cu, Sb, Bi are precipitated. Introduce a second nickel strip and close the flask with a rubber stopper containing a glass tube extending on the outside to the bottom of the flask. Boil the solution gently for another 20 minutes, then seal the end of the glass tube with a hot solution of $NaHCO_3$ in a 250 ml. beaker. Remove the flask from the hot plate, cool to below 15° C., and titrate with a 0·125N. iodine solution using starch as indicator.

For very accurate work it is necessary to exclude air during the titration by inserting the tip of the burette through a small hole in the stopper of the flask, which is kept corked until the addition of the standard iodine solution. When much tungsten is present the blue colour produced is apt to obscure the end point of the starch indicator, and lead is preferable to nickel as a reducing

agent. In the presence of small quantities of vanadium or molybdenum, lead is also preferable for reducing $SnCl_4$.

The iodine solution may be made by weighing 80 gm. iodine and 160 gm. KI into a large beaker and covering with water. When all has dissolved, filter through asbestos into a dark bottle, and dilute with water to 5 litres. Allow to stand for 2 weeks, and standardize against a National Bureau of Standards tin concentrate or tin alloy which has been carried through the steps outlined above. The strength of this iodine solution is such that all concentrates can be run on 0·5 or 1·0 gm. samples without using more than 50 ml. iodine solution. It is undesirable to reduce and titrate more than about 0·4 gm. tin. 1 ml. of 0·1N. iodine solution = 0·005935 gm. Sn or 1 ml. of 0·125N. iodine = 0·007419 gm. Sn.

In routine determination of non-ferrous metals tin is often determined by removing lead with H_2SO_4, copper with NH_4OH, then precipitating tin with H_2S and weighing as SnO_2. This is quite satisfactory for control purposes in the absence of interfering elements such as As, Sb, Bi, Cd, P, etc.

Tin may also be conveniently collected, after *aqua regia* decomposition of the sample, in a ferric hydroxide precipitation, followed by solution in HCl and reduction with Al, Fe, or Ni.[1]

A good paper on the analysis of tin bronzes by Price,[4] gives the methods which have been used for many years in the laboratories of the Tin Research Institute.

In many materials, such as refinery slimes, tin may be determined on the same sample with arsenic and antimony.[7] Arsenic is determined iodimetrically after distillation from HCl at a low temperature, antimony and tin are separated in the filtrate with H_2S and antimony determined in the reduced solution with $KMnO_4$. Tin is subsequently determined iodimetrically on the solution after boiling with test lead, strips of iron or nickel, or powdered antimony.

The Tin Research Institute, Fraser Road, Greenford, Middlesex, England, an international organization to assist users of tin, is always available for chemists who have special analytical problems with this metal.

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TITANIUM

TITANIUM occurs in ores, minerals, soils, ferrous and non-ferrous alloys, cemented carbides, metallic titanium, pigments, and is an important element in an industrial laboratory. As a general rule moderate amounts of this metal can be determined colorimetrically by the yellow to orange colour of titanium sulphate in the presence of H_2O_2. For larger quantities of titanium either gravimetric or volumetric methods may be employed.

GENERAL PROCEDURES

1. Colorimetric determination

Dissolve 0·5–5 gm. sample in 10–20 ml. HCl, 10–20 ml. HNO_3, and a few drops of HF if necessary, add 10 ml. 1:1 H_2SO_4 and evaporate to fumes of SO_3. If HF has been added, add more H_2SO_4 and evaporate a second time to SO_3 fumes to eliminate all fluorine. Take up in water and filter. If any residue containing titanium is left, fuse with $KHSO_4$ and add to the filtrate. A good solvent for titanium compounds in general is a mixture of HF, H_2SO_4, and HNO_3.

If members of the hydrogen sulphide group are present, remove these with H_2S in 5–10% of H_2SO_4. Add 1 gm. tartaric acid, make the filtrate slightly alkaline to the extent of 2 ml. excess NH_4OH per 100 ml. of solution, and pass in H_2S for 5 minutes. Titanium remains in solution while Fe, Co, Ni, and Zn precipitate as sulphides. Wash the precipitate well with dilute ammonium sulphide containing about 1% ammonium tartrate. Boil the filtrate to the complete expulsion of H_2S.

For very accurate work it is advisable to dissolve the precipitate

of sulphides and re-precipitate to recover minute quantities of occluded titanium. The separation above gives titanium, together with Al, Zr, V, W, U, Cr, P, if present. A separation with cupferron will now precipitate titanium from Al, Cr, Mn, and moderate amounts of P.[11] If Zr, V, W, U, or large amounts of P are present they will accompany titanium, but only V and P will interfere in the colorimetric procedure for titanium.

Adjust the volume of the solution to 150 ml. and add 30 ml. 1:1 H_2SO_4. Cool to 10° C., add some paper pulp and precipitate titanium with a freshly-prepared 6% solution of cupferron, adding the latter until there is an excess as indicated by the formation of a snow-white precipitate which rapidly disappears. Filter, wash 12 times with cold 5% H_2SO_4 and then 5 times with 5% NH_4OH. Transfer the paper and precipitate to a platinum crucible, ignite, cool, add $KHSO_4$ and fuse the residue. Extract the solidified melt with dilute H_2SO_4.

If vanadium and phosphorus are present these must be removed by carefully neutralizing the greater part of the free acid present by addition of a solution of NaOH and pouring the mixture into 150 ml. of a hot, normal solution of NaOH, filtering, and washing with hot dilute NaOH. The presence of ferric iron is necessary for the complete precipitation of titanium. It is advisable to repeat the precipitation to remove traces of interfering elements, the titanium being brought into solution with HNO_3 and H_2SO_4, or by fusing with $KHSO_4$.

Transfer the solution, which should not contain more than 0·005 gm. titanium, to a colour comparison tube. Add 5 ml. of 3% H_2O_2 and mix thoroughly. To another comparison tube add 45 ml. of cold 10% H_2SO_4, 5 ml. of the same H_2O_2 solution, and then add from an accurate burette measured amounts of standard titanium sulphate solution containing 1 ml. = 0·0005 gm. Ti, mixing after each addition until the colour of the standard is slightly less intense than the solution. Dilute the standard to the same volume as the unknown and mix. After preliminary comparison, add titanium sulphate solution to the standard, adding at the same time an equal volume of 10% H_2SO_4 solution to the unknown, and mixing after each addition until the colours match exactly.

Any other convenient method of colour comparison may, of

course, be employed.[1, 2, 3, 12] The colour produced by titanium with H_2O_2 is destroyed by HF, whereas that produced by vanadium is not affected. It is advisable to check the colour in this way after making the comparison. The colour comparison may be made in the same manner in $HClO_4$ solution, using a standard solution of titanium perchlorate in place of titanium sulphate.

The above procedure may be considerably shortened in the absence of interfering elements. For example, an initial fusion with Na_2O_2 and Na_2CO_3 separates titanium and iron as precipitates from Al, Cr, V, Mo, W, P. Likewise a NaOH separation gives the same result. If the iron content is low the colour of the ferric iron may be bleached with the addition of a measured quantity of H_3PO_4 to sample and standard in the colorimetric comparison.

2. Gravimetric determination

The decomposition of the sample and elimination of interfering elements are carried out as described above. It is necessary, of course, to eliminate completely many elements whose presence does not interfere in the colorimetric procedure.[4, 7, 8] After the cupferron precipitation and treatment with $Na_2O_2 + Na_2CO_3$, the only elements likely to be still present with titanium are Zr and W. Zirconium is separated by the following procedure: the nitric acid solution is carefully treated with a solution of Na_2CO_3 to neutralize the greater part of the free acid, and to the boiling hot solution is slowly added a 20% solution of ammonium salicylate in sufficient excess to precipitate the zirconium. The mixture is boiled gently for about half an hour or more, diluted to about 200 ml. and filtered hot. The precipitate is washed with a hot 20% solution of ammonium salicylate until its colour is only faintly yellow or white. Titanium passes into the filtrate.

Steinmetz [9] describes a convenient mercury cell for determining small amounts of titanium and similar metals in alloys. Johnson, Weaver, and Lykken [5] also describe a satisfactory unitized mercury cathode apparatus.

Titanium, together with Al, Zr, P, As, V, and U, can be quantitatively separated from such elements as Fe, Cr, Zn, Ni, Co, Sn, Mo, Cu, Bi, and Ag which are deposited in the mercury cathode.

Tungsten may be separated from titanium by the following procedure.[8] About 0·5 gm. of the mixed oxides is fused with 5 gm. Na_2CO_3 in platinum for 20 minutes. The crucible and contents when cold are placed in a nickel dish containing 10 gm. NaOH in 50 ml. water. The covered dish is placed on a boiling water bath for 2–3 hours, and the water lost by evaporation is replaced. The crucible is cleaned and rinsed with 50 ml. of hot water. The solution is allowed to cool or to stand overnight. The residue 1 is washed with half-saturated NaCl solution. The filtrate is treated with diluted HCl until phenolphthalein is decolourized, then heated on the water bath, and the red colour is discharged from time to time with a few drops of the acid. The precipitate 2 is washed in the same way as 1. Precipitates 1 and 2 are treated with a little normal HCl and after dilution to 100 ml., the titania is recovered by heating, making the solution ammoniacal, filtering, washing with NH_4NO_3 solution, and ignition. Unless the precipitate is small, it is leached with dilute acid, reprecipitated, etc. $TiO_2 \times 0{\cdot}5995 = Ti$.

3. Volumetric determination

The volumetric determination of titanium depends on the reduction of a ferric salt by a titanous solution, with the oxidation of the titanium from a valence of 3 to 4.[7, 8, 11] Potassium thiocyanate acts as the indicator for the disappearance of ferric ions. The procedures differ essentially in the choice of a reducing agent for the titanium solution.

(*a*) *Reduction with zinc amalgam*

Reagents

Zinc amalgam. To 100 gm. mercury add 3 gm. of zinc and heat on a water bath. Add a few ml. of 1:1 sulphuric acid. Cool, wash well, and separate from any solid matter in a separatory funnel.

Potassium thiocyanate. A saturated solution is diluted 1:1 with water.

Standard ferric ammonium sulphate. Dissolve 60 gm. of the salt in 600 ml. water and acidify with 20 ml. of sulphuric acid. Add potassium permanganate drop by drop as long as the pink

colour disappears. Dilute to 2 litres. Standardize against 0·20 gm. pure TiO_2. 1 ml. = 0·005 gm. TiO_2.

Procedure. Decompose a suitable weight of sample containing not more than 0·25 gm. TiO_2 by one of the following methods:

1. With nitric, hydrofluoric, and sulphuric acids, taking care to drive off all hydrofluoric acid by strong fuming.
2. Fusion with sodium carbonate.
3. Add 10 gm. of sodium or ammonium sulphate and 20 ml. concentrated sulphuric acid. Digest to complete solution on the hot plate. This last method is confined to fairly pure titanium pigments.

Take up in water and boil to solution, dilute to 100 ml., and make ammoniacal. Heat the solution to 60° C. and oxidize with bromine dropwise. Allow the precipitate to settle, filter, wash with hot water containing a little ammonia and ammonium chloride. Dissolve the precipitate in hydrochloric acid and dilute to 100 ml. Heat to 60° C. and make alkaline with sodium hydroxide solution, again adding bromine dropwise. It is important not to permit the temperature of the solution to exceed 60°, as if it boils there is some danger that metatitanic acid may be precipitated. The precipitate is filtered off and washed with hot water. It is then dissolved in hydrochloric acid and the acidity adjusted to about 10%. Heat to boiling and transfer to the Nakazono reductor. A stream of CO_2 is passed through the reductor and the titanium reduced by vigorous shaking for about 5 minutes using 15 ml. zinc amalgam. The zinc amalgam is tapped off under water, 3 ml. of the thiocyanate indicator added and the solution is titrated to a light straw colour with the standard ferric ammonium sulphate solution.

The Nakazono Reductor. The solution to be reduced is placed in *D* of Fig. 12. CO_2 is passed through *B*, *D*, *C*. Zinc amalgam is added and the flask *E* is filled together with the connecting tubes to stopcock *A* with freshly boiled distilled water. When reduction is complete the zinc amalgam is tapped off through *A* into *E* where it displaces water which rises into *D*. Some manipulation of the rubber tube connecting *E* to *A* may be necessary to accomplish this.

(*b*) *Reduction with test lead.* For high grade materials where the colorimetric method is unsuitable, the following procedure will give good results on routine analyses.

Weigh 0·25–2 gm. sample of the −325 mesh material into a Pyrex "copper" flask, add 25 gm. $NaHSO_4$, and fuse until all dark mineral is in solution. Cool and dissolve in 100 ml. 1:1 HCl. Add 10 gm. test lead to the solution and boil for 15 minutes.

Remove from the hot plate and decant the solution into a beaker. Filter and wash the test lead 5–6 times with water by decantation. Add 5 ml. of saturated KCNS and titrate with

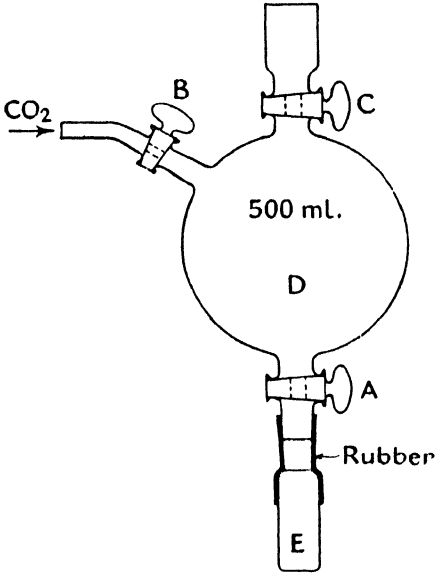


FIG. 12. Cell for reductions with zinc amalgam

ferric ammonium sulphate solution to a faint pink colour. The ferric ammonium sulphate solution consists of 30 gm. of this salt and 10 ml. H_2SO_4 per litre. This solution is equal to approximately 0·005 gm. TiO_2 per ml., and it is standardized by reducing 25 ml. with lead and titrating with standard $KMnO_4$ or $K_2Cr_2O_7$.

$$1 \text{ ml. of } 0{\cdot}1\text{N. } KMnO_4 = 0{\cdot}008 \text{ gm. } TiO_2$$

If members of the H_2S group are present they can be removed by gassing in 10% HCl, filtering, boiling off H_2S, and destroying any sulphur compounds in the filtrate by adding $KMnO_4$ to a

permanent pink colour. If Cr, U, V, and W are present they can be removed after the latter operation by precipitating Fe and Ti with NaOH. The precipitate is ignited, fused with $NaHSO_4$, and the determination carried out as outlined above.

$$Fe^{+++} + Ti^{+++} \rightarrow Fe^{++} + Ti^{++++}$$

$$Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O + Ti_2(SO_4)_3 \rightarrow$$
$$2Ti(SO_4)_2 + 2FeSO_4 + (NH_4)_2SO_4 + 24H_2O$$

$\frac{963{\cdot}7}{2}$ or 481·8 gm. ferric ammonium sulphate = 79·9 gm. TiO_2

30 gm. ferric ammonium sulphate = approx. 5 gm. TiO_2

30 gm./litre ferric ammonium sulphate = 0·005 gm. TiO_2 per ml.

(*c*) *Reduction with aluminium.* A recent publication by Rahm[6] describes a simple and effective procedure for titanium in pigments and ores. After solution of the pigment in a 500 ml. Erlenmeyer flask with $H_2SO_4 + (NH_4)_2SO_4$, or of the ore with $KHSO_4$ fusion, add 20 ml. HCl and 1–3 gm. aluminium metal. Exclude air from the acid solution by inserting one end of a delivery tube in the flask containing the sample, while the other end dips beneath a solution of sodium carbonate in a beaker. Titrate when cool with standard ferric chloride using KCNS as indicator.

SPECIAL PROCEDURES

The analysis of cemented carbides, in which titanium is often present, is cited in the chapter on Tungsten.

Thompson[10] gives full directions for the determination of titanium in titanium metal.

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TUNGSTEN

TUNGSTEN is found in many alloy steels, non-ferrous alloys, and cemented carbides, and its analysis is frequently required in metallurgical laboratories. The element is nearly always determined by separating it as tungstic acid by digestion in acids, with the aid of cinchonine, and weighing as WO_3.[4, 8] A number of interfering elements are often present and their separation makes the procedure for tungsten a lengthy and difficult one. Ignition of WO_3 should be carried out at 750° C. since volatilization may occur at higher temperatures. The procedure given below may obviously be shortened or modified in the absence of interfering elements.

GENERAL PROCEDURES

1. Tungsten in ores, concentrates, etc.

Transfer 1 gm. of the finely ground sample to a 400 ml. beaker, add 5 ml. water and manipulate the beaker to break up the material and distribute it evenly on the bottom.[3, 6, 7] Add 100 ml. HCl, cover the beaker with Speedyvap cover glass and heat for one hour at a temperature not exceeding 60° C., and with occasional stirring to prevent the formation of crusts or cakes on the bottom of the beaker. Now increase the heat and boil to a volume of about 50 ml. Stir the material on the bottom of the beaker until all caked residue is broken up, and then add 40 ml. HCl and 15 ml. HNO_3. Cover until danger of spattering is past, then remove the cover and continue the boiling until the volume of the solution has been reduced to about 50 ml. Add 5 ml. of HNO_3, break up all caked matter, and boil until the volume has been reduced to

10–15 ml. Add 150 ml. of hot water, stir thoroughly, and allow the solution to digest warm for 15 minutes. Add 5 ml. of cinchonine solution, made by dissolving 124 gm. cinchonine, $C_{19}H_{22}N_2O$, in a mixture of 500 ml. HCl and 500 ml. water, and digest the solution on a hot plate or water bath at 60–70° C. for at least 30 minutes.

Let the precipitate of tungstic acid settle, decant the supernatant liquid through an 11 cm. Whatman No. 40 paper containing paper pulp, and wash the precipitate 4 times by decantation with hot cinchonine wash solution made by diluting 25 ml. of the cinchonine solution and 30 ml. of HCl to 1 litre with hot water. Transfer the precipitate to the paper and wash the beaker, paper, and precipitate thoroughly. Add cinchonine solution to the filtrate and washings (No. 1), mix thoroughly and set aside to make sure that recovery of tungsten is complete. Transfer the washed precipitate to the original beaker by means of a jet of water; no more than about 25 ml. should be used. Add about 6 ml. NH_4OH, or enough to give a slight excess, cover the beaker and warm gently for a few minutes. Wash the beaker with warm 10% NH_4OH containing 10 gm. NH_4Cl per litre. Stir the solution well, filter through the same paper that was used before, collect the filtrate in a 400 ml. beaker and wash the original beaker, the filter, and the residue with the warm dilute NH_4OH. Reserve the residue (No. 2).

Evaporate the filtrate or gently boil it until most of the NH_4OH has been expelled. Add 20 ml. HCl and 10 ml. HNO_3 and boil to a volume of 10–15 ml. Dilute to 150 ml. with hot water, add 10 ml. of cinchonine solution, stir the solution thoroughly, digest at 80–90° C. for at least 30 minutes and then allow to cool. Add paper pulp, transfer the precipitate completely to an 11 cm. Whatman No. 40 paper and wash thoroughly with the hot cinchonine wash solution. This is the main precipitate and is to be ignited together with any additional tungsten obtained as to be described. Thoroughly mix the filtrate and washings (No. 3) and set aside until precipitation is complete.

If the material was completely decomposed any tungsten held in the reserved residue (No. 2) is usually combined with iron or aluminium, and can be dissolved by digesting the residue with warm 10% HCl, filtering, washing in turn with small amounts of a hot 0·5% solution of NH_4Cl and the NH_4OH wash solution.

The tungsten (Recovery A) is then precipitated by further treatment with acid and cinchonine as with the boiled NH_4OH extract, with which it should not be combined.

The residue (No. 4) still left after the treatments with dilute HCl and NH_4OH is usually free from tungsten. It may contain SiO_2, Sn, Nb, Ta. In this case ignite the paper and residue (No. 4) at a low temperature in a porcelain crucible, transfer the ash to a platinum crucible, and volatilize silicon by evaporation with HF and H_2SO_4. Fuse the residue with as little Na_2CO_3 as possible, cool, and extract with water. Filter, acidify the filtrate with HCl, boil to expel CO_2, and test for tungsten by adding 5 ml. cinchonine reagent and digesting the solution at the side of the steam bath for 30 minutes, and then at room temperature for several hours or overnight. If a precipitate appears in this solution or in the two reserved filtrates and washings (Nos. 1 and 3), filter all through the same paper and wash the combined precipitates with cinchonine wash solution. Extract with NH_4OH, precipitate, and wash as in the preceding recovery (Recovery B).

Transfer the papers containing the main precipitate and the recoveries (A and B) to a large weighed platinum crucible and heat at a low temperature until all carbon has been destroyed. Cool, moisten the precipitate with a little HF, evaporate to expel any SiO_2, and then ignite at 750° C. Cool in a desiccator, weigh as impure WO_3 and repeat the ignition until constant weight is obtained.

The tungstic oxide that is obtained must be examined for contaminants such as Mo, Ag, Fe, and P as follows. Fuse with as little Na_2CO_3 as possible, extract the melt with water, filter and wash any residue with a warm 1% Na_2CO_3 solution, then with hot water. Reserve the filtrate. Ignite the paper and residue and repeat the operation. Combine the filtrates, and set aside. Ignite the well-washed paper and residue, cool, weigh, and correct the weight of tungstic oxide for the oxides found. If silver is present, digest the first insoluble residue with NH_4OH, filter, wash the residue and then proceed with the ignition and re-fusion with Na_2CO_3. Treat the ammoniacal filtrate with $(NH_4)_2S$, recover any precipitate and ignite it with that obtained in the combined water extracts.

Acidify the water extracts, boil to expel CO_2, and then add

NH_4OH in excess. Ordinarily no precipitate should remain; if one does it must be recovered by filtration, washed, ignited, and the weight deducted from that of the tungstic acid. Add 3–5 gm. tartaric acid to the clear ammoniacal solution, saturate with H_2S, add H_2SO_4 until 1% by volume in excess, digest for one hour at 40–60° C. and filter. Wash the precipitate with H_2S water containing 5 gm. tartaric acid and 5 ml. H_2SO_4 per litre. Reserve the filtrate if tests for phosphorus and vanadium are necessary. Since the sulphides may still contain tungsten, dissolve the precipitate in hot dilute HNO_3 containing a little bromine, boil to expel the latter, add 1–2 gm. tartaric acid and make the solution ammoniacal. Again treat with H_2S and proceed as before. Finally ignite very carefully at a temperature not over 600° C., cool, weigh, and correct the tungstic oxide for the oxides formed.

$$WO_3 \times 0{\cdot}793 = W$$

The U.S. Bureau of Mines reports that for low grade tungsten ores the use of tannic acid and antipyrine (phenazone) has several advantages over cinchonine for the second precipitation of tungsten.[5]

2. Tungsten in high-speed steel, ferrotungsten, tungsten metal, etc.

Transfer 1 gm. of drillings to a covered 250 ml. beaker, add 50 ml. HCl and heat to incipient boiling.[1, 10] Add cautiously HNO_3 until the metal has all dissolved. Evaporate the liquid quickly until tungstic oxide begins to separate, and then add 10 ml. cinchonine solution. Boil slowly until the volume is reduced to about 25 ml. Add 10 ml. hot water and set aside for 30 minutes.

Filter through 11 cm. Whatman No. 40 paper containing paper pulp, wash with cinchonine wash solution. Dry and ignite in a platinum crucible, remove the SiO_2 with HF, ignite again, and weigh. Cover the residue with about twice its weight of dry Na_2CO_3 and place the crucible in the hottest part of the muffle for 5 minutes. Remove the crucible and when the fused mass is cold, extract with hot water and filter. Ignite the washed residue in the same crucible. The loss in weight is tungstic oxide.

3. Tungsten in cemented carbides

The analysis of simple and complex tungsten carbides is an important specialized field, and is fully covered in papers such as that of Furey and Cunningham,[2] and Touhey and Redmond.[9] Decomposition is usually effected in a platinum dish with HNO_3 and HF, or by fusion with sodium peroxide in a nickel crucible. Tungsten is separated with cinchonine or cinchonine-antipyrine, weighed, fused with $KHSO_4$, and contaminants like Ti, Nb, Ta removed with cupferron in the presence of tartrate and determined. Molybdenum, if present, is determined colorimetrically and its weight also deducted from the impure tungstic oxide.

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URANIUM

URANIUM occurs in a few minerals and ores, and its determination is occasionally required in an industrial laboratory. Its great importance in the field of atomic energy ensures that uranium will be encountered more frequently in future in many industrial laboratories. In the usual separations of uranium the chief interfering substances are CO_2 and vanadium. Uranium is generally separated from other elements and weighed as U_3O_8.[2, 4, 5, 6, 7, 9] In the absence of other elements the following procedure, applicable to complex ores, can be shortened accordingly.

GENERAL PROCEDURES

Weigh 0·5–10 gm. sample into a 400 ml. beaker, add 10–50 ml. HCl, 10–50 ml. HNO_3, and a few drops of HF if necessary. Evaporate to dryness and dehydrate with HCl several times. Add HCl, hot water, boil, filter, wash, and discard SiO_2. If the material is very refractory, fuse the residue with Na_2CO_3 or $KHSO_4$ and add to the main solution. If tungsten is present, indicated by the formation of insoluble tungstic acid in dilute HNO_3 and HCl, add cinchonine solution, allow to stand for an hour and filter off the precipitated tungsten as directed under Tungsten.

Adjust the acidity of the filtrate to 5–10% HCl or H_2SO_4 and remove Group 2 metals with H_2S. A useful means of removing large quantities of copper from uranium samples is with NH_4OH. This eliminates the repeated precipitation of bulky CuS or the removal of large quantities of copper by electrolysis. The

remaining Group 2 elements are generally present in small quantities and can be removed easily with H_2S. Filter and wash well with acidulated H_2S water. Boil the filtrate 10–15 minutes to remove H_2S, add 10 ml. H_2O_2, and boil thoroughly. Neutralize with NH_4OH and add 3 gm. $(NH_4)_2CO_3$ excess. Boil 20 minutes and filter off hydroxides and insoluble carbonates of Fe, Ni, Co, Zn, Al, Ti, Zr, Cr, Ca, Ba, Sr, Mg, etc. Wash thoroughly with hot water and reserve the filtrate for uranium. The presence of carbonate prevents the precipitation of uranium by NH_4OH.

Dissolve the precipitate in HNO_3 and re-precipitate Fe, etc., with $(NH_4)_2CO_3$. Filter and wash. Concentrate the combined filtrates from this precipitation to 250 ml. Acidify the filtrates with HNO_3, boil 10 minutes to expel CO_2, and neutralize with NH_4OH. Uranium is now separated from nearly all other elements except vanadium. The latter may be removed as lead vanadate or as sodium vanadate.

1. Precipitate vanadium as lead vanadate after re-acidifying the uranium solution with HNO_3 and adding 4 ml. excess, by 10 ml. of 10% lead acetate followed by 20 ml. concentrated ammonium acetate to neutralize the free HNO_3. Allow the lead vanadate to settle several hours, filter through double Whatman No. 40 paper, and wash well. Uranium passes into the filtrate which should be clear, not yellow. Remove the uranium from the lead by adding NH_4OH in excess to the hot filtrate, boiling and filtering without washing. The precipitate contains the uranium, together with traces of lead. Discard the filtrate.

Treat the precipitate on the filter with hot concentrated $(NH_4)_2CO_3$ containing a little free NH_4OH until all the uranium is dissolved, and then wash with the same solution diluted. Precipitate the lead remaining in the filtrate with H_2S. Allow to stand in a warm place, filter, and wash the precipitate with H_2S water containing a little $(NH_4)_2CO_3$. Boil the filtrate to expel H_2S and $(NH_4)_2CO_3$, and concentrate to 200 ml.

2. An alternative procedure to remove vanadium consists in treating the ammonium hydroxide precipitate of uranium, etc., with HCl and neutralizing with NaOH. Add about 5% excess NaOH, boil, cool, filter, and wash with 1% NaOH containing a little Na_2SO_4. Vanadium and aluminium remain in solution, while uranium is precipitated. For large quantities of vanadium

it is advisable to re-precipitate to liberate occluded vanadium. Dissolve the uranium precipitate with HNO_3.

The above separations are based on the fact that the presence of carbonate prevents the precipitation of uranium with NH_4OH or $(NH_4)_2S$.

Make the concentrated solution slightly acid with HNO_3 and boil to expel CO_2. Add NH_4OH in excess. Boil 1 minute and filter. No washing is necessary. Dry the precipitate and ignite as U_3O_8.

$$U_3O_8 \times 0{\cdot}8480 = U$$

Test the oxide by dissolving in HNO_3 and adding H_2O_2 for V and $(NH_4)_2CO_3$ for Al_2O_3.

Carry through all the above steps a blank to which has been added a known quantity of uranium acetate or nitrate as a check on the accuracy of the procedure.

It is sometimes useful to recall that uranium can be separated from other members of Group 3 in the following manner:

1. Electrolysis at a mercury cathode separates uranium from Fe, Cr, Zr, Ni, Co, which are deposited.
2. Cupferron separates hexavalent uranium from the precipitate of Fe, V, Zr, Ti, Nb, Ta. The solution containing about 10% of its volume of H_2SO_4 is oxidized by $KMnO_4$ reagent to a faint pink and then a 6% water solution of cupferron is added in excess. Paper pulp is added, the precipitate is filtered off and washed with 10% H_2SO_4 or HCl containing 0·2% cupferron. Uranium passes into the filtrate.
3. The presence of $(NH_4)_2CO_3$ prevents precipitation of uranium either by NH_4OH or $(NH_4)_2S$. In this way uranium can be separated from Fe, Al, Co, Ni, Zn, Ti, etc.
4. Iron can be separated from uranium by an ether extraction.
5. Uranium is precipitated with cobalt by α-nitroso β-naphthol in acetic solution but not in dilute HCl.
6. A zinc oxide separation removes uranium along with Fe, Cr, Ti, V, etc., from the filtrate of Co, Ni, Mn.
7. Treatment with NaOH of an acid solution of the NH_4OH precipitate of Group 3 gives U, Ti, Zr, Fe, Cr, precipitated as hydroxides free from Al, V. This is convenient to

remove vanadium from uranium after precipitation of all others with carbonate.

8. Chromium can be separated from uranium by oxidizing the solution completely with HNO_3, followed by precipitation with NH_4OH. Chromium passes into the filtrate.

Rabbitts [3] outlines a good procedure for uranium in ores, eliminating at the mercury cathode Fe, Co, Ni, Cu, Zn, Ga, Ge, Rh, Pd, Ag, Cd, In, Sn, Ir, Pt, Au, Hg, Tl, Cr, Mo, Re, Po, Bi, As, Se, Te, Pb, and Os. By a cupferron separation the following are removed: Nb, Ta, W, Th, Ce, Ti, V, and Zr. In a later publication [4] Rabbitts describes the cellulose column method and the microfluorometric procedure for uranium. These methods are in use at the Radioactivity Division of the Mines Branch at Ottawa.

The analytical chemistry of uranium is well covered in a recent book edited by Rodden [5] with the assistance of a number of other workers connected with the Manhattan Project. Special techniques were devised for rapidly handling large numbers of samples.

A good handbook of chemical methods for the determination of uranium in minerals and ores, prepared by the Chemical Research Laboratory, D.S.I.R., and published in 1950, is available from H.M. Stationery Office, London, for 1s.

SPECIAL PROCEDURES

1. Small quantities of uranium may be determined colorimetrically with ammonium thiocyanate.[1]

2. A fluorescent test for uranium has been developed by Sill and Peterson.[8]

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VANADIUM

VANADIUM is widely distributed in ores and is a very important alloying element in irons and steels. Its analysis is consequently frequently encountered in metallurgical laboratories. Vanadium is generally determined volumetrically. It can be separated from members of Group 2 by precipitation of the latter with H_2S in acid solution. If the quantity of these is large, a solution and re-precipitation should be practised to recover co-precipitated vanadium. Vanadium may be separated from members of succeeding groups by precipitation with $(NH_4)_2S$.

The element may be isolated from other members of Group 3 by several procedures.[2, 3] Fusion with Na_2CO_3 and KNO_3, and extraction of the melt with water, will separate vanadium as soluble sodium vanadate from Fe, Ti, Zr. For small quantities of vanadium, separate most of the iron with bicarbonate. Electrolysis at a mercury cathode will separate vanadium from Fe, Cr, Ni, Co. Precipitation of quinquevalent vanadium by cupferron will remove the element from U, Cr, P, Al. Chromium can be removed from vanadium by passing in SO_2 to a nitric acid solution, then pouring the reduced solution into hot 10% NaOH, filtering, and washing the residue containing the chromium. Vanadium can also be separated from chromium by adding glacial acetic acid and H_2O_2 to the neutral solution, boiling, adding lead acetate to precipitate lead vanadate, filtering, decomposing the precipitate with H_2SO_4, and removing the $PbSO_4$ by filtration, the vanadium remaining in solution. Chromium can also be eliminated by volatilization as chromyl chloride. Vanadium may be isolated from Co, Ni, and Mn by a zinc oxide separation. Vanadium may be separated with aluminium from

Fe, Ti, Zr, U, and Cr, by treatment of the ammonium hydroxide group with NaOH. Vanadium together with Al, Cr, and U may be separated from Fe, Ni, Co, and Mn by precipitating the latter with Na_2O_2 in alkaline solution.

GENERAL PROCEDURES

Weigh 0·5–5 gm. sample so that the vanadium present will not exceed 0·2 gm. Place in 600 ml. beaker, add 10–20 ml. HNO_3 and 10–20 ml. HCl, with a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and evaporate to heavy fumes of SO_3. Cool, add 50 ml. hot water, boil, and filter off SiO_2 and $PbSO_4$, washing with hot water. If the material is refractory it may be necessary to fuse the acid-insoluble residue in a platinum crucible with Na_2CO_3 and KNO_3, and add this to the original filtrate, dehydrating SiO_2 and filtering off this and $PbSO_4$ as given above.

Adjust the acidity to 5–10% H_2SO_4 and precipitate all Group 2 elements with H_2S. Filter and wash thoroughly with acidulated H_2S water. If the precipitate is large it is advisable to dissolve in HNO_3, add H_2SO_4 and evaporate to fumes, and re-precipitate with H_2S to recover co-precipitated vanadium. Boil off all H_2S and cool.

1. Titration of reduced vanadium with $KMnO_4$, after ammonium persulphate treatment

Carry out the titration by adding an excess of $KMnO_4$, cooling to 15° C., adding 5 ml. H_3PO_4, and then an excess of ferrous ammonium sulphate as shown by 0·1% potassium ferricyanide external indicator. Add 8 ml. of fresh 15% ammonium persulphate and stir 1 minute. Test with $K_3Fe(CN)_6$ to show the excess ferrous ammonium sulphate has been oxidized. Titrate with 0·025 or 0·05N. $KMnO_4$ solution to a pink end point which remains permanent for 1 minute.

This procedure depends on the fact that in cool acid solution containing no silver nitrate, ammonium persulphate oxidizes ferrous sulphate but does not react rapidly with quadrivalent vanadium, permanganate, bivalent manganese, or trivalent chromium. It is therefore possible to reduce vanadium by adding

an excess of ferrous sulphate, to destroy the excess with persulphate, and then to titrate the reduced vanadium with potassium permanganate. Tungsten is about the only important interfering element and may usually be removed initially as tungstic acid after solution of the sample in acids.

$$V_2O_5 + 2FeSO_4 + H_2SO_4 \rightarrow V_2O_4 + Fe_2(SO_4)_3 + H_2O$$

$$2FeSO_4 + (NH_4)_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4$$

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

1 ml. 0·05N. $KMnO_4 = 0{\cdot}00255$ gm. V.

We have found this to be the best procedure for vanadium. It is applicable to all types of products and is less subject to interference than other methods. It is employed by laboratories with long experience in vanadium such as those of Union Carbide and Carbon Co. and Vanadium Corporation of America.[5, 7]

A convenient vanadium compound for standardizing purposes is AnalaR ammonium vanadate, which contains a maximum of 0·015% impurities. A solution made by dissolving 1·1534 gm. ammonium vanadate in water made slightly ammoniacal with NH_4OH and diluting to a volume of 100 ml., has a value of 1 ml. = 0·005 gm. V.

2. Titration of reduced vanadium with $KMnO_4$, after reduction with ferrous ammonium sulphate

This procedure is satisfactory with experienced chemists, but is not of such universal application as the previous titration.

Add strong $KMnO_4$ solution to the sample until it is a dark purple colour and completely oxidized. Just drive out the pink colour with ferrous ammonium sulphate. Repeat this operation more carefully, taking two drops of ferrous ammonium sulphate to drive out the second pink colour. Allow the solution to stand for about half an hour.

The solution is now very carefully oxidized with $KMnO_4$ again. This time the end point is usually a faint pinkish-brown colour which should persist for half a minute, and should be produced by the addition of only 2–3 drops $KMnO_4$.

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

The solution is now immediately titrated with standard ferrous ammonium sulphate, the latter being run in slowly and the stirring done without violent agitation. The solution is tested from time to time with 0·1% potassium ferricyanide on a spot plate until the blue colour of ferrous iron appears. It is advisable to retain a portion of the sample in a small beaker. Diphenylamine can be used as an internal indicator if desired instead of the external potassium ferricyanide.

Towards the end of the titration at least 30 seconds should elapse between additions of ferrous ammonium sulphate. In solutions of high zinc concentration care must be taken that the proper ferrous blue is obtained. A light blue colour shows up between the zinc and ferricyanide which must be passed before the true blue of ferrous iron is obtained.

The blank on the standard solution is small. If much iron is present in the sample it is advisable to add 10 ml. of 1:3 H_3PO_4 to the filtrate to mask the iron in solution. In this case the blank is slightly increased.

1 ml. of 0·1N. ferrous ammonium sulphate = 0·0051 gm. V

3. Titration of reduced vanadium, using $K_2Cr_2O_7$

An alternative procedure to the foregoing is to add strong $KMnO_4$ solution to the sample after removal of Group 2 elements in 10% H_2SO_4 and boiling off H_2S. Next add moderately strong ferrous ammonium sulphate solution until the purple colour is discharged. Then add the $KMnO_4$ carefully until a light purple tinge is obtained.

Now add the standard ferrous ammonium sulphate solution from a burette, drop by drop, until the purple colour is exactly discharged.

$$V_2O_5 + 2FeSO_4 + H_2SO_4 \rightarrow V_2O_4 + Fe_2(SO_4)_3 + H_2O$$

Again set the burette to the zero point and add the standard ferrous ammonium sulphate solution until all vanadium is reduced, about 3 ml. in excess. Read the burette. Test with potassium and ferricyanide on the wax spot plate. The spot should now show a deep blue colour. Diphenylamine can be used as an internal indicator if preferred.

Titrate at once with standard potassium dichromate solution

from a second burette until the spot test no longer shows a blue colour. Standardize the ferrous ammonium sulphate standard daily against the $K_2Cr_2O_7$ standard, by means of a blank analysis made by placing 100 ml. of 1:2 H_2SO_4 in a 600 ml. casserole, diluting to 450 ml., and warming on the hot plate. Add 25 ml. of the standard ferrous ammonium sulphate solution, and titrate with the standard dichromate until the spot test no longer shows a blue colour.

$$K_2Cr_2O_7 + 2FeSO_4 + 5H_2SO_4 \rightarrow$$
$$Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 5H_2O + O_2$$

$$\left.\begin{array}{l} 2K_3Fe(CN)_6 + 3FeSO_4 \rightarrow 3K_2SO_4 + Fe_3[Fe(CN)_6]_2 \\ K_3Fe(CN)_6 + FeSO_4 \rightarrow K_2SO_4 + KFe[Fe(CN)_6] \end{array}\right\} \text{Turnbull's blue}$$

Subtract the ml. $K_2Cr_2O_7$ used from the ml. of ferrous ammonium sulphate added. The ferrous ammonium sulphate must be in terms of the dichromate. If the standards show a difference in strength, calculate from the result obtained above the ml. of ferrous ammonium sulphate used in the analysis in terms of $K_2Cr_2O_7$. Multiply the net titration by the factor for vanadium found for the dichromate solution and calculate to percentage.

Cr, Fe, Al, Mn, Zn, P do not interfere. Chlorides are removed with H_2SO_4. Nickel interferes by forming a brown colour with ferricyanide but the element is seldom present in sufficient quantity to cause serious difficulties. If uranium is present it is necessary to take as the end point of the $K_2Cr_2O_7$ titration that point where the blue colour of the spot test first disappears on standing about 5 seconds. The uranium will cause the return of the blue colour after an interval of 20–30 seconds, and this return should be disregarded in the titration.

The method is based on the fact that V_2O_5 is reduced to V_2O_4 by ferrous ammonium sulphate, and that the vanadium is more easily reduced than As, Sb, etc. The excess of ferrous iron may then be oxidized selectively by $K_2Cr_2O_7$ in the presence of the reduced vanadium, all of the iron becoming oxidized before the dichromate begins to oxidize the more easily reduced vanadium compound. The point where all iron is oxidized is easily recognized by the ferricyanide spot test.

Reagents

1. Strong $KMnO_4$. A saturated solution of $KMnO_4$ in water.

2. Ferrous ammonium sulphate reducing solution. Dissolve about 100 gm. of $FeSO_4(NH_4)_2SO_4.6H_2O$ in 500 ml. of water and add a little H_2SO_4.

3. Standard 0·1N. $K_2Cr_2O_7$. Dissolve 4·9035 gm. $K_2Cr_2O_7$ in 1 litre of water. 1 ml. 0·1N. $K_2Cr_2O_7 = 0·0051$ gm. V or 0·0091 gm. V_2O_5.

4. Standard ferrous ammonium sulphate solution. Dissolve 40 gm. of the salt in 1 litre of water containing 100 ml. H_2SO_4.

5. Potassium ferricyanide indicator. Dissolve a piece the size of a pea in 50 ml. of water. The indicator must be made fresh each day, as some ferrocyanide forms on standing.

In place of visual titration, potentiometric titration may be employed in all these procedures. The vanadium in H_2SO_4 solution is oxidized with HNO_3 or $KMnO_4$, and titration is made with ferrous ammonium sulphate and $K_2Cr_2O_7$ or $KMnO_4$ to the zero point of the instrument.[1, 4, 6]

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ZINC

ZINC is one of the most important non-ferrous metals, and its determination is of frequent occurrence in industrial laboratories. Zinc is separated from members of Group 2 by precipitation of the latter with H_2S in 5–10% acid solution. In the presence of appreciable quantities of cadmium and copper these should be separated by H_2S in an acid concentration exceeding 4N., followed by a second precipitation to set free the occluded zinc. Iron, aluminium, and other members of Group 3 may be separated from zinc by precipitation with $NH_4OH + NH_4Cl$, or when large amounts are present by precipitation of the zinc with H_2S in dilute H_2SO_4 solution with or without the presence of formic acid. Silica and lead may be removed by dehydration with H_2SO_4. Zinc can be separated from most other members of Group 3 by precipitation as sulphide in 0·01N. H_2SO_4 solution.

GENERAL PROCEDURE

Zinc is usually determined volumetrically by titration with potassium ferrocyanide. The general procedure below may obviously be shortened in the absence of interfering elements.[1, 2, 4, 9, 11]

Weigh 0·5–5 gm. sample into a 400 ml. beaker, add 10–20 ml. HCl, 10–20 ml. HNO_3, and a little HF if necessary. Add 10 ml. 1:1 H_2SO_4 and evaporate to strong fumes of SO_3. Cool, add hot water, boil, and filter off SiO_2, $PbSO_4$, etc. Wash well with hot water. Adjust the acidity to 5–10% H_2SO_4 and remove Group 2 elements with H_2S. Filter and wash thoroughly with acidulated H_2S water. If the quantity of precipitated sulphides is large and

small amounts of zinc are in question, it may be necessary to dissolve the sulphides in acid and re-precipitate with H_2S. Boil out all H_2S, oxidize with H_2O_2, and boil well.

If small amounts of Fe, Al, or Mn are present they may be removed by adding bromine water or ammonium persulphate, making ammoniacal, boiling, and filtering off the precipitated hydroxides. Wash well with a dilute NH_4OH-NH_4Cl solution. Dissolve the precipitate in HCl and re-precipitate with ammonium persulphate and NH_4OH. Boil, filter, and wash as before. Zinc is in the filtrate.

If Ni, Co, Cr, W, or large amounts of Fe, Al, Mn, V are present it is better to separate zinc as sulphide with H_2S in dilute H_2SO_4 solution. The unusual elements Tl, In, and Ga will accompany zinc in this precipitation. To the sulphuric acid solution of zinc that is free from members of the H_2S group and boiled free of H_2S, add a few drops of methyl orange or methyl red and then NaOH until the solution is neutral. Dilute so that the volume of the solution is at least 200 ml. and contains not more than 0·1 gm. zinc per 100 ml. Adjust the acidity with 5% H_2SO_4 so that the solution is as near 0·01N. as possible, 0·26 ml. H_2SO_4 per litre, or approximately 1 ml. of 5% H_2SO_4 per 200 ml. solution. Cool to room temperature and pass a rapid stream of H_2S through the solution for 30 minutes. Allow to settle for 10 minutes, filter, and wash with cold water. Transfer precipitate to original beaker with HCl, neutralize with NH_4OH, and add 3 ml. excess HCl. Dilute to 200 ml., heat to boiling, and titrate as directed below.

Precipitation of ZnS in a solution of formic acid buffered with ammonium formate and citrate has been found very useful for separating zinc from many elements of Group 3, particularly Al, Mn, Fe. To the filtrate after removal of Group 2 sulphides, boil to eliminate H_2S and reduce the bulk, and add NH_4OH just short of neutrality. Add 25 ml. of a 20% citric acid solution and make neutral to methyl orange with NH_4OH. Add 25 ml. of formic mixture and dilute to 200 ml. for each 0·2 gm. zinc. Pass in H_2S for 5 minutes to the warm solution and allow to stand under pressure of H_2S for 20 minutes. Filter and wash with cold 2·5% formic acid saturated with H_2S. Dissolve the ZnS off the paper with HCl, wash well, neutralize the excess acid with NH_4OH and

add 3 ml. HCl excess. Proceed with the titration using ferrocyanide.

Add 0·3 ml. of ferrous sulphate solution. Pour about one quarter of the sample solution into a 200 ml. beaker and run the standard potassium ferrocyanide solution, while stirring, into the remaining portion to an excess. Add all excepting 1–2 ml. of the solution to the 200 ml. beaker and continue the addition of standard $K_4Fe(CN)_6$ until the end point is passed by a few drops. Add the remainder of the solution in the 200 ml. beaker and wash out with water. Continue the titration 1–2 drops at a time until the end point is reached. The change of colour from blue to pea green at the end point is very sharp. It can best be observed by looking down through the solution and not from the side.

The change in colour is due to the reaction between the small amount of ferrous iron present and the ferricyanide in the standard. As long as an excess of zinc is present it removes the ferrocyanide as precipitated potassium zinc ferrocyanide $K_2Zn_3\{Fe(CN)_6\}_2$, and the iron remains as the blue ferro-ferricyanide. When the potassium ferrocyanide is in excess, the blue ferro-ferricyanide is decomposed into the colourless ferro-ferrocyanide. This causes the sudden change in the colour of the solution to a lighter shade.

$$2K_4Fe(CN)_6 + 3ZnCl_2 \rightarrow K_2Zn_3\{Fe(CN)_6\}_2 + 6KCl$$

$$3FeSO_4 + 2K_3Fe(CN)_6 \rightarrow Fe_3\{Fe(CN)_6\}_2 + 3K_2SO_4 \text{ (blue)}$$

$$K_4Fe(CN)_6 + FeSO_4 \rightarrow K_2Fe\{Fe(CN)_6\} + K_2SO_4 \text{ (white)}$$

If desired, uranium nitrate may be used as an outside indicator. Use a spot plate in which about two drops of 15% uranium nitrate solution have previously been placed in each depression. When the end point has been passed, indicated by the change in colour of the solution, add a portion of the reserve solution and titrate carefully until the end point is again passed. Now add the final few ml. of reserve solution and titrate carefully until the end point or brown tinge with uranium nitrate on the spot plate is apparent.

$$K_4Fe(CN)_6 + 2UO_2.(NO_3)_2 \rightarrow \underset{\text{brownish-red}}{(UO_2)_2Fe(CN)_6} + 4KNO_3$$

The potassium ferrocyanide solution is standardized by titrating against 0·3 gm. pure zinc carried through all the steps of

the operation outlined above. Allow the solution to age for a week or two before using, or agitate with air for a day. Since the factor of this solution will decrease with age it must be standardized at regular intervals.

Reagents

Ferrous sulphate solution. Dissolve 1·25 gm. of $FeSO_4.7H_2O$ in water, add 3 ml. of HCl, and dilute to 250 ml.

Potassium ferrocyanide solution. Dissolve 21·6 gm. $K_4Fe(CN)_6.3H_2O$ and 0·25 gm. potassium ferricyanide in 1 litre of water. 1 ml. = 0·005 gm. Zn.

Formic mixture. 200 ml. formic acid, 250 gm. ammonium sulphate, and 30 ml. ammonia per litre.

SPECIAL PROCEDURES

1. Routine volumetric

For control purposes on many products zinc is commonly determined without separation as the sulphide. The following procedure is typical. Dissolve the sample in HNO_3, HCl, HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to fumes of SO_3. Cool, add 100 ml. of water, 5 gm. NH_4Cl, cover and boil. If considerable insoluble is present, filter off, but a small residue may be disregarded. Cool, add 30 ml. NH_4OH and 0·25 gm. ammonium persulphate, cover and boil for 10 minutes. Filter on 12·5 cm. Whatman 31 or 531 paper and wash 4–5 times with zinc wash solution. Remove any traces of zinc in the beaker by washing with hot concentrated NH_4Cl solution. If the precipitate of hydroxides is large, re-dissolve in dilute HCl and re-precipitate as before, combining the filtrates.

Add methyl orange to the filtrate unless copper is present, in which case the latter serves as indicator. Neutralize with HCl from a dispensing burette, and add 5 ml. in excess. Add 10 ml. of iron indicator solution and place on the hot plate. When warm, add enough test lead to cover the bottom of the beaker and boil for 10 minutes. If much copper is present, remove the beaker from the hot plate, cool slightly and add a fresh portion of test lead. Boil and thus remove any remaining copper on the

fresh surface of test lead. Titrate the hot solution, which should have a volume of about 200 ml., with standard $K_4Fe(CN)_6$ in the usual manner, using uranium nitrate as the outside indicator.

Reagents

Zinc wash solution. Dissolve 100 gm. NH_4Cl in water, add 250 ml. NH_4OH, and dilute to 250 ml. Heat this solution to boiling for use.

Iron indicator solution. Dissolve 0·016 gm. iron wire in HCl and dilute to 2 litres with water.

2. Gravimetric

On some samples such as alloys it may be preferable to determine zinc by weighing as ZnO. This is carried out by precipitating Group 2 with H_2S in 5–10% acid solution, separating zinc from other members of Group 3 by precipitating with H_2S in very dilute H_2SO_4, and igniting the ZnS to ZnO.

Dissolve the sample in 10–20 ml. HNO_3, 10–20 ml. HCl, a few drops of HF if necessary, add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, add hot water, boil, and filter off SiO_2 and $PbSO_4$ if necessary.

Adjust the acidity to 5–10% H_2SO_4 and precipitate Group 2 elements with a vigorous stream of H_2S. Filter off the precipitated sulphides and wash well with acidulated H_2S water. If the precipitate is voluminous, dissolve in acid and re-precipitate with H_2S to free all occluded zinc. If copper is the only Group 2 element present it may be often conveniently removed electrolytically in the usual nitric:sulphuric solution. Zinc may then be determined on the solution following electrolysis.

Boil the filtrate to remove all H_2S, add a few drops of methyl orange or methyl red and neutralize with NaOH. Dilute so that the volume of the solution is at least 200 ml. and contains not more than 0·1 gm. zinc per 100 ml. Adjust acidity to as near 0·01 as possible, i.e. 1 ml. of 5% H_2SO_4 per 200 ml., cool to room temperature, and pass a rapid stream of H_2S through the solution for 30 minutes. Allow to stand 10 minutes, filter, and wash with cold water.

Dry the paper and precipitate at a low temperature in an open weighed porcelain or platinum crucible, burn the carbon at as low

a temperature as possible, and then gradually raise the heat to approximately 900° C. Finally cover the crucible, heat to 1000° C. for 5–10 minutes, raise the cover to allow escape of any oxides of sulphur, reheat for a few minutes, cool over a good desiccant, and weigh as ZnO. $ZnO \times 0{\cdot}8034 = Zn$.

In some products, such as brass, die castings, and electrolytic zinc, zinc is usually determined by difference.[2]

3. Oxide zinc

A procedure has been described for the determination of oxide zinc, based on the solubility of the latter and insolubility of zinc sulphide in ammonium chloride–ammonium acetate solution.[5] To 1 gm. of ore add 25 ml. of 25% NH_4Cl solution and 10 ml. of saturated ammonium acetate. Boil 10 minutes, filter, and wash with hot dilute NH_4Cl solution. Determine zinc on the filtrate.

The above procedure, however, is not applicable to zinc silicate, zinc phosphate, and lead:zinc:vanadium minerals, and a superior method for determining oxide zinc has been worked out at Rhodesia Broken Hill Development Company Limited, Broken Hill, Northern Rhodesia.[3] It is based on the solubility of all oxidized zinc minerals in 2% by volume H_2SO_4 saturated with SO_2. Zinc sulphide is insoluble in this solution. The procedure is as follows.

Weigh 0·5–1·0 gm. of −200 mesh sample into a 300 ml. stoppered Erlenmeyer flask fitted with a Bunsen valve. Add 50 ml. of 2% by volume of sulphuric acid saturated with sulphur dioxide. Stopper the flask and allow to stand in a warm place at 30–40° C. for one hour, swirling the flask for a few seconds every 10 minutes. Filter, and wash thoroughly with hot water. To the filtrate add 5 ml. 1:1 H_2SO_4 and boil off all sulphur dioxide. Proceed with the determination of zinc by any standard procedure, taking into consideration all possible interfering elements. This figure represents the oxidized, or non-sulphide, zinc.

A method for the determination of zinc oxide in zinc powder has been noted[6] in which the oxide in a 2 gm. sample of powder is dissolved by allowing to stand for 2 hours in 100 ml. of 30% ammonium acetate solution.

4. Small quantities of zinc may be determined in certain cases

with dithizone as given by Sandell,[8] and Young,[10] or absorptiometrically as described by Phillips and Holton.[7]

Chemists who have any special difficulties in zinc analysis are invited to contact the Zinc Development Association, Lincoln House, Turl Street, Oxford.

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ZIRCONIUM

ZIRCONIUM is found in some ores, steels, and refractories, and its determination may be occasionally encountered in any industrial laboratory. Nearly all zirconium compounds contain small quantities of hafnium, and the latter is classed analytically with zirconium.[7] Zirconium may be separated from Group 2 elements by precipitation of the latter with H_2S in 5–10% acid solution. It is separated with other members of Group 3 from succeeding groups by $(NH_4)_2S$.

Zirconium may be separated from Fe, Ni, Co, Mn, and Zn by removal of the latter as sulphides in ammoniacal tartrate solution, zirconium passing into the filtrate. The iron in acid solution is reduced with H_2S, tartaric acid equal to 5 times the approximate weight of the oxides present is added, the solution is made ammoniacal, and then H_2S is passed in until the sulphide precipitate has coagulated. The precipitate is filtered on Whatman No. 40 paper, care being taken to keep the funnel well filled, so that oxidation of the sulphides and consequent running-through is avoided. The sulphides are promptly washed, using the same precaution, with water containing a little NH_4Cl and $(NH_4)_2S$. If the cupferron precipitation of zirconium is to be used, the tartrate need not be destroyed, and it is sufficient to acidify to 10% H_2SO_4 by volume and to boil out the H_2S. If it is necessary for further work to remove the tartrate, the solution is acidified with 10 ml. 1:1 H_2SO_4, evaporated to a volume of 50 ml., 10 ml. HNO_3 added, and the solution evaporated to fumes of SO_3. After cooling, 10 ml. HNO_3 are again added and the mixture once more evaporated to fumes. Occasionally a third addition of

HNO_3 and evaporation may be necessary to completely destroy the tartaric acid.

Zirconium may be separated from titanium by precipitating the zirconium with Na_2HPO_4 or $(NH_4)_2HPO_4$ in a 10% by volume H_2SO_4 solution in presence of H_2O_2. The element is separated from tungsten by precipitation of the latter in acid solution with cinchonine, and from vanadium by fusion of the mixed oxides with Na_2O_2 or Na_2CO_3 and leaching out the soluble sodium vanadate with water. Zirconium is separated from Al, Cr, and U by precipitation of the zirconium with cupferron in 10% by volume H_2SO_4 solution. The uranium must be put into the hexavalent form by boiling with H_2O_2 prior to the cupferron precipitation. Zirconium may be separated from Nb and Ta by fusing the ignited phosphate precipitate with KOH, dissolving in water, filtering, igniting the residue, fusing with $K_2S_2O_7$, dissolving in acid, and reprecipitating the zirconium as ZrP_2O_7. Thorium and rare earth elements may be removed by precipitating them with an excess of oxalic acid, leaving the zirconium in the filtrate. Zirconium may be separated by electrolysis with a mercury cathode from Fe, Cr, Zn, Ni, Co.

GENERAL PROCEDURE

The following general method is suited for nearly all classes of zirconium analyses, and may, of course, be altered in the presence or absence of various interfering elements discussed above.[1, 3, 4, 5] In steels it is often desirable to make an ether separation to remove iron at the start of the analysis.

Weigh out 0·5–5 gm. sample into a 400 ml. beaker, decompose with 10–20 ml. HCl, 10–20 ml. HNO_3, and a few drops of HF if necessary. Add 10 ml. 1:1 H_2SO_4 and take to strong fumes of SO_3. Cool, dilute with hot water, boil, and filter off any SiO_2 or $PbSO_4$. If the sample is not completely decomposed by acid treatment, fuse the residue with Na_2CO_3 or with $Na_2O_2 + Na_2CO_3$. Occasionally it may be necessary to fuse with $KHSO_4$ a small residue which still persists after the above fusion.

Adjust the acidity to 5% H_2SO_4 by volume and pass in a rapid stream of H_2S to precipitate all Group 2 metals. If a voluminous precipitate is obtained it is desirable to dissolve in acid and re-

precipitate with H_2S to set free any occluded zirconium. Wash thoroughly with acidulated H_2S water.

Tartaric acid equal to 5 times the approximate weight of the oxides of Fe, Ni, Co, Mn, and Zn present is added. The solution is made ammoniacal and H_2S is passed in until the sulphide precipitate has coagulated. The precipitate is filtered on Whatman No. 40 or 42 paper, keeping the funnel well filled to prevent oxidation of the sulphides and consequent running through. Wash the precipitate promptly, using the same precaution, with water containing a little NH_4Cl and $(NH_4)_2S$.

Boil out the H_2S, oxidize with a little H_2O_2, and adjust the acidity to 10% H_2SO_4 by volume. Cool to about 10° C. and add an excess of 6% cupferron solution. The formation of a fine white precipitate of nitroso-phenyl hydroxylamine which redissolves indicates that an excess of the reagent has been added. The zirconium precipitate is white and curdy, but any titanium present is also quantitatively precipitated and it will impart a yellow colour to the precipitate. A brownish colour indicates that the previous separation from iron has been faulty. Filter and wash with cold 10% HCl. Aluminium, chromium, and uranium are in the filtrate.

Ignite the paper and precipitate very carefully in a weighed platinum crucible. If Ti, W, Nb, and Ta are absent the precipitate may be weighed as ZrO_2. If, as usually occurs, one or more of these elements are present the ignited precipitate is fused with $K_2S_2O_7$, dissolved in dilute H_2SO_4, and H_2O_2 added to oxidize titanium. To the clear solution containing about 10% H_2SO_4, add 25 ml. of a 20% solution of $(NH_4)_2HPO_4$, stir vigorously for a few minutes, and allow to digest for several hours. Stir in a little paper pulp, and filter on a Whatman No. 42 paper. Wash the precipitate thoroughly with cold 5% NH_4NO_3, transfer to a platinum crucible, ignite at a low temperature until the paper is charred, and gradually heat to about 1050° C. Cool, and weigh as ZrP_2O_7, unless the sample contains tungsten which has not been removed by acid digestion and cinchonine precipitation at the start of the analysis, or Nb and Ta. $ZrP_2O_7 \times 0{\cdot}3440 = Zr$.

If only TiO_2 is present with the zirconium it is best determined colorimetrically and its weight subtracted from the $ZrO_2 + TiO_2$.

If Nb and Ta are present, fuse the ignited phosphate precipitate

with KOH in a nickel crucible, dissolve in water, filter, and wash. Ignite the residue, fuse with $K_2S_2O_7$, dissolve in dilute H_2SO_4 and re-precipitate as before with $(NH_4)_2HPO_4$ in 10% H_2SO_4 solution. Filter, wash, ignite, and weigh as ZrP_2O_7 in the manner outlined above.

Tungsten is best separated at the start of the analysis by digestion in acid solution and cinchonine. Vanadium may be removed after the cupferron separation by fusion of the mixed oxides with Na_2O_2 or Na_2CO_3 and leaching out the soluble vanadate with water.

SPECIAL PROCEDURES

1. One of the best methods for zirconium is based on the fact that in a 10% H_2SO_4 or HCl solution phenylarsonic acid, $C_6H_5AsO(OH)_2$, precipitates white flocculent $ZrO(C_6H_6AsO_3)_2$ which is converted to ZrO_2 by igniting, treating with HF and H_2SO_4, fuming and re-igniting at 1000° C. Iron if present in quantities can be removed with ether or with a double precipitation of phenylarsonic acid. Titanium does not interfere if H_2O_2 is present when the precipitation is made, nor do Al, Cr, Mo, or V in small quantities. The procedure is outlined in the methods of the U.S. Steel Corporation.[6]

2. Kumins[2] has recently described a procedure for separating zirconium with mandelic acid from a hydrochloric acid solution. This specific reagent separates zirconium from Ti, Fe, V, Al, Cr, Th, Ce, Sn, Ba, Ca, Cu, Bi, Sb, Cd.

3. The use of fumaric acid for the isolation and determination of zirconium has been described.[8] From solutions 0·25N. in HCl the reagent separates zirconium from Al, Be, U, Ni, Ba, Ca, Fe, Mn, Th, and the ceria earths in a single precipitation; in a double precipitation V, Cr, Ti, and Sn are completely removed.

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MISCELLANEOUS ANALYSES AND DATA

I. ACIDITY OF SPECIAL SAMPLES

1. Acidity of oils and pyranols

From time to time the industrial chemist is requested to report on acidity of transformer oils, etc. The following procedure is used by the General Electric Company, Schenectady, N.Y.

Solutions

Sodium hydroxide. 0·01 normal, standardized to third place.

Titrating solvent. Mix one part benzene, by volume, with one part of ethyl alcohol. Add 0·5% by volume of a saturated solution of phenol red in ethyl alcohol.

Procedure. Place 100 ml. of titrating solvent into a 500 ml. Erlenmeyer flask and titrate with the standardized 0·01N. sodium hydroxide until a lasting red coloration is obtained.

Immediately add approximately 10 gm. of the sample, weighed to the third decimal place. Titrate again with the standardized sodium hydroxide using a swirling motion of the flask, until the same end point is reached.

For convenience, a pipette may be used to add the sample to the flask and the weight determined from the gravity. The specific gravity must be taken at the same temperature as that used when pipetted.

In cases of high acid values or where the addition of the sample produced cloudiness in the titrating solvent when the sodium hydroxide is added, a smaller portion of the sample may be used.

The acidity is expressed in milligrams of sodium hydroxide per gram of sample.

$$\frac{\text{ml. 0·01N. NaOH} \times 40 \times \text{Normality of 0·01N. NaOH}}{\text{weight in grams of sample}}$$
$$= \text{mg. NaOH per gram of sample}$$

2. Free acid in copper solutions

As a special case of the determination of acid in coloured solutions we may consider free acid in copper solutions.

If the copper content of the solution is not too high it is usually possible to titrate directly with 0·5N. Na_2CO_3, using methyl orange indicator. The end point is the change from pink or purple to a yellow, green, or yellow-orange. The number of millilitres of 0·5N. Na_2CO_3 used, multiplied by 0·0245, gives the number of grams of acid present in terms of H_2SO_4.

0·5N. Na_2CO_3. Weigh out 53 gm. Na_2CO_3 and make up to 2 litres with distilled water. 1 ml. 0·5N. Na_2CO_3 is equivalent to $\frac{98}{2} \times 0{\cdot}5 \times \frac{1}{1000}$ or 0·0245 gm. H_2SO_4.

When the copper content of the solution is high, the following procedure will give good results on electrolytes, leach solutions etc., in works practice where potentiometric titrations are not employed. It is based on the fact that when an excess of KI solution is added to a copper solution the copper is precipitated as cuprous iodide, and iron is reduced to the colourless ferrous state. The precipitate of Cu_2I_2 is removed by filtration and the excess iodine destroyed by careful addition of $Na_2S_2O_3$. The clear or faintly milky solution can then be titrated with standard alkali, using methyl orange.

Pipette out 5–50 ml. of the sample into a 250 ml. beaker, dilute slightly with water, and add sufficient 20% KI solution to precipitate all copper. Avoid an excess of KI, for cuprous iodide is soluble in an excess. Allow the precipitate to settle a few minutes on the hot plate, and filter through a large Whatman No. 42 paper.

Cuprous iodide has a tendency to creep over the edge of filter paper but this can be avoided by using a 12·5 cm. paper and not filling the funnel more than half full.

Wash thoroughly several times with cold water, discard paper and precipitate. Titrate the liberated iodine in the solution carefully with a saturated solution of $Na_2S_2O_3$. If an excess of $Na_2S_2O_3$ is added the latter will react with the acid in the sample, giving a turbidity due to liberated sulphur, and causing low results.

To the clear, colourless solution add 3 drops methyl orange and titrate to an orange-yellow colour with 0·5N. Na_2CO_3. The number of ml. of Na_2CO_3 used, multiplied by 0·0245, is the number of grams of acid present, in terms of H_2SO_4.

II. GAS ANALYSES

Nearly all industrial laboratories will have occasion from time to time to undertake gas analyses. This specialized field of analytical chemistry is fully covered in the texts of Dennis and Nichols,[5] Jacobs,[6] Parr,[7] Scott and Furman,[8] and Treadwell and Hall.[10] An excellent general reference handbook is the Burrell Manual for Gas Analysts,[2] and some useful data on absorbents are given in a booklet of the G. Frederick Smith Chemical Co.[9] A very good review of convenient apparatus and procedures for the analysis of gases by absorption and combustion is given by Brooks *et al.*[1]

Instruments for the detection and measurement of various toxic gases in air are available from such firms as Mine Safety Appliances Co., Pittsburgh, Pa.

The determination of hydrogen in steel has been described.[3 4]

Determination of CO_2, O_2, and CO in flue gases containing SO_2

In the metallurgical industries it is sometimes necessary to determine CO_2, O_2, and CO in gases from roasting, smelting, or waste heat boiler operations where considerable quantities of SO_2 are present. The order of absorption in the standard Orsat apparatus is carbon dioxide in potassium hydroxide, oxygen in

alkaline pyrogallol, and carbon monoxide in ammoniacal cuprous chloride. It is necessary in this case, therefore, to either remove sulphur dioxide before absorption of the sample in potassium hydroxide or to determine the sulphur content after absorption to correct for the presence of sulphur dioxide. Instead of determining the sulphur in the absorbent, SO_2 and CO_2 may be determined by absorption together in standard NaOH in the presence of hydrogen peroxide. The SO_2 is converted to Na_2SO_4 and the CO_2 goes to Na_2CO_3. Titrate with standard acid, using phenolphthalein, to obtain all the excess NaOH plus half the Na_2CO_3. When the colourless end point is reached add methyl orange and continue the titration to the pink end point. The methyl orange alkalinity, or total reading on the burette after both titrations, gives the sum of $NaOH + Na_2CO_3$. The difference between methyl orange and phenolphthalein alkalinity represents half the carbonate. The original NaOH added, less the quantity remaining as NaOH and that changed to Na_2CO_3, gives the quantity changed to Na_2SO_4. In this manner one obtains a measure of CO_2 and SO_2 which passed into the absorbent solution of NaOH, without determining the sulphate gravimetrically.

An alternative procedure is to remove SO_2 before passing the gas into the absorbent solution for carbon dioxide. In a private communication from S. R. Zimmerley of the U.S. Bureau of Mines, Salt Lake City,[11] it is indicated that the following procedure will give satisfactory results for control work.

Using mercury as the confining liquid, determine the four gases in a modified Orsat apparatus. Absorb the SO_2 first in a potassium iodide-iodine solution slightly acidified with HCl to minimize the absorption of CO_2. Then absorb the CO_2 as usual in KOH in the second pipette. Pass the residual gas successively into an alkaline solution of potassium pyrogallate to remove oxygen and finally into ammoniacal cuprous chloride to remove carbon monoxide. We have found, however, that the solubility of carbon dioxide in iodine solutions is too high to permit this procedure to be used for accurate work.

In Table 5 is presented a list of absorbents for gases, which may be useful to chemists when setting up absorption trains. The large number of blanks should serve to draw attention to a fertile field for investigation.

TABLE 5

Absorbents for Gases

Absorbent	H_2O	CO_2	SO_2	H_2S	Oxides of N	NH_3	Alcohol	C_2H_2	C_6H_6	Cl_2	HCl	C_2N_2	HCN	CO	O_2	PH_3	AsH_3	SbH_3	H_2Se
$CaCl_2$	Yes	—	No	—	Yes	Yes	Yes	—	—	—	—	—	—	—	—	—	—	—	—
H_2SO_4	Yes	No	—	—	Yes	Yes	—	Yes	—	—	—	—	—	—	—	—	—	—	—
P_2O_5	Yes	No	No	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—
KOH	—	Yes	Yes	Yes	Yes	—	—	—	Yes	Yes	Yes	Yes	Yes	No	No	—	—	—	—
Soda Lime (2 CaO, 1 NaOH)	Yes	Yes	Yes	—	—	—	—	—	—	Yes	—	—	—	—	—	—	—	—	—
Activated alumina	Yes	partial	partial	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dessichlora, barium perchlorate	Yes	—	—	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—
Dehydrite, magnesium perchlorate trihydrate	Yes	No	—	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—
Drierite, anhydrous calcium sulphate	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Anhydrone, anhydrous magnesium perchlorate	Yes	No	small partial	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—
Ascarite, sodium hyroxide asbestos	Yes	Yes	Yes	—	—	—	—	—	—	—	Yes	—	—	—	—	—	—	—	—
$CuSO_4$ anhydrous	Yes	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$CuSO_4$ solution	—	—	—	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Iodine	—	partial	Yes	Yes	—	—	—	—	—	Yes	—	—	—	—	—	—	—	—	—
Ammoniacal suprous chloride	—	Yes	—	—	—	—	—	Yes	—	—	—	—	—	Yes	Yes	—	—	—	—
Silver nitrate	—	—	—	Yes	—	—	—	Yes	—	Yes	Yes	—	Yes	—	—	Yes	Yes	Yes	—
Alkaline pyrogallol	—	Yes	Yes	—	—	—	—	—	—	—	—	—	—	No	Yes	—	—	—	—
Fuming sulphuric acid	Yes	—	—	—	—	Yes	—	Yes	Yes	—	—	—	—	—	—	—	—	—	—
Acid zinc-potassium chloride	—	—	—	No	—	No	—	—	—	No	No	—	—	—	—	—	—	—	Yes
H_2O_2 solution	—	—	Yes	No	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ammoniacal H_2O_2	—	—	Yes	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica gel	Yes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H_2SO_4 sat. with chromic acid	—	—	small quantities	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
50% chromic acid	—	—	large quantities	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5% $KMnO_4$	—	—	large quantities	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

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III. WATER

The chemical analysis of industrial and domestic waters is usually a constant and important operation in most industrial laboratories. The determinations described below will cover most aspects of water analysis encountered in industry, but occasionally others may be required. The references cited at the end of this section give complete details of all phases of water analysis. Good reviews are now given annually by Love.[11]

In the mineral analysis of waters usually a fairly large initial sample must be taken, often 1–5 litres, and evaporated to a convenient volume. During this operation care must be taken to eliminate contamination around the hot plates. Owing to the low percentage of nearly all constituents in water, generally expressed in parts per hundred thousand, blanks should be carried along with the sample in all determinations.

Results of water analyses are practically always expressed at the present time as parts per hundred thousand or parts per million. Sometimes for special work they are reported as grains per gallon. To convert these results the following relations are useful:

Parts per hundred thousand × 0·584 = grains per gallon (U.S.)
Parts per hundred thousand × 0·7 = grains per gallon (Imperial)
Grains per gallon (U.S.) × 1·71 = parts per hundred thousand
Grains per gallon (Imperial) × 1·43 = parts per hundred thousand.

The quantity of water taken for the following analyses will obviously depend on the sample.

1. Acidity or alkalinity

To 100 ml. of the sample in a porcelain casserole, or 250 ml. beaker on a white background, add 3 drops of phenolphthalein. If the solution turns pink, follow the procedure from *B*.

A. Carefully add to the sample 0·02N. NaOH from a burette, stirring thoroughly, until the colour changes to a faint permanent pink. The ml. of 0·02N. NaOH ÷ 0·9808 = acidity as H_2SO_4 in parts per 100,000. In the presence of iron and aluminium salts the end point is difficult to determine. Where a large number of determinations are made it is advisable to make the standard NaOH solution 0·0204N., in which case the number of ml. of NaOH used gives directly the H_2SO_4 in parts per 100,000.

To determine mineral acids + sulphates of iron and aluminium, titrate with phenolphthalein as above, but at boiling temperature.

To determine free mineral acids add 2 drops methyl orange indicator to 100 ml. of the sample and titrate with 0·02N. NaOH in the cold until the pink colour just disappears. The number of ml. of 0·02N. NaOH ÷ 0·98 = acidity as H_2SO_4 in parts per 100,000. In the presence of considerable quantities of iron or aluminium salts this result is not a true measure of the free mineral acids.

B. If the solution turned pink on the addition of phenolphthalein it is alkaline. Carefully add to the 100 ml. sample in a porcelain casserole, or 250 ml. beaker on a white background,

0·02N. H_2SO_4 from a burette, stirring vigorously. Titrate to the colourless end point. The ml. of 0·02N. H_2SO_4 = phenolphthalein alkalinity expressed as $CaCO_3$ in parts per 100,000. This gives the hydroxides + one-half the normal carbonates.

Now add 2 drops of methyl orange to 100 ml. of sample and titrate carefully until the yellow solution changes to a faint pink or orange colour. The ml. of 0·02N. H_2SO_4 = methyl orange alkalinity as $CaCO_3$ in parts per 100,000. This measures the total alkalinity, hydroxides + carbonates + bicarbonates. As a general rule the methyl orange titration is carried out on the same sample used for the phenolphthalein titration, 2 drops methyl orange being added after the colourless end point of the previous titration has been reached. In this case, of course, the methyl orange alkalinity is the total reading on the burette, i.e. phenolphthalein + methyl orange readings.

It is good practice in methyl orange titrations to have two beakers as references for the colour change, each filled with the same quantity of distilled water as the samples, together with the indicator. Add a few drops of acid to one and of alkali to the other. These reference solutions will enable one to distinguish the colour change at the end point more readily.

The following table summarizes the relationship between phenolphthalein and methyl orange alkalinities in presence of hydroxide, carbonate, and bicarbonate.

TABLE 6

Relationship between phenolphthalein and methyl orange alkalinities in presence of hydroxide, carbonate, and bicarbonate

Titration value	Hydroxide	Carbonate	Bicarbonate
P = phenolphthalein alkalinity M = methyl orange alkalinity			
$P = 0$	0	0	M
$P < \frac{1}{2}M$	0	2P	M − 2P
$P = \frac{1}{2}M$	0	2P	0
$P > \frac{1}{2}M$	2P − M	2(M − P)	0
$P = M$	M	0	0

For instance, where the phenolphthalein alkalinity is zero, hydroxides and carbonates are absent and the methyl orange alkalinity represents bicarbonates only. Where the phenolphthalein alkalinity is less than half the methyl orange value, hydroxides are absent, twice the "P" reading gives the carbonate present, and bicarbonates are the difference between the methyl orange reading and twice the "P" value. ✓

2. Free carbon dioxide

A. Owing to the ease with which CO_2 escapes from water, this determination should be made on a special sample as rapidly as possible after collection.

Thoroughly mix the sample, and place 100 ml. into a beaker or preferably a Nessler tube. Add 2 drops phenolphthalein and titrate rapidly with N/22 Na_2CO_3 solution, with gentle stirring, until a faint but permanent pink colour is produced. The number of ml. N/22 Na_2CO_3 solution = parts free CO_2 per 100,000. N/22 Na_2CO_3 is made by dissolving 2·41 gm. Na_2CO_3 in boiled water and making up to 1 litre.

B. Free or dissolved CO_2 in mine water is determined by placing a 250 ml. sample in a 400 ml. beaker, adding 2 drops phenolphthalein, and titrating to a faint but permanent pink with a standard Na_2CO_3 solution.

1 ml. N/10 Na_2CO_3 = 0·0022 gm. CO_2
1 ml. N/22 Na_2CO_3 = 0·0010 gm. CO_2

Take another 250 ml. sample and boil for 5–10 minutes to drive off all free CO_2. Cool rapidly and add 2 drops phenolphthalein. If there is no mineral acid present, free CO_2 will be driven off and the decomposition of bicarbonate will result in an alkaline reaction and a faint pink colour. If the sample is not pink, the acidity is due not to free CO_2 but to a mineral acid, such as H_2SO_4 from the oxidation of sulphide ore. The difference between the titration before and after boiling then represents free CO_2, since bicarbonates will not be present with a mineral acid in mine water.

Blanks of ordinary and of recently-boiled distilled water, should be carried along with the above titration.

8. Hardness

The hardness of a water is a measure of its tendency to consume soap before a permanent lather can be formed. It is due to the presence of calcium and magnesium compounds, and to a lesser extent iron and aluminium, which combine with the fatty acids in the soap to form insoluble salts like calcium and magnesium palmitates, stearates, oleates, etc. Hardness is expressed as parts $CaCO_3$, and while it may be found by calculation from the quantities of calcium and magnesium present in the sample, it is nearly always determined by adding successive increments of standard soap solution to a sample, shaking and finding the point at which a permanent lather is formed. The test is rapid and with careful manipulation gives quite satisfactory results.[7, 15, 18]

Standard calcium solution. Dissolve 0·5 gm. $CaCO_3$ with a little dilute HCl. Wash down sides of beaker with a little CO_2-free water. Neutralize with NH_4OH to a slight alkalinity, using litmus as indicator. Make up to 500 ml. with CO_2-free water. 1 ml. = 0·001 gm. $CaCO_3$.

Standard soap solution. Shake 100 gm. Castile soap in 1 litre of 80% ethyl alcohol. Let stand for 24 hours. Decant the clear supernatant liquid and store as stock solution. This solution is about 10 times stronger than the standard solution. Adjust the stock solution with alcohol until 1 ml. = 1 ml. standard $CaCl_2$ solution, making allowance for the lather factor of the soap solution.

The unfortunate term "lather factor" is simply the blank, and denotes the amount of standard soap solution required to produce a permanent lather in 50 ml. of CO_2-free distilled water. When standardizing, use 10 ml. of standard $CaCl_2$ in 40 ml. CO_2-free distilled water and titrate until the lather persists for 5 minutes. 1 ml. of standard soap solution = 0·001 gm. $CaCO_3$ after deducting lather factor. The lather factor for the soap used should be ascertained by making at least 4 determinations on 50 ml. portions of CO_2-free distilled water.

If the water is acid it should be first made neutral to methyl orange by the careful addition of 0·02N. Na_2CO_3. Add 50 ml. of the water to a 500 ml. glass-stoppered reagent bottle. Run in successive portions of the standard soap solution from a burette,

shaking vigorously after each addition, until a strong lather which will persist for 5 minutes is obtained. When it is considered this point has been reached, the bottle should be laid on its side. Deduct the lather factor from the burette reading, and this value multiplied by 2 gives the hardness in parts per 100,000 expressed as $CaCO_3$, when 1 ml. of the soap solution is exactly equal to 0·001 gm. $CaCO_3$.

Sometimes a transient end point, called a "ghost point", is reached after the conversion of the calcium salts. The addition of more soap solution will cause this temporary lather to disappear, and titration is continued to the true end point. If the hardness of the water necessitates more than 15 ml. of soap solution, take an aliquot portion and dilute with CO_2-free distilled water. The strength of the standard soap solution must be checked periodically. Permanent lather means one which does not disappear in 5 minutes.

As an alternative to the soap test for hardness, the latter may be determined by titration with potassium palmitate. Details of this procedure are given in the Solvay bulletin.[17]

Another alternative to the soap test is titration with reagents proposed by Schwarzenbach.[14] Chemical supply houses now furnish the following reagents for this method:

(*a*) Standard solution disodium ethylenediamine tetraacetate One ml. of this is usually equivalent to 1·00 mg. calcium carbonate.
(*b*) Buffer solution.
(*c*) Eriochrome black T indicator solution.

Total hardness is determined as follows: pipette 50 ml. of sample water into a 250 ml. Erlenmeyer flask. Add 10 ml. of the buffer solution, 4 drops of the indicator solution and mix. Titrate with the standard tetraacetate solution to a colour change from wine red to blue. The true end point is the final disappearance of the red hue and the appearance of a blue colour. To calculate total hardness as p.p.m. $CaCO_3$, multiply ml. of the titrating reagent by 20.

Calcium hardness is determined as follows: determine the total hardness as above. Pipette 100 ml. of sample into a 250 ml. flask and add 10 ml. saturated sodium oxalate solution. Thoroughly

mix and allow to stand for 15 minutes with occasional shaking. Remove the precipitated calcium oxalate by filtration through Whatman No. 40 paper and pipette 50 ml. of the clear filtrate into a 250 ml. Erlenmeyer flask. Determine the magnesium hardness as given above. To calculate the magnesium hardness as p.p.m. multiply ml. of titrating reagent by 22. The latter value is used instead of 20 because the sample water was diluted with the sodium oxalate solution. Subtract this value from p.p.m. total hardness to obtain calcium hardness.

While turbid waters are filtered prior to the soap hardness determination, work at Rhokana Corporation has shown that the presence of small quantities of colloidal matter such as fine clay does not significantly increase the consumption of soap.

With the results of the titration for alkalinity using phenolphthalein and methyl orange indicator, and for hardness using soap solution, much valuable information can be obtained from the following relationships:

H, or hardness by soap test = total hardness. This is the sum of the calcium and magnesium salts in water, whether present in alkaline form such as calcium bicarbonate, or as non-alkaline form, e.g. magnesium sulphate.

P, or phenolphthalein alkalinity = sum of hydroxides + half the carbonates. If hydroxides and bicarbonates are absent, the P reading represents half the normal carbonates; if bicarbonates are present the P reading gives half the normal carbonates. Bicarbonates and hydroxides cannot exist together in a water since they react to form normal carbonates.

M, or methyl orange alkalinity = total alkalinity. This is the sum of all alkaline salts in a water, calcium, magnesium, sodium, etc. It gives all the hydroxide, carbonate, and bicarbonate.

When 2P is greater than M, then 2P – M = hydroxide alkalinity, generally denoted by O. If M is greater than 2P, then M – 2P = bicarbonate alkalinity, which may be designated $\boxed{O}$.

When H is greater than M, some of the hardness salts must be present in a non-alkaline form, i.e. as sulphates of calcium or magnesium. H – M = permanent hardness, generally indicated by $\boxed{S}$.

If M is greater than H, part of the alkalinity must be due to sodium salts. M – H = alkalinity due to sodium salts, or sodium alkalinity, usually designated by S.

The hydroxide value, O, may represent calcium hydroxide, magnesium hydroxide, or sodium hydroxide, singly or together. The sodium alkalinity value, S, may indicate sodium hydroxide, sodium carbonate, or sodium bicarbonate, separately or together.

If S is greater than O, then S – O = sodium carbonate, denoted by N. When O is greater than S, then O – S = calcium hydroxide, usually designated [N].

These relationships may be used to give very complete information on waters from lime-soda treatment plants, boilers, etc.[2]

4. Determination of solids

A. *Total solids.* Evaporate 1 litre of a thoroughly representative sample in a weighed platinum dish on a water bath. Dry the dish in an oven at 105° C., cool in a desiccator, and weigh. The increase in weight is total solids, i.e. dissolved + suspended solids.

B. *Suspended solids.* If the water contains suspended matter, filter 1 litre of a representative sample through a previously weighed Gooch crucible. Dry at 105° C., cool in a desiccator, and weigh. Retain the filtrate for dissolved solids. For the determination of suspended solids in very difficultly filterable waters, such as some types of sewage effluents, a satisfactory procedure is given by Young and Leibowitz.[21]

C. *Dissolved solids.* Evaporate the filtrate from the determination of suspended solids in a weighed platinum dish. If suspended matter is absent, evaporate 1 litre of the original sample directly on the steam bath. Dry the dish at 105° C. in the oven, cool in a desiccator and weigh. For all but very exact work, evaporation can be quickly and satisfactorily carried out by evaporating rapidly in 1-litre Pyrex beakers to a low volume and transferring to platinum dishes in the final stages for weighing.

In rapid control analyses used in power plants the measurement of total dissolved solids is usually taken with a hydrometer or densimeter.[2]

D. *Organic and volatile matter.* Ignite the dish, after weighing at 105° C., as in *A* or *C* above, at a dull red heat to drive off all

organic matter. Cool, add a little CO_2 water to recarbonate any calcium or magnesium oxide. Rotate the dish to wet all the contents and then dry at 105° C. in an oven, cool in a desiccator, and weigh. The loss of weight represents approximately the organic and volatile matter. In the same manner, ignition of the Gooch crucible in *B*, after drying at 105° C., and weighing, will give a close check on the organic and volatile matter.

5. Dissolved oxygen

A. *Standard Winkler method.* The Winkler procedure for the determination of dissolved oxygen depends upon the formation of a precipitate of manganous hydroxide in a glass-stoppered bottle completely filled with the water under examination. The oxygen dissolved in the water is rapidly absorbed by the manganous hydroxide, forming a mixture of higher oxides which on acidification in the presence of an iodide releases iodine in a quantity chemically equivalent to the oxygen content of the sample. The liberated iodine is then titrated with a standard solution of sodium thiosulphate.

Fill a narrow-necked glass-stoppered bottle of 250–300 ml. capacity by leading water to the bottom of the bottle and allowing the water to run through and overflow for at least 5 minutes. Samples should be cooled to approximately 21° C. by means of a cooling coil. Different arrangements of cooling coils are given in references 2, 3, 10. Carefully withdraw any tubing from the bottle, leaving it full to the top. Insert the stopper so that no air is entrapped. Take the temperature of the water while it is running through.

(*a*). If nitrite nitrogen is present in quantities greater than 0·1 mg. per litre remove the stopper from the bottle and add 0·7 ml. H_2SO_4 and then 1 ml. of $KMnO_4$ solution. All solution additions to the sample are conveniently made by means of 10 ml. burettes to which tubes drawn out to fine jets, long enough to reach the bottom of the sample bottle, are attached. The greatest care must be taken to exclude all air. Insert the stopper and mix by inverting the bottle several times. If a noticeable excess of $KMnO_4$ is not present after 20 minutes, again add 1 ml. of the $KMnO_4$ solution. After 20 minutes destroy the excess of $KMnO_4$

by adding 1 ml. of the potassium oxalate solution, re-stopper the bottle at once, and mix its contents. Continue as in the following paragraph.

(*b*). If, as is generally the case, nitrite nitrogen is absent or less than 0·1 mg. per litre, the above procedure may be omitted and manganous sulphate solution added directly.

Add 1 ml. of manganous sulphate solution and 3 ml. of the alkaline KI solution to the bottle by means of the fine tubes attached to a burette, being very careful to exclude air. Replace stopper carefully, shake well, and let stand 5 minutes.

Add 2 ml. H_2SO_4 to the bottom of the bottle and replace stopper carefully to exclude air. Shake well and allow to stand 10 minutes. Pour contents into a porcelain casserole and titrate with 0·025N. $Na_2S_2O_3$, adding starch indicator solution when the colour has become faint yellow. Titrate to the colourless end point. 1 ml. of 0·025N. $Na_2S_2O_3 = 0{\cdot}0002$ gm. oxygen or 0·14 ml. oxygen at N.T.P.

$$\text{Dissolved oxygen} = \frac{\text{ml. titration} \times \text{oxygen factor} \times 100{,}000}{\text{ml. of sample titrated}}$$

$$= \text{parts oxygen per } 100{,}000 \text{ by weight}$$

If conversion to volume is desired, 1 gm. oxygen occupies 700 ml. at N.T.P.

Reagents

Potassium permanganate solution. Dissolve 6·32 gm. $KMnO_4$ in water and dilute to 1 litre.

Potassium oxalate solution. Dissolve 20 gm. potassium oxalate in water and dilute to 1 litre.

Manganese sulphate solution. Dissolve 480 gm. $MnSO_4.4H_2O$ in water and dilute to 1 litre.

Alkaline potassium iodide solution. Dissolve 500 gm. NaOH and 150 gm. KI in water and dilute to 1 litre.

Sodium thiosulphate solution, 0·025N. Dissolve 6·205 gm. $Na_2S_2O_3.5H_2O$ in water and dilute to 1 litre. If desired, the ordinary standard $Na_2S_2O_3$, having a value of 1 ml. = 0·0025 gm. Cu, made by dissolving 10 gm. $Na_2S_2O_3.5H_2O$ and 1·5 gm.

NaOH in 1 litre of water, may be used. The oxygen factor = copper factor × 0·1259.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$
$$Mn(OH)_2 + O \rightarrow H_2MnO_3$$
$$H_2MnO_3 + 2H_2SO_4 + 2KI \rightarrow K_2SO_4 + MnSO_4 + I_2 + 3H_2O$$
$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The effect of temperature upon the titration of iodine with the Winkler test for dissolved oxygen has been studied by Pinkney and Young.[12] The starch-iodine reaction was found to have its maximum sensitivity at approximately 10° C.

While the Winkler method is satisfactory for the determination of dissolved oxygen in most waters, the very low oxygen contents of boiler waters in modern power plants have necessitated modifications such as those of Haslam and Moses[9] and Schwartz and Gurney[13] given below.

B. *Method of Haslam and Moses.* A procedure for the determination of dissolved oxygen in boiler waters is that of Haslam and Moses.[9] In this method dissolved oxygen is absorbed by manganous hydroxide and on acidification with HCl chlorine is liberated. The latter reacts with *ortho*-tolidine to give a yellow colour which is measured in a Lovibond Nesslerizer using the chlorine discs. The chlorine liberated is proportional to the dissolved oxygen present in the sample.

$$Mn(OH)_2 + O \rightarrow H_2MnO_3$$
$$H_2MnO_3 + 4HCl \rightarrow MnCl_2 + 3H_2O + Cl_2$$

Reagents

Manganous chloride. 400 gm. $MnCl_2.4H_2O$ per litre.

Potassium hydroxide. 700 gm. KOH per litre.

ortho-tolidine. Dissolve 1 gm. in 100 ml. HCl, and make up to 1 litre with water.

Procedure. Allow water to flow through a Winkler flask for 10 minutes to ensure displacement of all air. If the water is not at room temperature use a cooling coil placed ahead of the Winkler sampling flask.

By means of a graduated funnel attached to the Winkler flask add 1 ml. manganous chloride solution and 1 ml. potassium

hydroxide solution. If reagents refuse to flow into flask, open the pinch cock on the inlet rubber tubing momentarily, taking care to close the pinch cock before air can be drawn in after reagents.

Mix the contents of the Winkler flask carefully by inverting several times. Allow to stand for 10 minutes and add 2 ml. HCl. Gently agitate the flask until the solution becomes clear.

Withdraw 50 ml. of clear solution into a Nessler cylinder and add 0·5 ml. *o*-tolidine solution. Allow to stand 5 minutes and match the colour against the permanent standard discs supplied with B.D.H. Lovibond nesslerizer for free chlorine.

These discs cover the ranges:

0·01–0·09 p.p.m. free chlorine
0·10–0·50 p.p.m. free chlorine.

To convert p.p.m. chlorine to ml. oxygen per litre, multiply by 0·158.

With care and accuracy in sampling, this procedure is stated to give reliable results within the range 0·0016–0·08 ml. O_2 per litre. The following substances interfere: nitrites, chlorates, ferric and manganic compounds, organic colouring matter.

It was found at Nchanga that better results were obtained when the *o*-tolidine solution was added directly to the sampling flask in the same way that the other reagents are added. This overcomes a slight loss of chlorine in a hot atmosphere when transferring the treated solution from sampling flask to Nessler cylinder. It was also found that sulphuric acid had fewer reducing contaminants tending to cause low oxygen values than hydrochloric acid.

The writer has not been able to get consistent results with this method at Nchanga or to check with results simultaneously by the Schwartz and Gurney procedure. Whether this was due to a peculiarity of the boiler water under investigation has not been determined, but we recommend the Schwartz and Gurney method in preference to the procedure of Haslam and Moses.

C. *Method of Schwartz and Gurney.* This procedure is one of the most reliable and satisfactory for the determination of dissolved oxygen in boiler water. Errors due to contamination of reagents and to varying sensitivites of starch are eliminated. The method consists in adding a small known quantity of iodine from a standard potassium bi-iodate solution to two samples, one of

which is a blank. The two determinations have a common sensitivity which is cancelled in the calculation.

Reagents

1. Manganous sulphate solution. 480 gm. of $MnSO_4.4H_2O$ or 400 gm. $MnSO_4.2H_2O$ dissolved in water, filtered and made up to 1 litre. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the S.G. of the solution to 1·27 at 20° C.

Manganese chloride solution. This may be used instead of manganous sulphate. 425 gm. $MnCl_2.4H_2O$ per litre.

2. Alkaline iodine reagent. 500 gm. of NaOH and 135 gm. NaI per litre. Alternatively 700 gm. KOH and 150 gm. KI per litre may be used.

3. Sulphuric acid. 1:1 with water.

4. Starch solution. To 0·5 gm. of starch in a mortar add a little cold water and grind to a paste. Pour into 100 ml. of boiling water, stir, and allow to settle overnight. Use the clear supernatant liquor.

5. Dilute acid for standardization. 1 vol. conc. H_2SO_4 in 9 vol. water (3·6N.).

6. Stock sodium thiosulphate, N/40. To 100 ml. of standard $Na_2S_2O_3$ used for copper determinations, wherein 1 ml. = 0·0025 gm. Cu, add 57 ml. of water. Alternatively dissolve 6·205 gm. $Na_2S_2O_3.5H_2O$ in water and dilute to one litre.

Standard potassium bichromate, N/40. 1·225 gm. $K_2Cr_2O_7$ per litre.

Standardization. Dissolve 2·5 gm. KI in about 25 ml. of water and 5 ml. of the dilute sulphuric acid in an Erlenmeyer flask. Add 20 ml. of the standard bichromate. Set the mixture in the dark for 5 minutes. Dilute to 200 ml. and titrate the liberated iodine with the N/40 thiosulphate, adding starch towards the end of the titration.

7. Sodium thiosulphate, N/200. 20 ml. of N/40 thiosulphate is accurately pipetted into a 100 ml. volumetric flask and diluted to the mark with water. This solution must be freshly prepared daily.

8. Potassium bi-iodate, N/200. 0·1625 gm. $KH(IO_3)_2$ per litre.

Apparatus. All rubber tubing used in sampling must be freed of sulphur by boiling for 6 hours in 20% NaOH solution and then flushed out overnight with water.

Three oxygen sampling flasks are required.

Procedure. Turn on the water supply to a big cooling coil. When cooling water is overflowing, connect the bottom of the coil to the sampling point with rubber tubing. Flush out the coil with the water to be sampled and connect the outlet of the large coil to the inlet of a small coil immersed in iced water, and flush out the small coil. To avoid air locks ensure that both coils are empty of water before connecting. After flushing connect the outlet of the small coil to the burette side of the first of three sampling flasks connected in series. Cautiously open the valve at the sampling point, permitting a gentle flow of water to fill the flasks. Be extremely careful to avoid entrapping air bubbles. When the flasks are full, increase the water flow and continue sampling for at least 10 minutes. The flow should be rapid enough to ensure a correct sample but not rapid enough to raise the temperature above 25° C.

This procedure applies to the collection of water samples by means of cooling coils, the first serving to reduce the temperature of the sample to that of the cooling water of the power station which may be considerably over 25° C., and the second cooling coil provided with ice water to reduce the temperature of the sample well below this figure. Obviously the cooling arrangements will depend on the conditions at each power plant.

Close the valve and then close all the cocks on the sampling flasks. The flasks are then treated as follows:

Blank. One flask is a blank and reagents are added in the following manner:

(*a*) From a burette add exactly 1 ml. KOH.KI solution to the burette on the flask. Open the burette cock and then cautiously manipulate the bottom cock on the flask until the KOH.KI solution is drawn into the flask. Avoid admitting air. Close both cocks and wash out the flask burette with distilled water.

(*b*) In the same manner as above add 1·5 ml. of 1:1 H_2SO_4.

Rotate the flask to mix the contents, and again wash out the burette.

(*c*) Finally add 1 ml. of manganese solution. Mix the contents of the flask.

(*d*) Open the top cock on the flask and then using the bottom cock run about 10 ml. to waste. Add a further 10 ml. to a 250 ml. measuring cylinder, rinse the cylinder and then add exactly 250 ml. of the contents of the flask.

(*e*) Pour the solution into a porcelain dish and add exactly 2·00 ml. of N/200 $KH(IO_3)_2$. Cautiously titrate the liberated iodine with freshly prepared N/200 $Na_2S_2O_3$, adding 1 ml. of starch solution towards the end of the titration. Record this titration. The solution is stirred during the titration with a thermometer. The temperature is recorded and must not exceed 25° C.

Sample. The other two flasks constitute a duplicate sample and are treated as follows:

(*a*) Add exactly 1 ml. of manganese reagent, taking all the precautions previously described.

(*b*) Add 1 ml. KOH.KI, mix thoroughly and stand for 3 minutes.

(*c*) Add 1·5 ml. 1:1 H_2SO_4 and rotate the flask until the precipitate is completely dissolved.

(*d*) Run a little of the sample to waste and use a further small quantity to rinse the measuring cylinder. Then transfer 250 ml. to a porcelain dish.

(*e*) Add exactly 2·0 ml. N/200 $KH(IO_3)_2$. Titrate with N/200 $Na_2S_2O_3$, adding 1·0 ml. starch solution towards the end of the titration.

(*f*) From the titre obtained subtract the quantity of N/200 $Na_2S_2O_3$ used in titrating the blank, and calculate the O_2 content of the boiler water.

1 ml. N/200 $Na_2S_2O_3 = 0{\cdot}112$ ml. O_2 per litre, when a 250 ml. sample is used.

A good procedure is outlined by Bairstow, Francis, and Wyatt[6] using the Spekker absorptiometer to measure the starch-iodide complex. Another method, proposed by Arnott, McPheat and Ling,[5] follows the normal Winkler procedure up to the point

where iodine is liberated. Iodine is then extracted with pure CCl_4, if necessary about four times, water is added, followed by an excess of standard $Na_2S_2O_3$. The CCl_4 layer, after shaking, is discarded, and the aqueous layer titrated with standard iodine.

For work of the highest accuracy it is recommended to determine the end point in the Schwartz and Gurney procedure by means of electrometric titration.[1, 8, 16, 20, 22]

A comprehensive review of the whole subject of dissolved oxygen determinations has recently been published.[22]

6. Chlorine

Since the chlorine ion is very stable in water it may be used as an index of concentration occurring in boilers or of dilution of sewage effluent in rivers, etc.

Take 100 ml. of water, add a few drops of phenolphthalein and if a red colour appears neutralize with 0·02N. H_2SO_4. If the water is acid to methyl orange, neutralize with 0·02N. Na_2CO_3. If the sample contains H_2S, acidify with H_2SO_4, boil for a few minutes, cool, neutralize with Na_2CO_3 and restore the original volume of sample. If the sample is highly coloured, decolorize by shaking with washed aluminium hydroxide, filter, wash, and take an aliquot portion of the clarified sample.

Add 1 ml. of 10% potassium chromate as indicator and titrate with standard silver nitrate containing 4·791 gm. $AgNO_3$ per litre to the appearance of a permanent faint red coloration. The number of ml. of silver nitrate used, multiplied by 10, gives parts per million chlorine. ✓

7. Mineral analysis

The methods for determining SiO_2, Fe, Al, Ca, Mg, Mn, S, Na, K, etc., are usually the standard ones discussed previously. Generally large samples must be evaporated to a convenient volume, and the method employed is that used for small quantities on other products.[7, 15, 18]

In water analyses, hypothetical combinations are usually made, in addition to giving the result of each element. The procedure for deciding on these combinations varies slightly with different authorities. The Association of Official Agricultural Chemists,[4] for instance, advises joining NO_2, NO_3, BO_2, and AsO_4 to Na;

I and Br to K; and PO_4 to Ca. Assign the residual basic ions in the following order: NH_4, Li, K, Na, Mg, Ca, Sr, Mn, Fe, and Al, to the residual acid ions in the following order: Cl, SO_4, CO_3, and HCO_3. In case HCO_3 is not present in a sufficient quantity to take up all the Ca, the residual Ca is linked with SiO_2 to form $CaSiO_3$, and Mn, Fe, and Al are calculated to the oxides Mn_3O_4, Fe_2O_3, and Al_2O_3.

On the other hand, the American Public Health Association [3] recommends combining Ca, Mg, NH_4, Na, and K with CO_3, OH, SO_4, NO_3, and Cl. In alkaline waters containing large amounts of silica, the latter is considered to be present as sodium silicate. Otherwise silica is considered as a separate item. Iron and aluminium oxides are considered as separate items.

The determination of water in caustic soda and other alkaline materials has been described by Suter.[19]

The determination of phosphate in boiler water is given under Phosphorus.

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IV. XANTHATES

From time to time most laboratories serving the mining industries are called on to determine xanthates. There are several methods of determining xanthate: Wark prefers titration with standard iodine in which the xanthate is oxidized to dixanthogen,[5] the Great Western Division of the Dow Chemical Company advocates decomposition of the xanthate with standard

acid and titration of the excess with standard alkali,[3] while others measure xanthate by precipitation with a cuprous salt and determination of the excess copper.

1. Acid-base titration

A. *Undecomposed xanthate.* Dissolve 5 gm. of the xanthate sample in cold water and wash into a 250 ml. volumetric flask. Add 20 ml. of a 10% $BaCl_2$ solution, shake, dilute to volume, and allow to settle. Pour the supernatant clear liquid through a dry filter.

The sample should be tested at this stage for the presence of sulphides and thiocarbonates, which are occasionally found in xanthates. To 20 ml. of the filtrate add 5 ml. of 10% lead acetate solution. If the resulting precipitate has a brown or red colour, sulphides or thiocarbonates are present. If the precipitate has a light yellow colour, a trace of them is indicated. If the precipitate is white both substances are absent. If the presence of sulphides or thiocarbonates is indicated by this qualitative test it is advisable to expose the xanthate sample to dry air for a short period to complete the oxidation of these substances before the determination of xanthate is made.

Pipette 25 ml. of the clear filtrate into a 400 ml. beaker, dilute to 250 ml., and add 0·1N. HCl with stirring as follows:

30 ml. for butyl, amyl, and hexyl xanthates
35 ml. for potassium ethyl xanthate and isopropyl xanthate
40 ml. for sodium ethyl xanthate.

Allow the liquid to stand 10 minutes, then add 3 drops methyl red indicator. Titrate the excess of acid back with 0·1N. NaOH until the red colour changes to yellow. Call the alkali consumption A ml. and calculate the results as follows:

$(40 - A) \times 2{\cdot}884 = \%$ sodium ethyl xanthate
$(35 - A) \times 3{\cdot}206 = \%$ potassium ethyl xanthate
$(35 - A) \times 3{\cdot}485 = \%$ potassium isopropyl xanthate
$(30 - A) \times 3{\cdot}766 = \%$ potassium secondary butyl xanthate
$(30 - A) \times 4{\cdot}047 = \%$ potassium amyl xanthate
$(30 - A) \times 4{\cdot}324 = \%$ potassium hexyl xanthate.

B. *Decomposed xanthate.* This procedure, used by the Great Western Division of the Dow Chemical Company,[2, 3] is a modifica-

tion of the acid-base titration method and involves a preliminary extraction of xanthate from associated impurities with acetone. It is applicable to xanthates in all stages of decomposition but not to xanthate in solution.

Weigh 1 gm. sample and transfer to a 250 ml. beaker. Add 50 ml. of acetone and stir thoroughly. Allow to stand 5 minutes and then filter through a small Buchner funnel, using a Whatman No. 5 filter paper, into a 250 ml. suction filter flask. Wash beaker with 4–5 portions of acetone and then wash residue with two more 10 ml. portions of acetone. When filtering add solution slowly to centre of paper to prevent impurities from going through.

Add the same amount of 0·2N. HCl to the filtrate, as given in the previous section A for 0·1N. HCl with undecomposed xanthates of various compositions. Allow the liquid to stand 10 minutes, add 3 drops methyl red indicator, and titrate with 0·2N. NaOH to the appearance of the yellow colour. Using the factors given in the preceding section, (ml. HCl – ml. NaOH) × Factor = % xanthate.

C. *Available xanthate.* The following procedure was given to the writer by the American Cyanamid Company in 1946.[1]

A 5 gm. sample of the finely powdered xanthate is washed into a 250 ml. volumetric flask with acetone and filled to the mark with acetone; 12–15 solid glass beads of about $\frac{1}{8}$ in. diam. are dropped in, the flask stoppered and shaken at frequent intervals for one-half hour. The beads furnish a ball mill action which aids materially in the extraction of the xanthate. A 25 ml. aliquot is then run through a small dry filter paper into 35 ml. of 0·1N. HCl in a 250 ml. beaker. The filter is washed with additional acetone. The beaker containing the filtrate and acid is placed in a water bath at about 50° C. for 15 minutes. The solution is stirred occasionally during this time. It is then removed from the bath, cooled to room temperature, and titrated with 0·1N. NaOH to the methyl red end point.

Available xanthate is calculated as follows:

$$\% \text{ Available xanthate} = \text{Mol. wt. of xanthate} \times \frac{(35 - \text{ml. } 0{\cdot}1\text{N. NaOH})}{50}$$

In this procedure the main precaution is to insure thorough extraction of the xanthate, particularly with the coarsely granular

materials. All xanthates should be ground finely in a mortar before weighing out the sample. A check on the completeness of extraction of a xanthate may be made by analysing a second aliquot from the extraction flask after longer shaking. If the analyses check within about 0·2% the extraction was complete.

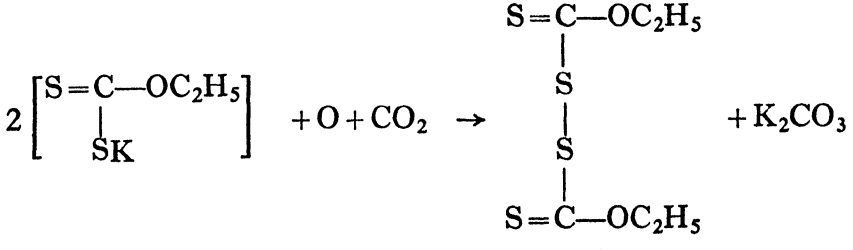
The acetone solution should not be allowed to stand for more than about two hours, and, preferably, the filtration into the standard acid should be finished within an hour from the first contact of the sample with acetone. An acetone solution of a xanthate falls off in grade at the rate of about 2 per cent. in 24 hours.

The molecular weights of the common xanthates in use at present are as follows:

	Mol. Wt.
Sodium ethyl xanthate	144·2
Sodium isopropyl xanthate	158·2
Sodium secondary butyl xanthate	172·2
Sodium amyl xanthate	186·2
Potassium ethyl xanthate	160·3
Potassium isopropyl xanthate	174·3
Potassium normal butyl xanthate	188·3
Potassium secondary butyl xanthate	188·3
Potassium amyl xanthate	202·3
Pentasol amyl xanthate	202·3
Potassium hexyl xanthate	216·3

2. Determination with cuprous salt

A. *Available collecting power.* One of the chief decomposition products of xanthates is di-xanthogen, which is formed as follows:



potassium ethyl xanthate — di-xanthogen

Since di-xanthogens themselves are good collectors, some concentrator staffs prefer to include them in the estimation of available xanthate. Di-xanthogens, unlike xanthates, are soluble in ether, and the loss in weight due to an ether extraction gives the di-xanthogen content.

Weigh 2 gm. of the sample into a small porcelain dish, add 15 ml. ether, and grind thoroughly. Filter through a dried weighed Gooch crucible and wash well with ether, using about 5 ml. for each wash. Dry the residue in an oven at 70° C. for 15 minutes, cool, and weigh. The loss in weight represents di-xanthogen.

Transfer the residue and asbestos to a 400 ml. beaker, dilute to 200 ml. with water, and when all the xanthate is in solution filter through a Whatman No. 31 or 531 paper, washing well with cold water. Precipitate the xanthate with copper as directed under B below. The xanthate found in the ether-insoluble precipitate, plus the di-xanthogen content, gives the total collecting power of the material.

B. *Available xanthate.* Dissolve 2 gm. of material in cold water and filter through Whatman No. 31 or 531 paper, washing well with cold water. If di-xanthogen has been determined by an ether extraction, the ether-insoluble residue may be dissolved in water, filtered, and washed. Make up to a definite volume.

Pipette 10 ml. of a solution containing 1 gm. cuprous chloride in 100 ml. of 25% HCl solution into a 600 ml. beaker containing 200 ml. water. Add from a burette or pipette 10 ml. of the filtered xanthate solution into this and stir thoroughly. Allow to stand for 15 minutes with occasional stirring. One gm. of copper or 1·6 gm. cuprous chloride will be required to precipitate 2·5 gm. of potassium ethyl xanthate.

$$2KC_3H_5OS_2 + Cu_2Cl_2 \rightarrow Cu_2(C_3H_5OS_2)_2 + 2KCl$$

Cupric salts cannot be used as part of the xanthate is then converted to di-xanthogen which is not precipitated by copper.

Filter off the copper xanthate precipitate through a Whatman No. 40 paper into a 250 ml. volumetric flask. Wash several times with cold water and make the flask up to the mark. Pipette off 100 ml. or other suitable quantity of this filtrate and determine the copper remaining in it. At the same time run the copper on the standard cuprous chloride solution.

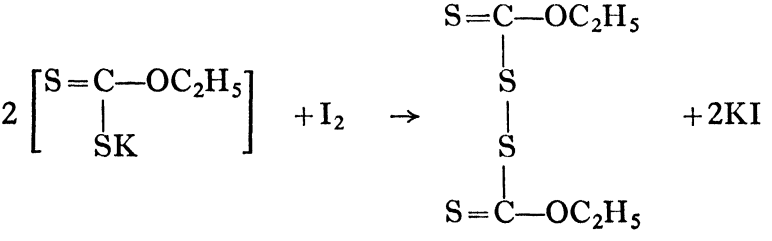
The copper in both standard and unknown solutions may be determined iodimetrically. Place the solutions in 300 ml. Erlenmeyer flasks, make just ammoniacal, and boil off the excess NH_4OH on an asbestos-covered plate. Acidify with about 10 ml. acetic acid and allow to boil for ½ minute. Remove, cool, add KI, and titrate in the usual way with standard $Na_2S_2O_3$ solution, using starch as indicator.

If preferred, copper may be determined electrolytically in the filtrate by adding 10 ml. 1:1 H_2SO_4 and evaporating to strong fumes of SO_3. Cool, add 1–2 ml. HNO_3, hot water, boil, cool, dilute to 150 ml. and electrolyse in the usual manner.

The difference in the copper content before and after the addition of the xanthate is a measure of the xanthate present. 1 gm. Cu = 2·5215 gm. potassium ethyl xanthate or 2·2681 gm. sodium ethyl xanthate.

3. Determination with iodine

Wark[5] recommends titrating 5 ml. of a 0·5 gm. per litre solution of potassium ethyl xanthate with 0·001N. iodine solution. For 20 ml. of the iodine solution he used about 0·25 ml. of 0·2N. KI and 0·2 ml. of 5 gm. per litre starch solution. The blank was then only 0·1 ml. The accuracy is not increased with larger quantities of xanthate and stronger iodine, since the di-xanthogen formed gives an emulsion with a faint bluish tinge which renders the detection of the end point more difficult.



potassium ethyl xanthate — di-xanthogen

In the procedure of Linch[4] a 1 gm. sample of xanthate is dissolved in 50 ml. water. Five ml. of 10% barium chloride solution is added and the solution, after stirring thoroughly, is allowed to stand two hours. About 150 ml. of water are added and the solution is titrated with 0·1N. iodine solution, adding

starch indicator solution near the end point. The colour at the end point may be blue or red, depending on the nature of the xanthate.

In our hands the iodine titration has not given as good results as the acid-base or cuprous salt procedures.

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V. STANDARD ACIDS AND BASES, AND INDICATORS

The preparation of standard solutions of acids and bases is generally performed by first making up approximate 1·0N. solutions, and then from these stock reagents diluting to 0·1N. or other normality as required. The strength of the final solution is preferably checked against a primary standard, e.g. for acids use a weighed quantity of Na_2CO_3 or for bases a weighed amount of potassium acid phthalate. A secondary standard may be used for some work, i.e. an unknown acid may be titrated against a standard solution of alkali whose value has previously been checked against a primary standard.

A very complete survey of the standardization of volumetric solutions has recently been made by the Analytical Chemists' Committee of Imperial Chemical Industries Ltd.[1]

1. Sulphuric acid

To prepare 1·0N. H_2SO_4 from commercial concentrated H_2SO_4 of s.g. 1·84 containing 96% H_2SO_4, take $\frac{49{\cdot}04 \times \frac{100}{1{\cdot}84}}{96}$ or 27·8 ml. and make to 1 litre with water.

The 0·1N. H_2SO_4 solution is made by withdrawing 100 ml. of the 1·0N. solution and diluting to 1 litre.

Standardize the 0·1N. acid by weighing out 0·1000 gm. Na_2CO_3, dissolving in 100 ml. water, adding 2 drops methyl orange, and titrating to the pink end point. 1 ml. of 0·1N. $H_2SO_4 = 0{\cdot}005303$ gm. Na_2CO_3. 0·1000 gm. $Na_2CO_3 = 18{\cdot}85$ ml. of 0·1N. H_2SO_4.

If a reliable secondary standard of NaOH solution is available, the 0·1N. H_2SO_4 may be checked against a measured volume of the standard alkali, using phenolphthalein as indicator.

2. Hydrochloric acid

To prepare 1·0N. HCl from commercial concentrated HCl of s.g. 1·187 containing 37% HCl, take $\dfrac{36{\cdot}46 \times \dfrac{100}{1{\cdot}187}}{37}$ or 83·1 ml. and make to 1 litre with water.

The 0·1N. HCl may be prepared by dilution of 100 ml. of the above normal solution to 1 litre.

Standardize in the same manner as for H_2SO_4 outlined above.

A concentrated C.P. acid usually comes to the laboratory in a bottle giving M, its molecular weight, d, its specific gravity, and its percentage analysis p. To prepare an aqueous solution of desired normality N, a convenient formula is $V = \dfrac{100}{bpd} MN$, where b is the basicity of the acid and V is the number of millilitres of concentrated acid required for one litre of the dilute solution.

3. Sodium hydroxide

Dissolve about 50 gm. of reagent grade NaOH in an equivalent weight of water, and place in large well-stoppered test-tubes kept in an upright position in a cupboard for about two weeks. In such concentrated NaOH solution any Na_2CO_3 or other impurity rapidly settles to the bottom of the test-tube.

To prepare 1·0N. solution withdraw 54 ml. of this 1:1 NaOH solution and make up to 1 litre with boiled water. From this stock solution prepare 0·1 NaOH by dilution of 100 ml. to 1 litre.

Standardize against potassium acid phthalate, a 0·1N. solution

of which contains 20·4220 gm. per litre. The purity, stability, and high molecular weight of potassium acid phthalate make it ideal for a primary standard in alkalimetry. Weigh out 1 gm. potassium acid phthalate, dissolve in CO_2-free water, add 2 drops phenolphthalein, and titrate with the NaOH solution to the first permanent pink. 1 gm. $KHC_8H_4O_4 = 48{\cdot}97$ ml. of 0·1N. NaOH.

$$\text{Normality of NaOH} = \frac{\text{gm. potassium acid phthalate}}{\text{ml. NaOH} \times \frac{204{\cdot}220}{1000}}$$

If an accurate secondary standard of H_2SO_4 or HCl is available, the 0·1N. NaOH may be checked against a measured volume of the standard acid, using phenolphthalein as indicator.

In all these solutions, if the strength is, for instance, 1·023N. and it is desired to adjust it to 1·0N., add 23 ml. water to 1000 ml. of solution. In general, if the solution is stronger than desired, dilute to a definite normality value by the following formula:

$$V_1 = \frac{V_2 \times N_2}{N_1}$$

where V_2 and N_2 represent the volume and normality of stock solution, respectively, and V_1 represents the volume to which the stock solution should be diluted to obtain the desired normality, N_1.

If it is desired to reduce a 96% solution, for example, to 93%, the calculation is as follows: the reduction is 3 in 96 or 3·125%. Take 96·875 gm. of 96% solution and make up to 100 gm. with water. This new solution will contain 96·875 × 96 or 93·00 gm.

To express analytical results on the dry basis, the formula is:

$$\%\text{ ``dry basis''} = \frac{\%\text{ on ``as received'' basis} \times 100}{100 - \%\text{ moisture in the original sample}}$$

% moisture in the original sample is expressed as the percentage of moisture in the moisture-free weight of the sample taken, e.g.

100 gm. of dry copper concentrates running 35% Cu takes up 1% moisture in transit. On the "as received" basis this sample would contain $\frac{100 \times 35}{101}$ or 34·65% copper. On the dry basis it would have $\frac{34{\cdot}65 \times 100}{100-1} = 35{\cdot}00\%$ copper.

4. Indicators

The indicators phenolphthalein, methyl orange, and methyl red serve for the great majority of determinations in acidimetry-alkalimetry in industrial laboratories. The preparation and properties of these indicators are summarized below:

	Colour Change		Transition range *p*H	Preparation
	acid	alkaline		
Phenolphthalein	colourless	red	8·2–10·0	1 gm./litre C_2H_5OH
Methyl orange	red	yellow	3·1–4·4	1 gm./litre H_2O
Methyl red	red	yellow	4·2–6·3	0·2 gm./litre H_2O

When using methyl orange as an indicator in acid–base titrations it is advisable to have as a reference colour a flask or beaker containing the same quantity of water as the titrating vessel, together with a few drops of acid or alkali and the indicator. This will enable one to more readily distinguish the colour change of methyl orange.

In Table 7 are illustrated the suitability of phenolphthalein, methyl orange, and methyl red in acid–base titrations for a number of reagents. There are still a number of gaps in our knowledge of the behaviour of these indicators under various conditions, in spite of the information given by standard references,[3, 4, 5] and it would appear to be a useful field for investigation.

A recent booklet[2] gives a good outline of the theory and many useful procedures on non-aqueous acid-base titrations.

TABLE 7

Suitability of common acid–base indicators for various reagents

	Phenol-phthalein	Methyl Orange	Methyl Red
Acetic acid	Yes	No	—
Alkali aluminates	Yes	—	—
Alkali silicates	Yes	—	—
Ammonia	No	Yes	Yes
Arsenic and Phosphoric acid: monobasic	No	Yes	—
Arsenic and Phosphoric acid: dibasic, soln. sat. with NaCl	Yes	—	—
Arsenic and Phosphoric acid: tribasic	Yes	—	—
Bases bound to: Boric acid	—	Yes	Yes
Bases bound to: Carbonic acid	—	Yes	—
Bases bound to: Hydrogen sulphide	—	Yes	Yes
Bases bound to: Phosphoric acid (primary salt)	—	Yes	—
Benzoic acid	Yes	No	—
Boric acid + polyvalent alcohols	Yes	No	No
Carbonic acid: free, in aqueous solution	Yes	No	—
Carbonic acid: as carbonate	—	Yes	—
Carbonic acid: as bicarbonate	—	Yes	—
Chromic acid, against strong base	Yes	—	—
Formic acid	Yes	No	—
Hydrocyanic acid	—	No	Yes
Hydrofluoric acid	Yes	No	—
Oxalic acid	Yes	No	—
Oxidizing acids like strong HNO_3	—	Yes	No
Phthalic acid	Yes	No	—
Strong acids	Yes	Yes	Yes
Strong amine bases	—	Yes	—
Strong bases	Yes	Yes	Yes
Sulphurous acid: monobasic	—	Yes	—
Sulphurous acid: dibasic	Yes	—	—
Weak organic bases	—	—	Yes

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