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It is necessary in a volume of this kind to draw heavily on the work of others, not only from publications but from unpublished data.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

CONTENTS

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