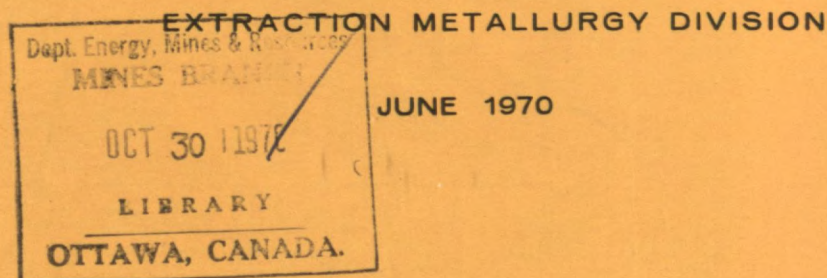CANADA

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OTTAWA

METHODS FOR THE ANALYSIS OF ILMENITE, TITANIUM-BEARING SLAGS AND OTHER ELECTRIC FURNACE SLAGS

PART III: A REVIEW AND COMMENTS ON SOME TYPICAL METHODS FOR THE SEPARATION AND DETERMINATION OF ALUMINUM

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by

A. Hitchen*

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SUMMARY

A review of some typical methods for the separation and determination of aluminum in a variety of materials is presented. A discussion is given of the nature of interferences and sources of error likely to be encountered in the application of several of the methods. For application to the analysis of ilmenite and titanium-bearing slags, the simplest and most attractive methods appear to be those which involve an extraction step followed by a chelometric titration using EDTA or DCYTA.

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MÉTHODES D'ANALYSE DE L'ILMÉNITE, DES LAITIERS TITANIFÈRES ET D'AUTRES LAITIERS PROVENANT DE FOURS ÉLECTRIQUES

PARTIE III: REVUE ET COMMENTAIRES SUR QUELQUES MÉTHODES TYPES DE SÉPARATION ET DE TITRAGE DE L'ALUMINIUM

par

A. Hitchen*

RÉSUMÉ

L'auteur passe en revue quelques méthodes types utilisées pour séparer l'aluminium et en déterminer la quantité contenue dans divers matériaux. Il examine la nature des interférences et les causes d'erreurs susceptibles de se produire lors de l'application de plusieurs de ces méthodes. Pour l'analyse de l'ilménite et des laitiers titanifères, les méthodes qui paraissent les plus simples et les plus pratiques sont celles qui comportent une phase d'extraction suivie d'un titrage chélométrique à l'aide d'EDTA ou de DCYTA.

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INTRODUCTION

As part of a research program concerned with the smelting of ilmenite ores to produce a titania-bearing slag suitable for pigment purposes and metallic iron, it was necessary to determine alumina in the slags and ores, both for thermal balance calculations and because the slag composition has a direct effect on the metal-slag equilibrium. The materials to be analyzed for this program were expected to have an alumina content in the range 0.5 to 10%. In addition to the alumina, the slags and ores were expected to contain different percentages of silica (1 to 5%), iron (5 to 50%), titanium (5 to 50%), calcium (0.1 to 2.0%), magnesium (1 to 10%) and smaller amounts (<0.5) of vanadium, chromium, manganese and phosphate.

A survey of the literature revealed surprisingly few methods which related specifically to the determination of aluminum in ilmenite ores and slags. It must be assumed, therefore, that it is being determined in this type of sample by methods that have been applied to other materials - e.g., iron ores, iron slags and alloys - after modification to take care of the unusually high titanium content.

This report reviews and describes some typical methods that have been applied to the determination of aluminum in various materials. The application of these methods has been mainly confined to materials of low titanium content, such as cements, clays, and silicate rocks, and, in the case of materials of high iron content,

to iron ores, steels, and alloys. Applications to ilmenite were noted in only two instances. No attempt has been made to give a comprehensive review of all these methods, because of the number involved and because many of the methods are obviously not applicable.

REVIEWS OF METHODS

A number of surveys of methods for aluminum have appeared [1,2], and standard texts discuss the most commonly used procedures [3,4,5]. Chalmers [6] has reviewed many methods for its separation and determination and describes briefly a few selected gravimetric and titrimetric methods. Reviews of methods for use with a wide variety of materials may be found each year in the Annual Reviews section of "Analytical Chemistry". Maxwell [7] describes methods used in rock and mineral analysis. Blair et al. [8] have reviewed and discussed previously published methods for the separation of aluminum from iron and have classified them according to the headings: precipitation, solvent extraction, chromatography, and mercury cathode electrolysis.

Despite the many methods that exist, aluminum remains one of the most difficult elements to determine accurately when present in admixture with other ions. The difficulty arises in part because of the lack of specific or reasonably selective reagents for its separation and/or determination, but essentially it is a consequence of the similar chemical behaviour of aluminum and those elements with which it is usually associated. Consequently, a preliminary separation of aluminum from interfering elements is invariably required.

METHODS FOR THE SEPARATION OF ALUMINUM

1. Mercury Cathode Electrolysis

In order to apply suitable separation procedures or techniques, some knowledge of the nature of the sample and the kind and amount of potentially interfering elements is desirable. For example, aluminum may be separated from many elements, such as iron, copper, zinc, lead, nickel, cobalt and cadmium (as well as a host of others), by electrolysis in acid solution with a mercury cathode [9,10]. The aluminum is not deposited and may then be precipitated from the electrolyte by ammonia, filtered off, and ignited to the oxide. Unfortunately, elements such as titanium, zirconium, vanadium and uranium are not deposited on the mercury cathode either, and will seriously interfere if an ammonium hydroxide precipitation is subsequently contemplated. Moreover, certain other elements - for example, chromium, manganese or molybdenum - may not be removed completely at the mercury cathode unless careful attention is paid to ensure optimum conditions for their deposition. Thus, the mercury cathode provides a valuable group separation from many interfering elements but involves uncertainties. Blair et al. [8] believed that mercury cathode electrolysis was the most suitable technique for analysis of iron-based materials, as it had the advantages of introducing no foreign elements and keeping reagent additions to a minimum.

2. Precipitation Methods

Separation of aluminum from elements such as iron, titanium and zirconium may be effected by precipitating these latter elements with sodium hydroxide or sodium peroxide [5]. The presence of significant amounts of magnesium, however, may cause some of the aluminum to be precipitated also. In any case, double or even triple precipitations may be necessary to recover all the aluminum, depending on the relative amounts of the elements present. In addition, zinc, vanadate, chromate, or molybdate will not be precipitated and will accompany the aluminum in the filtrate. Other elements - e.g., manganese, copper and nickel - divide and may be found partly in the filtrate and partly in the precipitate, depending on the amounts present and the conditions of precipitation. The elements zinc, copper, manganese and nickel, if present in the filtrate from the sodium hydroxide precipitation, cannot be separated from the aluminum after acidification of the filtrate and precipitation of the aluminum with ammonia, because, at the pH required for re-solution of their hydrous oxides, aluminum is appreciably soluble.

Cupferron has been used to separate elements, such as titanium, iron, zirconium and vanadium, from aluminum [5]. This reagent is especially useful for the separation of small amounts of the above-mentioned elements from large amounts of aluminum, as in clays, bauxite, or metallic aluminum. Murphy, Clabaugh and

Gilchrist [11], however, use cupferron to separate macro amounts, i.e. 0.1 to 0.5 gram, of titanium and/or zirconium from small amounts of aluminum in the analysis of barium titanate-barium zirconate ceramic dielectrics. These authors observed that significant amounts of aluminum, i.e. about 1 milligram, are coprecipitated with the titanium and zirconium cupferrates and that a double precipitation of the titanium and zirconium with cupferron is necessary to recover the aluminum. In order to improve the separation, they precipitate the titanium and zirconium from a warm (60°) solution by adding 90% of the calculated required quantity of cupferron before cooling and adding the remaining cupferron plus a little in excess. A denser precipitate results by this technique and less aluminum is coprecipitated. These authors also use cupferron to separate and determine the aluminum in the same material after the removal of the titanium and zirconium. The aluminum cupferrate is filtered off and ignited to Al_2O_3.

Cupferron has also been used by Codell and Norwitz [12] to separate small amounts of aluminum from titanium, iron, vanadium and tungsten in titanium alloys prior to determining the aluminum colorimetrically with aluminon (reagent).

3. Ion Exchange Methods

Ion exchange procedures are very useful as a means of separating aluminum from various elements. Samuelson [13] refers

to many methods for the separation or determination of aluminum in various minerals, alloys, and other products. Cation and anion exchange resins are both employed, depending on the nature of the sample and its particular composition. Lewis, Nardozzi and Melnick [14] use Dowex 1x8 anion exchange resin to absorb impurities such as iron, titanium and manganese from 9 to 10 M HCl solutions of iron ores, while calcium, magnesium and aluminum pass through in the effluent. The calcium, magnesium and aluminum are then determined by EDTA titration.

4. Solvent Extraction Methods

Aluminum has been separated from various elements by numerous methods using solvent extraction techniques [15,16,17]. The element extracted may be aluminum or it may be the contaminant(s). This technique has often been combined with a spectrophotometric finish, e.g., using 8-hydroxyquinoline [18].

Cupferron and diethyldithiocarbamate are organic reagents commonly used for the extraction of elements interfering in the determination of aluminum or other desired elements, e.g., calcium and magnesium. Other organic reagents have also been used; e.g., aluminum has been extracted with thenoyltrifluoroacetone in benzene to separate it from Fe, Cu, Sr, Y, Ca, and Zn [19].

METHODS FOR THE DETERMINATION OF ALUMINUM

1. Gravimetric Methods

Hillebrand et al., in their classic work on mineral and rock analysis [5], described methods for the decomposition of rocks and minerals, as well as some methods for the separation of aluminum from interfering elements that may be encountered. These included detailed gravimetric methods in which aluminum is precipitated with ammonium hydroxide or ammonium phosphate, and they discussed the many sources of errors that may be expected when these methods are used.

Precipitation with ammonia is so subject to contamination from other elements that there is little to recommend it for the determination of aluminum.

Precipitation with phosphate is still widely used, especially in the analysis of iron ores, and is a relatively rapid procedure in the hands of skilled analysts.

In the absence of interfering ions, the gravimetric basic succinate method that was proposed by Willard and Tang [20,21] is perhaps one of the best. In this method, the aluminum is precipitated from homogeneous solution in the presence of succinic acid, using urea as the hydrolytic reagent. It effectively separates aluminum from calcium, magnesium, barium, manganese, cadmium, cobalt, nickel and copper in a single precipitation, and from zinc or iron by a double precipitation. Phosphate prevents the complete

precipitation of aluminum. Titanium and zirconium, on the other hand, are precipitated under the same conditions as for aluminum and therefore will interfere. The basic benzoate method [3,22] is similar except that precipitation is brought about by the careful addition of ammonia, rather than by urea.

Oxine (8-hydroxyquinoline) has been widely investigated and used for the separation and determination of aluminum by gravimetric, titrimetric and colorimetric procedures. A preliminary separation of the aluminum from other elements, which may be made by mercury cathode electrolysis, by cupferron or by acctylacetone [17] or a combination of these methods, is usually necessary. The precipitate of aluminum oxinate finally obtained may be dried at 150° and weighed as $Al(C_9H_6ON)$ or ignited to Al_2O_3. It may also be dissolved in dilute hydrochloric acid solution and titrated bromatometrically [23,24,25] or it can be extracted with chloroform and determined spectrophotometrically [26,27]

2. Colorimetric and Fluorimetric Methods

Sandell in his book [28] describes a number of methods for the extraction and subsequent spectrophotometric determination of aluminum and discusses in detail many of the precautions that are required to avoid interference from other elements. Tikhonov [29] has reviewed photometric methods including some that use the newer reagents such as chromeazurol S, xylenol orange and methyl thymol blue. Of the solvent extraction-spectrophotometric methods,

the most commonly used one is that which employs 8-hydroxyquinoline

(oxine). This reagent has been investigated by Gentry and

Sherrington [18], who have established the optimum conditions

for the extraction of the aluminum. The extraction has also

been used to separate aluminum from nickel, iron and titanium [30].

The fluorimetric determination of aluminum after extraction of

its 8-hydroxyquinolate with chloroform has been described by

Tullo, Stringer and Harrison [31]. A similar method has been

employed to determine aluminum in uranium ores, solutions and

uranium products [32]. Barkley [33] describes a combined

spectrophotometric-fluorimetric method for the determination of

aluminum in phosphate ores and products from wet-process

phosphoric acid manufacture. In this method, small amounts, e.g., 0 to

10 μg, of Al are determined fluorimetrically, while larger amounts, e.g.,

10 to 100 μg, can be determined spectrophotometrically on the same

solution if the lower estimate of range has been exceeded, thus

avoiding the necessity to repeat the analysis.

Many other elements react with 8-hydroxyquinoline

under the conditions employed for the extraction of aluminum,

unless complexing or masking reagents such as cyanide, hydrogen

peroxide or EDTA are added. Some degree of selectivity is also

obtained by adjusting the pH of the solution.

Riley and his co-workers, for example, described

methods in which aluminum is extracted as the 8-hydroxyquinolate

into chloroform from solutions of rock samples. The method described in their first paper [34] fails if appreciable amounts of copper, cobalt and zirconium are present and, in a second paper [35], the method is reportedly made specific for aluminum by extracting the interferences with 8-hydroxyquinaldine prior to extracting the aluminum. In addition, quinalizarin-sulphonic acid is added to complex zirconium and ion exchange is employed to remove uranium. However, Dagnall, West and Young [36] subsequently demonstrated that 8-hydroxyquinaldine extracts considerable amounts of aluminum and hence this particular sequence does not provide reliable results.

Other colorimetric methods for the determination of aluminum are based on the formation of a strongly coloured lake with a suitable dye. The more common reagents used for this purpose are ammonium aurintricarboxylate, eriochromecyanin R, pontachrome blue black R, alizarin Red S, and hematoxylin, but there are many others [28]. These lake reaction methods are not ideal and suffer from interference by a great many other elements and anions. Close control of the pH, temperature and other conditions is frequently necessary for reproducible results. The advantage of these methods is in their great sensitivity and rapidity. In general, however, the rapidity is negated by the necessity for preliminary separations of the aluminum from interferences.

Corbett and Guerin [37] have made a study of several colorimetric reagents used for determining aluminum in iron and steel. They examined five reagents: alizarin Red S calcium, arsenazo, eriochrome cyanine-R, 8-hydroxyquinoline, and stilbazo. Interfering elements, such as iron, titanium, vanadium and nickel, are removed by a preliminary mercury cathode electrolysis and cupferron-chloroform extraction. Traces of elements such as manganese and chromium remain in the electrolyte after the mercury cathode electrolysis and will not be removed by cupferron-chloroform extraction, but these elements do not interfere at the levels expected. The only other elements likely to be present in irons and steels, and which are not removed by the separation procedures used, are magnesium, beryllium, and phosphorus. Of these latter elements, magnesium and phosphorus will not interfere in any of the methods at the levels expected; beryllium will not interfere in the oxine-extraction method, but it may interfere slightly if stilbazo or alizarin Red S - calcium is used, or seriously if the arsenazo or eriochrome cyanine-R methods are used, depending on the level of beryllium that is present. These authors recommended the use of arsenazo or alizarin Red S calcium reagent for the determination of aluminum in iron and steel, on the basis of sensitivity and stability of the reagents.

Chromeazurol S is one of the newer reagents that have been applied to the determination of aluminum [38,39,40]. So far it has not been widely used but it appears to be superior to many of the older reagents, e.g., aluminon, eriochromecyanine-R, or stilbazo, with respect to sensitivity, stability, reproducibility of results and tolerance to other elements. In addition, it has been used in a differential spectrophotometric method for the determination of large amounts of aluminum [41]. Its use is deserving of more attention, and its application to the analysis of actual production materials should be studied in more detail.

Xylenol orange and methyl thymol blue are two new reagents that have been recently suggested for the determination of aluminum [42-45] and may prove to be very useful in the future, especially if selectivity can be improved by employing masking agents such as ascorbic acid, thiourea, cyanides, thioglycolic acid, and EDTA or other chelating reagents. It is in the latter approach, as well as in the development of more specific reagents, that the best possibility for the improvement of colorimetric methods for aluminum lies.

3. Polarographic Methods

Direct polarographic methods have been described for the determination of aluminum in alloys, clays, cements, and other materials [46,47]. The half-wave reduction potential of aluminum

is -1.7 V. vs sce in most aqueous electrolytes, which is so close to the discharge potentials of sodium, potassium and barium ions that large concentrations of salts of these ions cannot be present or used as supporting electrolytes and hence lithium or tetraalkyl ammonium salts must be used instead. In addition, hydrogen ion is reduced prior to aluminum and large concentrations of hydrogen ion, i.e. low pH, obliterate the aluminum wave. On the other hand, aluminum begins to hydrolyze at pH levels above 4, so it is evident that critical control of the pH is necessary if aluminum is to be determined successfully. The pH of the unbuffered solutions must, in fact, be adjusted carefully to between 3.5 and 3.8 with a precision of $\pm$ 0.1 pH unit or better. Buffers cannot be used to control the pH, because weak acids will still produce a large hydrogen wave.

As a result of the foregoing difficulties, direct polarographic methods have not been attractive and other methods have been sought. Willard and Dean [48], in 1950, proposed the first indirect method for aluminum, which was based on the complexation of aluminum ion with di-o-hydroxyazo dyes. When excess dye is present in the solution containing aluminum ion, two polarographic waves are observed, the first due to the excess unreacted dye and the second to the reduction of the portion of the dye that is complexed by aluminum. The diffusion current of the aluminum-dye complex is proportional to the concentration of aluminum

(provided that an excess of dye is present). The advantage of this method is the fact that the half-wave potential of the aluminum-dye complex is -0.52 V. vs sce at pH 4.5 and is well in advance of the discharge potentials of hydrogen, sodium, potassium, and many other elements. However, the height of the second wave, i.e. the aluminum-dye complex, is greatly dependent on the pH. The wave height changes much more slowly between pH 4 and 5 - Willard and Dean recommend a pH of 4.6 $\pm$ 0.1, which they obtained by means of an acetate buffer.

The method, while convenient for some purposes, is subject to interference by many common ions associated with aluminum. For example, chloride, sulphate, calcium and potassium interfere because they precipitate the dye. Fluoride and citrate interfere because they complex the aluminum more strongly than the dye. Titanium, vanadium, copper and iron also seriously interfere. Many of these interfering elements can be removed by mercury cathode electrolysis, but, as has been mentioned previously, not titanium, vanadium, calcium, and many others.

Another disadvantage of the Willard and Dean method, and one that is frequently overlooked, is that an accurate estimate of the amount of aluminum present must be known beforehand in order to choose the proper amount of dye to be added, or conversely, to choose the correct size of sample aliquot to be

taken for a fixed amount of dye. Sufficient dye must be used to complex all the aluminum that is present; but only a slight excess of dye must be added, otherwise the first wave which is due to the unreacted dye will be so large as to make a small second wave due to the aluminum-dye complex difficult to measure. Increasing the sensitivity of the polarograph to magnify the aluminum-dye wave also magnifies the first wave, and, if the latter is too great, the compensating current or zero adjust control of the polarograph may be unable to compensate for it sufficiently to get the aluminum wave on the chart or scale at the sensitivity required to get a measurable aluminum wave. This disadvantage would disappear if a suitable dye could be found for which the aluminum-dye complex is reduced first. The disadvantage could perhaps also be overcome if derivative pulse or square-wave polarographic techniques were used. Unfortunately, these latter instruments are highly complex and expensive and, in addition, at least in their present stage of development, are subject to breakdowns so frequently that their use requires the services of a sophisticated instrument-maintenance group.

The Willard and Dean method can perhaps best be applied to routine types of material in which the aluminum content is known not to vary to any great extent, but for research projects in which the aluminum content may vary to an unknown degree this approach is simply not practicable.

Other methods based on the principles proposed by Willard and Dean have been described [49,50] and most of the remarks made pertaining to the Willard and Dean method can also be applied to them.

Rooney, for example, has described a method for the determination of trace amounts of aluminum in cast irons [49]. A preliminary separation of interfering elements is made by electrodeposition at the mercury cathode and/or extraction with diethyldithiocarbamate into chloroform. The aluminum is precipitated and extracted as cupferrate at pH 4.5 and is finally determined polarographically by the method of Willard and Dean, using a cathode-ray polarograph.

One of the attractive features of polarographic procedures is the fact that they are usually more tolerant to many contaminant metals. However, in the procedures described above, this advantage diminishes if the contaminant metal also forms complexes with the same reagent as aluminum, e.g., Solochrome violet R.S., or if it is reduced at the same potential as the aluminum-dye complex. In this respect, therefore, the polarographic methods based on an aluminum-dye complex are sometimes subject to the same interferences as the colorimetric methods based on the same dyes and there may often be no advantage of one method over the other. The preliminary methods of separation are common to either finish and once the aluminum

is obtained free from interfering elements the choice of finish, i.e. colorimetric or polarographic, is often based on personal preference rather than any inherent advantage. The polarographic method for aluminum requires more complex instrumentation and, what is really more important, highly skilled and experienced analysts to interpret the polarograms.

4. Titrimetric Methods

Many titrimetric methods have been proposed for the determination of aluminum [51,59]. As in the case of most other methods, separations are invariably required. In one widely used method, aluminum is determined by adjusting an aluminate solution to a fixed pH (usually 10.0); adding fluoride to complex the aluminum; and titrating the hydroxyl ion which is liberated in an amount equivalent to the aluminum present, using a standard acid solution. This reaction has been the basis of a number of procedures [52,53,55,59] and has been reviewed by Watts and Utley [59]. It can tolerate more impurities than nearly any other procedure but it is not satisfactory in the presence of titanium, zirconium, nickel or manganese and is not recommended for iron ores [58]. Titration methods have also been proposed in which the aluminum is precipitated by oxine and either the excess oxine in solution [60] or the oxine in the precipitate [61-63] is titrated. One example is a proposed ASTM method for aluminum in high-alloy steels,

which calls for removal of interfering elements with a mercury cathode electrolysis, extraction of cupferrates, and a sodium hydroxide separation. The aluminum is subsequently precipitated with oxine and titrated [64].

The introduction of EDTA to analytical chemistry by Schwarzenbach [65,66] opened up a whole new field of interest. Chelometric titrations with EDTA were soon applied to the determination of many metals and among them, naturally, was aluminum. A review of various methods for the determination of aluminum with EDTA has been presented by Flaschka, Barnard and Broad [67] and West [68]. Books have been written on the analytical uses of EDTA by Welcher [69], Flaschka [70] and Schwarzenbach [71] and they describe in some detail several of the methods used to determine aluminum in various materials.

Pribil [72] has reviewed some of the methods available for the complexometric determination of aluminum and has discussed the problems and difficulties involved. Because of the slow reaction of aluminum with EDTA under the conditions of the procedure, it is the usual practice to add an excess of EDTA and back-titrate with iron [73,74], zinc [75,76], manganese [77], thorium [78], or aluminum [79]. Cimerman, Alon and Mashall [80] describe procedures for the titrimetric determination of aluminum using EDTA. Amounts of aluminum from 5 to 15 mg were determined by a back-titration procedure after

removing the interference of other elements such as iron, copper, titanium, magnesium, manganese, calcium and phosphate by complexing agents or ion exchange. Khalifa and Ismail, in the only reference related specifically to the analysis of ilmenite [81], described methods for the determination of aluminum, iron, titanium, chromium, vanadium and copper, using a back-titration of EDTA with mercury [11]. The end-points were determined potentiometrically. In another paper [82] the same authors describe methods for the estimation of aluminum and tervalent vanadium in synthetic mixtures of various elements, in which they again employed a potentiometric method for the back-titration of the EDTA. In both of the above papers Khalifa and Ismail determined the sum of aluminum and other admixed elements by EDTA. The other elements were determined separately, e.g., zirconium by cupferron, iron by permanganate titration, copper by iodometric titration or electrolysis, chromate by titration with ferrous ion, vanadium by permanganate titration, and titanium by titration with EDTA after a sodium hydroxide separation. The aluminum was then calculated by difference. The inherent difficulty with this procedure is that the result for aluminum depends on the accuracy with which the other elements can be determined and if several of these elements are present the summation of errors involved may be

considerable. Moreover, the procedure is not attractive if aluminum is the only element desired, because of the necessity to determine the other elements as well.

Pribil and Vesely [83,84] proposed methods, based on EDTA titration, for the determination of iron, aluminum and titanium when these elements are present together in synthetic solutions. Titanium is precipitated by sodium hydroxide after using triethanolamine to complex the iron and aluminum. The sum of iron and aluminum is determined in the filtrate at pH 5 to 5.5 by back-titrating an excess of standard EDTA solution with a standard solution of lead nitrate. Aluminum is then determined by titration of the EDTA liberated from the aluminum-EDTA complex after addition of fluoride. The liberated EDTA is titrated at pH 5 to 5.5, using standard lead nitrate solution. Unfortunately, in neither of the above papers do Pribil and Vesely deal with the problem of zirconium, vanadium, or chromium. In applying this procedure to rock and mineral samples, it was found by Kiss [85] that results for aluminum showed significant scatter, which he attributed to salt effects.

Nestoridis [86] has described rapid methods for the analysis of Portland cement. The sum of aluminum and titanium (and presumably iron) is complexed by addition of excess EDTA, and the excess is back-titrated with a standard mixed copper-zinc sulphate solution at pH 5 using a mixed xylenol orange-PAN

indicator. The sum of aluminum and titanium is then determined by titration of the EDTA liberated on addition of fluoride. Titanium is determined colorimetrically in a separate aliquot and aluminum is calculated by difference. This method is similar, in some respects, to that of Evans [87] (see later) and it cannot be used for the analysis of ilmenite ores or slags for what are essentially the same reasons, i.e. the iron and titanium contents are too high. Although their effect was not investigated, zirconium, chromium and vanadium may be expected to interfere. In a more recent paper [88], Nestoridis accomplishes a sequential determination of titanium and aluminum in which the EDTA released from the titanium complex by the addition of phosphate is first titrated, after which the EDTA released from the aluminum complex by the addition of fluoride is also titrated. In this procedure, manganese interferes if amounts of it greater than 5 mg are present. Zirconium, if present, is determined as aluminum, and corrections have to be made after determining the zirconium separately. Moreover, current test work, to be described in a later report (Part IV) of this series, indicates that the fluoride used to release the EDTA from the aluminum complex may interfere if iron is also present, and that phosphate causes slightly low results for aluminum, possibly because of the formation of aluminum phosphate at pH 5 to 6.

An important advance in the chelometric titration of aluminum was made by Pribil and Vesely [89] with the observation

that 1,2-diaminocyclohexanetetraacetic acid (DCYTA), also known

as (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA), reacts

with aluminum quantitatively at ordinary temperatures, even in

the presence of high concentrations of sodium or potassium

salts. These authors used the reagent to determine the sum of

iron and aluminum in synthetic solutions. An excess of DCYTA

was added to a weakly acid solution (pH not stated) and this excess

was back-titrated at pH 5 to 5.5 with standard lead nitrate

solution. Aluminum is then determined by titration, at pH 5 to 5.5,

of the DCYTA liberated from the aluminum-DCYTA complex on

addition of fluoride, using 0.05 M lead nitrate solution as

titrant. However, experiments in Part IV of this series by the

present author have shown that this procedure gives low results

for aluminum and high results for iron. Evans [87] (see later)

has made a similar observation but does not give evidence to

substantiate his statement. In a later paper, Pribil and Vesely [90]

employed DCYTA to determine aluminum and tervalent chromium in

the presence of chromate in synthetic solutions containing only

these three ions. In a further extension of their research,

they describe procedures for the determination of calcium,

magnesium, iron, aluminum, and titanium in iron ores and slags,

using chelating reagents such as EDTA, EGTA and DCYTA [91] in

which aluminum was determined essentially as before, i.e. titration

of DCYTA liberated after addition of fluoride.

Burke and Davis [92] described a method for the determination of aluminum in a variety of alloys, in which excess DCYTA is back-titrated at pH 5-6 with a standard zinc solution, using xylenol orange as the indicator. The bulk of the interfering elements are removed at the mercury cathode; manganese by treatment with sodium chlorate; and titanium or zirconium by extraction with tri-n-octylphosphine oxide (TOPO). They did not investigate the extraction of large amounts of titanium or zirconium with TOPO and confined their work to amounts of these elements equivalent to or less than the amount of aluminum, i.e. about 20 mg.

Pritchard [93] has described a method to determine aluminum in silicate materials after fusion of the sample with sodium hydroxide and extraction of the melt with hydrochloric acid. An aliquot of the sample solution is then treated with a solution of sodium hydroxide, and an excess of standard DCYTA solution is added. The mixture is digested on a steam bath for 1 hour, then filtered and washed with a dilute solution of sodium hydroxide. The excess DCYTA in the filtrate is titrated at pH 5.5, using standard zinc solution and xylenol orange as the indicator. In the presence of much magnesium (>1 mg), care was required to avoid adsorption of aluminum on the magnesium hydroxide, and in experiments with synthetic solutions Pritchard restricted the amount of magnesium to 2 mg. In addition, under

the conditions of the procedure DCYTA decomposed slightly, and allowances had to be made for this in blank determinations. Pritchard claims that addition of DCYTA to an alkaline solution of the sample enhances the separation of aluminum from iron, titanium, magnesium, calcium and manganese but he does not give results of comparison tests. It should be noted, also, that in his samples, with the exception of silica, the amount of other elements present was considerably less than the amount of aluminum. He did not deal with the problem of larger amounts (> 4 mg) of iron or titanium, etc., and did not investigate the effect of vanadium, chromium, or zirconium or other elements.

Kiss [85] proposed a method for the determination of aluminum in rocks and minerals after extraction of iron and titanium with cupferron and chloroform. The aluminum is complexed with excess DCYTA in a nitric acid-perchloric acid solution at pH 3.5 and the excess DCYTA is back-titrated at pH 5.0 to 5.5, using a standard lead nitrate solution and xylenol orange as indicator. The cupferron remaining in the aqueous solution is destroyed before the titration of aluminum, and corrections have to be made for manganese and other co-titrated elements.

Evans [87] proposed a rapid method for the complexometric determination of aluminum in silicate and other rock materials. The iron, aluminum and titanium are complexed by the addition of excess DCYTA and the excess is back-titrated at pH 3.5 to 3.7

with a copper solution, using o-dianisidine-N N N'N'-tetraacetic acid as a metallofluorescent indicator. The iron is determined in a similar manner after masking the aluminum and titanium with fluoride. The titanium is determined spectrophotometrically and the aluminum is calculated by difference. Evans' method is suitable for the analysis of rock where the amount of iron and titanium in the sample does not usually exceed the amount of aluminum. This is not true for ilmenite ores and slags, however, since the amount of iron and titanium substantially exceeds the amount of aluminum, resulting in the possibility of a very large error in calculating the aluminum value by difference.

In any of the methods that have been reviewed, extreme care is required when determining micro quantities of aluminum to avoid introduction of trace amounts of aluminum from glassware and apparatus, and pure silica, polythene or Teflon should be used wherever possible. Barkley [33] showed that glassware could contribute as much as 5 mg of aluminum under certain conditions. Oelschlager [94] has demonstrated that small amounts of aluminum are removed from glassware in contact with strong sodium hydroxide solutions, and work by the present author, which is reported in Part IV of this series, confirms the need to use Teflon apparatus wherever possible. Furthermore, in practice, air-borne contamination of the solutions with microgram amounts of iron and other elements is very difficult to prevent, especially in laboratories in which other analyses are being performed.

It is the reproducibility of the blank, rather than its magnitude, that imposes the lower limit to the range of aluminum that can be determined. If a high pick-up of aluminum is obtained, however, it is unlikely that good reproducibility will be achieved. These remarks, of course, assume that the blank is due only to aluminum from various sources and not to the presence of adventitious or extrinsic contaminants that escape removal by the separation steps.

CONCLUSIONS

A review has been presented, in this report, of some typical methods for the determination of aluminum in a wide variety of materials with a view to their applicability to the analysis of ilmenite ores and slags.

A critical examination reveals that none of them is really suitable for this purpose. An evaluation of the various separations and determinative procedures led to the conclusion that isolation of aluminum from interfering elements would be needed, in nearly all cases, for the proposed application. It appeared, then, that the simplest and best approach would consist of a sodium hydroxide separation followed by a solvent extraction of the remaining interferences and a titration of the aluminum with a chelating reagent such as EDTA or DCYTA.

The investigation and development of the analytical procedure for the determination of aluminum in ilmenite ores and slags are described in Part IV of this series, now in preparation.

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