CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH

OTTAWA

METHODS FOR THE ANALYSIS OF ILMENITE, TITANIUM-BEARING SLAGS AND OTHER ELECTRIC FURNACE SLAGS
PART IV A. THE COMPLEXOMETRIC DETERMINATION OF ALUMINUM IN ILMENITE, TITANIFEROUS SLAGS, AND IRON ORES

A. HITCHEN

EXTRACTION METALLURGY DIVISION

MARCH 1973

Mines Branch Technical Bulletin 168

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

PART IV A. THE COMPLEXOMETRIC DETERMINATION OF
ALUMINUM IN ILMENITE, TITANIFEROUS SLAGS, AND IRON ORES

by

A. Hitchen*

SUMMARY

A procedure is described for the accurate and precise
determination of aluminum in ilmenite, titaniferous slags,
and iron ores. After fusion of the sample with sodium peroxide,
triple precipitations with sodium hydroxide-peroxide solutions
are performed to remove the bulk of interfering elements such
as iron and titanium. The interferences remaining in the filtrate
and accompanying the aluminum are removed by solvent extraction
in chloroform with sodium diethyldithiocarbamate at pH 2.
The aluminum in the aqueous layer is determined by means of
a back-titration of an excess of 1,2-cyclohexylenedinitrilo
tetraacetic acid (DCYTA) with standard zinc solutions at pH 5
to 5.5 and xylenol orange as the indicator.

*Chemist, Chemical Analysis Section,
 Extraction Metallurgy Division, Mines Branch, Extraction
 Metallurgy Division, Department of Energy, Mines and Resources,
 Ottawa, Canada.

Direction des mines

Bulletin technique TB 168

LES MÉTHODES POUR L'ANALYSE DE L'ILMÉNITE, DES SCORIES TITANIFÈRES ET D'AUTRES SCORIES PROVENANT DU FOUR ÉLECTRIQUE

IVe Partie A - LA DÉTERMINATION COMPLEXOMÉTRIQUE DE L'ALUMINIUM DANS L'ILMÉNITE, DANS LES SCORIES TITANIFÈRES ET DANS LES MINERAIS DE FER

par

A. Hitchen*

RÉSUMÉ

L'auteur décrit un procédé pour la détermination exacte et précise de l'aluminium dans l'ilménite, dans les scories titanifères et dans les minerais de fer. Après la fusion de l'échantillon avec du peroxyde de sodium,, il exécute trois précipitations avec les solutions d'hydroxyde-peroxyde de sodium afin d'enlever la quantité importante des éléments qui interfèrent comme le fer et le titane. Ensuite, il enlève les interférences qui restent dans le filtrat et qui accompagnent l'aluminium par l'extraction par solvant dans du chloroforme avec du diéthyldithiocarbamate de sodium à pH2. L'auteur détermine la quantité de l'aluminium dans la couche aqueuse par un tirage en retour d'un excès de l'acide 1, 2-diaminocyclohexane-tétracétique (DCYTA) avec les solutions titrées de zinc de pH 5 à 5.5 et le xylénol orange comme indicateur.

---

*Chimiste, Section des analyses chimiques, Division de la métallurgie extractive, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

CONTENTS (Cont'd)

TABLES

CONTENTS (Cont'd)

Page

TABLES

INTRODUCTION

In the previous report in this series[1], the lack of
a suitable accurate method for the determination of aluminum
in ilmenite and in ilmenite slags was pointed out, and the
requirements for such a method were outlined. The analytical
chemistry of aluminum was also reviewed in some detail.

The reaction between aluminum and both DCYTA (1,2-
cyclohexylenedinitrilotetraacetic acid), and EDTA (ethylene-
diaminetetraacetic acid) as well as most of the recent published
methods based on them were appraised in the previous paper.
DCYTA was the better because it reacts quantitatively with
aluminum at room temperature, whereas EDTA must be boiled to
complete the reaction. The principal objection to the published
methods employing DCYTA[2,3,4] relates generally to how
interfering elements are handled and to the lack of provision
for removing large amounts of titanium. For example, Pritchard[2],
in analyzing silicate rocks, relied on a single sodium hydroxide
separation to separate aluminum from iron, titanium, magnesium,
calcium, and manganese. DCYTA was added immediately after the
sodium hydroxide to complex the aluminum. Besides being
inadequate for recovering aluminum quantitatively if large
amounts of titanium are present, loss of aluminum by co-precipitation
was a problem if much magnesium was present. Other separations
that have been recommended for titanium removal include tri-n-
octyl phosphine oxide[3] and cupferron[5,6], both of which are

relatively inefficient if the titanium:aluminum ratio is high. Still another approach[7,8] is to determine the sum of titanium iron, and aluminum and then to subtract the separately determined titanium and iron values, a method which, as was pointed out in Part III of this series, is fraught with errors if the content of these elements greatly exceeds that of aluminum.

A particularly interesting method is the stepwise titration procedure of Nestoridis[9] in which titanium and aluminum are both complexed initially with EDTA and then released successively (titanium with phosphate and aluminum with fluoride), the liberated EDTA being back-titrated in each case. This gives a separate value for aluminum, has been applied to ilmenite, but is subject to intereference from manganese and zirconium.

Consideration of the problems associated with the methods described above suggested that the best approach would be to use a chelatometric titration with DCYTA after first removing the major impurities (titanium, iron, calcium, and magnesium) as completely as possible.

Sodium diethyldithiocarbamate is used as a extraction reagent for many elements and has been employed for both the extraction and subsequent colorimetric determination of small amounts of bismuth, iron, cobalt, chromium, nickel, uranium, and copper[10].

Small amounts of titanium can also be extracted from acid solutions at pH 2, and this method has been employed to remove titanium and iron from samples of cast iron[11] prior to extracting aluminum with cupferron. Large amounts of iron

were removed, as necessary, by either mercury cathode electrolysis or extraction from hydrochloric acid solution with isobutyl acetate before extracting the remaining impurities with the diethyldithiocarbamate.

To reduce the number of extractions, a prior sodium hydroxide separation to reduce the amount of titanium and iron was considered desirable.

Most of the samples (slags and titanium ores) were either difficult or impossible to dissolve in acids, so consideration was given to selecting a suitable general dissolution procedure which would be compatible with the over-all procedure. An alkaline fusion suggested itself because it presented the possibility of achieving preliminary separation of the bulk of the iron and titanium.

This report describes the development and successful application of a chelatometric titration procedure for determining aluminum in ilmenite ores, titaniferous slags, and iron ores. Interfering elements such as iron, titanium, and vanadium are removed in preliminary separation steps by a sodium hydroxide precipitation and solvent extraction using sodium diethyldithiocarbamate.

The method was subsequently applied to determining aluminum in a wider variety of ores and slags after suitable modifications were made to deal with different natures, compositions, and complexities of these materials. The procedure was applied to chromite ores, petroleum coke fly ash and slags, uranium ores, tin ores, manganese ores and slags,

and various minerals. The procedures and modifications used for these materials are described in a later section of this report, Part IV B.

APPARATUS AND REAGENTS

Apparatus

Beakers, glass, 600- or 800-ml

Beakers, Teflon, 400-ml and 600-ml with covers

Burettes, 50-ml

Magnetic stirrer and bars

pH meter

Separatory funnels, Squibb type, Teflon stopcock, 500 ml

Zirconium or iron crucibles with covers, 20- or 40- ml

Reagents

Ascorbic acid, reagent-grade

Carbon tetrachloride, reagent grade; (chloroform may be substituted for carbon tetrachloride).

DCYTA (1,2-cyclohexylenedinitrilo tetraacetate solution), 0.10 N. Dissolve 35.5 g of the acid in 200 to 240 ml of 1M NaOH and dilute to 1 litre with water. Prepare more dilute DCYTA solutions, if required, by dilution of this stock solution with water. Standardize the solution against pure lead (99.9%), pure zinc (99.9%) or pure aluminum wire or foil (99.9% or better).

Hexamethylenetetramine (Urotropine, hexamine), U.S.P. or reagent grade.

Hydrochloric acid, concentrated, reagent grade.

Sodium acetate, reagent grade, 25% w/v solution.

Sodium diethyldithiocarbamate, 10% aqueous solution. Prepare fresh daily and filter before use.

Sodium hydroxide pellets, reagent-grade.

Sodium hydroxide wash solution, 5 % w/v

Sodium peroxide, reagent-grade

Sulphuric acid, concentrated, reagent-grade

Xylenol orange indicator. Prepare a 0.25 % aqueous
solution of the tetrasodium salt. Pass this solu-
tion through a column of Dowex 50W ion exchange
resin in the H^+ form. Wash the column with not
more than 100 ml of water and dilute the eluate
to 250 ml i.e., 0.1 %. Note: This preparation
is essential otherwise poor end-points will be
obtained with untreated indicator.

Zinc chloride, 0.02 N or 0.10 N. Dissolve the appropriate
amount of zinc chloride in water and dilute to
volume or prepare by dissolving pure zinc metal in
a slight excess of hydrochloric acid and dilute
to volume with water. Standardize against the
standard DCYTA solution.

ANALYSIS PROCEDURES

1. Dissolving sample (ilmenite slags and ores)

Weigh a 0.5 to 1.0-gram sample and transfer to a
zirconium crucible. If the sample contains much coke or carboni-
ferous material, ignite at red heat for 5 minutes to remove it.
Cool, add 4 to 6 grams of sodium peroxide and mix well with a
dry stirring-rod or spatula. Brush any particles adhering to
the spatula or rod back into the crucible and add 5 or 6 pellets
of sodium hydroxide. Cover the crucible with a zirconium cover
and carefully fuse the mixture over a Fisher burner at a dull-
red heat for about 10 minutes or until the sample is completely
decomposed. Occasionally swirl the melt during the fusion period.

Cool, place the crucible and melt, including the
zirconium cover, in a 400-ml Teflon beaker; cover with a Teflon
beaker cover and carefully add about 75 to 100 ml of distilled
water. After the reaction has subsided and the melt is dis-

integrated, remove the cover and crucible and rinse them with a few drops of concentrated hydrochloric acid and water to dissolve any insoluble residue, adding the rinsings to the contents of the beaker. Place the beaker on a hot plate and bring to a boil. Continue boiling for a few minutes to decompose the excess peroxide. Remove the beaker from the hot plate and let the precipitate settle for 5 minutes or so before filtering. Filter the solution through Whatman No. 50 or 52 paper that has been previously washed with dilute (5 %) sodium hydroxide solution. Collect the filtrate in a 600-ml Teflon beaker. Transfer most of the precipitate to the paper with the aid of a stream of hot dilute (5 %) sodium hydroxide solution (it is not necessary to transfer the precipitate completely). Wash the precipitate 4 or 5 times with the hot sodium hydroxide wash solution.

Rinse the precipitate back into the original beaker and dissolve it in a slight excess of hydrochloric acid solution. Dilute to about 100 ml and bring to a boil. Meanwhile, dissolve 5 or 6 grams of sodium peroxide in about 100 ml of water in a 400 ml Teflon beaker and bring it to a boil. Pour the sample solution carefully and slowly into the peroxide solution with vigorous stirring so as to precipitate the Ti, Fe, and Zr again*.

---

*Sodium peroxide is used to reprecipitate the iron and titanium because it was found that a more readily filterable precipitate was obtained by this procedure than if sodium hydroxide alone was used. If necessary, sodium hydroxide can be used if some hydrogen peroxide is also added but sodium hydroxide has been found to contain more aluminum than sodium peroxide and a higher blank is obtained. If sodium peroxide is used, a blank correction is frequently not required, but it should be determined for each fresh supply of peroxide.

Boil the solution for a few minutes, remove from the hot plate, and allow the precipitate to settle. Filter the solution through the same filter paper that was used for the first filtration and combine the filtrate with the original filtrate. Wash the precipitate a few times with the hot dilute sodium hydroxide wash solution. Transfer the precipitate back to the 400-ml Teflon beaker, dissolve it again in dilute hydrochloric acid, and precipitate the titanium, iron, and zirconium once more as described above. Filter the solution and wash the precipitate with hot dilute sodium hydroxide solution. Discard the precipitate and combine the filtrates with the previous two filtrates. Add a few drops of methyl red indicator and acidify the combined filtrates with hydrochloric or sulphuric acid. Evaporate the solution to about 400 ml and then cool to room temperature.

Amounts of calcium or magnesium greater than about 20 mg can cause difficulty in the titration step. If they are likely to be present in such amounts, precipitate the aluminum with ammonia, discard the filtrate, then redissolve the aluminum hydroxide precipitate in hydrochloric acid and proceed with the extraction step. Generally, however, only relatively small amounts of calcium or magnesium are present in ilmenite ores and slags. Moreover, these elements are removed to a large extent in the sodium hydroxide precipitation step and therefore the amounts remaining with the aluminum in the filtrate will normally be of no concern.

2. Extraction of interferences

Add 10 to 20 ml of 25 % sodium acetate solution and 5 ml of glacial acetic acid to the filtrates, and adjust the pH to 1.8 to 2.0 with dilute hydrochloric or sulphuric acid and sodium hydroxide. Transfer the solution to a 500-ml Squibb-type separatory funnel and cool to below room temperature in ice cold water. Add 5 to 10 ml of freshly prepared and filtered 10 % DEDTC solution and shake for 1 minute. Add 30 ml of carbon tetrachloride (or chloroform) and shake for 2 minutes with occasional release of pressure. Allow the two phases to separate and drain off the lower organic layer and discard it. Continue the addition of further portions of the DEDTC solution and extract with carbon tetrachloride until the extract is colorless thus indicating the complete removal of extractable impurities. If more than 3 extractions are found to be necessary at this stage, readjust the pH of the solution to 2 again before extracting with more DEDTC. The addition of the DEDTC causes the pH of the aqueous solution to increase to 3.5 or 4 after only 2 or 3 additions, therefore there may be some precipitation of hydrous aluminum oxide. Moreover, a higher pH is not favourable for the extraction of some elements such as titanium. To avoid draining the solution into a beaker for each measurement, it is a great convenience to use a small-diameter combination pH electrode to readjust the pH directly in the separatory funnel.

3. Titration of aluminum

Drain the aqueous layer into a 600 to 800-ml glass beaker and rinse the separatory funnel several times with distilled water, adding the rinsings to the beaker. Adjust the pH of the solution to between 2.0 and 2.5 and add a measured excess of standard 0.02 M DCYTA solution, based on the estimated amount of aluminum present*. Adjust the pH to between 5.0 and 5.5 with dilute (5 %) sodium hydroxide solution, add 1 to 2 grams of solid hexamethylenetetramine and 0.1 to 0.2 g of solid ascorbic acid to prevent blocking of the indicator by trace amounts of any heavy metals that may have escaped extraction. Add sufficient xylenol orange indicator solution to colour the solution a distinct yellow and stir (magnetic stirrer) the solution. Back-titrate the excess DCYTA with a standard 0.02 N solution of zinc chloride until the pink end-point is reached. From the net amount of DCYTA consumed calculate the percentage of aluminum. 1 ml of 0.020 N DCYTA = 0.5390 mg Al.

PRELIMINARY INVESTIGATIONS

1. Determination of aluminum in solutions containing no other metal ions

Pure aluminum metal was dissolved in hydrochloric or sulphuric acid to establish the range over which aluminum can

---

*If a pink colour forms when the indicator is added, it indicates that insufficient DCYTA was present to provide an excess. The determination can be salvaged however. To do so, add sufficient 50 % sodium hydroxide to raise the pH to 12 or higher, and then add the necessary excess of DCYTA. Readjust the pH to 2.0 and, finally, to 5.0 as before; then continue with the titration.

be determined precisely and accurately. In these experiments, weighed amounts of the pure aluminum wire (99.9 % Al) or aliquots of a standard solution of aluminum were titrated with a standard solution of DCYTA using the back-titration procedure described in the report; the results were compared with those that were obtained from taking similar amounts of aluminum and, after dissolution, extracting the impurities etc. by the proposed procedure. The results of these experiments are given in Table 1.

Table 1 shows that from 1 to 300 mg of aluminum can be precisely and accurately determined by titration with DCYTA. Furthermore, aluminum is not extracted by diethyldithiocarbamate and carbon tetrachloride and can be determined accurately and precisely without having to destroy any organic material remaining in the aqueous layer after the extraction is performed. The precision and accuracy is usually better than 2 parts per thousand on 10 to 300 mg aluminum. On unextracted solutions containing small amounts (less than 1 mg) of aluminum, the end-point is not as sharp, hence the precision is not as good as with larger amounts. If small amounts of aluminum have been extracted, the subsequent titration end-point is even poorer and, at the 0.05-mg level, the end-point is not detectable. Such an end-point may be caused by decomposition of the DEDTC. The titrations could perhaps be improved if the extracted solutions were evaporated and the organic material destroyed, but the presence of sodium acetate and the large amounts of salts would make such a treatment impractical. In practice, therefore, the procedure that is proposed appears to be best applicable to amounts of aluminum greater than 1 mg.

TABLE 1

Determination of Aluminum in Solutions
Containing No Other Metal Ions

Aluminum Taken (mg)	Aluminum Found (mg	
	Not Extracted	Extracted
0.05	0.053*	e.p. not detectable
0.10	0.093*	0.06*
0.50	0.47*	0.31*
1.00	1.01*	0.99*
10.00	10.00**	10.00, 10.01**
20.00	20.00**	19.99, 20.00**
30.00	30.00**	29.92, 29.96**
55.04	55.03***	
102.49	102.42***	
103.90		103.80***
105.08	104.50***	
112.38	112.29***	
157.80	157.70***	
204.40		204.10***
210.30	208.90***	
211.67	211.98***	
251.12	251.28***	
317.50	315.60***	

*Titrated with 0.002 N DCYTA and 0.002 N $ZnCl_2$
**Titrated with 0.02 N DCYTA and 0.02 N $ZnCl_2$
***Titrated with 0.10 N DCYTA and 0.10 N $ZnCl_2$

Preliminary tests had shown that the pH of the solution to be extracted was important to the formation of an emulsion (honey-comb effect) during the extraction step. The appearance of an emulsion greatly hindered the separation of the two phases and prolonged the procedure. At pH 4, for example, emulsions were almost invariably produced and the possibility existed that in draining the emulsion, small amounts of aluminum would be lost. Moreover, at pH 4 there is the danger that aluminum will start to precipitate, especially if large amounts are present (although the results actually obtained at these pH levels did not indicate any loss of aluminum). However, it was found that, by lowering the pH of the solution to about 2, the formation of emulsions was almost completely eliminated, occurred in only a few tests, and that complete recovery of aluminum was still obtained. A disadvantage of using a low pH is that the diethyldithiocarbamate reagent decomposes more quickly (although in practice no ill effects were noted). Moreover, the optimum pH (2) to avoid the formation of an emulsion may not be the optimum pH for the extraction of all interfering elements. The results obtained by extraction of a number of interfering elements from a solution buffered to pH 2 are discussed under Preliminary Investigations, Section 6 C of this report. Subsequent observations indicated that emulsion formation and perhaps decomposition of the DEDTC could be inhibited by cooling the solution to 15°C or less by

immersing the separatory funnel in ice water. This step, though not absolutely necessary, is recommended because it helps in the phase separation.

During the preliminary experiments it was found that the pH of unbuffered solutions is greatly affected by the addition of the highly alkaline (> pH 10) sodium diethyldithiocarbamate solution. Therefore, if the DEDTC solution is added to an unbuffered solution during the extraction step, the pH of the solution can rise to a level at which aluminum precipitates as its hydrous oxide and can be removed mechanically with the chloroform. The addition of 10 to 20 ml of 25 % sodium acetate solution and 5 ml of glacial acetic acid serves to buffer the solution adequately for the extraction step in most cases. The amount of acetate added is not critical because the final adjustments to pH 2 are made by adding either hydrochloric or sulphuric acid. The acetate does not interfere in the subsequent DCYTA titration and, in fact, has been found to be beneficial if magnesium or calcium is present.*

2. Effect of initial pH on the titration

Very little information is given about the optimum pH conditions for complexing the aluminum in any of the papers dealing with the titration of aluminum with DCYTA. For example,

---

*See Preliminary Investigations, Section 6 B of this report.

Pribil and Vesely[4,13,14], Burke and Davis[3], and Evans[7] mention only that the excess DCYTA is added to an acidic solution without stating the pH, (presumably because their samples were prepared in a strongly acid solution to begin with). On the other hand, Pritchard[2] adds the excess DCYTA to a strongly alkaline (ca 2.5 % NaOH) solution, acidifies the filtrate to bromocresol green indicator with hydrochloric acid, and finally adjusts the solution to a blue colour with sodium hydroxide solution. Thus the pH of the solution would range from less than 3.8 to about 5.5 using this indicator. Kiss[6] is the only author to state a specific pH (3.5) at which to add the excess DCYTA solution. A number of experiments were therefore under-taken to establish the optimum pH conditions at which to complex the aluminum with DCYTA.

a) Series A. In the presence of excess DCYTA

Solutions containing 10.00 or 20.00 mg of aluminum were first adjusted to the desired initial pH value, then 0.1 to 0.2 g of ascorbic acid and 25.00 or 50.00 ml of 0.02 N DCYTA solution were added. The pH was then adjusted to pH 5.0 to 5.5 by adding 2 to 4 g of hexamethylenetetramine and either dilute hydrochloric acid or dilute sodium hydroxide solution. The excess DCYTA was back-titrated with standard 0.02 N zinc chloride solution using xylenol orange as the indicator. The results of these tests are given in Table 2.

The results in Table 2 show that it is necessary to adjust the pH to 3 or lower before adding the standard DCYTA;

TABLE 2

Series A.   Effect of Initial pH on the Titration

Initial pH	Al Taken (mg)	Al Found (mg)	% Recovery
2.0	20.00	20.00	100.00
3.0	20.00	20.00	100.00
4.0	20.00	12.9	64.5
5.0	20.00	4.6	23.0
10.0	20.00	13.1	65.5
12.0	10.00	9.17	91.7
	"	8.70	87.0
	"	9.33	93.3

otherwise low results for aluminum will be obtained. At pH values between 4 and 10 and before adding the DCYTA, a slight precipitate was visible (due presumably, to the presence of some insoluble hydrous aluminum oxide). This precipitate apparently does not react with the excess DCYTA and this undoubtedly accounts, in part, for the low results that are obtained. At pH 10 and 12, the recoveries of aluminum again increase because the hydrous aluminum oxide dissolves to form the aluminate ion. When the pH is lowered to 5, the aluminum is again able to react with the DCYTA because the aluminate ion reverts to the aluminum ion but the recoveries are still low, presumably due to the formation of undissociated hydroxo aluminum compounds that react only slowly with DCYTA.

In practice, it has been found that the DCYTA can be added to a solution at a higher pH* but afterward the solution must be adjusted to less than pH 3 in order to allow the aluminum-DCYTA complex to be formed before adjusting the pH to its final value of 5.0 to 5.5 for back-titration.

In the course of these experiments, it was observed that, if insufficient DCYTA is added to complex all the aluminum, a pink-coloured aluminum-indicator complex forms on addition of the xylenol orange. The formation of the pink colour, which does not disappear when the pH is readjusted to 2, or on addition of more DCYTA thus appears to be irreversible under these conditions. Therefore the indicator must <u>not</u> be added until the DCYTA is present in excess and the solution has been adjusted to pH 2.

It is possible for an insufficient amount of DCYTA to be added because of an incorrent estimate of the amount of aluminum present, therefore further experiments were made to determine the procedure to be followed in this event to avoid having to repeat the analysis. These experiments are described in the following section.

b) <u>Series B</u>. <u>In the presence of insufficient DCYTA</u>

If, as has just been noted, insufficient DCYTA is added to complex all the aluminum, an irreversible aluminum-xylenol orange complex is formed when xylenol orange indicator is added and adjustment of the pH is made, so that, normally,

---

*At pH levels above 10 the colour of the solution turns blue because of the acid-base properties of the xylenol orange indicator but on lowering the pH the yellow form of the indicator reappears.

the sample has to be discarded and the analysis repeated. Therefore, further experiments were undertaken to determine conditions that would avoid this possibility.

In doing some preliminary tests, it was observed that if a solution containing the pink Al-dye complex was made highly basic (above pH 10), the pink colour was almost completely discharged and was replaced by the blue colour due to the basic characteristics of the xylenol orange. This observation suggested that it was possible to disrupt the Al-dye complex in highly alkaline solutions. Further additions of DCYTA could then be made and the pH could finally be lowered to the level required for back-titration of the excess DCYTA.

To explore this possibility, experiments were carried out to observe the effect on the aluminum-dye complex under such conditions as insufficient DCYTA having been added or the indicator having been inadvertently added before the DCYTA. In these tests, the pH of the solutions was adjusted to 12 or higher to confirm that the aluminum-dye complex could be broken and the aluminum could be freed to combine with the DCYTA. In series B-1, Test 1 was performed to determine the effect when DCYTA was added to a solution that had a high pH initially. Tests 2 and 3 of Series B-1 were conducted to illustrate the importance of adjusting the pH to less than 3 before finally titrating the solution at pH 5.5. The tests in Series B-2 were done identically to those in Series B-1 but simulate the effects of salts arising from the use of sodium peroxide and sodium hydroxide in the preparation of the samples.

Series B-1. In the absence of sodium salts

1)   Solutions containing 10.00 mg of aluminum and 0.2 g
of ascorbic acid in a volume of about 300 ml of water were
adjusted to pH 12 with sodium hydroxide solution; the xylenol
orange indicator was added first and then an excess of standard
DCYTA solution. The pH was carefully lowered to 5.0 to 5.5
using hydrochloric acid and finally hexamine was added as a
buffer. The excess DCYTA was titrated with standard zinc
solution.

2)   Solutions containing 10.00 mg of aluminum were
adjusted to pH 2.0 with hydrochloric acid. A standard solution
of DCYTA was added but in an amount insufficient to complex
all the aluminum (about one half of the amount of DCYTA
theoretically required). Hexamine buffer and xylenol orange
indicator were added to produce the pink Al-dye complex and
the pH was adjusted to between 12 and 13 with sodium hydroxide
solution. An excess of standard DCYTA solution was added and
the pH carefully lowered to 5.0 to 5.5 but not lower, with
hydrochloric acid. The excess DCYTA was titrated with standard
zinc solution.

3)   The procedure in 2) was repeated except that, after
the final excess of DCYTA solution was added, the pH was first
lowered to 2.0 before final adjustment to 5.0 to 5.5. The
amount of aluminum recovered in these three tests was calculated
and the results are summarized in Table 3 under Series B-1.

Series B-2. In the presence of sodium salts

The above series of tests were repeated in an identical
manner except that 10 ml of 12 M hydrochloric acid was added to

the solution of aluminum before any pH adjustments were made.
This amount of acid was chosen in order to simulate the
effect due to the presence of the large amount of salts derived
from the fusion of the sample with sodium peroxide and sodium
hydroxide. The aluminum recovered in these tests is recorded
in Table 3 under Series B-2.

TABLE 3

Effect on the Titration of Aluminum When
DCYTA is Added in Two Increments, in the
Absence and in the Presence of Sodium Salts
(Series B-1 and B-2)

Test No.	pH			Al Present mg	Al Found (mg)	
	Initial	Intermediate	Final		Series B-1 (NaCl absent)	Series B-2 (NaCl Present)
1	12	–	5.5	10.00	9.68*	10.00*
2	2	12	5.5	10.00	9.20*	10.00*
3	2	12 → 2	5.5	10.00	9.68**	9.95**

*Sluggish end-point
**Sharp end-point

Table 3 shows that, if insufficient DCYTA to complex
all the aluminum is added, the titration can still be completed
successfully if the solution is first made highly basic (pH 12
to 13), an excess of DCYTA added, the pH then lowered to 2,
and finally adjusted to pH 5 to 5.5. The end-point can still
be detected, although it will be sluggish, if the pH is
lowered just to pH 5.5 but a sharper end-point is obtained if
the pH is lowered to 2 before final adjustment to 5.5. In order
to obtain complete recovery, however, it is necessary to have

present a large amount of sodium chloride salt. This is fortuitous

because large amounts of sodium chloride will be present in any

case, due to the neutralization of the alkaline filtrate from

the peroxide fusion step. Results obtained in the following section

indicate that the chloride is a factor in the complete recovery

of aluminum which was observed in the above tests, perhaps because

the chloride prevents the formation of undissociated hydroxo-

aluminum compounds but the results are not conclusive.

3. The effect of large amounts of chloride, sulphate, acetate,
    perchlorate and nitrate on the titration

The results of the preceding tests led to the investiga-

tion of the effect of adding similar amounts of other acids such

as sulphuric, acetic, perchloric, and nitric to solutions contain-

ing aluminum. The acids were added, rather than the equivalent

sodium salts, because of convenience and also because the acids

would be used to neutralize the alkaline solutions obtained in

preparing the samples. The tests were done according to

Procedures 2 and 3 of Series B-2 described in the preceding section,

substituting 10 ml of one of concentrated sulphuric acid, glacial

acetic acid, 72 % perchloric acid, or concentrated nitric acid

for the hydrochloric acid. The results of these tests were compared

with results obtained on solutions containing either 10 ml of

concentrated hydrochloric acid or no acid. In all tests, 10 ml

of DCYTA solution was initially added, so that only about one half

of aluminum present was complexed before the pH of the solutions

was adjusted. In some tests, a total of 25 ml of DCYTA solution

was added (equal to about 6 ml DCYTA in excess) and in others

30 ml of DCYTA solution was added (equal to about 11 ml DCYTA

in excess). The results are summarized in Table 4.

TABLE 4

Effect of Large Amounts of Chloride,
Sulphate, Acetate, Perchlorate and Nitrate
on Titration when DCYTA is Added in Two Increments

Procedure No.	2	3[a]	3	3
Total Amount of DCYTA added (ml)	25	25	25	30

Aluminum Taken = 10.00 mg   Aluminum Found (mg)

Anion Added As				
No Acid	9.54*	9.74**	9.82*	10.00*
HCl	10.00*	10.00*	10.00*	10.00*
H_2SO_4	9.38**	9.90**	9.95**	8.96** [b]
				9.90** [c]
HAc	9.92**	9.38**	9.95**	– [d]
				9.90* [e]
$HClO_4$	9.28**	10.00*	9.69**	10.00*
HNO_3	9.95**	10.00*	9.74**	10.00*

* sharp red end-point   ** slow or orange end-point

(a) The pH of the solution in this series of tests was raised to
between 12 and 13, the excess of DCYTA was added, the pH was
lowered to 2.0 and again raised to 12 before lowering it to 2.0
once more. The pH was finally adjusted to 5.0 to 5.5 for the
back titration.

(b) This result was obtained on the first titration. The colour
slowly turned red during the titration and the final end-point
was difficult to detect.

(c) The solution in the same beaker on which Result (b) was obtained
was again adjusted to pH 12 to 13 and an additional 10.00 ml
of DCYTA solution was added, i.e., total = 40 ml. The solution
was readjusted to pH 2 and then to 5.5 for the final titration.
The end-point was better but still slow.

(d) The solution turned deep red when adjusted to pH 5.5 and no
titration could be made. No explanation can be given for
this behaviour other than for some reason the aluminum
reacted with the xylenol orange instead of with the DCYTA.

(e) The solution in the same beaker on which Result (d) was obtained was again adjusted to pH 12 to 13, readjusted to pH 2 and then to 5.5. This time no trouble was observed and the end-point was sharp although no additional DCYTA was added.

The results in Table 4 show that, except in the case of hydrochloric acid, variable recoveries of aluminum are obtained depending on the procedure that is followed. If no acid is added, the recoveries of aluminum are low by 0.2 to 0.5 mg except when a relatively large excess of DCYTA is added (about 50% above theoretical). In the presence of large amounts of sulphate, acetate, perchlorate, and nitrate salts, the recoveries of aluminum are always low but improved recoveries are sometimes obtained if the pH of the solution is readjusted to 12 to 13 a few times. One explanation of the observed effect is that in the latter procedure a large part of the pink aluminum-indicator complex is broken when the pH is raised to 12, the aluminum that is set free combining with the DCYTA when the pH is lowered. However, a small amount of aluminum often remains combined (or may recombine) with the xylenol orange, so it is necessary to raise the pH again to 12 to 13 to liberate more aluminum from this complex. This technique works better in the presence of chloride, perchlorate, and nitrate than it does in the presence of either sulphate or acetate. An alternative explanation is that undissociated hydroxo-aluminum compounds that only slowly react with DCYTA are produced as the pH is lowered from 12 to 2. The true explanation is more likely a combination of both the above possibilities.

If a substantial excess (about 50 % above the theoretical amount of DCYTA is added), complete recovery of the aluminum is

obtained except in the presence of sulphate and acetate. With the latter anions it is necessary to add more DCYTA and/or to readjust the pH of the solution to 12 to 13 several times to improve the recovery. It should be pointed out that sulphate and acetate didn't cause any trouble in the analysis of ilmenite samples. This may have been because an excess of DCYTA was always added initially and also because, in nearly all cases, chloride was present from the neutralization of the alkaline filtrates from the precipitation step. Therefore it was never necessary to employ the above technique.

The procedure, suggested to be used in the event insufficient DCYTA is added to complex all the aluminum, appears to be most effective in the presence of chloride, therefore the use of hydrochloric acid is advocated to neutralize the alkaline filtrates and to overcome the undesirable effects of sulphate or acetate.

4. Effect of tartaric acid on the titration

Tartaric acid is a well-known complexing reagent that is frequently used to prevent the precipitation of metals such as iron, titanium, and aluminum in the presence of strong alkalies. In an attempt to prevent the precipitation of aluminum or the formation of hydroxyl compounds, if the pH of the solution is adjusted before the titration, and to explore the possibility of its use as a buffer in the extraction step instead of acetate, the addition of tartaric acid was considered. Therefore, experiments to determine its effect on the titration of aluminum were done.

Solutions containing 10 to 20 mg of aluminum were treated with various amounts of tartaric acid, the pH was adjusted to the desired initial pH value, then a measured excess of standard DCYTA solution was added and the pH finally adjusted to a value of 5.0 to 5.5 by adding hexamethylenetetramine and either dilute hydrochloric acid or sodium hydroxide solutions. The excess DCYTA was titrated with standard zinc chloride solution using xylenol orange as the indicator. The results of these tests are given in Table 5.

TABLE 5

Effect of Tartaric Acid on the Titration

Initial pH	Amount of Tartaric Acid Added (grams)	Aluminum Taken (mg)	Aluminum Found (mg)
2.0	2	10.00	2.79
2.0	4	10.00	1.05
4.0	2	20.00	9.60
5.0	2	20.00	8.20

The results in Table 5 show that tartaric acid seriously interferes in the titration of aluminum with DCYTA. The interference is greater at the lower initial pH values before the DCYTA is added. The results clearly indicate the formation of a tartaric acid-aluminum complex that is stronger than the DCYTA-aluminum complex. The use of tartaric acid or tartrates as buffer agents in the extraction step or in the titration must therefore be avoided.

5. Effect of fluoride ion on the titration

Pribil and Vesely[4] determined aluminum in slags and ores by titrating the DCYTA liberated when ammonium fluoride was added to a solution in which all the aluminum was complexed with DCYTA. The iron-DCYTA complex is supposedly not affected by the addition of fluoride. In order to explore the possibility of using this technique, the effect of fluoride on the determination of aluminum was investigated by carrying out the following experiments in which fluoride was added to solutions containing known amounts of aluminum or aluminum and iron that had been previously titrated with DCYTA. The amount of DCYTA thus liberated was titrated with zinc solution and the results were compared with those that were obtained prior to the addition of fluoride. The last two experiments were carried out to establish that aluminum is completely complexed by fluoride and that the fluoride does not inhibit the titration of the free DCYTA by zinc.

a) To a solution, containing 20.00 mg of aluminum in a volume of about 300 ml of water and adjusted to pH 2.0, was added 25.00 ml of a standard 0.05 N DCYTA solution. Hexamethylene-tetramine buffer was added and the excess DCYTA was titrated at pH 5.5 with 0.05 N zinc chloride solution using xylenol orange as indicator. The amount of aluminum titrated was calculated.

b) To the titrated solution from (a) was added 20 ml of 1 M ammonium fluoride. The pH of the solution was adjusted to 2.0, as recommended by Pribil and Vesely, and then the solution was boiled for 3 minutes. After cooling the solution and readjusting the pH to 5.5, the liberated DCYTA was titrated with standard

0.05 N zinc chloride solution and the amount of aluminum cal-
culated from the amount of DCYTA liberated.

(c) To a solution containing 20.00 mg of aluminum and
11.2 mg of ferric iron, previously adjusted to pH 2.0, was
added 25.00 ml of 0.05 N DCYTA solution. The excess DCYTA was
titrated with standard zinc solution as in (a) and the amount of
aluminum calculated after correcting for the amount of iron added.
Note: In this experiment, the net amount of DCYTA used corresponds
to the sum of Al and Fe present.

(d) The solution obtained after titration in (c) was
treated with ammonium fluoride in the same manner as (b) and the
amount of aluminum calculated from the amount of DCYTA liberated
by the fluoride.

(e) A solution containing 20.00 mg of aluminum was
adjusted to pH 2.0 and 20 ml of 1 M ammonium fluoride was added.
The solution was allowed to stand for 5 minutes at room temperature,
then 25.00 ml of 0.05 N DCYTA solution was added and the solution
titrated at pH 5.5 with standard 0.05 N zinc chloride as before.

(f) A solution was prepared in the same manner as (e)
except that it was boiled for 3 minutes after the addition of the
fluoride, then cooled, 25.00 ml of 0.05 N DCYTA solution was
added and the solution titrated at pH 5.5 with 0.05 N zinc chloride
solution.

The results of these experiments are shown in Table 6.

TABLE 6

The Use of Fluoride to Selectively Liberate Aluminum
from its DCYTA Complex and the Effect of
Fluoride on the Titration

Experiment	Al Taken (mg)	Fe Taken (mg)	Al Found (mg)	Fe Found (mg)
(a)	20.00	Nil	20.00	
(b)	20.00	Nil	19.75	
(c)	20.00	11.2	19.85*	
(d)	20.00	11.2	19.10**	12.8**
(e)	20.00	Nil	-0.33	
(f)	20.00	Nil	0.00	

* Calculated after correcting for the amount of DCYTA theoret-
ically required to titrate the iron present.

** Calculated from actual titration values for (c) and (d)

The results in Table 6 show that aluminum is liberated
from its DCYTA complex by the addition of fluoride and that the
amount of aluminum present can be calculated from the amount of
DCYTA liberated. They also show that the sum of the amount of
aluminum and iron present can be titrated stoichiometrically.
However, when fluoride is added to complex the aluminum and
liberate an equivalent amount of DCYTA, the results for aluminum
tend to be low and the corresponding results for iron are high.
Evans[7] mentions a similar effect and states that in the presence
of free DCYTA the iron(III) chelate causes further reaction
between the aluminum and free DCYTA to take place. However,

Evans does not give references or results of experiments to substantiate his statements. On the other hand if fluoride is added before the DCYTA, the aluminum is completely complexed by the fluoride and cannot be titrated; the fluoride does not interfere with the titration of free DCYTA by zinc. This is confirmed by the results in Table 6, agrees with Evans' work, and shows that iron can be determined with DCYTA after complexing aluminum and titanium with fluoride.

6. Effect of diverse ions on the titration

        (a) Titration without extraction of interfering ions

It was anticipated that many elements besides aluminum would react with DCYTA because this reagent is similar in many respects to EDTA. Little information, however, is available on the extent of such interference in the determination of aluminum under the conditions of the proposed method. Therefore a systematic investigation to establish the effect of diverse ions on the titration of aluminum with DCYTA was undertaken.

Solutions containing known amounts of aluminum and/or the potential interfering-ion were titrated using the titration step (3) of the proposed procedure (page 9. The results of these tests are given in Table 7.

TABLE 7

Effect of Diverse Ions on the Titration (No Separations)

Element Added (mg)		Aluminum Added (mg)	"Apparent" Al Found (mg)	Treatment	Comments
As^{+3}	10	10.00	10.00	ascorbic acid	
As^{+5}	10	10.00	9.98	"	
Ba^{+2}	10	10.00	10.00	"	
Bi^{+2}	10	10.00	11.20	"	
Ca^{+2}	20	10.00	9.72	"	
	100	10.00	–	"	Solution cannot be titrated.
Ce^{+4}	10	10.00	10.74	"	Ce^{+4} reduced to Ce^{+3}
	100	10.00	13.34	"	by ascorbic acid
Cd^{+2}	11.2	0.00	2.55	"	Quant recovery of Al + Cd indicated
	11.2	20.00	22.70	"	
CN^{-1}	10	10.00	10.00	"	
	200	10.00	10.00	"	
Co^{+2}	12.4	0.00	5.71	"	Quant recovery of Al + Co indicated
	12.4	20.00	25.30	"	
Cr^{+3}	10.5	0.00	0.07	"	
	10.5	10.00	9.96	"	
	200	10.00	–	"	Deep green colour of Cr^{+3} made end-point undetectable
Cr^{+6}	10	10.00	9.96	no ascorbic acid	Highly yellow coloured solution but e.p. easily detectable
	200	10.00	10.00	"	
Cu^{+2}	10	0.00	4.14	ascorbic acid	Blue colour produced on adding DCYTA. Quant recovery of Al + Cu indicated
	10	20.00	24.10	"	

TABLE 7 (Cont'd)

Element Added (mg)		Aluminum Added (mg)	"Apparent" Al Found (mg)	Treatment	Comments
Fe^{+3}	2.8	0.00	1.33	ascorbic acid	Fe^{+3} reduced to Fe^{+2} by ascorbic acid
	2.8	0.00	1.32	"	
	2.8	20.00	21.10	"	
	11.2	0.00	5.23	"	
	11.2	20.00	24.30	"	
	2.8	0.00	1.59	H_2O_2 added	
	11.2	20.00	24.40	"	
Hg^{+2}	10	10.00	11.31	ascorbic acid	End-point fades
La^{+2}	10	10.00	11.84	"	
	100	10.00	26.8	"	
Mg	20	10.00	10.00	"	
	100	10.00	–	"	Solution cannot be titrated
Mn^{+2}	10.2	0.00	3.23	"	End-point fades
	10.2	20.00	24.20	"	
Mo^{+6}	10	10.00	9.92	"	
	100	10.00	5.87	"	
Ni^{+2}	10.3	0.00	4.76	"	Quant recovery of Al + Ni indicated
	10.3	20.00	24.50	"	
NO_3^{-}	10	10.00	10.00	ascorbic acid	
	200	10.00	10.00	"	
Pb^{+2}	10.2	0.00	1.22	"	Quant recovery of Al + Pb indicated
	10.2	20.00	21.30	"	
PO_4^{-3} (10 mg P)	30.7	10.00	8.92	"	White ppte appears at pH 4
(100 mg P)	307	10.00	9.07	"	
Sn^{+2}	10	10.00	10.04	"	
	20	10.00	9.50	"	White ppte at pH 2 poor e.p.
	50	10.00	9.00	"	"
	100	10.00	–	"	Ppte appears at pH 4. Indicator turned pink and e.p.was undetectable

TABLE 7 (Cont'd)

Element Added (mg)		Aluminum Added (mg)	"Apparent" Al Found (mg)	Treatment	Comment
Sr^{+2}	10	10.00	10.00	ascorbic acid	
Th^{+4}	10	10.00	11.25	"	Quant.recovery of Al + Th indicated
Ti^{+4}	2.4	0.00	0.59	"	
	7.2	0.00	2.06	"	Ppte appeared at pH 2,
	7.2	20.00	20.90	"	which dissolved on adding ascorbic acid. E.p. difficult to detect.
	7.2	0.00	2.16	H_2O_2 added	Ppt appeared at pH 2.
	2.4	0.00	1.12	added H_2O_2 at	End point difficult
	2.4	20.00	17.40	pH 2 and boiled	to detect
	7.2	0.00	2.60	5 mins,cooled,	
	7.2	20.00	12.40	added ascorbic acid and titrated	
V^{+5}	2.5	0.00	1.53	ascorbic acid	V^{+5} reduced to V^{+4}
	2.5	0.00	12.40	no ascorbic acid	Colorless solution at pH 2,X.O. indicator turned pink, e.p. difficult to detect
	12.6	0.00	7.38	ascorbic acid	Yellow solution at pH 2.
	12.6	0.00	7.47	"	On adding ascorbic acid
	12.6	20.00	27.40	"	the solution turned blue and then colorless. E.p.easy to detect.
	2.5	0.00	0.00	H_2O_2 added	
	12.6	0.00	0.00	"	
	2.5	20.00	20.00	"	E.p. easy to detect
	12.6	0.00	0.00	"	
	12.6	20.00	20.00	"	
Zr^{+2}	10.0	10.00	11.40	ascorbic acid	
	20.00	10.00	12.00	"	
	10.0	10.00	11.36	no ascorbic acid	
	10.0	10.00	10.50	H_2O_2 added	White ppte appeared at pH 5.5

The results in Table 7 show that many elements
seriously interfered in the titration of aluminum with DCYTA.
Arsenic(III), arsenic(V), barium, and strontium do not interfere
at the 10-mg level. Nitrate and cyanide do not interfere in
amounts up to 200 mg. Chromium(VI) does not interfere when
present in amounts up to 200 mg; at least 10 mg of chromium(III)
is tolerable but amounts of chromium(III) in excess of about
50 mg interfere with the detection of the end-point because of
the deep green colour of the chromium(III) ion. Therefore, if
large amounts are encountered, it is better to convert the chromium
to the chromate form and avoid the use of ascorbic acid in the
titration, if other conditions permit it. An alternative procedure
would be to volatilize the chromium as chromyl chloride. Vanadium
interferes, even in the presence of ascorbic acid, but it does
not interfere when hydrogen peroxide is present. Phosphate inter-
feres to some extent and causes low results possibly because
of the formation of small amounts of aluminum phosphate that
precipitate at pH 5. Molybdenum(VI) does not interfere if
present at the 10-mg level but, at the 100-mg level, it causes low
results for aluminum. Tin does not interfere if present at the
10-mg level but, if 20 to 50 mg are present, a white precipitate
(hydrous tin oxide?) appears that makes the end-point difficult to
detect and low recoveries of aluminum are obtained. At the
100-mg level, tin produces a pink colour with the indicator to
render the end-point undetectable.

One surprising result of the study is the unexpected
interference of calcium and magnesium. Calcium at the 20-mg

level interferes slightly and magnesium in same amount inter-
fered even less, except that the indicator is coloured a slight
orange to red which makes the end-point more difficult to detect.
In the presence of large amounts of calcium or magnesium, however,
the indicator turns red and the titration cannot be made. This
interference is discussed in the next section and procedures are
suggested for eliminating it. All the other elements such as
Ti, Fe, Cu, Ni, Co, Bi, Hg, Mn, Pb, Cd, La, Ce, Th and Zr inter-
fere at all levels of concentration.

In the tests conducted with zirconium ion it should be
noted that this ion interfered whether or not ascorbic acid was
present but if hydrogen peroxide was added the interfering effect,
though not entirely eliminated, was decreased. This decrease
may have been due, in part, to the formation of complex zirconium
peroxy compounds or to polymers but further investigation of this
behaviour was not attempted. Additional tests and discussion
of the effect of zirconium are given in Sections 7 and 8 of this
report.

The results of the titration interference study show
that isolation of the aluminum will be required invariably because
nearly all of the elements investigated will be present to a
greater or lesser extent in most samples in which aluminum is to
be determined.

(b) Effect of calcium and magnesium on the titration

The interference of calcium and magnesium in the
titration of aluminum was unexpected, so it was concluded that,
at the pH (5 to 5.5) at which the titration was done, the calcium

and magnesium competed with the aluminum for the DCYTA. There-
fore, if insufficient DCYTA is added to complex all the calcium
or magnesium as well as the aluminum, there will be a small amount
of aluminum left uncomplexed and this will react with the
indicator to produce the pink colour and render the titration
impossible. To test this hypothesis, a solution was prepared
which contained 20 mg of calcium and 10.00 mg of aluminum. An
excess of DCYTA was added, sufficient to complex all the calcium
and aluminum, and the excess DCYTA was then titrated at pH 5 to
5.5 with standard zinc solution using xylenol orange. The
amount of aluminum recovered was 10.05 mg and no interference
due to calcium was observed, either with the indicator or by
consumption of DCYTA. Apparently, in the back-titration step,
the zinc easily displaces the calcium from its DCYTA-Ca complex
and the net result is that only the aluminum is determined.
Because magnesium interferes even less than calcium the same
procedure can be applied in the presence of small amounts of
magnesium.

The above procedure fails, however, if amounts of
calcium or magnesium exceeding about 20 mg are present because
it is then necessary to use excessive amounts of DCYTA to complex
all the elements. In the event that more than 20 mg of either
calcium or magnesium are present, an ammonia precipitation of
the aluminum will serve to remove the bulk of calcium and
magnesium. The aluminum hydroxide can then be dissolved in
hydrochloric acid and the solution can be extracted with
diethyldithiocarbamate to remove other interfering elements

before titrating with DCYTA. During these tests, however, it
was observed that acetate ion exhibited an unusual masking effect
and that this effect could be used to eliminate the interference
of calcium and magnesium. Therefore if solutions containing
100 mg amounts of either calcium or magnesium and 10.00 mg of
aluminum were titrated with 50 ml of DCYTA (an amount insufficient
to complex all the aluminum and calcium or magnesium), in the
presence of about 2.5 to 3 grams of sodium acetate, the aluminum
was titrated without interference. The aluminum recovered was
10.05 mg in the presence of 100 mg of calcium and 9.95 mg in the
presence of 100 mg of magnesium. A slow colour change occurred
at the end-point but it did not cause difficulty.

In the proposed procedure for the determination of
aluminum in ilmenite slags, the interference of calcium or
magnesium is not expected because the sodium hydroxide removes
the bulk of the calcium and magnesium along with the titanium
and iron, and whatever, if any, left with the aluminum will be
prevented from interfering by the sodium acetate buffer present
in the titration step.

Tests were made on ilmenite slags, containing higher
than usual amounts of magnesia (about 15%), to illustrate the
correctness of the above supposition and these tests and the
results obtained are described in Section E on the analysis of
samples.

(c) Titration after extraction of interfering ions

To establish the effect of several diverse ions on the
recovery of aluminum that was present either singly or in admixture if

the extraction step was included in the procedure, the following

tests were performed. Solutions, buffered to pH 1.8 to 2.0

with acetate and containing the diverse ions and known amounts

of aluminum,were extracted with sodium diethyldithiocarbamate

and chloroform. The aluminum remaining in the aqueous layer was

determined by DCYTA titration. The results of these tests are

given in Table 8.

TABLE 8

Recovery of Aluminum from Synthetic Solutions
of Diverse Ions Extracted with DEDTC

Solution	Amount of Diverse Ion Present	Colour of Carbamate in ppte	in CHCl$_3$	Al Added (mg)	Al Found (mg)
1	None	–	–	10.00	10.00
2	10 mg Cr^{+3}	Violet	Green	10.00	9.97
3	10 mg Ni^{+2}	Yel-Green	Green	10.00	9.94
4	10 mg Mn^{+2}	Pink	Violet	10.00	9.92
5	10 mg V^{+5}	Deep Yellow	Yellow	10.00	10.00
6	10 mg Co^{+2}	Light Green	Deep Green	10.00	9.97
7	10 mg Ti^{+4}	Orange Yellow	Orange	10.00	9.94
8	10 mg Ti^{+4} (+H$_2$O$_2$)	"	"	10.00	9.94
Mixture A	10 mg each of Cu, Ni, Co, Fe and Ti	Mixed Violet to Orange	Mixed	10.00	9.97
Mixture B	10 mg each of Fe, Mn, V, Cr and Ti	Mixed Violet to Orange	Mixed	10.00	9.92
Mixture C	10 mg each of Cu, Zn, Pb and Bi	Mixed	Mixed	10.00	9.95

The results in Table 8 show that aluminum can be

completely separated from diverse interfering ions that are

usually associated with it, if they are present in small amounts.

The results, therefore, suggest that aluminum can be separated from small amounts of the diverse ions remaining after a bulk separation of the latter using either a mercury cathode electrolysis or a sodium hydroxide precipitation separation. Rooney, for example[11], found that pH 2 was optimum for the extraction of small amounts (1 mg) of titanium but did not investigate the extraction of other elements. In a later paper[12] Rooney used DEDTC to extract large amounts (100 mg) of iron and small amounts of other interferents from cast irons.

The solvent extraction of large amounts of titanium is not practical because excessive amounts of DEDTC and chloroform or carbon tetrachloride are required. Iron, on the other hand, is more easily extracted and we have found that several hundred milligrams of iron can be extracted by DEDTC without loss of aluminum. This observation suggests that the determination of aluminum in iron ores can be simplified by eliminating either a mercury cathode electrolysis or a sodium hydroxide precipitation step and going direct to solvent extraction after dissolving the sample.

(d) Effect of cyanide as a masking agent for diverse ions in the titration

Cyanide is used as a masking agent to prevent interference from many elements in titrations with EDTA. Therefore, to explore the possibility of using cyanide in a similar role for the titration of aluminum with DCYTA, the following tests were done. The solution containing the potential interfering element and a known amount of aluminum was treated with 200 mg of NaCN

at pH 2. An excess of DCYTA was added and the excess was back-titrated at pH 5.5 with standard zinc solution and xylenol orange as the indicator. The results of these tests are shown in Table 9.

TABLE 9

Recovery of Aluminum When Cyanide is Used as a Masking
Agent in the Titration of Solutions Containing
Diverse Interfering Ions

Interfering Element (mg)	Al Added (mg)	Apparent Al Found (mg)	Comments
None	10.00	10.00	
100 mg Ca	10.00	8.98	White ppte formed on adding DCYTA
11.2 mg Cd	10.00	12.45	Quant recovery of Al and Cd
20 mg Cu	10.00	1.90	White ppte formed on adding CN^- to Cu^{+2}
20 mg Fe	10.00	5.39	
20 mg Mn	10.00	17.59	
20 mg Zn	10.00	13.78	

The results shown in Table 9 indicate that cyanide is not a suitable masking agent for interfering ions in the titration of aluminum with DCYTA. The complete recovery of aluminum, as indicated by the first result in Table 9, confirms that cyanide does not interfere in the titration of excess DCYTA with zinc solution.

The low values obtained for aluminum in the presence of copper and iron suggested that the zinc may be titrating

ferrocyanide and cuprocyanide after the DCYTA was titrated.
This opinion was confirmed by experiments in which standard
potassium ferrocyanide solutions were titrated at pH 5.5 with a
standard zinc solution using xylenol orange as the indicator.
Stoichiometric equivalent results were obtained. This observation
is of importance in any complexometric back-titration procedure
in which cyanide is used to mask iron or copper etc. by forming
complex cyanides. If these back-titration procedures employ
as a back-titrant reagents such as zinc that are capable of
reacting with these complex cyanides then gross errors will
be experienced. On the other hand, the error will not occur if
a direct titration with EDTA or DCYTA is used.

The low result obtained in the presence of calcium
is due to insufficient DCYTA solution being added, as explained
in Section B.

7. Effect of zirconium in the extraction step

Zirconium is a serious interference in the titration
of aluminum with DCYTA and some zirconium would be introduced
to the sample if the fusions with sodium peroxide were carried
out in zirconium crucibles. The zirconium thus introduced would
undoubtedly be virtually completely removed along with the iron
and titanium during the sodium hydroxide separation steps but
it was desirable to see if zirconium would be extracted with
DEDTC at pH 2.

Accordingly several tests were done in which small
amounts of zirconium were added to known amounts of aluminum
and, after adding 5 ml of glacial acetic acid and 15 ml

of 25 % sodium acetate solution and adjusting the pH to 2, the
solutions were extracted with DEDTC and chloroform. The results
of these tests are shown in Table 10.

TABLE 10

Separation of Zirconium from Aluminum by
Extraction with DEDTC

Test No.	Present Al mg	Zr mg	Al Found (mg)	Difference (mg)
1	20.00	24	20.97	+ 0.97
2	20.00	24	20.42	+ 0.42
3	20.00	2.4	20.62	+ 0.62
4	20.00	2.4	20.37	+ 0.37
5	20.00	nil	20.10	+ 0.10

The bulk of the zirconium is extractable but a small
amount (1 to 3 mg) remains and is titrated as aluminum.

In Tests 1 and 2, a persistent emulsion formed which
was extremely difficult to break up and the high recoveries of
aluminum may be due in part to zirconium trapped in the entrained
emulsion that could not be completely removed. On the other
hand, in Tests 3 and 4 no emulsion was produced and the separation
proceeded smoothly. The results, however, show high recoveries
for aluminum, and the differences are of about the same order
of magnitude as in Tests 1 and 2.

The pH of the solution cannot be maintained constantly
at 2 during the extraction because the addition of the DEDTC
raises the pH and, in the above tests, the pH at the finish of the

extraction step was between 3.5 and 3.7. Thus some hydrolysis of the zirconium may have occurred which prevented its complete extraction. Another possible explanation is the formation of zirconium polymers or acetate species that are not extracted. Complete recovery of the aluminum in the absence of zirconium is shown by the result for Test 5.

As was stated previously, any zirconium present or introduced into the sample by fusion with sodium peroxide in zirconium crucibles would be expected to be removed during the sodium hydroxide separation step, especially if iron and titanium are also present.

Accordingly experiments were carried out to verify this supposition and the results of these experiments are discussed in the next section.

8. Effect of fusion with peroxide in zirconium crucibles on the extraction and titration of aluminum with DCYTA

Experiments were done to establish what effect the fusing of peroxide in zirconium crucibles would have on the extraction, and titration of various amounts of aluminum. In these experiments, 6 grams of sodium peroxide and 5 or 6 pellets of sodium peroxide were fused in zirconium crucibles. The melt was leached with water in Teflon beakers and, after boiling, the solutions were filtered to remove ZrO_2. To the solutions were added known amounts of aluminum and, after addition of acetate buffer and adjustment of pH, the solutions were extracted and titrated with DCYTA to determine the aluminum. The results are compared with those obtained by taking identical amounts of

aluminum and treating them in the same manner with peroxide etc.,
but omitting the fusion step, in Table 11.

TABLE 11

Effect of Fusion with Peroxide in Zirconium Crucibles
on the Extraction and Titration

Aluminum Taken (mg)	Aluminum Found (mg)				
	Fusion in Zr Crucibles	Mean	Without Fusion in Zr Crucibles	Mean	
10.00	10.01, 10.05	10.03	10.01, 10.01	10.01	
20.00	20.06, 20.12	20.09	19.99, 20.00	20.00	
30.00	29.95, 30.03	29.99	29.92, 29.96	29.94	
0.00	0.11, 0.11	0.11	0.04 0.04	0.04	

Table 11 indicates that the fusion of peroxide in
zirconium crucibles has little, if any, effect on the recovery
of aluminum. It is estimated that 50 to 150 mg of zirconium can
be introduced by the fusion attack, depending on the fusion
conditions employed. The results from the fusion step tend to
be slightly higher than those without the fusion step and this
may be caused by the presence of trace amounts of zirconium
that escape the precipitation or extraction stages of the
procedure. The difference in results, however, are very small
so, after correcting each for the blank determination, no signi-
ficant difference is revealed.

B.1   Analysis of samples

The results of the experiments in the foregoing sections
show that aluminum can be determined by titration with DCYTA
after precipitating interfering elements with sodium hydroxide
and extracting with DEDTC and either chloroform or carbon tetra-
chloride. Sodium hydroxide removes most of the iron, titanium,
and magnesium and small amounts of other precipitable ions.
However, small amounts of aluminum are either co-precipitated or
adsorbed on the precipitate, especially in the presence of magnesium'
therefore multiple precipitations are usually required to recover
the aluminum. In addition, elements such as vanadium, chromium,
zinc, and sometimes manganese, copper, and nickel accompany the
aluminum and are found in the filtrate. The proposed extraction
procedure using DEDTC, however, has been shown to be effective
in separating these elements, at the levels expected in ilmenite
ores and slags, from the aluminum; therefore attention was
focused on determining the number of sodium hydroxide precipitations
that would be necessary to recover all the aluminum.

a)   Minimum number of sodium hydroxide precipitations
      required

To establish the minimum number of sodium hydroxide
precipitations required, certified standard samples of iron ore
and ferrotitanium were fused with sodium peroxide and sodium
hydroxide in zirconium crucibles. The melts were leached with
water and the solution was boiled to decompose the peroxide and
then filtered. The precipitate, after washing with hot dilute
(5%) sodium hydroxide solution, was dissolved in dilute hydro-

chloric acid and reprecipitated again with hot (5%) sodium peroxide solution. The above procedures were repeated several times, the first two filtrates from precipitation were combined and the succeeding filtrates were kept separate. The aluminum in each individual fraction was determined by titration with DCYTA after extracting the remaining interfering elements with DEDTC.

The results in Table 12 show that three precipitations with sodium hydroxide-peroxide, including the original fusion-leaching step, are sufficient to recover all the aluminum from the samples. In fact, two precipitations are sufficient to recover all but 0.1 to 0.2 mg of the aluminum and a third precipitation could be omitted unless higher accuracy is desired. The fourth precipitation yields amounts of aluminum that are less than 0.05 mg (i.e. 0.01 % or less on a 0.5-g sample). This amount of aluminum is equivalent to 0.1 ml of 0.02 N DCYTA solution and therefore is at the limits of detection and precision of the method.

b) <u>Recovery of aluminum from synthetic titaniferous slags and from "spiked" ilmenite and iron ore samples</u>

Because no certified standard samples of ilmenite were available, two techniques were applied to check the recovery of aluminum. One technique consisted of preparing synthetic titaniferous slags from pure titanium dioxide and certified standard iron ores containing known amounts of aluminum and the other technique used was to "spike" ilmenite, slags, and iron ores with known amounts of aluminum, and in each case determine the amount of aluminum recovered.

TABLE 12

Recovery of Aluminum in the Filtrates after Successive
Precipitation Steps with Sodium Hydroxide

Sample	Al Found (mg)			Total Al (mg)	% Al Found	Certified % Al	
	1st and 2nd Ppt'n	3rd Ppt'n	4th Ppt'n			Certified	Range
NBS 116A	15.76	0.13	< 0.05	15.89	3.18	3.25	3.15 - 3.34
ferrotitanium	15.85	0.10	< 0.05	15.95	3.19		
BCS 302	18.86	0.16	< 0.05	19.02	3.80	3.83	3.78 - 3.88
Iron Ore	18.78	0.13	< 0.05	18.91	3.78		

1) Several synthetic titaniferous slags were prepared
by mixing 0.5 g of a certified iron ore with 0.5 g of pure
titanium dioxide (NBS TiO_2 #154a) and fusing the mixture with
sodium peroxide in zirconium crucibles. The recovery of aluminum
was determined by the proposed procedure and compared with the
certified amount present.

2) Several ilmenite , titaniferous slag, and iron ore
samples were fused with sodium peroxide in zirconium crucibles
and known amounts of aluminum were added to the samples as
they were being leached with water. The results of these tests
are shown in Tables 13 and 14.

TABLE 13

Recovery of Aluminum from Synthetic Titaniferous Slags

Sample	Al Present Range (mg)	Certified Average Al (mg)	Al Found (mg)
N.B.S. # 26 Crescent iron ore	2.62 - 2.88	2.70	2.82, 2.93
B.C.S. # 302 Northamptonshire iron ore	18.90 - 19.40	19.15	18.81, 18.26
B.C.S. #303 Iron ore sinter	17.85 - 18.15	18.05	17.78, 17.97

TABLE 14

Recovery of Aluminum from "Spiked" Ilmenite Samples
and Iron Ore Samples

Sample No.	Weight of Sample	Al Added (mg)	Al Found (mg)
2174 Ilmenite ore	0.5 g	nil	5.13
	0.5 g	10.00	14.89
	0.5 g	20.00	24.96
3108 Ilmenite slag	0.5 g	nil	16.02
	0.5 g	10.00	25.48
	0.5 g	20.00	36.00
1551 Iron ore	0.1 g	nil	7.92
	0.1 g	6.00	13.63
1561 Iron ore	0.1 g	nil	6.18
	0.1 g	6.00	12.21

The results shown in Tables 13 and 14 show that the recovery of aluminum is essentially complete and within acceptable limits of error. Recoveries from other certified standards are given in Table 18.

c) Comparison of Results Obtained by the Proposed Method with Those Obtained by a Cupferron Gravimetric Method

In addition to the "spiking" technique several of the ilmenite samples were analyzed for aluminum by the proposed method and the results were compared with results obtained by a cupferron method[15]. The results are shown in Table 15.

TABLE 15

Comparison of Results Obtained by DCYTA
Method and Cupferron Method

| Sample | Aluminum Found (% Al_2O_3) | |
	Cupferron Method	DCYTA Method
2827	3.26, 3.40	3.84, 3.80
2832	3.39, 3.37	3.40, 3.39
2834	3.74, 3.74	3.76, 3.76
2846	3.71, 3.64	3.74, 3.78
2958	4.78, 4.71	4.95, 5.05

The results in Table 15 show that the DCYTA method
compares favourably with the cupferron method and the precision
is better in most cases. The DCYTA results are believed to be
more reliable than the cupferron results because the cupferron
procedure is more subject to losses of aluminum. The DCYTA
method is also shorter than the cupferron method and can be
completed in about $1\frac{1}{2}$ days instead of the 3 days required by
the cupferron method, the extra time in the cupferron method
being taken up by the necessity to destroy the cupferron before
the second precipitation of the iron and titanium and
because the aluminum cupferrate must be allowed to stand overnight
before filtering and ignition. In addition, the ignited residue
must be treated with hydrofluoric and sulphuric acids to remove
silica. In the DCYTA method, it is not necessary to remove silica
because it does not interfere, and samples of titaniferous slags
containing 20 to 35 % silica have been analyzed without having
to remove the silica.

d) Determination of Aluminum in High-Magnesium Titaniferous Slags

Titaniferous slags and furnace products differ from ilmenite ores in that they may contain much larger amounts of calcium and magnesium, derived from fluxes and from the furnace lining.

In order to show that the proposed sodium hydroxide precipitation step was sufficient, by itself, to remove the bulk of the calcium and magnesium along with the iron and titanium and to prevent their interference in the titration of aluminum, the following tests were carried out:

Samples of titaniferous slags that contained larger than usual amounts of magnesium (about 15 % MgO instead of 2 to 5 % MgO) were chosen for the test. Duplicate samples were fused with sodium peroxide and sodium hydroxide in zirconium crucibles. The duplicate samples were now divided into two parts, A and B. Samples A were analyzed according to the proposed procedure. Samples B were leached with water and the precipitate was dissolved in hydrochloric acid and boiled to destroy the peroxide. A single ammonia precipitation was then done to separate the aluminum, iron, titanium, etc. from the bulk of the calcium, magnesium, and sodium salts. The solutions were filtered and the filtrates containing the magnesium, calcium, etc. were discarded. The precipitate was dissolved in hot hydrochloric acid solution and the aluminum was separated from the iron, titanium, and zirconium by doing triple precipitations with hot sodium hydroxide-sodium peroxide solutions according to the proposed procedure. The remainder of the analysis was completed in the same manner as for Sample A.

TABLE 16

Determination of Aluminum in High-Magnesium Titaniferous Slags

Sample	Sample Weight	MgO Present	Aluminum Found	
			Sample A Proposed Procedure	Sample B Additional Ammonia Separation to Remove Ca & Mg
3054	0.5 g	15.9 %	2.79 %	2.78 %
3105	0.5 g	13.2 %	2.60 %	2.58 %

The results which are given in Table 16 show that an additional ammonia precipitation step to remove magnesium and calcium is unnecessary, at least at the levels these elements are present in titaniferous slags and ores. If any magnesium and calcium escape the sodium hydroxide separation step the presence of sodium acetate in the titration step is sufficient to prevent their interference.

e)   Analysis of Titaniferous Slags and Ores

The method was applied to the analysis of titaniferous slags and ores and typical results that were obtained on duplicate, weighed samples are shown in Table 17.

As can be seen from the results in Table 17, the reproducibility is good on titaniferous slags containing 0.4 to 3 % aluminum. Greater percentages of aluminum in the slags were not encountered but there is no reason to believe that higher percentages would be less precise.

TABLE 17

Determination of Aluminum in Titaniferous Ores and Slags

Sample No.	Description	% Aluminum Found (duplicate weighed samples)
2613	Ore	0.93, 0.92
2714	"	1.04, 1.02
2715	"	0.75, 0.75
2827	Slag	2.03, 2.01
2832	"	1.80, 1.79
2834	"	1.99, 1.99
2846	"	1.98, 2.00
2850	"	1.93, 1.93
2864	"	2.26, 2.22
2865	"	1.96, 2.04
2958	"	2.62, 2.67
2983	Ore	0.87, 0.87
3008	"	0.38, 0.37
3009	"	1.05, 1.04
3010	"	1.37, 1.38
3104	Slag	3.10, 3.08
3106	"	2.17, 2.15
3107	"	2.86, 2.84
3108	"	3.20, 3.21
3109	"	2.30, 2.32
3141	"	2.80, 2.85

f)   Analysis of Certified Standard Samples

A number of certified standard samples of several iron ores, a plastic clay, and a ferrotitanium were analyzed for aluminum by the proposed method in order to show the applicability of the method to samples other than titaniferous ores and slags.

The results shown in Table 18 are in good agreement with the certified values and generally fall within the reported range of values. The results for the plastic clay appear to be a little higher than the reported values but this may be largely because only a relatively small amount (between 13 and 14 mg) of aluminum was titrated, so an error of + 0.1 mg in the amount of aluminum determined would be sufficient to account for most of the bias.

CONCLUSIONS

The procedure presented in this report is applicable to the determination of aluminum in titaniferous ores and slags. It is a simple and precise method and suitable for routine analyses. The method is applicable to the determination of from 0.5 to 300 mg of aluminum. Interfering elements are readily removed by sodium hydroxide-sodium peroxide separation and by extraction with sodium diethyldithiocarbamate and chloroform. An advantage of the method is that it is unnecessary to remove silica or to destroy organic material remaining after the extraction. The method is also applicable to iron ores and slags, ferrotitanium alloys, and plastic clays. A later section of this report describes the application of the procedure to

TABLE 18

Results on the Determination of Aluminum in
Certified Standard Samples

| Sample No. | Description | % Al_2O_3 | | Found |
| | | Reported | | |
		Range	Cert.Value	
NBS 26	Crescent Iron Ore	0.99- 1.09	1.02	0.98,0.99
BCS 175/1	Liberian Iron Ore	1.05- 1.19	1.10	1.09,1.10
BCS 302	Northamptonshire Iron Ore	7.15- 7.34	7.24	7.19,7.15
NBS 98	Plastic Clay	25.44-25.68	25.54	**25.80,25.75**,25.75 25.60,25.38,25.77
NBS 116A	Ferrotitanium	3.15-3.34(% Al)	3.25(% Al)	3.18,3.19 (% Al)

to the determination of aluminum in chromites, coke fly ash, uranium ores, tin ores, manganese ores and slags, and various minerals (Part IV B).

ACKNOWLEDGEMENTS

The author acknowledges the capable assistance of G. Zechanowitsch, C. Lalonde, and L. Desjardins, Technicians, Chemical Analysis Section, Extraction Metallurgy Division, on testing and analyzing the samples. In particular, the observations and suggestions of Mr. Lalonde were helpful in devising the techniques used to overcome the difficulties in the determination when an excess of calcium or magnesium were present or when an insufficient amount of DCYTA was added. Mr. Zechanowitsch, whose careful work materially aided in establishing the optimum conditions for the precipitation and extraction steps, also deter-mined aluminum in a number of the samples by a cupferron method for purposes of comparison. Mr. Desjardins assisted in the early stages of the investigation.

REFERENCES

1. Hitchen, A., "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" Mines Branch Technical Bulletin TB 124, Department of Energy, Mines and Resources, Ottawa, Canada, June 1970.

2. Pritchard, D.T., Anal. Chim. Acta. 32, 184 (1965).

3. Burke, K.E., and Davis, C.M., Anal. Chem. 36, 172 (1964).

4. Pribil, R., and Vesely, V., Chemist-Analyst 55, 68 (1966).

5. Corbett, J.A., and Guerin, B.D., The Analyst 91, 490 (1966).

6. Kiss, E., Anal. Chim. Acta., 39, 223 (1967).

7. Evans, W. H., The Analyst 92, 685 (1967).

8. Nestoridis, A., ibid. 95, 51 (1970).

9. Nestoridis, A., Anal. Chim. Acta 49, 335 (1970).

10. Morrison, G. H., and Freiser, H.,"Solvent Extraction in
     Analytical Chemistry", John Wiley and Sons, Inc.,
     New York, 1957.

11. Rooney, R.C., Anal. Chim. Acta 19, 428 (1958).

12. Rooney, R.C., The Analyst 83, 546 (1958).

13. Pribil, R., and Vesely, V., Talanta 9, 23 (1962).

14. Pribil, R., and Vesely, V., ibid. 10, 1287 (1963).

15. Murphy, T.J., Clabaugh, W.S., and Gilchrist, R., J. of
     Research of Nat. Bur. Standards, A-Phys. and Chem.,
     64A, No. 6, 535 (Nov.-Dec. 1960).