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DEPARTMENT OF
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MINES BRANCH
OTTAWA

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

*PART II: RAPID METHODS FOR THE
DETERMINATION OF IRON AND TITANIUM
IN ILMENITE ORES AND SLAGS*

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A. HITCHEN

EXTRACTION METALLURGY DIVISION

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

PART II: RAPID METHODS FOR THE DETERMINATION OF IRON
AND TITANIUM IN ILMENITE ORES AND SLAGS

by

A. Hitchen*

SUMMARY

Procedures are described for the rapid determination of titanium and iron in ilmenite ores and slags. Three fusion procedures are described which are suitable for decomposing the material and taking it into solution. Iron is determined by dichromate titration after reduction in a silver reductor. The combined titanium and iron titre is determined by dichromate titration after reduction with liquid zinc amalgam, and the titanium is then found by difference. The accuracy and precision of the methods are satisfactory for routine control purposes and technicians may easily be trained in their use. A single analysis for both titanium and iron may be completed in between 45 and 60 minutes.

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

Direction des mines
Bulletin technique TB 121

MÉTHODES D'ANALYSE DE L'ILMÉNITE, DES LAITIERS
TITANIFÈRES ET D'AUTRES SCORIES PROVENANT DES FOURS
ÉLECTRIQUES. PARTIE II: MÉTHODES DE TITRAGE RAPIDE DU
FER ET DU TITANE DANS LES MINÉRAIS D'ILMÉNITE
ET LES LAITIERS

par

A. Hitchen*

RÉSUMÉ

L'auteur examine certaines méthodes de titrage rapide du fer et du titane dans les laitiers et les minerais d'ilménite. Il décrit trois méthodes de fusion qui peuvent servir à décomposer le matériau en vue d'en faire une solution. La teneur en fer est établie par titrage au bichromate après réduction dans l'argent. La teneur combinée en fer et en titane est déterminée par titrage au bichromate après réduction dans un amalgame de zinc liquide, et on obtient ensuite la teneur en titane par soustraction. Ces méthodes sont assez précises pour les vérifications ordinaires et les techniciens peuvent facilement en apprendre l'usage. Un seul titrage de fer et de titane peut être effectué en 45 à 60 minutes.

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

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INTRODUCTION

Part I of this series (Technical Bulletin TB 120, March 1970) (21), has reviewed some of the methods used for the determination of titanium and/or iron and their application to the analysis of ilmenite and other iron- or titanium-bearing materials. Of the methods that were reviewed, those which involved a simple reduction step and a titrimetric finish were considered to offer the greatest possibilities on the basis of speed, simplicity, suitable accuracy, and the ease with which technicians could be trained in their use.

The methods proposed by Fonseka and de Silva (1) appeared to be the most applicable and these methods were investigated initially.. S. Suzuki (2), and Hope et al. (3), reduced titanium with liquid zinc amalgam, using a simple separatory funnel instead of a Nakazono reductor (4), and the procedure described in this report employs a similar technique to reduce iron and titanium. Iron is determined on a separate aliquot by using a silver reductor to reduce it selectively. Both of the reduced solutions are titrated with standard potassium dichromate solution, using diphenylamine sulphonate as the indicator. The titanium content is then determined from the difference in the two titrations.

APPARATUS AND REAGENTS

Apparatus

Separatory funnels, 250 ml, Squibb type, Teflon stopcock.

Burette, 50 ml.

Nitrogen gas cylinder equipped with suitable regulator, etc.

Silver reductor, prepare according to references 5,6,7, and 8.

Platinum crucibles, capacity 30 to 40 ml.

Zirconium crucibles.

Silica or Vycor crucibles.

Reagents

Carbon tetrachloride, reagent grade.

Ferric sulphate, reagent grade, 5% w/v in 5% v/v sulphuric acid solution. Deaerate before use by bubbling nitrogen gas through the solution in a graduated cylinder.

Hydrochloric acid, 36%, reagent grade.

Liquid zinc amalgam.

Wash 150 grams of reagent-grade, 20-mesh zinc granules with dilute sulphuric acid, and then warm for 1 hour on a steam plate in a hood with about 250 ml of mercury and 50 ml of 25% v/v sulphuric acid. Cool, wash with dilute (2%) sulphuric acid, and separate the liquid portion of the amalgam from the solid by means of a separatory funnel. Reserve the solid portion for the

preparation of more amalgam. Store the liquid amalgam under dilute (2%) sulphuric acid, and wash it with the dilute acid before use.

Phosphoric acid, 85%, reagent grade.

Potassium dichromate - 0.05 or 0.10 N solutions. Prepare by dissolving 2.4516 or 4.9032 grams of the primary standard-grade reagent in distilled water and dilute to 1 litre.

Potassium pyrosulphate, reagent grade.

Sodium carbonate - borax fusion mixture.

Mix together equal parts by weight of reagent-grade anhydrous sodium carbonate and anhydrous sodium borate powder. Do not use hydrated crystals of either compound, otherwise spattering will occur upon fusing.

Sodium diphenylamine sulphonate indicator, Analoid tablets.

Sodium hydroxide pellets, reagent grade.

Sodium peroxide powder, reagent grade.

Sulphuric acid, 98%, reagent grade.

Sulphuric acid, 1 M, reagent grade. Deaerate immediately before use by bubbling nitrogen gas through the solution contained in a small wash bottle.

Sulphuric acid-hydrochloric acid mixture. Mix equal volumes of 1 M HCl and 1 M H₂SO₄. This solution is used to wash the silver reductor.

ANALYSIS PROCEDURES

1. Sample Dissolution (Slags and Ilmenite Ores)

Weigh a 0.5- to 1-gram sample and transfer it to a 40-ml platinum crucible. Ignite the sample at red heat for about 5 minutes to remove any coke or carbonaceous material. Cool, add 10 grams of a 1:1 mixture of sodium carbonate-borax, and mix thoroughly with the sample, using a glass rod or spatula. Brush back into the crucible any particles adhering to the rod or spatula. Fuse the sample and mixture over a Fisher burner at bright-red heat, with occasional swirling, until the sample is completely decomposed (about 10 minutes). Cool, transfer the crucible to a 400-ml beaker, cover the beaker, and leach with about 100 ml of 25% v/v hot sulphuric acid. Heat the solution on the hot plate until the sample is dissolved and the solution is clear. Transfer the solution to a 250-ml volumetric flask, rinse the crucible and beaker with dilute (5-10% v/v) sulphuric acid, cool, and dilute to volume with water. Mix the sample well and take 50- or 100-ml aliquots for the determination of iron and titanium. The solution at this point should be clear without any sign of a precipitate*.

*The presence of a precipitate at this stage is indicative of incomplete fusion of the sample, or, as is more likely, the presence of large amounts of silica, in which case an additional 5 grams of Na_2CO_3 should be used in the fusion.

2. The Determination of Iron

Activate the silver reductor before use, by washing the column with 50 ml of 0.5 M HCl + 0.5 M H₂SO₄ wash solution. Transfer a 50-ml aliquot of the sample solution to a small beaker and add a few drops of concentrated hydrochloric acid. Pass this solution through the silver reductor and collect the effluent in a clean 250-ml beaker. Rinse the column with 50 to 60 ml of the 0.5 M HCl + 0.5 M H₂SO₄ wash solution, collecting the rinsings in the same beaker. Add 5 ml of concentrated (85%) phosphoric acid and 1 diphenylamine sulphonate indicator tablet. Titrate the iron (II) with standard dichromate solution to a violet end-point. Record the volume of dichromate solution used as (A). Calculate the percentage of iron, using the factor of 1 ml 0.05 N K₂Cr₂O₇ = 2.792 mg Fe.

3. The Determination of Titanium plus Iron

Transfer a 50-ml aliquot of the sample solution to a 250-ml, Squibb-type separatory funnel. Add 15 to 20 ml of liquid zinc amalgam. Displace the air in the funnel with a stream of nitrogen from a cylinder, using a glass tube suspended in the funnel with the open end just above the surface of the sample. Remove the tube and stopper the funnel immediately. Shake the funnel vigorously for 1½ to 2 minutes to reduce both the titanium and iron. Rinse the stopper with a small amount of previously deaerated 1 M sulphuric acid solution. Add 15 to 20 ml of carbon

tetrachloride, as recommended by Smith (9), to separate the zinc amalgam from the aqueous solution, and drain the amalgam, together with a portion of the tetrachloride, into a small beaker*.

Immediately add 30 ml of deaerated ferric sulphate solution to the sample solution in the funnel and mix by swirling. Add 5 ml of concentrated (85%) phosphoric acid and 1 diphenylamine sulphonate tablet. Without removing the solution from the funnel, titrate the iron (II) produced with standard dichromate solution to a violet end-point. Record the volume of dichromate solution used as (B). Calculate the volume of dichromate solution (C) used to titrate the titanium by subtracting the volume of dichromate solution used to titrate the iron (II) obtained from the silver reductor, i.e. $B - A = C$. Calculate the percentage of titanium from the volume C, using the factor of 1 ml 0.05 N $K_2Cr_2O_7 = 2.395$ mg Ti.

PRELIMINARY INVESTIGATIONS

1. Determination of Iron

Initially, attempts were made to determine iron in ilmenite ores by reducing the iron with stannous chloride, which is said not to reduce titanium (5). Samples weighing 0.2 gram were fused with potassium pyrosulphate in platinum crucibles and

*This amalgam may be recovered, washed with dilute (2%) sulphuric acid, and reused several times before discarding.

leached with dilute sulphuric acid and a little hydrochloric acid to give the yellow iron (III) chloride. The siliceous residue was filtered off and ignited in platinum, and after the silica was removed in the usual way, the residue was fused with potassium pyrosulphate, dissolved, and added to the original filtrate. The iron (III) was then reduced carefully with a few drops of stannous chloride in excess. After removal of the excess of stannous chloride with mercuric chloride, the ferrous ion was titrated with a standard solution of dichromate, using diphenylamine sulphonate as indicator.

With some samples little or no trouble was encountered using this procedure, but with others, although the yellow colour of the iron initially disappeared, on continued addition of stannous chloride a deep brown-orange colour began to appear. The appearance of this secondary coloration made it difficult to judge when sufficient stannous chloride had been added to reduce all the iron. In the subsequent titration with potassium dichromate, gross errors were obtained.

It was established that the effect was not due to titanium, vanadium, or organic matter. Platinum was suspected because of its known interference with the stannous chloride reduction (reference 5, p. 392) and because platinum crucibles had been used. This was confirmed by experiments in which portions of potassium pyrosulphate were fused in platinum crucibles and the

melt was dissolved in dilute sulphuric acid containing a small amount of hydrochloric acid. Stannous chloride was added and a deep brown-orange colour appeared as before, proving that the trouble was due to the presence of dissolved platinum. The depth of the brown colour was dependent on how much pyrosulphate was used and for how long the fusion was carried out.

Since the interference in the stannous chloride method came from the platinum crucible the use of other types of crucible was considered, but for various reasons they cannot be used. The initial fusion of the sample with pyrosulphate can be done in Vycor, porcelain or silica crucibles, for example, but the treatment of the insoluble residue for the recovery of iron and titanium requires the use of hydrofluoric acid to remove the silica, and for this purpose platinum is necessary. Subsequent fusion of the residue with pyrosulphate will thus introduce platinum in any case. On the other hand, fusion of the sample with an alkaline flux in platinum can also dissolve small amounts of platinum, and Vycor, porcelain or silica crucibles cannot be used because they will be destroyed. For the above reasons, further investigation of the stannous chloride method for the determination of iron was discontinued.

Fusions with alkaline fluxes in zirconium crucibles can be resorted to - for example, if it is necessary to use the stannous chloride method - but experience with the silver reductor

has proven that the latter is so much simpler and easier to use that the stannous chloride reduction method was not reconsidered. Other reasons for avoiding the use of zirconium crucibles are given on page 18 of this bulletin.

To overcome this serious interference by platinum, it was decided to investigate the use of a silver reductor to determine iron. A number of synthetic solutions containing known amounts of iron and titanium were prepared in 10% sulphuric acid containing a small amount of hydrochloric acid, i.e. about 1% v/v*. These solutions were passed through the silver reductor and the iron (II) produced was titrated with standard dichromate and diphenylamine sulphonate indicator. Reduction and recovery of the iron were complete, with no evidence of interference from the titanium.

Accordingly, solutions of the ilmenite ores were prepared, duplicate samples were passed through the silver reductor, and the iron was determined. Very good agreement between the duplicate samples was obtained and no brown colour due to reduced platinum salts was observed.

Typical results obtained on ilmenite samples analyzed for iron by the stannous chloride method and by the silver reductor method are compared in Table 1.

*Hydrochloric acid was added because a small amount appeared to be necessary to accomplish complete reduction of the iron in the silver reductor. Moreover, the hydrochloric acid had the additional advantage of providing a deep yellow colour (due to ferric chloride) that was useful for seeing that the reductor was functioning properly.

TABLE 1

Determination of Iron in Ilmenite Ores by Stannous Chloride Reduction Method and Silver Reductor Method

Sample	%Fe	
	Stannous Chloride Method	Silver Reductor Method
3162	40.86, 41.40	39.94, 39.92
3163	51.18, 48.71	40.00, 42.16
3164	52.65, 45.14	42.35, 42.31
3165	53.22, 54.35	41.99, 41.59
3166	52.93, 54.75	39.88, 40.09
3167	44.90, 44.40	40.04, 40.76
3168	49.70, 50.06	49.02, 49.25
3169	49.25, 52.54	50.38, 50.10
3170	49.52, 61.89	50.44, 50.18
3197	57.78, 63.10	50.87, 50.02

The results in Table 1 show that the silver reductor method has a much greater precision than the stannous chloride method. The gross errors caused by the presence of platinum have been eliminated. Further investigations using the silver reductor were considered unnecessary, since the efficiency and accuracy of the method had been well established by several previous authors (1,11,12).

2. Determination of Titanium plus Iron

Attention was now turned to investigating the use of the Jones reductor to reduce the titanium and iron. Synthetic solutions containing known amounts of titanium and/or iron were prepared in 10% sulphuric acid together with a small amount of hydrochloric acid, i.e. about 1% v/v. These solutions were warmed slightly and passed through the Jones reductor, and the effluent was collected in a previously deaerated solution of 5% ferric sulphate in 5% v/v sulphuric acid.

The resultant iron (II) was titrated with standard 0.1 N dichromate solution with diphenylamine sulphonate indicator. Corrections were made for the amount of dichromate required to titrate the iron present. The results of these tests are given in Table 2.

The results in Table 2 show that titanium was either not completely reduced in the column, or partially reoxidized by air that was incompletely removed from the ferric sulphate collecting solution, or was perhaps reoxidized due to the formation of peroxide in the reductor. In addition, mechanical difficulties were encountered in using a Jones reductor, due to hydrogen-gas formation. The gas bubbles slowed the rate at which the solution could be passed through the column and, in an attempt to speed up the flow rate, a slight suction was applied to the bottom of the reductor as recommended by Hillebrand (5). The increased flow rate may have resulted in incomplete reduction of the titanium.

TABLE 2

Determination of Titanium in the Presence of Iron
after Reduction with the Jones Reductor

Ti Present mg	Fe Present mg	Std. 0.1 N $K_2Cr_2O_7$ used		Ti Found mg	Diff. mg	% Ti Recovery
		Total ml	Net ml for Ti			
59.71	Nil	12.20	12.20	58.44	-1.27	97.87
"	"	12.20	12.20	58.44	-1.27	97.87
"	30.43	17.50	12.05	57.72	-1.99	96.67
"	30.43	17.75	12.30	58.92	-0.79	98.68
"	30.43	17.30	11.85	56.76	-2.95	95.06
"	30.43	17.60	12.15	58.20	-1.51	97.47
119.42	30.43	30.05	24.60	117.83	-1.59	98.67

In view of the low recoveries obtained by use of the Jones reductor, it was decided to try a liquid zinc amalgam technique to reduce the iron and titanium and compare the results with those obtained by the Jones reductor. The reduction technique used was that which is proposed in this report. After addition of excess ferric sulphate solution the resultant iron (II) was titrated with standard 0.1 N dichromate as before. Corrections were made for the amount of dichromate required to titrate the iron present. The results of these tests are given in Table 3.

The results in Table 3 show that 99 to 99.5% of the titanium is reduced or recovered as compared to 95 to 98% using the Jones reductor. The slightly low recoveries from using the

TABLE 3

Determination of Titanium in the Presence of Iron
after Reduction with Liquid Zinc Amalgam

Ti Present mg	Fe Present mg	Std. 0.1 N $K_2Cr_2O_7$ used		Ti Found mg	Diff. mg	% Ti Recovery
		Total ml	Net ml for Ti			
59.71	Nil	12.35	12.35	59.16	-0.55	99.08
59.71	Nil	12.40	12.40	59.40	-0.31	99.48
119.42	Nil	24.70	24.70	118.31	-1.11	99.07
59.71	30.43	17.85	12.40	59.40	-0.31	99.48
119.42	30.43	30.18	24.73	118.46	-0.96	99.20

liquid zinc amalgam technique are in agreement with the observations of Khan and Stephen (13) in their work with iron, and with Chalmers, Edmond and Moser (14). The results could possibly be improved if more scrupulous care was taken to remove oxygen from the solutions, or from the nitrogen gas as recommended by Khan and Stephen, but this was not considered necessary for the purpose for which the method was intended. In view of the better reduction with the liquid zinc amalgam, and of the ease with which it could be carried out, this procedure was the one that was finally adopted for routine use.

3. Fusion Procedures

In order to assess the precision of the method, a number of ilmenite ore and titaniferous slag samples were dissolved

and the iron and titanium were determined. The samples were brought into solution by using three different fusion procedures, and the values obtained for iron and titanium were compared. The three fusion procedures used are as follows:

A. Sodium carbonate-borax fusion

Samples weighing 0.5 to 1.0 g were ignited and then mixed and fused with 10 g of a 1:1 mixture of the flux in a platinum crucible. The melt was dissolved in 100 ml of 25% v/v sulphuric acid solution and diluted to 250 ml in a volumetric flask.

B. Sodium peroxide-sodium hydroxide fusion

Samples weighing 0.5 to 1.0 g were fused with 6 g of sodium peroxide and a few pellets of sodium hydroxide in a zirconium crucible. The melt was digested with a small volume of water and finally dissolved in an excess of hydrochloric or sulphuric acid sufficient to give a final concentration of about 10% v/v when diluted to 250 ml in a volumetric flask. The solution was boiled to decompose peroxides and then cooled and diluted to volume.

C. Potassium pyrosulphate fusion

Samples weighing 0.5 to 1.0 g were fused with 7 to 10 g of potassium pyrosulphate in a platinum or Vycor crucible.

The melt was digested in 100 ml of 25% v/v sulphuric acid solution and the insoluble siliceous residue was filtered off. The paper and residue were ignited in a platinum crucible, and treated with HF + H₂SO₄ to volatilize silica. The residue remaining was fused with a small amount of pyrosulphate, combined with the original solution, and the whole was diluted to 250 ml in a volumetric flask.

The results of these tests are shown in Table 4.

The results in Table 4 show that the titanium and iron can be determined with satisfactory precision, using any one of the three fluxes described. The carbonate-borax fusion has the advantage that all the sample is soluble in the acid leach solution without further treatment. The peroxide fusion requires that the acidified solution be boiled to decompose the peroxide. The pyrosulphate fusion has the disadvantage of being more lengthy because of the need to remove silica and recover iron and titanium from the residue. Of the three fusion techniques the carbonate-borax is the simplest to use. However, it was found that the platinum crucibles were contaminated by small amounts of iron, which were very difficult to remove except by repeated ignitions and fusions with pyrosulphate and boiling in hydrochloric acid solution. The contamination is probably caused by the absorption of ferrous iron during the fusion with the carbonate-borax flux.

TABLE 4

Comparison of Analysis Results for Titanium and Iron
after using Three Fusion Procedures to Decompose Ilmenite
Ore and Slags

Sample	Fusion Method	%TiO ₂	%Fe
2358 Slag	Na ₂ CO ₃ - Borax	-	-
	Na ₂ O ₂ - NaOH	44.14	10.75
	K ₂ S ₂ O ₇	44.68, 45.15	10.63, 10.66
2359 Slag	Na ₂ CO ₃ - Borax	60.95	2.05
	Na ₂ O ₂ - NaOH	60.42, 60.42	1.89, 2.02
	K ₂ S ₂ O ₇	60.77, 60.34	1.87, 1.81
2360 Slag	Na ₂ CO ₃ - Borax	48.50, 48.34	2.24, 2.09
	Na ₂ O ₂ - NaOH	48.50, 48.34	2.24, 2.09
	K ₂ S ₂ O ₇	47.94, 48.04,	2.10, 2.10,
		48.58	2.85
2421 Slag	K ₂ S ₂ O ₇	71.23, 71.31	10.75, 10.72
2530 Slag	Na ₂ CO ₃ - Borax	44.35, 44.29	10.33, 10.32
2531 Slag	Na ₂ CO ₃ - Borax	60.45, 60.97	1.68, 1.65
2532 Slag	Na ₂ CO ₃ - Borax	44.67, 44.55	2.26, 2.37
2613 Ore	Na ₂ CO ₃ - Borax	36.80, 37.07	40.76, 40.76
	Na ₂ O ₂ - NaOH	36.76, 36.59,	41.02, 41.04,
		36.35	41.04
	K ₂ S ₂ O ₇ - analyst A	37.15, 36.00,	40.76, 41.04,
		37.15	41.04
	K ₂ S ₂ O ₇ - analyst B	37.32, 36.92	40.90, 40.82

Shell (15) has reported similar losses of iron to platinum crucibles when silicates, limestones and refractory oxides were fused with carbonate or carbonate-borax mixtures. He

recommended the use of cast silver crucibles, instead of platinum, for fusion of the samples. In a later paper (16), he claimed that the fusions could be performed in platinum crucibles provided an oxidizing atmosphere was maintained. No losses of iron were observed if the samples were fused in an electric furnace or if the silica residue was ignited in an electric furnace after a preliminary fusion of the sample over a gas burner. Loss of iron always occurred if flame fusion of the sample was followed by flame ignition of the silica residue.

During the course of this work a comprehensive investigation by Russell, Spangenburg and Steele (17), of the use of platinum ware for silicate analysis, appeared in the literature. Serious contamination of the platinum with iron was noted by these workers when fusions of materials containing iron were made with alkaline fluxes. The use of crucibles made from a platinum:gold (95:5) alloy was recommended instead of the usual platinum crucibles. If platinum crucibles were to be used, a sinter at 440°C with a mixture of sodium peroxide and sodium hydroxide was preferred by them because platinum attack was reduced and less iron was absorbed.

The contamination of the crucibles by iron in our work was relatively small, however; and for control purposes the error which was tolerable was neglected. The results in Table 4 do not indicate any bias in either direction when the fusions are made

in platinum with the carbonate-borax flux. Nevertheless, the crucibles were ignited and fused once with pyrosulphate before being used again, to minimize the possible error due to carry-over of iron from one sample to the next. For accurate work it would be better to avoid platinum ware, but this will necessitate some sacrifice in speed. The sodium peroxide-sodium hydroxide procedure would be a suitable alternative if only titanium and iron are to be determined, otherwise the zirconium introduced from the crucible may cause difficulty in determining certain other elements that may be desired.

DISCUSSION

A. The Silver Reductor

Hillebrand et al. (5) state that solutions passed through a silver reductor must be free from platinum salts, because these are reduced to platinum which, in turn, forms a platinum-silver couple and leads to unwanted reductions, e.g., reduction of titanium to the trivalent state. Miller and Chalmers (12), on the other hand, state that platinum (IV) introduced by the fusion is reduced to platinum (II), is carried through the column, and slowly reacts with ceric sulphate to give a fading end-point.

In the proposed method, the samples are fused with a sodium carbonate-borax flux in platinum crucibles. Thus it is

possible for small amounts of platinum to be dissolved and be present in the sample aliquot taken for analysis. Based on the actual aliquot taken, the amount of platinum thus present would be only a fraction of the amount of platinum dissolved during the fusion. It is conceivable, however, that after a large number of samples are passed through the column, and if platinum is deposited, the platinum could gradually build up on the silver reductor to a point where it would contribute a significant error. Very little work, if any, appears to have been done relating to this aspect of the problem and to establish to what extent the interference actually is serious.

Hillebrand et al. (5), in the first edition of their book (1929), suggested the addition of a small amount of platinum in the preparation of a Jones reductor to increase its activity, but this suggestion does not appear in their second edition.

No interference due to platinum was noticed with the relatively small numbers of samples that were analyzed during the short period of time in which the project was carried out. Darkening slowly occurred at the top of the silver reductor column and gradually worked its way down, but this darkening may have been due to the photodecomposition of silver salts such as silver chloride rather than the deposition of platinum. When the darkening had progressed about half-way down the column, it was replaced in use with a new silver reductor. To avoid the

possibility of serious interference from platinum deposition, more frequent replacement of the silver reductor may be necessary, but in view of the lack of information no guidelines can be laid down. Alternatively, fusion with a sodium peroxide-sodium hydroxide flux in zirconium crucibles, or fusion with potassium pyrosulphate in silica or porcelain crucibles, could be used to avoid the introduction of platinum.

According to Miller and Chalmers (12), if vanadium, platinum or palladium is present, a sharp end-point will be observed when all the ferrous iron is titrated. This end-point fades as slow oxidation of the lower valency states of these elements takes place. Our experience with ilmenite ores and slags that contain small amounts, i.e. about 0.1%, of vanadium confirms the above remarks. Our samples would also contain small amounts of platinum introduced by the fusion step, and whether the fading end-point is due primarily to vanadium or to platinum is not known but, presumably, both elements contribute in some degree. The ferrous end-point is very sharp, however, and the subsequent fading of this end-point is not at all serious. Some post-titration precipitation of iron and titanium phosphates occurs, but during the titration no precipitate appears and no interference is noticeable. The same remarks hold true for solutions obtained from the liquid zinc amalgam reduction step.

B. The Liquid Zinc Amalgam Reductor

In order to obtain reproducible results it is necessary to exclude air during the reduction step. Failure to take this precaution will lead to results that are erratic and several per cent low. These observations are in agreement with those of Pilkington and Smith (18). The necessary precautions can be easily carried by the proposed procedure without elaborate apparatus.

In view of the poisonous nature of mercury vapour, which is a cumulative effect, most authors prefer a Jones reductor for most reductions in routine work. However, in determinations for elements like titanium, liquid amalgams offer certain advantages such as:

- 1) Complete reduction can be achieved in a few minutes without the formation of troublesome hydrogen-gas bubbles as is the case with a Jones reductor.
- 2) Very reliable results can be obtained.
- 3) The amalgams can be used repeatedly several times before exhaustion.
- 4) Exclusion of air from the reduction apparatus is easily carried out.
- 5) It is unnecessary to transfer the sample from one container to another to carry out the titration.

- 6) The volume of solution to be titrated is much less because no large volume of wash solution is used as in the case of a column or Jones reductor.

While there is some danger of spillage when transferring the amalgam at different points in the procedure, this danger can be easily prevented by exercising due care.

The proposed method for titanium, in common with all methods using aluminum, zinc amalgam or the Jones reductor, is subject to interference by vanadium, chromium, molybdenum, uranium or other elements whose ions are reduced by zinc amalgam. Vanadium is reduced to vanadium (III) or vanadium (II), and chromium (III) is partially reduced to chromium (II) (19), all of which will titrate in the subsequent dichromate titration for iron plus titanium and lead to high results. Since, in the silver reductor step (for the separate determination of iron), chromium (III) is not reduced, while vanadium (V) is reduced to vanadium (IV) which is not titrated by dichromate, the burden of the error will fall on the titanium figure. The amount of vanadium and chromium is usually less than 0.5% in most high-grade ores and slags, and because of the similarity in the volumetric factors with that of titanium the error will be of the same order. Because of the non-quantitative nature of the reductions, they must be ignored or corrected for by assuming quantitative reduction*.

*A similar but lesser interference occurs when stannous chloride is used as the reductant in obtaining the iron value (20).

CONCLUSIONS

Iron in ilmenite ores and slags can be determined by reducing it with a silver reductor without interference by titanium. The sum of titanium and iron can be determined by reducing these elements with liquid zinc amalgam. Titanium is determined by difference. The results obtained by these procedures are sufficiently rapid, accurate and precise for routine analysis and control of electric furnace smelting conditions.

A decided advantage of the proposed procedure for using liquid zinc amalgams over other suggested procedures is the use of a simple separatory funnel in which to carry out the reduction and titration. The addition of carbon tetrachloride to the funnel after the reduction step facilitates the removal of the amalgam without loss of any of the reduced solution or, conversely, without retention of small droplets of the amalgam with the solution. It has the added advantage that transfer of the solution to another container for titration is unnecessary. Complete removal of excess carbon tetrachloride is also unnecessary, because it does not interfere. Large quantities of borax do not interfere with either the reduction or the titration and, in some instances, may be beneficial if, for example, fluorspar is present due to its use as a flux in smelting operations.

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