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*METHODS FOR THE ANALYSIS OF
ILMENITE, TITANIUM-BEARING SLAGS
AND OTHER ELECTRIC FURNACE SLAGS
PART 1: A REVIEW AND COMMENTS ON
SOME TYPICAL METHODS FOR THE
DETERMINATION OF TITANIUM AND IRON*

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

PART I: A REVIEW AND COMMENTS ON SOME TYPICAL METHODS
FOR THE DETERMINATION OF TITANIUM AND IRON

by

A. Hitchen*

SUMMARY

A review has been made of some typical methods for the determination of titanium and iron. Comments on these methods have been made with the view of deciding on their applicability to the determination of titanium and iron in ilmenite ores and slags. The advantages and disadvantages of some of the methods are discussed.

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Direction des mines

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MÉTHODES D'ANALYSE DE L'ILMÉNITE, DES LAITIERS
TITANIFÈRES ET D'AUTRES LAITIERS PROVENANT DES FOURS
ÉLECTRIQUES. PARTIE I: REVUE ET COMMENTAIRES AU
SUJET DE QUELQUES MÉTHODES-TYPE DE
TITRAGE DU FER ET DU TITANE.

par

A. Hitchen*

RÉSUMÉ

L'auteur passe en revue quelques méthodes-type de titrage du fer et du titane. Il discute ces méthodes en vue de déterminer leurs possibilités d'application au titrage du fer et du titane dans les minerais d'ilménite et les laitiers.

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INTRODUCTION

As part of a research program concerned with the smelting of ilmenite ore to produce pig iron and an upgraded titania slag suitable for pigment purposes, the analysis of the feed material and the slag for titanium, iron, and other constituents was required at various stages of the smelting operation. In order to assess and control the smelting conditions and the quality of the slag, it was required that the slag material be analyzed for titanium and iron at frequent intervals, i.e. every 1 to 2 hours, on a 24-hour basis for several weeks.

A REVIEW OF SOME TYPICAL METHODS FOR THE DETERMINATION OF TITANIUM AND IRON

A search of the literature revealed that there is comparatively little information concerning the analysis of ilmenite ores or titaniferous slags. There are, however, many methods for the determination of iron and/or titanium in other materials. These methods vary considerably in technique and depend greatly on whether small or large amounts of iron or titanium are to be determined, the nature of the material to be analyzed, and how much sample is available for analysis.

The methods under review here are restricted to those involving macro amounts of sample, i.e. more than about

0.05 to 0.1 gram, with the exception of a few other methods which are felt to be pertinent and of interest. Some of the macro methods have been modified or adapted for the purpose of micro and semi-micro analysis, and, so far as theoretical principles are concerned, the only differences are in the apparatus used and the technique followed.

Procedures for the determination of major or macro quantities of titanium and/or iron fall largely into two categories, namely titrimetric and gravimetric, although procedures employing spectrophotometry, differential spectrophotometry, polarography, coulometry, etc., have also been used in certain applications.

1. Methods for the Determination of Iron

Iron seldom occurs alone and most of the methods described in the literature are not specific for iron. Gravimetric methods nearly always require a preliminary separation, whereas some titrimetric methods are almost without interference. In gravimetric methods the iron is often precipitated as the hydrated ferric oxide or a basic ferric salt, using reagents such as ammonia (1), formate (2,3), or benzoate (1,4). Cupferron has also been used as a precipitant for iron (5). In most gravimetric methods the precipitate is ignited and weighed as ferric oxide.

The simplest and best of the titrimetric methods appear to be the EDTA or chelometric methods (6,7,8a) and a few of the redox reactions for which separations are unnecessary.

Small amounts of iron can be determined spectrophotometrically using 1,10-phenanthroline (9,10), thiocyanate (9), or Tiron (11). Solvent extraction is often used to isolate the iron from interfering elements before the spectrophotometric finish. Iron can also be determined by polarographic or amperometric methods (12,13,14). There is very little advantage to be gained by using polarographic or spectrophotometric methods for the determination of iron in ilmenite ores and slags, because the titrimetric methods are simpler and faster. The methods may be useful, however, if small amounts of iron, i.e. 1% or less, are to be determined. In most cases, a preliminary separation of the iron from interfering elements would likely be necessary, although the 1,10-phenanthroline spectrophotometric method seems relatively free of interference from titanium, chromium, and vanadium. This method, however, is usually restricted to determining less than 5% of iron (10).

2. Methods for the Determination of Titanium

Gravimetric methods for the determination of titanium are similar to those employed for iron, namely, precipitation by ammonia or cupferron followed by ignition of the precipitates and weighing as TiO_2 (5). Preliminary separations from interfering elements are generally necessary.

The spectrophotometric determination of titanium is most often accomplished by the peroxide methods (9), although the ascorbic acid procedure (15) is less subject to interferences. The Tiron-titanium complex has also been the basis for a spectrophotometric procedure (16). All these spectrophotometric methods are intended for the determination of titanium in the lower ranges. However, differential spectrophotometry using the peroxide method has been employed for large amounts of titanium or where high accuracy is desirable (17).

Titrimetric methods for the determination of titanium have largely depended on the reoxidation of a reduced solution of the metal but a few other methods such as bromatometric titration of titanium 8-hydroxyquinolate (18), direct reduction with chromous sulphate (19), titration with EDTA (20,21,22) or amperometric titration with cupferron (23) have been advocated. An advantage of the redox titrimetric method is that, as in the case of iron, preliminary separations are frequently unnecessary.

A number of instrumental procedures employing coulometric titration (24,25) or polarography (26 to 32) have also been used.

APPARATUS AND REAGENTS FOR REDUCTION AND DETERMINATION OF TITANIUM AND IRON

Many forms of apparatus suitable for carrying out the reduction of solutions of titanium and iron have been recommended.

Various reducing agents, ranging from solid reagents such as cadmium, lead, zinc, aluminum and amalgamated zinc to liquid amalgams of zinc, bismuth, cadmium and lead, have been proposed. Electrolytic cathodic reduction is attractive in principle but requires special equipment and conditions for the reduction. It has the advantage of not introducing foreign elements.

Stephen (33,34) in a number of papers has given an extensive account of the development and uses of reductors of all kinds, and standard text-books (1,5,35) give detailed information on both the uses of solid or liquid metal reductors, and the precautions that must be observed in their use.

The most frequently used reductor using solid reducing agents is the column or Jones type (36). Japanese workers have made much use of liquid amalgams, employing a Nakazono-type reductor (37) or a simple separating funnel (38). Solid reducing agents, such as aluminum, may be added directly to the solution (39,40,41). The excess aluminum dissolves in the solution and does not interfere in the subsequent titration. Silver as a reductant for iron was suggested by several workers (42,43,44,45), but Walden, Hammett and Edmonds (46) were the first to systematically investigate its use and it is commonly referred to as a Walden reductor.

The possibility that peroxide will form during the use of the various reductors has been examined by several investigators, and many contradictory views have been presented. This lack of agreement has been commented on by Kolthoff and Belcher (47). It is not intended here to reconcile or outline these opinions, except to state that the experiments of Chalmers, Edmond and Moser (48) and of Khan and Stephen (49) appear to have definitely established that peroxide is formed.

Chalmers, Edmond and Moser investigated the determination of iron by reduction with tin (II) chloride, zinc amalgam and silver reductor methods. These workers found that there is a small but definite amount of interaction between mercury (I) chloride and iron (III), but that it is sufficiently slow to make its effect negligible during a normal titration. They also found that detectable amounts of peroxide are produced when solutions of iron (II) are shaken with liquid zinc amalgam in the presence of air, but not if the air is displaced by carbon dioxide. Similar results were obtained when other reductants, such as copper wire, copper foil, mercury, zinc, lead, tin, bismuth and silver, were shaken with hydrochloric acid in the presence of air. Accordingly, these workers recommend that for accurate work it is essential to remove aerial oxygen from the solutions and to conduct the reduction in an inert atmosphere.

Khan and Stephen (49) described experiments in which they examined the formation of peroxide using various reducing agents. They found that satisfactory results for iron can only be obtained when oxygen is completely excluded from the solutions in contact with the reducing agent. They noted that even the small amount of oxygen present as an impurity in commercial nitrogen is sufficient to cause the formation of peroxide, and that its formation is prevented only by removal of the last traces of oxygen, e.g. by passing the nitrogen gas over hot reduced copper.

It should be stated at this point, however, that the errors due to peroxide formation, while significant, are small and are of more importance when only small amounts of titanium or iron are to be determined. For many routine analyses, the error, i.e. about 1% relative, can be tolerated, and this error can be minimized even further without taking elaborate steps to remove the last traces of oxygen completely.

The titanium (III) ion, unlike iron (II), is relatively unstable and is easily oxidized by aerial oxygen, but the titration can be performed in an inert atmosphere such as carbon dioxide or nitrogen, or by adding an excess of the oxidizing titrant and back-titrating the excess. Alternatively, an excess of ferric sulphate solution may be added and the ferrous equivalent titrated with a suitable oxidizing titrant.

Reduced titanium and/or iron solutions can be titrated with a variety of standard reagents; potassium permanganate, potassium dichromate, ceric sulphate, potassium bromate, and ferric solutions have all been employed. Various indicators, including diphenylamine, diphenylamine sulphonate, diphenylbenzidine, methylene blue, indigo carmine and sodium or potassium thiocyanate, have been recommended. The titrations may also be completed potentiometrically (50,51,52,53).

Titanium can be determined in the presence of iron, after reduction of both elements, by titration with a standard oxidizing solution with detection of the end point (a) potentiometrically (50), or (b) using indigo carmine (54), or (c) using two indicators, methylene blue for the titanium and o-phenanthroline ferrous complex for the iron (40,55).

SUMMARIES OF AND COMMENTS ON SOME METHODS FOR THE DETERMINATION OF TITANIUM AND/OR IRON

Space limitations permit only a few methods to be discussed in this bulletin, but these are representative of those that have been proposed by various authors. For a more comprehensive review of the literature, one should consult some of the general references (5,8b,8c,47,56) or refer to the original papers that are cited therein.

Hope, Moran and Ploetz (57) have described a method for the determination of titanium in pigments, using a liquid

amalgam technique. The reduction is performed in a separatory funnel and sodium carbonate is added to provide an atmosphere of carbon dioxide. The titanium (III) is titrated with standard ferric alum solution, using potassium thiocyanate as the indicator.

The determination of titanium (III) in titaniferous slags by dissolving the samples in an acid solution of standard vanadium (V) has been proposed by MacCardle and Scheffer (58). The iron is determined separately by a volumetric dichromate method.

McNabb and Skolnik (59) determined titanium and iron by titration with permanganate. The reduction is performed using a Jones reductor. In one aliquot the sum of titanium and iron is determined, and in another aliquot the iron is determined after air oxidation of titanium in the presence of mercuric chloride is completed. Titanium is calculated by difference.

In 1949, Shippy (55) described a procedure for the simultaneous determination of titanium and iron in titanium ores, using potassium permanganate as the titrant, with methylene blue as indicator for the titanium end-point and 1,10-phenanthroline ferrous complex as the indicator for the iron end-point. Reduction of both metals is carried out simultaneously, using the Jones reductor.

In 1952, Rahm (39) proposed a titrimetric method for the determination of titanium in pigments and ores. A 0.3-0.5 gram sample is fused with 30-50 grams of potassium bisulphate for 30

minutes, and, after dissolving the melt in dilute sulphuric acid, the titanium (and iron) is reduced with aluminum metal rather than the Jones reductor. The titanium (III) is then titrated under an atmosphere of carbon dioxide with standard ferric chloride solution, using potassium thiocyanate as the indicator. Based on his results obtained using both the Jones reductor and the aluminum metal reduction procedures, Rahm concluded that the aluminum reduction procedure is significantly more precise. A procedure for iron was not reported in his paper.

In an attempt to improve on the method of Shippy (55), Page and Gainer (40) described procedures for the determination of titanium and iron in titaniferous materials by cerate titrimetry. As in the method of Rahm, the samples are fused with potassium bisulphate and the melt is extracted with dilute sulphuric acid. The titanium (IV) and iron (III) are reduced, with either aluminum foil or liquid zinc amalgam, in a carbon dioxide atmosphere. The titanium (III) is titrated with cerium (IV) sulphate at a temperature of 65-70°C, using methylene blue as the indicator. The solution is cooled to 25-30°C and the iron (II) is titrated with cerium (IV) sulphate, using N-phenylanthranilic acid as the indicator. The method has the advantage that both iron and titanium can be determined in the same sample weight, but it requires heating the sample prior to titration of the titanium and maintaining the temperature within the rather narrow limits

specified. These authors also found that fusion with 50 grams of potassium bisulphate for 45 minutes is necessary for the complete solution of an 0.2- to 0.25-gram sample of most ilmenite ores, and implied that this is about the maximum amount of sample that can be taken using their procedure. Shippy, however, was able to fuse an 0.2- to 0.3-gram sample with 7 grams of potassium bisulphate in a platinum crucible.

Fonseka and de Silva (60) described a titrimetric procedure for the determination of titanium and iron in titaniferous material, and applied it to the analysis of ilmenite, rutile and silica rocks. The solution of titanium and iron is passed through a Jones reductor and the reduced solution is collected in an excess of ferric alum solution. The titanium (III) liberates an equivalent amount of iron (II) and this, together with the iron (II) obtained from the reduction of iron (III) in the sample, is titrated with standard dichromate, using diphenylamine sulphonate as the indicator. The iron (III) is separately determined by reduction in a silver reductor and titrated with the same dichromate.

Chang, Cheung and Kim (61) determined titanium in chromium-bearing titaniferous magnetite ores, using a liquid zinc amalgam to reduce titanium, iron, and chromium. Chromium (II) is selectively reoxidized to chromium (III) with arsenic (V) and mercury (II). The titanium (III) is titrated with standard iron (III) solution, using potassium thiocyanate as the indicator.

Denton and Whitehead (62) devised an automatic apparatus for the determination of titanium in large numbers of samples, mostly liquid, obtained in the paint industry. The titanium is reduced with cadmium in a column-type reductor and titrated with standard ferric alum solution to a potentiometric end-point. The determination is carried out automatically and a result could be obtained in 7 minutes. The use of such an instrument achieves a large saving in man-hours over the conventional methods when very large numbers of similar-type samples are to be analyzed on a routine basis. Presumably the system can be used to analyze solid samples after they have been brought into solution by a suitable method. Iron does not interfere, because the titanium (III) is titrated with ferric alum solution.

Dilts and Furman (24) described a coulometric method for the determination of titanium and iron with electrolytically-generated cerium (IV) ion and amperometric end-point detection. A Jones reductor is used to reduce the titanium and iron. These authors applied the method only to mixtures of the pure elements and did not investigate the presence of potentially interfering elements, nor did they apply it to the analysis of ores or other material. Moreover, the method is limited to the determination of less than 5-mg amounts of titanium or iron, because of the insolubility of titanium sulphate in the generating medium. For a discussion of other difficulties associated with the method, the original paper should be consulted.

Malmstadt and Roberts (25) described a constant-current coulometric method, with automatic spectrophotometric end-point detection, for the determination of iron in titanium sponge, alloys, and ores. The ferric iron is automatically titrated with electrogenerated titanium (III) ion. The method, while accurate, rapid, and useful over a range of iron of 0.01 to 20% or more, requires complex, expensive equipment which may not always be easily available or whose procurement may not be justified in terms of its limited use for a short-term project. The method is subject to interference by vanadium, copper and molybdenum, but not from nickel, tungsten, chromium, magnesium, manganese, zirconium, tin, or aluminum. For the determination of iron in the presence of vanadium, these authors recommend using another method.

Khalifa and Ismail (22) described EDTA methods for the analysis of ilmenite, based on potentiometric back titration of excess EDTA with mercury (II). Using these methods, iron, titanium, aluminum, copper, vanadium and chromium are determined.

Polarographic methods have been proposed for the determination of titanium. Berger and Cadoff (26) used a sulphuric acid-EDTA-sodium acetate supporting electrolyte at pH 4.7 to determine titanium in paint pigments. Banerjee, Budke and Miller (27) reported the use of a sulphuric acid-potassium pyrosulphate medium for the determination of titanium in niobium and tantalum ores. Graham et al. (28,29,30) used a sulphuric acid-ammonium

sulphate-tartaric acid medium to determine titanium in rocks, minerals and various alloys after removing the iron by means of a mercury cathode. Potts (31) used a similar medium to determine titanium in paint pigment. Hitchen (32) used an acetate-EDTA electrolyte to determine titanium in lead zirconate-lead titanate ceramic materials.

CONCLUSIONS

Of the methods reviewed in this report, those which involved a simple reduction step and a titrimetric finish appeared to be the most applicable for the control of a short-term research project.

Spectrophotometric and polarographic methods, as well as other instrumental methods employing coulometry, for instance, were considered to be unsuitable on the basis of being too time-consuming or complex, or requiring elaborate and expensive instrumentation that was unavailable.

The investigation and development of rapid methods for the determination of titanium and iron in ilmenite ores and slags, based on the reduction of titanium and iron with liquid zinc amalgam, or of iron with a silver reductor, followed by titration with dichromate, are described in Part II of this series, now being prepared.

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