CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

THE DETERMINATION OF TITANIUM IN LEAD ZIRCONATE-LEAD TITANATE ELECTRONIC CERAMICS. A COMPARISON OF TITRIMETRIC METHODS WITH POLAROGRAPHIC AND DIFFERENTIAL SPECTROPHOTOMETRIC METHODS

A. HITCHEN

EXTRACTION METALLURGY DIVISION

OCTOBER 1972

Technical Bulletin TB 153 Price 75 cents

Available by mail from Information Canada, Ottawa,
and at the following Information Canada bookshops:

HALIFAX
1735 Barrington Street

MONTREAL
1182 St. Catherine Street West

OTTAWA
171 Slater Street

TORONTO
221 Yonge Street

WINNIPEG
393 Portage Avenue

VANCOUVER
657 Granville Street

or through your bookseller

Price: 75 cents Catalogue No. M34-20/153

Price subject to change without notice

Information Canada
Ottawa, 1972

Mines Branch Technical Bulletin TB 153

THE DETERMINATION OF TITANIUM IN LEAD ZIRCONATE-LEAD TITANATE ELECTRONIC CERAMICS A COMPARISON OF TITRIMETRIC METHODS WITH POLAROGRAPHIC AND DIFFERENTIAL SPECTROPHOTOMETRIC METHODS

by

A. Hitchen*

ABSTRACT

Three procedures for the determination of titanium in lead zirconate-lead titanate powders and process solutions which are simple, rapid, precise and accurate, are described. Two of the methods are based on reduction of the titanium with a) liquid zinc or lead amalgams or b) metallic aluminum, followed by titration of the reduced titanium with a standard ferric sulphate solution using sodium thiocyanate as the indicator. The third method is a polarographic procedure using an acetate + EDTA electrolyte. Relatively few elements interfere and procedures are suggested to overcome some of those that do. The accuracy and precision of the methods compare favourably with the much longer differential spectrophotometric method.

*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 153

LA DÉTERMINATION DU TITANE DANS LES CÉRAMIQUES ÉLECTRONIQUES COMPOSÉES DU ZIRCONATE DE PLOMB ET DU TITANATE DE PLOMB

UNE COMPARAISON DES MÉTHODES TITRIMÉTRIQUES AUX MÉTHODES DE POLAROGRAPHIE ET DE SPECTROPHOTOMÉTRIE DIFFÉRENTIELLE

par

A. Hitchen*

RÉSUMÉ

L'auteur décrit trois méthodes simples, rapides et précises pour la détermination du titane dans les poudres composées du zirconate de plomb et du titanate de plomb et dans les solutions. Les deux méthodes sont basées sur la réduction du titane avec a) du zinc liquide ou des amalgames de plomb ou b) de l'aluminium métallique suivi par le tirage du titane réduit avec une solution titrée de sulfate ferrique utilisant du thiocyanate de sodium comme indicateur. La troisième méthode est un procédé polarographique utilisant un acétate + une électrolyte EDTA. Relativement peu d'éléments interfèrent et l'auteur suggère des procédés pour surmonter ceux qui interfèrent. La précision des méthodes se compare favorablement à celles de la méthode beaucoup plus longue de spectrophométrie différentielle.

---

*Premier agent scientifique, 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

INTRODUCTION

An interdivisional research program on the development of chemical processes for the production of electronic ceramics of greater purity and homogeneity than those previously available has been completed at the Mines Branch. Details of the process developed for the production of lead zirconate-lead titanate powders, for use in such ceramics, have been described by McNamara and Gow[1]. One of the aims of the program was to study the effect of small changes in stoichiometry of the powders on the electrical and physical properties of the finished ceramic transducers[2,3].

To permit the evaluation of this aspect, an important part of the program was the development of rapid, accurate, and precise analytical methods that were necessary to establish the extent of the changes in stoichiometry and also to provide for production control of the powders. Earlier publications have described the development of the analytical methods used for the determination of lead[4] and zirconium[5] and a summary of analytical methods[6] includes a description of the differential spectrophotometric method employed to determine titanium. The differential spectrophotometric method for the determination of titanium has been found to be precise but it is slow and complicated and requires extreme care to ensure accurate results.

It was therefore decided to investigate the use of other methods that would offer the same precision as the differential method but would be simpler and more rapid. In

addition, such methods would enable the analyses to be done by alternative procedures in doubtful, or difficult, cases.

Murphy, Clabaugh and Gilchrist[7] described a gravimetric method for determining zirconium and titanium in barium titanate-barium zirconate ceramic materials in which separations of the titanium and zirconium were made by employing cupferron and 8-hydroxyquinoline as reagents. Dosch and Conrad[8] proposed a cation exchange method to separate titanium and zirconium from bismuth and lead in PZT ceramics. The titanium and zirconium were separated from each other by a second cation-exchange separation following which each was precipitated with cupferron and finally determined gravimetrically. Both of the foregoing procedures were briefly investigated but neither offered any advantages with respect to speed, precision or simplicity. Both procedures involved many intermediate treatment steps before the titanium was isolated.

Various other methods have been suggested for the separation of titanium from interfering elements. The mercury cathode, for example, has long been used to separate titanium from iron, copper, lead, zinc and many other elements but unfortunately zirconium remains with the titanium in solution. Most procedures use 8-hydroxyquinoline or cupferron to separate the titanium from many other elements or to precipitate the titanium from many other elements or to precipitate the titanium after it has been isolated from other elements by other means. Complexing agents such as EDTA have been employed to mask potentially interfering elements and to render the precipitation

more specific. Pribil and Malat[9], for example, claim that only titanium, tungsten, molybdenum, vanadium, and uranium are precipitated by 8-hydroxyquinoline from an acetic acid-ammonium acetate buffered solution. On the other hand, zirconium, uranium, iron, aluminum, copper, magnesium, beryllium, and antimony in addition to the titanium, are precipiated from an ammoniacal ammonium acetate solution. Majumdar and Chowdhury[10] precipitated titanium with cupferron from an ammonium acetate buffered solution containing EDTA. Lead and zirconium were among a host of other elements that were said not to interfere with the precipitation. The titanium was ignited and determined gravimetrically. Neither of the above two procedures were believed to be applicable to the lead titanate-lead zirconate materials because a double or perhaps triple precipitation of the titanium would undoubtedly have to be made to ensure its complete separation from the lead and zirconium. Each titanium precipitate would have to be destroyed either by ignition or by treatment with nitric, sulphuric, and perchloric acids before the next precipitation could be made. This feature of each of the above methods detracts from their potential usefulness because the destruction of the organic precipitate is not without difficulty and has to be performed with extreme care if losses are to be avoided. Neither method may be considered rapid or simple.

Attention was therefore turned to other possible methods. Because of the successful use of EDTA as a titrant for lead and zirconium in these lead zirconate-lead titanate materials[4,5]

the use of an EDTA-titrimetric method appeared attractive. This approach had the advantage that only one titrant, EDTA, would be required to determine each of the major constituents - lead, zirconium, and titanium.

A number of trial experiments to determine titanium were made using EDTA as a titrant but it soon became apparent that in order to be successful a separation of the titanium from the lead and zirconium would first have to be made. If any of the methods employing cupferron or 8-hydroxyquinoline previously mentioned were used to isolate the titanium, then finishing the determination by titrating the titanium with EDTA after destruction of the organic matter would offer no advantage over igniting the precipitate and determining it gravimetrically. Further investigations along these lines with EDTA were therefore discontinued.

The writer[11] has reviewed and made comments on some typical methods for the determination of iron and titanium. Of the methods commented upon in this report, those which were based on a simple reduction step and a titrimetric finish appeared to be the most applicable to the determination of titanium in the lead zirconate-lead titanate material.

The reduction of titanium has been accomplished in several different ways. The Jones reductor[12] is perhaps the most frequently used column-type of reductor but this procedure has not proven entirely satisfactory in our laboratories[13]. Liquid zinc amalgam has been employed by several workers[13,14,15,16,17] for the analysis of various materials though the use of aluminum

metal has been recommended by others[16,18,19] as having certain advantages over the Jones reductor.

Polarographic methods for the determination of titanium in various materials have been suggested and lead, titanium and niobium in lead zirconate-lead titanate ceramics were determined by Goode, Herrington and Jones[20] by means of cathode-ray polarography. These workers used a sodium acetate + EDTA electrolyte to determine the titanium and niobium and a 1 M hydrochloric acid medium to determine the lead. A polarographic method employing an ammonium acetate-acetic acid-EDTA electrolyte has been used in our own laboratories for the determination of molybdenum in binary alloys of molybdenum and uranium[21]. It was found that titanium also gave an analytically useful wave in this medium. Subsequently a more detailed investigation of the behaviour of titanium in this electrolyte was carried out and is described in a separate report[22].

This report describes the results of an investigation in which three different methods were developed to determine titanium in lead zirconate-lead titanate materials. Two of the methods are based on reduction of the titanium by means of a) liquid zinc or lead amalgam or b) aluminum metal with subsequent titration of the reduced titanium with standard ferric sulphate solution. The third method is a polarographic procedure employing an ammonium acetate-acetic acid-EDTA supporting electrolyte. The results obtained by each of these methods are compared to results obtained by the differential spectrophotometric method. These results indicate that the precision and accuracy of the methods compare favourably with each other.

After completion of the work described in this report there appeared a method for the analysis of lead zirconate-lead titanate material which is based on "Coprex" analysis[23]. The elements lead, titanium, zirconium, and lanthanum are precipitated as the hydroxides or carbamates at pH 9 using iron as a co-precipitant. The mixed precipitate is collected on a Millipore paper, dried and analyzed by an X-ray spectrochemical technique. No analysis data for samples are reported but from the calibration graphs illustrated for each of the elements it is believed that the precision to be expected is not as satisfactory as the precision obtained for the methods described herein. The advantage of the X-ray method, however, is that only a 10-mg sample is required for the determination of all four elements.

APPARATUS AND REAGENTS

I. Titrimetric Procedures Using Amalgams or Aluminum Metal Reductants

Apparatus

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

Burette and titrant reservoir similar to that described by Pilkington and Smith[19] for maintaining the titrant under an atmosphere of nitrogen.

Distilling flask, round bottom, 500 ml, with side arm modified by bending upwards rather than downwards.

Heating mantle, 500 ml, to fit above distilling flask.

Variable rheostat, for controlling the heat of the mantle.

Cylinder of compressed nitrogen gas equipped with

regulating valve.

Magnetic stirrer and bar.

Reagents

0.02 M Ferric Sulphate

Dissolve 11 grams of $Fe_2(SO_4)_3.xH_2O$ (containing about 72% $Fe_2(SO_4)_3$) in 500 ml of distilled water containing 20 ml of 18 M sulphuric acid and warm to dissolve. Add 0.1 N potassium permanganate solution until a pink colour is obtained, cool, and dilute to 1 litre. Allow the solution to stand overnight and filter to remove any undissolved residue. Transfer the solution to the titrant reservoir and de-aerate the solution with nitrogen. Maintain it under a nitrogen atmosphere at all times.

Standardize the solution against known amounts of titanium that have been reduced by either of the amalgam procedures or with aluminum metal as proposed in this report. Correct the titrations for a blank in the usual way. Ferric ammonium sulphate may be substituted for the ferric sulphate. (Use 19.3 grams $FeNH_4(SO_4)_2.12\ H_2O$ per litre).

Sodium thiocyanate solution

Dissolve 45 grams of sodium thiocyanate salt in water and dilute to 100 ml. De-aerate with nitrogen before use.

Zinc or lead amalgam

Wash 15 grams of zinc or lead granules with hydrochloric acid to remove surface oxides and then with distilled water to remove the acid. Dry the metal and add to 300 grams of mercury in a beaker or casserole and warm to dissolve the metals. Caution: use a fume hood. Cool, separate the liquid amalgam from the solid residue and wash the liquid amalgam with 1% v/v sulphuric or hydrochloric acid just before use. Store the amalgam under a layer of the dilute acid when not in use. Retain the solid residue for the preparation of fresh amalgam.

Aluminum metal, Fisher, a certified-grade 20-gauge wire, or 1/32-inch sheet. The wire was found to be the most convenient to use. A length of wire weighing 3 grams was cut and the same length of wire was used for all determinations to permit a constant blank correction to be used.

Sulphuric acid wash solution, 2 N

De-aerate the solution with nitrogen before use or store in a dispensing reservoir under nitrogen.

Carbon tetrachloride, Reagent grade.

II. Polarographic Procedure

Apparatus

L & N Electrochemograph Type E

H-type polarographic cells, Sargent-Welch Cat. No. S-29400

Capillary tubing, Sargent-Welch Cat. No. S-29417

pH meter

Water bath equipped with thermostat and heat to maintain a temperature of 25.0 ± 0.1°C.

Reagents

0.2 M EDTA

Dissolve 74.5 grams of reagent-grade disodium ethylenediaminetetraacetate dihydrate in water and dilute to 1 litre.

5 M Ammonium acetate

Dissolve 385 grams of reagent-grade ammonium acetate in water and dilute to 1 litre.

1 M Acetic acid

Dilute 58 ml of reagent-grade glacial acetic acid to 1 litre with water.

Other chemicals used are of reagent grade.

ANALYSIS PROCEDURES

I. Procedure Using Liquid Zinc or Lead Amalgam as the Reductant

Transfer a sample (either a solution or a solid)*, containing 10 to 50 mg of titanium to a 150-ml beaker and add 5 to 10 ml of 18 M sulphuric acid. Evaporate the solution to fumes of sulphuric acid and continue fuming until the sample is decomposed and any nitric or perchloric acid is removed. Cool, add 10 to 15 ml of water and 20 ml of 12 M hydrochloric acid.

*If desired, a larger sample may be taken into solution by boiling it with 72% perchloric acid and diluting to a known volume in a volumetric flask. Aliquots may then be taken for each of the determinations required, i.e., Pb, Zr, and Ti.

Warm the solution to dissolve the sample, transfer it to a 250 ml separatory funnel and dilute to about 100 ml with water.

Add 10 ml of liquid zinc or lead amalgam and displace the air in the solution and separatory funnel by flushing for several minutes with nitrogen. Rinse the tip of the flushing tube with a few ml of de-aerated 2 N sulphuric acid. Stopper the funnel and shake vigorously for several minutes to reduce the titanium. If lead amalgam is employed, shake for 5 to 10 minutes using a mechanical shaker. Rinse the stopper carefully with de-aerated 2 N sulphuric acid and add 10 ml of carbon tetrachloride to separate the aqueous layer from the amalgam. Drain the amalgam into a waste beaker*. Add 3 ml of de-aerated 45% sodium thiocyanate solution to the sample in the funnel and again flush the upper part of the funnel with nitrogen to maintain an inert atmosphere. Titrate the reduced titanium with de-aerated standard ferric sulphate solution to the first permanent orange-red end-point while maintaining a flow of nitrogen over the surface of the sample solution. Correct the volume of ferric sulphate consumed for a blank obtained by performing the reduction step on the reagents, minus the sample, in the same manner.

II. Procedure Using Aluminum Metal as the Reductant

Transfer a sample, either a solution or a solid sample, containing 10 to 50 mg of titanium to a 150-ml beaker and add 5 to 10 ml of 18 M sulphuric acid. Evaporate the solution to fumes of sulphuric acid to remove any nitric or perchloric

*The amalgam can be collected and re-used several times before finally discarding if it is first washed with dilute(1%) sulphuric acid.

acids. Cool, add 100 ml of water and sufficient sulphuric acid, if necessary, to make the final volume about 4% in sulphuric acid. Filter the solution through Whatman No. 40 or 42 paper and wash the lead sulphate precipitate with cold 4% v/v sulphuric acid solution. Transfer the solution to a 500-ml round-bottom distilling flask that serves as the reduction vessel, add 20 ml of 12 N hydrochloric acid and dilute to between 250 and 300 ml with water. Pass nitrogen gas through the side arm of the flask to maintain an inert atmsophere over the surface of the solution and add 3 grams of aluminum wire formed into a coil to facilitate inserting it into the flask. Heat the solution moderately to start the reaction and let it proceed to completion. If it appears to be too violent, cool the solution occasionally in a beaker of cold water to moderate it. Finally, after all the metal has dissolved and the reaction has ceased, cool the solution to less than 60° while maintaining a flow of nitrogen. Add a magnetic stirring bar and 3 ml of de-aerated 45% sodium thiocyanate solution and titrate the reduced titanium with standard ferric sulphate solution to the first permanent red end-point. Determine a blank by carrying the reagents through the reduction step in the same manner as the sample and deduct the value obtained* from the ferric sulphate solution consumed in the titration of the samples.

*If the same weight of aluminum is not used with each sample the blank will have to be determined in terms of ml of ferric sulphate per gram of aluminum and the corrections made accordingly. This procedure has the disadvanatage that each piece of aluminum has to be weighed individually. If wire is used it is a simple matter to cut it to the same length each time.

III. Polarographic procedure

Transfer a sample, either a solution or a solid sample, containing 10 to 25 mg of titanium to a 150-ml beaker and add 5 ml of 18 M sulphuric acid. Evaporate the solution to fumes of sulphuric acid to remove any nitric or perchloric acid and continue the fuming until the residue is just moist and less than 1 ml of sulphuric acid remains. Cool, add 50 ml of 0.2 M EDTA solution and bring to a boil for several minutes. Cool the solution to room temperature and add 10 ml of 5 M ammonium acetate and 10 ml of 1 M acetic acid. Dilute to between 80 and 85 ml with water and check the pH of the solution with a pH meter. Adjust the solution, if necessary, with sodium hydroxide or sulphuric acid solution to pH 5.0 ± 0.1. Transfer the solution to a 100 ml volumetric flask, adjust exactly to the mark at 25.0°C with water and mix well. Transfer a portion of the solution to a polarographic cell in a water bath maintained at 25.0°C ± 0.1°C and de-aerate the solution with nitrogen. Immerse a dropping mercury electrode in the solution and record 4 waves* from 0.0 to minus 1.0 volt vs the S.C.E. using a suitable range and damping position on the instrument**. The half-wave potential of the titanium wave in the above supporting electrolyte having a pH of 5.0 ± 0.1 should be minus 0.46 ± 0.01 volts vs the S.C.E.*** Calculate the diffusion current by

*For a more accurate estimate of the titanium, process two or more replicate samples and record 1 or more waves on each solution.

**Range 20 microamperes full scale and damping position 2 on the L and N instrument used in this work.

***Slight variations in the half-wave potential will occur if the pH of the solutions differ from this value but the wave height will remain unaffected.

subtracting the average residual current measured at minus 0.25 volt from the average limiting current measured at minus 0.70 volts. Process a number of standard titanium solutions in the same way, using the same capillary and instrument settings, and obtain an average factor in terms of mg of titanium per microampere of diffusion current. Using this average factor calculate the amount of titanium in the samples.

PRELIMINARY INVESTIGATIONS

I. Titrimetric Procedures

A. Reduction with liquid zinc or lead amalgam and titration with standard ferric sulphate solution

The application of this method to this specific problem warranted no concern with impurities in general. However, small amounts of other elements such as iron or niobium, for example, may sometimes be incorporated in the ceramic powders to give specific electrical or physical properties. A study was therefore made to determine the conditions under which interference by the above elements would not occur but which would still permit the quantitative determination of titanium.

The liquid zinc amalgam technique described in this report has also been used to determine iron and titanium in ilmenite ores and titanium-bearing slags[13] and the advantages and disadvantages of using liquid amalgams is discussed therein. In the procedure for the ilmenite ores and slags, the iron and titanium are both reduced with the zinc amalgam and after addition of an excess of ferric sulphate solution the total ferrous iron that results is titrated with standard potassium

dichromate solution. The dichromate that is consumed is therefore equivalent to the sum of the iron and titanium in the sample. In order to avoid the interference by iron the procedure in this report uses a standard ferric sulphate solution to titrate the reduced titanium directly. If any iron is present in the sample it is also reduced along with the titanium but the ferrous iron that is formed is not titrated by the ferric sulphate.

The use of ferric sulphate as a titrant thus avoids the interference by iron but will not prevent the interference of other substances that are reduced by the zinc amalgam and are titrated by ferric sulphate. Niobium constitutes such an interference but the extent to which it is reduced under the conditions of the method was not known so an investigation was made to ascertain if niobium was in fact reduced, to what extent, and how its interference could be prevented.

a) Reduction and Titration of Titanium with Amalgams

i) Comparison of liquid zinc and lead amalgams as reductants for titanium.

A series of preliminary tests were made to determine the optimum conditions for the reduction of titanium in solutions containing hydrochloric and sulphuric acids with either a liquid zinc amalgam or a liquid lead amalgam. In these tests, an aliquot of a solution containing the titanium was transferred to a separatory funnel and the required amounts of hydrochloric and sulphuric acids were added. The

solution in the funnel was diluted to 100 ml with water and the amalgam added. Air was removed from the solution and the funnel by means of nitrogen and the reduction was made by shaking the funnel for various times. The rest of the operation was performed as recommended in the procedure described in this report (p 10). The ferric sulphate solution was standardized against a standard potassium dichromate solution after the iron had been reduced in a silver reductor. The amounts of titanium, the various reagents, and the other conditions as well as the results that were obtained are given in Table 1.

b) Reduction and Titration of Niobium

i) Comparison of liquid zinc and lead amalgams as reductants for niobium.

A few experiments were performed to determine if niobium were reduced by either liquid zinc or lead amalgams under the same conditions as are used to reduce titanium.

In these experiments, the conditions of acidity with respect to sulphuric acid, hydrochloric acid and volume of solution were kept identical for both amalgams. Known amounts of niobium were present and the solutions were shaken for 3 to 4 minutes in the absence of air with either liquid zinc or lead amalgam. The reduced solution was titrated under nitrogen with de-aerated standard ferric sulphate solution after removal of the amalgam. The results of these tests are shown in Table 2.

TABLE 1

Reduction of Titanium with Liquid Zinc or Lead Amalgams

Effect of Acid Concentration and Shaking Time

Test	Acid Concentration HCl	Acid Concentration H_2SO_4	PbHg ml	ZnHg ml	Ratio of Solution to Amalgam	Shaking Time min	Ti Present mg	Ti Found* mg	% Ti Recovery*
1	2.4M	1M		10	10/1	3-4	15.00	15.00	100.0
2	3.0M	"		"	"	"	15.00	14.97-15.03	99.8-100.2
3	2.4M	"	15		6/1	"	15.00	14.48-14.73	96.5- 98.2
4	3.6M	"	"		"	"	15.00	15.00	100.0
5	4.8M	"	"		"	"	15.00	14.88-14.97	99.2- 99.8
6	6.0M	"	"		"	"	15.00	15.03	100.2
7	7.2M	"	"		"	"	15.00	15.18-15.21	101.2-101.4**
8	2.4M	"	"		3/1	5	6.00	5.95	99.2
9	"	"	"		"	"	7.50	7.45	99.4
10	"	"	"		"	"	18.00	17.80	99.0
11	"	"	"		"	"	22.50	22.28	99.2
12	"	"	"		6/1	10	15.00	14.90-14.96	99.3- 99.7
13	3.3M	"	"		"	"	15.00	14.90	99.3
14	4.0M	"	"		"	"	15.00	15.00	100.0
15	2.4M	2.0M	"		"	"	15.00	14.93-15.00	99.5-100.00
16	"	3.0M	"		"	"	15.00	14.96	99.7

* minimum and maximum recoveries based on 1 to 4 titrations

** the high acidity destroyed the red-end-point colour and yellow was observed instead.

TABLE 2

Comparison of the Reduction of Niobium by Liquid Zinc and Lead Amalgam

Acid Concentration HCl	Acid Concentration H_2SO_4	Volume of Solution, ml	PbHg ml	ZnHg ml	Shaking Time min	Niobium Present mg	Niobium Found* mg
2.4 M	1.0 M	100		10	3-4	5	1.48
"	"	"		10	"	5	0.89
"	"	"		10	"	10	1.93
"	"	"	15		"	0	0.00
"	"	"	"		"	1	0.00
"	"	"	"		"	2	0.00
"	"	"	"		"	3	0.00
"	"	"	"		"	4	0.00
"	"	"	"		"	10	0.00

*the niobium is calculated on the basis that it is reduced to Nb^{+3} before titrating it. Corrections were made for a blank titration.

ii) Effect of acid concentration and shaking time on the reduction of niobium with liquid lead amalgam.

A number of tests were carried out to determine the effect of acid concentration and shaking time on the reduction of niobium with liquid lead amalgam. The effect of changing the ratio of amalgam to solution volumes was also studied. The reduction and titration steps were done in the absence of air as in the preceding section. The results are shown in Table 3.

B. Reduction of Titanium with Aluminum Metal

The use of aluminum metal to reduce titanium has been advocated by several workers[16,18,19]. To explore this possibility a number of solutions containing 15 or 30 mg of titanium were reduced with aluminum wire using the procedure described in this report which is based on that used by Pilkington and Smith[19]. The reduced titanium was titrated with standard ferric sulphate solution using sodium thiocyanate as indicator. The ferric sulphate solution was standardized against potassium dichromate after reducing the iron by means of a silver reductor. After correcting for a blank titration, the amount of titanium recovered was calculated and is shown in Table 4.

II. Polarographic Procedures

A description of the investigation and development of the polarographic method for the determination of titanium is given in a separate report[22] and the reader is referred to it for details and a discussion of several factors influencing the behaviour of titanium as well as the effect of some elements

TABLE 3

Effect of Acid Concentration and Shaking Time on the Reduction of Niobium with Liquid Lead Amalgam

Test	Acid Concentration HCl	Acid Concentration H_2SO_4	PbHg ml	Ratio of Solution to Amalgam	Shaking Time min	Niobium Present mg	Niobium Found mg
1	2.7 M	1.0 M	15	3:1	5	5.00	0.00
2	"	"	"	"	"	5.00	0.00
3	"	"	"	"	"	5.00	0.00
4	"	"	"	6:1	"	5.00	0.00
5	"	"	"	"	10	5.00	0.00
6	"	"	"	4.5:1	"	5.00	0.00
7	"	2.0	"	6:1	5	5.00	0.18
8	"	"	"	"	"	10.00	0.41
9	"	3.0	"	"	"	5.00	0.15
10	3.3	1.0	"	"	10	5.00	0.44
11	4.0	"	"	"	10	5.00	0.47

that may cause interference or difficulties in the determination of titanium.

TABLE 4

Reduction of Titanium with Aluminum Metal

Ti Taken mg	Ti Found mg	Difference mg	% Recovery
15.00	14.83	- 0.17	99.0
15.00	14.87	- 0.13	99.2
30.00	29.71	- 0.29	99.1
30.00	29.75	- 0.25	99.2

Briefly, neither zirconium nor lead interfere with the determination of titanium because zirconium is not reduced and lead is reduced only at a more negative potential, i.e., minus 1.2 volts versus the saturated calomel electrode.

ANALYSIS OF SAMPLES

A number of solution and solid samples of lead-titanium-zirconium oxide mixtures were analysed for titanium by the proposed procedures and the results were compared with values obtained by the differential spectrophotometer method. The results obtained by each of the proposed procedures are shown in Table 5.

TABLE 5

Determination of Titanium in Lead Zirconate-Lead Titanate Products - Comparison of Results by a Differential Spectrophotometric Method, Amalgam and Aluminum Reduction - Titrimetric Methods and a Polarographic Method

Sample	Titanium Found (As Ti)[a]				
	Diff.Spect. g/l or %	PbHg g/l or %	ZnHg g/l or %	Al Reduction g/l or %	Polarography g/l or %
1091	6.88 ± 0.01 %	6.89 ± 0.06 %			
1094	6.13 ± 0.00 %	6.18 ± 0.01 %			
1087	8.15 ± 0.01 %	8.17 % (b) 8.15 % (c) 8.20 % (c) 8.13 % (d)			
683	1.18 ± 0.00 g/l				1.18 ± 0.01 g/l
684	1.13 ± 0.00 g/l				1.14 g/l
686	1.27 ± 0.00 g/l				1.26 g/l
688	1.07 ± 0.01 g/l				1.06 g/l
690	1.02 ± 0.00 g/l				1.02 g/l
693	0.92 ± 0.00 g/l				0.92 ± 0.01 g/l
694	0.77 ± 0.00 g/l				0.76 g/l
2244R	1.00 ± 0.00 g/l			1.00 ± 0.00 g/l	
2245	1.04 ± 0.00 g/l			1.04 ± 0.00 g/l	1.05 ± 0.01 g/l
2246	1.61 ± 0.01 g/l			1.61 ± 0.00 g/l	1.59 ± 0.02 g/l
2660	0.85 ± 0.00 g/l			0.85 ± 0.00 g/l	0.85 ± 0.00 g/l
2661	0.84 ± 0.00 g/l			0.84 ± 0.00 g/l	0.83 ± 0.01 g/l
2281	6.11 ± 0.03 %			5.94 ± 0.03 %	
2282	6.14 ± 0.01 %			6.14 ± 0.00 %	
2283	6.06 ± 0.00 %			6.03 ± 0.02 %	
2284	5.77 ± 0.02 %			5.78 ± 0.00 %	
2285	5.82 ± 0.01 %			5.79 ± 0.02 %	
2286	5.67 ± 0.01 %			5.66 ± 0.03 %	

TABLE 5 (Cont'd)

Sample	Titanium Found (As Ti)[a]				
	Diff. Spect. g/l or %	PbHg g/l or %	ZnHg g/l or %	Al Reduction g/l or %	Polarography g/l or %
2289	5.11 ± 0.01 %		5.14 ± 0.00 %	5.14 %	5.19 ± 0.01 %
2290	4.59 ± 0.01 %		4.64 %	4.61 %	4.62 ± 0.04 %
2291	4.58 ± 0.01 %		4.62 ± 0.01 %	4.59 %	4.63 ± 0.04 %
2292	4.56 ± 0.02 %		4.57 ± 0.01 %	4.58 %	4.56 ± 0.01 %
2295	3.82 ± 0.01 %		3.83 ± 0.01 %	3.80 %	3.84 ± 0.03 %
2296	8.41 ± 0.00 %		8.38 %	8.35 %	8.40 ± 0.04 %
2682	5.56 ± 0.00 %		5.56 ± 0.01 %	5.54 %	5.58 ± 0.02 %
2683	5.56 ± 0.01 %		5.56 ± 0.01 %	5.54 %	5.55 ± 0.01 %
2684	5.39 ± 0.01 %		5.40 ± 0.00 %	5.37 %	5.38 ± 0.02 %
2685	7.76 ± 0.02 %		7.78 ± 0.02 %	7.76 %	7.79 ± 0.04 %
2686	7.76 ± 0.02 %		7.86 ± 0.00 %	7.74 %	7.80 ± 0.01 %
2687	7.47 ± 0.02 %		7.49 ± 0.03 %	7.45 %	7.47 ± 0.05 %

(a) Where an indication of range is given it means that the analysis was performed on duplicate or more samples or aliquots. Where no range is given only one sample was taken for analysis.

(b) No niobium was added.

(c) Niobium equivalent to 5% was added to the sample.

(d) Niobium equivalent to 7.5% was added to the sample.

DISCUSSION

I. Titrimetric Procedures

A. Reduction with Liquid Zinc or Lead Amalgams

a) Reduction and Titration of Titanium

i) Comparison of liquid zinc amalgam with liquid lead amalgam as reductants for titanium.

The results in Table 1 show that the liquid zinc amalgam gives virtually 100% reduction of the titanium at relatively low acidities. Quantitative reduction of the titanium with the lead amalgam can be achieved in 3 to 4 minutes if the hydrochloric acid concentration is maintained between 3.6 M and 6.0 M. However, increasing the hydrochloric acid concentration further, i.e., to 7.2 M, causes an apparently higher than 100% recovery of titanium because the red end-point due to the ferric thiocyanate is destroyed and the end-point that is actually observed is probably due to an excess of yellow Fe^{+3} ions. On the other hand, in 2.4 M HCl + 1 M H_2SO_4 slightly lower recoveries of titanium are obtained by using a liquid lead amalgam if the solution is shaken for less than 5 minutes and between 99 and 100% reduction of the titanium can be obtained only if the shaking time is increased to 5 or 10 minutes. The longer time required for reduction by the lead amalgam procedure merely reflects the fact that the lead amalgam is a less powerful reductant than the zinc amalgam because of the difference in their reduction potentials[24].

Changing the ratio of amalgam to solution volumes has no significant effect on the recoveries. The slightly low recoveries of titanium obtained at the lower acidities used in the liquid lead amalgam technique are in agreement with previous observations in our laboratories[13] and with those of Khan and Stephen[25] and Chalmers, Edmond and Moser[26]. The results could perhaps be improved if more scrupulous care were taken to remove oxygen from the solutions and/or from the nitrogen gas as recommended by Khan and Stephen but this degree of improvement is not considered necessary for the purpose for which the method is intended. For the analysis of samples, the ferric sulphate solution is therefore standardized against known amounts of titanium that are carried through the proposed procedure rather than against potassium dichromate. In this way correction is made for most of the bias.

b) Reduction and Titration of Niobium

i) Comparison of liquid zinc amalgam with liquid lead amalgam as reductants for niobium.

The results in Table 2 show that niobium is reduced by zinc amalgam but the reduction is not stoichiometric. The amount of niobium reduced is calculated on the assumption that Nb^{+5} is reduced to Nb^{+3}. Hillebrand and Lundell comment on the difficulties in reducing niobium[27]. On the other hand, niobium is not reduced by lead amalgam under the conditions given in Table 2.

ii) Effect of acid concentration and shaking time on the reduction of niobium with liquid lead amalgam.

The results in Table 3 show that niobium is not reduced by lead amalgam if the acidity is carefully controlled. The maximum acidity that can be tolerated appears to be about 2.7 M hydrochloric acid and 1 M sulphuric acid. Increasing either the hydrochloric or sulphuric acid concentrations above these levels allows some reduction of the niobium to take place. Increasing the ratio of amalgam to solution volumes or increasing the shaking time from 5 to 10 minutes had no apparent effect. Concentrations of acid less than the minimum in Table 3 were not investigated because the results of Test 3 in Table 1 indicated that the reduction of titanium would not be complete.

B. Reduction of Titanium with Aluminum Metal

The results in Table 4 indicate that only about 99% of the titanium is reduced by means of aluminum metal. This is in agreement with the results obtained by reduction with the liquid lead amalgam and the explanation is perhaps the same in each case, i.e., incomplete removal of oxygen from the solutions or from the nitrogen or incomplete reduction of the titanium.

It is therefore recommended that the ferric sulphate solution be standardized against known amounts of titanium that are taken through the procedure in the same manner as the sample rather than against potassium dichromate. Standardization in this way need be done only when a fresh reagent solution is

prepared because the ferric sulphate solution is stable and is always stored under nitrogen. However, de-aeration of all the reagents and wash solutions is essential to ensure accurate and precise results.

In some preliminary tests, it was observed that the aluminum metal also reduced some of the lead to metallic lead and some erratic values were obtained. It was believed that these spurious results were caused by small particles of lead remaining suspended in the solution and that these particles eventually reduced the ferric iron thereby giving a fading end-point. The bulk of the lead was therefore removed by precipitating it as lead sulphate before the reduction step. This precaution eliminated the trouble. A loss of titanium may occur by co-precipitation with the lead sulphate but the loss is very small and is not significant. Any small amounts of lead remaining after removal of the lead sulphate may be precipitated in the reduction step but these particles redissolve in the acid after the aluminum has disappeared.

The acidity of the solution affects the efficiency of the reduction of titanium. If too much acid is present the quantity of hydrogen gas evolved is increased and a larger amount of aluminum must be used to compensate for this. Pilkington and Smith[19] used a volume of about 150 ml for the reduction of titanium with sheet aluminum, but we found that, at this volume, the reaction was so violent, if aluminum wire was used, that considerable spraying from the vigorous hydrogen evolution resulted. The volume of solution was therefore increased to

between 250 and 300 ml with water without addition of more acid in order to decrease the violence of the reaction. Intermittent cooling of the solution in a beaker of water was also necessary to control the rate of dissolution of the aluminum.

In some preliminary tests, a strong odour of hydrogen sulphide was detected when the sodium thiocyanate indicator was added to hot solutions of the reduced titanium and a rapidly fading end-point was obtained. These observations are in agreement with those of Rahm[18]. Cooling the solution to less than 60°C before adding the indicator, as recommended by Rahm overcame the interference.

The blank correction obtained in the aluminum reduction procedure is considerably greater than the blank obtained in either of the liquid amalgam procedures e.g. 0.60 ml vs 0.08 ml. Nevertheless the blank is reproducible if an identical amount of aluminum metal is used with each sample. If different weights of aluminum metal are used, however, the blank correction has to be calculated on the basis of ml of ferric sulphate solution per gram of aluminum and the corrections made accordingly. Tin and titanium are frequently present as impurities in aluminum and are usually responsible for the blank titration involved. Copper and antimony are also objectionable because they interfere with the titration.

Niobium is also reduced to some extent by aluminum metal but there is no way to avoid this interference like it is avoided in the procedure employing the liquid lead amalgam.

II. Analysis of Samples

A. Reduction with zinc or lead amalgam

Table 5 shows that reduction of the titanium with either liquid zinc or lead amalgam gives results that compare very favourably, both with respect to accuracy and to precision, with results obtained by the differential spectrophotometric method and with the other methods described in this report. Lead and zirconium do not interfere and other possible interferences such as iron or niobium were not present. Iron does not interfere if either a zinc or a lead amalgam is used as a reductant.

For the determination of titanium in lead zirconate-lead titanate samples that contain no niobium, virtually 100% reduction of the titanium can be obtained with liquid zinc amalgam at relatively low acid concentrations. The 100% reduction of titanium with lead amalgam is accomplished at somewhat higher acid concentrations. However, if niobium is present the zinc amalgam procedure cannot be used because some of the niobium will be reduced. On the other hand, if lead amalgam is used, the higher acidities necessary to achieve 100% reduction of the titanium cannot be employed because niobium is also reduced under these conditions. Therefore for samples that contain niobium, the maximum acidity is fixed at 2.4 M hydrochloric acid + 0.5 to 1 M sulphuric acid in order not to reduce the niobium. The titanium is about 99% reduced at this acidity and the amount of titanium present is calculated by using an empirical factor obtained by standardizing the ferric sulphate solution against

known amounts of titanium carried through the procedure using the same amounts of acid, etc. For example, some of the samples reduced by the lead amalgam procedure were "spiked" with niobium and no interference was apparent.

If no interferers are present in the samples, the liquid zinc amalgam procedure is preferred because of its slightly greater reduction efficiency. The lead in the samples is also reduced to the metallic state but it dissolves in the amalgam and in effect the reducing agent becomes a mixed zinc-lead amalgam. One of the sources of error to be aware of, however, in employing the liquid zinc amalgam is the possible existence of small particles of lead metal resulting from the reduction step that remain suspended in the solution instead of dissolving in the amalgam. These particles of lead may reduce some of the ferric sulphate and cause a fading end-point. The effect is more pronounced if the amalgam has been used many times and does not contain as much zinc as a fresh amalgam. The zinc amalgam should not be used more than 2 or 3 times before discarding it. In the analyses of the samples, however, no difficulties were encountered from this potential source of error.

B. Reduction with Aluminum Metal

Reduction of the titanium with aluminum metal by the proposed method gives results that compare favourably with results obtained by the other methods given in Table 5. The bulk of the lead is removed as lead sulphate and the small amount left in solution does not interfere. Zirconium does not interfere and iron would not constitute an interference but niobium would.

The samples that were analyzed, however, were free from both iron and niobium.

C. Polarographic Procedure

The determination of titanium in the lead zirconate-lead titanate materials by the polarographic method yields results that compare very well with the results obtained by the other methods. The precision of the method is excellent from a polarographic viewpoint and is only marginally less than the precision of the other methods. There does not appear to be any bias in the method so far as accuracy is concerned. These desirable factors are undoubtedly due to the very well-defined characteristics of the titanium wave in the medium employed. No maximum suppressor is required.

No interfering elements were present in the samples. Elements such as iron, chromium, etc., that are sometimes added to lead zirconate-lead titanate compounds would cause difficulties only if present in the samples in amounts that give rise to polarographic waves that are prior to and have a height greater than the titanium wave. Ferric iron is a more serious interference than ferrous, therefore the iron should first be reduced to the ferrous form. This reduction step would simultaneously reduce any Cr(VI) to Cr(III) and shift the chromium wave to minus 1.3 volts vs the S.C.E. where it would not interfere with the titanium wave. Niobium does not interfere because it is reduced at more negative potentials[22].

SUMMARY

This report describes three simple, rapid, precise and accurate methods for the determination of titanium in lead zirconate-lead titanate material. The first two methods are based on reduction of the titanium with a) liquid zinc or lead amalgams or b) metallic aluminum followed by titration of the reduced titanium with standard ferric sulphate solution. The third method is a polarographic procedure using an acetate-EDTA electrolyte. Relatively few elements interfere and procedures are described to overcome the effects of some of those that do. Once the manipulative skills are acquired each method is simply and rapidly carried out. The results obtained by any of the proposed methods are in excellent agreement with the results obtained by the differential spectrophotometric method.

Each of the proposed methods is easier and faster than the differential spectrophotometric method because in the latter method a great deal more attention has to be paid to the calibration of the volumetric ware, the adjustment of the acid concentration and the preparation of the standard titanium solutions. In addition, the lead must be removed prior to the colorimetric finish by either solvent-extraction or precipitation with sulphuric acid. In the proposed methods using amalgam reduction or the polarographic method, the lead does not have to be removed in a separate step.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of G. Zechanowitsch, Chemical Analysis Section, Extraction Metallurgy

Division, who did the preliminary reduction tests, using the lead and zinc amalgams, and the careful determination of the titanium content of the samples, using the differential spectrophotometric method.

REFERENCES

1. MacNamara, V. M., and Gow, W. A., "A Chemical Precipitation Method for the Production of a Homogeneous, High Purity Powder Applicable to the Lead Zirconate Titanate Solid-Solution Series", Mines Branch Investigation Report IR 63-39, Department of Mines and Technical Surveys (now Department of Energy, Mines and Resources) Ottawa, Canada (1963).

2. Webster, A. H., MacDonald, R.C., and Bowman, W. S., "The System $PbO-ZrO_2-TiO_2$ at 1100°C," Bull. Can. Ceramic Soc. 34, 97 (1965).

3. Webster, A. H., Weston, T. B., and Craig, R. R., "Some Ceramic and Electrical Properties of Bodies Fabricated from Coprecipitated Lead-Zirconium-Titanium Hydroxides", Bull. Can. Ceramic Soc. 34, 121 (1965).

4. Hitchen, A., "The Determination of Lead by a Solvent Extraction-EDTA Titration Method", Mines Branch Research Report R 128, Department of Mines and Technical Surveys, Ottawa, Canada, March 1965.

5. Hitchen, A., "The Complexometric Titration of Zirconium in Perchloric Acid Solution, and its Application to the Analysis of Lead Zirconate-Titanate Ceramics", Mines Branch Research Report R 171, Department of Mines and

Technical Surveys, Ottawa, Canada, November 1965.

6. Barkley, D. J., Hitchen, A., Zechanowitsch, G., Zimmerman, J. B., and Ingles, J. C., "The Chemical Determination of Lead, Titanium and Zirconium in Precipitates Used for the Production of Homogeneous Lead Zirconate-Lead Titanate Solid Solutions", Bull. Can. Ceramic Soc. 34, 130 (1965).
7. Murphy, T. J., Clabaugh, W. S., and Gilchrist, R., Nat. Bur. Standards J. Res., Section A, 64, 535 (1960).
8. Dosch, R. G., and Conrad, F. J., Anal. Chem. 36, 2306 (1964).
9. Pribil, R., and Malat, M., Coll. Czech. Chem. Communs. 15, 120-31 (1950); C.A. 45, 3286 (1951).
10. Majumdar, A. K., and Chowdhury, J.B.R., Anal. Chim. Acta. 15, 105 (1956).
11. Hitchen, A., "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", Mines Branch Technical Bulletin TB 120, Department of Energy, Mines and Resources, Ottawa, Canada, March 1970.
12. Jones, C., Trans. Am. Inst. Mining Engrs. 17, 411 (1888-9).
13. Hitchen, A., "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", Mines Branch, Technical Bulletin TB 121, Department of Energy, Mines and Resources, Ottawa, Canada, March, 1970.

14. Suzuki, S., and Horiike, T., J. Chem. Soc. Japan, Pure Chem. Sect. 72, 143 (1951): Chem. Abstr. 46, 3450 (1952).

15. Nakazono, T., J. Chem. Soc. Japan 42, 526, 761 (1921): Chem. Abstr. 16, 1543 (1922).

16. Paige, J. O., and Gainer, A. B., Anal. Chem. 31, 1399 (1959).

17. Hope, H. B., Moran, R. G., and Ploetz, A. C., Ind. Eng. Chem., Anal. Ed. 8, 48 (1936).

18. Rahm, J. A., Anal. Chem., 24, 1832 (1952).

19. Pilkington, E. S., and Smith, P. R., Anal. Chim. Acta. 32, 552 (1965).

20. Goode, G. C., Herrington, J., and Jones, W. T., Anal. Chim. Acta, 35, 91 (1966).

21. Hitchen, A., "Polarographic and Amperometric Methods Applied to Metallurgical Analysis", Mines Branch Information Circular IC 158, Department of Mines and Technical Surveys, Ottawa, Canada, April 1964.

22. Hitchen, A., "The Polarographic Determination of Titanium; Application to the Analysis of Lead Zirconate - Lead Titanate Electronic Ceramics", Mines Branch Technical Bulletin TB 152, Department of Energy, Mines and Resources, Ottawa, Canada, September 1972.

23. Vincent, S. M., "Analyses of Lead Zirconate-Lead Titanate Solids Containing Lanthanum", Bell Telephone Laboratories Technical Memorandum, April 12, 1971.

24. Vogel, A. I., "Quantitative Inorganic Analysis", 3rd ed. Longmans, Green and Co. Ltd., London, 1961.

25. Khan, M.A.S., and Stephen, W. I., Anal. Chim. Acta. 41, 43 (1968).

26. Chalmers, R. A., Edmonds, D. A. and Moser, W., Anal. Chim. Acta. 35, 414 (1966).

27. Hillebrand, W. F., and Lundell, G.E.F., "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc. New York, 1953.