CANADA

Dept. Mines & Technical Surveys
PATENT BRANCH
24 1966
LIBRARY
OTTAWA, CANADA.

THE COMPLEXOMETRIC TITRATION OF ZIRCONIUM IN PERCHLORIC ACID SOLUTION, AND ITS APPLICATION TO THE ANALYSIS OF LEAD ZIRCONATE-TITANATE CERAMICS

A. HITCHEN

PARTMENT OF MINES AND
HNICAL SURVEYS, OTTAWA

EXTRACTION METALLURGY DIVISION

MINES BRANCH

RESEARCH REPORT

R 171

*R172 not published

Price 75 cents

NOVEMBER 1965

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
Mackenzie Building, 36 Adelaide St. East

MONTREAL
Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 75 cents Catalogue No. M38 -1/171

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1965

Mines Branch Research Report R 171

THE COMPLEXOMETRIC TITRATION OF ZIRCONIUM IN PERCHLORIC ACID SOLUTION, AND ITS APPLICATION TO THE ANALYSIS OF LEAD ZIRCONATE-TITANATE CERAMICS

by

A. Hitchen *

ABSTRACT

A rapid, simple, precise and accurate method is described for the titrimetric determination of zirconium. The sample, after a fuming with perchloric acid, is diluted with water and titrated with a standard solution of disodium ethylenediamine tetraacetate (EDTA), using Xylenol Orange as the indicator. Except for bismuth, iron (III), tin, antimony, niobium, mercury (I), arsenate, sulphate and fluoride, relatively few ions interfere; and procedures for overcoming the interferences or eliminating the interfering ions are described. Because titanium and lead do not interfere, this titration procedure has been successfully applied to the direct determination of zirconium in lead zirconate-lead titanate ceramic materials. A special fuming technique makes possible the "activation" of up to 205 mg of zirconium and is a major factor in obtaining the high precision.

* Senior Scientific Officer, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Rapport de recherches R 171

LE TITRAGE COMPLEXOMÉTRIQUE DU ZIRCONIUM DANS UNE SOLUTION D'ACIDE PERCHLORIQUE ET SON APPLICATION À L'ANALYSE DES CÉRAMIQUES AU ZIRCONATE ET AU TITANATE DE PLOMB

par

A. Hitchen*

RÉSUMÉ

L'auteur décrit un procédé rapide, simple et précis d'effectuer le dosage titrimétrique du zirconium. L'échantillon, après fumage à l'acide perchlorique, est dilué avec de l'eau et titré à l'aide d'une solution régulière de tétraacétate d'éthylénédiamine de bisodium (EDTA), en utilisant du Xylenol Orange comme indicateur. Sauf pour le bismuth, le fer (III), l'étain, l'antimoine, le niobium, le mercure (I), l'arséniate, le sulfate et le fluorure, relativement peu d'ions font de l'interférence, et l'auteur décrit les procédés utilisés pour combattre les interférences ou éliminer les ions interférents. Parce que le titane et le plomb ne causent pas d'interférence, le présent procédé de titrage a été appliqué avec succès au dosage direct du zirconium dans les céramiques à titanate de plomb et à zirconate de plomb. Un procédé spécial de fumage rend possible l'"activation" de près de 205 mg de zirconium et c'est un facteur important dans l'obtention d'une haute précision.

*Agent scientifique sénior, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

INTRODUCTION

An extensive research program on the development of chemical processes for the production of pure homogeneous electronic ceramics of closely controlled composition is being carried out on an interdivisional basis at the Mines Branch. One phase of this work, involving the production of lead zirconate-titanate powders, has been described by McNamara and Gow (1). Other recent publications have included studies of the phase relationships, and of the ceramic and electrical properties of the ceramics produced from these powders (2, 3).

Another important part of this program is the development of rapid, accurate and precise analytical methods for production control and for characterization of the final products. A recent publication (4) describes the development of the procedure used for the determination of lead, and an earlier summary of analytical methods (5) includes a discussion of the difficulties experienced in obtaining accurate values for zirconium using the well-known mandelic acid gravimetric method (6). In view of these difficulties, a gravimetric method employing 8-hydroxyquinoline and cupferron as reagents (7) and a similar method employing a prior ion exchange separation (8) were investigated. Neither offered any advantages with respect to either speed or precision. Polarographic and absorptiometric methods were considered, on the basis of previous experience, to be unlikely to provide the required accuracy.

It was therefore decided to investigate the use of an EDTA-titrimetric method, since this approach had proved so successful in the determination of lead in these same materials (4). In most of the published papers on the subject, zirconium is determined indirectly, i.e. by the addition of excess EDTA and back-titration with bismuth or iron (9, 10, 11, 12, 13). This is probably related to the difficulty of converting zirconium to a form in which it will react rapidly with EDTA during the course of a direct titration. The few papers which describe a direct titration procedure (14, 15, 16, 17) appear to confirm this. Thus, Pribil and Veselý (17) considered it necessary, after dissolving the sample in hot nitric acid, to allow the solution to stand 12-15 hr in 0.5N nitric acid to permit depolymerization of the zirconium entities. Even with this treatment, titration of more than 35 mg of zirconium was not recommended. These same authors, in another paper (16), state that zirconium solutions containing hydrochloric, sulphuric or perchloric acids are not suitable for complexometric determinations and the results are always low. On this basis, they recommend using only a nitric acid medium under controlled conditions. On the other hand, Volodarskaya and Derevyanko (14) found it possible to determine zirconium in non-ferrous alloys, using hydrochloric or sulphuric acid media. However, these workers, too, limited themselves to about 20 mg of zirconium. Experiments were therefore carried out to establish the feasibility of rapidly determining, by direct EDTA titration,

a sufficient weight of zirconium to give the desired level of precision. This report describes the result of the study. It shows that, contrary to previous reports, a large amount of zirconium can be titrated directly with EDTA. It is further shown this titration can be carried out in perchloric acid medium, which is most convenient for the analysis of lead zirconate-titanate ceramics. Moreover, and of great importance, the technique necessary to achieve this requires not more than 30 minutes, rather than 12 to 15 hr as reported by other investigators. A comprehensive investigation of the effect of interfering ions outlines the possibilities and limitations of the procedure, and a precision study shows that, when used for the determination of zirconium in lead zirconate-titanate materials, a precision comparable to that previously reported from this laboratory for the determination of lead (4) is possible.

An added advantage is that the same standard solution and titration set-up are employed for both lead and zirconium determinations, with a resultant saving in time, bench space and expense.

APPARATUS AND REAGENTS

Apparatus

Precision burette: 100-ml, Advanced free-piston burette (Advanced Instruments, Inc., Newton Highlands, Mass. (18)), modified by the substitution of a Teflon stop-cock and a drawn-down tip.

Reagents

0.01 M EDTA solution. Dissolve 3.722 g of the disodium dihydrate salt in water and dilute to 1 litre.

NOTE: Since commercial zirconium is a mixture of zirconium and hafnium, and since the reagent reacts quantitatively with both these elements, the results of the titration of the sample by this method are obtained in millimoles of combined zirconium and hafnium and the equivalence of the reagent depends on the relative proportions of the two elements. Therefore, to obtain results for the zirconium plus hafnium content of the samples which will be concordant with the amount added in the preparation of the powder being analyzed, standardize the EDTA solution, by the proposed method, against a solution of the zirconium salt used in the preparation of the lead zirconate-titanate material. This zirconium solution must be carefully and accurately standardized gravimetrically by the cupferron or mandelic acid method. The EDTA solution thus standardized will have an empirical equivalence factor that will enable one to calculate the number of milligrams of zirconium (plus hafnium) oxide in the sample taken for analysis.

If it is known the lead zirconate-titanate material is free from hafnium, standardize the EDTA solution against hafnium-free zirconium oxide, by the proposed method or against pure lead (99.99%) in acetate buffer pH 5.0 - 5.5, using Xylenol Orange indicator (4), to determine the exact normality of the solution.

Perchloric acid -- reagent grade, 72 per cent.
Xylenol Orange indicator -- 0.1 per cent in water.
The other reagents used are of A.R. quality.

ANALYSIS PROCEDURES

The procedures finally adopted are as follows:

A. Solutions and Unsintered Solid Samples

Transfer a sample containing 20 to 150 mg ZrO_2 to a 600-ml beaker and add 25 to 30 ml of 72 per cent perchloric acid. Evaporate to fumes of perchloric acid and boil the fuming acid solution until it becomes pale yellow-green in colour. Continue to boil for 2 to 5 min. Cool, rinse down the inside of the beaker with water, and dilute to 400-500 ml. Add several drops of Xylenol Orange indicator and titrate with 0.01 M EDTA solution. Near the end-point, warm the solution to 70-80° C and complete the titration. The colour change at the end-point is extremely sharp from red to pure yellow.

B. Sintered Lead Zirconate-Titanate Samples

Method 1. Sodium Peroxide Fusion (recommended method)

Fuse a weighed 0.2 to 0.5 g sample with about 10 times its weight of sodium peroxide together with 5 or 6 pellets of sodium hydroxide in a nickel crucible at 400-450° C for 30 min in a muffle furnace. Cool, place the crucible in a 600-ml covered beaker, and fill the crucible carefully with water. After the reaction has subsided, rinse the contents of the crucible into the beaker and add 35 to 40 ml of 72 per cent perchloric acid. If some insoluble particles adhere to the crucible, use some of the acid to dissolve them, and rinse this solution into the beaker also. Evaporate the solution to heavy fumes of perchloric acid and proceed as directed above for unsintered samples.

Method 2. Nitric Acid-Hydrofluoric Acid-Sulphuric Acid Treatment

Transfer a weighed 0.2 to 0.5 g sample to a small Teflon beaker and add 20 ml of concentrated nitric acid and 5 to 10 ml of concentrated hydrofluoric acid. Digest on a hot plate for a few minutes to disintegrate the sample.

Carefully add about 2 ml of concentrated sulphuric acid and evaporate the solution to heavy fumes of sulphuric acid. Repeat the treatment with nitric and hydrofluoric acids if necessary, to ensure the complete disintegration of the sample. Cool, rinse down the sides of the beaker with a little water, and evaporate again to fumes of sulphuric acid. Repeat this treatment to ensure the complete removal of fluoride. Finally, continue the fuming of the solution to remove excess sulphate until dryness is almost but not quite reached. Rinse the sample into a 600-ml beaker with a little water and add 25 to 30 ml of 72 per cent perchloric acid. Evaporate the solution to fumes of perchloric acid and proceed as directed above for unsintered samples.

Method 3. Ammonium Fluoride-Perchloric Acid Treatment

Transfer a weighed sample to a small Teflon beaker and add 10 ml of concentrated hydrofluoric acid and 5 to 10 ml of concentrated ammonium hydroxide. Digest on a hot plate to disintegrate the sample. Add 10 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid, and evaporate the solution almost to dryness. Repeat the treatment with hydrochloric and nitric acids, to decompose the ammonium salts* and remove the bulk of the fluoride. Finally, add 10 ml of 72 per cent perchloric acid and evaporate the mixture to dryness. Add a further 10 ml of 72 per cent perchloric acid and evaporate to dryness again to ensure complete removal of fluoride. Add 25 to 30 ml of 72 per cent perchloric acid and warm the mixture to dissolve the salts**. Transfer the solution to a 600-ml beaker, evaporate it to heavy fumes of perchloric acid, and proceed as directed above for unsintered samples.

NOTE: If desired, a larger sample may be taken into solution by any of the above methods and diluted to a known volume, e.g. 500 ml, in a volumetric flask. Aliquots may then be taken from this solution for each of the required determinations, i.e. Pb, Ti and Zr. Slight differences due to lack of homogeneity can be avoided by this technique, but it has the disadvantage that it is more troublesome to dissolve a larger sample than a smaller one, especially sintered samples.

---

* The ammonium salts are removed to ensure the removal of fluoride and as a safety precaution in order to avoid any possible explosive decomposition of ammonium perchlorate.

** Occasionally some samples do not redissolve. No explanation has been found for this unexpected behaviour.

PRELIMINARY INVESTIGATIONS

Standardization of the EDTA Solutions

In chemical behaviour hafnium is very similar to zirconium, and it is titrated with EDTA under the conditions of the proposed method. Hafnium is also precipitated with mandelic acid in the gravimetric method and is finally weighed as hafnium oxide. Thus, in either method hafnium is included in the zirconium result. However, because of the difference in equivalent weights of the two elements the results for zirconium plus hafnium by the two methods will not coincide and cannot be properly compared unless corrections are made for the hafnium content. Because the hafnium content may differ slightly between different batches of zirconium salts used to prepare the lead zirconate-titanate material, it is necessary to standardize the EDTA solution used for the determination of zirconium against a standard solution of zirconium prepared from the same batch of zirconium salt that is used in the preparation of the lead zirconate-titanate material. Standardization in this way will give an empirical equivalence factor for ZrO_2 plus HfO_2 that will permit the correlation of results by the gravimetric method and by the titrimetric method.

It is essential to standardize the standard zirconium solution carefully by either the cupferron (19) or mandelic acid (6) gravimetric method in which the zirconium (plus hafnium) precipitate is ignited to the combined ZrO_2 plus HfO_2 oxides. Table 1 shows typical results for the standardization. It will be seen that standardizing the zirconium solution gravimetrically by precipitating the zirconium (plus hafnium) with ammonium hydroxide gave slightly erratic and higher results than did the cupferron or mandelic acid methods. These erratic results were attributed to the presence of small amounts of aluminum as an impurity in the zirconium salt.

TABLE 1

Comparison of Cupferron, Mandelic Acid and Ammonium Hydroxide Methods for the Gravimetric Standardization of Pure Zirconium Solutions

	Cupferron Method	Mandelic Acid Method	Ammonium Hydroxide Method
Aliquot taken, ml	10	15	10
ZrO_2 + HfO_2, mg per 10 ml	113.04, 113.02, 113.11 Ave. 113.06	113.07, 113.03 Ave. 113.05	113.41, 113.79, 113.57 Ave. 113.59

Investigation of the EDTA Titration of Zirconium in Hot Nitric Acid

A large number of titrations, upon synthetic zirconium solutions containing lead and titanium, were carried out using the procedure recommended by Pribil and Veselý (17). It was concluded from the results of these experiments that the method, while simple and accurate for most routine analyses, was unsuitable for application to the analysis of lead zirconate-titanate materials, for the following reasons: 1) it lacked the high accuracy and precision desired; 2) only relatively small amounts of zirconium, e.g. less than 35 mg of zirconium, could be titrated; and 3) the solution had to stand for 15 hr or overnight before the titration could be completed. Furthermore, the procedure could not easily be adapted to the analysis of solid samples of lead zirconate-titanate materials, especially the sintered type of material.

Determination of Zirconium in Various Acid Media

In view of the difficulty of dissolving the solid samples in nitric acid, attention was directed to the use of other mineral acids for carrying out the titration. Phosphoric acid dissolved the unsintered samples completely, but formed insoluble phosphates with zirconium, titanium and lead when the solution was diluted with water. Hydrochloric acid, like nitric acid, has the disadvantage that solid samples are not readily dissolved by it. Sulphuric and perchloric acids would be the most desirable solvents for the titration, because they dissolve solid samples more readily than nitric or hydrochloric acids, and moreover, if the latter acids, together with hydrofluoric acid, were required to dissolve more refractory samples, these acids could be volatilized readily by evaporation to fumes of the higher boiling acids.

Preliminary tests were made to determine the effect of each of these four common mineral acids--nitric, hydrochloric, sulphuric, and perchloric--on the titration of zirconium with EDTA.

Aliquots of a standard zirconium chloride solution containing 20 to 200 mg ZrO_2 were either boiled or fumed heavily with an appropriate amount of the concentrated mineral acid being studied, and finally diluted to 500 ml with water. The concentration of acid after dilution was about 0.5 to 0.6N. After dilution, all the zirconium solutions were titrated with standard 0.01M EDTA solution, using Xylenol Orange indicator. Near the end-point each solution was warmed to 70-80°C and the titration completed. The results of these tests are given in Table 2.

TABLE 2

Determination of Zirconium in Different Acid Media

ZrO_2 Taken, mg	ZrO_2 Found, mg			
	0.5N HCl	0.5N HNO_3	0.5N $HClO_4$	0.5N H_2SO_4
20.49	20.50	20.39	20.50	13 to 19
51.22	51.19	50.95	51.21	46.9
102.44	102.37	100.37	102.48	---
204.88	---	---	204.83	---

The results given in Table 2 show that perchloric or hydrochloric acid is better than either nitric or sulphuric acid for the direct titration of zirconium. Sulphuric acid, in particular, was found to be unsuitable, in spite of literature references to the contrary (14, 20). In the analysis of lead zirconate-titanate materials, moreover, lead would be precipitated as lead sulphate with a possible slight loss of zirconium due to co-precipitation effects (5). In other experiments it was found that in sulphuric acid medium, titanium caused some interference with the detection of the end-point at pH 2.0, the pH at which the titration was carried out. In addition, only relatively small amounts of zirconium could be titrated and the amount of titanium that could be tolerated placed an upper limit on the amount of zirconium that could be taken for analysis. Therefore, attempts to determine zirconium by either direct or back-titration procedures in sulphuric acid medium were abandoned in favour of direct titration in perchloric acid.

Perchloric acid is preferred to hydrochloric acid because it can be used to dissolve most solid lead zirconate-titanate materials by simply boiling the sample in the acid. Sintered samples usually require more drastic treatment. In addition, lead perchlorate is very soluble in an aqueous solution, whereas lead chloride is less soluble.

The Effect of Perchloric Acid Concentration on the Titration of Zirconium with EDTA

Experiments were carried out to establish the range of concentration of perchloric acid in which the titration of zirconium with EDTA could be performed. The results of these experiments are given in Table 3.

TABLE 3

The Effect of Perchloric Acid Concentration on the Titration of Zirconium with EDTA

Test No.	Volume of 72% $HClO_4$ Before Fuming	Approx. Acid Normality of Final Solution	ZrO_2 Taken=56.55mg ZrO_2 Found, mg
1.	5 ml	0.1	56.35
2.	10 ml	0.2	56.56
3.	20 ml	0.4	56.39
4.	30 ml	0.5 to 0.6	56.52
5.	50 ml	1 to 1.2	56.71*
6.	75 ml	1.5 to 2	56.96*
7.	100 ml	2 to 2.4	--- **

*end-point orange in colour, indistinct and unreliable.

**end-point not detectable.

The Effect of Zirconium Content on the Titration

Experiments were undertaken to establish the range of concentration over which zirconium could be determined in 0.5N perchloric acid solution. Amounts of zirconium from 20 to 200 mg of ZrO_2 were titrated with standard 0.01 M EDTA solution. Amounts of zirconium from 0.2 to 1 mg of ZrO_2 were titrated with standard 0.01 M EDTA solution. The results of these experiments are given in Table 4.

TABLE 4

The Effect of Zirconium Content on the Titration

ZrO_2 Taken, mg	ZrO_2 Found, mg
0.205	0.206
1.024	1.026
20.49	20.50
51.22	51.21
102.44	102.48
204.88	204.83

The Effect of Titanium on the Titration of Zirconium with EDTA in 0.5N Perchloric Acid

Experiments were carried out to determine the effect of titanium on the titration of zirconium with EDTA in 0.5N perchloric acid solution. The titanium used in these experiments was added in the form of a dilute standardized solution of titanous chloride in 10 per cent hydrochloric acid in order to avoid the introduction of sulphate ion that is generally used in the preparation of titanium solutions. The titanium (III) is readily oxidized to titanium (IV) when the solution is fumed with the perchloric acid. The results of these experiments are given in Table 5.

TABLE 5

The Effect of Titanium on the Titration of Zirconium with EDTA in 0.5N Perchloric Acid

Test No.	TiO_2 Taken, mg	ZrO_2 Taken= 56.55 mg
		ZrO_2 Found, mg
1.	none	56.52
2.	47.5	56.59
3.	47.5*	56.59
4.	95.0	56.55
5.	190.0	56.59
6.	380.0	56.52

*In addition to the titanium, 600 mg of Pb was added to the form of lead nitrate before fuming the solution with perchloric acid.

Interference Study of Some Elements in the EDTA Titration of Zirconium in 0.5N Perchloric Acid Solution

Although lead and titanium were the only elements that would be present in the lead zirconate-titanate material in amounts sufficient to warrant concern as potential interferences, an interference study was undertaken to determine the effect of some other elements that would possibly be present as impurities in the raw materials or be introduced as contaminants at various phases of the research program in the production of the lead zirconate-titanate material. The results of an interference study are also of great interest if the procedure is to be adapted to the analysis of other zirconium-bearing material. The results of these tests are given in Table 6.

The criterion used to decide if an element interfered was whether or not recovery of the zirconium at the 20-mg level was within ±0.05 mg of the amount taken or within ±0.15 mg at the 60-mg level.

TABLE 6

Titration of Zirconium in the Presence of Various Elements

I. NON-INTERFERING ELEMENTS

Elements that do not interfere with the determination of zirconium (10-100 mg element; 20-60 mg ZrO_2)
Ag^{+}, Al^{+3}, As^{+3}, Ba^{+2}, Be^{+3}, B^{+3}, Ca^{+2}, Cd^{+2}, Ce^{+3}, Co^{+2}, Cr^{+6}, Cu^{+2}, Dy^{+3}, Er^{+3}, Fe^{+2}*, Gd^{+3}, Hg^{+2}, K^{+}, La^{+3}, Li^{+}, Mg^{+2}, Mn^{+2}, Mo^{+6}, Nd^{+3}, Ni^{+2}, Pb^{+2}, Pr^{+3}, Sm^{+3}, Sr^{+2}, Th^{+4}, Ti^{+4}, U^{+6}, V^{+5}, Y^{+3}, Yb^{+3}, Zn^{+2}.

*Hydroxylamine hydrochloride added to reduce Fe^{+3} to Fe^{+2}.

Titration of Zirconium in the Presence of Various Elements

II. INTERFERING ELEMENTS

Cations	As^{+5}, Bi^{+3}, Fe^{+3}, Hg^{+*}, Nb^{+5}, Sb^{+5}, Sn^{+2}, Sn^{+4}
Anions	F^{-**}, $SO_4^{=**}$

*In the presence of Hg^{+} the end-point is not sharp and the results are 0.1 to 0.5 mg high. The other metals interfere by consuming EDTA or by forming precipitates. Sn^{+2} and Sn^{+4} do not interfere in 0.5N hydrochloric acid solution.

**An indistinct end-point is produced in the presence of these anions.

Experiments in Overcoming Interferences

1. Changes in Acid Concentration

A few titrations were carried out in 1 to 2M perchloric acid to see whether the interference of bismuth and iron could be prevented by using a higher acid concentration. A slight improvement was noted but the endpoint faded and was not distinct enough. The Xylenol Orange apparently forms with these elements a complex that is less intensely coloured at the higher acid concentration but which still obscures the true end-point in spite of the fact that a colour change is observed in the vicinity of the end-point. It was also noticed, in these experiments, that when amounts of perchloric acid in excess of about 35 ml were fumed, the resulting solution on dilution with water frequently smelled strongly of chlorine due to the break-down of perchloric acid. This probably contributed to the fading of the indicator.

2. Use of Mercury Cathode Electrolysis for the Separation of Zirconium from Bismuth, Iron and Lead in Perchloric Acid Medium

Electrolysis with a mercury cathode serves as a simple and convenient method for the separation of elements such as aluminum, titanium and zirconium from iron, copper, bismuth, lead and many other elements which can be deposited, under suitable conditions, on the mercury (21). This method should serve, therefore, as an excellent means of removing bismuth and iron as well as several other elements from lead zirconate-lead titanate material, thus preventing them from interfering in the determination of zirconium. Most mercury cathode separations have been carried out in a

dilute sulphuric acid solution, but, because sulphuric acid is not satisfactory for the subsequent determination of zirconium, it is necessary to perform the electrolysis in a perchloric acid solution. This medium has the added advantage that lead perchlorate is soluble. Experiments were therefore carried out to determine the feasibility of a mercury cathode electrolysis of a perchloric acid solution for the separation of bismuth and iron from zirconium.

Synthetic solutions were prepared that contained zirconium, bismuth, ferric iron, titanium, and lead. These solutions were evaporated to heavy fumes with 30 ml of 72 per cent perchloric acid to remove nitrate and chloride ions that were associated with the preparation of the solutions. After cooling, the solutions were diluted with water to about 250 ml and electrolyzed on a mercury cathode until bismuth and iron were removed. After completion of the electrolysis, the electrolyte was transferred to a 600 ml beaker and evaporated to fumes of perchloric acid, cooled, diluted with water to 500 ml and titrated with standard 0.01M EDTA solution, using Xylenol Orange as indicator. The results of these experiments are given in Table 7.

TABLE 7

Separation of Zirconium from Iron, Bismuth and Lead by Mercury Cathode Electrolysis

Test No.	Fe Taken, mg	Bi Taken, mg	TiO_2 Taken, mg	Pb Taken, mg	ZrO_2 Taken, mg	ZrO_2 Found, mg	Diff, mg
1.	--	--	--	--	20.49	20.49	0.00
2.	40	20	--	--	20.49	20.49	0.00
3.	40	20	--	--	20.49	20.49	0.00
4.	40	20	--	--	20.49	20.40	- 0.09
5.	40	20	30	150	50.12	49.79	- 0.33

Tin, antimony and arsenic are also removed by means of the mercury cathode. In other experiments it was found, however, that these elements form precipitates with zirconium when fumed with perchloric acid and it is better, therefore, to remove them by volatilization with hydrobromic and hydrochloric acids rather than by mercury cathode electrolysis, i.e., after it is established that perchloric acid is to be used.

3. Chemical Reduction of Iron by Means of Various Reducing Agents

Although a mercury cathode electrolysis is suitable for the removel of iron and other interfering elements, it would be desirable to have a simpler method for eliminating the interference of iron if it is the only significant interference present in the samples. Attention was therefore directed to developing a suitable procedure in which a chemical reductant could be used to reduce ferric iron to ferrous iron, which was found not to interfere.

A series of tests was carried out in which solutions containing 20.49 mg of ZrO_2 and 40 mg of Fe^{+3} were evaporated to heavy fumes with 25-30 ml of 72 per cent perchloric acid and then diluted to 50-100 ml with water. The resultant solutions were treated with the various reducing reagents that are listed in Table 8, using a separate zirconium-iron solution with each reagent. In one test, using stannous chloride as the reductant, the zirconium-iron solution was boiled with 30 ml of 12M hydrochloric acid instead of with perchloric acid. Each solution was finally diluted with water to about 500 ml and titrated at 70-80°C with 0.01M EDTA solution, using Xylenol Orange indicator. The results of these experiments are given in Table 8.

TABLE 8

The Use of Chemical Reductants for the Elimination of Iron Interference

ZrO_2 Taken = 20.49 mg			Fe Taken = 40 mg	
Reductant	Amount Used	Treatment	ZrO_2 Found, mg	Remarks
Aluminum wire or granules	200-300 mg	Boiled until Al dissolved	20.85 20.77	Sharp end-point. "
Zinc granules	200-300 mg	Boiled until Zn dissolved	20.77	"
Sodium sulphite	200-300 mg	---	---	No end-point detected.
Ascorbic acid	200-300 mg	---	---	No end-point detected.
Stannous chloride	200-300 mg	0.5N $HClO_4$	---	Indistinct end-point, unreliable.
Stannous chloride	200-300 mg	0.5N HCl	20.50	Sharp end-point.
Hydroxylamine hydrochloride	200-300 mg	---	20.50	Sharp end-point.

4. Interference of Niobium

Synthetic solutions containing niobium and zirconium were prepared. The investigation of the effect of niobium was made more difficult because it was not possible to dissolve niobium oxide in either hydrochloric or perchloric acid and hence it was necessary to use sulphuric acid. It had been found in previous experiments that sulphate interfered to some extent in the direct titration of zirconium, so that it was essential to remove the sulphate ion before the effect of niobium could be determined.

Experiments were carried out in which the sulphate was removed either by precipitating the zirconium and niobium with ammonium hydroxide or by precipitating the residual sulphate with barium chloride after most of the sulphuric acid had been removed by fuming. The zirconium was finally determined in the presence of niobium by direct titration with standard 0.01 M EDTA solution in either 0.5N hydrochloric acid or 0.5N perchloric acid, using Xylenol Orange indicator according to the proposed procedure. The results of these experiments and the procedures used are summarized in Table 9.

TABLE 9

The Determination of Zirconium in the Presence of Niobium

Zr Taken = 20.49 mg			
Test No.	Procedure	Nb_2O_5 Taken, mg	ZrO_2 Found, mg
1.	Pure Zr precipitated with NH_4OH and titrated hot in 0.5N $HClO_4$	None	20.49
2.	Zr and Nb precipitated with NH_4OH to remove $SO_4^=$; titrated hot in 0.5N HCl	7	20.10
3.	Same as 2 but titrated hot in 0.5N $HClO_4$	7	20.10, 20.10
4.	" " " " " "	14	20.10, 20.10
5.	" " " " " "	50	18.76
6.	" " " " " "	200	13.53
7.	Sulphate converted to $BaSO_4$ with $BaCl_2$, titrated hot in 0.5N HCl; not fumed with $HClO_4$	7	20.23, 20.10
8.	Fumed with $HClO_4$; 10 ml of HCl added to dissolve Nb precipitate and sulphate converted to $BaSO_4$ with $BaCl_2$; titrated hot in 0.5N $HClO_4$ + 0.15N HCl	7	19.83
9.	Sulphate converted to $BaSO_4$ with $BaCl_2$ followed by fuming with $HClO_4$; titrated hot	7	19.70

Precision of the Zirconium Determination

A statistical study was made of the precision of the zirconium titration in the presence of titanium and lead. A solution of titanium and zirconium dissolved in nitric acid was prepared for use in this study. The zirconium content as determined by the mandelic acid gravimetric method and by the proposed method was 12.88±0.01 g ZrO_2/l. The titanium content as determined by a hydrogen peroxide differential spectrophotometric method (22) was 4.70±0.00 g TiO_2/l.

For the study, 5-ml aliquots of the zirconium-titanium solution were taken. To some of these aliquots a known amount of lead was added and to other aliquots a known amount of zirconium was added as a "spike"; the remaining aliquots were left without additions of lead or zirconium, for purposes of comparison. Each of these solutions was evaporated to fumes of 30 ml of 72 per cent perchloric acid and boiled for several minutes. After cooling, the solutions were diluted to about 500 ml with water and titrated with 0.01 M EDTA and Xylenol Orange indicator. The results of these tests are given in Table 10.

TABLE 10

Precision of the Zirconium Determination

TiO_2 Present, mg	Pb Present, mg	ZrO_2 "Spike", mg	Total ZrO_2 Present, mg	Total ZrO_2 Found, mg	Average ZrO_2 Found, mg	Standard Deviation*, mg
23.5	--	--	64.40	64.46, 64.46, 64.46, 64.48, 64.47, 64.46, 64.43, 64.46, 64.46, 64.40	64.45±0.05	±0.007
23.5	503.79	--	64.40	64.33, 64.38, 64.40, 64.47, 64.36, 64.40, 64.38, 64.42	64.39±0.08	±0.015
23.5	--	5.03	69.43	69.41, 69.41	69.41±0.00	--
23.5	--	20.14	84.54	84.45, 84.42, 84.52, 84.55, 84.45, 84.50, 84.50	84.48±0.07	±0.017
23.5	--	50.35	114.75	114.85, 114.37	114.61±0.24	--

*See reference 23.

ANALYSIS OF SAMPLES

A. Solutions and Unsintered Ceramic Material

Zirconium was determined in a number of solutions and unsintered solid samples of lead-titanium-zirconium oxide mixtures using the proposed method and the results compared with values determined gravimetrically using the mandelic acid method (6). The results are given in Table 11.

TABLE 11

Determination of Zirconium in Lead Zirconate-Titanate Samples: Comparison of Results of Mandelic Acid Gravimetric Method and EDTA Titration Method

Sample No.	ZrO_2 Found	
	Mandelic Acid Method	EDTA Method
4608	5.74 g/l	5.72 g/l
4611	3.16 "	3.17 "
4826	12.88 "	12.88 "
5306	5.62 "	5.60 "
5307	4.63 "	4.63 "
5308	5.61 "	5.61 "
5309	5.57 "	5.58 "
1211	19.12±0.02 %	19.12±0.03 %
1213	19.39±0.05 "	19.35±0.03 "
1214	16.94±0.01 "	16.97±0.01 "
1215	17.09±0.00 "	17.10±0.00 "
4373	26.18 "	26.24 "
2033	17.39 "	17.33±0.02 "
R-4	17.32±0.02 "	17.20±0.00 "
R-5	17.25±0.07 "	17.18±0.01 "
R-6	17.27±0.02 "	17.24±0.02 "
R-7	17.28±0.04 "	17.26±0.00 "

B. Sintered Ceramics (Effect of Sample Dissolution Procedure)

The analysis of the finished electronic ceramics is complicated by the fact that the high-temperature sintering treatment has rendered them insoluble in perchloric, sulphuric, nitric, or hydrochloric acid. Since it was desired to have a method that was applicable to the finished products as well as to the raw materials, it was also necessary to evaluate the method, using samples that had been taken into solution by the methods of attack which would be applicable to the refractory ceramic materials.

To study the application of the method to sintered material, a sample was prepared from pure lead oxide, zirconium dioxide and titanium dioxide so as to have the composition 68.00 per cent PbO, 20.00 per cent ZrO_2, and 12.00 per cent TiO_2. The sample was ground, dried, calcined at 1000°C for one hour, then reground after calcining until 100 per cent of the material passed through a -100 mesh screen and 95 per cent passed through a -200 mesh screen.

Portions of this sample, containing 40 to 100 mg of ZrO_2, were decomposed by two different methods of attack, as follows:

1. A 0.2 to 0.5 g sample was decomposed by the sodium peroxide fusion method (Method 1) described on pages 3-4 of this report In one series of tests the decomposed sample was removed from the nickel crucible with water only. The results of these tests are given in Table 12, Column A. In this series of tests, a thin film of insoluble material remained adhering to the walls of the crucible after the peroxide melt was leached with water, and it was felt this might lead to slight losses of zirconium. Therefore, in a second series of tests, the nickel crucible, after leaching of the peroxide melt with water, was rinsed with perchloric acid in order to dissolve the film of material, and the rinsings were added to the bulk of the sample solution. The results of these tests are given in Table 12, Column B. The remainder of the procedure in each of the above series of tests was as described for the treatment of the peroxide fused samples on pages 3-4 of this report.

2. A 0.2 to 0.5 g sample was decomposed and the zirconium determined by the nitric acid-hydrofluoric acid-sulphuric acid procedure (Method 2) described on page 4 of this report. In this procedure lead sulphate remained insoluble in the acid solution. In one series of tests the lead sulphate was left in the solution without filtering it off. The results of these tests are given in Table 12, Column C. In another series of tests, the lead sulphate was dissolved by adding 5 to 10 g of ammonium chloride to produce a clear solution before titrating the zirconium with EDTA. The results of this series of tests are given in Table 12, Column D.

TABLE 12

Analysis of Standard Lead Zirconate-Titanate Sample: Effect of Decomposition Procedure

ZrO_2 = 20.00%

Peroxide Fusion		Acid Treatment	
A	B	C	D
19.91 % ZrO_2	20.06 % ZrO_2	19.93 % ZrO_2	19.99 % ZrO_2
19.88	20.08	19.95	19.92
19.88	19.96	19.89	19.96
19.99	20.10	19.99	
		20.07	
		20.01	
19.91±0.07	20.05±0.09	19.96±0.10	19.96±0.04

DISCUSSION

Optimum Concentration of Perchloric Acid

The results given in Table 3 show that zirconium may be accurately determined by direct titration with EDTA solution in 0.1 to about 0.6N perchloric acid. When amounts of perchloric acid in excess of 35 to 40 ml are used, the resulting solution on dilution with water frequently smells strongly of chlorine due to the breakdown of perchloric acid. In addition, even when no chlorine odour can be detected, the colour change at the end-point is indistinct and unreliable.

In the fuming step for the dissolution of the samples, about 5 to 10 ml of perchloric acid is fumed off and thus, if less than 10 ml of perchloric acid is used, insufficient acid remains to ensure the proper conditions for the titration of zirconium. Therefore, from 25 to 30 ml of 72 per cent perchloric acid was chosen as a convenient amount of acid to add in order to allow for

losses on fuming. The resultant solution after dilution with water is about 0.3 to 0.5N in perchloric acid. Moreover, this amount of acid minimizes "bumping" during the dissolution step and avoids possible hydrolysis of the zirconium and titanium when the solution is subsequently diluted with water.

The Effect of Zirconium Content on the Titration

The results given in Table 4 show that zirconium may be accurately determined by the proposed method in the range of 0.2 to 200 mg of ZrO_2 in 0.5N perchloric acid solution, i.e., the method is applicable for the determination of substantially larger amounts of zirconium than by previously reported methods (9, 16, 17).

In the titration of amounts of zirconium of 1 mg or less a sharp end-point was obtained, and in practice as little as 10 micrograms has been detected. The procedure is therefore adaptable to the analysis of barren solutions that contain only 1 mg Zr/l. The long waiting period required in previous EDTA methods (16, 17) is unnecessary. In fact, when solutions of zirconium in perchloric acid are diluted and allowed to stand overnight, the subsequent titrations are somewhat slower in reaching the end-point, possibly as a result of the formation of complex hydrolytic polymers. The zirconium, however, may be permitted to stand overnight in the concentrated perchloric acid before dilution without affecting the final titration.

It is believed that the success of the proposed method is due to the fact that the zirconium is boiled in the perchloric acid for a length of time sufficient to depolymerize existing complex polymers of zirconium and convert them to a form in which they are readily titrated with EDTA. Merely evaporating the solution to light or moderate fumes of perchloric acid is insufficient. Zielen and Connick (24) have studied the hydrolytic polymerization of zirconium in perchloric acid solutions and conclude that at low concentrations of zirconium, e.g. about 10^{-4}M, in the presence of high concentrations of perchloric acid, e.g. 1 to 2M, the principal species of zirconium ion is the unhydrolyzed monomer, Zr^{+4}. At higher concentrations of zirconium and lower concentrations of perchloric acid, they postulate the existence of various polymeric species. Thus, in the present work it seems likely that the zirconium exists in the concentrated perchloric acid either as the Zr^{+4} monomer or, more probably, the zirconyl ion ZrO^{+2}. This on dilution and standing, is slowly hydrolyzed to various polymeric species which do not react as readily with EDTA as does the ZrO^{+2} monomer. If, on the other hand, the solution is diluted and titrated immediately, the ZrO^{+2} monomer is not converted to the other species to any great extent before it is able to react with the EDTA.

The solutions are titrated at 70-80° C, a temperature that is lower than that usually reported in the literature for EDTA titrations of zirconium in other acid media. It is believed this is possibly because zirconium is complexed to a lesser extent by perchlorate ion than by other anions, especially sulphate, and therefore is able to form the zirconium-EDTA complex more readily than otherwise. At temperatures lower than 60° C the rate of titration is slower, but occasionally it has been observed (25) that some zirconium solutions are rapidly titrated by EDTA at temperatures as low as 40 to 50° C to within 0.1 to 0.2 ml of the end-point. This phenomenon is believed to be dependent on time and temperature effects associated with the previous preparation of the sample, which would affect the degree of complex formation or hydrolysis of zirconium in the perchloric acid.

The Effect of Titanium on the Titration of Zirconium with EDTA in 0.5N Perchloric Acid Solution

The results given in Table 5 show that relatively large amounts of titanium (and lead) can be tolerated in the direct titration of zirconium with EDTA in 0.5N perchloric acid solution. The end-point in these titrations was very sharp and without the slightest hint of interference due to titanium. These results are especially important in the application of the method to the analysis of lead zirconate-titanate products, and is a distinct advantage over other recently described titrimetric methods for the determination of zirconium in which the titanium must be restricted to less than 5 mg (9) or to less than 40 mg (16).

Interferences

It is seen that, of the ions studied in Table 6, only bismuth, iron (III), arsenate, antimony, tin, niobium, mercury (I), sulphate and fluoride interfere. The effect of sulphate has been discussed in the section of this report on the determination of zirconium in various acids. Sulphate is easily removed by precipitating the zirconium with ammonium hydroxide. Trace amounts of fluoride cause the results to be consistently low by a few tenths of a milligram of ZrO_2, while larger amounts cause indistinct end-points and much lower results. Additions of fluoride-complexing agents, such as boric acid or aluminum, failed to eliminate the interference, nor could fluoride be removed merely by fuming with perchloric acid even if the fuming was repeated several times with intervening rinsings of the walls of the beaker. The fluoride could be eliminated, however, by carefully fuming the perchloric acid solution to dryness at least twice. Baking the residue too long after dryness was reached, however, made it almost impossible to redissolve the residue in perchloric acid.

Tin, antimony and arsenate interfere with the titration of zirconium with EDTA in perchloric acid medium. Tin interferes because it is precipitated, presumably as its hydrous oxide, when fumed with perchloric acid. The precipitate so formed adsorbs or traps some of the zirconium and prevents it from being titrated by the EDTA. In hydrochloric acid medium, neither tin (II) nor tin (IV) interferes, as evidenced by the successful use of stannous chloride to reduce iron (III) (see section on the use of chemical reductants). Antimony and arsenate interfere because they precipitate the zirconium, possibly in the form of its antimonate and arsenate respectively. These precipitates do not redissolve on adding EDTA, and thus the zirconium cannot be titrated. The three metals, tin, antimony and arsenic, however, are easily removed by treatment of the solution with hydrochloric and hydrobromic acids, followed by evaporation of the solution to fumes of perchloric acid to volatilize the metals as their bromides. They can also be removed by mercury cathode electrolysis (21) but, when fumed with perchloric acid prior to electrolysis, these metals form precipitates, so it is better to volatilize them as their bromides.

Niobium in large amounts interferes in the titration of zirconium with EDTA, because it is precipitated, in part, as the hydrous oxide which adsorbs zirconium. Unfortunately, tartrate cannot be used to keep the niobium in solution because tartrate also forms a complex with zirconium which prevents the determination of zirconium by direct titration. It should be possible to apply the back-titration procedure of Fritz and Johnson (9) when the amounts of zirconium and niobium are small, but their procedure is not applicable in the presence of large amounts of niobium. A more detailed discussion of the effect of niobium is given on page 24 of this paper. Tantalum would be expected to behave in a manner similar to that of niobium.

The results in the presence of mercury (I) are slightly high, by 0.1 to 0.5 mg, because of an indistinct end-point.

Bismuth and iron (III) interfere because they consume EDTA at the pH required for the titration of zirconium, and also because they form slightly coloured complexes with Xylenol Orange indicator which mask the sharpness of the end-point. At a higher pH, for instance about 2, the reaction of bismuth and iron (III) with EDTA is stoichiometric and the end-point is sharp. In 0.5N perchloric acid, however, bismuth and iron form weaker complexes with EDTA and Xylenol Orange, and, on titration of these elements with EDTA, only a gradual colour change is observed near the end-point. At this acid concentration, the titration results of a solution containing zirconium, iron and/or bismuth are not equivalent to the sum of the elements present and the end-point colour is an indistinct orange rather than a pure yellow. Increasing the acid concentration to 1M or 2M does not mask the interference of bismuth and iron. Moreover, the end-point obtained in the titration of pure zirconium solutions is indistinct at these higher acid concentrations (see

Table 3). The interference of iron is easily overcome by reducing it with hydroxylamine hydrochloride but bismuth must be removed, either by a mercury cathode electrolysis as discussed in the following section, or by some other procedure.

The results given in Table 6 show that molybdate ion does not interfere with the titration of zirconium. It was observed, however, that at the 100-mg level of molybdate the rate of titration was considerably slower and several minutes had to be allowed for attainment of the correct end-point. A slight precipitate was formed during the titration of the zirconium with EDTA, but this precipitate redissolved as the titration continued until at the end-point the solution became completely clear. The precipitate probably consisted of zirconium molybdate that slowly redissolved as the EDTA was added. This effect is believed to be the cause of the slow rate of titration. Therefore, in order to avoid slow titration rates and to ensure accurate results, it is suggested that when the ratio Mo/Zr exceeds 2/1, or when amounts of molybdenum in the samples greater than 100 mg are expected, a preliminary separation of molybdenum and zirconium should be carried out.

Mercury Cathode Electrolysis

The results given in Table 7 show that when a mercury cathode electrolysis separation was employed the recovery of zirconium was complete and no interference from either bismuth or iron was observed. This separation can thus serve as a satisfactory means for the removal of bismuth and iron, as well as many other elements from zirconium in a perchloric acid solution. Care, however, has to be taken that no zirconium is lost by trapping some of the electrolyte solution between the surface of the mercury and the electrolyte cell wall, or in removing it from the cell. These are believed to be the reasons for the slight losses noted in Tests 4 and 5 in Table 7.

The Use of Chemical Reductants to Eliminate the Interference of Iron

The results given in Table 8 show that:

(a) aluminum and zinc reductants gave slightly high results;

(b) sulphite and ascorbic acid gave poor end-points and unsuccessful titrations;

(c) stannous chloride gave good results in hydrochloric acid solution but poor results in perchloric acid; and

(d) hydroxylamine hydrochloride gave good results in perchloric acid solution.

The successful use of a chemical reductant to reduce iron is dependent on having a uniform excess of the reductant throughout the solution in order to prevent the reoxidation of ferrous iron by air. This accounts for the good results obtained with stannous chloride in hydrochloric acid solution and with hydroxylamine hydrochloride in perchloric acid solution. On the other hand, aluminum and zinc are ineffective in either of these acid solutions because reduction of the iron takes place and is maintained only at the solution-metal interface and not homogeneously. Thus, localized reoxidation of ferrous iron can take place at the surface of the solution in contact with air. This could perhaps be avoided if the reduction were carried out in an inert atmosphere, but would involve a more complicated set-up.

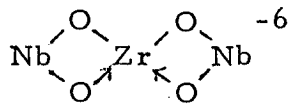
Sodium sulphite and ascorbic acid are also unsatisfactory as reductants, not because they do not reduce iron or fail to prevent reoxidation but, rather, because they interfere with the detection of the end-point. Sulphite is oxidized to sulphate and this may be the explanation for some of the erratic results observed with this reagent. It is also possible that the zirconium forms a complex with sulphite which behaves in a similar manner as the zirconium sulphate complex toward EDTA. The unlikely possibility of of incomplete reduction of ferric iron by the sulphite remains. In any event, whatever the reason, the use of sulphite as a chemical reductant for ferric iron is not satisfactory. Ascorbic acid interferes by forming a complex with zirconium that does not react with EDTA. Volodarskaya and Derevyanko (14) make a similar observation with reference to ascorbic acid and they recommend hydroxylamine hydrochloride for the reduction of ferric iron in hydrochloric or sulphuric acids.

The methods that utilize stannous chloride in hydrochloric acid, or hydroxylamine in perchloric acid solution, for the reduction of iron are more convenient to use than those that employ the mercury cathode for the removal of iron. They have the advantage that they are considerably faster and there is less possibility of loss of zirconium by manipulation. These methods, however, also have a disadvantage because they cannot prevent the interference from other metals such as bismuth. Nevertheless, the chemical reductant methods are useful and convenient to use for those samples in which iron is the only interfering element present. If bismuth or mercury is present in addition to or instead of iron, it is necessary to employ the mercury cathode to remove them. Alternatively, the cation exchange method reported by Dosch and Conrad (8) may be used and the zirconium determined by EDTA titration by the proposed method instead of gravimetrically using cupferron.

The Determination of Zirconium in the Presence of Niobium

The results given in Table 9 show that slightly low recoveries of zirconium are obtained when small amounts of niobium are present. The recoveries of zirconium become smaller as the amount of niobium is increased. The low results are believed to be due to a combination of effects: 1) the formation of soluble complex niobates, 2) coprecipitation of zirconium with hydrous niobium oxide, and 3) adsorption or occlusion of zirconium ions on the hydrous niobium oxide or barium sulphate precipitates. In Tests 2, 3 and 4 the solutions that were titrated were perfectly clear and no trace of precipitate was observed. In Tests 5 and 6 there was a considerable amount of precipitate, presumably hydrous niobium oxide, that undoubtedly adsorbed or occluded some of the zirconium, and led to low results.

The results of Tests 7, 8 and 9 show that sulphate can be removed by precipitation as barium sulphate but slightly low recoveries of zirconium are obtained, probably because of the adsorption of zirconium on the precipitate of barium sulphate. The adsorption effect is seen to be somewhat less in hydrochloric acid solution (Test 7) than in perchloric acid solution (Tests 8 and 9). The results of Test 7 agree well with those of Tests 2, 3 and 4 in which niobium and zirconium were precipitated with ammonium hydroxide to remove the sulphate. The loss of 0.3 to 0.4 mg of zirconium oxide in Tests 2, 3, 4 and 7, as well as part of the loss in Tests 5, 6, 8 and 9, is believed due to the formation of complex niobates containing zirconium, as suggested by Schoeller (26, 27), in which the zirconium is masked and is unable to react with the EDTA. These small aggregates or mixed polymers that form are still in true solution, but the end-members mask the inner ones, e.g.



and prevent their titration with EDTA. The red colour of the zirconium-Xylenol Orange complex slowly reappears when the solution is vigorously stirred with a stirring rod, and this behaviour suggests the existence of some weakly bonded zirconium-niobium species. The stirring mechanically disrupts the bonds between the weakly held zirconium ions and the niobium complexes, thus freeing the zirconium to react with the EDTA. Simply heating the solution does not liberate the zirconium ions as rapidly as does vigorous stirring. The effect, however, is slow and not pronounced. Those zirconium ions that are more completely "buried" within the niobium-zirconium polymers are prevented entirely from reacting with the EDTA.

Precision Study

The colour change of the Xylenol Orange from red to yellow is extremely sharp and it is this property that contributes greatly to the high precision with which zirconium can be determined.

The results of the precision study, Table 10, show that the method is highly precise and accurate in the presence of lead and titanium. A calculation of the combined uncertainty resulting from errors in reading the burette during (a) standardization of the titrant and (b) the titration of the sample indicates that it is sufficient to account for almost all the error in the method.

Analyses of Samples

Table 11 shows that the proposed method gives results that are in excellent agreement with results obtained by the mandelic acid gravimetric method. Lead and titanium do not interfere in the direct titration of zirconium with EDTA and need not be removed prior to the titration.

Unsintered solid samples and solution samples are easily dissolved by boiling in perchloric acid without further treatment.

A determination of zirconium on a single sample of either an unsintered solid or a solution of lead zirconate-titanate material can be completed in about one hour if the result is to be reported on an "as received" basis.

The results in Table 12 show that zirconium can be accurately and precisely determined in sintered lead zirconate-titanate material after the sample has been decomposed either by a sodium peroxide fusion or by a multi-acid treatment as described. The results in Columns A and B of Table 12 indicate there is a slight loss of zirconium if the crucible is not rinsed with acid. The results in Columns C and D of Table 12 show there is no significant adsorption or coprecipitation of zirconium by the lead sulphate produced during the acid decomposition procedure. The slightly lower results of the acid treatment procedure are attributed to the presence of trace amounts of fluoride that were incompletely removed and also, to a lesser degree, to the presence of the small amount of sulphate that remained in the solution. Almost one-half of the individual results of the acid-treated samples are in excellent agreement with the peroxide results, which indicates that fluoride had probably been almost completely removed from these particular samples.

A small amount of nickel is introduced into the solution by the peroxide fusion, but it can be minimized by fusing the material at as low a temperature as is necessary to effectively decompose the sample. Fusion at 400 to 450°C for 30 min was sufficient for the samples that were studied.

Addition of sodium hydroxide produces a better melt at lower temperatures. At 500°C the nickel crucible is attacked to a greater extent and its useful life is shortened.

A determination of zirconium on a single sample of sintered lead zirconate-titanate material may be completed in about 3 hr. The proposed method is thus considerably more rapid than the gravimetric method, which requires 3 to 4 days for completion.

CONCLUSIONS

This report describes a titrimetric procedure for the determination of zirconium in lead zirconate-titanate material which is simple, rapid, precise and accurate. The zirconium is determined in a perchloric acid solution by direct titration with EDTA in the presence of lead and titanium. Relatively few elements interfere, and procedures are described for the removal of those that do. The use of the titrimetric method for this determination is recommended over the gravimetric mandelic acid method because the avoidance of chemical separations permits greater speed and accuracy. In the method, as is common with most other methods for the determination of zirconium, the analytical result includes both zirconium and hafnium. The proposed method has the following advantages over recently described titrimetric methods (9, 16) for the determination of zirconium:

1. Preliminary isolation of a precipitate is not necessary.
2. Relatively large amounts of zirconium may be titrated.
3. Relatively large amounts of titanium and thorium can be tolerated without interference.
4. It is not necessary to allow the solution to stand for 15 hr or so before completing the titration.
5. A back-titration is not necessary.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of G. Zechanowitsch, Technician, Chemical Analysis Section, Extraction Metallurgy Division for useful suggestions pertaining to the analysis of lead zirconate-lead titanate material and for the gravimetric zirconium determinations used for comparison purposes. Thanks are due also to V. McNamara, Senior Scientific Officer, Hydrometallurgy Section, Extraction Metallurgy Division, for discussions arising from problems encountered in this work. The solution of titanium and zirconium used in the statistical study was prepared

and supplied by V. McNamara and his co-workers; the zirconium and titanium contents of this solution were carefully determined by G. Zechanowitsch.

REFERENCES

1. V.M. McNamara and W.A. Gow, "A Chemical Precipitation Method for the Production of a Homogeneous High-Purity Powder Applicable to the Lead Zirconate Titanate Solid Series", Mines Branch Investigation Report IR 63-39, Department of Mines and Technical Surveys, Ottawa, Canada, April 3, 1963.

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

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

4. A. Hitchen, "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. D.J. Barkley, A. Hitchen, G. Zechanowitsch, J.B. Zimmerman and J.C. Ingles, "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. (in press).

6. C.A. Kumins, Anal. Chem. 19, 376 (1947).

7. T.J. Murphy, W.S. Clabaugh and R. Gilchrist, Nat. Bur. Standards J. Res., Section A, 64, 535 (1960).

8. R.G. Dosch and F.J. Conrad, Anal. Chem. 36, 2306 (1964).

9. J.S. Fritz and M. Johnson, Anal. Chem. 27, 1653 (1955).

10. G.W.C. Milner and G.A. Barnett, Anal. Chim. Acta 14, 414 (1956).

11. G.W.C. Milner and J.W. Edwards, Anal. Chim. Acta 20, 31 (1959).

12. G.W.C. Milner and J.W. Edwards, The Analyst 80, 879 (1955).

13. C.F. Hirn and C.A. Lucchesi, Anal. Chem. 31, 1417 (1959).

14. R.S. Volodarskaya and G.N. Derevyanko, Zavod. Lab. 29, 28-29 (1963); English translation, Industrial Laboratory 29, 25 (1963).

15. J. Körbl and R. Pribil, Chemist-Analyst 45, 102 (1956).

16. R. Pribil and V. Veselý, Talanta 11, 1197 (1964).

17. R. Pribil and V. Veselý, Chemist-Analyst 53, 43 (1964); see also correction in Chemist-Analyst 54, 31 (1965).

18. I.C.P. Smith, Chemistry and Industry, p. 1117, (1957).

19. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 1953.

20. O. Budevsky, L. Pencheva, R. Russinova and E. Russeva, Talanta 11, 1225 (1964).

21. G.E.F. Lundell and J.I. Hoffman, "Outline of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, 1938.

22. W.T. Neal, The Analyst 79, 403 (1954).

23. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", 3rd ed. (The MacMillan Company, New York, 1952), p. 271.

24. A.J. Zielen and R.E. Connick, J. Amer. Chem. Soc. 78, 5785 (1956).

25. G. Zechanowitsch, private communication, 1965.

26. W.R. Schoeller, "Analytical Chemistry of Tantalum and Niobium", Chapman and Hall, Ltd., London, 1937.

27. I.M. Kolthoff and P. Elving, "Treatise of Analytical Chemistry: Part II" (Interscience Publishers, New York, 1964), p. 206.