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THE POLAROGRAPHIC DETERMINATION OF TITANIUM; APPLICATION TO THE ANALYSIS OF LEAD ZIRCONATE - LEAD TITANATE ELECTRONIC CERAMICS

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by

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ABSTRACT

A polarographic method for the determination of titanium using a 0.5 M ammonium acetate + 0.1 M acetic acid + 0.1 M disodium ethylenediaminetetraacetate (EDTA) supporting electrolyte is described. The titanium polarographic wave is well-defined in this medium. Relatively few elements interfere, and procedures are suggested to overcome some of those that do.

The method has been used to determine titanium in lead zirconate-lead titanate ceramic powders and solutions. The results compare favourably with results obtained by a differential spectrophotometric method.

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DOSAGE POLAROGRAPHIQUE DU TITANE: APPLICATION À L'ANALYSE DES CÉRAMIQUES ÉLECTRONIQUES À BASE DE ZIRCONATE DE PLOMB ET DE TITANATE DE PLOMB

par

A. Hitchen*

RÉSUMÉ

L'auteur décrit une méthode polarographique de dosage du titane à l'aide d'un électrolyte indifférent comprenant 0.5 M d'acétate d'ammonium, 0.1 M d'acide acétique et 0.1 M de tétraacétate d'éthylènediamine et de sodium. Le polarogramme du titane est très bien défini dans ce milieu. Il y a relativement peu d'éléments qui créent de l'interférence et l'auteur propose certaines méthodes pour contrer les effets de quelques éléments de ce genre.

La méthode a été utilisée pour doser le titane dans des poudres et des solutions de céramiques à base de zirconate de plomb et de titanate de plomb. Les résultats obtenus se comparent favorablement à ceux qu'on obtient en utilisant une méthode de spectrophotométrie différentielle.

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INTRODUCTION

As part of a research program for the development of lead zirconate-lead titanate powders for the production of electronic ceramics of high purity and homogeneity[1] it was necessary to provide rapid, accurate, and precise analytical methods for the determination of titanium in these powders and in the process solutions used in the development work.

The determinate of titanium by means of polarography appeared to be feasible for the range of concentrations expected and an investigation was undertaken to develop a suitable procedure. Several methods have been proposed for the determination of titanium in various materials. For example, Banerjee, Budke and Miller[2] used a potassium pyrosulphate-sulphuric acid medium to determine titanium in niobium and tantalum ores. Graham, et al[3,4,5] used a sulphuric acid-ammonium sulphate-tartaric acid medium to determine titanium in rocks, minerals and various alloys while Potts[6] used a similar medium to determine titanium in paint pigments. The polarography of molybdenum, titanium and niobium in solutions of certain organic acids was studied by Headridge and Hubbard[7]. Sinyakova[8] and Pecsok and Maverick[9] have studied the polarographic behaviour of titanium in an EDTA medium and found that reversible waves could be obtained over a fairly wide range of pH. In a later investigation Berger and Cadoff[10] utilized a sodium acetate-ammonium sulphate-EDTA medium at pH 4.7 to determine titanium in paint pigment. Goode, Herrington and Jones[11] used a 0.2 M sodium acetate + 0.1 M EDTA medium (buffered at pH 4.0), a cathode-ray polarograph, and a high-precision comparison

technique to determine titanium and niobium in lead zirconate-lead titanate ceramics. A polarographic method employing an ammonium acetate + acetic acid + EDTA electrolyte has been used in our laboratories for the determination of molybdenum in binary alloys of molybdenum and uranium[12]. In the course of the work on molybdenum it was found that titanium gave an analytically useful wave in this medium.

This report describes the results of an investigation of the behaviour of titanium in an ammonium acetate + acetic acid + EDTA electrolyte and a study of several factors that influence its behaviour. An investigation to determine those elements that may interfere in the determination of titanium has also been made.

As a result of these studies a method has been developed and successfully applied to the determination of titanium in lead zirconate-lead titanate solutions and powders. A comparison of the results obtained by the proposed polarographic method with those obtained by a differential spectrophotometric method and by reduction using liquid amalgams or aluminum metal is described in a separate report[13].

<div align="center">APPARATUS AND REAGENTS</div>

Apparatus

Leeds and Northrup 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 heater to
maintain a temperature of 25.0 ± 0.1°C.

Reagents

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

5 M ammonium acetate solution. 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 reagent-grade.

EXPERIMENTAL PROCEDURE

The procedure finally adopted is as follows:

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 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 solution 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 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 ± 0.1°C and de-aerate the solution with nitrogen.
Immerse a dropping mercury electrode in the solution and record
4 replicate waves* from 0.0 to minus 1.0 volt vs the S.C.E. using
a suitable current range and damping position on the instrument**.
The half-wave potential of the titanium wave in the above-
mentioned supporting electrolyte should be within 0.01 of
minus 0.46 volt vs the S.C.E.*** Calculate the diffusion current
by subtracting the average residual current measured at minus 0.25
volt from the average limiting current measured at minus 0.70
volt. 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 milligrams of titanium per
microampere of diffusion current. Using this factor, calculate
the amount of titanium in the samples.

PRELIMINARY INVESTIGATIONS

A. Relationship Between Diffusion Current and Concentration
    of Titanium

        In order to establish that a linear relationship
existed between the diffusion current and the concentration of

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*For a more accurate estimate of the titanium, process two or
more replicate samples and record one 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. See Table 4 in this
report.

titanium, a number of solutions containing known amounts of titanium in the 0.5 M ammonium acetate + 0.1 M acetic acid + 0.1 M EDTA electrolyte at pH 5.0 were prepared and the polarograms were recorded. The results of these tests are given in Table 1. Smaller or greater amounts of titanium were not investigated because they were outside the range of interest for the method.

TABLE 1

Relationship between the Diffusion Current and
the Titanium Concentration in 0.5 M Ammonium Acetate
+ 0.1 M Acetic Acid + 0.1 M EDTA Supporting Electrolyte

Ti Concentration (mg/100 ml)	Diffusion Current (microamperes)	Factor mg Ti/microampere
6.0	3.77 ± 0.15	1.59
12.0	7.28 ± 0.08	1.65
24.0	14.80 ± 0.04	1.62
60.0	36.6 ± 0.3	1.64

B. Interfering Elements

Impurities, in general, were not present in the lead zirconate-lead titanate ceramic materials, and with the exception of a few elements, interferences were of no concern. Lead and zirconium were the only elelments present in amounts sufficient to warrant attention as potential interferences but an interference study is of great interest if the procedure is to be adopted to the analysis of other titanium-bearing material. An investigation was therefore undertaken to determine the polarographic behaviour of a number of diverse ions in the proposed

electrolyte and to ascertain which elements may cause interference or difficulties in the determination of titanium. Accordingly, solutions of the elements in the 0.5 M ammonium acetate + 0.1 M acetic acid + 0.1 M EDTA electrolyte were prepared and the polarogram recorded. No maximum suppressor was added to these solutions, in order to observe any maximum occurring on any of the waves. The results and comments on these tests are shown in Table 2.

TABLE 2

Polarographic Behaviour of Diverse Elements in
0.5 M Ammonium Acetate + 0.1 M Acetic Acid + 0.1 M EDTA

Element	Approximate Concentration mg/100 ml	$E_{\frac{1}{2}}$ vs S.C.E.	Comments
Ag(I)	10	>0	
As(III)	7.5	N.R.	
As(V)	7.5	-0.9 to -1.5	the residual current is flat until minus 0.8 V then a gradual current increase occurs with a maximum at minus 1.38 V.
Bi(III)	20	-0.71	F.W.D.
Ca(II)	5	N.R.	
Cd(II)	10	-1.3	F.W.D.
Ce(III)	15	N.R.	
Ce(IV)	15	N.R.	
Co(II)	5	N.R.	
Cr(III)	5	-1.31	F.W.D. (purple complex)
Cr(VI)	5	0	
Cu(II)	5	-0.43	W.D.
Fe(II)	5	-0.18	F.W.D.
Fe(III)	10	~ -0.3	very sudden jump at minus 0.28 V distorted wave slope but W.D. limiting current plateau.
Hg(II)	20	>0	
Mg(II)	5	N.R.	
Mn(II)	5	N.R.	
Mn(VII)	5	N.R.	
Mo(VI)	10	-0.83	W.D.*
Nb(V)	10	-0.85, -1.2	1st wave W.D., 2nd wave I.D.
Ni(II)	5	N.R.	

Table 2 (continued)

Element	Approximate Concentration mg/100	E½ vs S.C.E.	Comments
Pb(II)	20	-1.2	F.W.D.
Sb(III)	10	-0.7, -0.9	F.W.D. large maximum
Sb(V)	10	-0.2 to -1.0	current rises from minus 0.28 V gradually but continuously to minus 1.0 V.
Sn(II)	10	(-0.35),-1.3	1st wave anodic, 2nd wave F.W.D.
Sn(IV)	10	(-0.35),-1.3	1st wave anodic, 2nd wave F.W.D.
Th(IV)	20	N.R.	
Ti(IV)	5	-0.5, -1.15	**
U(VI)	25	-0.5	W.D.
V(V)	5	>0,-1.0 to -1.4	reduction begins at >0 V 2nd wave is I.D. at minus 1.0 V.
Zn(II)	5	N.R.	
Zr(IV)	10	N.R.	

W.D. - well-defined wave;   F.W.D. - fairly well-defined wave;
I.D. - ill-defined wave;   N.R.   - no reduction

*Two species are present which combine to form a single wave
 at pH 5. At other values of pH two waves appear.

**Two waves were observed. The second wave at minus 1.15 V was
 much smaller than the first wave which indicates the existence
 of two species not in equilibrium. See also reference (10).
 In this test the titanium solution was not boiled with the
 EDTA before addition of the acetate, which may account for
 the appearance of the second wave.

C. Effect of Time and Temperature on the Titanium Wave Height

Because of the well-known fact that titanium reacts
only slowly with EDTA in complexometric titrations unless
hydrogen peroxide is present[14] a number of experiments were
performed to see if the titanium readily formed an EDTA complex
in the proposed electrolyte at room temperature.

A solution of a lead zirconate-lead titanate solid sample was prepared in perchloric acid. A 10-ml aliquot containing 7.59 mg of titanium was evaporated to fumes after addition of about 2 ml of sulphuric acid. The evaporation was continued until the perchloric acid and excess sulphuric acid was removed and only a moist residue remained. The residue was treated at room temperature with 50 ml of 0.2 M EDTA solution, 10 ml of 5 M ammonium acetate solution and 10 ml of 1 M acetic acid. The solution was transferred to a 100-ml volumetric flask, diluted to volume with water, and mixed. A portion of the solution was immediately de-aerated in a polarographic cell and the titanium wave recorded from 0.0 to minus 1.0 volt vs the saturated calomel electrode. The wave was recorded at intervals for 80 minutes. The solution was left standing for 48 hours, and the titanium wave was recorded again. The results of this test are given in Table 3.

TABLE 3

Effect of Time of Standing after Solution
Preparation on Height of Titanium Wave

	5 mins	10 mins	45 mins	75 mins	80 mins	48 hrs
Wave height (microamperes)	2.820	2.840	3.015	3.205	3.235	3.820

In view of the excessively long time for the final wave height to be reached at room temperature other experiments were carried out to hasten the process. In these experiments the EDTA solution was added to the sample first and the solution was then boiled for several minutes before cooling it

to room temperature. The ammonium acetate and acetic acid were added as before and finally the solution was diluted with water to volume in a volumetric flask and the titanium wave recorded, again as already described. The procedure was successful and enabled complete complexation of the titanium to be obtained in a matter of a few minutes rather than hours. This was the procedure adopted in subsequent experiments.

D.   Effect of pH on the Wave Height and the Half-Wave Potential ($E_\frac{1}{2}$)

In order to determine the effect of varying the pH of the supporting electrolyte on the titanium wave height or its half-wave potential, a number of solutions containing 10 mg of titanium were prepared in the proposed supporting electrolyte by the following procedure: an aliquot of solution containing 10.00 mg of titanium was transferred to a 150-ml beaker; fifty ml of 0.2 M EDTA solution was added and the solution was boiled for several minutes; the solution was cooled to room temperature; 10 ml of 5 M ammonium acetate solution and 10 ml of 1 M acetic acid were added; the pH was adjusted to the desired value with sodium hydroxide, or with sulphuric acid, and finally the solution was diluted to volume with water in a 100-ml volumetric flask; a portion of the solution was transferred to a polarographic cell and de-aerated with nitrogen. On each solution four waves were recorded, without damping, at potentials from 0.0 to minus 1.0 volt vs the saturated calomel electrode and the average of the maximum wave heights was calculated. The half-wave potential was also determined on each solution. The results of these tests are shown in Table 4.

TABLE 4

Effect of pH on Wave Height and Half-wave Potential of Titanium in 0.5 M Ammonium Acetate + 0.1 M Acetic Acid + 0.1 M EDTA

pH	Average Wave Height (microamperes)	$E\frac{1}{2}$, volts vs S.C.E.
3.55	5.96 ± 0.04	-0.30 ± 0.01
3.87	5.97 ± 0.03	-0.33 ± 0.00
4.85	6.07 ± 0.03	-0.44 ± 0.00
6.35	5.99 ± 0.04	-0.62 ± 0.00

E.   Stability of the Sample Solutions

In order to determine the stability of the titanium in the proposed electrolyte, duplicate aliquots of two lead zirconate-lead titanate solutions with about 2 ml of sulphuric acid were evaporated to fumes to remove nitric or perchloric acid. The residue was treated with 50 ml of 0.2 M EDTA solution, boiled for a few minutes, and cooled to room temperature. Ten ml of 5 M ammonium acetate solution, 10 ml 1 M acetic acid and 10 ml of water were added and the pH checked to see that it was 5.0 ± 0.1. The solution was diluted to volume in a 100 ml volumetric flask and mixed. The titanium waves were recorded on each solution on each of two days with a 96-hour interval between recordings. The results of these tests are given in Table 5.

TABLE 5

Stability of Titanium in the Supporting Electrolyte

| Sample | Wave Height (microampers) | | | |
| | Recorded Immediately | | Recorded after 96 hrs | |
	Solution A	Solution B	Solution A	Solution B
2245	3.35	3.30	3.35	3.37
2246	2.52	2.52	2.52	2.49

F. Reproducibility and Precision of Measuring the Titanium
   Wave Heights

In order to determine the day-to-day reproducibility
of the method and the precision with which the titanium diffusion
current could be measured, a number of solutions containing known
amounts of titanium were prepared and the polarographic waves
were recorded. These solutions were prepared fresh each time
on different days over the course of a week. On some days only
a single solution at each level of titanium concentration was
prepared while on other days two or more solutions were prepared.
Four waves were recorded on each solution. The diffusion
current of each wave was carefully measured by subtracting the
average residual current at -0.25 volt from the average limiting
current at -0.70 volt. These results are given in Table 6.

G. Analysis of Samples

A number of solutions and solid samples of lead
zirconate-lead titanate mixtures were analysed by the proposed
polarographic method and the results were compared with results
obtained by a differential spectrophotometric method. These

TABLE 6

Reproducibility and Precision of Wave Height Measurements for Titanium

Ti Taken	Diffusion Current in Microamperes (Average and Range of 4 Recorded Waves)									
	1st Day	2nd Day		3rd Day					4th Day	
	A	A	B	A	B	C	D	E	A	B
12 mg	7.48±0.02	7.48±0.02		7.68±0.08	7.72±0.02	7.72±0.04	7.70±0.00	7.68±0.02	7.58±0.02	7.50±0.02
24 mg	15.10±0.06	14.60±0.04	14.64±0.02	15.10±0.04	15.26±0.06	15.28±0.04	15.16±0.06	15.16±0.08	14.72±0.02	14.66±0.02

results appear in Table 7. Additional results appear in a separate report[13] in which a comparison is made of results obtained by a differential spectrophotometric method and by reduction using liquid amalgams or aluminum metal.

TABLE 7

Determination of Titanium in Lead Zirconate-Lead Titanate Products

| Sample | Titanium Found (as Ti) * | |
	Differential Spectrophotometric Method	Polarographic Method
683	1.18 ± 0.00 g/ℓ	1.18 ± 0.01 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
2292	4.56 ± 0.02 %.	4.56 ± 0.01 %
2295	3.82 ± 0.01 %	3.84 ± 0.03 %
2296	8.41 ± 0.00 %	8.40 ± 0.04 %
2682	5.56 ± 0.00 %	5.58 ± 0.02 %
2685	7.76 ± 0.02 %	7.79 ± 0.04 %

*Average of 2 determinations on each sample.

DISCUSSION

A. Relationship Between Diffusion Current and Concentration of Titanium

A plot of the results in Table 1 showed a linear relationship between the diffusion current and the concentration

of titanium over the range of interest with the curve passing through the point of origin. From an examination of the polarograms it is estimated that the minimum amount of titanium that can be determined with the instrument used in this work is about 0.1 mg of titanium per 100 ml i.e. $\sim 2 \times 10^{-5}$ M.

No maximum suppressor is required and the titanium wave is very well-defined in the range of concentrations investigated. The residual currents and limiting currents are virtually flat and parallel to each other and to the voltage axis, so advantage was taken of this fact in measuring the wave height.

Initially the wave heights were calculated from measurements made at the half-wave potential. This was done with lines drawn through the midpoints of the oscillations on the residual current and on the limiting current plateau. The vertical distance between the two lines at the half-wave potential was then measured. Because of the well-defined titanium wave it was later found simpler to measure the average residual and limiting currents at minus 0.25 and minus 0.70 volt respectively versus the saturated calomel electrode and to calculate the diffusion current as the difference between the two measurements. This procedure gave a slightly better reproducibility and precision than if the measurements had been made at the half-wave potential because it was unnecessary to draw lines and because only measurements at two points were required.

It must be emphasized that this procedure is not applicable at all concentrations of titanium nor to all types of polarographic waves and it is employed only for the particular conditions recommended in the proposed method. For example, if the residual and limiting currents are not parallel to either each other or the voltage axis, as would be expected at low concentrations of an element, the measurements would have to be made at the half-wave potential or by some other method as suggested by Meites[15].

To utilize the two point measurement technique that is described in the procedure for measuring the wave heights, a concentration of at least 5 mg of titanium per 100 ml of supporting electrolyte is necessary and in practice sufficient sample is taken to give a concentration of 10 to 25 mg of titanium per 100 ml.

B. Interfering Elements

Of the elements whose polarographic behaviour was studied As(III), Ca, Co, Ce(IV), Mg, Mn, Ni, Th, Zn and Zr gave no reduction waves in the proposed electrolyte. As(V), Bi(III), Cd(II), Cr(III), Mo(VI), Nb(V), and Pb(II) are reduced at potentials considerably more negative than titanium and will not interfere. Niobium gives rise to two waves of approximately equal height with half-wave potentials of minus 0.85 V and minus 1.2 V vs the saturated calomel electrode. The first wave coincides with that of molybdenum(VI) while the second coincides, with that of lead and chromium(III). The niobium wave at minus 0.85 V is well defined and may be analytically useful, but

the wave at minus 1.2 V is ill-defined because of the close
proximity of the hydrogen reduction potential. Ferrett and
Milner[16] studied the polarography of niobium in various support-
ing electrolytes and found that, in EDTA solutions, niobium
produced waves whose half-wave potentials varied with the pH
of the solution. In 0.1 M EDTA at pH 4.75, they found that
the half-wave potential of the first niobium wave was minus 0.835
volt vs the saturated calomel electrode and, in 0.2 M EDTA at
pH 5.0, the half-wave potential of the second wave was minus 1.1
volt. These values are in reasonably close agreement with the
values, of minus 0.85 and minus 1.2 V, obtained in the acetate-
EDTA electrolyte proposed in this report. Ferrett and Milner
verified that the reduction process for niobium was $Nb^{+5} \rightarrow Nb^{+4}$
for the first step and $Nb^{+4} \rightarrow Nb^{+3}$ for the second step and it
seems reasonable to assume that the same process takes place
in the acetate-EDTA electrolyte used in our work and is due
to the same mechanism that Pecsok and Maverick proposed for the
reduction of the Ti- EDTA acid complex[9].

Ce(III) does not give a visible wave but the current
gradually increases over the full potential scale and the
current increase is more evident between minus 0.7 and minus 1.2 V.
The oscillations due to the dropping mercury electrode are more
visible in the presence of Ce(III) than with Ce(IV). Likewise
with Sb(V) the current gradually increased between minus 0.2
and minus 1.0 volt without giving a visible wave. Elements
such as Ag, Hg, Cr(VI) and V(V) are reduced at 0 volt and,
though they do not give waves in the vicinity of the titanium

wave, they may cause difficulty if they are present in amounts greater than that of titanium. However, such concentrations are unlikely in lead zirconate-lead titanate ceramics. Iron(II) gives a fairly well-defined wave at minus 0.18 V vs the saturated calomel electrode and will not interfere unless present in excessive amounts. On the other hand, iron(III) will cause interference because its reduction potential is too close to the titanium wave. No definite wave for Fe(III) appeared, instead a very sudden jump in current occurred at minus 0.28 volt. The slope of the wave was somewhat distorted, but the limiting current plateau was virtually flat. Cu(II), Sn, and U(VI) are direct interferences with titanium because they give rise to waves that are very close to or coincide with the titanium wave. However, tin as well as antimony and arsenic can be easily removed by evaporating the samples with hydrobromic, hydrochloric, and sulphuric acids to volatilize these elements as their bromides or chlorides. The presence of these elements in lead zirconate-lead titanate material in amounts sufficient to cause interference is highly unlikely.

In order to avoid the interference due to high concentrations of sulphate as reported by Berger and Cadoff[10] the sample solutions are fumed with sulphuric acid until only 1 ml or less of the acid remains. This amount of acid corresponds to between 0.15 and 0.2 M sulphuric acid when the solution is diluted to 100 ml, therefore, its concentration is much less than that at which it begins to interfere, i.e., 0.7 M.

In the determination it is also necessary to have sufficient EDTA present to complex all the foreign metals. For example, lead and zirconium will compete with the titanium for the EDTA and if insufficient EDTA is present the Ti-EDTA will dissociate and the lead and zirconium complexes will form in preference.

The amount of sample taken for analysis generally contained from 135 to 200 mg of lead and from 30 to 75 mg of zirconium in addition to 10 to 25 mg of titanium. The amount (50 ml) of 0.2 M EDTA added was 4 times the amount required to complex the maximum amount of lead, titanium, and zirconium present, therefore the excess of EDTA was large enough to prevent interference by either lead or zirconium.

C. Effect of Time and Temperature on the Height of the Titanium Wave

A plot of the results in Table 3 shows a linear relationship between time and diffusion current. The exact time at which the maximum wave height was reached was not determined but the approximate time was inferred to be at least 3 hours after the solution was prepared. This time was calculated by assuming that the maximum wave height (the wave height that was measured after 48 hours) was 3.82 microamperes, by extrapolating the wave height versus the time curve to the time corresponding to this maximum wave height, by assuming that the same rate of reaction between the titanium and EDTA was maintained.

The titanium-EDTA complex formed more rapidly, and the maximum wave height was obtained much more quickly if the mixture had been boiled than if it simply had been mixed at

room temperature. It was found that it was necessary to add the EDTA to the titanium and boil the mixture <u>before</u> adding the ammonium acetate and acetic acid, otherwise the titanium-EDTA complex would be slow in forming. Berger and Cadoff[10] also found that the order of addition of reagents was important; they added the EDTA to the titanium first but did not indicate that they heated the solutions before adding the other reagents.

D. <u>Effect of pH on the Wave Height and the Half-Wave Potential of Titanium</u>

A plot of the results in Table 4 showed that the half-wave potential of the titanium wave varied linearly with the pH of the solution but the wave height was constant as is evident in the table over the range pH 3.5 to 6.5. The effect of pH greater or less than these values was not investigated. The slope of the curve in the pH-dependent range is minus 0.114 volt per pH unit; this agrees with minus 0.114 volt per pH unit obtained by Pecsok and Maverick in 5.1 millimolar EDTA + 0.1 M acetic acid + 0.2 M perchloric acid medium[9].

In the acetate-EDTA electrolyte used in our work at pH values less than 3.5, some of the EDTA precipitates and there is then insufficient EDTA in solution to ensure the complexation of all the titanium, lead and zirconium in the samples (see section B, Interfering Elements). Thus it is necessary to adjust the pH to a value greater than 3.5 to maintain the EDTA in solution. In the analytical procedure that was finally adopted, the pH of the solutions was adjusted to 5.0 ± 0.01 at which value the half-wave potential of titanium was minus 0.46 ± 0.01 volt versus the saturated calomel electrode. Adjusting the

pH to ± 0.1 unit was done to facilitate measuring the residual

and limiting currents at minus 0.25 and minus 0.70 volt

respectively. If large variations in pH were permitted the

measurements of the wave height would have to be made at

different potentials, e.g., at 0.2 volt on either side of the

observed half-wave potential. Moreover, close adjustment of

the pH ensures that the titanium wave always appears at the

same half-wave potential and will not be confused with, for

example, a wave due to another reducible element having a

half-wave potential near that of titanium. Because of the

strong buffering action of the solution, the adjustment is

easily and quickly made by means of a pH meter.

Pecsok and Maverick state that they had difficulty

preparing 0.1 M EDTA solutions that contained more than 3 milli-

molar titanium at pH 4 and more than 0.8 millimolar titanium at pH 6

and that at higher concentrations of titanium a colloidal TiO_2

precipitate appeared[9]. In the acetate-EDTA electrolyte used

in our work we encountered no difficulty and no colloidal

precipitate was observed up to a 12 millimolar concentration of

titanium (see Table 1) even after the solutions had stood for

several weeks. This difference in behaviour may be related to

the fact that the titanium was first boiled with EDTA or

perhaps may be due to the presence of the acetate. Pecsok and

Maverick[9] make no mention of boiling or warming the titanium

with the EDTA solutions prior to polarography nor do Berger and

Cadoff[10], although Goode et al heated their solutions for

30 minutes after addition of the sodium acetate buffer[11].

So it is likely that boiling the titanium-EDTA solution established equilibrium conditions quickly and increased the stability of the solutions, perhaps by the breaking down of polynuclear hydroxo-compounds which react only sluggishly with EDTA. Similar phenomena are observed in the behaviour of aluminum and zirconium in titrations with EDTA[14].

Another difficulty occurs when titanium is complexed with EDTA in the presence of excessive amounts of sulphate[10]. Two waves appear, the first of which is due to the Ti-EDTA complex and the second due to the Ti-sulphate complex. The titanium-sulphate complex is formed at the expense of the Ti-EDTA complex but though each wave is proportional to the concentration of the individual complexes, the sum of the wave heights cannot be used to calculate the titanium concentration directly because of the difference in the diffusion current coefficients. Moreover, because it is highly unlikely that the ratio of one species to the other would be reproducible (even under the same conditions) each time a solution is prepared, the measurement of one wave only cannot be made. So, to be certain that only the Ti-EDTA complex is formed, the concentration of sulphate is kept low and the pH is controlled within certain limits.

It should be noted that the above types of reaction are not the same as that or those when an element or complex is reduced in two stages. In the latter type of reaction, only one species is originally present in the solution which is reduced first to an intermediate product or valence state that undergoes further reduction at the electrode with the height of

each reduction step being proportional to the original concentration of the element or complex.

E.   Stability of the Sample Solution

The results of the tests recorded in Table 5 show that the titanium complex in the solution is stable for at least 4 days as indicated by the wave height remaining constant during that period.   There was no sign of any precipitate to suggest that hydrolysis of either titanium or zirconium was taking place.   Berger and Cadoff[10], however, state that the diffusion current decreases with time in the medium they employed and that erratic results are obtained if the solutions are left standing for more than 3 days.

In our work, it was observed that, at pH values less than about 3, white crystals appeared in the solution when first prepared but these were believed to be EDTA crystals and they dissolved when the pH was adjusted to higher levels.

F.   Reproducibility and Precision of Measuring the Titanium Wave Height

The results in Table 6 show that on any given day the precision with which the diffusion current can be measured is excellent.   This is due to the nearly ideal wave characteristics of the titanium complex in the proposed electrolyte. The reproducibility of the diffusion currents recorded on solutions freshly prepared on different days is good.   The slight variations in wave height that are observed are to be expected and are attributed to the normal day-to-day variations in capillary characteristics and to instrumental limitations of the polarographic method in general.   The precision and

reproducibility is well within 2% relative error that is normally expected in the concentration range used[15,17].

G. Analysis of Samples

The results obtained by the polarographic procedure compare very favourably with the results obtained by the differential spectrophotometric method. The precision of the method is excellent and there does not appear to be any bias so far as accuracy is concerned. The very well-defined characteristics of the titanium wave in the medium undoubtedly contribute to the success of the method. In addition, no maximum suppressor is required.

Lead and zirconium do not interfere and not other interfering elements were present in the samples. Elements such as iron or chromium that are sometimes added to lead zirconate-lead titanate compounds would cause difficulties only if present in amounts that would result in polarographic waves that would precede and be higher than the titanium wave. Ferric iron is a more serious interference than ferrous, therefore the iron should first be reduced to the ferrous form. Chromium(VI) can also be reduced to chromium(III) and this would shift the chromium wave to minus 1.3 volt vs the S.C.E. where it would not interfere with the titanium wave. Niobium will not interfere because it is reduced at a more negative potential i.e. at minus 0.85 volt vs the S.C.E.

No attempt was made to determine the lead simultaneously with the titanium, in spite of lead giving a wave in this medium, because the close proximity of the hydrogen reduction wave made a precise measurement of the lead wave impossible. Moreover, high

concentrations of lead such as are present in the lead zirconate-lead titanate material, i.e., between 50 and 60 % Pb in solids or between 10 and 20 g Pb/l in solutions cannot be determined with the necessary precision by means of normal D.C. polarographic methods. The lead is therefore determined by a solvent extraction - EDTA titration procedure[18]. Zirconium is also determined by a complexometric titration procedure in perchloric acid[19].

CONCLUSIONS

This polarographic method for the determination of titanium is simple, rapid, precise, and accurate. The titanium wave in the proposed electrolyte has excellent polarographic characteristics for the concentrations of titanium investigated i.e., 6 to 60 mg Ti/100 ml. These characteristics enable the wave height of titanium to be measured to a high degree of precision by means of two-point measurements, i.e., at minus 0.25 and minus 0.70 volt vs the S.C.E. Though few elements interfere, there are procedures to counter some of those that do.

The method is applicable to the determination of titanium in lead zirconate-lead titanate ceramic powders and solutions and it compares favourably with differential spectro-photometry. The polarographic method is simpler and faster than differential spectrophotometry which requires that the lead be removed prior to the colorimetric finish by either solvent-extraction or precipitation with sulphuric acid. In addition, the spectrophotometric method demands the calibration of the volumetric wave and very careful work in the adjustment of the acid concentration, and the preparation of standard titanium solutions.

ACKNOWLEDGEMENTS

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