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THE COMPLEXIMETRIC TITRATION OF ZIRCONIUM BASED ON THE USE OF FERRIC IRON AS THE TITRANT AND DISODIUM-1,2-DIHYDROXYBENZENE-3,5-DISULFONATE AS THE INDICATOR

D. L. Manning
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D. L. Manning, A. S. Meyer, Jr., J. C. White

August 12, 1955

ANALYTICAL CHEMISTRY DIVISION

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TABLE OF CONTENTS

THE COMPLEXIMETRIC TITRATION OF ZIRCONIUM BASED ON THE USE OF FERRIC IRON AS THE TITRANT AND DISODIUM-1,2-DIHYDROXYBENZENE-3, 5-DISULFONATE AS THE INDICATOR

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ABSTRACT

Zirconium is converted to a stable complex by the addition of an excess of disodium dihydrogen ethylene diamine tetra-acetate (EDTA) to a dilute sulfuric acid solution containing zirconium. The excess EDTA is titrated with iron(III) to a disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) end point at a pH of 4.8. Fluoride ion interferes; by complexing the fluoride with beryllium, however, the titration can be conducted in the presence of as much as 4 g of fluoride. Such anions as sulfate, tartrate and phosphate do not interfere. Cationic interferences are relatively few since most metals form weaker complexes with EDTA than do either zirconium or iron. By slight modifications in the procedure, the method is applicable to the determination of zirconium in the presence of moderate amounts of trivalent iron, divalent nickel and trivalent chromium. The method is rapid and simple. The coefficient of variation is less than one per cent.

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INTRODUCTION

The ever-increasing importance of zirconium and its compounds has led to the development of a number of methods for its determination. Most of the investigations have been concerned with the development of organic precipitants such as mandelic acid and its halo-derivatives[3, 7]. These reagents are decidedly better than phosphate[4] and cupferron[5] as quantitative reagents. In order to eliminate the ignition step and to save time, colorimetric and volumetric methods have been devised. Manning and White[8] developed a differential spectrophotometric method for zirconium. Kolthoff and Johnson[6] have reported an amperometric method based on the use of n-nitro phenylarsonic acid. A procedure for the amperometric titration of zirconium with cupferron was recently published by Olson and Elving[10]. This latter method is applicable to the determination of zirconium in the presence of fluoride but has the disadvantage that cupferron is quite unstable in solution.

A selective method based on the titration of zirconium with disodium ethylenediaminetetraacetate (EDTA) to an eriochromecyanine end point was developed by Fritz and Fulda[1]. Anions such as sulfate, phosphate and fluoride interfere in that method. Fritz and Johnson[2], however, reported on the successful determination of zirconium in the presence of such anions as sulfate, phosphate, tartrate and small amounts of fluoride by adding an excess of EDTA, then titrating the excess with bismuth nitrate using thiourea as the indicator. In the presence of uranium(VI), however, the detection of the end point by this method is difficult if not impossible. Milner and

Phennah[9] determined zirconium in zirconium-uranium alloys by isolating the zirconium as the insoluble mandelate followed by dissolution of the precipitate in five per cent sulfuric acid. An excess of EDTA was added following which the excess is titrated with a solution of iron(III) using salicylic acid as the indicator. Sweetser and Bricker[11] developed a titrimetric procedure whereby the excess EDTA is titrated with iron(III) to a spectrophotometric end point using salicylic acid as the indicator.

The proposed method consists of the addition of an excess of EDTA to a solution which contains zirconium followed by titration of the excess with iron(III) to a disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) end point at a pH of 4.8. The color change at the end point is from yellow to purple. The method is applicable to the determination of zirconium in the presence of sulfate, tartrate, phosphate, small amounts of fluoride and hexavalent uranium. Cationic interferences are relatively few because zirconium and iron(III) form extremely stable complexes with EDTA; thus, in the back-titration with iron(III), the purple color of the iron(III)-Tiron complex is not obtained until the metal-EDTA complexes, which are less stable than the iron(III)-EDTA complex, have been dissociated.

Fluoride in concentrations less than 0.1 M does not interfere in the titrimetric method. Even higher concentrations of fluoride can be tolerated by the addition of beryllium to the solution prior to the addition of EDTA. The interference from fluoride is thus eliminated through the formation of the stable $BeF_4^=$ complex. Beryllium does not form a stable complex with EDTA. On account of the toxic nature of beryllium, it is suggested that, whenever possible, the interference from fluoride be eliminated by volatilization as hydrogen fluoride instead of relying on complexation with beryllium. Boron

in the form of boric acid, and aluminum were considered as alternate reagents for reducing the fluoride ion concentration by complex ion formation. Preliminary tests, however, indicated that boron was not effective in removing the fluoride interference. Aluminum was rejected because it forms a stable complex with EDTA.

The proposed method, with a slight modification, is also applicable to the determination of zirconium in the presence of iron, nickel and chromium. These metals form stable complexes with EDTA and therefore interfere seriously with the determination of zirconium. The interference can be overcome by forming the EDTA complex of zirconium in addition to those of the interfering metals. A large amount of fluoride as sodium fluoride is then added to the solution to dissociate the zirconium-EDTA complex selectively by forming the stable $ZrF_6^{=}$ ion thus liberating an equivalent amount of EDTA. The liberated EDTA which is utilized as a measure of the zirconium is titrated with the iron(III) solution to a Tiron end point. The presence of fluoride affects adversely the stability of neither the iron(III)-EDTA nor the iron(III)-Tiron complex. With this modification the procedure can be made specific for zirconium in the presence of any metal ion the EDTA complex of which is not dissociated by fluoride.

REAGENTS

Standard zirconium solution, 5 mg per ml. Dissolve 5 grams of ZrF_4 in a solution composed of 50 ml of water and 50 ml of concentrated H_2SO_4 by heating to fumes of SO_3 and maintaining the solution at the boiling point of H_2SO_4 for about one hour. Allow the solution to cool, then dilute to exactly 500 ml. Standardize by determining the zirconium content of a 25-ml aliquot of the solution gravimetrically with mandelic acid.

EDTA solution, 0.05 M. Dissolve 17 grams of disodium dihydrogen ethylenediaminetetraacetate in one liter of water. Standardize against pure zinc metal, dissolved in a solution adjusted to pH 10, using eriochrome black T as the indicator.

Iron(III) solution, 0.025 M. Dissolve 12.1 grams of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in about 100 ml of 3 N HCl. Heat the mixture until solution is complete. Cool, then dilute to 1 liter with water.

Acetate buffer solution, pH 4.8. Dissolve 100 grams of ammonium acetate in 300 ml of water. Add concentrated hydrochloric acid until a pH of 4.8 is indicated by means of a pH meter. Dilute the solution to 500 ml with water.

Sodium fluoride solution, 10 mg fluoride per ml. Dissolve 5.5 grams of NaF in 250 ml of water.

Beryllium chloride solution, approximately 10 mg Be per ml. Add 5 grams of pure beryllium metal to a 400-ml beaker which contains about 200 ml of water, then place in a well-ventilated hood. Add concentrated HCl, a few ml at a time, until the metal is completely dissolved. Add an additional 50 ml of concentrated HCl, then dilute to 500 ml with water. If the solution appears turbid, filter through Whatman No. 40, or equivalent, filter paper.

Ammonium hydroxide, 7 M. Mix equal volumes of concentrated NH_4OH and water.

Disodium-1,2-Dihydroxybenzene-3,5-Disulfonate.

APPARATUS

A Beckman, Model H-2, pH meter equipped with standard glass and calomel electrodes was used for all pH measurements. A magnetic stirrer was used to stir the solutions during the course of the titrations.

PROCEDURES

I. Determination of Zirconium in the Presence of Sulfate and Small Amounts of Fluoride

Transfer an aliquot of the sample solution containing from 15 to 40 mg of zirconium in about five per cent sulfuric acid solution to a 150-ml beaker. Adjust the volume to about 50-ml by adding water. Add a 10-ml aliquot of the standard EDTA solution and adjust the pH to within the range 5.5 to 6.5 by adding dropwise 7 M NH_4OH. Allow the solution to stand at room temperature for about ten minutes, then transfer to a 250-ml erlenmeyer flask. Add 10 ml of the acetate buffer solution then adjust the volume to about 100 ml with water. Add approximately 100 mg of Tiron, then titrate the excess EDTA with the 0.025 M iron(III) solution until the color changes from yellow to purple. The end point is noted as that when the purple color persists for about one minute. The purple color usually fades after about five minutes due to the iron(III) complexing the EDTA away from the zirconium followed by subsequent dissociation and fading of the iron(III)-Tiron complex. This transition does not affect the detection of the end point.

II. Determination of Zirconium in the Presence of Fluoride

Follow Procedure I with the exception that about 15 ml of a solution of $BeCl_2$ (10 mg Be per ml) is added before the addition of the 10 ml of 0.05 M EDTA solution. When the solution is adjusted to within the pH range of 5.5 to 6.5 with 7 M NH_4OH, the excess beryllium, over that required to complex the fluoride present, usually precipitates. Add 20 ml of the acetate buffer then stir for a few minutes until a clear solution is obtained. Titrate the excess EDTA with the standard iron(III) solution. Add small increments of

the iron(III) solution slowly in the vicinity of the end point and note the permanency of the reddish-purple iron-Tiron color. The end point is taken when the color persists without any sign of fading for about one minute.

III. Determination of Zirconium in the Presence of Moderate Amounts of Iron(III), Nickel(II) and Chromium(III)

Transfer a sample aliquot containing from 15 to 40 mg of zirconium in 5 per cent H_2SO_4 which contains only trace amounts of fluoride ion to a 150-ml beaker. Follow Procedure 1 through the titration of the excess EDTA with the 0.025 M iron(III) solution to the Tiron end point.

Add 200 mg of fluoride (as NaF) then stir the solution for a few minutes. Titrate the liberated EDTA from the zirconium-EDTA complex to a Tiron end point with the iron(III) solution.

RESULTS

The zirconium content of some relatively pure solutions of zirconium sulfate in 1 M H_2SO_4 was determined by the titrimetric method following Procedure 1. The zirconium solutions were previously analyzed by the gravimetric mandelic acid method. Table I lists some of the typical results which were obtained.

Table I

Application of the EDTA Volumetric Method to the Titration of Zirconium

Conditions: Solution - 1 M H_2SO_4
EDTA solution, 10 ml
Buffer, 10 ml
Tiron, 100 mg
Titers, 1 ml EDTA = 3.48 mg of Zr
1 ml iron(III) = 0.65 ml of EDTA

Titrant ml	Zirconium Present (A) mg	Zirconium Found (B) mg	Difference (B-A) mg
3.40	27.2	27.1	-0.1
3.32	27.2	27.3	0.1
3.35	27.2	27.2	0.0
3.45	27.2	26.8	-0.4
8.40	15.8	15.2	-0.6
5.40	22.8	22.6	-0.2
5.50	22.8	22.4	-0.4
5.18	22.8	23.0	0.2
5.23	22.8	22.9	0.1
		Average	0.2
		Coefficient of Variation, per cent,	0.8

The results of these tests indicate that the titrimetric procedure is applicable to the determination of zirconium with a precision comparable to that obtainable by gravimetric methods, i.e., a coefficient of variation of less than one per cent under ideal conditions.

Occasionally a precipitate is formed when excess EDTA is added to solutions containing zirconium in the presence of sulfate ions. Boiling the solution will not dissolve the precipitate. The formation of the precipitate can usually be avoided either by taking a smaller aliquot for the determination of zirconium or by the addition of about 10 ml of 10 w/v per cent of ammonium tartrate to the test solution before the addition of excess EDTA. This phenomenon was also reported by Fritz and Johnson[2] who

indicated that the precipitate probably consists of a sulfate or mixed sulfate-tartrate complex with zirconium.

The Effect of Small Amounts of Fluoride

Tests were conducted to determine the maximum fluoride ion concentration that could be tolerated. Known amounts of zirconium were determined in the presence of small concentrations of fluoride by Procedure I. The results of the tests are given in Table II.

Table II

The Effect of Fluoride on the Determination of Zirconium by the EDTA Volumetric Method - Procedure I

Conditions: EDTA, 10 ml
Buffer, 10 ml
Tiron, 100 mg
Titers, 1 ml EDTA = 3.48 mg of Zr
1 ml iron(III) = 0.69 ml of EDTA

Fluoride mg	Titrant ml	Zirconium Present (A) mg	Zirconium Found (B) mg	Difference (B-A) mg
0	3.17	27.2	27.2	0.0
5	3.15		27.3	0.1
10	3.15		27.3	0.1
20	3.25		27.0	-0.2
30	No permanent end point observed			
40	"			
50	"			
100	"			

About 20 mg of fluoride apparently is the maximum amount that can be tolerated in the analysis without interfering with the determination of zirconium. As much as 30 mg of fluoride ion partially dissociates the zirconium-EDTA complex through the formation of the stable $ZrF_6^=$ ion and the liberation of an equivalent amount of EDTA. The EDTA so reduces the concentration of uncomplexed iron that the iron-Tiron complex is no longer stable.

This accounts for the very rapid fading of the iron-Tiron color in the titration and the fact that no definite end point is obtained in the presence of higher concentrations of fluoride ion.

Elimination of Interference from Fluoride with Beryllium

Some results from the titration of zirconium in the presence of fluoride by the method of Procedure II in which beryllium was added to reduce the effective fluoride-ion concentration are shown in Table III.

Table III

Determination of Zirconium in the Presence of Fluoride by Modified EDTA Volumetric Method

Conditions: Standard zirconium solution in 5 per cent H_2SO_4, 5 ml
EDTA solution, 10 ml
Acetate buffer, 20 ml
Tiron, approximately 100 mg
Titers, 1 ml EDTA = 3.48 mg Zr
1 ml iron(III) = 0.69 ml EDTA

Fluoride as NaF	Beryllium as $BeCl_2$	Titrant	Zirconium		
			Present (A)	Found (B)	Difference (B-A)
g		ml	mg		
0.0	0.0	3.21	27.2	27.1	-0.1
0.1	0.15	2.88		27.1	-0.1
0.4	0.15	2.85		27.1	-0.1
1.0	0.15	2.85		27.1	-0.1
1.0	0.15	3.00		26.8	-0.4
2.0	0.25	2.60		27.2	0.0
4.0	0.5	2.00		27.4	0.2

It was necessary to apply a correction to these results as a consequence of the presence of iron in the beryllium chloride solution used to complex the fluoride. This "blank" was equivalent to 0.005 mg of zirconium per mg of beryllium added.

The effectiveness of beryllium in eliminating the interference of fluoride is clearly demonstrated by these data. Even in the presence of such gross quantities of fluoride as 4 g, the precision of the determination is of the same order as that ordinarily found under ideal conditions. Furthermore, the distinctness of the end point was not impaired.

In this series of tests, the method was applied to the determination of zirconium in the form of the metal and the oxide. A sample of metal of known purity was dissolved in hydrofluoric acid and diluted with water so that the solution was approximately 1 M with respect to HF. An aliquot which contained 22.2 mg of zirconium was titrated after the addition of 150 mg of beryllium as beryllium chloride. The average of duplicate determinations was 21.9 mg with a relative standard error of 0.5 per cent.

A sample of zirconium oxide was dissolved in a mixture of hydrofluoric and sulfuric acids. The aliquot taken was approximately 1 M with respect to either acid; again 150 mg of beryllium was added before titration. The average of duplicate determinations was 25.1 mg of zirconium as compared to 25.0 mg taken. The relative standard error was 0.5 per cent.

The results of these applications reveal the versatility of the method and demonstrate the ease and precision with which zirconium can be determined in hydrofluoric acid solutions. The usual procedure for such analyses would include a step to remove HF prior to analysis. This time-consuming step is completely unnecessary when this modification is adopted.

Modification for Determination of Zirconium in Presence of Iron, Nickel, and Chromium

The results from the titration of zirconium in the presence of varying amounts of iron, nickel and chromium(III) are given in Table IV. Procedure III was followed in making these analyses.

Table IV

Determination of Zirconium in the Presence of Iron, Nickel and Chromium by the Modified EDTA Volumetric Method

Conditions: EDTA, 10 to 25 ml
Buffer, 10 ml
Tiron, about 100 mg
Fluoride, 200 mg
Stir 5 minutes after adding fluoride
Titers, 1 ml EDTA = 3.48 mg of Zr
1 ml iron(III) = 0.69 ml of EDTA

Metal Ion Added			Titrant		Zirconium		
Iron	Nickel	Chromium	Excess EDTA	Liberated EDTA	Present A	Found B	Difference B-A
mg			ml		mg		
0	0	0	3.25	11.25	27.2	27.1	-0.1
2	-	-	2.29	11.27		27.1	-0.1
7	-	-	5.32	10.93		26.4	-0.8
15	-	-	17.48	11.00		26.5	-0.7
2	2	-	7.00	11.10		26.7	-0.5
5	5	-	2.10	11.20		26.9	-0.3
-	5	-	7.05	11.28		27.1	-0.1
-	10	-	3.77	11.20		26.9	-0.3
-	-	1	10.20	11.22		26.9	-0.3
-	-	5	9.38	11.25		27.0	-0.2
-	20	-	17.10	6.90	16.3	16.5	0.2
3	-	-	5.75	6.70		16.1	-0.2
7	-	-	2.70	6.67		16.8	0.5
15	-	-	12.10	6.83		16.4	0.1
						Average	-0.3

A negative bias, although quite small, is obvious. In general, the precision is, again, of the same order as that for solutions of zirconium containing far less iron, chromium, or nickel. The solutions that contained more than five mg of trivalent chromium could not be successfully titrated due to the presence of the reddish-purple chromium-EDTA complex. The color of this complex obscured the detection of the end point. Although trivalent chromium reacts slowly with EDTA at room temperature, the presence of 10 to 20 mg of chromium produces enough color with EDTA to mask the end point completely. The maximum amount of chromium that can be tolerated is about 5 mg.

In titrating the excess EDTA, the color changes from yellow to purple at the end point. After the addition of the fluoride, the color of the solution quickly changed back to yellow and upon titrating the liberated EDTA, the color changed from a yellow to a reddish-purple at the end point. It is necessary to add the increments, 0.05 ml, of the iron solution slowly in the vicinity of the end point and to observe if the reddish-purple color of the iron-Tiron complex fades. The end point is taken when the color is stable for a period of approximately two to three minutes. The detection of the end point in the presence of iron, nickel and chromium ions is not as distinct as is the case for titration when these ions are absent. More erratic results are to be expected until the operator becomes more familiar with the end point.

The Effect of Time on the Formation of the Zirconium-EDTA Complex in Neutral Solutions at Room Temperature

A previous report[2] on the determination of zirconium with EDTA in the presence of sulfate recommends that the solution be adjusted to a pH of 2, then boiled in order to convert the zirconium quantitatively to the zirconium-EDTA complex. A series of tests was conducted to determine if the conversion is quantitative at a pH of 6 at room temperature since the complexing power of EDTA in general increases with increasing alkalinity.

Aliquots containing a known amount of zirconium in 1 M H_2SO_4 were treated according to Procedure I. After adjusting the pH of the solutions to 6.0 they were allowed to stand at room temperature for the indicated periods. The solutions were then diluted, followed by the addition of the acetate buffer and titration of the excess EDTA. The results are presented in Table V.

Table V

The Effect of Time on the Formation of the Zirconium-EDTA Complex in the Presence of Sulfate

Conditions: EDTA, 20 ml
Buffer, 10 ml
Tiron, 100 mg
Titers, 1 ml EDTA = 3.48 mg of Zr
1 mg iron(III) = 0.65 ml of EDTA

Standing Time Minutes	Titrant ml	Zirconium Present (A) mg	Zirconium Found (B) mg	Zirconium Difference (B-A) mg
10	6.75	54.3	54.5	0.2
30	6.79		54.4	0.1
60	6.71		54.6	0.3
120	6.72		54.5	0.2
2 days	6.71		54.4	0.1

The results indicate that the zirconium-EDTA reaction in solutions which contain sulfate is apparently complete at room temperature at a pH of about 6 within a period of ten minutes. Tests were not conducted to determine if the reaction is complete in less time because the time required to adjust the pH of a series of test solutions is usually of the order of ten minutes. The preliminary boiling step can be eliminated, thus materially increasing the efficiency of the method.

SUMMARY

The proposed method compares favorably with other titrimetric procedures that have been developed for the determination of zirconium. The method is applicable to the determination of zirconium in the presence of sulfate and moderate amounts of iron, nickel, and chromium. It has an advantage over the method of Fritz and Johnson[2] in that moderate amounts of hexavalent uranium and trivalent iron do not obscure the color change at the end point. Fluoride does not interfere when present in amounts up to 20 mg; however, when fluoride

is present in amounts in excess of 20 mg the direct method is not applicable, but can be made quite satisfactory by the addition of beryllium chloride in order to complex the fluoride. The method is comparable to the amperometric procedure proposed by Olson and Elving[10]. Their method does not require the prior removal of the fluoride ion, but has the disadvantage that the cupferron solution used as a titrant is quite unstable. The titrimetric procedure results in a considerable saving of time over the usual gravimetric methods. It appears more easily adapted to the determination of zirconium than titrimetric methods in which the end point is detected spectrophotometrically or amperometrically.

ACKNOWLEDGMENT

The authors acknowledge the assistance of C. D. Susano in the preparation of this report.

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