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TITRIMETRIC DETERMINATION OF ZIRCONIUM

By
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March 1955

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Technical Information Service, Oak Ridge, Tennessee
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F. H. Spedding, Director, Ames Laboratory

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TITRIMETRIC DETERMINATION OF ZIRCONIUM*

by M. O. Fulda and J. S. Fritz

ABSTRACT

A brief literature survey on the present gravimetric, colorimetric, spectrographic, and volumetric methods for the determination of zirconium has been presented.

A new method for the quantitative determination of zirconium has been proposed. The method is titrimetric and is carried out in acid solution with EDTA (disodium dihydrogen ethylenediaminetetraacetate), a stable, soluble complex being formed. A visual indicator gives a sharp end point. Thorium, molybdenum, bismuth, antimony, and tungsten constitute important interferences, but most other metals do not affect the results. Tin and titanium reduce the sharpness of the end point but do not otherwise interfere. Iron must be completely reduced to the ferrous state before titration. Copper interference is avoided by complexing it with thiourea. Anion interferences were also studied. This method constitutes an approach to the determination of zirconium in more difficult samples.

In order to check the applicability of the proposed method in a practical manner, several samples of zircon sands and zirconium-zinc alloys were analyzed for zirconium by this method and the results compared with the results of analyses by the method of Kumins (30), using the precipitation of zirconium mandelate with mandelic acid and ignition to zirconium oxide. The results of the proposed titrimetric method agree very well with the results of the gravimetric method.

I. INTRODUCTION

The mineral zircon was discovered by Werner who found it to be a mineral separate from diamond (36). He named it from the Latin, silex circonius, or the Arabian, zerk, a precious stone. He was not aware, however, that another element besides iron, aluminum, silicon and oxygen was present. The German chemist, Klaproth, discovered zirconia, ZrO₂, while analyzing a zircon in 1789 (62).

* This report is based on a M.S. thesis by M. O. Fulda, submitted March, 1955 at Iowa State College, Ames, Iowa. This work was performed under contract with the Atomic Energy Commission.
The metal was first prepared by Berzelius in 1824 (37). Now the Kroll process is used. In the Kroll process zircon ore is heated with graphite in an electric arc to produce zirconium carbide and drive off the silicon. The zirconium carbide is treated with chlorine gas to form zirconium tetrachloride and this is reduced to spongy zirconium with molten magnesium in an inert atmosphere. The magnesium and magnesium chloride are distilled off under high vacuum (68).

The possibilities of zirconium as a structural material are interesting to metallurgists and chemical engineers. Its ability to withstand high temperatures and stresses is of importance in the field of jet engines and in its resistance to corrosion it may rival tantalum. When freed from hafnium, it has a low absorbing power for neutrons; this additional observation is important in the design of nuclear reactors and explains the increased interest in the separation of these two elements (32). Also, zirconium does not amalgamate with mercury, a property which is made use of in mercury vapor applications. Zirconium alloys are used in armor plate steels, deoxidizers and scavengers, and where resistance to heat and corrosion is needed. Zirconia, zirconium oxide, is used in refractories. It is resistant to the action of heat, slags, and most acids (37).

Zirconium, therefore, is increasing in importance and more rapid and selective methods of control analysis are needed. Most of the methods now available are either timeconsuming or not selective enough. The majority of the methods are gravimetric for macro amounts and colorimetric for micro or semimicro amounts, while comparatively few volumetric methods have been offered. The volumetric methods are usually not very selective and are indirect, requiring a preliminary separation of a precipitate.

This work was undertaken to develop a rapid direct titrimetric method for zirconium which would also be selective. The titration is carried out in acid solution with EDTA (disodium dihydrogen ethylenediaminetetraacetate); a visual indicator gives a sharp end point. First a discussion of the titration, the factors affecting the titration, and the treatment of interferences, is given in this report. Then some practical analyses of samples containing zirconium are given.
Some excellent reviews of the analytical chemistry of zirconium have been published (2a; 13; 61; 65, p.321). The report of the Technical Information Service of the Atomic Energy Commission (TID-3010) is especially useful. It covers the entire field of zirconium chemistry through 1950 (61).

1. Gravimetric

A large number of gravimetric procedures have been proposed for macro amounts of zirconium. The classical method is a precipitation as ZrOHPO$_4$, zirconyl hydrogen phosphate, from 10 per cent sulfuric acid solution. This separates zirconium from all metals but quadrivalent cerium. The precipitate cannot be ignited to a definite composition, however, and has to be fused with sodium carbonate and the hydrous oxide precipitated with ammonia from hydrochloric acid solution (65, p.321). For small amounts the phosphate precipitate can be ignited and weighed as ZrP$_2$O$_7$ (4; 65, p. 321). Willard determined larger amounts by precipitation from homogeneous solution by heating with triethyl phosphate (66).

Most of the recent developments are in the use of organic precipitants and direct ignition of the precipitate to the oxide. The methods using mandelic acid (18, 23, 30, 38) and para bromo or para chloromandelic acid (19, 26, 44, 45) are done in this manner, the only interference being hafnium. The precipitate from the halogen derivatives can be washed with water; the precipitate from the mandelic acid must be washed with a 2 per cent HCl-5 per cent mandelic acid solution. Tetrachlorophthalic acid is as specific, but much less reagent is required (41). Other organic precipitants are ammonium benzoate (22), benzilic acid (27, 57), tannin (46), benzoic acid (47), paradimethylaminoazophenylarsonic acid (51), fumaric acid (55), metanitrobenzoic acid (58), cinnamic acid (59), hydrazine sulfate (60), metacresoxyacetic acid (56), and cupferron (2a; 65, p.321). A thermogravimetric analysis using the precipitate with 8-hydroxyquinoline was unsuccessful (3).

Another inorganic precipitant in addition to phosphate is selenious acid. The precipitate, Zr(SeO$_3$)$_2$, is ignited to the oxide (13). Zirconium can also be separated as BaZrF$_6$ using barium nitrate-hydrofluoric acid solution as the precipitant (2a; 21, p.1499).
2. **Colorimetric**

For micro amounts of zirconium colorimetric methods of analysis are used. Being used for a different range of concentrations than the method proposed in this report, these methods do not compete; therefore it will be sufficient to merely mention a few of them.

Most of the authors of colorimetric measurements of zirconium use Alizarin Red S as the color forming reagent (15, 17, 53). Other reagents used are quercetin (16), thorin (22), hematoxylin (55), m-(2-hydroxynaphthylazo) mandelic acid (43), and chloranilic acid (54). The use of fluorescence analysis using flavanol (la) and morin (67) and a method applying flotation analysis to fluorescence analysis (42) have been mentioned in the literature. Kiefer and Boltz (24) determined the excess phosphate from a precipitation of zirconium as the phosphate spectrophotometrically as the molybdiphosphoric acid complex.

3. **Spectrographic**

Spectrographic methods are used for extremely small amounts of zirconium (22), for the determination of zirconium in hafnium (25, 34, 40), and for the analysis of very difficultly soluble alloys such as zirconium-niobium.

4. **Volumetric**

The majority of the methods for the volumetric determination of zirconium which are found in the literature are indirect methods involving precipitation and a determination of the excess precipitant or dissolution of the precipitate in an excess of a standard solution and a determination of the excess. The reason for this is that zirconium has a constant oxidation state and forms a colorless ion in solution. These indirect methods involve so many operations that it might be more practicable to ignite the precipitate to the oxide and weigh it as such.

White (64) developed many indirect methods. In one a zirconia precipitate is dissolved in potassium fluoride solution and the basicity titrated. In another zirconium is precipitated with p-chloromandelic acid. The precipitate is dissolved in excess standard sodium methylate in methyl alcohol-benzene solution, and the excess sodium methylate titrated with standard acetic acid with thymol blue as the indicator. Another method of White is the dissolution of the zirconia precipitate in excess standard acid and the titration of the excess acid.
Sawaya and Yamashita (48) determined zirconium by dissolving the hydrous oxide precipitate in potassium fluoride and standard 0.1 N nitric acid and titrating the excess standard acid. The reaction for dissolution of the hydrous oxide is

$$\text{Zr(OH)}_4 + 6 \text{KF} + 4 \text{HNO}_3 \rightarrow \text{K}_2\text{ZrF}_6 + 4 \text{KNO}_3 + 4 \text{H}_2\text{O}.$$  

Dahr and Das Gupta (9) determined zirconium volumetrically after isolation of zirconium oxalohydroxamate. The precipitate is dissolved in dilute hydrochloric acid and hydrolyzed to hydroxylamine. Excess standard titanous chloride is added and back titrated with Fe(III) solution.

Graham, et al. (14), developed a polarographic method for zirconium in magnesium base alloys based on the polarographic reducibility of m-nitrobenzoic acid. Again the precipitate must be isolated and redissolved.

A few direct titrations have been reported for zirconium. Kolthoff and Johnson (28) did a direct amperometric titration of solutions containing no interfering ions with a mean error of ± 5.3 per cent and a deviation of ± 0.8 per cent. Larsen and Grammil (29, p.569) did electrometric titrations in their calculation of the solubility product of zirconium hydroxide. The usual strong acid-base curves were obtained, but the end point was calculated from an extrapolation because precipitation and coagulation obscured the inflection point. Cozzi (7) determined zirconium by reduction at the dropping mercury electrode. Although these types of titration are direct, they are usually not very rapid.

Recently EDTA, ethylenediaminetetraacetic acid, has been used by Milner and Phennah (39) to titrate zirconium in binary alloys with uranium after dissolving the mandelic acid precipitate in perchloric acid. Excess EDTA is added to the sample in acid solution and back titrated with Fe(III). Salicylic acid is the indicator which is used. The accuracy claimed for 100 milligrams of zirconium is 1 per cent.

From this review it can be seen that a direct and rapid method for the determination in the presence of interfering cations is needed. This is the work which this report reports.

Ethylenediaminetetraacetic acid, EDTA, was first reported by Fick and Ulrich (11) in 1936. They prepared it by reacting ethylenediamine, hydrogen cyanide, and formaldehyde, and saponifying the
product to EDTA. As shown by Schwarzenbach and Ackermann (50) it is essentially a dicarboxylic acid because the first two pK's are so close (pK\(_1\) = 1.995, pK\(_2\) = 2.672, pK\(_3\) = 6.161, pK\(_4\) = 10.252). This compound has the ability to form very stable, water soluble complexes with many metal ions. The log of the formation constant for the reaction

\[ M^{+n} + Y^{-4} \rightleftharpoons MY^{(n-4)} \]

where \( M^{+n} \) represents the metal ion, \( Y^{-4} \) the EDTA ion, and \( MY^{(n-4)} \) the complex, was reported for many ions by Cabell (5) and compared with those values for other complexing agents. The author was unable to find a value for the log \( K \) for the zirconium complex with EDTA in the literature.

The reagent is not specific; however, with the proper choice of conditions and indicators, the reagent can be made specific.

EDTA has found application in many other fields besides analytical chemistry. Two extensive bibliographies on the uses of EDTA are available. One is entitled, "Sequestrene," and is published by Alrose Chemical Co. (1b). It covers the literature to June, 1952. The other is entitled, "Bibliography of Ethylenediaminetetraacetic Acid," and is published by Versenes Incorporated, formerly Bersworth Chemical Co. (2b).

III. EDTA TitrATION OF ZIRCONIUM

A. Factors Affecting the Titration

1. Indicators

The general reactions involved in the titration are

\[ Zr(IV) + H_2Y^{-2} = ZrY + 2H^+ \]  \hspace{1cm} (1)
\[ ZrIn_a + H_2Y^{-2} + (ab - 2)H^+ = ZrY + aH_bIn, \]  \hspace{1cm} (2)

where \( Y \) and \( In \) represent the EDTA and indicator radicals, respectively. After the bulk of the zirconium has reacted according to reaction 1, the highly colored zirconium-indicator complex is destroyed (reaction 2), marking the end point. In addition to being highly colored, the zirconium-indicator complex must be less stable than the
zirconium-EDTA complex. Furthermore, reaction 2 must be fairly rapid, so that the end point will not be overrun.

Several indicators were tried. Alizarin Red S has been used for the colorimetric determination of zirconium (63) but is useless for the EDTA titration because of the very slow reaction of the zirconium-indicator complex with EDTA. Carminic acid, chloranilic acid, and Chrome Azurol S also are unsatisfactory. Both Alizarol Cyanone RC and Eriochrome Cyanine RC give sharp and vivid end points. The Alizarol Cyanone RC end point is often slow if a direct EDTA titration is attempted, but it is fast if a slight excess of EDTA is added and this excess back titrated hot with standard zirconium. Either direct or back titration is possible with Eriochrome Cyanine RC, but the end point in the direct titration should not be approached too rapidly.

2. Effect of pH

With either Alizarol Cyanone RC or Eriochrome Cyanine RC indicator, satisfactory end points can be obtained in the pH range 1.0 to 2.0. Best accuracy is obtained, however, if the final pH is between 1.3 and 1.5. Results for zirconium are high above pH 1.5 and low below pH 1.3.

Dewell (8), using ion exchange studies, found that zirconium ions in solution changed to complex ions and formed colloids above pH 2.0 according to the reaction

\[ \text{ZrO}^{2+} + \text{H}_2\text{O} \rightarrow \text{ZrOH}^+ + \text{H}^+. \]

This would explain why no end point was observed by the author above pH 2.0. In EDTA solution zirconium begins to precipitate at pH 3.0; this was found by Cabell (6) and confirmed by the author.

3. Effect of heat

Heating the solution to 70° to 90°C. speeds the reaction and permits a rapid back titration of excess EDTA with zirconium. A direct titration in hot solution is not possible. When the solution is heated at pH to 1.3 to 1.5 without excess EDTA, no end point is observed even with 100 per cent excess EDTA. When the solution is heated for 15 minutes without excess EDTA, a jelly-like substance, possibly the hydrous oxide of zirconium, precipitates and absorbs
the indicator. Perhaps the formation of complex ions and colloids which Dewell (8) described as happening above pH 2.0 occurs at a lower pH at higher temperatures.

4. Extraction attempts

Fritz and Ford (12) extracted thorium prior to a titration with EDTA according to the method of Levine and Grimaldi (33). In this extraction mesityl oxide is the organic solvent and aluminum nitrate is the salting out agent. This separated thorium from the rare earths and large amounts of fluoride and phosphate. A separation such as this for zirconium would be very useful because fluoride and phosphate are important interferences in the EDTA titration (see Interference Study). Many alloys if zirconium are soluble only in hydrofluoric acid, and the phosphate precipitation is, as mentioned earlier, a very good separation scheme for zirconium.

Several combinations of mesityl oxide and salting out agents were tried. Aluminum nitrate, zinc nitrate, calcium nitrate, lithium nitrate, and magnesium nitrate were tried; but no quantitative separations were obtained. Scadden and Ballou (49) used a mixture of dibutyl ether, dibutylphosphoric acid, and monobutylphosphoric acid and only extracted 98 per cent of the zirconium present. This was the most quantitative extraction that could be found in the literature.

5. Buffer attempts

It was mentioned earlier that the best pH to use is 1.3 to 1.5. The pH change during the titration is very slight for titrations of 10 milliliters or less; however, to maintain such a close pH tolerance it would seem advisable to use a buffer system. Sodium periodate-periodic acid (pKa = 1.54), sodium oxalate-oxalic acid (pKa = 1.19), sodium saccharide-saccharin (pKa = 1.60), and sodium dichloroacetate-dichloroacetic acid (pKa = 1.30) buffer systems were tried, but all of them interfered in the titration. No suitable buffer was found.

B. Reagents and Apparatus

1. Indicators

a. Alizarol Cyanone RC. A 0.4 per cent aqueous solution of this dye, obtained from National Aniline Division, Allied Chemical and Dye Corp., was used as an indicator.
b. Eriochrome Cyanine RC. A 0.4 per cent aqueous solution of this dye, obtained from Geigy Co., was used as an indicator.

c. Eriochrome Black T. A 1 per cent solution of this dye, obtained from Hach Chemical Co., in triethanolamine (10) was used as an indicator.

2. Standard solutions

a. EDTA. Reagent grade disodium dihydrogen ethylenediaminetetraacetic acid, available commercially from Hach Chemical Co., was used for this solution. To prepare a 0.05 M solution 70 grams of the salt were dissolved in 3.5 liters of water. This solution was standardized against pure zinc metal as described by Fritz and Ford (12) and Brown and Hayes (5) or against the 0.05 M standard zirconium solution.

b. Hafnium Chloride. A 0.05 M solution in (5 + 95) hydrochloric acid was prepared by dissolving 11.4 grams of HfO(OH)_2 in 50 milliliters of concentrated hydrochloric acid and diluting to one liter. This solution was standardized by evaporating an aliquot and igniting the residue to the oxide. The zirconium content was 2.1 per cent by weight as determined by spectrographic analysis.

c. Thorium Nitrate. A 0.05 M solution in 0.02 to 0.03 M nitric acid was prepared and standardized as described by Fritz and Ford (12). The standardization is done gravimetrically by precipitation of thorium oxalate and ignition to thoria.

d. Zirconyl Chloride. Zirconyl chloride octahydrate containing less than 100 parts per million hafnium was used for this solution. A 0.05 M solution in (5 + 95) hydrochloric acid was prepared by dissolving 16 grams of the reagent in 50 milliliters of concentrated hydrochloric acid and diluting to one liter.

3. Miscellaneous

All other chemicals used in this work were reagent grade unless otherwise specified. The zinc amalgam was 20 mesh zinc lightly amalgamated as directed by Kolthoff and Sandell (29, p. 569).
4. Apparatus

All pH measurements were made with a Beckman Model G pH meter using a glass-calomel electrode system. Magnetic stirrers were used for all of the titrations. Other apparatus were normal laboratory equipment.

C. Procedures

1. Procedure for direct titration

The zirconium concentration of the solution before the titration was 0.15 to 0.25 millimoles of zirconium per 50 milliliters of solution. The pH was adjusted to 1.4 with dilute ammonium hydroxide (1 + 9) or dilute perchloric acid (1 + 9), two drops of the indicator solution were added, and the solution was titrated with 0.05 M EDTA to the disappearance of the pink color of the zirconium-indicator complex.

2. Procedure for direct titration in the presence of iron

If iron was present, 10 grams of amalgamated zinc was added to 50 milliliters of the solution which contained 0.15 to 0.25 millimoles of zirconium and up to 1.0 millimole of iron. The pH had to be less than 1.0 in order to insure complete reduction of the iron. The mixture was stirred about five minutes, then the pH was adjusted to 1.2 to 1.4 with dilute ammonium hydroxide (1 + 9). Two drops of the indicator solution were added, and the solution was titrated with 0.05 M EDTA to the disappearance of the pink color of the zirconium-indicator complex while bubbling nitrogen through the solution by means of a gas washing tube. Magnetic stirring was used.

3. Procedure for back titration

The same procedure was used as for the direct titration, and a slight excess of EDTA was added. When necessary, the pH of the solution was readjusted to 1.4 with dilute ammonium hydroxide (1 + 9). The solution was heated almost to boiling and back titrated with 0.05 M zirconyl chloride to the first permanent pink color.
D. Stoichiometry

Since aqueous solutions of zirconium polymerize above pH 2, there was some doubt as to whether the titration with EDTA could be made stoichiometric. A test for stoichiometry was made by titrating aliquots of a zirconyl chloride solution which had been standardized by evaporation and ignition to the oxide and by mandelic acid precipitation and ignition to the oxide. The EDTA solution used to titrate the zirconium was standardized against pure zinc metal by methods reported in the literature (5, 12). Stoichiometric results were obtained only when a correction was applied for the approximately 2 per cent hafnyl chloride present in the reagent grade zirconyl chloride. This assumes that the hafnium was titrated with the zirconium. The hafnium content of the solution was determined independently by the spectrographic laboratory and reported as the Hf/Zr ratio. The calculation of the metal ion molarity is

\[
M = \frac{\text{Hf/Zr}}{\text{Hf/Zr} + 1} \times \frac{\text{g}}{221.4} + \frac{\text{Zr/Hf}}{\text{Zr/Hf} + 1} \times \frac{\text{g}}{113.1}
\]

\[V\]

\[
\text{Hf/Zr} = \text{spectrographic ratio}
\]

\[
g = \text{weight in grams of combined oxides from evaporation and ignition}
\]

\[
V = \text{volume in liters of aliquot evaporated}
\]

\[
M = \text{metal ion molarity of solution}
\]

To check the stoichiometry further a standard zirconyl chloride solution was prepared from zirconyl chloride containing less than 100 parts per million hafnyl chloride, and this solution was titrated with two different standard EDTA solutions. The results given in Table 1 show that at least within ordinary titration error the method is stoichiometric, a one to one zirconium–EDTA complex being formed.
Table 1. Direct Titration of Zirconium

<table>
<thead>
<tr>
<th>Zr taken (mg)</th>
<th>Theoretical EDTA (ml)</th>
<th>Experimental EDTA (ml)</th>
<th>Difference (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.8</td>
<td>5.24</td>
<td>5.24</td>
<td>0.00</td>
</tr>
<tr>
<td>22.8</td>
<td>5.24</td>
<td>5.24</td>
<td>0.00</td>
</tr>
<tr>
<td>22.8</td>
<td>5.24</td>
<td>5.25</td>
<td>-0.01</td>
</tr>
<tr>
<td>22.8</td>
<td>9.47</td>
<td>9.47</td>
<td>0.00</td>
</tr>
<tr>
<td>22.8</td>
<td>9.47</td>
<td>9.48</td>
<td>-0.01</td>
</tr>
<tr>
<td>22.8</td>
<td>9.47</td>
<td>9.49</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Some hafnium usually accompanies zirconium and will be titrated as zirconium unless the hafnium-zirconium ratio is determined and taken into account in the calculations as indicated. If it is not convenient to determine this ratio, it can usually be assumed to be constant in a series of samples. The EDTA can then be standardized against a sample containing a known weight of zirconium plus hafnium, the concentration of the EDTA solution being expressed as the zirconium-hafnium titer.

E. Interference Study

Table 2 lists the interfering and non-interfering ions. The fact that ions such as copper(II), nickel(II), and lead(II) do not interfere although their EDTA complexes are very stable (log K formation is approximately 18 (5)) indicates that both the zirconium-EDTA and zirconium-indicator complexes are very strong.

The direct titration procedure must be followed if aluminum is present. This is because once the zirconium-indicator complex has been broken by adding excess EDTA, the indicator is free to react with the aluminum. The direct titration succeeds because the aluminum reacts with the indicator too slowly to interfere, especially at room temperature.
Table 2. Interference Study

<table>
<thead>
<tr>
<th>Ion added&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Direct titration</th>
<th></th>
<th>Back titration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDTA Theoretical (ml)</td>
<td>EDTA Experimental (ml)</td>
<td>EDTA Theoretical (ml)</td>
<td>EDTA Experimental (ml)</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.24</td>
<td>interferes</td>
<td>5.21</td>
<td>5.25</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>5.21</td>
<td>interferes</td>
</tr>
<tr>
<td>Ba&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>5.21</td>
<td>5.20</td>
</tr>
<tr>
<td>Be&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.23</td>
<td>5.21</td>
<td>5.25</td>
</tr>
<tr>
<td>Bi&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>interferes</td>
<td>5.21</td>
<td>interferes</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>5.21</td>
<td>5.20</td>
</tr>
<tr>
<td>Cd&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>5.21</td>
<td>5.21</td>
</tr>
<tr>
<td>Ce&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>3.50</td>
<td>3.51</td>
</tr>
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<td>5.26</td>
<td>5.21</td>
<td>5.20</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>3.50</td>
<td>3.50</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>interferes</td>
<td>4.50</td>
<td>4.51&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>4.47</td>
<td>4.46&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.50</td>
<td>3.51&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.33</td>
<td>5.34</td>
<td>5.21</td>
<td>interferes</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>interferes</td>
<td>5.21</td>
<td>interferes</td>
</tr>
<tr>
<td>Hg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>4.17</td>
<td>4.18</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>4.50</td>
<td>4.50</td>
</tr>
<tr>
<td>La&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.24</td>
<td>3.50</td>
<td>3.51</td>
</tr>
<tr>
<td>Li&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>5.21</td>
<td>5.20</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>5.41</td>
<td>5.39</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.24</td>
<td>5.22</td>
<td>5.41</td>
<td>5.41</td>
</tr>
</tbody>
</table>

<sup>a</sup>Approximately equal to zirconium concentration.

<sup>b</sup>Thiourea (0.5 grams) added before the titration.
Table 2 (Continued)

<table>
<thead>
<tr>
<th>Ion added</th>
<th>Direct titration</th>
<th>Back titration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDTA</td>
<td>EDTA</td>
</tr>
<tr>
<td></td>
<td>Theoretical (ml)</td>
<td>Experimental (ml)</td>
</tr>
<tr>
<td>Mo^{+++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>5.24</td>
<td>5.24</td>
</tr>
<tr>
<td>Ni^{++}</td>
<td>5.24</td>
<td>5.24</td>
</tr>
<tr>
<td>NH_{4}^{+}</td>
<td>5.24</td>
<td>5.24</td>
</tr>
<tr>
<td>Pb^{++}</td>
<td>5.24</td>
<td>5.22</td>
</tr>
<tr>
<td>Sb^{+++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Sn^{++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Sn^{+++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Ti^{+++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Ti^{++++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>Th^{++++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>UO_{2}^{++}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>VO^{2+}</td>
<td>5.24</td>
<td>5.33</td>
</tr>
<tr>
<td>Zn^{++}</td>
<td>5.24</td>
<td>5.24</td>
</tr>
<tr>
<td>C_{2}H_{3}O_{2}^{−}</td>
<td>5.41</td>
<td>5.38</td>
</tr>
<tr>
<td>F^{−}</td>
<td>5.41</td>
<td>interferes</td>
</tr>
<tr>
<td>Mandelate</td>
<td>5.24</td>
<td>5.25</td>
</tr>
<tr>
<td>MoO_{4}^{2−}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>SO_{4}^{2−}</td>
<td>5.41</td>
<td>interferes</td>
</tr>
<tr>
<td>Tartrate</td>
<td>5.24</td>
<td>interferes</td>
</tr>
<tr>
<td>VO_{3}^{−}</td>
<td>5.24</td>
<td>5.21</td>
</tr>
<tr>
<td>WO_{4}^{2−}</td>
<td>5.24</td>
<td>interferes</td>
</tr>
</tbody>
</table>
Two methods can be used to get stoichiometric results if copper(II) is present. Copper interferes in a direct titration, but no interference is noted if excess EDTA is added and the solution is heated several minutes before back titration. Apparently the copper–EDTA complex is almost as strong as the zirconium–EDTA complex. If 0.5 gram of thiourea is added to the solution before the titration, a strong, colorless copper-thiourea complex forms which removes the copper interference completely. The solution can then be titrated directly or by the back titration procedure.

Although iron(III) forms a very strong complex with EDTA \((\log K = 25)\), iron(II) forms a comparatively weak complex \((\log K = 14.7)\) \cite{6}. Interference from iron can be avoided by a preliminary reduction with zinc amalgam. The titration must be carried out in an inert atmosphere because iron(II) is very easily oxidized to iron(III) in the presence of EDTA causing the end point to fade. Table 3 shows a study of iron interference.

**Table 3. Iron Interference Study**

<table>
<thead>
<tr>
<th>Mole ratio Fe/Zr</th>
<th>Theoretical EDTA (ml)</th>
<th>Experimental EDTA (ml)</th>
<th>Difference (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>5.33</td>
<td>5.36</td>
<td>+0.03</td>
</tr>
<tr>
<td>2/1</td>
<td>5.33</td>
<td>5.34</td>
<td>+0.01</td>
</tr>
<tr>
<td>4/1</td>
<td>5.33</td>
<td>5.33</td>
<td>0.00</td>
</tr>
<tr>
<td>5/1</td>
<td>2.13</td>
<td>2.15</td>
<td>+0.02</td>
</tr>
<tr>
<td>10/1</td>
<td>2.13</td>
<td>2.13</td>
<td>0.00</td>
</tr>
<tr>
<td>15/1</td>
<td>2.13</td>
<td>2.13</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Interference by tin(IV) is avoided by adding excess EDTA to a rather acidic sample \((\text{pH} \text{ about 0.5})\) and then back titrating at room temperature with standard zirconyl chloride solution. Titanium(IV) interference is avoided by a similar procedure, but EDTA must be added in excess of the amount equivalent to the combined zirconium and titanium. The solution is then heated almost to boiling and back titrated \((\text{at pH 1.2 to 1.4})\) with standard zirconyl chloride solution. The presence of either tin or titanium decreases the sharpness of the end point.
When nickel is present in an amount equimolar to the zirconium concentration, a reproducible error of 2 per cent is encountered in the direct titration; but no interference is encountered in the back titration. The reasons for the behavior in the direct titration are not apparent.

No interference is caused by perchlorate, chloride, nitrate, or acetate. Anions which complex zirconium strongly or precipitate zirconium, such as phosphate, molybdate, sulfate, fluoride, and oxalate, interfere seriously.

Hafnium and thorium interferences were investigated quantitatively. Mixtures of known amounts of zirconium and hafnium and zirconium and thorium were prepared and titrated. The results given in Table 4 confirm the quantitative nature of these two interferences.

Table 4. Titration of Mixtures

<table>
<thead>
<tr>
<th>Theoretical EDTA (ml)</th>
<th>Experimental EDTA (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent to Zr 3.66</td>
<td></td>
</tr>
<tr>
<td>Equivalent to Th 2.59</td>
<td></td>
</tr>
<tr>
<td>Equivalent to sum 6.25</td>
<td>6.25, 6.22, 6.22</td>
</tr>
<tr>
<td>Equivalent to Zr 2.71</td>
<td></td>
</tr>
<tr>
<td>Equivalent to Hf 2.64</td>
<td></td>
</tr>
<tr>
<td>Equivalent to sum 5.35</td>
<td>5.32, 5.33, 5.32</td>
</tr>
</tbody>
</table>

IV. ANALYSES OF SAMPLES CONTAINING ZIRCONIUM

A study of a new method of analysis would not be complete without a few practical analyses of unknown samples and a comparison of the results with those of another method. Samples of zircon sands and zirconium-zinc alloys were available. The method used for comparison was the mandelic acid precipitation of zirconium proposed by Kumins(30), this being the most selective and commercially available reagent for zirconium and hafnium.
Three spectrographic determinations, one on reagent grade zirconyl chloride octahydrate, one on a zirconium zinc alloy, and one on a zircon sand sample showed a Hf/Zr ratio of 2.0 ± 0.1. This means that about 2 per cent of the zirconium in the samples was actually hafnium. Using this factor of 2 per cent, the author found that the "molecular weight" of zirconium to be used in the volumetric determination should be 92.97 instead of 91.22, an increase of 1.92 per cent. The value for the "molecular weight" of zirconium oxide is 124.97 instead of 123.22, an increase of 1.42 per cent. When not taken into account, this difference causes discrepancies when results for the titrimetric procedure are compared with those of the gravimetric procedure.

A. Zircon Sand Samples

When received, these samples were in the form of a powder from a sodium hydroxide fusion. The samples were leached with water to remove some of the sodium hydroxide, dissolved in hydrochloric acid and diluted to volume in a volumetric flask so that a 10-milliliter aliquot contained 0.15 to 0.25 millimoles of zirconium. The zirconium was determined titrimetrically by the back titration procedure and gravimetrically by the mandelic acid procedure of Kumins (30). Table 5 shows a comparison of results by the two procedures.

<table>
<thead>
<tr>
<th>Titrimetric determination</th>
<th>Gravimetric determination</th>
<th>Deviation from gravimetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range % Zr</td>
<td>No. detns.</td>
<td>Average % Zr</td>
</tr>
<tr>
<td>19.99 - 20.89</td>
<td>2</td>
<td>20.44</td>
</tr>
<tr>
<td>21.18 - 22.27</td>
<td>2</td>
<td>21.86</td>
</tr>
<tr>
<td>21.66 - 21.77</td>
<td>3</td>
<td>21.71</td>
</tr>
<tr>
<td>21.51 - 21.62</td>
<td>3</td>
<td>21.55</td>
</tr>
<tr>
<td>39.78 - 40.00</td>
<td>3</td>
<td>39.85</td>
</tr>
<tr>
<td>39.55 - 39.55</td>
<td>3</td>
<td>39.55</td>
</tr>
<tr>
<td>34.63 - 34.76</td>
<td>3</td>
<td>34.70</td>
</tr>
<tr>
<td>34.50 - 34.78</td>
<td>3</td>
<td>34.74</td>
</tr>
</tbody>
</table>
Some hydrous oxide of silica slowly precipitated in the volumetric flask. As little of this precipitate as possible was allowed in the aliquots by carefully pipetting aliquots from above the precipitate. The precipitate does not interfere in the titrimetric procedure in small amounts; in large amounts it adsorbs the indicator. The precipitate does interfere in the gravimetric procedure, but it can be removed by evaporation with hydrofluoric acid after the zirconium mandelate precipitate has been ignited to the oxide. The fact that all of the titrimetric determinations in Table 5 deviate negatively from the gravimetric determinations indicates that perhaps all of the silica was not removed in the gravimetric determinations.

B. Zirconium-Zinc Alloys

When received, these samples were in the massive form. Some could be broken and ground up with a mortar and pestle; others had to be cut into smaller pieces with an abrasive cutter. Samples containing 250 to 400 milligrams of zirconium were weighed and dissolved in bromine and ethyl acetate. The solution was evaporated almost to dryness, and the residue was dissolved in 10 milliliters of concentrated hydrochloric acid with heating. The alloys dissolved very readily in bromine and ethyl acetate; however, an alternate solvent mixture was nitric and perchloric acids. Dilute nitric acid (1 ~ 9) was added until the vigorous bubbling caused by the dissolving zinc subsided; then 10 milliliters of concentrated perchloric acid was added, and the solution was heated for one to three hours or until solution was complete. The solutions were transferred to 200-milliliter volumetric flasks and diluted to volume. Ten-milliliter aliquots were used for the titrimetric determination by the back titration procedure, and 50-milliliter aliquots were used for the gravimetric determination by the mandelic acid precipitation method of Kumins (30). Table 6 shows a comparison of the results by the two procedures.
### Table 6. Analyses of Zirconium-Zinc Alloys for Zirconium

<table>
<thead>
<tr>
<th>Volumetric determination</th>
<th>Gravimetric determination</th>
<th>Deviation from gravimetric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td>% Zr</td>
<td>% Zr</td>
</tr>
<tr>
<td>24.34 - 24.47</td>
<td>24.45</td>
<td>24.59</td>
</tr>
<tr>
<td>2.80 - 2.82</td>
<td>2.81</td>
<td>2.90</td>
</tr>
<tr>
<td>8.80 - 9.04</td>
<td>8.91</td>
<td>9.07</td>
</tr>
<tr>
<td>12.53 - 12.59</td>
<td>12.58</td>
<td>12.60</td>
</tr>
<tr>
<td>13.07 - 13.15</td>
<td>13.12</td>
<td>13.37</td>
</tr>
<tr>
<td>2.44 - 2.47</td>
<td>2.46</td>
<td>2.34</td>
</tr>
<tr>
<td>10.16 - 10.31</td>
<td>10.24</td>
<td>10.35</td>
</tr>
</tbody>
</table>

### V. Suggestions for Future Work

Work must be done to avoid the interferences of fluoride, phosphate, sulfate, and other ions. Hydrofluoric acid and sulfuric acid are good solvents for ores and alloys of zirconium, and phosphate is a good quantitative precipitant for the separation of zirconium. Possibly an extraction procedure such as that used by Fritz and Ford (12) for thorium can be worked out.

For titrations involving 25 to 50 milliliters of EDTA solution the pH change during the titration may be considerable. The use of a buffer which does not interfere in the titration would be an improvement on the proposed method.

From a more general outlook titration with complexing agents is an approach offering wide opportunity for rapid and selective determinations. Perhaps the applications can be extended to non-aqueous systems.
VI. LITERATURE CITED


64. White, J. C. Oak Ridge National Laboratory report ORNL-1515, 1953.


