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Determination of Thorium in Plutonium-Thorium Oxides and Carbides

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DETERMINATION OF THORIUM IN PLUTONIUM-THORIUM OXIDES AND CARBIDES

by

L. F. Walker and D. J. Temer

ABSTRACT

Thorium is determined in (PuTh)C and (PuTh)O₂ by complexometric titration with ethylenediaminetetraacetic acid (EDTA) following separation on anion-exchange resin. Carbides are first oxidized by ignition in air at about 800°C. Oxide or oxidized carbide samples are dissolved in acids by the sealed-reflux technique or by heating in beakers. The plutonium is selectively sorbed from the 12M hydrochloric acid solution of the fuel on a Bio-Rad AG1-X2 anion-exchange resin column, and the eluted thorium is titrated with EDTA using xylenol orange as the indicator. The average recovery of thorium in 20 samples is 99.98% with a relative standard deviation of 0.07%.

INTRODUCTION

In order to avoid the use of plutonium in reactor fuel, a Th-²³³U fuel cycle is being considered as a possible alternative. A start-in fuel, in which plutonium has been substituted for the ²³³U, has been used. Because thorium cannot be determined directly in the presence of plutonium or uranium, a need exists for a method of determining thorium in carbides, oxides, or nitrides, of (Pu-Th) or (U-Th) reactor fuel.

A method for determining thorium in solution is well known.¹ Thorium cannot be determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA) in the presence of either plutonium or uranium because (1) plutonium and uranium form stable EDTA complexes,² and (2) the plutonium ion color masks the xylenol orange end-point, so a separation before analysis is necessary.

Thorium⁴⁺ is separated from Pu⁴⁺ using anion-exchange resin³ in 12M hydrochloric acid. The

thorium⁴⁺ passes through the column while the Pu⁴⁺ is retained. The thorium is collected and fumed to dryness with perchloric and nitric acids to eliminate carbonaceous materials that cause difficulties in end-point detection. The residue is taken up in water, the pH adjusted to 2.5, xylenol orange is added, and the thorium is titrated with a dilute solution of Na₄ EDTA. To maintain the pH at 2.5 ± 0.1 during the titration the tetrasodium salt of EDTA is preferred to the disodium salt. The Na₄ EDTA titrant is standardized against a thorium reference solution the same day the samples are analyzed.

II. APPARATUS AND REAGENTS

Apparatus

Balance. A single-pan Mettler balance with hook to hold weight burette, sensitivity of ± 0.1 mg.

Column. Ion-exchange resin column as shown in Fig. 1.

Fig. 1.
Ion-exchange resin column.

Electrode. A semi-micro, combination pH electrode.

Weight burette. A modified Friedman LaMer burette, as shown in Fig. 2.

Miscellaneous lab equipment. pH meter, hot

Fig. 2.
Weight burette.

plate, magnetic mixer, beakers (50 or 100 mL) and other common glassware.

Polyethylene bottle. A size 9L bottle with dispensing spigot to store Na_4EDTA solution (Na_4EDTA solutions etch glass).

Reagents

EDTA. Baker analyzed tetrasodium salt, 0.025 M.

Hydrochloric Acid. 12M, 1M, 0.1M, reagent grade.

Ion-exchange resin. Bio-Rad AG1-X2, 100-200 mesh.

Nitric acid. 15.5M, reagent grade.

Sodium hydroxide. 0.3M, reagent grade.

Perchloric acid. 11.6M, reagent grade.

Thorium nitrate reference solution. Dissolve thorium metal in HNO₃, evaporate the solution to dryness, and dissolve the residue in water to a concentration of 20-25 mg Th/g of solution. The thorium is determined gravimetrically as the oxalate.

Xylenol orange. 0.1% in 20% ethanol.

III. PROCEDURE

1. Ignite carbide samples in a fused-silica or platinum dish in air at about 800°C to incinerate the carbon.

2. Dissolve the oxide or oxidized carbide sample by the sealed-reflux technique⁴ or transfer the sample by washing with water to a 100 ml beaker. Add 5 ml of 15.5M HNO₃, 10-20 drops of 1.3M HF, and 5ml of 70% HClO₄. Evaporate the water at ≈100°C on a hot plate or steam bath, cover the beaker with a watch glass, and heat until the sample dissolves.

3. Transfer the solution obtained by the sealed-reflux technique by washing with water into a 100 ml beaker. Evaporate the solution to dryness on a hot plate or steam bath. If the sample was dissolved in a beaker, rinse the watch glass, and allow the combined rinse and solution to evaporate to dryness.

4. Redissolve the residue in 1M HCl.

5. Transfer aliquots containing 100-125 mg of Th, preferably on a weight basis, to 50 ml beakers.

6. Evaporate the aliquots to dryness on a hot plate or steam bath.

7. Cool the sample residue and dissolve in 12M HCl.

8. Transfer the solution quantitatively, using a minimum amount of 12M HCl, to a washed 5-ml Bio-Rad AG1-X2 anion-exchange resin column, and collect the eluate in a 100-ml beaker.

9. Wash the column with a minimum of three column volumes* of 12M HCl.

10. Add 5 ml of 70% HClO₄ and 2 ml of 15.5M HNO₃ to the eluate.

11. Evaporate the eluate slowly to dryness on a hot plate or steam bath and allow the residue to cool.

12. Dissolve the residue in a small amount of water and again evaporate to dryness.

13. Dissolve the residue in about 20 ml of water and add 6 drops of 0.1% xylenol orange solution.

14. Stir the solution with a magnetic mixer and monitor the solution's pH with a combination electrode.

15. Maintain the pH of the solution at 2.5 ± 0.1 during the titration by adding dilute NaOH or HCl solution as required.

16. Titrate the thorium in the aliquot with 0.025M EDTA (added from a weight burette) until the xylenol orange indicator turns yellow.

17. Titrate a thorium reference solution following steps 13 through 16 to determine the EDTA titer.

$$\text{EDTA Titer} = \frac{\text{mg Th in reference soln}}{\text{g EDTA soln}}$$

18. Calculate the thorium content of the sample as follows.

$$\% \text{Th} = \frac{(\text{EDTA titer, mg Th/g soln})(\text{wt of EDTA, g})(100\%)}{\text{wt of aliquot, mg}}$$

19. A blank correction is not required.

IV. EXPERIMENTAL

A. Thorium Reference Solutions

Iron-free thorium reference solutions were prepared by dissolving the pure metal in HNO₃, evaporating the solution to dryness, and dissolving the residue in water. The solutions were diluted to contain 20-25 mg Th/g of solution.

Weighed aliquots containing approximately 100 mg Th were titrated directly with the EDTA solution, with xylenol orange as the indicator. The end point (from purple to golden yellow) is sharp and easily seen. The EDTA titer is determined from the results of three or more titrations against the reference solution. An average relative standard deviation (RSD) of 0.04% was found over 12 sets of 3 or more aliquots of reference solution as shown in Table I.

Data on prepared solutions containing both plutonium and thorium appear in Table II. After removal of plutonium, the average recovery for

*A column volume is equal to the void volume of the column.

TABLE I
THORIUM REFERENCE SOLUTIONS

<u>Aliquots Analyzed</u>	<u>EDTA titer^a RSD</u>
4	0.05%
4	0.03%
4	0.01%
3	0.06%
4	0.05%
4	0.04%
3	0.02%
4	0.00%
5	0.07%
4	0.04%
5	0.03%
10	0.05%
	0.04%

^aBecause the actual titer of EDTA solution changes with time, only those reference aliquots analyzed the same day can be compared. Entries represent determinations done on different days.

thorium as determined by titration is 99.98% with a RSD of 0.07%. Since the recovery of thorium is quantitative, one can omit the elution of thorium reference solutions through the anion-exchange resin. Thus, one is able to standardize the EDTA titrant while other work is in progress.

Blank

A blank (no thorium or plutonium) was eluted through the ion-exchange column and titrated. It required an amount of EDTA equivalent to 0.006 mg Th. This represents an error <0.01% in a typical 100-mg Th sample, which is far below the accuracy of the method. Thus, the blank correction is assumed to be zero in these studies.

C. Samples

Samples containing 100 mg Th with or without 25 mg Pu were analyzed as described in the procedure. On several samples, the eluate was collected in frac-

tions, and each fraction was titrated separately. The results are shown in Table III. These tests indicate that three column volumes of eluent are needed to recover the thorium quantitatively.

D. Precision

Precision for reference solutions (0.04% RSD) is better than for samples containing both thorium and plutonium (0.07% RSD). Error in the weight of complexant added and variation in pH, which affects the end point of the titration, are two sources of error in the determination. An error of 10 mg in the addition of complexant introduces a relative error of 0.07% in the determination of thorium.

E. Columns

Before use, the columns are packed with Bio-Rad AG1-X2 anion-exchange resin dispersed in 1M HCl and then rinsed with 5-10 column volumes of 12M HCl. After the thorium is eluted, the plutonium may be eluted from the resin with three column volumes of 1M HCl. The column is regenerated for the next sample or set of samples by rinsing with three column volumes of 12M HCl. The amount of resin used in each column was estimated to sorb 1 g of Pu. In practice, 100 mg of Pu did sorb at the top 15% of the bed volume. This permits the analysis of several samples before the resin becomes saturated and the plutonium has to be eluted.

V. INTERFERENCE

Interference from the cations of iron, zirconium, and zinc, which form stable complexes with EDTA and from the anions SO_4^{2-} , PO_4^{3-} , and F^- , which form stable thorium complexes, was considered. Uranium, a likely impurity in the mixed oxide or carbide fuel, is removed along with plutonium by the ion-exchange resin column.² Fluoride ion volatilizes when the samples are fumed to dryness with HClO_4 .

Interference was tested by adding the cation or anion to a sample containing 100 mg Th. The sample was then analyzed as described in the procedure. At the 1% impurity level, cerium interferes with the

TABLE II
SAMPLE SIMULATION

EDTA Titer (mg/g)	Pu in Sample (mg)	Th in Sample (mg)	wt of EDTA (g)	Th recovery (%)
6.303	24.2211	96.5393	15.3114	99.97
6.303	24.3905	94.5559	14.9906	99.93
6.303	24.2443	96.5439	15.3172	99.89
6.303	24.4215	94.6084	15.0032	99.95
6.303	24.2162	95.2838	15.1025	99.90
6.303	24.6062	97.3866	15.4527	100.01
6.303	24.2724	97.3317	15.4490	100.04
6.303	24.3857	95.7970	15.1867	99.92
6.303	24.4268	97.2005	15.4230	100.01
6.247	24.7941	101.2687	16.1956	99.91
6.247	24.1115	101.9995	16.3387	100.07
6.247	24.4307	101.1074	16.1847	100.00
6.247	24.2090	101.8408	16.3160	100.08
6.247	24.4559	102.0600	16.3207	99.90
6.247	24.1373	101.3317	16.2084	99.92
6.247	24.0564	100.0742	16.0364	100.11
6.247	24.3789	100.5530	16.0923	99.98
6.247	11.7455	100.6765	16.1178	100.01
6.239	---	100.8050	16.1711	100.09
6.239	---	102.3800	16.4047	99.97
				Avg 99.98
				RSD 0.07%

TABLE III
THORIUM ELUTION STUDY

Volume of Eluent^a	Th Recovery (%) Volume of Eluent^b
1	35.46
2	62.97
3	1.57
4	0

^aExpressed in term of multiples of the void volume of the column.

^bEach result is the average of three runs.

TABLE IV
INTERFERENCE STUDY OF VARIOUS IONS

Ions Tested	Form Used	Th Recovery (%)	
		1.0% Level	0.1% Level
Fe ⁺³	FeCl ₃ · 6H ₂ O	99.96	Not tested
Zr ⁺⁴	ZrOCl ₂ · 8H ₂ O	99.92	100.02
Ce ⁺⁴	(NH ₄) ₂ Ce(NO ₃) ₆	100.40	99.99
SO ₄ ⁼	H ₂ SO ₄	99.97	99.99
PO ₄ [≡]	H ₃ PO ₄	96.11	100.01

determination but iron and zirconium are removed by the ion-exchange column. Sulfate does not interfere at the 1.0% level but phosphate interferes by complexing with thorium, giving a low apparent recovery. None of the metals or anions tested interfered at the 0.1% level. Table IV summarizes the results of triplicate samples tested with the impurity at both the 1.0% and 0.1% level.

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