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DETERMINATION OF TRACES OF THORIUM IN URANIUM SOLUTIONS

by

M. O. Fulda
Analytical Chemistry Division

June 1956

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
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ABSTRACT

A colorimetric method was developed for the determination of 1 to 100 ppm of thorium in uranium solutions. The indicator was thorin and the standard deviation was 7 per cent at 1 ppm and 2 per cent at 100 ppm.

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INTRODUCTION

A method was required for the determination of traces of thorium in uranium solutions. In the generally accepted colorimetric determination of thorium with thorin (o-(2 hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid disodium salt) uranium interferes when the ratio of uranium to thorium is greater than 200 to 1[1]. Earlier work by Hyde and Tolmach[2] had demonstrated that thorium is completely extracted from aqueous solution at pH 1.0 by TTA (thenoyltrifluoroacetone), whereas under the same conditions only one per cent of the uranium is extracted. In another series of experiments Horton and Thomason[3] separated thorium from rare earths by extraction with TTA and then used a colorimetric method with thorin to determine the thorium.

On the basis of the results of these earlier investigations, work was undertaken to develop an analytical procedure which involved (1) separation of thorium from uranium by solvent extraction with TTA, followed by (2) colorimetric determination of thorium using thorin.

SUMMARY

A method was developed for the determination of 1 to 100 ppm of thorium in uranium solutions. The thorium is removed from the interfering uranium by solvent extraction using a solution of TTA (thenoyltrifluoroacetone) in xylene. A spectrophotometric analysis with thorin completes the analysis.

Average recoveries of 93.9 to 105.4 per cent were obtained for samples containing known quantities of thorium. The standard deviation was 7.3 per cent at 1 ppm and 2.1 per cent at 100 ppm.

Although this study was limited to solutions containing 1 to 100 ppm of thorium, the range of thorium concentration can be extended by proper selection of sample size.

DISCUSSION

EXPERIMENTAL PROCEDURE

Samples that contained 10 to 100 μg of thorium and up to 500 milligrams of uranium were adjusted to pH 1.0 and extracted with 0.5M TTA in xylene. Any extracted uranium was stripped from the organic phase with 0.1M nitric acid. The thorium was then re-extracted into 2.0M nitric acid and determined spectrophotometrically with thorin reagent. A detailed procedure for the analysis of samples is given in the Appendix.

EFFECT OF VARIABLES

Uranium Interference

Samples that contained 50 and 500 mg of uranium and no thorium were adjusted to pH 1.0 and extracted with 0.5M TTA in xylene. The organic phase was then washed with 0.1M nitric acid to remove the uranium. The extent of uranium interference was measured by extracting the organic phase with 2.0M nitric acid and determining the apparent thorium content of the aqueous phase by the thorin method. The data in the following table show that two washings with 0.1M nitric acid were needed to avoid interference from uranium.

URANIUM INTERFERENCE IN THE DETERMINATION OF THORIUM

Uranium Taken, mg	Apparent Thorium Recovery, µg	
	single wash	double wash
50	3.0	0.0
50	3.2	0.0
500	3.0	0.0
500	3.2	0.0

Acid Concentration

The results in Figure 1 show that thorium was completely extracted from 0.1M nitric acid solution by TTA and was completely recovered from the TTA by extraction with 2.0M nitric acid.

Samples that contained 20 µg of thorium were extracted with 0.5M TTA at acidities of 0.1 to 2.0M nitric acid. After extraction, the aqueous phase was analyzed for thorium.

Samples that contained 20 µg of thorium in 0.1M nitric acid were extracted with 0.5M TTA in xylene. The organic phase was then extracted with 2.0, 5.0, and 8.0M nitric acid. All of the thorium was recovered in each experiment.

Extraction Time

Samples that contained 20 µg of thorium in 0.1M nitric acid were extracted with 0.5M TTA in xylene for one and three minutes. Less than 1 µg of thorium remained in the aqueous phase after one minute and no detectable thorium remained after three minutes.

Two one-minute washings of the organic phase with 2.0M nitric acid gave complete recovery of the thorium.

RESULTS

A plot of absorbance versus μg of thorium indicated that Beer's law was followed in the range from 1 to 100 μg of thorium. The absorbances observed showed that the most accurate results would be obtained in the range from 10 to 100 μg of thorium. Subsequent sample sizes were adjusted to contain 10 to 100 μg of thorium.

Known solutions that contained 1 to 100 ppm of thorium and 50 g/l of uranium were analyzed to determine the accuracy of the method. The data in the table are the results of duplicate analyses of these solutions. The average thorium recovery ranged from 93.9 to 105.4 per cent.

RESULTS OF ANALYSIS OF STANDARD THORIUM-URANIUM SOLUTIONS

Thorium Concentration, ppm	Sample Size, ml	Recovery, %	Average Recovery, %
0.89	10.00	102.7-106.8	104.8
1.77	10.00	100.5-102.6	101.6
3.54	10.00	102.8-105.6	104.2
8.87	1.00	93.4-94.4	93.9
17.7	1.00	92.3-100.5	96.4
44.2	1.00	100.8-100.8	100.8
62.0	1.00	103.4-105.0	104.2
70.9	1.00	102.2-103.8	103.0
88.7	1.00	105.1-105.6	105.4

Two of these solutions were analyzed in replicate to define the precision of the method. The results in the table show a standard deviation of 7.3 per cent at 1 ppm and 2.1 per cent at 100 ppm thorium.

PRECISION OF THORIUM ANALYSIS

Thorium Concentration, ppm	Sample Size, ml	No. Analyses	Average Recovery, %	Standard Deviation, %
0.98	10.00	10	99.5	7.3
97.4	1.00	7	101.7	2.1

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2. Hyde, E. K. and Tolmach, J. TTA Extraction of Dilute Solutions of Thorium Nitrate and Uranyl Nitrate. Argonne National Laboratory, ANL-4248 (Declassified).

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APPENDIX

PROCEDURE FOR ANALYSIS OF SAMPLES

Preparation of Standard Curve

1. Prepare solutions containing 10 to 100 μg of thorium per ml.
2. Pipet accurately 1 ml of each solution into 50-ml volumetric flasks. Add 15.0 ml of 1.0M nitric acid and 5.0 ml of 0.1 per cent aqueous thorin solution.
3. Dilute the solutions to volume and mix well.
4. Transfer the solutions to 5-cm absorption cells and measure the absorbances at 545 millimicrons against a reagent blank. To prepare the reagent blank, add 15.0 ml of 1.0M nitric acid to 5 ml of 0.1 per cent aqueous thorin solution and dilute to 50.0 ml.
5. Prepare a standard curve by plotting absorbance versus μg of thorium.

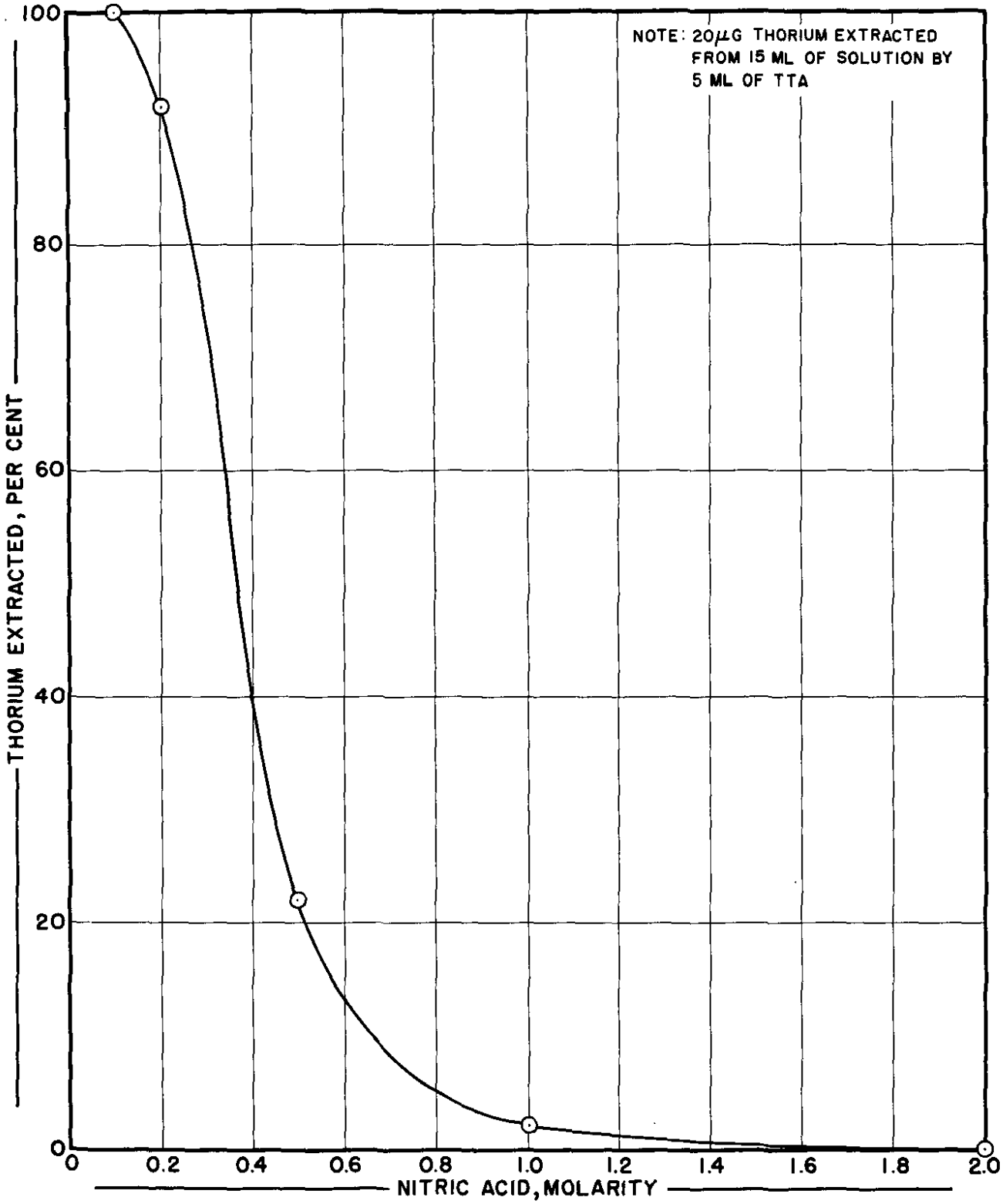
Analysis of Samples

1. Pipet a sample containing 10 to 100 μg of thorium into a 50-ml beaker.
2. Adjust the volume of this solution to about 10 ml with distilled water.
3. Adjust the pH of this solution to 1.0 ± 0.1 with dilute nitric acid or dilute sodium hydroxide. Use a pH meter with glass and calomel electrodes.
4. Wash the electrodes with 0.1M nitric acid, and wash the solution into the extraction flask with 0.1M nitric acid.
5. Add 2 ml of 0.5M TTA (thenoyltrifluoroacetone) in xylene to the flask. Stir the solutions vigorously for five minutes. Remove the aqueous layer and discard.
6. Add 10 ml of 0.1M nitric acid, and stir the solutions vigorously for two minutes. Remove the aqueous layer and discard.
7. Repeat step 6.
8. Add 3.0 ml of 2.0M nitric acid to the extraction flask, and stir the solutions vigorously for one minute.
9. Transfer the aqueous layer to a 50-ml volumetric flask.

10. Repeat step 8 with 5.0 ml of 2.0M nitric acid.
11. Transfer the aqueous layer to the same volumetric flask.
12. Discard the organic layer and wash the extraction flask with acetone.
13. Pipet accurately 5 ml of 0.1 per cent aqueous thorin solution into the solution in the volumetric flask and dilute to volume with distilled water.
14. Transfer the solution to a 5-cm absorption cell and measure the absorbance at 545 millimicrons against a reagent blank. To prepare the reagent blank, add 15.0 ml of 1.0M nitric acid to 5.0 ml of 0.1 per cent thorin solution and dilute to 50.0 ml.
15. Determine the quantity of thorium in the sample from the standard curve.
16. Calculate the thorium concentration in ppm as follows:

$$\text{thorium, ppm} = \frac{\mu\text{g of thorium from standard curve in step 15}}{\text{sample size, ml} \times \text{density of sample}}$$

FIGURE 1



EFFECT OF CONCENTRATION OF ACID ON EXTRACTION OF THORIUM BY TTA