0

CC-2962

An-I

Iowa State College

Contract No. W-7405-eng-82

* * *

Analytical Section

PRECIPITATION OF THORIUM OXALATE FROM
NITRIC ACID SOLUTIONS

By

A. S. Ayers

Problem No. 117

October 5, 1945

Manuscript Received: December 19, 1945

Report Received: January 15, 1946

Issued:

JAN 14 1946

Photostat Price \$ 1.80
Microfilm Price \$ 1.80
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

80911

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CLASSIFICATION CANCELLED
DATE 12-15-78
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch SG

1. Introduction

It has been known for a long time that thorium is precipitated by oxalic acid in acid solutions, but a survey of the literature showed no study of the limits of the acidity and oxalic acid excess which yield quantitative results. V. I. Spitzin reports on the solubility of thorium oxalate in varying concentrations of several acids⁽¹⁾, but the effect of an excess oxalic acid is not included. Since solutions are sometimes presented for analysis that contain more than the recommended two per cent mineral acid⁽²⁾, it would be advantageous to be able to quantitatively remove the thorium without otherwise altering the solutions. This was especially of interest in solutions containing bismuth, since it was hoped that small amounts of thorium could be precipitated in nitric acid solutions containing large quantities of bismuth. In removing the bismuth first by a bismuth oxychloride precipitation, there is every opportunity for carrying off the thorium.

2. Experimental Work

Standard solutions of thorium nitrate were made from reagent grade thorium nitrate and analyzed by evaporating aliquots to dryness and igniting in platinum. Aliquots of these solutions were acidified with known amounts of nitric acid, diluted to known volumes and heated almost to boiling. A small amount of filter pulp was added, then a weighed amount of oxalic acid introduced. The oxalic acid concentration was varied from the theoretical amount to six times that quantity (500 percent excess). The nitric acid content ranged from 0.0 to 2.6 normal. The samples were allowed to cool to room temperature and then filtered through S&S White Ribbon paper (or its equivalent). Some authors recommend allowing the thorium oxalate to stand for 10-12 hours⁽²⁾, but the use of filter pulp permits filtration after 1 1/2-2 hours with accurate results. The precipitates were dried, charred at a low temperature and then ignited in platinum in the muffle at 1000°C. Ignition at lower temperatures

(700-800°) produces an oxide that is slightly hygroscopic; higher temperatures prevent this. The results obtained are tabulated in Table 1.

3. Conclusions

At oxalic acid concentrations higher than 0.45 normal in the solution after precipitation reproducible results were not obtained. It may well be noted here that the density of the precipitate depended upon the nitric acid concentration; at 1.5 to 1.8 normal nitric acid the moist precipitate occupied approximately one-half as much space on the filter as at 0.4 to 0.6 normal nitric acid. This is of importance in the handling of large quantities of thorium. The variation of the low nitric acid samples can be explained by noting that a soluble complex oxalate is formed from thorium oxalate in neutral or slightly acid solutions.

A graphic representation of the results is presented following Table 1; here normality of nitric acid is plotted against grams of thorium dioxide recovered, with a different curve for each value of the normality of the excess oxalic acid used.

4. Recommended Procedure

An aliquot containing about 1.5 grams of thorium (as metal) is taken for analysis as this is the maximum amount that can be handled readily in an analysis. This is diluted to a volume of 200-300 ml and heated to boiling. A small amount of macerated filter pulp is added and then the oxalic acid is stirred in as crystals. If the solution is 0.2 N in HNO_3 , 100 per cent excess oxalic acid is adequate; 1.0 N HNO_3 requires 200 per cent and 1.8 N, 400 per cent excess. The solution is removed from the hotplate, allowed to cool to room temperature and then filtered through a medium speed ashless filter paper. The precipitate and paper are placed in a weighed platinum crucible, dried at 110°, charred at 300° and ignited at 1000°. The conversion factor of Th/ThO_2 is 0.8785.

REFERENCES

- (1) Spitzin, V. I., J. Russ. Phys. Chem. Soc., 47, 557-701 (1901).
- (2) Scott, W. W. "Standard Methods of Chemical Analysis", Fifth Edition, page 953.

8091-5

TABLE 1
TABULATION OF RESULTS OF OXALATE PRECIPITATIONS

HNO ₃ Normality	Per Cent Excess H ₂ C ₂ O ₄	H ₂ C ₂ O ₄ In Supernatant Liquid, Normality	Per Cent Recovery		
0.1*	0	0.000	99.45,	99.80,	99.90
0.2*	10	0.0058	99.80,	99.75,	99.50
0.3*	10	0.0058	99.70,	99.50,	99.45
0.4*	10	0.0058	99.70,	99.50,	99.75
0.1*	25	0.0145	99.85,	99.80,	100.10
0.3*	25	0.0145	100.00,	99.95,	99.75
0.4*	25	0.0145	99.50,	99.50,	
0.4*	50	0.029	99.50,	99.40,	99.75
0.6*	50	0.029	99.55,	99.50	
0.4*	100	0.058	100.0 ,	99.45,	99.85
0.6*	100	0.058	100.20,	100.15,	99.90
0.2	125	0.125	99.85,	100.00	
0.4	125	0.125	100.00,	99.80	
0.6	125	0.125	99.30,	99.80	
0.8	125	0.125	99.55,	99.80	
1.0	125	0.125	99.45,	99.85	
0.0	240	0.236	100.15		
0.2	240	0.236	100.10		
0.4	240	0.236	100.00,	99.80	
0.6	240	0.236	99.85,	100.10	
0.8	240	0.236	100.05,	100.00	
1.0	240	0.236	100.05,	100.00	
1.2	240	0.236	99.90		
1.4	240	0.236	99.55		
0.6	350	0.348	99.95		
0.8	350	0.348	100.05		
1.0	350	0.348	100.00		
1.2	350	0.348	99.95		
1.4	350	0.348	100.00		
1.6	350	0.348	99.80		
1.4	450	0.445	100.00		
1.6	450	0.445	99.90		
1.8	450	0.445	100.00		
2.0	450	0.445	99.30		
2.4	450	0.445	99.55		
2.4	450	0.445	98.30		

*These values are for samples of 0.7671 g ThO₂ while the remainder are for 1.3046 g ThO₂ per sample. All sample volumes were 200 ml.

8091-4

4

THORIUM RECOVERY vs NITRIC ACID NORMALITY AT VARIOUS OXALIC ACID CONCENTRATIONS

CC-2962

8091-5