UNCLASSIFIED

Report No. BMI-260

THE DETERMINATION OF RARE EARTHS IN THORIUM

by

E. J. Center
W. M. Henry
R. D. Householder

May 15, 1952

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

Contract No. AT-(30-1)-Gen-228

UNCLASSIFIED

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Price \$0.30

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.

CONFIDENTIAL

-4-

Report No. BMI-260

ABSTRACT

A quantitative method for the determination of individual rare earths in thorium down to a level of 0.05 ppm. is described. The procedure consists of a chromatographic cellulose-column separation followed by a solution-type spectrographic determination. Values are given for the recovery of a number of rare earths using this combined procedure.

CONFIDENTIAL

CONFIDENTIAL

-5-

Report No. BMI-260

TABLE OF CONTENT:

	<u>Page</u>
INTRODUCTION	6
CELLULOSE-COLUMN SEPARATION	7
Reagents	7
Preparation of Column	8
Preparation of Cellulose	8
Packing the Column (Figure 1)	8
Procedure	8
SPECTROGRAPHIC DETERMINATION	10
Apparatus	11
Procedure	12
Standards	12
RECOVERY OF RARE EARTHS	14

CONFIDENTIAL

CONFIDENTIAL

-6-

THE DETERMINATION OF RARE EARTHS IN THORIUM

by

E. J. Center
W. M. Henry
R. D. Householder

INTRODUCTION

Tentative project specifications for product thorium prepared at Battelle Memorial Institute by solvent extraction are given below:

- (1) Each individual impurity (except as noted) less than 5 ppm.
- (2) Uranium less than 1 ppm.
- (3) Cerium, lanthanum, neodymium, praseodymium, yttrium, each less than 0.5 ppm.
- (4) Dysprosium, cadmium, less than 0.1 ppm.
- (5) Samarium, gadolinium, boron, europium, each less than 0.05 ppm.

Since a quantitative analysis of low-level individual rare earths is required, a spectrographic procedure would appear ideal. However, the ratio of thorium to rare earths is too high to permit a direct spectrographic determination. The relatively low volatility of the rare-earth elements precludes the use of the familiar carrier-distillation procedure⁽¹⁾. Thus, a preliminary chemical separation is indicated.

(1) Scribner, B. F., and Mullin, H. R., "Carrier-Distillation Method for Spectrographic Analysis and its Application to the Analysis of Uranium-Rare Materials", Journal of Research of the National Bureau of Standards, Vol. 37, December, 1946.

CONFIDENTIAL

A chromatographic cellulose-column technique was selected as a means of concentrating the rare earths prior to a spectrographic determination. This method is similar to the procedures described by N. F. Kember⁽²⁾ and T. V. Arden⁽³⁾, but has been modified to meet the requirements of this project.

Preliminary tests indicate that a similar procedure can be used for the determination of rare earths in uranium.

CELLULOSE-COLUMN SEPARATION

Preliminary spectrographic studies indicated that a quantitative analysis of the rare earths at specification limits could be conveniently obtained on one ml. of solution containing not more than 1 mg. of thorium, prepared from a 25-g. sample of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (10 g. Th). Column experiments showed that a 25-g. sample could be concentrated to meet spectrographic specifications by a double cellulose-column separation. The first pass through the column reduced the thorium to approximately 20 mg. and the second pass to less than 0.1 mg. while quantitatively retaining the rare earths.

Reagents

Water: Water containing less than 0.2 ppm. of total solids.
Water used was first distilled and then passed through a mixed-bed ion-exchange resin.

Ammonium Hydroxide: Prepared water was saturated with NH_3 . This should be prepared daily.

Ether-Nitric Acid: 100 ml. of absolute ethyl ether to 12.5 ml. of 1.42 specific gravity HNO_3 .

Hydrogen Peroxide: 30 per cent reagent.

Paper: Schleicher and Schuell filter paper clippings.

(2) Kember, N. F., CRL-AE-23 "The Extraction of Thorium Nitrate With Ether Containing Nitric Acid in the Presence of Activated Cellulose, and the Application of This Process to the Analysis of Monazite Sands and Uranio-Thorianite", September, 1948

(3) Arden, T. V., CRL-AE-36 "A Study of the Preparation of Pure Uranium Oxide From a Sample of Pitchblende Ore, by Extraction With Ether Containing Nitric Acid, in the Presence of Activated Cellulose", July, 1949

Preparation of Column

- (1) Clean the glass with dichromate cleaning solution, wash well, and dry.
- (2) Coat the column with 2 per cent Silicone in carbon tetrachloride (Dow Corning B. C. 200).
- (3) Bake the column at 250° C. for 2 hours.

Preparation of Cellulose

- (1) Shred S&S filter paper clippings, add them to a boiling HNO_3 mixture (3.6 ml. HNO_3 to 100 ml. H_2O), and boil for 15 minutes. (Use the HNO_3 mixture in the ratio of 3 liters of acid to 450 g. of paper.)
- (2) Filter on a Buchner funnel, wash first with water, then alcohol, and then ether.
- (3) Spread out the cellulose and allow to dry.

Packing the Column (Figure 1)

- (1) Fit the bottom of the column with a pledget of glass wool to form a level surface. A porcelain disk is preferable.
- (2) Half-fill the column with 12.5 per cent HNO_3 -ether solution and add the cellulose in small quantities, pressing firmly after each addition.

Procedure

Weigh a 25-g. ⁽⁴⁾ sample of thorium nitrate [$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$] and transfer to a 150-ml. beaker. Add 30 ml. of 2 N HNO_3 and warm until solution is complete. Heat to boiling and add 2 to 3 drops of 30 per cent H_2O_2 with constant stirring, continue to boil to remove excess peroxide. Cool sample to room temperature.

(4) Up to 50 grams of thorium nitrate may be used.

FIGURE 1. CELLULOSE COLUMNS

Prepare a column containing 7 inches of activated cellulose pulp (Figure 1, Column A). Condition the column by passing 250 ml. of 12.5 per cent ether-nitric mixture through the pulp. Add 9 g. of activated dry cellulose pulp to the aqueous solution of the sample (sample should be completely absorbed by the paper; if not, add more paper). Add 60 ml. of the ether-nitric solution to the sample and stir thoroughly. Decant the solution (leaving the pulp in the beaker) into the column, allowing the liquid to pass through at a rate of about 30 ml. per 3 minutes. Add 30 ml. of ether-nitric reagent to the beaker containing the pulp, and mix. When the surface of the liquid of the first portion has reached the top of the paper in the column, add the second portion, permitting the same rate of travel through the paper as before. Repeat this procedure until 1200 ml. of solvent has passed through the column. Discard the organic effluent.

Wash the pulp in the beaker and in the column with portions of aqueous 2 N HNO_3 , using about 400 ml. in all. Place the effluent on a steam bath to remove ether and then reduce the volume on a hot plate to approximately 5 ml. (5). Add 15 ml. of H_2O and heat to boiling; add 1 to 2 drops of 30 per cent H_2O_2 , and boil to remove excess peroxide.

Prepare a column containing 9 inches of cellulose pulp (Figure 1, Column B). Absorb the sample in approximately 9 g. of dry cellulose and transfer the sample and cellulose to the top of the prepared column, washing in with ether-nitric reagent. Pass solvent through the column (30 ml. per 3 minutes) until the effluent reaches a volume of 1500 ml. Allow the column to drain and discard the ether-nitric mixture. Pass 400 ml. of warm 2 N HNO_3 through the column at the normal rate. Remove ether on a steam bath and then evaporate on a hot plate until the volume is below 1 ml. The sample is now ready for spectrographic analysis. (The amount of thorium remaining at this point is less than 0.1 mg.)

SPECTROGRAPHIC DETERMINATION

Immediate consideration was given to the copper-spark method of excitation. The advantages of this type of excitation, for extreme sensitivity

(5) If the thorium nitrate is known to contain appreciable amounts of calcium and magnesium, an oxalate or hydroxide purification of the rare earths should be made at this point. A hydroxide separation has been found to be somewhat more convenient than the oxalate and is made as follows: Reduce the aqueous solution from the first column separation to approximately 200 ml. Add NH_4OH until precipitation is complete, stir, and allow to stand over night. Filter on an open paper and wash with 5 per cent NH_4OH . Dissolve precipitate with hot 25 per cent HNO_3 and reduce the volume to about 5 ml. Proceed as above.

especially where sample quantity is limited, is thoroughly discussed by Fred, et al. (6). For this particular application, however, the use of copper rods was somewhat unfavorable. The solutions to be analyzed contained nitric acid and, despite considerable care in acidproofing the electrodes, occasional attack and consequent salting was observed. The copper rods to be used necessitated a machining operation or an acid cleaning treatment. The copper spectrum, while comparatively simple, was still profuse enough in lines to make the identification and detection of some of the rare-earth elements extremely difficult. For these several reasons, standard-grade graphite rods were used in place of copper rods. The graphite rods were made acid proof to prevent sample penetration. They had the advantage of being expendable after initial use and contributed few and easily identified lines to the analysis spectrum. Since in this application the sole interest was in rare-earth elements, these impurities in the graphite were not harmful. The disadvantage of CN bands occurring by sparking graphite rods in air was easily overcome by the use of a nitrogen-free atmosphere. Due to pressing requirements for analysis, a thorough investigation of various atmospheres was not made. Three gases, oxygen, argon, and carbon dioxide, were tried. Of these three, oxygen gave the best line-to-background ratio. In our experience, the detection limit of a rare-earth element was nearly the same using the prepared graphite rods in an oxygen atmosphere as with the copper rods. The method as developed provided the sensitivities of detection required.

Apparatus

Initial experimental work was done using the second order 2.5 Å per mm. dispersion of a Baird 3-meter grating spectrograph. Exposures in two separate wavelength regions, 3125-3880 and 3850-4540 Å, were deemed necessary for optimum detection of all the rare-earth elements. Later work was done on an Applied Research Laboratories 1.5-meter grating spectrograph. This spectrograph provides the facility for simultaneously photographing a very extensive wavelength region by the use of two cameras. The second order, 3.45 Å per mm., spectra in the region 2200-4700 is obtained with one exposure.

An Applied Research Laboratory synchronously interrupted high-voltage spark was used for excitation source. The conditions used were 4/3-kva capacitance with 0.32-mh. inductance, forty-five seconds exposure time.

Eastman Spectrum Analysis No. 1 and 103-0 plates or film were used, with the 103-0 finally being adopted. They were developed in ARL.

(6) Fred, M. C., Russell, R. G., Albrecht, W. W., Nicholson, N. H., and Corvill, E. Report K2554 "Spectrochemical Analysis by the Copper-Spark Method", March 1, 1945.

developing equipment at 70° F. for four minutes. The per cent transmission of the spectral lines was determined using an ARL densitometer.

Electrodes used for the sample were 1/4-inch-diameter standard graphite rods cut to a length of 1-1/2 inches. The sample ends of these electrodes were ground smooth and covered with an acid-proof coating. The samples were placed on the ends of the electrodes by means of a 0.2-ml. micropipette graduated in 0.01 ml. Apparatus used for containing an oxygen atmosphere during excitation was similar to that described by Ellenburg and Owen⁽⁷⁾.

Procedure

The samples as received, after the cellulose-column separation, contained essentially only rare-earth elements and a minor amount of thorium in solution. The sample solution is taken to dryness and any organic material decomposed by addition of nitric acid. The internal standard, palladium, is added at this point. The solution is adjusted to volume with 1-1 nitric acid so that 0.6 ml. is equivalent to 10 g. of thorium, as received, prior to column separation. The amount of palladium added for an internal standard is 10 micrograms per ml. of sample solution.

0.06-ml. portions of the samples are transferred to the ends of pairs of electrodes by means of a micropipette and dried by heating under an infrared lamp. If too much salt is obtained on the electrode, it may be necessary to further dilute the samples, adding an equivalent amount of internal standard. After drying, the electrodes containing the samples are placed as counterelectrodes in the excitation stand using a 3-mm. gap spacing. Oxygen is passed through the atmosphere chamber surrounding the electrodes for 30 seconds before starting the spark. The samples are then excited in the high-voltage spark using 4/3 kva capacitance, 0.32-mh. inductance, 45-second exposure. A 20-micron slit opening is used in the spectrograph. After development of the film, the per cent transmission of the spectral lines is measured on the densitometer. Because of the heavy exposure, some background is encountered and this is corrected for in the usual manner before drawing the analysis curves. The lines used and the range of analysis are shown in Figure 4.

Standards

Synthetic standards were prepared from pure rare-earth elements in the usual manner, by additions from stock solutions, to cover the ranges indicated in Figure 4.

(7) Ellenburg and Owen, *Anal. Chem.* 25, 115 (1953).

FIGURE 2 WORKING CURVES SHOWING LINES AND RANGES

C-1813

RECOVERY OF RARE EARTHS

The results in Table 1 were obtained by spiking samples of thorium nitrate with various amounts of rare earths, and measuring their retentions after removal of the thorium.

A series of experiments with rare-earth tracers⁽⁸⁾ was carried out to confirm the cellulose-column method. The results of these experiments are also given in Table 1. The tracers used were samarium-153, cerium-praseodymium-144, europium-152, -154, and thulium-170. The amounts used were determined in part by the specific activities of the tracer samples available.

The second series of tracer experiments described in Table 1 was essentially a check on the analytical procedure now being used, which involves a double cellulose-column concentration of the impurities. In all cases, at least 96 per cent recoveries of the individual rare earths were obtained.

(8) Tracer experiments were carried out by G. D. Calkins and R. B. Blackmore.

15
TABLE 1. RECOVERY OF RARE EARTHS

$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g.	Cellulose Column	12.5% Nitric Ether, ml	Rare Earths Added	Rare Earths Recovered	Thorium Remaining as ThO_2	Method of Determination
2	1 Pass, long column	1500	Y 0.09 mg.	0.12 mg.	Less than 0.2 mg.	Spectrographic
2	Ditto	1500	Nd 0.14 mg.	0.10 mg.	Less than 0.2 mg.	"
2	"	1500	Pr 0.13 mg.	0.13 mg.	Less than 0.2 mg.	"
4.5	"	1500	Sm 2260 ppm.	2187 ppm.		Radio-Tracer
5.0	"	1500	Ce 0.50 ppm.	0.50 ppm.		Ditto
5.0	"	1500	Eu 340 ppm.	340 ppm.		"
5.0	"	1500	Tm 750 ppm.	750 ppm.		"
5.0	"	1500	Ho 455 ppm.	441 ppm.		"
2	"	1500	Ce 100 mg.	98.3 mg.	Less than 0.2 mg.	Chemical
2	"	1500	Ce 100 mg.	96.6 mg.	Less than 0.2 mg.	"
2	"	1500	Ce 100 mg.	99.2 mg.	Less than 0.2 mg.	"
2	"	1500	Ce 100 mg.	96.4 mg.	Less than 0.2 mg.	"
25	1 Pass, short column	1200	Ce 500 mg.	494 mg.	20 mg.	"
50	2 Passes, long columns	(1)	Ce 0.50 ppm.	0.49 ppm.		Radio-Tracer
50	Ditto	(1)	Eu 340 ppm.	331 ppm.		Ditto
50	"	(1)	Tm 1000 ppm.	866 ppm.		"

(1) 12-14 ml. used to elute thorium nitrate from first column; 1500 ml. for second column.

CONFIDENTIAL

- 15 -

CONFIDENTIAL