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IN-1275
April 1969

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ANALYSIS OF IRRADIATED
ZIRCONIUM CLAD THORIUM TUBES

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
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Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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IN-1275
Issued: April 1969
Chemistry
TID-4500

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U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
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ABSTRACT

Four irradiated and two unirradiated zirconium clad thorium tubes were dissolved and analyzed for uranium and thorium. The zirconium cladding was removed by dissolution in hydrofluoric acid. An insoluble double salt of zirconium and thorium was converted to the hydroxide of zirconium and thorium with sodium hydroxide and then dissolved with fuming perchloric acid. The thorium core of the sample was dissolved in nitric acid catalyzed with hydrofluoric acid.

SUMMARY

Two unirradiated and four irradiated zirconium clad thorium tubes, submitted by the Reactor Experiments Group, were analyzed for total and isotopic uranium and total thorium. The two unirradiated samples contained approximately 0.5 and 1.5 g of added U-233. Each of the six samples was a tube measuring 2-1/2-cm OD x 18-cm long, and each contained about 60 g of thorium and 100 g of zirconium.

The zirconium cladding was removed from the samples by selective dissolution with 750 ml of cold 10M HF under reflux in an all polyethylene system. The undissolved core of thorium metal was removed from the hydrofluoric acid, washed thoroughly with water to remove all traces of zirconium, and then dissolved in 200 ml of hot nitric acid catalyzed with 0.04M HF. The hydrofluoric acid-zirconium solution contained a thorium bearing residue. The residue, a double salt of thorium and zirconium, was heated with 50% sodium hydroxide to form insoluble metallic hydroxides, filtered, and dissolved in fuming perchloric acid.

All three fractions were analyzed for both thorium and uranium. Thorium in the hydrofluoric acid-zirconium fraction was determined by emission spectroscopy and found to be negligible (<20 ppm). Thorium in the dissolved residue fraction was determined gravimetrically after precipitation as the oxalate and ignition to the oxide. The residue fraction contained from 1 to 2% of the total thorium. Thorium in the nitric acid-thorium fraction was determined volumetrically by an EDTA back-titration procedure. Uranium was determined by an isotopic dilution mass spectrometric technique after separation from the thorium and zirconium. The separation was accomplished by anion exchange using Bio-Rad AG 1-X8, 200 to 400 mesh resin in the chloride form.

The irradiated samples were too large and the dissolution too complicated to process in the Remote Analytical Facility. Therefore, the dissolution of these samples was performed in the cave in X-cell which is equipped with master slave manipulators.

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ANALYSIS OF IRRADIATED ZIRCONIUM CLAD THORIUM TUBES

I. INTRODUCTION

Analytical chemistry support for the PAED reactivity measurements program of the Reactor Experiments Group required the dissolution and analysis of four irradiated and two unirradiated zirconium clad thorium tubes. The tubes were 2-1/2-cm OD x 18-cm long, and contained approximately 60 g of thorium. The thorium was clad with approximately 100 g of zirconium and was enriched with U-233.

Because the radiation level of the irradiated samples was high, 7.5 to 8.3 Ci, dissolution of these samples was performed in the X-Cell cave[1]. This cave is a 4-1/2- x 3- x 3-1/2-ft lead shielded chamber equipped with two master-slave manipulators.

The zirconium cladding was dissolved with 10M HF under total reflux in an all plastic apparatus. The thorium core then was transferred to a glass apparatus and dissolved under total reflux with a 15M HNO₃-0.04M HF mixture. A residue containing both zirconium and thorium remained in the hydrofluoric acid solution. This double salt was removed by filtration, treated with sodium hydroxide to form the corresponding hydroxides, and then dissolved with perchloric acid.

All three fractions were analyzed for thorium and uranium. Thorium was determined in the nitric acid fraction volumetrically with EDTA, in the residue fraction gravimetrically as the oxide after precipitation as the oxalate, and in the hydrofluoric acid fraction spectrochemically using an emission spectrograph. Uranium was determined in all three fractions by isotopic dilution mass spectrometry.

This report describes in detail the dissolution and analysis of these samples.

- [1] R. C. Shank et al, Annual Report of ICPP Analytical Section for 1961, IDO-14588 (May 1962).

II. EQUIPMENT

The apparatus used for the hydrofluoric acid dissolution of zirconium was fabricated almost entirely of plastic material and is illustrated in Figure 1. The dissolver was a calibrated 1-liter, wide mouth, Nalgene bottle. The dissolver was calibrated with a magnetic stir bar inside so that samples could be dissolved, mixed, and diluted to volume in the same container. A glass reflux condenser containing a polyethylene condenser tube was attached to the dissolver through a No. 10 neoprene stopper. A reagent line also entered the dissolver through this stopper. A vent was installed in the off-gas system to prevent liquid in the scrub train (Figure 2) from flowing back into the dissolver. The dissolver was placed in an 8-in. diam x 4-in. high polypropylene container which was securely fastened to the top of a magnetic stirring apparatus with doubled coated masking tape. The reaction of hydrofluoric acid and zirconium is exothermic and the secondary container was used as a safety factor in case the dissolver decomposed under heat of reaction.

The apparatus for the nitric acid dissolution of thorium is illustrated in Figure 3. The dissolver was a calibrated 1-liter boiling flask with a 50/30 F ball and socket joint and a side arm delivery tube for reagent additions. The dissolver was calibrated with a magnetic stir bar inside so that samples could be dissolved, diluted to volume, and mixed in one container. A vent section containing a vent tube and a line leading to the off-gas scrub train was attached to the condenser through a 35/25 F ball and socket joint. The vent tube prevented liquid from the scrub train from flowing back into the dissolver. Heat for the dissolution was supplied with a 115 V 1-liter heating mantle which was controlled by a powerstat located outside the cave.

The same scrub train (Figure 2) was used for both the hydrofluoric and nitric acid dissolutions. It consisted of three filter flasks connected in series through which the off-gases were drawn by vacuum. The first flask was empty and served as a trap for liquids which might escape the reflux condenser. The second flask contained water and the third flask contained a 25 w/v% sodium hydroxide solution to neutralize volatile acids. This train constituted an effective system for removing acid vapors and volatile fission products. The two vapor traps were both equipped with Kjeldahl traps.

A stainless steel filter tube (Figure 4) was used to filter the thorium-zirconium double salt from the hydrofluoric acid solution after the zirconium was dissolved. The filter tube was connected to a 1-liter Nalgene bottle, and vacuum was applied through the same system used for sampling (Figure 5). The vacuum held a membrane filter on the face of the filter tube and transferred the solution to the empty Nalgene bottle.

Reagents were added to the dissolvers from hand-pumped pressure reservoirs located outside the cave. Aliquots of the dissolved samples were taken for analysis using the remote sampling apparatus illustrated in Figure 5. This apparatus consisted of two filter flasks connected in series to serve as traps for "hot" liquids. A vacuum source acting through these two flasks drew small portions of the sample from the dissolver and trapped them in a sample bottle.

A photograph of the assembled dissolution apparatus in the X-Cell cave is shown in Figure 6.

Fig.1 Apparatus For The Hydrofluoric Acid Dissolution Of Zirconium

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Fig 2 Off-Gas Scrub Train

INC-C-12849

Fig.3 Apparatus For The Nitric Acid Dissolution Of Thorium

INC-A-12846

Fig. 4 Stainless steel filter tube.

INC-C-12851

Fig. 5 Remote Sampling Apparatus

Fig. 6 Assembled apparatus in the RAF Cave

(a) Each Fraction is Analyzed for Thorium and Uranium

INC-A-12847

Fig. 7 Dissolution scheme

III. DISSOLUTION

The dissolution scheme for processing the zirconium clad thorium tubes is illustrated in Figure 7. One side of a U-shaped, 15-in. length of 1/16-in. Monel wire was passed through the sample tube; the sample and wire were placed in the plastic dissolver (Figure 1); and the apparatus was assembled as previously described. The Monel wire was left in place during the dissolution so the thorium core could be removed after the zirconium had dissolved. Small increments of 10M HF were added to the dissolver from a hand-pumped pressure reservoir. The reaction of zirconium and hydrofluoric acid is exothermic and the reaction rate was controlled by the rate at which the acid was added. The dissolution of the zirconium cladding was complete after the addition of 750 ml of 10M HF.

The reflux condenser was raised above the dissolver and the thorium core was lifted out using the Monel rod previously inserted through the sample. The core was washed thoroughly with water to remove all traces of both zirconium and fluoride and was transferred to the 1-liter glass dissolver. The hydrofluoric acid solution in the plastic dissolver was diluted to volume in the precalibrated dissolver and mixed with a magnetic stirring apparatus. A residue remained in the hydrofluoric acid solution and was separated by filtering with the stainless steel filter tube and a Gelman Metrical VM-6 25-mm filter. The residue was retained and analyzed as a separate fraction.

The residue (including the filter) was washed with water, transferred to a Teflon beaker, and converted to the metallic hydroxides with 25 ml of a hot 50% NaOH solution. The resulting solids were filtered on a Whatman No. 40 filter paper, washed with water, dissolved by fuming with nitric and perchloric acids, and diluted to 100 ml in a volumetric flask. All dissolution work on the residue was performed in a hood rather than in the X-Cell cave.

The thorium core was placed in the glass dissolver (Figure 3), and the equipment was assembled as previously described. Concentrated nitric acid catalyzed with 0.04M HF was added from a hand-pumped pressure reservoir and the rheostat to the heating mantle was adjusted so that the solution was heated to boiling. A total of 200 ml of acid was added in small increments to dissolve the sample. The rate of acid addition as well as the temperature of the heating mantle were used to control the rate of reaction. Dissolution was completed in 2 to 3 hr. Considerable foaming was experienced during the dissolution and attempts to avoid foaming by dissolving the sample in dilute acid were unsuccessful. The foaming was controlled by adding the acid in small increments.

Following dissolution, the system was vented and cooled. The condenser was washed with water and removed. The sample was diluted to volume with distilled water and then mixed thoroughly on the magnetic stirring apparatus. A residue remained in several of the samples. Emission spectrographic analysis showed the residue to be silica and to be free from uranium. No attempt was made to dissolve the residue.

Aliquots were taken for chemical analysis from the thorium and zirconium solutions using the remote sampling apparatus. Top and bottom aliquots were analyzed to confirm homogeneity of the samples.

IV. CHEMICAL ANALYSIS

Each sample was separated into three fractions during dissolution: a 1M HF solution (1 liter) containing approximately 100 g of Zr, a dissolved residue fraction containing from 1 to 2 g each of zirconium and thorium in 100 ml of dilute perchloric acid, and a 2M HNO₃ solution (1 liter) containing approximately 60 g of Th. All fractions were analyzed for thorium and uranium. The nitric acid fraction was also analyzed for zirconium.

Emission spectroscopy was used to determine thorium in the zirconium solution and to determine zirconium in the thorium solution. These data indicate excellent separation was achieved during dissolution with less than 20 ppm cross contamination of either zirconium or thorium. The low level of zirconium in the nitric acid-thorium fraction permitted a complexometric thorium analysis using EDTA (IDO-14316, Th-2, tentative, 1965).

Thorium in the residue fraction was determined gravimetrically as the oxide after first being separated from zirconium by oxalate precipitation. An aliquot from the dissolved residue was treated with an excess of 5% oxalic acid solution, digested by heating for one hour to precipitate the thorium oxalate, and filtered. After washing with water, the residue and paper were placed in a tared platinum crucible and ignited at 750° C in a furnace. The resulting thorium oxide was weighed and calculated as grams of thorium per sample. Although zirconium was not determined quantitatively in the dissolved residue, X-ray fluorescence analysis of the solid before dissolution showed an approximate 1:1 ratio of thorium and zirconium. X-ray diffraction analysis was not able to identify the solid residue because no comparable reference diffraction patterns were available. However, the residue is believed to be a thorium fluorozirconate double salt.

Uranium was determined in all three solutions by isotopic dilution mass spectrometry after a preliminary separation from zirconium and thorium by ion exchange. Dowex 1- X10 in the chloride form and an 8M HCl media were used for the separation. The uranium-chloro complex remained on the resin and the zirconium and thorium ions were removed by washing with 8M HCl. The uranium was eluted with a 0.1M HNO₃ solution and was analyzed by mass spectrometry. Details of this separation procedure are given in Appendix A. The analytical data for thorium and uranium are reported in Tables I, II, and III.

TABLE I

RESULTS OF THORIUM ANALYSES

<u>Sample Code</u>	<u>Thorium, g^[a]</u>		
	<u>Residue Fractions</u>	<u>HNO₃ Fraction</u>	<u>Total^[b]</u>
21	1.231	62.91	
	1.239	62.76	
		62.76	64.04
54	0.577 ^[c]	62.46	
	0.582 ^[c]	62.01	
		62.24	62.82
22	1.025	63.97	
	1.028	63.76	
		63.92	64.91
7	1.230	60.51	
	1.224	60.36	61.66
29	0.903	62.79	
	0.905	62.79	
		62.65	
		62.93	63.69
36	0.897	59.12	
	0.893	60.51	
		60.02	60.77

[a] Thorium in the HF-fraction was determined by emission spectroscopic techniques and found to be < 20 mg.

[b] The total thorium is the sum of the average of the two fractions.

[c] The thorium in this residue fraction is probably low due to partial loss of sample.

TABLE II

RESULTS OF TOTAL URANIUM ANALYSES

Sample Code	Uranium, g			
	HF Fraction	Residue Fraction	HNO ₃ Fraction	Total ^[b]
21	0.00792	0.00976	0.638	0.658
	0.00794	0.00974	0.643	
54	0.0145	0.00736 ^[a]	1.416	1.437
	0.0147	0.00734 ^[a]	1.415	
22	0.0116	0.00690	0.743	0.762
	0.0116	0.00690	0.745	
7	0.00482	0.0026	0.296	0.303
	0.00572	0.0026	0.295	
29	0.00890	0.0083	0.880	0.896
	0.00894	0.0083	0.878	
36	0.0094	0.0122	1.012	1.033
	0.0104	0.0122	1.011	

[a] The uranium in this residue fraction is probably low due to partial loss of sample.

[b] The total uranium is the sum of the averages of the three fractions.

TABLE III

RESULTS OF URANIUM ISOTOPIC ANALYSES

<u>Sample Code</u>	<u>WEIGHT % OF ISOTOPES</u>				
	<u>U-233</u>	<u>U-234</u>	<u>U-235</u>	<u>U-236</u>	<u>U-238</u>
21	96.57	1.35	0.05	--	2.03
54	95.97	1.34	0.07	--	2.62
22	95.04	3.95	0.19	0.01	0.81
7	89.43	1.74	0.09	0.01	8.73
29	94.65	4.23	0.22	0.01	0.89
36	91.73	4.19	0.22	0.01	3.85

APPENDIX A

ION EXCHANGE SEPARATION OF URANIUM FOR ISOTOPIC DILUTION

MASS SPECTROMETRIC ANALYSIS

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1. PROCEDURE

1. Add 1 ml of sample containing 0.2 to 5 mg of uranium to a 10-ml test tube containing 1 mg of a uranium spike. For these samples which contained U-233, a U-235 spike was used.
2. Add, in excess, 0.1M KMnO_4 dropwise to oxidize the uranium to the VI oxidation state.
3. Add 3 ml of conc HCl , stopper the tube and mix thoroughly. The excess KMnO_4 will be reduced.
4. Prepare an ion exchange column as follows: Add Dowex 1- X10, 200 to 400 mesh resin to a 70-x 6-mm micro ion exchange column and condition the resin by washing with 8 ml of conc HCl .
5. Transfer the sample from step 3 to the ion exchange column and wash with 3 ml of 8M HCl . Discard the wash solutions which contain residual thorium and zirconium.
6. Elute the uranium with 3 ml of 0.1M HNO_3 . Collect the eluate in a 5-ml centrifuge tube.
7. Evaporate the sample to dryness under a heat lamp. Organic material is eluted from the resin and must be destroyed before mass spectrometric analysis.
8. Heat the sample over a Meker burner to destroy organic matter and then cool the sample.
9. Add 2 drops of conc HNO_3 and repeat steps 7 and 8.
10. Determine the isotopic uranium ratios mass spectrometrically and calculate the uranium concentration in the sample.