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DETERMINATION OF URANIUM ISOTOPES IN IRRADIATED THORIUM

Savannah River Laboratory

Aiken, South Carolina

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DETERMINATION OF URANIUM ISOTOPES
IN IRRADIATED THORIUM

by

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ABSTRACT

Uranium isotopes in irradiated thorium were determined by alpha pulse height analysis coupled with mass analysis. Pa^{233} (U^{233} parent) was determined by gamma spectrometry. The precision of a single determination of U^{232} in U^{233} product was $\pm 5\%$ at the 95% confidence limit. The analysis of U^{232} in U^{233} product was confirmed by a method that combined low geometry alpha counting, mass analysis, and coulometry.

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DETERMINATION OF URANIUM ISOTOPES IN IRRADIATED THORIUM

INTRODUCTION

Uranium-233, a nuclide of interest in the breeder reactor program, can be produced by irradiating Th^{232} with thermal neutrons.^(1,2) The irradiation of thorium also produces U^{232} and U^{234} , which are undesirable because:

- One product in the U^{232} decay chain is thallium-208, which is a very energetic gamma emitter and increases the amount of shielding required for the U^{233} product.^(3,4) (See Appendix A.)
- Uranium-234 dilutes the U^{233} product and prevents the determination of U^{233} by alpha pulse height analysis (APHA) because the alpha energies are in the same range:

U^{233}	4.72 - 4.82 Mev
U^{234}	4.72 - 4.77 Mev

Two experimental assemblies that contained target slugs of thorium were irradiated at the Savannah River Plant. The amount of uranium product per unit weight of thorium and the U^{232} concentration in the U^{233} product were needed for planning irradiations for the production of 120 kg of U^{233} . To obtain these concentrations, quantitative determinations were needed for total thorium, total Pa^{233} (parent of U^{233}), total uranium, and the isotopic content of the uranium.

SUMMARY

The quantity and isotopic content of uranium produced by thermal neutron irradiation of thorium was determined by alpha counting, mass spectrometry, and APHA. An anion exchange technique was adapted for initial separation of thorium, protactinium, and uranium. Thorium was determined by colorimetry and protactinium by gamma spectrometry. The precision of a single determination of U^{232} in U^{233} product was $\pm 5\%$ at the 95% confidence limit. The U^{232} content of the U^{233} product was confirmed by an independent method that employed low geometry alpha counting, mass analysis, and coulometry.

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DISCUSSION

DISSOLUTION OF IRRADIATED THORIUM METAL

Irradiated thorium metal dissolves efficiently in 15M HNO_3 - 0.05M HF. Massive thorium metal is attacked slowly by concentrated phosphoric or perchloric acid and dilute nitric, sulfuric, or hydrofluoric acid. Concentrated nitric acid renders the metal passive, and hydrochloric acid leaves a black residue of unknown composition that is believed to be ThO or ThH_2 .⁽⁵⁾ Shuler et al.⁽⁶⁾ have shown that F^- or SiF_6^- in nitric acid catalyzes the dissolution of Th or ThO_2 . In all mineral acids except hydrofluoric and sulfuric, Pa^{233} , the parent of U^{233} , forms an unstable solution and eventually precipitates or becomes colloidal.⁽⁷⁾ With hydrofluoric acid it forms the stable complex ion PaF_7^- .

Thorium metal wafers that weighed 30 to 70 g were cut from the center of irradiated elements and were dissolved as follows: About 300 ml of 15M HNO_3 - 0.05M HF were added to each wafer, and the mixture was heated at incipient boil for four hours. Another 100 ml of 15M HNO_3 - 0.05M HF were then added; the metal was completely dissolved after about two more hours at incipient boil. The solution was then diluted to one liter.

SEPARATION OF URANIUM, THORIUM, AND Pa^{233}

Thorium, protactinium, and uranium in the sample solution were separated by anion exchange by the method of Kraus, Moore, and Nelson.^(8,9) A 100- μl aliquot of the dissolved sample was diluted one thousandfold in 10M HCl , and one ml of the diluted sample was passed through a column of "Dowex" 1-X10, 50-100 mesh resin* (Figure 1) at 1.3 to 1.7 ml/(min)(cm^2). Thorium and most of the fission products passed through the column because they do not form anionic complexes. The column was washed with two column volumes of 10M HCl , and the effluent and washes were collected for thorium analysis. Protactinium was eluted with three column volumes of 9M HCl - 0.5M HF. Uranium was eluted last with two column volumes of 0.1M HCl .

FIG. 1 ION EXCHANGE COLUMN

*"Dowex" is a trademark of Dow Chemical Co.

The anion exchange separation was evaluated by analyzing a synthetic solution that contained known amounts of reagent-grade thorium nitrate, U^{235} , Zr^{95} - Nb^{95} , and Pa^{233} (separated from Np^{237} by anion exchange) in 6M HNO_3 . An aliquot of the synthetic solution was diluted one thousandfold in 10M HCl, and one ml of the dilution was passed through the anion column. The separated thorium and protactinium were determined by the methods described in the next section; U^{235} was determined by 2π alpha counting. The recoveries are shown in Table I.

TABLE I
Recoveries from Synthetic Solution

<u>Constituent</u>	<u>Recovery (a), %</u>
Thorium	98.3 $\pm$ 1.0
Pa^{233}	95.0 $\pm$ 9.5
U^{235}	98.2 $\pm$ 2.6

(a) Each analysis was performed in triplicate. The precision is at the 95% confidence limit for a single determination.

DETERMINATION OF THORIUM AND Pa^{233}

The thorium fraction from the ion exchange column was analyzed by the Thorin method.⁽¹⁰⁾ The eluted Pa^{233} was counted by gamma spectrometry. Pa^{233} decays to U^{233} with a half life of 27.0 days; therefore, the concentration of Pa^{233} must be added to the determined concentration of U^{233} to obtain the total U^{233} produced. (See Appendix B for the specific activity used.) The gamma detector was calibrated with Pa^{233} that had grown into secular equilibrium in an alpha-standardized Np^{237} solution.

DETERMINATION OF URANIUM ISOTOPES BY MASS ANALYSIS AND ALPHA PULSE HEIGHT ANALYSIS

Simple 2π alpha counting could not be used for the determination of uranium isotopes. Instead APHA was necessary to determine the ratio of the alpha contributions from U^{232} and U^{233} - U^{234} (combined peak). Mass analysis was used to calculate the contribution of the U^{234} to the U^{233} - U^{234} alpha peak.

For mass spectrometric analyses, one to two milligrams of uranium were separated from each sample solution by anion exchange and were purified by ether extraction. After evaporation of the ether, the residue was oxidized to destroy organic material and was diluted to a known volume with water. Table II shows the mass analysis data obtained with a thermal emission mass spectrometer.

TABLE II

<u>Uranium Mass Analyses</u>		
<u>Mass No.</u>	<u>Sample A ^(a), wt %</u>	<u>Sample B ^(b), wt %</u>
232	0.016	0.020
233	93.40	92.98
234	4.21	5.14
235	0.195	0.219
236	0.007	0.009
237	(c)	(c)
238 ^(d)	2.17	1.62
239	(c)	(c)

(a) An average of 18 scans. Calculated molecular weight: 233.6

(b) An average of 10 scans. Calculated molecular weight: 233.2

(c) Not detected.

(d) An impurity normally present in thorium.

The value for mass 232 is not sufficiently precise or accurate as an independent method of measurement of U^{232} because: (1) traces of Th^{232} from the original sample could be present in the separated uranium, and (2) the tungsten filament of the mass spectrometer contains some Th^{232} impurity. Even though the conditions used for mass analysis were believed to eliminate thorium emission, the mass 232 analysis still has an estimated error of $\pm 15\%$ at the concentration shown.

In preparation of samples for APHA, an aliquot of the uranium solution eluted from the anion column was electro-deposited on platinum from a hydrochloric acid medium.⁽¹¹⁾ This method was chosen as the best of three methods that were evaluated for preparing APHA sources. The other two methods were direct evaporation on stainless steel and evaporation on stainless steel of a hexone extraction of the separated uranium. Figure 2 shows a comparison of the data from plates

FIG. 2 ALPHA PULSE HEIGHT ANALYSES OF URANIUM ISOTOPES

prepared by the three methods. These data were produced with a Frisch grid chamber and multichannel analyzer. The electrodeposited mounts had a resolution of 1.5% vs. ~3.5% for directly evaporated mounts. With the better resolution, the contribution of U^{232} to the U^{233} peak did not need to be calculated. Table III shows the amount of U^{232} obtained by APHA analysis of electrodeposited samples.

The concentration of U^{234} must be known if APHA is used to determine U^{232} in U^{233} product. The data in the second column of Table III were calculated directly from APHA scans uncorrected for U^{234} . The last column takes into account the correction for U^{234} as obtained by mass analysis. The higher the level of irradiation, the more significant the U^{234} correction becomes. With or without the U^{234} correction, the U^{232} concentrations exceeded the maximum limit of 170 ppm.

TABLE III

Alpha Pulse Height Analyses of U^{232} in U^{233} Product (a)

Sample	Parts of U^{232} per Million Parts of U^{233}	
	Analysis Uncorrected for U^{234}	Analysis Corrected for U^{234}
A (4.48 kg U^{233} /ton Th)	188	193 $\pm$ 10
B (5.75 kg U^{233} /ton Th)	235	243 $\pm$ 10

(a) Each analysis performed in quadruplicate. Precision is at the 95% confidence limit for a single determination. All results were corrected for Pa^{233} decay. The specific activities used are in Appendix B.

DETERMINATION OF U^{232} BY LOW GEOMETRY ALPHA COUNTING, MASS ANALYSIS, AND COULOMETRY

As shown in Figure 3, the determined U^{232} concentrations were higher than the U^{232} concentrations reported⁽²⁾ for slightly different reactor loadings. Because of the importance of accurate analytical data on which to base plans for reactor loading in the production program, it was deemed advisable to verify the analytical results by an independent method. A combination of low geometry alpha counting (LGAC), mass analysis, and coulometry was devised to verify the results in Table III.

FIG. 3 U^{232} IN U^{233} PRODUCT VS PRODUCED U^{233}

Portions of the purified samples prepared for mass analysis were taken for LGAC and coulometric analysis. Aliquots for LGAC were electrodeposited on platinum from a hydrochloric acid medium.⁽¹¹⁾ Uranium losses during electrodeposition averaged 3%. To determine these losses, uranium was removed from the spent plating solution by ion exchange, then eluted and mounted for 2 π alpha counting.

The combined data from the LGAC and coulometric analyses are shown in Table IV.

TABLE IV

U²³² in U²³³ Product by Coulometric-LGAC Method

Sample	Separated Solution		U ²³² in U ²³³ Product, ppm (a, b)
	U Conc by Coulometric Method, mg/ml ^(a)	Activity by LGAC, d/(min)(ml)	
A	0.204 $\pm$ 0.003 (n=3)	5.76 $\times$ 10 ⁶	166 $\pm$ 24 (n=10)
B	0.523 $\pm$ 0.009 (n=3)	1.67 $\times$ 10 ⁷	249 $\pm$ 17 (n=4)

(a) Corrected for Pa²³³ decay.

(b) Precision at the 95% confidence limit for a single determination.

The U²³² in the U²³³ product (last column of Table IV) was calculated from the following equation, which assumes that only U²³², U²³³, and U²³⁴ contribute to the counting rate:

$$ae + b(1 - e) = \frac{c}{d} \quad \text{or} \quad e = \frac{c - bd}{d(a - b)}$$

where

a = the specific activity of U²³² (from Appendix B), d/(sec)(mg)

b = the specific activity of U²³³ + U²³⁴ (calculated from Table II and data in Appendix B), d/(sec)(mg)

c = uranium activity (from LGAC), d/(sec)(mg)

d = total concentration of U²³², U²³³, and U²³⁴ (calculated from the coulometrically determined total uranium concentration on the basis of the isotopic concentrations in Table II), mg/ml

$$e = \frac{\text{wt } U^{232}}{\text{wt}(U^{232} + U^{233} + U^{234})}$$

$$1 - e = \frac{\text{wt}(U^{233} + U^{234})}{\text{wt}(U^{232} + U^{233} + U^{234})}$$

This evaluation of e is based on the difference between two large, experimentally determined values ($c - bd$) and, therefore, is subject to a relatively large error. e is corrected for the U^{234} concentration on the basis of Table II, and the U^{232} concentration is expressed as ppm of U^{233} (Table IV).

CONCLUSIONS

Differences between the two methods (Tables III and IV) are rather large with Sample A but in good agreement with Sample B. The range of results on both samples overlap so the methods are in agreement. As predicted, the range of error is smaller for the APHA method than for the coulometric-LGAC method because the latter involves the difference between two large numbers.

APPENDIX A

FORMATION OF URANIUM ISOTOPES

U^{233} is produced by thermal neutron irradiation of Th^{232} and subsequent decay as shown in Equation 1.

Reactions that reduce the yield of U^{233} are the neutron induced fission of U^{233} and (n, γ) reactions on Pa^{233} and U^{233} . Both of these (n, γ) reactions produce U^{234} as a final product.

Three fast neutron $(n, 2n)$ reactions produce U^{232} , the most detrimental contaminant in U^{233} . Equation 2 shows how >90% of the U^{232} is formed.

Minor amounts of U^{232} are produced by:

The quantity of U^{232} produced is minimized if the uranium target slugs are placed in positions exposed only to thermal neutrons, thereby reducing the fast neutron $(n, 2n)$ reactions until large quantities of U^{233} build up, fission, and supply appreciable quantities of fast neutrons.

Even small amounts of U^{232} (~10 ppm) are undesirable because of the high gamma energy of its decay products (listed in the table on the following page). Tl^{208} (2.6 Mev), one of the highest energy gamma emitters known, emits 88% of the gamma activity above 1.2 Mev⁽³⁾; the remaining 12% comes from Bi^{212} .

Decay Chain of U^{232}

Isotope	Half Life	Type of Decay	Major Energies, Mev		
			α	β	γ
U^{232}	73.6 y	α, γ	5.3	-	0.058
Th^{228}	1.9 y	α, γ	5.3- 5.4	-	0.084
Ra^{224}	3.6 d	α, γ	5.7	-	0.24
Rn^{220}	54 s	α	6.3	-	-
Po^{216}	0.16 s	α	6.8	-	-
Pb^{212}	10.6 h	β	-	0.34	-
Bi^{212}	60.5 m	α, β, γ	6.0	0.3	2.2, 1.8, 1.3
66% Po^{212}	3×10^{-7} s	α	8.8	-	-
34% Tl^{208}	3.1 m	β, γ	-	1.8	2.6
Pb^{208}	Stable		-	-	-

The activity of the decay chain reaches a maximum after 10 years and then follows the decay of 74-year U^{232} . Knolls Atomic Power Laboratory reports that a uranium metal sphere with a 3.06-cm radius (1 kg) produced by irradiating thorium to 4200 g/ton in the Materials Testing Reactor would emit 690 r/hr at its surface after 10 years.⁽³⁾ Los Alamos reports that 100 ppm of U^{232} in a 3-cm-radius metal sphere of U^{233} would result in 1300 r/hr at the surface in 10 years.⁽⁴⁾

APPENDIX B

HALF LIVES AND SPECIFIC ACTIVITIES

There is a variation of several per cent in the uranium and protactinium half lives quoted by different authors. The values used in this report were:

<u>Isotope</u>	<u>Half Life</u>	<u>Specific Activity, d/(sec)(mg)</u>
Pa ²³³	27.0 d	7.70×10^{11}
U ²³²	73.6 y	7.73×10^8
U ²³³	1.62×10^5 y	3.52×10^5
U ²³⁴	2.48×10^5 y	2.28×10^5

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