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DETERMINATION OF U^{232} AND U^{233}
IN IRRADIATED THORIUM

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NOVEMBER, 1965

BATTELLE-NORTHWEST
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DETERMINATION OF U^{232} AND U^{233}
IN IRRADIATED THORIUM

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DETERMINATION OF U^{232} AND U^{233} IN IRRADIATED THORIUMINTRODUCTION

This report describes the early development work and the analytical methods in current use at Battelle-Northwest for the analysis of uranium in irradiated thorium.

In 1963, gram quantities of thorium metal and oxide were irradiated in Hanford reactors to study U^{233} production. Prime interest of the study was the production of U^{233} with minimum U^{232} content; an upper impurity limit of 1 ppm U^{232} was an initial goal. Measurements were required of the amount and isotopic purity of U^{233} produced under various conditions. Thus, three analytical problems were presented:

- (1) The dissolution of irradiated thorium metal and thorium oxide samples
- (2) The quantitative separation of microgram amounts of uranium from thorium, protactinium, and fission products
- (3) The accurate measurement of U^{233} and U^{232} .

The analytical methods developed for the small scale tests were later placed in routine use for the production tests of 1964 and 1965.

SUMMARY

Analytical methods for the determination of uranium in irradiated thorium have been developed. These methods of dissolution, separation, and measurement are outlined in Figure 1. The detailed procedures are presented in the appendices.

Thorium oxide is usually dissolved by heating in a 12N HCl-0.04N HF mixture.

"Blue" oxides which are particularly resistant to chemical attack are dissolved by prolonged heating with 15N HNO_3 -0.04N HF. Thorium metal is dissolved in dilute acid (2N HCl-0.04N HF) to control the reaction rate.

Uranium is separated from the thorium-protactinium-fission product matrix by either anion exchange or liquid-liquid extraction of the chloride complex from 9 to 12N HCl. Samples in nitrate solution must first be converted to the chloride.

In the anion exchange method, uranium, protactinium, zirconium, and niobium are coadsorbed on a Dowex 1 x 8 resin column while thorium and most fission products pass through. Protactinium, zirconium, and niobium are eluted with 9N HCl-1N HF. Uranium is eluted with 0.1N HCl.

In the extraction method, uranium, protactinium, zirconium, and niobium are coextracted with 10% triisooctylamine in xylene. Protactinium, zirconium, and niobium are scrubbed from the organic phase with 7N HCl-1N HF. Uranium is stripped with 0.05N HNO_3 .

Uranium recovery is about 93% by anion exchange and about 97% by amine extraction. Decontamination factors are of the order of 10^6 for thorium and most fission products and 10^4 for protactinium, zirconium, and niobium.

U^{233} is measured by two techniques. Natural uranium is added as an isotopic diluent prior to sample dissolution and the U^{233}/U^{238} atom ratio of the purified fraction is measured with a thermal emission mass spectrometer. A second measurement is obtained by total alpha

FIGURE 1
Determination of U^{232} and U^{233}
in Irradiated Thorium

counting in a gas-flow proportional counter and subsequently correcting for chemical yield and for alpha contributions of U^{232} and U^{234} . The estimated relative standard deviation for the isotopic dilution U^{233} measurement is about $\pm 3\%$; that for the alpha counting technique is about $\pm 5\%$. Agreement between the techniques is normally within 5%.

U^{232} is determined by alpha energy analysis using a silicon surface barrier detector and a multichannel pulse height

analyzer. Alpha spectra of good resolution are obtained from residue-free sources prepared by electrodeposition of uranium from nitrate solution onto platinum. As little as 0.2 part U^{232} per million parts U^{233} can be measured. The estimated relative standard deviation of the ratio measurement is $\pm 5\%$ at this level.

EXPERIMENTAL AND DISCUSSION

U^{233} is produced by thermal neutron irradiation of Th^{232} . The scheme for

this nuclear transmutation and other simultaneous processes which determine the composition of the irradiated material are outlined in Figure 2. Concentration ranges observed for important constituents in typical Hanford irradiated thorium material are presented in Table I.

Dissolution of Thorium Oxide and Thorium Metal

The most satisfactory dissolution method for refractory ThO_2 is to heat with concentrated HCl or HNO_3 , 0.01 to 0.06N in HF . The catalytic properties of fluoride and fluorosilicate

FIGURE 2

Neutron Irradiation of Thorium
 (a) U^{233} and U^{234} formation
 (b) U^{232} formation

TABLE I

COMPOSITION OF TYPICAL HANFORD IRRADIATED THORIUM MATERIAL

Constituent	Concentration Range	
Th ²³²	88-99	wt%
Th ²³⁰	0.2-80	μg/g Th ²³²
U ²³³	30-3000	μg/g Th ²³² (a)
U ²³²	0.3-130	μg/g U ²³³ (a)
U ²³⁴	0.004-0.04	atom ratio U ²³⁴ /U ²³³
Pa ²³³	0.4-5.0	atom ratio Pa ²³³ /U ²³³ (b)
Radiation	50-400	rad/hr ^(b,c)
Color (ThO ₂)	white to deep blue ^(d)	

(a) 200 days after end of irradiation

(b) At end of irradiation

(c) For 0.2 g sample of irradiated thorium

(d) Irradiated ThO₂ samples ranged in color from pure white to completely blue, with a number of samples containing both white and blue particles.

ions in ThO₂-HNO₃ systems were first reported by Schuler.⁽¹⁾ He investigated the effects of HNO₃ and fluoride ion concentration on dissolution rate at 98 °C. Detailed studies of the equilibria of thorium(IV) fluoride ion complexes in acid solution have been made by Dodgen.⁽²⁾ Virtually all experimental work has been confined to HNO₃ systems because of their compatibility with stainless steel. Investigations of HCl media have been mostly qualitative.

The dissolution rate of ThO₂ in HNO₃ or HCl solution is strongly dependent upon the method of oxide preparation. Oxides made by ignition of the hydroxide or salts of the volatile oxy-acids at temperatures not exceeding 550 °C are readily soluble in mineral acids alone. An oxide that is not significantly attacked unless fluoride ion catalyst is present is produced by higher temperature denitration methods such as "flame spray." The "sol gel"

process yields a crystalline oxide which is even more slowly dissolved. If sol gel material is compacted to high density and then irradiated, a blue oxide is formed. This blue oxide is very resistant to chemical attack. Prolonged heating with fluoride-catalyzed HNO₃ will eventually dissolve blue thorium oxide. Hydrochloric acid media is relatively ineffective in the dissolution of sol gel material.

Data for fluoride-ion catalyzed dissolution tests in both HNO₃ and HCl are presented in Figure 3. The ThO₂ was prepared by ignition of thorium oxalate at 1000 °C for 1 hr. A specified weight of oxide was added to 15 ml of the matrix acid in a 50 ml Teflon beaker and heated to 80 °C. The HF catalyst was added, and the temperature was increased to 98 °C at a 9 °C/min gradient with constant stirring. Dissolution time was measured from time of fluoride addition.

FIGURE 3
Dissolution of Thorium Oxide in Nitric
and Hydrochloric Acids with Fluoride Catalysis

One gram of ThO₂ can be dissolved by heating at 98 °C in 15 ml of HNO₃ or HCl containing 0.004N to 0.06N fluoride ion catalyst. A wide range of acid concentrations will dissolve the oxide in less than 15 min. The maximum catalyst concentration which will not precipitate thorium fluoride is 0.04N fluoride ion. Dissolution is most rapid in HNO₃, but concentrated HCl is preferred because later separation and purification procedures require a chloride system.

Blue oxides are dissolved in concentrated HNO₃ and then are converted to chloride solution. The conversion is accomplished by carbonate-free precipitation as the hydroxide of thorium and uranium and redissolution in concentrated HCl. When only a few milligrams of thorium are present, direct evaporation of the nitrate sample followed by addition of concentrated HCl is effective.

Thorium metal is readily attacked by HNO₃ or HCl. The use of dilute

acid permits control of reaction rate and minimizes oxide formation through excessive heat generation. However, small metal-oxide residues usually remain unless fluoride ion is present. Metal samples are normally dissolved in 2N HCl-0.04N HF.

Separation of Uranium Fraction by Anion Exchange

A chloride anion exchange system was selected for the separation of uranium and thorium. The uranium chloride complex is strongly adsorbed on Dowex 1 x 8 anion exchange resin from 6N or greater HCl. Thorium is

not adsorbed. Protactinium, zirconium, and niobium, which are coadsorbed with the uranium, may be removed by fluoride complexing. Data for the adsorption of many elements on Dowex 1 from HCl and HF are given in Table II.

The procedure for the anion exchange separation of uranium as the chloride complex was adapted from the work of Kraus.⁽³⁾ The method is presented in block diagram form in Figure 4. Uranium, protactinium, zirconium, and niobium are quantitatively adsorbed from 12N HCl; some ruthenium

TABLE II

ADSORPTION PROPERTIES OF VARIOUS IONS ON ANION EXCHANGE RESINS

Ion	Adsorbed from 12M HCl	Adsorbed from 12M HCl-.5M HF	Adsorbed from 8M HCl-.3M HF	Eluted by 0.1M HCl	Ion	Adsorbed from 12M HCl	Adsorbed from 12M HCl-.5M HF	Adsorbed from 8M HCl-.3M HF	Eluted by 0.1M HCl	Ion	Adsorbed from 12M HCl	Adsorbed from 12M HCl-.5M HF	Adsorbed from 8M HCl-.3M HF	Eluted by 0.1M HCl
Ac(III)	-	-			In(III)	x	s		x	Ru(IV)	x	x	-	
Ag(I)	-	-			Ir(III)	-	-		-	Sb(III)	x	s	-	
A.Earth	-	-			Ir(IV)	x	x		-	Sb(V)	s	x	x	
A.Metal	-	-			Mn(II)	-	-		-	Sc(III)	s			
Al(III)	-	-			Mo(VI)	x	x	x	-	Se(IV)	x		x	
Am(III)	-	-			Nb(V)	x	s	-	-	Sn(II)	s	s	-	
As(III)	s	s	x		Ni(II)	-	-		-	Sn(IV)	x	x	-	
As(V)	-	-			Np(IV)	x	x	-	-	Tc(VII)	x	x	-	
Au(III)	x	x	-		Np(VI)	x	x	x		Te(IV)	x		-	
Be(II)	-	-			Os(III)	x	x	-	-	Th(IV)	-			
Bi(III)	x	x	-		Pa(V)	x	-		-	Ti(III)	s		x	
Cd(II)	x	x	-		Pb(II)	x	x	-	-	Ti(IV)	x	-		
Co(II)	x	-			Pd(II)	x	x	-	-	Tl(I)	-			
Cr(III)	s	s	x		Po(IV)	x	-	-	-	Tl(III)	x	x	-	
Cr(VI)	x	-	-		Pt(IV)	x	x	-	-	U(IV)	x	x	x	
Cu(I)	s	s	-		Pu(III)	-	-		-	U(VI)	x	x	x	x
Cu(II)	s	-			Pu(IV)	x	-	-	-	V(IV)	x			
Fe(II)	s	-			Pu(VI)	x	-	x		V(V)	x		x	
Fe(III)	x	x	x		R.Earth	-	-		-	W(VI)	x	s	x	
Ga(III)	x	x	x		Re(III)	-	-		-	Y(III)	-			
Ge(IV)	x	-			Re(VII)	x	x	-	-	Zn(II)	x	x	s	
Hf(IV)	x	-			Rh(III)	-	-		-	Zr(IV)	x	-		
Hg(II)	x	x	-		Rh(IV)	x	x	-	-					

Note: Adsorption data for 12M HCl from Reference 4.
Adsorption data for HCl-Hf systems from References 5, 6, and 7.

- = negligible
s = 0.3 < distribution coefficient < 1.0
x = quantitative

FIGURE 4

Uranium Separation by Anion Exchange, Dowex 1

is also adsorbed. Thorium and rare earths pass through the column. Flow rate is maintained at 20 drops/min.

Protactinium, niobium, and zirconium are removed by washing with eight column volumes of 9N HCl-1N HF. Protactinium elutes sharply in the first column volume while niobium elutes gradually and irregularly, beginning in the second column volume, rather than as a well defined fraction. Decontamination factors for protactinium and zirconium are at least 10^4 . The factor for niobium is much smaller.

More efficient niobium removal from the column is obtained with 8N

HCl-0.05N HF. With this reagent, niobium elutes immediately after the protactinium as a broad but definite fraction in the second and third column volume. At this fluoride ion concentration, as much as 25% increase in the niobium decontamination factor can be obtained, but protactinium often "tails" badly, reducing the protactinium factor to as low as 10^3 .

Effective protactinium removal is most important when processing short-cooled samples in which protactinium concentration is high. Protactinium decontamination might be sacrificed for improved niobium removal when

well aged material is involved. Both wash solutions have been used in sequence with short-cooled samples which contain relatively large amounts of fission products.

Uranium is eluted with three column volumes of 0.1N HCl, leaving any adsorbed ruthenium on the resin column. Uranium recovery was measured for six samples of irradiated ThO₂ by comparison of alpha counting results with data obtained by isotopic dilution methods. Recovery for the anion exchange of the chloride complex ranged between 84 and 99%. Average recovery was 93%.

Separation of Uranium by Liquid-Liquid Extraction

Of the tertiary amine liquid-liquid extraction systems which have been reported for uranium, separa-

tion from chloride solution with triisooctylamine (TIOA) appeared to be best suited for irradiated thorium material. Extraction data are given in Table III.

A tertiary amine extraction of the uranium(VI) chloride complex proceeds as follows:

Complex formation:

Amine extraction:

As indicated in Table III, 99% of the uranium is extractable into 5% TIOA from 6N or greater HCl. Uranium may be stripped into an aqueous phase

TABLE III
SEPARATION OF URANIUM BY LIQUID-LIQUID EXTRACTION⁽⁸⁾
TRIISOOCTYLAMINE

<u>Aqueous</u>	<u>Organic</u>	<u>U(VI)^(b)</u>	<u>Th(IV)</u>	<u>Nb⁹⁵</u>	<u>Percent Extracted^(a)</u>			<u>Sr, Cs, Am, Cm, R.E.</u>
					<u>Zr⁹⁵</u>	<u>Ru¹⁰⁶</u>		
1 <u>M</u> HCl	5% TIOA	40	--	--	--	--		
2 <u>M</u> HCl	5% TIOA	--	--	0.3	0.02	74.3		Negligible
2.2 <u>M</u> HCl	5% TIOA	--	0.003	--	--	--		Negligible
4 <u>M</u> HCl	5% TIOA	95	--	3.1	0.4	72.5		Negligible
4.5 <u>M</u> HCl	5% TIOA	--	0.005	--	--	--		Negligible
6 <u>M</u> HCl	5% TIOA	99	--	--	--	--		Negligible
6.5 <u>M</u> HCl	5% TIOA	99	--	90.2	0.7	69.8		Negligible
6.7 <u>M</u> HCl	5% TIOA	99	0.010	--	--	--		Negligible
7 <u>M</u> HCl	5% TIOA	99	--	96.8	89.6	58.6		Negligible
8.9 <u>M</u> HCl	5% TIOA	99	0.016	96.8	89.6	58.6		Negligible
11.1 <u>M</u> HCl	5% TIOA	99	0.020	96.8	89.6	58.6		Negligible

PERCENT U(VI) STRIPPED FROM 5% TIOA

Water	99.8
0.1M HNO ₃	99.2
0.1M HCl	98.9

(a) 5% TIOA solution in xylene. Two minute extraction at 20 °C. Equal volumes of aqueous and organic.

(b) Yellow oil or gel may form at high uranium concentrations.

as the UO_2^{++} ion by simply reducing chloride ion concentration and shifting equilibria in the reverse direction.

Numerous separation tests were performed with 5% TIOA using a Th- U^{235} -Pa 233 standard and various combinations of separation and decontamination methods. The tests are summarized in Table IV.

Protactinium(V) is extracted along with uranium into TIOA. Coextracted protactinium can be removed with 7N HCl-1N HF or 7N HCl-0.5N HF, the greater fluoride ion concentration being most efficient.

Of the fission products present in significant amounts, only zirconium, niobium, and ruthenium are appreciably extractable from 7N HCl. Zirconium and niobium can be removed with 7N HCl-1N HF solution; however, niobium is more efficiently removed with a lower fluoride ion concentration. Extracted ruthenium is not removed.

Uranium can be quantitatively stripped with 6N H_2SO_4 or any of the reagents listed in Table III. Two 0.05N HNO_3 strips have proved most satisfactory. Ruthenium(IV) is not removed with uranium and remains in the organic phase.

TABLE IV
TRIISOOCTYLAMINE LIQUID-LIQUID SEPARATIONS TESTS

Step	Test (a)			
	1	2	3	4
	Percent Extracted			
5% TIOA Extraction	x	x	x	x
1st 7N HCl Scrub	x	x	x	x
2nd 7N HCl Scrub	x	-	x	x
1st 7N HCl-1N HF Scrub	93 Pa 0.25 U	86 Pa	75 Pa ^(b)	x ^(b)
2nd 7N HCl-1N HF Scrub	7 Pa 0.1 U	12 Pa	20 Pa ^(b)	x ^(b)
3rd 7N HCl-1N HF Scrub	-	2 Pa	4 Pa ^(b)	x ^(b)
7N HCl Scrub	x	x	-	-
Two 0.05N HNO_3 Strips	94 U	97 U 0.4 Pa	97 U 0.5 Pa	-
Two 1M NH_4CO_3 Strips	-	-	-	98 U 4 Pa
Stripped Organic	0.2 U	0.1 U	0.2 U	<0.1 U

NOTE: x = step performed, but no measurements taken.

- = step not performed.

(a) 40 mg Th/ml- U^{235} -Pa 233 -7N HCl was the standard solution. Equal volume extraction at 20 °C. Steps performed in sequence. Percentages denote distribution to that phase. Values given are averages of two or more runs.

(b) 7N HCl-0.5N HF scrub solution.

FIGURE 5

Uranium Separation by Liquid-Liquid Extraction
with 10% Triisooctylamine in Xylene

A separation procedure based upon the data of Tables III and IV is outlined in Figure 5.

Uranium(VI) and protactinium(V) are quantitatively extracted from 7N HCl-0.04 HF into an equal volume of 10% TIOA in xylene. Ninety percent of the zirconium(IV), 97% of the niobium(V), and 59% of the ruthenium(IV) are simultaneously extracted.

Protactinium, zirconium, and most of the niobium are removed from the organic as fluoride complexes with three 7N HCl-1N HF scrubs. Decontamination factors are at least 10^4 for protactinium and zirconium, but as much as 20% of the niobium may not be removed. More efficient niobium

removal from the organic phase can be obtained by reducing fluoride concentration in the strip to 0.5M, but protactinium decontamination suffers proportionally.

Uranium is stripped into two equal-volume 0.05 N HNO₃ scrubs, leaving ruthenium(IV) in the organic phase. Uranium recovery ranged between 95 and 98% in tests using a Th-U²³⁵-Pa²³³ standard. Uranium recovery has also been measured for 32 irradiated ThO₂ samples by comparison of alpha counting results with data obtained by isotopic dilution methods. For these samples, recovery ranged between 86 and 106%. Average recovery was 95%.

Liquid-liquid extraction has been adopted for routine use because the separation requires less time and uranium recovery is slightly greater.

Supplementary Methods for Decontamination of the Uranium Fraction

Highest purity U^{233} is usually produced at relatively low total irradiation. Fission product content of such material is small and the fraction of the niobium that is carried with the uranium through anion exchange or amine extraction contributes negligible activity. Late in 1964 tests were performed in a reactor central core at long exposures, resulting in the generation of gross amounts of fission products. Although Nb^{95} does not directly interfere with the uranium measurement, it can present sufficient radiation hazard that further decontamination is desirable.

Several solvent extraction methods were investigated in connection with niobium removal. Most of the procedures which extract niobium produce a uranium fraction in a solution media unsatisfactory for direct assay. Uranium extraction systems are better suited. The methylisobutyl ketone(hexone)-aluminum nitrate procedure⁽⁹⁾ outlined in Figure 6 proved most successful.

Anion exchange or amine extraction uranium fractions must be converted to 2.8M aluminum nitrate-1N acid deficient-0.1% tetrapropylammonium nitrate (TPAN) solution if more than 1 ml of solution is to be processed. Uranium(VI) and any zirconium(IV) and niobium(V) are coprecipitated with 2 mg of ferric ion by addition of carbonate-free ammonium hydroxide. The hydroxide precipitate is redissolved in a

FIGURE 6
Supplementary Decontamination Cycle
for High Fission Product Content Samples

drop or two of dilute HNO_3 and 10 ml of the aluminum nitrate reagent are added. Up to 1 ml of a sample solution less than 8N in HNO_3 concentration may be processed directly by addition to this amount of reagent.

Uranium is extracted into an equal volume of hexone as tetrapropylammonium uranyl trinitrate. As much as 4 mg total uranium can be tolerated. Larger amounts require proportionally higher TPAN concentration. The organic phase is scrubbed twice with the 2.8M aluminum nitrate reagent, and uranium is finally stripped into an equal volume of 0.1N HNO_3 . Only 0.04% of the zirconium-niobium initially present appears in the uranium fraction. Greater than 1% of gold(III), boron(III), cerium(IV), mercury(I), indium(III), palladium(II), ruthenium(IV), thorium(IV), the trivalent rare earths, and yttrium(III) will extract if present.⁽⁹⁾

Tests performed with $\text{U}^{233}\text{-Zr}^{95}\text{-Nb}^{95}$ standard solutions indicate that uranium recovery is better than 99%. About 1% of zirconium-niobium activity is entrained in the organic phase during extraction, but less than 0.02% survives scrubbing and is stripped with uranium. The zirconium-niobium decontamination factor is at least 5×10^3 .

Measurement of U^{233}

Direct radioassay is the simplest technique for U^{233} measurement. The purified uranium fraction is diluted to calibrated volume, and a measured aliquot is dried on platinum and counted in a gas-flow proportional counter. The observed count rate,

corrected for counter efficiency and chemical yield of the uranium separation process, corresponds to the summed alpha activity of the uranium isotopes present.

As indicated in Table I, the $\text{U}^{234}/\text{U}^{233}$ atom ratio is 0.004 to 0.04 in irradiated thorium material containing a natural uranium internal standard. This corresponds to a U^{234} count rate which is approximately 0.2 to 2.0% of the U^{233} count. Similarly, U^{232} is present in part per million range or about 0.2 to 20% of the U^{233} count. The U^{235} and U^{238} of the natural uranium isotopic diluent contribute negligible count because of their very low specific activity. Exclusive of chemical yield correction, a total alpha count will be biased not more than 5% high with respect to true U^{233} content so long as U^{232} concentration does not exceed 10 ppm. If U^{232} and U^{234} content is known, total alpha data can be corrected algebraically to produce a good approximation of the true U^{233} value.

Uncertainty in chemical yield usually exceeds all other sources of error combined and is accountable for virtually all residual error after correction of total alpha data for uranium isotopic impurities. Initially, recovery can be estimated from test runs with standard solutions. Better yield values are obtained by comparison of total alpha results and isotopic dilution measurements on actual thorium samples. Experience indicates that after an initial testing period to establish chemical yield and isotopic correction data, total

alpha results, accurate to within $\pm 5\%$ are possible without further yield measurements so long as analytical procedures and irradiation parameters remain unchanged.

Mass spectrometric analysis provides a more accurate measurement of U^{233} . An aliquot of the uranium fraction is further purified by diethyl ether extraction from $2N\ HNO_3$ - $15N\ NH_4NO_3$ solution. Dilute HNO_3 is added and the ether is evaporated. The resulting aqueous solution is analyzed on a thermal ionization mass spectrometer. Measurement of the U^{233}/U^{238} atom ratio permits direct calculation of U^{233} from the known amount of natural uranium added as isotopic diluent. The U^{233}/U^{234} atom ratio is also determined to permit correction of the total alpha count and the alpha energy analysis data for U^{234} .

The U^{233} result is independent of chemical yield and uranium isotopic impurities. Accuracy of the technique is primarily a function of the amount of U^{238} introduced from sources other than the isotopic diluent itself. Appreciable uranium can be concentrated from the large quantities of HCl and HNO_3 used in the separation and purification process. Uranium present as a trace impurity in laboratory glassware may be leached into the sample during analysis. Uranium contamination from these sources is minimized by the use of purified reagents and preleached glassware. Thorium metal samples frequently contain detectable uranium. Accuracy of the isotopic dilution method is estimated to be better

than $\pm 3\%$. U^{233} results calculated from total alpha data and from isotopic ratio measurements should agree within 5%.

Measurement of U^{232}

U^{232}/U^{233} ratios in the parts million range are determined by alpha energy analysis. Suitable sources are prepared by electrodeposition of uranium as the basic hydrous oxide on a platinum disk cathode from $1N\ NH_4NO_3$ solution initially adjusted to pH 1.5. The solution in the near vicinity of the cathode becomes basic as the result of the reduction of hydrogen ion at the cathode. Both hydrogen and nitrate ions are reduced at the cathode while oxygen is liberated at the anode. The reduction of nitrate ion consumes more than one hydrogen atom per electron. The net cell reaction is a loss of hydrogen from the solution resulting in a gradual increase in the solution pH which prevents the uranium deposit from redissolving. Deposition is nearly quantitative. To convert the deposit to an oxide the source is ignited prior to counting.

A $100\ mA/cm^2$ current gives nearly quantitative deposition of $1\ \mu g$ of uranium in about 2 hr. That amount of U^{233} is adequate for counting. Deposition need not be quantitative since only the U^{232}/U^{233} ratio is determined.

The alpha energy analysis system consists of a $200\ mm^2$ silicon surface barrier detector mounted in a modified filtrator apparatus.⁽¹⁰⁾ The source holder is maintained at a positive 250 V bias with respect to

the detector to minimize contamination of the detector surface with recoil nuclei from alpha decay. Detector output is converted to a voltage pulse in a charge-sensitive preamplifier and the pulses are amplified and delivered to a 400 channel pulse height analyzer.

An alpha energy spectrum for a typical uranium fraction separated from irradiated thorium is illustrated in Figure 7. The energy versus channel number relationship is obtained by counting a Np^{237} - Pu^{239} - Am^{241} mixed source under conditions identical to those for uranium samples and plotting the channel number of the peak maxima versus their respective alpha energy. Such a calibration is plotted as a broken line in the figure.

Channel bands of equal width are summed for each uranium isotope and corrected for background. An adjust-

ment for a small unresolved U^{234} component in the U^{233} peak is calculated from the $\text{U}^{233}/\text{U}^{234}$ atom ratio. Finally the $\text{U}^{232}/\text{U}^{233}$ ratio is calculated from the corrected total counts of the respective channel bands.

The U^{232} concentration in the example of Figure 7 is 0.92 parts U^{232} per million parts U^{233} . Ratios considerably below this value would produce significant enough U^{232} count to permit accurate measurement. Accuracy of corrected $\text{U}^{232}/\text{U}^{233}$ ratios is estimated to be better than $\pm 5\%$.

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FIGURE 7

Alpha Energy Spectrum of a Typical Separated Uranium Fraction

APPENDIX ASAMPLE DISSOLUTIONA-I. Dissolution of Irradiated
Thorium Oxide

1. Accurately pipette the natural uranium internal standard into a 40 ml screw cap glass vial. The amount of natural uranium added should be approximately equal to the amount of U^{233} in the sample.
 2. Add between 0.1 and 0.2 g irradiated ThO_2 , accurately weighed to within ± 0.1 mg, to the vial. This is conveniently accomplished by weighing the oxide into gelatin capsules.
 3. Add 7 ml 12N HCl-0.04N HF solution to the vial.
 4. Digest on a hot plate, just below boiling temperature, with occasional swirling, until the sample is completely dissolved. Add 12N HCl-0.04N HF as required to maintain a 6 to 7 ml volume during dissolution.
 5. If uranium is to be separated by anion exchange, dilute the sample to 10 ml with 12N HCl. If the separation is by amine extraction, dilute the sample to 10 ml with water.
 6. Warm gently to dissolve any crystallized thorium salts, then cool to room temperature.
- amount of natural uranium added should be approximately equal to the amount of U^{233} in the sample.
2. Add between 0.1 and 0.2 g irradiated ThO_2 , accurately weighed to within ± 0.1 mg, to the vial. This is conveniently accomplished by weighing the oxide into gelatin capsules.
 3. Add 10 ml 16N HNO_3 -0.04N HF solution to the vial.
 4. Digest on a hot plate, just below boiling temperature, with occasional swirling until the volume is reduced to about 5 ml.
 5. If the sample is not completely dissolved, add 10 μ l 29N HF (ThF_4 will precipitate) and continue digestion, maintaining the volume at 5 to 6 ml by 16N HNO_3 addition. Repeat the 29N HF addition about once every hour until the sample is dissolved.
 6. Heat on a hot plate until the solution is reduced to about 1 ml or until thorium nitrate begins to crystallize. Add 12N HCl dropwise with continued heating until evolution of oxides of nitrogen ceases.
 7. If uranium is to be separated by anion exchange, dilute the sample to 10 ml with 12N HCl. If the separation is by amine extraction, dilute the sample to 7 ml with 12 N HCl and add 3 ml water.
 8. Warm gently to dissolve any crystallized thorium salts, then cool to room temperature.

A-II. Dissolution of "Blue" Irra-
diated Thorium Oxide

1. Accurately pipette the natural uranium internal standard into a 40 ml screw cap glass vial. The

A-III. Dissolution of Irradiated
Thorium Metal Samples

1. Accurately pipette the natural uranium internal standard into a 40 ml screw cap glass vial. The amount of natural uranium added should be approximately equal to the amount of U^{233} in the sample.
2. Add between 0.1 and 0.2 g irradiated thorium metal, accurately weighed to within ± 0.1 mg, to the vial.
3. Add 3 ml water.
4. Add 12N HCl-0.04N HF solution to the vial dropwise. The rate of addition is used to control reaction rate.
5. When the metal mass has dissolved, dilute the sample to 10 ml with 12N HCl-0.04N HF solution and heat on a hot plate at just below boiling temperature until any residues are dissolved.
6. Dilute to 10 ml with 12N HCl-0.04N HF solution. Cool to room temperature.

APPENDIX BURANIUM SEPARATION AND DECONTAMINATIONB-I. Separation and Decontamination
of Uranium by Anion Exchange

1. Prepare an 8 ml Dowex 1 x 8, 100 to 200 mesh, chloride form resin bed in a 9 mm glass column equipped with a stopcock to control flow rate. Polyethylene chips make a suitable HF resistant plug to retain the resin in the column.
2. Wash the column with 16 ml 0.1N HCl, then equilibrate with 12N HCl.
3. Add the sample to the column, adjusting flow rate to about 20 drops/min. Allow the column to drain completely.
4. Rinse the sample vial with 10 ml 9N HCl and run the solution through the column. Repeat twice more.
5. Scrub the column with 70 ml 10N HCl-1N HF. Allow the column to drain completely.
6. Rinse the column with 20 ml 9N HCl. Stop the flow when the liquid level reaches the top of the resin bed. Discard the column effluents.
7. Elute the uranium with 20 ml 0.1N HCl, discarding the first 4 ml and accumulating the remainder in a 25 ml volumetric flask.
8. Dilute the contents of the flask to volume with water and mix thoroughly.

B-II. Separation and Determination
of Uranium by Amine Extraction

1. Add 10 ml vol/vol triisooctylamine in xylene to the 40 ml vial

containing the sample.

2. Stir to an emulsion 3 min on a vortex mixer. Allow the phases to separate, centrifuging if necessary. Discard the aqueous phase.
3. Add 10 ml 7N HCl to the vial and stir 1 min. Discard the aqueous phase.
4. Add 10 ml 7N HCl-1N HF solution to the vial and stir 3 min. Discard the aqueous phase.
5. Add 10 ml 7N HCl-1N HF solution to the vial and stir 3 min. Transfer the organic phase to a clean 40 ml vial. Add 10 drops 10% TIOA in xylene to the aqueous phase, mix briefly, combine the organic phase with the previous one. Discard the aqueous phase.
6. Add 10 ml 7N HCl-1N HF to the combined organic phases and stir 3 min. Discard the aqueous phase. Add 10 drops 7N HCl, swirl gently, and discard the aqueous phase.
7. Add 10 ml 0.05N HNO₃ to the vial and stir 3 min. Transfer the aqueous phase to a 25 ml volumetric flask. Repeat with a second 10 ml 0.05 N HNO₃ portion.
8. Dilute the contents of the flask to volume with 1N HNO₃ and mix thoroughly.

B-III. Supplementary Decontamination
Cycle for High Fission Pro-
duct Content Samples

1. Transfer an aliquot of the product solution of procedure B-I or B-II to a 40 ml glass vial. If the

- aliquot is 1 ml or less, omit steps 2 through 4 below.
2. Add one or two drops of 10 mg Fe^{+++} /ml solution and swirl to mix.
 3. Add concentrated, carbonate-free NH_4OH dropwise, with gentle swirling, until $\text{Fe}(\text{OH})_3$ precipitates, then add 10 drops excess. Centrifuge. Discard the aqueous phase.
 4. Dissolve the precipitate in two or three drops 6N HNO_3 .
 5. Add 10 ml 2.8M aluminum nitrate-1N acid deficient-0.1% (wt/vol) tetrapropylammonium nitrate reagent (ANN-TPAN)* and 10 ml methylisobutyl ketone to the vial.
- Stir 3 min on a vortex mixer, centrifuge, discard the aqueous phase.
6. Add 10 ml of the ANN-TPAN reagent. Stir 1 min, centrifuge, discard aqueous phase. Repeat the scrub with an additional 10 ml ANN-TPAN reagent.
 7. Add 10 ml 0.1 N HNO_3 . Stir 3 min, transfer the aqueous phase to a 25 ml volumetric flask. Repeat the uranium strip with an additional 10 ml 0.1N HNO_3 , combining the aqueous phases.
 8. Dilute the contents of the flask to volume with 0.1N HNO_3 and mix thoroughly.

* ANN-TPAN reagent: Dissolve 1050 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water to a 900 ml total volume, warming if necessary. Add 6.7 ml concentrated ammonium hydroxide and stir until the precipitate dissolves. Add 10 ml 10% tetrapropylammonium hydroxide solution and stir. Dilute 1 liter with water.

APPENDIX C

U²³² AND U²³³ MEASUREMENTC-I. Preparation of Sources for
Determination of U²³³ by
Total Alpha Counting

Pipette a measured aliquot of the product solution of procedure B-I, B-II, B-III, Appendix B, onto a platinum disc for alpha counting. The alpha counting rate should be at least 100 counts/min. Platinum discs are recommended because traces of HCl are usually present.

C-II. Preparation of Solutions for
Determination of U²³³ and U²³⁴
by Mass Spectrometry

1. Transfer an aliquot of the product solution of procedure B-I, B-II, B-III, Appendix B, into a 40 ml vial. The amount should be chosen to provide approximately 2 μg U²³³.
2. Add 10 ml, 2N HNO₃-NH₄NO₃ saturated solution, about 1 g NH₄NO₃ crystals, and 7 ml anhydrous diethyl ether to the vial. Stir to an emulsion for 5 min. Transfer the ether phase to a clean 40 ml vial.
3. Add an additional 7 ml ether to the vial. Stir 5 min. Transfer the ether phase.
4. Add 15 ml, 2N HNO₃-NH₄NO₃ saturated solution to the combined ether phases. Stir 1 min.
5. Transfer about 500 μl of the ether phase to a 1 dram vial containing 500 μl 0.1N HNO₃. Evaporate the ether. The vial contains about 0.05 μg of both

U²³³ and U²³⁸, amounts sufficient for most mass spectrometric measurements. The U²³³/U²³⁸ and U²³³/U²³⁴ atom ratios are to be determined.

C-III. Preparation of Sources for
Determination of U²³² by
Alpha Energy Analysis

1. Transfer the remainder of the ether layer of Step 5, procedure C-II, to a 100 ml beaker containing 10 ml 1N NH₄NO₃-0.1N HNO₃ solution. Evaporate the ether.
2. Adjust to pH 1.0 to 1.5 with dilute NH₄OH.
3. Transfer the solution to an electrodeposition cell consisting of a platinum disc for alpha energy analysis connected as cathode and a platinum stirrer-anode.
4. Electrolyze at 100 mA/cm² with continuous stirring until a pH of 8 or greater is reached.
5. Ignite the uranium hydroxide deposit on the source plate to red heat in a gas burner flame. The activity of the plate should be approximately 20,000 disintegrations/min U²³³, an amount sufficient for most alpha energy analyzers. Count until at least 50,000 counts have been accumulated in the U²³³ channel band. If U²³² content is very low, count until a U²³² total significant with respect to background is accumulated.

APPENDIX D

CALCULATIONS

D-I. Values Adopted for the
Constants Used in Calculations

Nuclide	Atomic Weight	Average Alpha Energy, MeV	Half-Life, yr
U ²³²	232.0372	5.3	72
U ²³³	233.0395	4.8	1.62×10^5
U ²³⁴	234.0409	4.75	2.48×10^5
U ²³⁵	238.0508		
Th ²³²	232.0382		

Formula weight ThO₂ = 264.0370Avogadro's Number = 6.02257×10^{23} D-II. Calculation of U²³³ from Mass
Spectrometric Isotopic Dilution Data $\mu\text{g U}^{233}/\text{g Th} =$

$$\frac{[R_{3/8}][0.97894][\mu\text{g U}^{238} \text{ added}]}{\text{g Th}}$$

where $R_{3/8}$ = atom ratio of U²³³ to U²³⁸0.97894 = atomic weight U²³³ /
atomic weight U²³⁸g Th = grams of thorium in
sample taken.D-III. Calculation of U²³² in U²³³
from Alpha Energy Analysis
and U²³³/U²³⁴ Atom Ratio $\mu\text{g U}^{232}/\text{g U}^{233} =$

$$\frac{C_{5.3}/SA_{232}}{(C_{4.8})(F_{233})/SA_{233}} \times 10^6$$

where $C_{5.3}$ = counts observed at
5.3 MeV $C_{4.8}$ = counts observed at
4.8 MeV

$$SA_{232} = \frac{6.02257 \times 10^{23}}{232.0372} \times \frac{0.69315}{72 \times 5.256 \times 10^5}$$

$$= 4.754 \times 10^{13} \text{ disintegrations/min/g U}^{232}$$

$$SA_{233} = \frac{6.02257 \times 10^{23}}{233.0395} \times \frac{0.69315}{1.62 \times 10^5 \times 5.256 \times 10^5}$$

$$= 2.1038 \times 10^{10} \text{ disintegrations/min/g U}^{233}$$

$$F_{233} = \frac{(R_{3/4})(HL_{233})^{-1}}{(R_{3/4})(HL_{233})^{-1} + (HL_{234})^{-1}}$$

$$= \text{fraction of counts observed at 4.8 MeV due to U}^{233}$$

 $R_{3/4}$ = atom ratio of U²³³ to U²³⁴ $HL_{233} = 1.62 \times 10^5 \text{ yr}$ $HL_{234} = 2.48 \times 10^5 \text{ yr}$ D-IV. Calculation of U²³³ from
Total Alpha Counting $\mu\text{g U}^{233}/\text{g Th} =$

$$\frac{(CPM_{\text{obs}})(C_{4.8/T})(F_{233})}{(CE)(CY)(A)(\text{g Th})(SA_{233})} \times 10^6$$

where CPM_{obs} = total alpha counts/min
observed $C_{4.8/T}$ = ratio of counts observed
at 4.8 MeV to counts
observed at all alpha
energies from alpha
energy analysis F_{233} = see Section D-III, above
CE = counting efficiency of

alpha counter. Approximately 0.0502 for 2 π windowless flow counters used

CY = chemical yield of separations process
A = fraction of total sample taken for counting

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