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THE DETERMINATION THORIUM ISOTOPIC RATIOS
BY RADIOCHEMICAL METHODS

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THE DETERMINATION OF THORIUM ISOTOPIC
RATIOS BY RADIOCHEMICAL METHODS

By W. Y. Matsumoto

INTRODUCTION AND HISTORY

Thorium-230 has been proposed as a source material for uranium-232 and its daughter thorium-228, both of which have an attractive potential for application in compact power sources. Fig. 1 (tabulated comparison of heat output from U^{232} and Th^{228} with other isotopes used or considered for heat sources)⁽¹⁾ illustrates their significant advantage with respect to their heat generation per unit weight. Another attractive feature can be seen in Fig. 2 (radioactive decay chain of U^{232})⁽¹⁾ as it would be possible to milk multigram quantities of Th^{228} from a stored stock of relatively long lived U^{232} . A feasible route to the production of U^{232} and Th^{228} is shown in Fig. 3 (diagram of a two step irradiation process to produce U^{232} and Th^{228} from Th^{230})⁽¹⁾. However, this route would be practical only if sufficient quantities of thorium with a thorium-230 isotopic abundance of 2% or greater are available.

The analytical work reported here was carried out to determine whether the uranium milling industry in the United States could supply quantities of thorium sufficiently rich in Th^{230} to make the scheme practicable. Th^{230} is normally found only associated with uranium ores since it occurs as a daughter product in the natural U^{238} decay chain and is relatively short-lived (80,000 year half-life) compared to geologic times.

The chemistry of thorium has been fairly well investigated with much of the recent work generated by its consideration for use in breeder reactors to produce fissionable U^{233} . Several good reviews on thorium chemistry have been published (2-5). However, trace analysis of thorium has been less well covered and published literature on the isotopic analysis of microgram quantities of thorium is virtually

nonexistent. Much of the literature available on the trace analysis of thorium reports lower limits of ten to one-hundred parts per million for one to five gram samples (6-8). The thorium content of uranium ores, particularly those rich in Th^{230} and therefore of the highest interest, may be on the order of a few to less than one ppm. The samples which we wished to analyse, uranium ores and uranium mill tailings, presented an additional difficulty in that they were often chemically complex mixtures and difficult to work with in any significant quantity.

Ko, Robertson, Treibs and Weiler (9,10) at Hanford investigated several methods for the separation of thorium (including ion exchange, coprecipitation with non-isotopic carriers and solvent extraction techniques) and its determination (spectrophotometric and spectrographic) in trace quantities. They found that the commonly used spectrophotometric methods were not well suited for the analysis of the sample types encountered due to difficulties in the control of interfering substances. They succeeded in developing a spectrographic method which was relatively free from interferences and which had a sensitivity of 1 ppm for 1 gram samples. However, for the determination of the thorium isotopic ratio they relied on a thermal ionization mass spectrometer which required a minimum sample size of 30 micrograms.

Winning this quantity of purified thorium from many of the samples processed turned out to be no small task. It was found that the process necessary for the dissolution of ore samples and the extraction thorium from the solution could be carried out on a laboratory scale for samples up to about 1 gram with quite good efficiency. For larger samples the efficiency of the process either decreased rapidly with increasing sample size or required the use of prohibitively large equipment, reagent quantities and time.

The sample size necessary for the complete analysis for both total thorium and the thorium isotopic ratio was reduced to 1 gram or less through the development of highly sensitive radiochemical methods.

DISSOLUTION

The dissolution of the ore samples and the subsequent purification of thorium followed a similar procedure to that used by Ko, et.al. (9,10). (Fig. 4) A weighed amount of the finely ground sample was evaporated to near dryness several times in a 50 ml platinum crucible with a mixture of sulfuric and hydrofluoric acids, evaporated to dryness twice with nitric acid, the soluble residue dissolved in hot water and filtered into a 50 ml pyrex beaker. The crucible and filter is rinsed with hot 6 N hydrochloric acid. If any insoluble residues remain after this treatment the filter is ashed, treated with sulfuric and hydrofluoric acids and the residue fused with a small amount of sodium carbonate. The sodium carbonate melt is dissolved in dilute hydrochloric acid and filtered into the sample. Any residue which may remain is discarded.

SEPARATION AND PURIFICATION

The dissolved sample is diluted to about 60 ml with water and transferred to a lusteroid centrifuge cone, 10 mg of lanthanum is added as purified lanthanum nitrate solution, stirred and precipitated with HF. The fluoride precipitate is washed twice with a mixture of 1 N HF and 0.5N HNO_3 , dissolved with 75 ml of 1 N HCl and reprecipitated with HF. The precipitate is transferred to a small beaker with nitric acid and evaporated to dryness after adding about 3 ml of perchloric acid. The dry salts are dissolved by warming with 3 ml of 1 N HNO_3 and transferred to a 60 ml separatory funnel with 12 ml of water. The thorium is extracted into 20 ml of 10% (w/v) solution of 2-thenoyltrifluoroacetone (TTA) in benzene. The organic phase is washed three times with 10 ml portions of 0.2 N HNO_3 , and the thorium is back extracted with 20 ml of 2 N HNO_3 . The nitric acid solution is concentrated to 1 ml by evaporation and

aliquoted for subsequent analysis. The thorium recovery at this point is 80% to 90% determined with Th^{234} and Th^{230} tracers.

THORIUM-230

Thorium-230 was determined by absolute alpha counting using a General Electric Model GEI-32911 alpha scintillation counter. With samples evaporated as a spread source onto 1-1/2" diameter stainless steel planchets the measured counting efficient was 36.3%. Alpha disintegrations from isotopes other than Th^{230} were determined to be insignificant in all samples analysed by alpha energy analysis. The alpha energy analyser was of the 2π ionization chamber type coupled to a Radiation Counter Laboratories Model 20600, 256 channel pulse height analyser (Fig. 6). With the separation procedures employed, Th^{228} and Th^{232} would be the only alpha emitters expected to be present in the sample aliquot counted. Since the specific activity of Th^{230} is 2×10^5 times greater than that of Th^{232} and Th^{228} is a product of Th^{232} decay, the error generated by ignoring their alpha contribution is of the order of 0.1% or less with Th^{230} isotopic abundances of 1% or more. The sensitivity of the method is conservatively estimated at 2×10^{-4} micrograms of Th^{230} based on a 15 minute counting time. The combination of the chemical separation procedures and alpha energy analysis makes the method quite specific.

THORIUM-232

Thorium-232 was determined by neutron activation [REDACTED] and subsequent measurement of the Pa^{233} produced (Fig. 7) with a multi-channel gamma scintillation spectrometer.

The samples were prepared for irradiation by sealing them under vacuum in small high purity quartz ampoules about 4 mm in internal diameter and 30 to 40 mm long (Fig. 8). Approximately 20 ampoules can be packed into a single irradiation capsule which was then irradiated for [REDACTED] a total exposure of about 4×10^{18} nvt.

After a cooling period of about one week to allow the short-lived activation products to decay off, the ampoules were opened in a specially designed breaker box and the contents transferred to 5 ml volumetric flasks with a mixture of 10 N H_2SO_4 and 0.25 N HF . This acid system was chosen to solubilize the Pa^{233} and prevent its loss by hydrolysis and absorption on the walls of the sample container.

Duplicate thorium-232 standards were analysed with each batch of samples irradiated, obviating the need for precise neutron flux and cross-section measurements. The average difference between duplicate standards in three separate irradiations was 0.72%.

Protoactinium-233 was separated and purified when necessary by coprecipitation with lanthanum fluoride and subsequent extraction into diisobutylcarbinol (2,6-dimethyl-4-heptanol)(11,12).

The samples for gamma energy analysis were placed in 1 dram screw cap vials and the 0.31 Mev gammas from Pa^{233} counted in a 3" x 3" NaI (Tl) scintillation well crystal coupled to a Radiation Instrument Development Laboratory Model 34-9, 400 channel pulse height analyser. (Fig. 9).

Both the direct irradiation of ore samples followed by the separation of Pa^{233} from the irradiated mixture, and irradiation of separated thorium followed by gamma energy analysis for Pa^{233} with and without chemical separation of the Pa^{233} were tried with comparable results. The latter method was the one adopted for use since complications arising from handling the highly radioactive activation products produced by the direct irradiation of the sample matrix are avoided. The thorium separation procedure used was found to be sufficiently effective so that Pa^{233} was, with the exception of a single case, the only significant isotope detected in the gamma energy analysis of the irradiated samples after ten days decay. (Figures 10 and 11)

The sensitivity for the determination of Th^{232} is conservatively estimated at 1.2×10^{-4} micrograms. A good estimate for the sensitivity of any neutron activation procedure may be obtained from the equations shown in Figure 12. As can be seen, high values for the available neutron flux, activation cross-section and the counting efficiency enhance the sensitivity for activation analyses. For a large number of elements it can be shown that neutron activation is by far the most sensitive analytical method known. A review, "The Use of Neutron Activation in Analytical Chemistry" was published by G. W. Leddicotte, et. al., in the proceedings of the second United Nations International Conference on the Peaceful Uses of Atomic Energy, 1958.

RESULTS

To test the reliability of the radiochemical method developed, several uranium ore and uranium mill residue samples were analysed for total thorium and thorium isotopic ratios by both the radiochemical and emission spectrographic-mass spectrographic methods. The results from these tests are shown in Figure 13. As can be seen, good agreement was obtained between the two methods within the limits of experimental error.

SUMMARY

A sensitive analytical method was needed to determine the total thorium content and the thorium-230 isotopic abundance in a number of uranium ore and mill tailing samples available in the United States. A procedure was developed using absolute alpha counting to determine thorium-230 and neutron activation analysis to determine thorium-232. The method is highly specific with a sensitivity on the order of 10^{-10} grams for either isotope and has been shown to give reliable data for the various sample types of interest.

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COMPARISON OF SPECIAL ISOTOPES

ISOTOPE	HALF-LIFE	HEAT GENERATION, WATTS PER GRAM			
		ALPHA	BETA	GAMMA	$\alpha + \beta + \gamma$
SHORT HALF - LIVES					
THORIUM - 228 *	1.9y	153.2	3.2	9.1	161.0
POLONIUM - 210	138.0d	141.0	—	—	141.0
CURIUM - 242	163.0d	119.7	—	0.2	119.8
CERIUM - 144 (PURE) *	285.0d	—	20.25	1.25	20.9
CERIUM - 144 (RECOVERABLE) *	285.0d	—	4.7	0.3	4.8
PROMETHIUM - 147	2.6y	—	0.4	—	0.4
LONG HALF - LIVES					
URANIUM - 232 *	74.0y	4.17	0.07	0.21	4.34
STRONTIUM - 90 (PURE) *	28.0y	—	0.78	—	0.78
STRONTIUM - 90 (RECOVERABLE) *	28.0y	—	0.5	—	0.5
PLUTONIUM - 238	90.0y	0.54	—	—	0.54
TRITIUM	12.3y	—	0.34	—	0.34
KRYPTON - 85	10.4y	—	0.53	0.01	0.53
RADIUM - 226 *	1620.0y	0.15	0.004	0.03	0.17

* INCLUDES OUTPUT OF RADIOACTIVE DAUGHTERS

FIGURE 1

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RADIOACTIVE DECAY OF U-232

* 7.7 GRAMS Th-228 PER YEAR FROM STORAGE
OF ONE Kg U-232

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U-232 AND Th-228 PRODUCTION

FIGURE 3

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DISSOLUTION OF ORE SAMPLES

FIGURE 4

THORIUM SEPARATION AND PURIFICATION

FILTRATE FROM ORE DISSOLUTION OR AQUEOUS SAMPLE

DILUTE TO 60ML IN A LUSTEROID CENTRIFUGE TUBE WITH NITRIC ACID AND WATER SO THAT THE FINAL ACID CONCENTRATION IS BETWEEN $2N$ AND $6N$. ADD 10 MG OF La^{+++} CARRIER. PRECIPITATE WITH 5 - 6 ML OF HYDROFLUORIC ACID. CENTRIFUGE AND DISCARD SUPERNATE.

PRECIPITATE

WASH TWO TIMES WITH $1N$ HF - $0.5N$ HNO_3 SOLUTION. CENTRIFUGE AND DISCARD SUPERNATE EACH TIME. DISSOLVE PPT. WITH 75 ML OF $1N$ HCL, ADD 5 - 6 ML OF HF, CENTRIFUGE AND DISCARD SUPERNATE.

PRECIPITATE

TRANSFER WITH HNO_3 TO A 50 ML BEAKER, ADD 3 ML OF $HClO_4$ AND EVAPORATE TO DRYNESS. DISSOLVE RESIDUE WITH 3 ML OF $1N$ HNO_3 , TRANSFER TO A 60 ML SEP. FUNNEL WITH 12 ML OF WATER. ADD 20 ML OF 10% THENOYLTRIFLUOROACETONE (TTA) IN BENZENE SOLUTION AND SHAKE 20 MINUTES. DISCARD AQUEOUS PHASE.

ORGANIC PHASE

WASH 3 TIMES WITH 10 ML PORTIONS OF $0.2N$ HNO_3 . DISCARD WASHES EACH TIME. STRIP WITH 20 ML OF $2N$ HNO_3 , FOLLOWED BY 10 ML OF $2N$ HNO_3 . DISCARD ORGANIC PHASE.

AQUEOUS PHASE

CONCENTRATE AND PLACE IN A 1 ML VOLUMETRIC FLASK. ALPHA COUNT ALIQUOT FOR THORIUM-230 DETERMINATION. SEAL ALIQUOT FOR THORIUM-232 DETERMINATION IN A QUARTZ IRRADIATION AMPOULE.

FIGURE 6

Figure 7

FIGURE 8

FIGURE 9

Pd²³³ GAMMA ENERGY SCANS

Figure 10

Figure 11

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CALCULATION OF SENSITIVITY OBTAINABLE

BY NEUTRON ACTIVATION ANALYSIS

$$A = \frac{W N \phi \sigma (1 - e^{-\lambda t}) \lambda E_p E_c}{M},$$

$$W' = \frac{M A'}{N \phi \sigma (1 - e^{-\lambda t}) \lambda E_p E_c}$$

where: A = The activity of the radionuclide produced in a time, t, after the start of the irradiation.

W = weight of the element taken for analysis.

M = Atomic weight of the element being determined.

N = 6.023×10^{23} .

ϕ = The neutron flux (n / cm² / sec.).

σ = The activation cross section (cm²).

λ = The decay constant ($0.693 / T_{1/2}$, where $T_{1/2}$ is the half-life of the radionuclide produced.

E_p = Efficiency of chemical separations used.

E_c = Radiation counting efficiency.

W' = Weight of element required to produce A' activity of radionuclide.

Figure 12

THORIUM AND THORIUM-230 ISOTOPIC ABUNDANCE
BY RADIOCHEMICAL AND EMISSION SPECTROGRAPHIC
PLUS MASS SPECTROGRAPHIC ANALYSIS

<u>SAMPLE</u>	<u>TOTAL THORIUM</u>		<u>PERCENT THORIUM-230</u>	
	<u>R.A.</u>	<u>E.S.</u>	<u>R.A.</u>	<u>M.S.</u>
A	6.3 x 10 ⁵	4.3 x 10 ⁵	0.34	0.33
B	1.19	1.09	2.14	2.32
C	62.4	72.5	4.47	4.71
D2	22	16	0.84	--
D3	3.4	3.9	1.9	--
D4	21.2	21.5	0.25	--
D5	55	65	0.08	--
D6	3.3	3.3	2.0	--
D8	8.9	7.6	0.44	--
D10	10	10	0.70	--
E	159	151	2.58	2.28
F	2.78	3.0	0.26	0.30
G	11.3	8.0	0.08	--

NOTE: TOTAL THORIUM IS IN UNITS OF MICROGRAMS/GRAM.

R.A.: DETERMINED BY RADIOCHEMICAL ANALYSES.

E.S.: DETERMINED BY EMISSION SPECTROGRAPHIC ANALYSIS.

M.S.: DETERMINED BY MASS SPECTROGRAPHIC ANALYSIS.

FIGURE 13