ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

THE RATIO OF THE (n, γ) TO $(n, 2n)$ CROSS SECTION FOR
THORIUM-232 BOMBARDED WITH FISSION NEUTRONS

by

R. A. Hasse and P. Kafalas

Chemical Engineering Division

July 1957

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
Introduction.	1
Theoretical Background.	3
Description of Apparatus and Method	4
Experimental Method	4
Method of Irradiation	4
Calibration and Description of Instruments	6
Analytical Procedures.	8
Results and Discussion	10
Appendix I - Analytical Procedures	18
Gravimetric Determination of Thorium	18
Determination of Thorium-231	18
Determination of Protactinium-233	20
Paper Chromatographic Method	20
Direct Method	21
Appendix II - Calculations	22
Calibration of Neptunium-237 (Protactinium-233) Standard . . .	22
Thorium-231 Calibration	22
Protactinium-233 and Thorium-231 Content	23
In-Pile Decay Correction for Thorium-231	23
References	25

THE RATIO OF THE (n, γ) TO $(n, 2n)$ CROSS SECTION FOR
THORIUM-232 BOMBARDED WITH FISSION NEUTRONS

ABSTRACT

Thorium-232 was exposed to an unmoderated neutron flux produced by uranium-235 fission. The ratio of the integrated cross sections for the (n, γ) and $(n, 2n)$ reactions $[\bar{\sigma}(n, \gamma)/\bar{\sigma}(n, 2n)]$ was determined to be 14.0 .

ANL-5761

1

THE RATIO OF THE (n, γ) TO $(n, 2n)$ CROSS SECTION FOR THORIUM-232 BOMBARDED WITH FISSION NEUTRONS

by

R. A. Hasse and P. Kafalas

INTRODUCTION

Thorium-232 has been considered for many years as a potential source of fissionable material. The addition of thorium directly to a reactor fuel makes possible the gradual conversion of thorium-232 to the thermally fissionable isotope uranium-233. Thorium-232 has also been considered as a possible blanket material for fast breeder reactors. However, a limiting factor in its usefulness as a fertile material is the ratio of the U^{232}/U^{233} built up. The fission cross section of uranium-232 for thermal neutrons is about one-tenth that of uranium-235, making it less useful as a reactor fuel.

Uranium-232 contamination is important for a second reason.⁽¹⁾ After the fuel rod or blanket material has been reprocessed, the uranium will contain uranium-232 as a contaminant. Uranium-232 has a half-life of 74 years. Its decay chain contains many short-lived alpha emitters, as well as beta and gamma emitters. The alpha activity of the purified fuel will increase with time because of the growth of the uranium-232 daughters.

Figure 1 summarizes the events leading to the formation of uranium-233 and uranium-232. The rate of disappearance of any isotope in the scheme, neglecting its rate of formation, is given by the sum of the decay rate and the rate of reaction:

$$(1) \quad -\frac{dN}{dt} = N(\lambda + \phi\sigma_a) \quad ,$$

where N is the amount of the given species present, ϕ is the flux, σ_a is the cross section for neutron absorption, and λ is the decay constant for the species. Table 1 summarizes the ratio $\lambda/\phi\sigma_a$ for each isotope of interest in the scheme presented in Figure 1. This ratio determines which of the processes, decay or absorption or both, is important in the disappearance of a given isotope. A flux of 10^{12} n/sec/cm² was assumed for the calculations. It can be seen from Table 1 that decay is always far more likely to occur than capture, i.e., $\lambda \gg \phi\sigma_a$, except for thorium-232 and protactinium-231. Therefore, the primary sources of uranium-232 will be the two schemes

and

FIGURE 1
FORMATION OF U-233
AND U-232 FROM Th-232

Table 1

RATIO OF DECAY TO NEUTRON ABSORPTION
RATE FOR ISOTOPES OF FIGURE 1

Isotope	$\lambda (\text{sec}^{-1})$	σ_a	$\lambda / \sigma_a \phi$
Th ²³¹	7.69×10^{-6}	100 mb ↓	7×10^7
Pa ²³¹	6.9×10^{-13}		7×10^0
Pa ²³²	6.07×10^{-6}		6×10^7
Th ²³³	4.95×10^{-4}		5×10^9
Pa ²³³	2.95×10^{-6}		3×10^7
Th ²³²	1.58×10^{-18}		2×10^{-5}

The two primary reactions that occur when thorium-232 is exposed to a fission neutron spectrum are $\text{Th}^{232} (n, \gamma) \text{Th}^{233}$ and $\text{Th}^{232} (n, 2n) \text{Th}^{231}$. The object of this work is to determine the ratio of the integrated cross sections for the two reactions. This ratio may be defined as

$$(2) \quad R = \frac{\bar{\sigma}(n, \gamma)}{\bar{\sigma}(n, 2n)},$$

where $\bar{\sigma}$ refers to the integrated cross section over the entire energy range of the fission neutrons. The quantity R is valuable in estimating the relative amounts of uranium-233 and uranium-232 formed in the thorium breeder material.

THEORETICAL BACKGROUND

When thorium-232 is irradiated in a fission neutron flux, the following reactions may occur: (n, γ) , $(n, 2n)$, (n, f) , (n, α) , and (n, p) . Only the first two are treated here.

The cross section for the (n, γ) reaction may be approximated, up to the intermediate neutron energy range (500 kev), by the $\frac{1}{v}$ law:

$$(3) \quad \sigma(n, \gamma) = \sigma^* \frac{v^*}{v}$$

Here, σ^* is the known (n, γ) cross section at a known neutron velocity v^* , and v is the neutron velocity for which one wishes to determine $\sigma(n, \gamma)$. Above the intermediate energy range, the $\frac{1}{v}$ law may be replaced by the $\frac{1}{E}$ law:

$$(4) \quad \sigma(n, \gamma) = \sigma^* \frac{E^*}{E}$$

Here, σ^* is the known (n, γ) cross section at a known neutron energy E^* , and E is the energy for which one wishes to determine $\sigma(n, \gamma)$.

An equation of the form

$$(5) \quad \sigma(n, 2n) = \frac{\sigma_c (E - E_{th})^2}{2 T^2}$$

may be assumed to describe the variation of $\sigma(n, 2n)$ with neutron energy.⁽²⁾ Here, σ_c is defined as the cross section for the formation of the compound nucleus ($\text{Th}^{232} + n$), E_{th} is the threshold energy for the reaction, E is the energy for which $\sigma(n, 2n)$ is to be determined, and T is the nuclear temperature of the product nucleus.

Actually, σ_c and T are also functions of the neutron energy. A value for T may be approximated by means of the equation

$$(6) \quad T = \left(\frac{E}{a} \right)^{1/2},$$

where a is a constant.⁽³⁾ Values for σ_c may be obtained from tables or graphical data.⁽⁴⁾

The equations given above, combined with data for the uranium-235 fission neutron energy spectrum, such as that given by L. Cranberg *et al.*,⁽⁵⁾ enable one to estimate a value for $\overline{\sigma}(n, \gamma) / \overline{\sigma}(n, 2n)$ (see Results and Discussion).

The ratio, $\bar{\sigma}(n, \gamma)/\bar{\sigma}(n, 2n)$, may be equated to $N_{\text{Th}233}/N_{\text{Th}231}$, where N refers to the total number of thorium-233 or thorium-231 atoms formed during any given irradiation of thorium-232. Thus,

$$(7) \quad \frac{\bar{\sigma}(n, \gamma)}{\bar{\sigma}(n, 2n)} = \frac{N_{\text{Th}233}}{N_{\text{Th}231}} .$$

The ratio $\frac{N_{\text{Th}233}}{N_{\text{Th}231}}$ is what was actually determined by this work.

DESCRIPTION OF APPARATUS AND METHOD

Experimental Method

The thorium-232 was irradiated in the form of thorium oxide. Each sample contained approximately one-half gram of the oxide. After irradiation the samples were dissolved in concentrated hydrochloric acid and made into stock solutions from which all samples for analysis were taken.

The actual values determined were the amounts of thorium-233 and thorium-231 formed during the irradiation period. It was shown before that the ratio $N_{\text{Th}233}/N_{\text{Th}231}$ is equal to $\bar{\sigma}(n, \gamma)/\bar{\sigma}(n, 2n)$.

The amount of thorium-231 contained in the sample was determined by a direct analysis for thorium-231 (25.0-hr half-life). The thorium-233 (23.3-min half-life) was allowed to decay to protactinium-233 (27.2-day half-life). An analysis for protactinium-233 was then made. Since, for such a short irradiation time, the only method for the formation of protactinium-233 is the decay of thorium-233, the amount of protactinium-233 found may be set equal to the amount of thorium-233 formed.

Method of Irradiation

The flux used to irradiate the thorium-232 was that produced by uranium-235 fission. This flux was obtained by using an enriched uranium converter thimble (see Figure 2) and a neutron flux supplied by the ANL research reactor, CP-5. The uranium in the converter thimble was enriched to ten per cent uranium-235.

The sample of thorium-232, sealed in quartz tubing, was placed in the converted thimble. The thimble was then lowered into a $4\frac{3}{4}$ -in. diameter vertical hole, approximately 5 ft 6 in. below the top, in CP-5. This is in the graphite region. The thimble temperature was monitored by a thermocouple attached to the outside of the converter thimble. The temperature of the thimble was allowed to vary from 200° to 300°C. Temperature adjustments were made by raising or lowering the thimble. Each irradiation lasted for about four hours at a reactor power of 2 megawatts.

FIG. 2
ENRICHED URANIUM CONVERTER THIMBLE
AND GRAPHITE PLUG ASSEMBLY

BORON CARBIDE

URANIUM METAL CUP

ALUMINUM

It was possible to insert or remove the converter thimble with the pile in operation by means of the external shielding shown in Figure 3. A movable boral shutter lay directly over the hole on top of the pile floor, except when the thimble was being inserted or removed. The thimble was raised or lowered by means of a pulley supported by a superstructure above the shielding (not shown in Figure 3).

As shown in Figure 2, any possible leakage of thermal neutrons from the pile flux through the uranium thimble, or through the cap of the thimble, which contains no uranium, is prohibited by a boron carbide lining in the thimble. This insures a pure uranium-235 fission neutron spectrum, with possibly some of the slower neutrons removed by the boron carbide. A graphite plug attached to the cap of the thimble prevents any fast neutrons produced by the uranium-235 fission from escaping up the hole and passing through the boral shutter.

Calibration and Description of Instruments

A well-type scintillation counter was calibrated to obtain an absolute disintegration rate of thorium-231. The counter used was a multi-purpose counter ANL Model MPC-1 with a well-type NaI(Tl) crystal. The counter was calibrated with thorium-231 separated quantitatively from uranium-235 by means of an anion exchange resin (Dowex Ag 2-X10, 200-400 mesh).

A sample of uranium-235 was converted to uranous uranate (U_3O_8) by a method described by J. H. Patterson.⁽⁶⁾ The uranous uranate was then allowed to stand for several weeks to allow the first daughter, thorium-231, to grow into a state of secular equilibrium. A sample of the uranous uranate was then weighed and dissolved in 8 N hydrochloric acid and diluted to 10 ml in a volumetric flask. One-milliliter aliquots of this solution were then forced through an anion exchange column with nitrogen gas. The column was washed with 8 ml of 8 N hydrochloric acid. The uranium-235 remained on the column. The effluent was then diluted to 10 ml in a volumetric flask. Three-milliliter aliquots of the effluent were used to calibrate the counter. Data and calculations may be found in Appendix II. The calibration factor, the reciprocal of the counting efficiency, was determined as 8.12 disintegrations per count recorded.

A quantitative determination of protactinium-233 was obtained by using a 4 in. x 4 in. NaI(Tl) crystal and an Argonne 256-channel pulse height analyzer. The crystal was calibrated with protactinium-233 in secular equilibrium with neptunium-237.

A sample of neptunium-237 in secular equilibrium with its first daughter, protactinium-233, was deposited on a platinum disc. The amount of neptunium-237 present was determined by low-geometry alpha counting. The disc and sample were then covered with Saran-wrap and sealed on the

FIGURE 3
SHIELDING AND REMOTE HANDLING
ARRANGEMENT EMPLOYED AT THE PILE.

back of the disc with scotch tape. The sample, used as a standard, was then placed face down on a 4 in. x 4 in. NaI(Tl) crystal. Using the Argonne 256-channel pulse height analyzer, the γ -ray spectrum was printed out by a Bristol Recorder. The area under the peak at 320 kev was used as a standard reference (see Figure 4). This peak is due entirely to the protactinium-233 present in the standard. It should be mentioned that this peak is not due to a single γ ray, but rather to several of them. However, the peak is well defined and no difficulties were encountered in using it as a reference standard. Samples to be analyzed for protactinium-233 were mounted in the same manner as the standard, confining the sample area to match that of the standard. A simple comparison of the area under the 320-kev peak for the unknown sample to that of the standard yielded the protactinium-233 content of the unknown. The standard sample used contained 1.547×10^5 dpm of protactinium-233. Calculations may be found in Appendix II.

The calibration of the 256-channel analyzer was not constant from day to day. This was due primarily to electronic irregularities, which were overcome by counting the standard each time a sample was run. Results obtained in this manner were reproducible within one per cent.

Analytical Procedures

The samples of irradiated thorium-232 were dissolved in concentrated hydrochloric acid with the addition of a few drops of very dilute fluosilicic acid. This solution was then diluted to 25 ml in a volumetric flask. All samples taken for analysis were taken from this stock solution. The thorium content was determined by a gravimetric and a spectrophotometric method. The deviation between the results obtained by the two methods was two per cent. All detailed analytical methods are presented in Appendix I.

Gravimetric Method

The thorium was precipitated from a hydrochloric acid solution by the addition of a saturated solution of oxalic acid. The oxalate was collected on a filter circle and ignited to thorium oxide at 900° C. The oxide was then weighed to determine the thorium content of the sample solution.

Thoron Method⁽⁷⁾

The compound known as thoron reagent [1-(0-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid] forms a stable colored complex with thorium. This complex is red in hydrochloric acid and will precipitate when the concentration of thorium exceeds 50 $\mu\text{g/ml}$.

A sample of appropriate thorium content was taken and fumed to dryness with a mixture of nitric and perchloric acids to remove any organic

9

material. The residue was taken up in a hydrochloric acid and the organic reagent added. The solution was then diluted to volume and the optical density determined versus a reference solution of the organic reagent.

Protactinium Analysis

Protactinium-233 was determined by two methods. In the first method, a sample of the stock solution was taken, and a known amount of protactinium-231 tracer was added. The thorium was precipitated by adding concentrated hydrofluoric acid. The supernate was then evaporated to one drop. The protactinium was isolated by paper chromatography.⁽⁸⁾ The paper containing the protactinium was destroyed by fuming to dryness with a nitric-perchloric acid mixture. The protactinium was then taken up in concentrated hydrofluoric acid and deposited on a platinum disc in the same manner as the counting standard (see Calibration of Instruments). The alpha activity (protactinium-231) was determined to obtain the chemical yield. The sample was then covered with Saran-wrap and the protactinium-233 content was determined.

The second method for protactinium involved no separations. A sample of the stock solution was deposited directly in the same manner as the counting standard. A sample of unirradiated thorium-232 of approximately the same size was also deposited on a platinum disc in the same manner. The protactinium-233 content of the irradiated thorium-232 was determined using the unirradiated thorium-232 as a blank. The two methods gave results that differed by less than two per cent.

Thorium-231 Analysis

The thorium was separated from protactinium and any fission product activity by a modification of a method given by R. J. Prestwood.⁽⁹⁾ A sample of unirradiated thorium-232 was run through the separation at the same time. This thorium-232 blank was used to correct for the activity due to thorium-232 and its daughters in the sample containing the thorium-231. The total thorium concentration in the purified solutions was determined by both the gravimetric and thoron methods given above. Three-milliliter aliquots of the purified solutions were counted in the calibrated well-type scintillation counter to determine the thorium-231 activity present.

RESULTS AND DISCUSSION

By means of the analytical methods given in the previous section, the amounts of thorium-233 and thorium-231 present when the samples were removed from the pile were determined. Two samples were used, each from a separate irradiation. The results are summarized in Table 2. The results from the two samples agreed within four per cent.

Table 2

RESULTS OF EXPERIMENTAL DETERMINATION
OF $\bar{\sigma}(n, \gamma)/\bar{\sigma}(n, 2n)$

Sample No.	Atoms Pa^{233} per mg ThO_2	Atoms Th^{231} per mg ThO_2	$\frac{\bar{\sigma}(n, \gamma)}{\bar{\sigma}(n, 2n)}$
1	6.06×10^8	4.41×10^7	13.74
2	5.41×10^8	3.81×10^7	14.20

It was necessary to apply an in-pile decay correction for the amount of thorium-231 built up. This was accomplished by means of the equation

$$(8) \quad N_B = \frac{N_B^* \lambda_B t}{1 - e^{-\lambda_B t}},$$

where N_B^* is the number of atoms of the isotope present at the end of the irradiation, N_B is the total number of atoms produced during the irradiation, λ_B is the decay constant, and t is the length of time the sample was in the pile. The correction is negligible for protactinium-233. The calculations may be found in Appendix II.

The decay curves for the two separated isotopes are given in Figures 5 and 6. The curve for protactinium-233 gives a straight line and a half-life of 27.2 days. After 30 to 40 hours of counting, the decay curve for thorium-231 begins to deviate from a straight line, appearing to be a composite of the thorium-231 activity and a long-lived activity. After following the activity for 700 hr it was found that the contaminating activity was constant. No evidence for a contaminating isotope could be found by a γ -ray spectrum taken 600 hr after the sample was removed from the pile.

The possible events responsible for another isotope would be either (n, α) , (n, f) or (n, p) reactions on thorium-232 or (n, γ) , $(n, 2n)$, (n, p) , or (n, α) reactions on some impurity in the thorium. The (n, α) reaction on thorium-232 would lead to thorium-229 with a 7300-year half-life. The Q for the $\text{Th}^{232}(n, \alpha)\text{Ra}^{229}$ reaction is +8.54 Mev and the coulomb barrier height is about 30 Mev. The (n, p) reaction would lead to Ac^{232} , which has never been observed.

A spectrographic analysis of the thorium oxide showed the only contaminant present in large enough quantities to give any measurable amount

13

of reaction leading to active products was aluminum (3000 ppm). None of the possible reactions of aluminum with neutrons could lead to an isotope that would cause the observed effects.

Another explanation for the bending of the thorium-231 decay curve would be attribution to faulty thorium determinations for the sample solutions. Thus, if insufficient correction was made for the thorium-232 present, the curve would bend as observed. However, it would require an error of about 30 per cent in the thorium yields to produce the results observed after 40 hours of counting. Since the amount of thorium was checked by two independent methods, this cause must be ruled out.

Another possible explanation is the instability of the solutions. After the first 30 to 40 hours of counting, the sample solutions began to show a residue on the bottom of the container. These solutions contained only thorium and a small amount of dissolved mesityl oxide. The residue was a brown sediment, probably decomposed mesityl oxide. If this sediment contained thorium, the counting efficiency would be increased. However, upon examination, the amount of activity found in the sediment was much too low to explain the deviation observed in the decay curve.

It is possible that a combination of a long-lived activity and a small error in the thorium determinations caused the results observed. The contribution of a very small error in the thorium determinations would be unnoticeable until after a long period of counting. After several hundred hours the fraction of the total activity contributed by thorium-232 and its daughters becomes quite large due to the growth of the daughter activities (see Figure 7) and the disappearance of the thorium-231. Thus, a very small error in the total thorium determinations could cause a fairly large error in the counting rates after an extended period of time.

The thorium-231 decay curve was treated as though it consisted of two distinct activities. The long-lived component was treated as a constant activity for the length of this experiment. This treatment yielded a half-life of 25.0 hours for thorium-231. The zero time on the decay curve shown in Figure 6 corresponds to 23.75 hours from the time the sample was removed from the pile. The activity present at the time the sample was removed from the pile was calculated from the activity present at the zero time on the decay curve using the equation

$$(9) \quad N = N_0 e^{-\lambda t}$$

A rough theoretical approximation for $\frac{\bar{\sigma}(n, \gamma)}{\bar{\sigma}(n, 2n)}$ was made by using equations 3, 4, 5, and 6 and data for the uranium-235 fission neutron energy spectrum given by L. Cranberg, *et al.*⁽⁵⁾ The data given by Cranberg was plotted as a linear function, energy versus the per cent of total neutrons at

15

a given energy. This curve was then divided into narrow energy increments. An average energy and neutron velocity for each increment was then estimated. Using the equations given before, approximate cross sections for the (n, γ) and $(n, 2n)$ reactions were calculated for each increment. These cross sections were then multiplied by the fraction of the total area under the curve contained within the given increment. The sum of these products was taken to be $\bar{\sigma}$, i.e., the integrated cross section with respect to the uranium-235 fission neutron spectrum. A value of approximately 10 was obtained for the ratio $\bar{\sigma}(n, \gamma)/\bar{\sigma}(n, 2n)$. This indicates a fair agreement between experiment and theory. Values for $\bar{\sigma}$ could not be obtained by this experiment because the total flux to which the samples were exposed was not determined.

As was shown before, the two important sources of uranium-232 (see Figure 1) are the schemes

and

This indicates the future work that might be done. A determination of the cross sections for the reactions $\text{Pa}^{231} (n, \gamma) \text{Pa}^{232}$ and $\text{U}^{233} (n, 2n) \text{U}^{232}$ for a flux similar to the one used in this experiment would allow a good approximation to be made of the ratio of uranium-232/uranium-233 built up. One might also wish to determine the absolute cross sections for the reactions treated in this experiment rather than the ratio of the cross sections.

ACKNOWLEDGEMENTS

We wish to acknowledge the aid of Dr. C. E. Crouthamel with many analytical problems and also the assistance of Dr. D. C. Stuepegia in operating the Argonne 256-channel pulse height analyzer. We wish to acknowledge also the assistance of C. Gatrousis, R. Heinrich, and B. Tani in the irradiation of the samples. Acknowledgement should go to A. Madson for his help in the thorium determinations and to Dr. J. C. Hindman for supplying the neptunium-237.

APPENDIX I

ANALYTICAL PROCEDURESGravimetric Determination of Thorium

1. Approximately 20 mg of thorium in solution was placed in a 50-ml centrifuge tube, and concentrated ammonium hydroxide was added slowly until the hydrated thorium hydroxide just began to precipitate. One drop of concentrated hydrochloric acid was added to dissolve the precipitate.

2. The solution was boiled for one minute and an excess of a saturated solution of oxalic acid was added. The precipitate was then allowed to stand overnight.

3. The thorium oxalate was collected on a number 42 Whatman 7/8-in. filter circle, using a chimney apparatus. The filter circle and precipitate were then placed in a Coors 000 crucible and ignited in a furnace at 900° C for 30 min. The residue was weighed as thorium oxide (ThO_2).

Thorium-231

Five principal steps were used to decontaminate the thorium.⁽⁹⁾ A fluoride precipitation removed most of the protactinium. A thorium iodate precipitation effected the removal of the rare earths. A thorium oxalate precipitation left zirconium in the supernate. An anion exchange column removed zirconium, iron, and uranium, as well as any remaining protactinium. A mesityl oxide extraction gave decontamination from the alkali and alkaline earth metal ions (including radium), lanthanum, and cerium.

Carriers:

Bismuth - 10 mg Bi/ml	$\text{Bi}(\text{NO}_3)_3$ in dilute nitric acid.
Zirconium - 10 mg Zr/ml	ZrOCl_2 in water.
Extraction solution	2.4 <u>M</u> $\text{Al}(\text{NO}_3)_3$ in 1.2 <u>M</u> HNO_3 .

1. Approximately 0.1 g of thorium in a hydrochloric acid solution was placed in a Lusteroid centrifuge tube. Thorium fluoride was then precipitated by slowly adding an excess of concentrated hydrofluoric acid. The mixture was centrifuged, and the precipitate was washed with dilute hydrofluoric acid. The supernate and all washings were discarded.

2. The thorium fluoride was dissolved in a mixture of aluminum nitrate and nitric acid. The hydrated thorium hydroxide was then precipitated with an excess of concentrated ammonium hydroxide. The precipitate was washed four or five times with concentrated ammonium hydroxide to remove all the aluminum. The supernate and washings were discarded.

3. The thorium hydroxide was dissolved in 10 ml of concentrated nitric acid. Fifteen milliliters of water and 10 ml of 1 M iodic acid were then added. The thorium iodate precipitate was centrifuged and washed with a solution 4 M in nitric acid and 0.25 M in iodic acid. The washings were discarded.

4. Two milliliters of concentrated hydrochloric acid were added to the precipitate and heated with stirring over an open flame until the precipitate dissolved and the solution boiled. The solution was then diluted to 10 ml. A few drops of hydriodic acid were added to release the iodine from the iodate ion. The free iodine was then extracted with four carbon tetrachloride extractions of 250 ml each.

5. Five drops of the zirconium holdback carrier and 10 ml of a saturated oxalic acid solution were added to the aqueous fraction and boiled for one minute. The oxalate precipitate was centrifuged and the supernate discarded.

6. Two milliliters of concentrated nitric acid and 100 mg of potassium chlorate were then added to the thorium oxalate. The mixture was heated cautiously to boiling to destroy the oxalate. The solution was then diluted to 15 ml and thorium hydroxide precipitated with an excess of concentrated ammonium hydroxide. The precipitate was centrifuged and the supernate discarded.

7. The precipitate was dissolved in 5 ml of concentrated hydrochloric acid. The solution was then transferred to an anion exchange column (Dowex Ag - 2 x 10, 200-400 mesh) which had been previously washed with concentrated hydrochloric acid. The solution was forced through the column in about 5 min with nitrogen gas. The column was flushed with 5 ml of concentrated hydrochloric acid and the effluents were combined. An excess of concentrated ammonium hydroxide was added to the effluent and the precipitate was centrifuged. The supernate was discarded.

8. The precipitate was dissolved with 2 ml of 6 M nitric acid. A ten-milliliter portion of the aluminum nitrate-nitric acid extraction solution was then used to transfer the solution to a 60-ml separatory funnel. Twenty milliliters of mesityl oxide were added and the mixture was agitated for 45 sec. The water layer was discarded. The organic fraction was then washed with two 5-ml portions of the extraction solution. The thorium was back-extracted into two 10-ml portions of water. The organic phase was discarded.

9. The hydroxide was precipitated with an excess of concentrated ammonium hydroxide. The supernate was discarded after centrifugation. The precipitate was dissolved with 15 drops of concentrated hydrochloric acid, and 5 drops of the bismuth carrier were added. The solution was then

diluted to 10 ml and saturated with hydrogen sulfide. The mixture was filtered through a number 40 filter paper and the bismuth sulfide precipitate discarded. Thorium hydroxide was then precipitated with concentrated ammonium hydroxide.

10. The precipitate was dissolved in concentrated hydrochloric acid and diluted to 10 ml in a volumetric flask. A three-milliliter aliquot of this solution was counted in the calibrated well-type scintillation counter to determine the thorium-231 content. The thorium blank was counted in the same manner and appropriate corrections were made for the thorium-232 activity present in the sample containing the thorium-231.

11. A five-milliliter portion of the above solution was used to determine the thorium content by the gravimetric method given above. A second sample of appropriate size was used to determine the thorium content by the thoron method.⁽⁷⁾

Protactinium-233

Paper Chromatographic Method⁽⁸⁾ The protactinium was separated from the thorium by precipitating thorium fluoride. The protactinium was then separated from other activities by a chromatographic method. A protactinium-231 tracer was used to determine the chemical yield.

1. One milliliter of the stock solution was placed in a Lusteroid centrifuge tube and a known amount of protactinium-231 tracer was added (~ 1000 c/m on a platinum disc). The thorium was precipitated as the fluoride by slowly adding an excess of concentrated hydrofluoric acid (very little protactinium will carry if the acid is added slowly). The mixture was centrifuged and the precipitate discarded.

2. The supernate was evaporated to one drop. The drop was then placed about 2 in. from one end of a strip of Whatman-3MM chromatography paper, 45 cm long and 15 mm wide. This end of the paper was placed in a concentrated hydrofluoric acid solution (being careful not to allow the spot containing the supernate to touch the solution). The hydrofluoric acid was allowed to rise up the paper about 30 cm. The paper was then removed and dried under a heat lamp.

3. The paper was cut into narrow horizontal strips. Each strip was then counted in a well-type scintillation counter to locate the protactinium which was just behind the solvent boundary.

4. The strips containing the protactinium were dissolved in a nitric-perchloric acid mixture and fumed to dryness. The protactinium was then picked up with one or two drops of concentrated hydrofluoric acid.

5. The protactinium was deposited on a platinum disc in the same manner as the counting standard (see Calibration of Instruments). The alpha activity (protactinium-231) was determined with a 2π α -proportional counter to determine the chemical yield. The sample was then covered with Saran-wrap and the protactinium-233 activity determined by the Argonne 256-channel pulse height analyzer with a 4 in. x 4 in. NaI(Tl) crystal.

Direct Method An aliquot of the stock solution was deposited directly in the same manner as the counting standard. A sample of unirradiated thorium of a similar size was mounted in the same way. The sample containing the protactinium-233 was counted and the thorium blank was used as a correction.

APPENDIX II

CALCULATIONSCalibration of Neptunium-237 (Protactinium-233) Standard

A sample of neptunium-237 was deposited on a platinum disc. The amount of neptunium present was determined by low-geometry alpha counting.⁽¹⁰⁾ The disintegration rate R was calculated from the relationship

$$R = \frac{A}{G_p (G_s/G_p)}$$

The quantity G_p is the geometry (solid angle for a point source for the particular arrangement employed), G_s/G_p is a correction for the deviation from a point source, and A is the counting rate observed.

Data and Results:

$$\begin{aligned} A &= 81.505 \text{ c/m} \\ G_p &= 0.0005295 \\ G_s/G_p &= 0.9952 \\ R &= 1.547 \times 10^5 \text{ dpm.} \end{aligned}$$

$$\text{Decay constant for protactinium-233} = 1.771 \times 10^{-5} \text{ min}^{-1}$$

$$N_{Pa} = \frac{1.547 \times 10^5}{1.771 \times 10^{-5}} = 8.735 \times 10^9 \text{ atoms}$$

Thorium-231 Calibration

Thorium-231, in secular equilibrium with uranium-235, was separated from a weighed amount of uranium-235 and was counted in a well-type scintillation counter. The calibration factor was defined as the number of disintegrations per count recorded.

$$\text{Disintegration Rate of Th}^{231} \text{ Standard} = 1.596 \times 10^4 \text{ dpm}$$

$$\text{Activity Observed} = 1.966 \times 10^3 \text{ c/m}$$

$$F = \frac{1.596 \times 10^4}{1.966 \times 10^3} = 8.12 \text{ dpc}$$

Protactinium-233 and Thorium-231 Content

The amount of protactinium and thorium isotopes present when the sample was removed from the pile was calculated by means of the equation

$$N = N_0 e^{-\lambda t}$$

Here, N is the number of atoms present at a given time, N_0 is the number of atoms present at the time the sample left the pile, λ is the decay constant, and t is the time elapsed.

Sample Number 1

Number of Th^{231} atoms found = 1.82×10^7 atoms/mg ThO_2

$$\lambda = 2.77 \times 10^{-2} \text{ hr}^{-1}$$

$$t = 28.25 \text{ hr}$$

$$N_0 = 3.98 \times 10^7 \text{ atoms/mg ThO}_2$$

Number of Pa^{233} atoms found = 4.59×10^8 atoms/mg ThO_2

$$\lambda = 2.55 \times 10^{-2} \text{ day}^{-1}$$

$$t = 10.88 \text{ days}$$

$$N_0 = 6.06 \times 10^8 \text{ atoms/mg ThO}_2$$

Sample Number 2

Number of Th^{231} atoms found = 1.78×10^7 atoms/mg ThO_2

$$\lambda = 2.77 \times 10^{-2} \text{ hr}^{-1}$$

$$t = 23.75 \text{ hr}$$

$$N_0 = 3.44 \times 10^7 \text{ atoms/mg ThO}_2$$

Number of Pa^{233} atoms found = 4.98×10^8 atoms/mg ThO_2

$$\lambda = 2.55 \times 10^{-2} \text{ day}^{-1}$$

$$t = 3.2 \text{ days}$$

$$N_0 = 5.41 \times 10^8 \text{ atoms/mg ThO}_2$$

In-Pile Decay Correction for Thorium-231

If no decay were to occur, the amount of a given species formed in a neutron flux is described by

$$N_B = \sigma N_A \phi t$$

where N_B is the species formed, N_A is the species from which N_B is formed, σ is the cross section for the reaction, ϕ is the flux, and t is the length of time the sample is in the flux. If decay of species B does occur during its formation, the amount present after an irradiation time t is given by

$$N_B^* = \frac{\sigma N_A \phi}{\lambda_B} \left(1 - e^{-\lambda_B t} \right) ,$$

where λ_B is the decay constant for species B. (11)

When one determines the amount of species B present at the end of an irradiation period, N_B^* is obtained. It is possible to determine N_B by using the relationship

$$\frac{N_B}{N_B^*} = \frac{\sigma N_A \phi t}{(\sigma N_A \phi / \lambda_B) (1 - e^{-\lambda_B t})}$$

or

$$N_B = \frac{N_B^* \lambda_B t}{(1 - e^{-\lambda_B t})}$$

This correction is negligible for protactinium-233.

Correction for Thorium-231:

Sample Number 1

$$N_B^* = 3.98 \times 10^7 \text{ atoms/mg ThO}_2$$

$$\lambda_B = 2.77 \times 10^{-2} \text{ hr}^{-1}$$

$$t = 4 \text{ hr}$$

$$N_B = 4.41 \times 10^7 \text{ atoms/mg ThO}_2$$

Sample Number 2

$$N_B^* = 3.44 \times 10^7 \text{ atoms/mg ThO}_2$$

$$\lambda_B = 2.77 \times 10^{-2} \text{ hr}^{-1}$$

$$t = 4 \text{ hr}$$

$$N_B = 3.81 \times 10^7 \text{ atoms/mg ThO}_2$$

REFERENCES

1. R. C. Feber, "Implications of the Uranium-232 Decay Chain Activity for the Processing of Irradiated Thorium and Recovered Uranium-232," KAPL-1271 (1955).
2. E. Segre, "Experimental Nuclear Physics," New York; John Wiley and Sons, Inc., 1953, Vol. 2, p. 354.
3. Ibid, p. 306.
4. H. Feshbach and V. F. Weisskopf, Phys. Rev., 76, 1550 (1949).
5. L. Cranberg, G. Frye, N. Nereson, and L. Rosen, Phys. Rev., 87, 662 (1956).
6. J. H. Patterson, "Manual of Special Materials Analytical Laboratory Procedures," ANL-5410 (1955).
7. P. F. Thomason, M. A. Perry and W. M. Byerly, Anal. Chem., 21, 1239 (1949).
8. C. E. Crouthamel and A. J. Fudge, "Paper Chromatographic Analysis of Irradiated Uranium in a Hydrofluoric Acid Medium," in press, J. Inorg. Nucl. Chem.
9. R. J. Prestwood, "Collected Radiochemical Procedures," LA-1721 (Rev.) (1954).
10. A. H. Jaffey, "The Actinide Elements," Edited by G. T. Seaborg and J. J. Katz, Chapt. 16, Div. IV, Vol. 14B, New York; McGraw-Hill Book Co., Inc., 1954.
11. G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," New York; John Wiley and Sons, Inc., 1955, p. 132.