

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Alpha Spectrometric Evaluation of SRM-995 as a Potential Uranium/Thorium Double Tracer System for Age-Dating Uranium Materials

F.E. Stanley¹, S.E. Glover¹, A.M. Stalcup¹, H.B. Spitz¹, Donna Beals²

1. *University of Cincinnati; Cincinnati, OH 45221*

2. *Savannah River National Laboratory; Aiken, SC 29808*

Corresponding Author: Dr. Henry B. Spitz
henry.spitz@uc.edu
Office: 513-556-2003
Fax:

Abstract:

Uranium-233 ($t_{1/2} \sim 1.59\text{E}5$ years) is an artificial, fissile isotope of uranium that has significant importance in nuclear forensics. The isotope provides a unique signature in determining the origin and provenance of uranium-bearing materials and is valuable as a mass spectrometric tracer. Alpha spectrometry was employed in the critical evaluation of a ^{233}U standard reference material (SRM-995) as a dual tracer system based on the in-growth of ^{229}Th ($t_{1/2} \sim 7.34\text{E}3$ years) for ~ 35 years following radiochemical purification. Preliminary investigations focused on the isotopic analysis of standards and unmodified fractions of SRM-995; all samples were separated and purified using a multi-column anion-exchange scheme. The $^{229}\text{Th}/^{233}\text{U}$ atom ratio for SRM-995 was found to be $1.598\text{E}-4$ ($\pm 4.50\%$) using recovery-corrected radiochemical methods. Using the Bateman equations and relevant half-lives, this ratio reflects a material that was purified ~ 36.8 years prior to this analysis. The calculated age is discussed in contrast with both the date of certification and the recorded date of last purification.

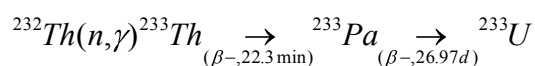
Keywords: Age-Dating, Alpha Spectrometry, Nuclear Forensics, Uranium, SRM-995, Thorium

Introduction

Determining the age of nuclear materials, i.e. the time that has passed since last radiochemical purification, is of significant importance to the field of nuclear forensics. [i,ii] Such information is invaluable in determining the provenance of the material. The ability to accurately gather age-dating information in a timely-manner is also a significant deterrent to nuclear terrorism and is of key importance in routine treaty verification as well as ongoing safeguards efforts. [iii]

Radioactive decay of actinides provides unique chronometers inherent to a given material. Several isotopic ratios have been exploited to determine nuclear material production ages. For example, enriched uranium can be age-dated based on the $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ratios. [iv,v] Additional nuclide ratios, such as the $^{229}\text{Th}/^{233}\text{U}$ ratio, may be exploited for special applications. [ii] The $^{229}\text{Th}/^{233}\text{U}$ ratio is distinct from the previous examples in that the ^{233}U is a synthetic nuclide and its content in uranium materials is usually negligible.

Uranium-233 is produced by neutron irradiation of ^{232}Th . [ii] This is a multistep process, as shown:



The decay of ^{233}U ($t_{1/2} \sim 159\,200$ yrs) to ^{229}Th ($t_{1/2} \sim 7\,340$ yrs) [vi] is useful as a special applications chronometer. Uranium-233 is also a valuable mass spectrometry tracer for uranium materials. [vii] The presence of ^{233}U in environmental samples may provide key insights into operator activities, such as the occurrence of nuclear fuel reprocessing. [ii,viii]

The present work used alpha spectrometry in a preliminary, critical evaluation of a ^{233}U standard reference material (SRM-995) as a potential uranium/thorium double tracer system for age-dating uranium materials. To be useful as a dual tracer, knowledge of both the ^{233}U and

^{229}Th content is required; the SRM must also have negligible ^{234}U and ^{230}Th content. Analyses were conducted on uranium and thorium control standards prior to determining the isotopic content of the SRM-995. Although the uranium content of SRM-995 was certified, information was not available for potential impurities (e.g. Th progeny). Results of these analyses were used to determine the radiological age of the reference material and revealed several deficiencies associated the proposed double tracer concept. A discussion of these considerations and the age-dating results is provided.

Materials and Methods

Materials

Deionized water was generated in-house and used in the preparation of all solutions requiring dilution. All acids (reagent grade), hydrogen peroxide, collodion, acetone, the 30 mL Nalgene bottles, and the 35 mm analytical funnels were obtained from Fisher Scientific (Pittsburgh, PA). Bio-Spin chromatography columns (Cat. No. 732-6008), AG 1x4 resin (100-200 mesh) and AG 1x8 resin (100-200 mesh) were purchased from Bio-Rad Laboratories, Inc. (Hercules, CA). Ammonium hydroxide was obtained from Pharmco Products, Inc. (Brookfield, CT). The isoamyl acetate was purchased from Thermo Scientific, Inc. (Waltham, MA). The 11/16" diameter stainless steel electrodeposition disks were obtained from A.F. Murphy Die and Machine Co, Inc. (Quincy, MA). Steel washers (OD = 31.9 mm; ID = 22.1 mm; thickness = 1.0 mm) were obtained from Boker's, Inc. (Minneapolis, MN) for recoil disk preparation.

The materials analyzed in this work included a certified ^{233}U solution standard, a thorium standard, and a separate uranium standard derived from depleted uranium. The ^{233}U standard was SRM-995 from the National Institute of Standards and Technologies (NIST; Gaithersburg,

MD). The thorium standard was prepared in-house by dissolving $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ from Johnson Matthey, & Co (London, UK) “SpecPure” Lot S3H72; the nuclide content of this material was determined previously using alpha spectrometry. [ix] The depleted uranium standard was prepared in-house from New Brunswick Laboratories (Argonne, IL) certified reference material NBL CRM U-002.

Initial Sample Preparation

Samples consisted of aliquots of the U-233 SRM (with ingrown Th-229) solution with and without U or Th tracer solutions added; they were readied by transferring appropriate volumes of the analyte standard solutions into 150 mL beakers. These solutions were then dried on a hotplate between 120 and 140 °C. The dried samples were dissolved in 8 M nitric acid, dried again, and then dissolved in ~ 1 mL of 8 M nitric acid prior to conducting anion exchange separation procedures. Reagent blanks were processed in an identical manner to the analyte samples.

The starting aliquots of the thorium analysis of SRM-995 were prepared to contain ~ 100 ng of ^{233}U to ensure that usable quantities of the ^{229}Th daughter nuclide obtained following purification. In contrast, only ~ 1 ng of ^{233}U from SRM-995 was used for the uranium measurements.

Anion Exchange Chromatography

A total of three anion exchange columns were used to separate and purify samples prior to counting; the procedure, described by LaMont and Hall [v], was followed for all samples. Figure 1 summarizes the separations process. The first column separated the uranium and thorium, and then each fraction underwent additional column purification prior to electrodeposition.

Radiochemical Separation of Uranium and Thorium: Uranium/thorium separations were carried out on 1 mL columns of Bio-Rad AG 1x8. Prior to sample loading, the columns were rinsed with 5 mL of 0.1 M HCl, 5 mL of 9 M HCl and an additional 2 mL of 0.1 M HCl to remove trace contaminants. The columns were then preconditioned, by rinsing with 10 mL of 8 M HNO₃, in preparation for sample introduction. The samples were loaded to the columns and original sample containers were rinsed three times with 1 mL washes of 8 M HNO₃ that were also loaded onto the columns. Uranium is weakly bound by the resin under these conditions. The uranium fractions were eluted into acid-cleaned 150 mL beakers by rinsing the columns with 10 mL HNO₃. The thorium fractions were then eluted into separate acid cleaned, 150 mL beakers with 10 mL of 9 M HCl. Both the uranium and thorium fractions underwent further purification, as described below.

Uranium Purification: Uranium fraction aliquots, containing less than 50 µg of uranium, were transferred to clean beakers for dry down on a hot plate between 120 and 140 °C. When the entire uranium fraction was to proceed to analysis, this step was ignored and the sample was dried down without transfer. The fractions were then dissolved in 3 mL of 9 M HCl and dry down was repeated. These samples were dissolved in 3 mL of 9 M HCl prior to column loading.

Further purification of the uranium fractions was carried out on 0.5 mL columns of Bio-Rad AG 1x4. Prior to sample loading, the columns were rinsed with 5 mL of 8 M HNO₃, 5 mL of 0.1 M HCl and 5 mL of 9 M HCl. The samples were then loaded onto the columns. The original sample beakers were rinsed twice with 1 mL of 9 M HCl; these rinses were also added to the columns. The columns were rinsed, to waste, with 2.5 mL of 9 M HCl and 1.25 mL of HNO₃ sequentially. The uranium fractions were then eluted into 100 mL beakers with 4 mL of HNO₃.

Purified uranium fractions received 2 mL of 0.36 M sodium bisulfate and were taken to dryness on a hot plate set between 120 and 140 °C. The samples were dissolved in 5 mL of concentrated HNO₃. Hydrogen peroxide was then added to the sample solutions, in a drop-wise fashion, until reaction (bubbling/fizzing) was no longer observed. The samples were then dried, dissolved in 5 mL of concentrated nitric acid, and dried once more. These fractions were stored dry and covered until electrodeposition occurred; minimal time was allowed to elapse prior to deposition.

Thorium Purification: Thorium fractions obtained from the primary separation step were taken to dryness on a hot plate set between 120 and 140 °C, dissolved in 2 mL of 8 M HNO₃, and dried down again. The samples were then dissolved in 4 mL of 8 M HNO₃. Hydrogen peroxide was then added to the sample solutions, in a drop-wise fashion, until reaction was no longer observed. The samples were dried down and dissolved in 4 mL of 8 M HNO₃ prior to column loading.

Secondary purification of the thorium fractions was carried out on 0.5 mL columns of AG 1x8. Prior to sample loading, the columns were rinsed with 5 mL of 9 M HCl, 5 mL of 0.1 M HCl, and 5 mL of 8M HNO₃. The samples were loaded onto the columns. The original sample beakers were rinsed in triplicate with 1 mL washes of 8 M HNO₃ and these rinses were added to the column beds. The columns were then rinsed, to waste, with 5 mL of 8M HNO₃ to remove iron and uranium. The thorium fractions were eluted into 100 mL beakers with 5 mL of 9 M HCl.

Purified thorium fractions received 2 mL of 0.36 M sodium bisulfate and were taken to dryness on a hot plate set between 120 and 140 °C. The samples were dissolved in 5 mL of

concentrated nitric acid, and dried again. Fractions were stored in a dry state and covered until electrodeposition occurred; minimal time was allowed to elapse prior to deposition.

Electrodeposition Cell Assembly

Disposable electrodeposition cells were assembled in-house and, with the exception of the electrode components, were strictly used only once for a single sample. The cells consisted of: 1) a 30 mL Nalgene bottle with the bottom removed and a hole in the cap, 2) a truncated analytical funnel acting as the cell cover, 3) a Pt wire serving as the anode, 4) an 11/16" stainless steel disk with an attached wire serving as the cathode, and 5) the sample planchet. A representation of the cell is provided in Figure 2 for clarity. In this setup, the sample planchet was placed between the rim of the bottle and the cathode and locked in place by attaching the cap. All cells were tested for leaks prior to introducing sample solutions.

Electrodeposition

Dried samples were first dissolved in 6 mL of 0.75 M H₂SO₄ and then transferred to the electrodeposition cells along with 2 drops of thymol blue pH indicator. The sample beakers were rinsed twice with 3 mL of 0.75 M H₂SO₄. Rinses were added to the electrodeposition cells to produce a total cell volume of 12 mL. The pH of the analyte solutions was adjusted by drop-wise addition of concentrated ammonium hydroxide. The target pH was ~ 1.7 and ~ 2.0 for the thorium and uranium fractions, respectively. To minimize equipment cross contamination, the sample solution color (indicating the solution pH) was visually compared to separate solutions prepared using a Fisher Scientific (Pittsburgh, PA) Accumet Model 15 pH meter.

Samples were electrodeposited onto 11/16" stainless steel disks for 1 hr at a constant current of 0.75 A using a Model 3015B Protek (Hudson, MA) dual DC power supply. The samples were then quenched by the addition of 1.5 M NH₄OH to the electrodeposition cells and

plating was continued for an additional 1 minute. The cells were disassembled and the sample planchets were thoroughly rinsed with DI water prior to being dried on a hot plate (~ 300 °C) for 10 minutes.

Suppression of Recoil Species

Recoil suppression films were employed throughout this work to prevent contamination of detector surfaces caused by recoil daughter nuclei. Alpha spectrometer recoil films were prepared and used according to a method previously developed by NIST personnel. [x]

Stock film solution was prepared by mixing equal volumes of isoamyl acetate and collodion. Using a disposable transfer pipette, one drop of the prepared mixture was placed on a water surface within a bowl deep enough to accommodate a wire loop. The film was allowed to solidify for approximately one minute and removed using the wire loop. The loop was then passed over a steel washer, seated on top of an inverted 30 mL Nalgene bottle, to transfer the film from the wire to the washer, forming a recoil “disk.” All films were allowed to dry for at least four hours and were discarded following single use.

Alpha Spectrometry

The nuclide content of each sample was determined by alpha spectrometry. All alpha spectrometry data was collected using Canberra Industries Inc. Model 7401 Alpha Spectrometers (Meriden, CT) with Canberra 450 mm² PIPS silicon diode detectors. The detectors were energy calibrated using sources of ~ 0.83 Bq each: ²³⁴U, ²³⁸U, ²³⁹Pu, ²⁴¹Am. Detector backgrounds and sample were counted for 100 000 s.

The alpha spectrometers were controlled manually and signal output was monitored by a Dell (Round Rock, TX) PC running Windows XP. Data management was carried out using the Genie 2000 Alpha Acquisition & Analysis (V2.0) software package.

Results and Discussion

Analysis of SRM-995 Fractions

Thorium and uranium fractions of SRM-995 were evaluated (Figure 3) following the measurement of quality control standards. Thorium aliquots in these investigations were 100 times more concentrated than uranium aliquots because of the relatively small amount of ^{229}Th expected to have grown into the material.

The alpha energy spectrum obtained by measuring the thorium fraction of SRM-995, (Figure 3A) clearly exhibits a wide peak at ~ 4850 keV that is caused by numerous, closely related α -decay energies for ^{229}Th . [xi] Thorium-228 was also measured in this fraction resulting in a calculated $^{228}\text{Th}/^{229}\text{Th}$ atom ratio equal to 0.108 ($\pm 4.46\%$, 1σ). The origin of the ^{228}Th is likely due to the presence of ^{232}U , an undesired contaminant arising from (n,2n) reactions on either ^{233}Pa or ^{233}U in the ^{233}U production scheme. [2]

Similar analyses were performed using the uranium fraction of SRM-995. The alpha energy spectra collected for the SRM uranium fractions were dominated by the ^{233}U alpha particle at ~ 4760 keV (Figure 3B). The alpha particle energy of ^{233}U is not distinct from that of the ^{229}Th daughter and further supports the need for radiochemical separations. No other uranium isotopes were detected in the SRM by alpha spectrometry. The $^{234}\text{U}/^{233}\text{U}$ activity ratio is expected to be $\sim 10^{-4}$ based on certificate values [xii], so ^{234}U should contribute very little to the alpha energy peak observed in the spectrum.

Analysis of Controlled Mixtures

Controlled mixtures of the ^{238}U or ^{232}Th quality control standards and SRM-995 were analyzed using alpha spectrometry so that the ^{229}Th and ^{233}U content in the SRM could be

determined using recovery-corrected radiochemical methods. As with the previous analyses, the thorium aliquots investigated here were 100 times more concentrated than the uranium aliquots since only a relatively small amount of ^{229}Th will have grown into the material. Typical alpha energy spectra for these investigations are shown in Figure 4.

The alpha energy spectrum for the thorium fraction of SRM-995 with the Th-232 tracer added is illustrated in Figure 4A. Alpha energy peaks for ^{228}Th , ^{229}Th , ^{230}Th , and ^{232}Th are clearly observed. Table 1 lists the thorium isotopic energy and activity for each thorium isotope of interest. These results were used to calculate the thorium content in SRM-995 based on the known input of ^{232}Th ($8.58\text{E}-2$ Bq). The quantity of ^{229}Th in the initial aliquot was determined to be $1.084\text{E}+11$ ($\pm 3.68\%$, 1σ) atoms.

Similar analyses were performed using controlled mixtures of the ^{238}U tracer and the uranium fraction of SRM-995. The alpha spectrum for the uranium fraction is shown in Figure 4B. Two peaks dominate the spectrum: one attributable to ^{238}U and the second attributable to a combination of ^{233}U and ^{234}U . The contribution of ^{234}U from the ^{238}U tracer was subtracted from the $^{233+234}\text{U}$ peak based on previous evaluation of the isotopic content of the NBL CRM U-002 (tracer). Summarized results for this sample are provided in Table 2. The resulting data was used to calculate the uranium content of the initial SRM-995 aliquot based on the known input of ^{238}U (0.534 Bq). The quantity of ^{233}U in the starting aliquot was determined to be $6.78\text{E}+12$ ($\pm 2.60\%$, 1σ) atoms. Based on these findings, a $^{229}\text{Th}/^{233}\text{U}$ ratio of $1.60\text{E}-4$ ($\pm 4.50\%$, 1σ) was calculated for SRM-995.

Age Determination for SRM-995

The Bateman equation and the relevant half-lives of the parent and decay products were used to predict the expected $^{229}\text{Th}/^{233}\text{U}$ ratio as a function of time passed since radiochemical

purification for SRM-995 assuming all thorium was removed at t_0 . The $^{229}\text{Th}/^{233}\text{U}$ ratio increases linearly following purification according to predictions shown in Figure 5. Results obtained using SRM-995 indicate that the material was purified 36.8 (± 3.2 , 2σ) yrs ago (~ 1975). This calculated date is earlier than the date reported on the SRM-995 material certificate (August 1980 [xii]) and purification (January 1979 [xiii]). It is important to note that the SRM-995 certificate does not report the time of purification or account for the time required for material testing prior to certification. The difference that exists between the calculated and expected purification dates may be a function of both the relatively large error associated with the ^{229}Th half-life and incomplete thorium removal at the time of last purification. The impact of potentially incomplete thorium removal, however, cannot be fully assessed, as the thorium isotopic content of SRM-995 has never been certified.

Conclusions

Alpha spectrometry was used in the critical evaluation of SRM-995, a ^{233}U standard solution, as a potential uranium/thorium dual tracer system for age-dating uranium materials. Several constraints were identified in using the proposed strategy, including: 1) spectral overlap in alpha spectrometry occurs for ^{233}U and ^{234}U , 2) original thorium isotopic content of SRM-995 was not certified, 3) a significant quantity of ^{233}U is required to achieve a usable quantity of ^{229}Th , and 4) ^{228}Th present in the SRM may complicate the analysis of some real-world samples. In addition to these constraints, widespread adoption of this strategy would require further efforts to investigate additional lots of SRM-995 beyond the single vial investigated in this work. A potential, partial solution to the issues discussed above would be the use of mass spectrometry rather than alpha spectrometry in conjunction with the evaluated approach. In both cases,

however, the uncertainty in the half-life of ^{229}Th will be a major contributor to the uncertainty calculation of the time since purification.

The age determined for this material exceeds the time that has passed since material certification and purification. This difference could be impacted by the incomplete removal of thorium as well as the large error associated with the established half-life value of ^{229}Th . This point further stresses the fact that the thorium isotopic content of this material has not been fully certified.

Acknowledgements

This research was supported by the U.S. Departments of Homeland Security and Defense through the Nuclear Forensics Graduate Fellowship Program and a grant from the U. S. Department of Energy for the University of Cincinnati Nuclear Forensics Graduate Academic Program. The Department of Homeland Security sponsored the production of this material under DOE Contract Number DE-AC09-08SR22470 for the management and operation of Savannah River National Laboratory,

References

- ⁱ Mayer K, Wallenius M, Ray I (2005) *Analyst* 130: 433-441
- ⁱⁱ Moody KJ, Hutcheon ID, Grant PM (2005) *Nuclear Forensic Analysis*. CRC Press Taylor and Francis Group, Boca Raton, FL.
- ⁱⁱⁱ Smith DK, Kristo MJ, Niemeyer S, Dudder GB (2008) *J Rad Nuc Chem* 276: 415-419
- ^{iv} Wallenius M, Morgenstern A, Apostolidis C, Mayer K (2002) *Anal Bioanal Chem* 374: 379-384
- ^v LaMont SP, Hall G (2005) *J Rad Nuc Chem* 264: 423-427

vi IAEA Interactive Nuclide Database

<http://www-nds.iaea.org/relnsd/vchart/index.html>

vii Varga Z, Suranyi G (2007) *Analytica Chimica Acta* 599: 16-23

viii Tumey SJ, Brown TA, Buchholz BA, Hamilton TF, Hutcheon ID, Williams RW (2009) *J Rad Nuc Chem* 282: 721-724

ix LaMont SP, Maddison AP, Filby RH, Glover SE (2001) *J Rad Nuc Chem* 248: 509-515.

x Inn KGW, *et al.* (2008) *J Rad Nuc Chem* 276: 385-390

xi Firestone RB, Shirley VS (1998) *Table of Isotopes*, 8th edn. John Wiley and Sons, Inc., Somerset, New Jersey.

xii National Institute of Standards and Technologies (1980) *Certificate: Standard Reference Material 995*.

xiii Kenneth G.W. Inn (personal communication regarding U-233 purification; October 6th, 2011)

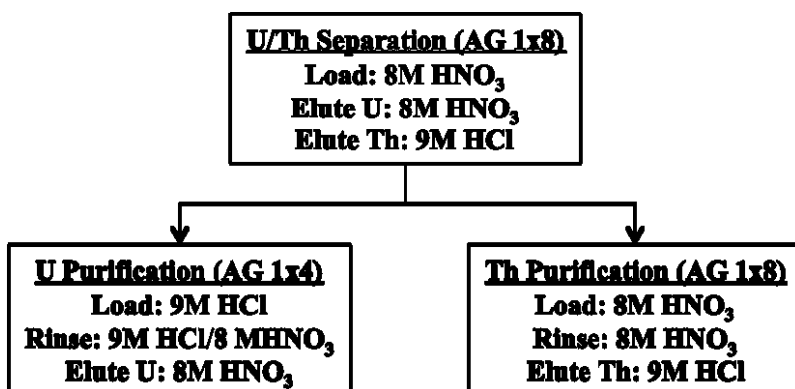


Figure 1. Flow diagram illustrating the anion exchange separation scheme.

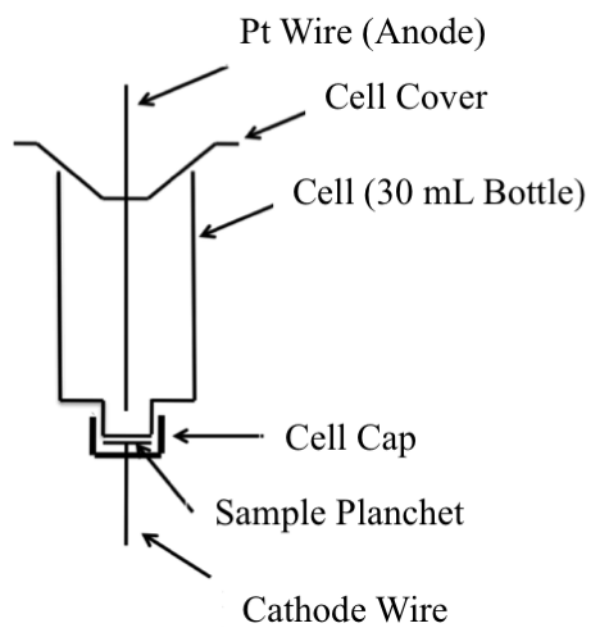


Figure 2. Illustration of the employed electrodeposition cells.

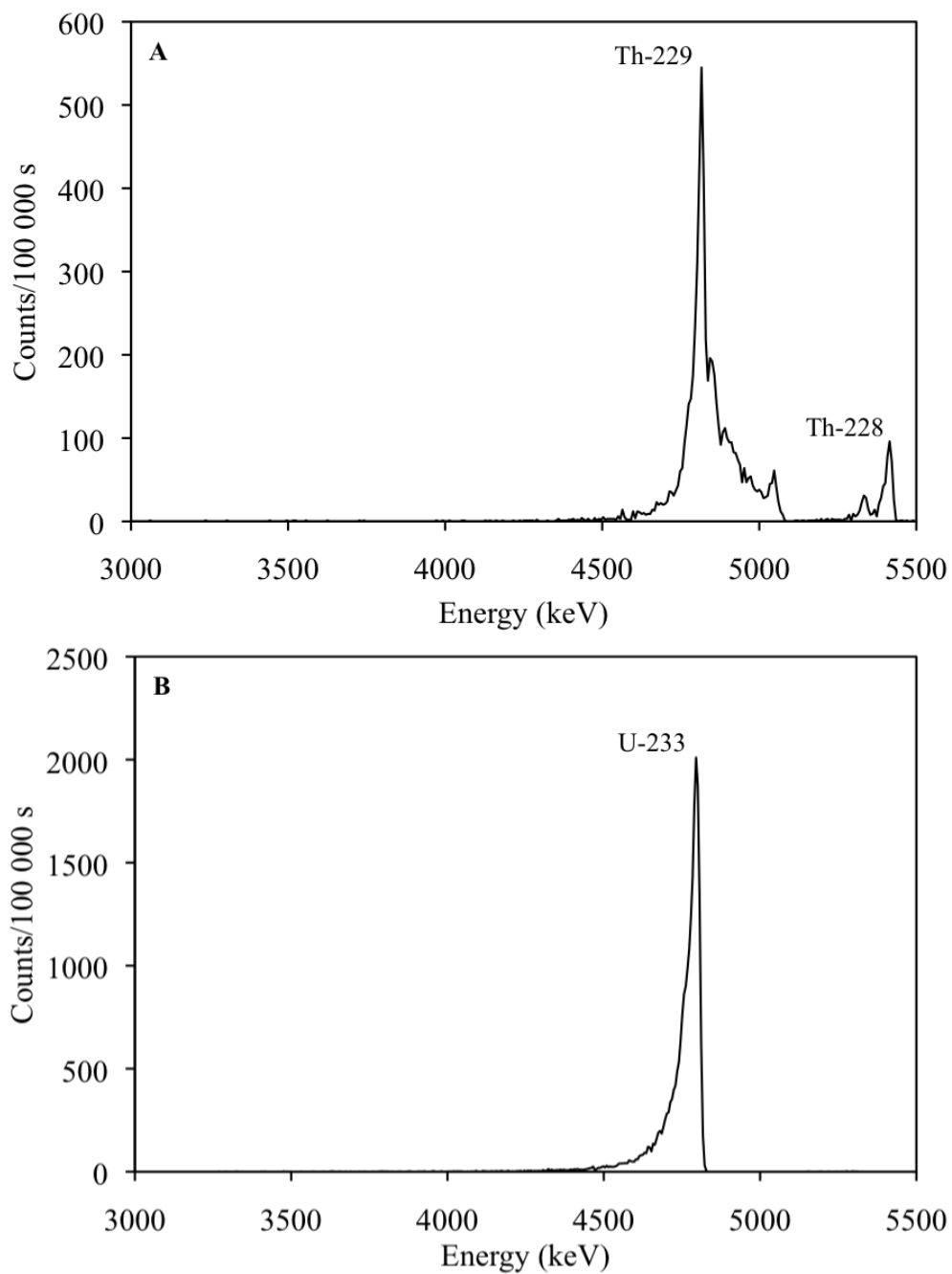


Figure 3. Alpha spectrometry results for a purified A) thorium fraction and B) uranium fraction of SRM-995.

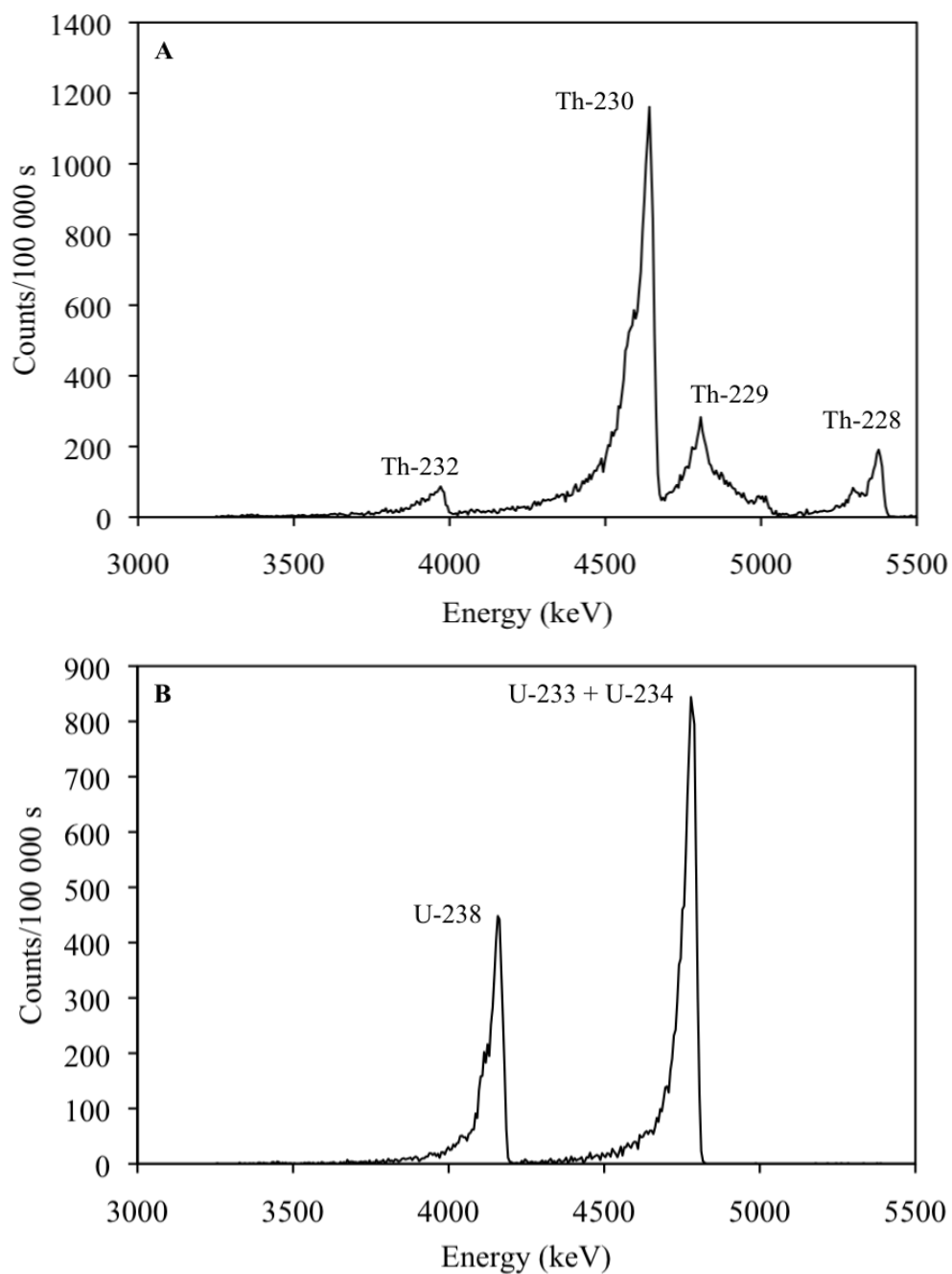


Figure 4. Alpha spectrometry results for a purified: A) thorium fraction of a controlled mixture of SRM-995 and the thorium QC standard; B) uranium fraction of a controlled mixture of SRM-995 and the uranium QC standard.

Nuclide	Energy (keV)	Activity (Bq)
Th-228	5330	0.131
Th-229	4856	0.474
Th-230	4608	0.987
Th-232	3940	0.0858

Table 1. Thorium isotopic energy and activity associated for each thorium isotope of interest.

Nuclide	Energy (keV)	Activity (Bq)
U-233+U-234	4749	0.951
U-233 _{Calculated}	4749	0.936
U-234 _{Calculated}	4749	0.015
U-238	4133	0.534

Table 2. Uranium isotopic energy and activity associated with each uranium isotope of interest. Note: Because of differences in aliquot concentrations, uranium isotopic results must be multiplied by 100 for comparison with the thorium results.

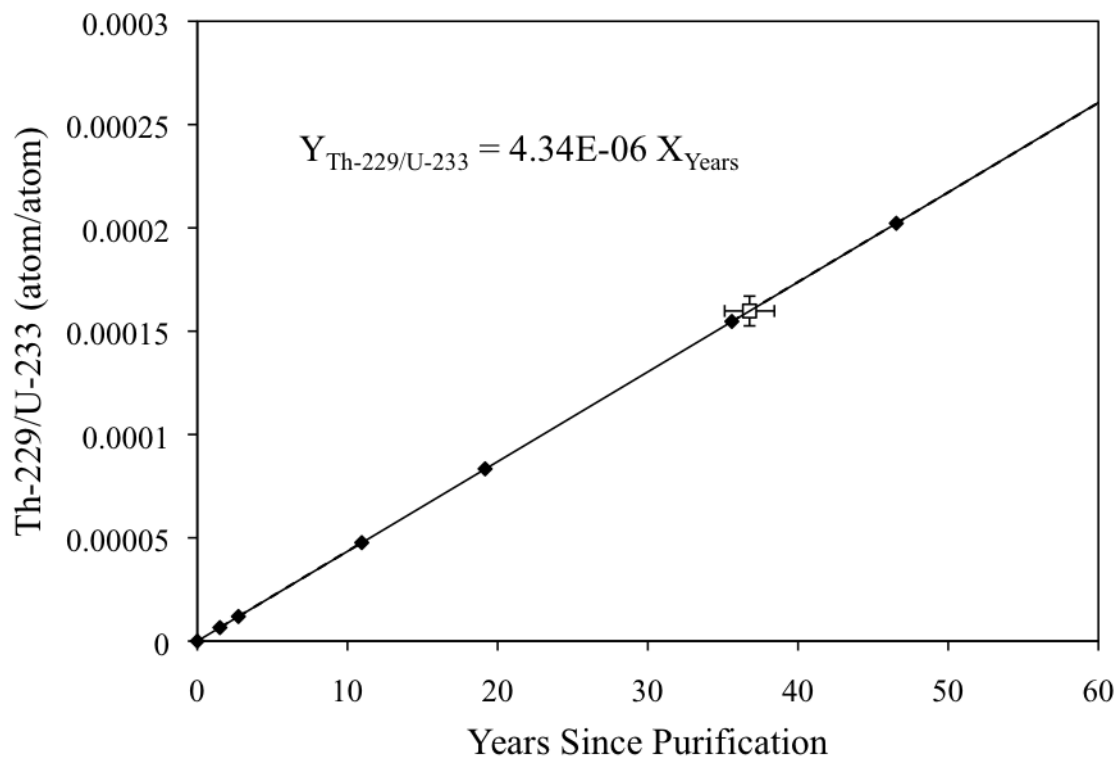


Figure 5. Model results of the expected Th-229/U-233 atom ratio as a function of time elapsed since initial sample purification. Filled markers (◆) represent calculated data, open markers (□) represent experimentally determined data.