LA-UR-13-20075

Approved for public release; distribution is unlimited.

Title: Design and Application of TIMS-Based Thorium Measurement Methods in the Actinide Analytical Chemistry Group at Los Alamos National Laboratory

Author(s): Stanley, Floyd E.
Spencer, Khalil J.
Kuhn, Kevin J.
Tandon, Lav

Intended for: Report

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Design and Application of TIMS-Based Thorium Measurement Methods in the Actinide Analytical Chemistry Group at Los Alamos National Laboratory

F.E. Stanley, K.J. Spencer, K. Kuhn, L. Tandon

Los Alamos National Laboratory; Chemistry-Actinide Analytical Chemistry (C-AAC)

TA-3, Bldg. 29; Diamond Drive; Los Alamos, NM 87545

Introduction:

Quantitation of inter-related actinides in nuclear materials, whether they be intercepted (e.g. stolen fuel pellets) or purposefully collected (e.g. cotton swipe samples), is essential in modern nuclear forensics and safeguards. Well-designed procedures may provide insight into a material's "age" (i.e. time since last purification), suggest processing/preparation routes, and point to involved parties.^{1,2}

In the present work, we detail the design and preliminary application of a thermal ionization mass spectrometry (TIMS) based approach to the analysis of thorium-230 within uranium-bearing materials. These efforts are in-line with a chronometric-type analysis strategy and focused on identification of appropriate preparation procedures, development of required spiking materials (i.e. ^{229}Th), and evaluation of uranium certified reference materials (CRMs). The presence of thorium in these materials is expected to be largely due to a combination of the decay of parent uranium (e.g. ^{234}U) to daughter nuclides (e.g. ^{230}Th), and thorium persistence following last purification.

Experimental:

Materials

Uranium certified reference materials (CRMs) were sourced from the New Brunswick Laboratory (NBL-Chicago, IL;

USA). A well characterized ^{233}U has been in use for some time in the C-AAC and was used to prepare a ^{229}Th spike due to purchasing delays. A thorium ICP-MS standard was purchased from High-Purity Standards (North Charleston, SC; USA). Optima grade acids were purchased from Fisher Scientific (Pittsburgh, PA; USA) and used as received. High purity colloidal graphite was purchased from the Ultra Carbon Corporation (Bay City, MI; USA).

Preparation of a Provisional ^{229}Th Spike

In the absence of an externally certified ^{229}Th , a provisional spike material was prepared by "milking" an in-house ^{233}U concentrate using the separation procedure detailed below. The U stock (99.995 wt % ^{233}U) contained ~1.02 mg of U per gram of nitric acid solution and was used to obtain several hundred nanograms of ^{229}Th .

Analysis/validation of the ^{233}U stock and isolated thorium material was carried out prior to investigations involving U CRMs. It should be noted that sample spiking requirements for the ^{233}U concentrate differed from those outlined below and relied upon the use of a uranium assay standard (natural composition) and Th ICP-MS standard (^{232}Th).

Sample Preparation

Sample fractions proceeding to U isotopic analysis were portioned to contain microgram levels of U. These fractions were transferred to vials containing known

quantities of ^{233}U and dried. The samples were then reconstituted in 12 M HCl and dried again. Finally, these fractions were dissolved in approximately 1 mL of 12 M HCl prior to separations.

Sample size requirements for fractions proceeding to Th analysis were estimated based on expected ^{230}Th in-growth and available knowledge pertaining to ^{234}U prevalence. For young materials or those of low enrichment, larger quantities of uranium are needed to isolate sufficient thorium for TIMS analysis. Conversely, old/highly enriched materials allow for reduced sample requirements. As an aid, ideal ingrowth of ^{230}Th was plotted for various U CRMs as a function of time elapsed since last purification (Figure 1).

Following determination of material quantity requirements, samples proceeding to Th isotopic analysis were transferred into vials containing known quantities of ^{229}Th . These fractions were dried, reconstituted in 12 M HCl, and dried a second time. Finally, samples were dissolved in about 1 mL of 12 M HCl prior to separations.

Separations

The separation of U and Th was carried out on a 2 mL Lewatit ion-exchange column in chloride form; this column was preconditioned with 8-10 mL of concentrated HCl prior to sample loading to equilibrate the resin and remove any blank Th. Re-dissolved samples were loaded onto the column, along with 2 sample vial rinses of ~ 0.5 mL of 12 M HCl. The thorium was not retained by the column and eluted immediately into a pre-cleaned vial. Further elution of any residual Th was achieved through the addition of ~ 5 mL of 12 M HCl to the column. A separate, pre-cleaned vial was then placed under the column and the U was eluted by the addition of ~ 6 mL of 0.1 M HCl.

TIMS Instrumentation

TIMS analyses were conducted using an IsoProbe T thermal ionization mass spectrometer from GV Instruments Limited (Now Isotopx: Middlewich, Cheshire; UK). The instrument incorporates nine variable position Faraday Cup detectors, all equipped

Figure 1. A plot of relative Th in-growth for U CRMs of varied enrichment.

with 10^{11} Ohm resistors, and one static Daly detector. Instrument performance and programming were controlled using the GV Instruments IonVantage software package as installed on a Dell (Rock Round, TX; USA) Optiplex PC.

Prior to use, the TIMS system was warmed for at least 30 minutes under electronic conditions similar to those to be employed in upcoming analyses. Following warm-up, instrument tuning was conducted before the analysis of each sample. Faraday Cup inter-detector gain values were determined on a weekly basis.

Uranium Analysis

Uranium isotopic measurements were conducted using triple rhenium filament assemblies and a traditional total evaporation approach.³ Faraday Cup detectors were employed at all detection positions and the major isotope ion beam intensity was targeted at ~ 4.0 V.

Thorium Analysis

Thorium isotopic measurements were conducted using single rhenium filament assemblies, carbon loading, and sequential isotope detection. Isotope detection employed a three-step measurement scheme that sequentially exposed the ^{232}Th , ^{230}Th , and ^{229}Th ion beams to the axial Daly detector; the detector position/nuclide assignments for this method are listed in Table 1. Baseline measurement and peak centering steps were included in this method preceding blocks of 15 three-cycle isotopic analyses; total block duration was ~ 225 seconds.

	L3	L2	L1	Daly	H1	H2	H3
Step 1	Th-229	Th-230		Th-232			
Step 2			Th-229	Th-230		Th-232	
Step 3				Th-229	Th-230		Th-232

Table 1. Detector/nuclide assignments used in the TIMS analysis of thorium.

Results and Discussion:

Measuring Thorium in Uranium CRMs

Aliquots of CRM U 900 and U 930 uranium isotope standards were investigated as thorium containing systems; repeat measurements ($N=3$) were carried out to determine ^{230}Th content in these materials. The results of these efforts are summarized in Table 2 and compared with values anticipated based on available materials data and predicted ^{230}Th ingrowth.

U-900	Th-230 (mole)	Exp. Uncertainty	Analysis Date
Trial 1	2.48E-12	1.74%	11-Dec-2012
Trial 2	2.49E-12		11-Dec-2012
Trial 3	2.50E-12		11-Dec-2012
Internal Std. Unc.	6.67E-15		
Average	2.49E-12		
Expected	2.51E-12		
Deviation (%)	0.77%		
U-930	Th-230 (mole)	Exp. Uncertainty	Analysis Date
Trial 1	7.12E-12	1.69%	13-Dec-2012
Trial 2	7.10E-12		13-Dec-2012
Trial 3	7.11E-12		13-Dec-2012
Internal Std. Unc.	4.16E-15		
Average	7.11E-12		
Expected	7.27E-12		
Deviation (%)	2.17%		

Table 2. Results for Th-230 measurements in distinct U CRMs. Th-230 values are normalized to 1 g of solution.

As listed, Th detection proved highly reproducible for the trials detailed above. Instrument-based measurement precisions of 0.06 and 0.27 % (standard uncertainty; $k=1$) were observed for samples containing ~ 1 ng of ^{230}Th . While this loading level was typically employed, measurements were successfully carried out for samples containing as little as ~ 85 fg of ^{230}Th . Additionally, the experimental trials are in good agreement with anticipated result; once expanded uncertainty ($<2\%$, $k=2$) is accounted for, these values are statistically identical.

Extrapolation of Material Age

For both U 900 and U 930, the data above was paired with repeated TIMS-based measurements of ^{234}U to extrapolate a material “age.” Results are summarized in Table 3 and compared with reference values provided by NBL.⁴ In both cases, the determined age was found to be in agreement with the expected value once expanded uncertainties were considered.

While the current data set clearly requires expansion, the obtained deviation and uncertainties are in line with previously accepted methods. For example, recent work notes several percent deviation and uncertainty values for MC-ICP-MS, TIMS, and alpha spectrometric approaches to age-dating uranium materials using the $^{230}\text{Th}/^{234}\text{U}$ chronometer.⁵ The authors of Reference 5 also suggest that sub-percent level confidence in such chronometric measurements remains highly unlikely in light of combined Type B uncertainty contributions; these errors are associated with external information, such as manufacturer’s specifications, certificate values, etc.

It should be noted that Williams and Gaffney recently investigated U 900 as part of an MC-ICP-MS-based chronometric investigation.⁶ Once mandatory mathematical corrections were applied to account for distinct analysis dates, the findings of their report ($^{230}\text{Th}/^{234}\text{U} \sim 1.46 \text{ E-}4$) and the current TIMS-based efforts were found to be in good agreement. This comparison strongly supports the use of the proposed strategy in the quantitation of thorium. Unfortunately, no such comparison is currently available for U 930.

U900		Exp. Uncertainty
$^{230}\text{Th}/^{234}\text{U}$ (atom/atom):	1.51E-04	2.9E-06
Obtained Age (years):	53.7	1.87% / 1.0 years
Expected $^{230}\text{Th}/^{234}\text{U}$ (atom/atom):	1.53E-04 (± 0.084%)	
Expected Age (years):	54.15 (± 0.046)	
Difference (years):	0.50	
U 930		Exp. Uncertainty
$^{230}\text{Th}/^{234}\text{U}$ (atom/atom):	1.48E-04	3.9E-06
Obtained Age (years):	52.9	2.65% / 1.4 years
Expected $^{230}\text{Th}/^{234}\text{U}$ (atom/atom):	1.53E-04 (± 0.113%)	
Expected Age (years):	54.10 (± .061)	
Difference (years):	1.2	

Table 3. TIMS-based chronometric results for CRM U 900 and U 930. Expanded uncertainties in obtained ages are for $k = 2$.

Special Considerations of Error

Various sources of uncertainty must be considered in connection with the analytical measurements detailed in this work; examples range from material weighing to the half-life values ($t_{1/2}$) of ^{230}Th and ^{234}U . The majority of such factors are reasonably well-known, controlled, and taken into account in final data reduction.

A special uncertainty concern does exist in the present work and will be addressed prior to future investigations. At this time, the provisional ^{229}Th spiking material has not been characterized to the extent typical for commercially available reference materials and contributes significantly to a typical Th measurement uncertainty budget; the ^{229}Th spike characterization comprises ~66.3% of the Th measurement uncertainty index. This spike, while necessary in the absence of an external reference material, will be replaced with a newly-available, highly-characterized reference material from NBL.

Conclusions:

A TIMS-based thorium measurement method has been developed within the C-AAC at Los Alamos National Laboratory, and applied to the quantitation of nanogram levels of ^{230}Th in uranium bearing materials. Repeat analysis of CRM U 900 and U 930 indicated high precision analytical performance and suggested minimal deviation from anticipated values, though Th content in these materials has not previously been certified. Extension of the proposed approach to the chronometric evaluation of the same CRMs yielded age values that were statistical identical to expected findings, and method performance was found to be comparable to previously accepted instrumental techniques.

One weakness in the current approach was discussed (i.e. use of a provisional ^{229}Th spike), but will be corrected prior to future investigations through the purchase and use of an exceptionally well-characterized reference material.

Supplemental:

Separations Performance

Preliminary investigations were conducted to determine the performance associated with the Lewatit-based separation scheme employed in this work. These efforts focused on the processing and analysis of two distinct uranium systems:

- 1) A solution of U 900 containing an added quantity of natural Th.
- 2) The ^{233}U used in the preparation of the ^{229}Th provisional spike.

In each of the above cases, the experimental decontamination factor (defined: Initial

U/Th divided by final U/Th) was determined to be on the order of 10^5 ; specific results obtained via preliminary TIMS isotopic analysis were 34 000 and 22 000. Additionally, a thorium recovery value of ~100% was calculated from the above efforts.

References:

- ¹ K.J. Moody, I.D. Hutcheon, P.M. Grant. Nuclear Forensic Analysis. CRC Press Taylor and Francis Group. Boca Raton, FL. (2005).
- ² F.E. Stanley. A Beginner's Guide to Uranium Chronometry in Nuclear Forensics and Safeguards. J. Anal. At. Spectrom. 27 (2012) 1821.
- ³ E.L. Callis, R.M. Abernathy. High-Precision Isotopic Analyses of Uranium and Plutonium By Total Sample Volatilization and Signal Integration. Int. J. Mass Spectrom. Ion Proc. 103 (1991) 93-105.
- ⁴ R. Essex; New Brunswick Laboratory. (Personal Communication- July 25th, 2012).
- ⁵ M. Wallenius, A. Morgenstern, C. Apostolidis, K. Mayer. Determination of the Age of Highly Enriched Uranium. 374 (2002) 379-384.
- ⁶ R.W. Williams, A.M. Gaffney. ^{230}Th - ^{234}U Model Ages of Some Uranium Standard Reference Materials. Proc. Radiochim. Acta 1 (2011) 31-35.