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Uranium isotope abundance ratios in natural uranium metal certified reference material 112-A

K. Mathew*, P. Mason, A. Voeks, U. Narayanan

New Brunswick Laboratory, U.S. Department of Energy, 9800 South Cass Avenue, Building 350, Argonne, IL 60439, United States

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ABSTRACT

Certified reference material (CRM) 112-A, uranium metal assay standard, with “natural” U isotopic composition and CRM 145, uranium assay standard solution made by dissolving CRM 112-A metal were analyzed using TRITON Thermal Ionization Mass Spectrometer (TIMS) to characterize the uranium isotopic abundances. The certified ^{235}U/^{238}U “major” ratio of 0.0072543 (40) in CRM C112-A and CRM 145 is determined using the total evaporation (TE) and modified total evaporation (MTE) methods. In the MTE method, the total evaporation process is interrupted on a regular basis to allow correction of background from peak tailing, internal calibration of the secondary electron multiplier (SEM) detector versus the Faraday cups, peak-centering, and ion source re-focusing. For the “minor” ^{234}U/^{238}U and ^{236}U/^{238}U ratio measurements using MTE, better precision and accuracy are achieved compared to the TE analyses. The certified ^{234}U/^{238}U ratio of 0.000052841 (82) in CRM C112-A and CRM 145 is determined using a conventional analysis technique that incorporates an internal mass bias correction utilizing the measured ^{235}U/^{238}U ratio and correction for peak tailing from ^{235}U and ^{238}U. The ^{236}U/^{238}U isotope abundance ratio in CRM C112-A and CRM 145 is estimated to be $<5 \times 10^{-9}$. The CRM 112-A and CRM 145 materials show no evidence for any statistically significant unit-to-unit variations in uranium isotope abundance ratios. The homogeneity of both CRMs is established. The measurements leading to the certification of uranium isotopic abundances are discussed.

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1. Introduction

To eliminate problems originating from stoichiometry of uranium oxide, Rodden [1] proposed the use of a uranium metal as an assay standard. A scalped dingot (source material for CRM112-A) was purchased from Mallinckrodt Chemical Works and uranium assay measurements were performed.

CRM 112-A had been widely used, especially in geochemical applications, as a natural uranium isotope reference standard, even though the material has not been certified for the uranium isotopic composition yet. Historically, a ‘consensus value’ of 137.88 had been used in the geochemistry and nuclear safeguards community for the ^{238}U/^{235}U ratio of CRM 112-A [2–5]. Recently, in a collaborative effort between several nuclear safeguards and geochemistry laboratories initiated by the Institute for Reference Materials and Measurements (IRMM), the consensus value was revised by comparing CRM 112-A with IRMM CRMs [6]. No US certified reference material was used for the estimation of the new consensus values for ^{234}U/^{238}U and ^{235}U/^{238}U. The present analytical effort was undertaken to provide characterized values for the uranium isotopic abundances that are traceable to the NBL U series CRMs widely used within the US and international nuclear safeguards community. In addition, the homogeneity of the materials needed to be established by demonstrating the absence of unit-to-unit variations in the isotope abundance ratios. Uncertainty estimates for the uranium isotopic abundances presented here include contributions from the uncertainties in the isotopic ratios of the CRM used for calibration of the mass spectrometer.

2. Materials and methods

Sufficient care was taken to ensure that natural and/or background (i.e., environmental or laboratory contamination) uranium did not contaminate the uranium metal samples during the characterization analyses. These steps included the use of pre-cleaned Teflon or quartz beakers and sample containers, use of ultra high purity acids and water, use of pre-cleaned zone refined rhenium filaments, and careful design of sample handling to eliminate potential cross-contamination. Additional details on each of these steps are provided below.

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* Corresponding author. Tel.: +1 630252 2428; fax: +1 630252 6256.
E-mail address: kattathu.mathew@ch.doe.gov (K. Mathew).

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2.1. Preparation of bottles and vials used for processing isotopic characterization samples

The Teflon bottles for dissolving CRM metal pieces and for processing isotopic characterization samples were prepared as follows:

- 500-mL reagent bottles from Ultrex II nitric acid were cleaned on the outside in dilute micro cleaning solution and refluxed on a steam bath with 8 M Ultrex II nitric acid to clean the inside. Prior to refluxing, caps were soaked in distilled deionized water in a Teflon container. All rinsing were done with distilled deionized water. Bottles and caps were placed on low particulate wipes and covered with the same and allowed to air dry.

The Savillex vials used for storing the mass spectrometry solutions were pre-cleaned as follows:

- New Savillex vials were soaked in warm (40 °C) micro cleaning solution for 12 h.
- The vials and caps were wiped with absorbent laboratory wipes and cleaned with distilled deionized water.
- The vials (and caps) were soaked in 1:4 trace metal grade nitric acid for 24 h.
- Ultrex II nitric acid (0.5 mL) was added to the vials, closed tight and set on a hot plate for 6 h. For refluxing, the hot plate was set at ~100 °C. The vials were allowed to cool and the acid was removed.
- The previous step was repeated a second time.

2.2. Preparation of the CRM 112-A characterization samples

CRM 112-A isotopic characterization samples were prepared as follows:

- CRM 112-A metal pieces of about 1 g were placed in glass beakers and heated in 8 M nitric acid to remove the oxide coating. After rinsing in deionized distilled water and drying with acetone they were weighed on a 4-place balance and transferred to Teflon bottles (cleaned as described above) previously weighed on a 3-place balance. Aluminum weighing pans and plastic and metal tweezers were used for the metal cleaning and weighing.
- Approximately 25 mL of 8 M Ultrex II nitric acid was added to each bottle which was then loosely capped. The metal was dissolved by placing the bottles on a steam bath. After dissolution was complete, bottles were removed from the steam bath and allowed to cool. Solutions were diluted to ~200 g with distilled deionized water. (*Note*: exact amount of acid and water were adjusted such that 5 mg U/g solutions were obtained.) Bottles were weighed on a 3-place balance and mixed thoroughly by swirling. The caps were removed and wiped with absorbent wipes. The bottles were re-capped and labeled by pen for Teflon. Paper labels were not affixed.

2.3. Preparation of the CRM 145 characterization samples

CRM 145 isotopic characterization samples were prepared as follows:

- CRM 145 ampoules were opened and the contents transferred to Teflon bottles (cleaned as described in Section 2.1) previously weighed on a 3-place balance. The bottles with CRM solutions were weighed and sufficient quantities of 1 M Ultrex II nitric acid were added to each bottle to obtain solutions containing 5 mg U/g solution. Final weights of the bottles with the dilute solution were taken and the solutions were mixed by swirling.

2.4. Mass spectrometry

In a laminar flow hood, 2.5 mL and 0.5 mL of the 5 mg U/g solutions were poured out into two pre-cleaned Savillex vials (see Section 2.1 for cleaning procedure used). 1.0 mg U/g solutions were prepared from the second aliquot (0.5 mL) by diluting to 2.5 mL using 1 M Ultrex nitric acid.

The high-purity zone-refined Re double filaments used for all analyses were preconditioned for U analysis by outgassing at ~4.7 A for 30 min. The sample loads for TE experiments consisted of 1 μg of U which was dispensed onto high-purity zone-refined Re double filaments and dried according to a standard filament loading routine.

Each of the eight units of CRM 112-A and three units of CRM 145 identified for the isotopic characterization were analyzed in triplicate by the total evaporation (TE), conventional, and modified total evaporation (MTE) analysis techniques using a ThermoFisher Scientific TRITON multi-collector TIMS instrument. The ^{235}U/^{238}U ratio was characterized by pooling the TE and MTE results. The ^{234}U/^{238}U minor ratio was characterized by conventional analysis using the pooled ^{235}U/^{238}U ratio for internal normalization. The ^{234}U/^{238}U ratio from MTE technique served as verification measurements.

The TE measurements consisted of consecutive 1-s integrations until the U sample was exhausted. During TE analysis all of the isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U are measured simultaneously using the cup configuration shown in Table 1. The TE analyses were run at a 15 V summed signal intensity. Isotopic ratios are then determined by dividing the integrated signal intensities of ^{234}U, ^{235}U, ^{236}U, and ^{238}U. Although the ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U ratios are all determined in TE measurements, NBL does not ordinarily use minor ratios (i.e., ^{234}U/^{238}U and ^{236}U/^{238}U) from TE experiments for reportable measurements. This is due to a persistent but variable bias (associated with major isotope peak tailing) in minor ratio data that, due to the nature of TE analysis, can only be corrected for using an assumed abundance correction with an associated high-uncertainty.

The ^{234}U/^{238}U ratio was characterized using a conventional analysis method that also incorporates an internal mass bias correction utilizing the pooled ^{235}U/^{238}U ratio result from the TE and MTE experiments. The conventional analysis technique includes measurement of the backgrounds on the lower and higher mass side of the ^{234}U isotope. The background corrected ^{234}U/^{238}U ratios are corrected for mass bias on a cycle per cycle basis using the measured ^{235}U/^{238}U ratio. The cup configuration used for the conventional analysis is shown in Table 2. Sample loads for the conventional analysis consisted of 10 μg of U which was dispensed onto high-purity zone-refined Re double filaments and dried according to a standard filament loading routine. The drying routine consisted of heating the filaments at 1.0 A for 1 min (after the drop had completely evaporated) followed by heating at 1.5 A and 2.0 A for 10 s each.

The conventional analyses were performed at a summed U signal intensity of approximately 24 V for a total of 60 cycles. The signal intensities of ^{234}U, ^{235}U, and ^{238}U were sufficient for measurement in Faraday cups. Each measurement cycle included background measurements at masses 233.7 and 234.4, equidistant from the mass of 234.05 of the isotope ^{234}U. These background measurements were necessary to correct isotopic ratio measurements for peak tailing effects from the ^{235}U and ^{238}U peaks. A 4-s delay between scans was also incorporated into the measurement routine to allow for amplifier decay.

Sample loads for the MTE analyses consisted of 5 μg of U which was dispensed onto high-purity zone-refined Re double filaments