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A new highly enriched ²³³U reference material for improved simultaneous determination of uranium amount and isotope amount ratios in trace level samples

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ABSTRACT

A highly-enriched ²³³U reference material (>0.99987 $n(^{233}U)/n(U)$) has been prepared and characterized for use as an isotope dilution mass spectrometry spike. An ion exchange separation was performed on 1 g of high purity ²³³U to further reduce trace amounts of contaminant Pu in the material. The purified ²³³U was then prepared as a master solution which was analyzed for molality of uranium by modified Davies and Gray titration. A portion of the master solution was quantitatively diluted and dispensed for reference material units. Selected units were analyzed for verification of uranium amount and to characterize uranium isotope amount ratios by multicollector inductively couple plasma mass spectrometry. Modelling of spike-corrected isotopic data show that the new spike will enable simultaneous measurements of uranium amount and isotope amount ratios with resulting uncertainties that are substantially less sensitive to over spiking than widely used ²³³U certified reference materials.

1. Introduction

Isotope dilution mass spectrometry (IDMS) is a well-established analytical method for measuring trace amounts of substance. When high quality isotopic spikes and appropriately calibrated mass spectrometric measurements are used, IDMS can be a primary analysis method that is traceable to the mole [1-3]. Enriched ²³³U has long been utilized as an IDMS spike for traceable and precise measurements for amount of uranium and for the relative proportions of uranium isotopes, e.g. Ref. [4-8]. Highly enriched ²³³U is particularly valuable as a spike for nuclear safeguards and nuclear forensics analyses [9-13] where it can enable uranium amount and isotopic composition to be determined from a single mass spectrometric analysis. In these disciplines, it may be necessary to analyze unique samples such as individual particles collected from safeguards inspections [14] and nuclear forensics investigations or ingrown uranium for U-Pu model age determinations. Accurately measured values for isotopic composition with small uncertainties are necessary for both particle analysis and radiochronometry. Traditional IDMS analysis techniques for samples with an unknown isotopic composition entail splitting a sample and performing separate measurements for amount and isotopic composition. This technique can yield precise and accurate results if there is ample analyte but might not feasible for the small quantities of uranium in a particle or in a Pu sample. Furthermore, the potential for heterogeneity between particles makes it undesirable to measure uranium amount for one particle and isotopic composition from another particle. Although, analysis of bulk samples or composite particle samples can address the sample size issue, important information can be lost due to the "averaged" values that are inherent to these measurements.

Accurate uranium amount and isotopic composition can be accomplished for IDMS measurements by optimizing the spike-to-sample ratio of a relatively highly enriched ²³³U spike (approximately 99%). Optimal spiking is, however, particularly difficult for nuclear safeguards and forensics samples as the amount of uranium in a particle or a plutonium sample is generally not known and can vary by orders of magnitude. Furthermore, no assumptions can be made about the isotopic composition of the uranium being analyzed. The potential impact of over-spiking or under-spiking on the uncertainties for amount measurements and

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spike corrected isotopic ratio data can be minimized by using a wellcharacterized spike that has been enriched to a very high degree (>99.9%). The 233 U reference material, described here, was developed to meet the specialized needs of the nuclear safeguards and nuclear forensic analytical communities for measuring both amount and composition from a single uranium mass spectrometric analysis.

The ²³³U nuclide is a synthetic isotope of uranium that has a half-life of $(1.592 \pm 0.002) \times 10^5$ a $(k = 1)^1$ [15] and is primarily produced as the result of thermal neutron capture by ²³²Th [16]. It is not part of the uranium fuel cycle but is observed as a trace constituent (<1 µg g⁻¹) in uranium that has a significant reprocessed component. The ²³³U nuclide also occurs as part of the ²⁴¹Pu decay chain, so some quantity of ²³³U is present in most plutonium materials, either as a contaminant remaining from plutonium production and processing or ingrown from ²⁴¹Pu. The longest-lived nuclide in the ²⁴¹Pu decay chain is ²³⁷Np which has a half-life of (2.144 ± 0.002) × 10⁶ a (k = 1) [17]. ²³⁷Np decays by alpha particle emission to the relatively short-lived ²³³Pa nuclide (27 d half-life) which, in turn, decays to ²³³U by beta emission. The ²³⁷Np half-life is significantly longer than those of the ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu and ²⁴²Pu isotopes that make up the bulk of most plutonium materials and decay to uranium isotopes ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U respectively. Therefore, ²³³U should be a relatively minor component of radiogenic uranium in an unknown sample of plutonium.

The observations that ²³³U is absent from natural and "virgin" uranium, occurs only as a trace constituent in reprocessed uranium, and is a minor component of uranium ingrown from plutonium make this nuclide an ideal isotopic spike for measuring trace samples of uranium (ng to fg levels). Several ²³³U Certified Reference Materials (CRMs) have been prepared by reference material providers (Table 1) but the enrichments of these spikes limit their usefulness for some nuclear safeguards and for ensics analyses. Although these $^{233}\mathrm{U}\,\mathrm{CRMs}$ have relatively low uncertainties for the molality (mol g^{-1}) of ^{233}U in the spike solutions, 2 of them (CRM 111-A [18] and IRMM-051 [19]) have proportions of uranium isotopes that make it difficult to recover low-uncertainty uranium isotope amount ratio values from mass spectrometric analyses of isotope dilution samples. One of the ²³³U CRMs (CRM 111 [20]) has lower levels of the ²³⁴U, ²³⁵U, and ²³⁸U isotopes but still has a proportion of ²³⁴U that can result in large uncertainties for $n(^{234}U)/n$ (²³⁸U) isotope amount ratio measurements. Furthermore, this CRM does not provide a certified value for the relative abundance of ²³⁶U, leaving it to the user to determine whether a spike correction is necessary and to quantify the magnitude of any needed correction.

To enhance measurement capabilities for sample-limited analyses of uranium, a collaborative project was initiated by the United States Department of Homeland Security (DHS) and the National Nuclear Security Administration (NNSA) to produce a very highly enriched ²³³U isotope dilution mass spectrometry reference material (henceforth referred to as the U-233 Spike). The starting material for the U-233 Spike, UTHX001-A, was provided from a stock of legacy ²³³U material preserved by NNSA [21] and stored at Oak Ridge National Laboratory (ORNL). DHS supported project coordination by staff at the National Institute of Standards and Technology (NIST) and preparation and characterization of the reference material at Lawrence Livermore National Laboratory (LLNL) and ORNL.

2. Experimental

2.1. Reference material preparation

Labware used for the preparation of the U-233 Spike reference material included new fluorinated ethylene propylene (FEP) Teflon bottles for uranium solutions (125 mL, 500 mL, and 2 L), perfluoroalkoxy (PFA) sample vials, and 30 mL FEP Teflon bottles for reference material units. The bottles and vials were cleaned prior to use by washing with Citranox detergent (Alconox Inc., White Plains, NY USA),² rinsing with deionized water, and then adding an acid solution consisting of 0.8 mol L⁻¹ HNO₃ (Seastar Chemicals Inc., Sydney, Canada) and 0.05 mol L⁻¹ HF (Seastar Chemicals Inc., Sydney, Canada). The bottles and vails containing the nitric acid solutions were then capped and fluxed on a hotplate at 120 °C for 24 h.

The transfer of the reference material solution to the unit bottles was performed using a MicroLab 600 dispenser (Hamilton Company, Reno, NV, USA). The dispenser was outfitted with a new 10 mL dispensing syringe and product transfer tubing (i.e. intake and dispensing tubing) and was then thoroughly flushed with a 0.8 mol L^{-1} HNO₃ solution. Immediately prior to dispensing the reference material solution to unit containers, approximately 30 mL of the ²³³U solution was dispensed to pre-condition the apparatus (3 dispensing cycles).

The quantitative transfer of relatively small masses of solution (between 0.5 g and 3.0 g) was necessary to aliquot samples for titrimetric analysis, to prepare dilutions of uranium solutions, and to dispense both sample and spike aliquots for IDMS analyses. New flat-bottom polyethylene ampoules (Canus Plastics Inc., Ottawa, Canada) with tips drawn out to a thin capillary were used as disposable pipettors for these solution transfers (no ampoule was used to dispense solution from more than 1 container). The mass of the samples was determined by the difference of the ampoule weight before and after dispensing. This method allows the mass of a solution subsample to be measured with high precision and minimizes the potential for bias due to evaporation. All masses were measured on electronic balances that were within their annual calibration periods and were checked with certified weights immediately prior to use. Corrections for air buoyancy based on ambient laboratory conditions were applied to all weighing data used for this project.

Uranium processing blanks are regularly measured for the laboratory where the reference material was prepared. During the period of project activities, these uranium processing blanks were less than 50 pg and included sample dissolution reagents, ion exchange separation, multiple drying cycles, and mass spectrometric analysis.

Fig. 1 is a schematic of the U-233 Spike reference material preparation and characterization process. The starting material for the project was obtained from a batch of high purity ²³³U stored at ORNL. Approximately 6 g of this material was designated by NNSA for reference material production and a precise uranium isotopic composition for this material was measured by Mathew et al. [22]. A 1 g portion of the UTHX001-A ²³³U was subsampled and transferred to LLNL in 2 Teflon vials. Screening analyses for uranium isotopic composition and plutonium content were performed at LLNL upon receipt of the ²³³U. These analyses indicated the $n(^{233}U)/n(U)$ isotope amount fraction was greater than 0.999 and that plutonium was present at approximately 14 µg g⁻¹ (relative to uranium).

To ensure that the ²³³U was suitable for use as a high purity spike, an ion exchange separation was performed. The ²³³U was dissolved in 4 mol L⁻¹ HNO₃ and transferred into a single larger PFA vial (30 mL). A 4 mL bed of TEVA extraction resin (Eichrom, Lisle, IL, USA) was prepared in a plastic column and preconditioned with 20 mL of 0.1 mol L⁻¹ HCI (Seastar Chemicals Inc., Sydney, Canada) followed by 15 mL of 4 mol L⁻¹ HNO₃. A pre-cleaned and weighed 125 mL Teflon bottle was positioned under the column. The ²³³U solution was loaded onto the column and then rinsed with another 70 mL of 4 mol L⁻¹ HNO₃. Most of the

¹ Unless otherwise specified, uncertainties cited for values in this report will be expanded uncertainties ($U = ku_c$) with a coverage factor (k) of 2 for an approximately 95 % level of confidence.

² Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1

²³³U certified reference materials for IDMS analysis. Certified values for molality and uranium isotope amount fraction of commercially available ²³³U spike CRMs. Uncertainty values represent expanded uncertainties. CRM 111 and CRM 111-A are distributed by National Nuclear Security Administration NBL Program Office (Lemont, IL, USA). IRMM-051 is a CRM from the European Commission Joint Research Center, Geel (Geel, Belgium).

Reference Material	Molality of U (μ mol g ⁻¹)	Isotope Amount Fraction				
		n(²³³ U)/n(U)	$n(^{234}U)/n(U)$	$n(^{235}U)/n(U)$	$n(^{236}U)/n(U)$	$n(^{238}U)/n(U)$
CRM 111 CRM 111-A IRMM-051	$\begin{array}{c} 2.1023 \pm 0.0011 \\ 2.06684 \pm 0.00052 \\ 0.010303 \pm 0.000018 \end{array}$	$\begin{array}{c} 0.999245 \pm 0.000006 \\ 0.994911 \pm 0.000006 \\ 0.980430 \pm 0.000058 \end{array}$	$\begin{array}{c} 0.000181 \pm 0.000002 \\ 0.001847 \pm 0.000002 \\ 0.009145 \pm 0.000002 \end{array}$	$\begin{array}{c} 0.000011 \pm 0.000002 \\ 0.000790 \pm 0.000002 \\ 0.002142 \pm 0.000054 \end{array}$	not reported 0.000166 ± 0.000002 0.000241 ± 0.000003	$\begin{array}{c} 0.000563 \pm 0.000004 \\ 0.002286 \pm 0.000004 \\ 0.008042 \pm 0.000019 \end{array}$

uranium passed through the column but the Pu in the solution was selectively adsorbed onto the TEVA resin. This purified ²³³U represents the "Master" solution for the U-233 Spike project. A small aliquot of the Master solution (0.1 g) was taken for uranium and plutonium IDMS and preliminary U isotope amount ratio analysis. These analyses indicated that the Master solution had a uranium mass fraction of approximately 9.4 mg g⁻¹, a Pu mass fraction of only 0.5 ng g⁻¹, and that the isotopic composition of the uranium had not been detectably altered by the purification process.

A total of 8 subsamples of the Master solution were created and carefully weighed for measurement of the molality (mol g⁻¹) of uranium in the solution. These included 2 samples transferred to FEP bottles for IDMS verification measurements at LLNL. The other 6 samples were dispensed to Teflon vials, dried to a uranium nitrate, and shipped to ORNL for titrimetric amount measurements. A "Stock" solution was then prepared for the U-233 Spike units by transferring a (35.8331 \pm 0.0010) g subsample of the Master solution to a previously cleaned and weighed 2-Liter FEP bottle. This aliquot was diluted to a mass of (1797.123 \pm 0.045) g with 1 mol L⁻¹ HNO₃ which represents a dilution factor of 50.15280 \pm 0.00073. After dilution, the stock bottle was capped and manually shaken to ensure mixing.

In preparation for production of the reference material units, previously cleaned 30 mL FEP Teflon bottles were dried and labelled with numbers corresponding to the planned fill order. Each bottle was then carefully weighed in triplicate on a 5-place (0.01 g) electronic balance (Mettler-Toledo XPE-105, Columbus, Ohio, USA). To reduce bias and variability during weighing due to static electricity, the bottles were placed in an aluminum sleeve with a carefully measured tare weight. In total, 165 units of the U-233 Spike were created during a single work session by transferring approximately 10 mL of the Stock solution to the prepared 30 mL FEP bottles using the preconditioned Hamilton MICROLAB 600 dispenser. The bottles were then capped and reweighed as previously described. The average mass of dispensed solution was 10.6729 g with a standard deviation of only 0.0022 g. After the filled sample units were weighed, they were dried in a Class-100 ducting HEPA-filter laminar flow hood using a Teflon coated heating block set to a temperature of approximately 90 °C. The dried units were capped and individually packaged by wrapping the top of the bottle with Teflon tape which, in turn, was wrapped with vinyl tape to prevent loosening of the cap or unravelling of the Teflon tape. The sealed bottles were then heatsealed in aluminized Mylar sleeves.

2.2. Modified Davies and Gray titrimetric measurements

The 6 aliquots of Master solution prepared at LLNL were measured for amount of uranium at ORNL by the modified Davies and Gray titrimetric method, as described in ASTM 1267–17 [23]. As a quality control measure, ORNL was only provided with approximate masses of uranium in the samples so they were essentially measured as unknowns. A 0.0045 mol L⁻¹ potassium dichromate (K₂Cr₂O₇) solution was prepared for this project using SRM 136f [24]. The titrant was standardized against a uranium solution (Table 2) prepared from CRM 112-A uranium metal standard [25]. The uranium standard solution titrations were performed in 2 sets of 5 titrations that bracketed the sample analyses so that any change in the titrant solution over the course of the project would be encompassed in the measurement variability. The resulting titrant equivalency factor (TEF) for uranium was (13.6502 \pm 0.0055) $\mu mol \ g^{-1}$ and the relative standard deviation of the titrations was 0.026 %, which fell within the recommendations of the ASTM method.

The 6 Master solution samples transferred from LLNL were carefully opened and 1 mL of 1 mol L⁻¹ HNO₃ (Certified ACS Plus, Fisher Scientific, Fair Lawn, NJ, USA) was added to each. The vials were then capped and inverted several times to capture any loose material. The uranium nitrate was allowed to dissolve overnight, then the solutions were quantitatively transferred to titration beakers by rinsing with 1 mL 1 mol L^{-1} HNO₃ a total of three times. Likewise, 4 mL of 1 mol L^{-1} HNO₃ was added to analysis blanks and quality control samples prepared for the project. A 1 mL aliquot of 1 mol L^{-1} H₂SO₄ (Certified ACS Plus, Fisher Scientific, Fair Lawn, NJ, USA) was added to all samples before fuming. The procedure outlined in ASTM 1267-17 was followed for the remainder of the sample preparation and the sample titrations. The ²³³U samples were measured over the course of two days with the order of measurement being samples ORNL 1, 3, and 5 measured on Day 1 and samples ORNL 6, 4, and 2 measured on Day 2. These measurements were performed within a sequence that included analysis blanks and quality control (QC) solutions of CRM 112-A (prepared independently of the TEF calibrant) and CRM 129-A [26]. The average relative bias for the QC measurements was 0.024 % and -0.005 %, respectively, demonstrating that the measurements were in control. The mass of the 6 Master solutions samples dispensed at LLNL and the dilution factor for the Stock solution were used to calculate molality of uranium in the Stock solution from the amount measurement results.

2.3. Isotope dilution mass spectrometry measurements

The molality of uranium in the Master solution and the Stock solution were measured by IDMS at LLNL as an independent verification of the modified Davies and Grav titrations. Three of the U-233 Spike units (unit numbers: U004, U044, and U160) were randomly selected for Stock solution analysis. The solutions in these units were carefully diluted so that isotopic composition measurements and multiple replicate IDMS analyses could be performed for each sample. Two IDMS "reverse-spikes" were used for this project (Table 2). Both solutions were created from CRM 112-A, but one (2016 U Reverse Spike) was prepared before project activities began and the second (2017 U Reverse Spike) was prepared during project activities. Carefully weighed aliquots of the 2017 U Reverse spike were added to the 2 samples of the Master solution that were dispensed to FEP bottles. Aliquots of the 2016 U reverse spike were added to multiple subsamples from the U004, U044, and U160 units. A quantitative dilution of the 2017 U Reverse Spike (Dilution 1) was prepared and aliquots of that solution were added to an additional set of subsamples from unit U044 to enable comparison of results for the 2 reverse spikes. All IDMS samples were allowed to equilibrate and were then diluted for uranium isotope amount ratio analyses.

2.4. Uranium isotope amount ratio measurements

Isotope amount ratio measurements for characterization of the U-



Fig. 1. Schematic of the production and characterization process for determining the attributes of the U-233 Spike refence material. Heavy arrows indicate transfer of material for unit production and attribute characterization. Lighter arrows indicate material transfer for verification analyses. "D&G" is modified Davies and Gray titrimetric analysis for uranium amount.

Table 2

CRM 112-A calibration solutions. Weighing, mass fraction, and molality data for CRM 112-A solutions prepared for calibration of SRM 136f for modified Davies and Gray titrations and for reverse IDMS spike solutions. The masses of uranium metal and solutions were corrected for air buoyancy based on ambient conditions at ORNL and LLNL. Uncertainty values are expanded uncertainties.

Calibrant/Spike	Mass (g)	Mass Fraction/Molality					
Preparation B (TEF titrations)							
U Metal	5.41141 ± 0.00020	$0.99975 \pm 0.00066 ~\rm g~g^{-1}$					
Solution	535.780 ± 0.028	42.4215 \pm 0.0027 μ mol g ⁻¹					
2016 U Reverse Spike	(IDMS)						
U Metal	3.03042 ± 0.00020	$0.99975 \pm 0.00066 ~\rm g~g^{-1}$					
Solution	1111.456 ± 0.026	$11.45461 \pm 0.00082 \ \mu mol \ g^{-1}$					
2017 U Reverse Spike (IDMS)							
U Metal	2.84834 ± 0.00019	$0.99975 \pm 0.00066 ~\rm g~g^{-1}$					
Solution	78.0150 ± 0.0036	$153.385 \pm 0.013 \ \mu mol \ g^{-1}$					
Aliquot	0.08961 ± 0.00010	$153.385 \pm 0.013 \ \mu mol \ g^{-1}$					
Dilution 1	1074.941 ± 0.049	$0.012786 \pm 0.00001 \; 5 \; \mu mol \; g^{-1}$					

233 Spike were made on a Nu-Plasma HR (Charlestown, MA, USA) multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using 3 different measurements routines. The $n(^{238}U)/n(^{233}U)$ isotope amount ratios for the IDMS samples were determined using a routine that measured the isotopes on Faraday cups. For isotopic composition measurements of the Master solution and the 3 reference material units, ²³³U was measured on a Faraday cup and the other uranium isotopes were measured on ion counters. The $n(^{235}U)/n(^{233}U)$, $n(^{236}U)/n(^{233}U)$, $n(^{238}U)/n(^{233}U)$ ratios were measured in single analysis routine but it was necessary to measure the $n(^{234}\text{U})/n(^{233}\text{U})$ ratio in a separate routine due to the arrangement of Faraday cups and ion counters in the mass spectrometer. All mass spectrometry data were corrected for mass fractionation using exponential mass bias correction factors determined from analyses of CRM U010 [27,28] that were performed in sequence with the U-233 Spike samples. Detector baselines and instrument background corrections were performed for all analyses and Faraday-ion counter detector gains were calibrated using CRM U010. The $n(^{234}\text{U})/n(^{233}\text{U})$ isotope amount ratio data was also corrected for an empirically determined ²³³U hydride formation ratio of 2.0 × $10^{-6} n(^{233}UH^+)/n(^{233}U)$ with an estimated relative expanded uncertainty of 25 %. CRM U005-A [28,29] and CRM U030-A [28,30] were analyzed as quality controls samples for the mass spectrometry measurements. The results for these standards indicated that $n (^{234}U)/n$ (^{238}U) , $n(^{235}\text{U})/n(^{238}\text{U})$, and $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurements were accurate within CRM uncertainties.

When ²³³U is produced by neutron capture, small quantities of ²³²U are also created. The relative proportion of ²³²U in ²³³U materials is of particular concern for users due to the energetic 2.6 MeV gamma emission from ²⁰⁸Tl in the ²³²U decay chain. An alpha spectrometry screening measurement was made on two samples of the Stock solution to determine the $n(^{232}U)/n(^{233}U)$ ratio. The samples were purified using UTEVA extraction resin (Eichrom, Lisle, IL, USA) to remove interfering nuclides (primarily ²²⁹Th and ²²⁸Th) and the uranium was electroplated

onto stainless steel planchets. The samples were counted for 15 days on an Ortec ULTRA AS silica detector (Oak Ridge, TN, USA). Regions of interest were defined for 232 U (encompassing 5.263 MeV and 5.320 MeV alpha particles) and for 233 U (all alpha particle energies from 4.309 MeV to 4.824 MeV). The measured activities were converted to atom ratios using appropriate decay constants and branching ratios for the measured alpha energies.

3. Results

3.1. Molality of uranium

The molality of uranium in the 233 U Stock solution was calculated from modified Davies and Gray amount measurements of the Master solution (Table 3). These results and the IDMS verification measurements results (Appendix A) are shown in Fig. 2. The titrimetric data indicate the molality of uranium for the reference material Stock solution is (0.79990 \pm 0.00043) μ mol g^{-1}. Individual uranium molality measurements for the titration and IDMS data sets are internally consistent and measurements overlap within uncertainties. The titrimetric data appear to show a trend of decreasing molality corresponding to the order of sampling, as indicated by the sample numbers. There is a 0.030 % difference between the mean values for measurements performed on Day 1 and Day 2 but a t-test performed to assess day-to-day variability does not indicate a statistically significant difference between the measurements days.

The 2017 U Reverse Spike IDMS analyses indicate a somewhat lower (-0.06 %) average molality of uranium than the modified Davies and Gray titrations and the 2016 U Reverse Spike data are lower still (-0.13 %). This pattern is confirmed by a fixed effect Analysis of Variance (ANOVA) performed on the molality data which indicates a statistically significant method-to-method bias (*F* statistic of 24.0, for an *F* critical of 3.5).

To assess sample variability, the 2016 Reverse Spike IDMS measurements included multiple replicate molality measurements for the three U-233 Spike units. These measurements do not indicate a statistically significant sample-to-sample bias for the uranium molality data (F statistic of 3.8, for an F critical of 4.6).

3.2. Isotope amount ratios

Uranium isotope amount ratio data for the ²³³U reference material are summarized in Table 4 and shown in Fig. 3. ANOVA performed on the characterization data sets do not show a statistically significant sample-to-sample bias for the isotope amount ratio data with the exception of $n(^{234}\text{U})/n(^{233}\text{U})$ ratio which yields a *F* statistic value of 32.6 for a *F* critical value of 5.14. In general, the measured isotope amount ratios for the sample units are consistent with measurements for UTHX001-A as received at LLNL and the Master solution after purification. The reference values calculated from the characterization measurements are also consistent with the values reported in Mathew et al.

Table 3

Sample data and measurement results for titrimetric analyses. Modified Davies and Gray characterization measurement data and results for molality of uranium in the ²³³U Stock solution. Stock Solution Mass Equivalent (italics) is the mass of the analyzed Master solution aliquot multiplied by the gravimetrically determined dilution factor for the Stock solution. Calculated values for the molality of uranium in the Stock solution was determined based on the Stock solution mass equivalent and the amount of uranium in the sample as calculated from the titrant mass and the uranium TEF. Uncertainty values are expanded uncertainties.

Analysis Sample	Master Solution Samples Mass (g)	Stock Solution Mass Equivalent (g)	Titrant Solution Mass (g)	Molality of U in Stock Solution (μ mol g $^{-1}$)
ORNL 1	2.65109 ± 0.00051	132.959 ± 0.024	7.7939 ± 0.0010	0.80017 ± 0.00055
ORNL 2	2.59328 ± 0.00051	130.060 ± 0.024	7.6221 ± 0.0010	0.79997 ± 0.00038
ORNL 3	2.73388 ± 0.00051	137.112 ± 0.024	8.0356 ± 0.0010	0.80000 ± 0.00054
ORNL 4	2.62481 ± 0.00051	131.642 ± 0.024	7.7122 ± 0.0010	0.79971 ± 0.00038
ORNL 5	3.21437 ± 0.00051	161.210 ± 0.023	9.4467 ± 0.0010	0.79990 ± 0.00049
ORNL 6	2.51575 ± 0.00051	126.172 ± 0.024	7.3914 ± 0.0010	0.79967 ± 0.00038
Reference Value for	Molality of U in Stock Solution		0.79990 ± 0.00043	



Fig. 2. Characterization data (filled circles) and verification measurement data (open squares and diamonds) for the molality of uranium in the U-233 Spike Stock solution. Error bars for individual measurements are expanded uncertainties. The reference value for molality of uranium (mean of titrimetric measurements) is shown as a solid line on the chart with an expanded uncertainty envelope indicated by the dashed lines. The dotted lines represent the 0.1% ORNL data quality criteria for modified Davies and Gray titrations.

Table 4

Isotope amount ratio measurement data. Summarized measurement data for uranium isotope amount ratios of the U-233 Spike material. UTHX001-A values are from a test analysis performed on the ²³³U material as received at LLNL. Values for Mathew et al. (italics) are derived from published data for the UTHX001-A material. The Reference Values are the mean of the combined data for U004, U044, and U160. Uncertainties shown for the summarized replicate measurements are 1 standard deviations. Uncertainties for the UTHX001-A, Mathew et al. and the Reference Values are expanded uncertainties.

Analysis	$n(^{234}\text{U})/n(^{233}\text{U})$	$n(^{235}\text{U})/n(^{233}\text{U})$	$n(^{236}\text{U})/n(^{233}\text{U})$	$n(^{238}\text{U})/n(^{233}\text{U})$
Master Solution $(n = 8)$ Spike Unit U004 $(n = 3)$ Spike Unit U044 $(n = 3)$ Spike Unit U160 $(n = 3)$ UTHX001-A (as received) Mathew et al. Reference Values for the U-233 Spike	$\begin{array}{l} (6.37\pm0.14) \ x \ 10^{-5} \\ (6.259\pm0.029) \ x \ 10^{-5} \\ (6.357\pm0.003) \ x \ 10^{-5} \\ (6.231\pm0.019) \ x \ 10^{-5} \\ (6.48\pm0.16) \ x \ 10^{-5} \\ (6.277\pm0.022) \ x \ 10^{-5} \\ (6.28\pm0.11) \ x \ 10^{-5} \end{array}$	$\begin{array}{c} (0.962 \pm 0.013) \ x \ 10^{-5} \\ (0.937 \pm 0.020) \ x \ 10^{-5} \\ (0.944 \pm 0.007) \ x \ 10^{-5} \\ (0.946 \pm 0.018) \ x \ 10^{-5} \\ (0.95 \pm 0.030) \ x \ 10^{-5} \\ (0.943 \pm 0.0087) \ x \ 10^{-5} \\ (0.942 \pm 0.015) \ x \ 10^{-5} \end{array}$	$\begin{array}{l} (0.1981\pm 0.0018) \ x \ 10^{-5} \\ (0.1981\pm 0.0012) \ x \ 10^{-5} \\ (0.1957\pm 0.0015) \ x \ 10^{-5} \\ (0.1964\pm 0.0021) \ x \ 10^{-5} \\ (0.1955\pm 0.0031) \ x \ 10^{-5} \\ (0.1878\pm 0.0065) \ x \ 10^{-5} \\ (0.1967\pm 0.0024) \ x \ 10^{-5} \end{array}$	$\begin{array}{l} (5.07\pm0.28) \ x \ 10^{-5} \\ (4.96\pm0.07) \ x \ 10^{-5} \\ (4.92\pm0.13) \ x \ 10^{-5} \\ (4.78\pm0.34) \ x \ 10^{-5} \\ (5.28\pm0.15) \ x \ 10^{-5} \\ (5.0709\pm0.0059) \ x \ 10^{-5} \\ \textbf{(4.89\pm0.50)} \ x \ 10^{-5} \end{array}$

except for the $n(^{236}\text{U})/n(^{233}\text{U})$ ratio which is significantly higher in this study (5% on average). The ^{233}U isotope amount fraction, $n(^{233}\text{U})/n(\text{U})$, calculated from the reference values is 0.9998769 \pm 0.0000052, which is essentially identical to the value of 0.99987521 \pm 0.00000027 measured by Mathew et al. on samples of the bulk UTHX001-A material.

Alpha spectrometry screening measurements indicated a low abundance of ²³²U with an uncertainty-weighted mean value for the $n(^{232}U)/n(^{233}U)$ isotope amount ratio of $(1.4 \pm 0.3) \times 10^{-8}$ for a reference date of August 03, 2018. Assuming each unit for the U-233 Spike has approximately 8.5 µmol of ^{233}U , this isotope amount ratio corresponds to $a^{232}U$ activity of (22.9 ± 4.9) Bq per unit. Therefore, the maximum activity for the problematic 208 Tl decay would be (8.2 ± 1.9) Bq per sample unit assuming secular equilibrium with ^{232}U and a 0.3593 ± 0.0007 (k = 1) branching fraction for alpha decay of 212 Bi [31].

4. Discussion

4.1. Suitability of the U-233 spike reference material

The goal of this project was to prepare a highly reliable reference material for uranium amount measurements by IDMS. To assure that the reference material will meet user needs, it is necessary to evaluate material stability, homogeneity, and the reproducibility of characterized attributes. Further, it is important to demonstrate the metrological traceability of characterized attribute values and to assign measurement uncertainties that are consistent with international standards.

Reference material units of the U-233 Spike should be stable indefinitely. The molality of the uranium Stock solution dispensed to individual reference materials units was determined for this study. This molality value, in conjunction with the well-characterized mass of solution dispensed to each unit and the isotope amount fraction of ²³³U, allow the amount of ²³³U in a unit of the U-233 Spike to be precisely calculated. Unit-specific amounts of ²³³U and the mass of each unit container will be provided to users to facilitate accurate molality calculations for in-house preparation of spike solutions. The units do not contain any free liquids with the uranium material being a film of dried nitrate at the bottom of each bottle. The advantage to providing the 233 U amount as an absolute quantity, along with a well-constrained container weight, is that any changes to the form of the quantified material within the primary container will not alter the reference material attribute values. Although the 233 U nuclide is radioactive and decays by α particle emission to 229 Th, it has a half-life of 1.59×10^5 a. Therefore, the change in the amount of ²³³U in a unit over the planned lifetime of the reference material batch (20-30 years) can be corrected quantitatively and is significantly smaller (–0.015 % change for 30 a) than the amount uncertainty (0.058 %-0.059 %, see section 4.2). The other uranium nuclides characterized for isotope amount ratios have longer half-lives than ²³³U, so changes in the amount of these isotopes due to radioactive decay will be negligible.

Heterogeneous reference material units would significantly diminish the utility of the U-233 Spike. The amount of uranium is independently characterized for each unit, so the primary concern for this reference material is variability of the isotopic composition of uranium between units. There are several mechanisms that can result in variable uranium composition between sample units. These include differential contamination, a heterogeneous Stock solution, and changes to the Stock solution during unit production. To minimize the potential for unit-to-unit variability due to contamination, work was performed in a dedicated low-contamination work space that was specifically refurbished for preparation of high-purity isotopic reference materials; all labware was



Fig. 3. Uranium isotope amount ratio measurement data. Error bars are expanded uncertainties as reported by the analysis laboratories. Uncertainties for the measurements result from Mathew et al. (squares) are smaller than the data symbols in some charts. Reference values for the U-233 Spike uranium isotope amount ratios, shown as solid lines on the charts, are based on measurement of the U-233 Spike units (filled circles). The expanded uncertainty envelopes for the reference values are indicated by the dashed lines. The UTHX001-A (open triangle) and Master Solution (open diamonds) data points are preliminary measurements made upon receipt at LLNL and after the separation was performed for the Master solution.

cleaned for ultra-trace low-contamination work; only high-purity reagents were used for project activities; and the dispensing apparatus was equipped with a new volumetric syringe and product transfer lines that were carefully cleaned and preconditioned for production of the reference material units. Furthermore, the relatively high uranium concentration of the spike Stock solution (0.2 g L⁻¹) would require a contamination event far in excess of measured uranium blanks to have a discernable impact on the characteristics of the reference material. The Stock solution for the U-233 Spike units was agitated (by shaking) after it was created from the Master solution. To minimize the potential for the Stock solution composition to drift during sample dispensing, the 165 reference material units were dispensed in a single work session (about 1 h).

An observed trend of decreasing molality with successive samples of the Master solution that were prepared for analysis by modified Davies and Gray titration is not due to sampling issues or a temporal drift in the measurement routine. Instead, the observed distribution of the data is a results of variable uranium blank corrections for titrimetric data in combination with the order of the sample analyses. The Day 1 titrimetric data indicate molality values that are, on average, 0.03 % higher than the Day 2 data. Since Day 1 analyses included samples 1, 3, and 5 and Day 2 samples were 2, 4, and 6. This difference created the appearance of an irregular pattern of decreasing molality with sample number. Furthermore, the difference between the measurement results for the two analysis days is largely due to the uranium blanks measured for each day. The mean Day 1 uranium blank was measured at (24 \pm 13) µg and the Day 2 blank was (36 \pm 3) µg. If an average blank of 30 µg is used to correct titration data for both days, the relative difference in mean values changes from 0.030 % to -0.019 %, the relative standard deviation of the data decreases from 0.024 % to 0.018 %, and the decreasing trend for the sample data essentially disappears. Although the Day 2 blank data is less variable, there is no independent evidence that either set of the uranium blanks is more accurate. Therefore, the uranium blank corrections for each day of analysis were maintained. The uncertainties for the measured blanks and the measurement variability for the data were incorporated in the uncertainty budget for the molality of the Stock solution (see section 4.2).

The uranium IDMS and isotopic composition measurements provide data that can be used to evaluate unit-to-unit variability for the U-233 Spike. The 3 units of the U-233 Spike were analyzed for uranium amount and isotope amount ratios under repeatability conditions as defined in the International Vocabulary of Metrology (VIM) [32]. ANOVA performed on the IDMS data for the 2016 U Reverse Spike samples do not indicate a statistically significant unit-to-unit variability (see results section) nor do the isotopic data indicate unit-to-unit variability with the exception of the $n(^{234}U)/n(^{233}U)$ ratio measurements which indicate a unit-to-unit bias at greater than a 99% level of confidence. This variability, however, is likely to be an analytical artifact rather than an indication of unit variability. The isotopic composition of extraneous uranium that could reasonably be expected to create unit-to-unit variability in the U-233 Spike (presumably by differential contamination) would be dominated by ²³⁸U and ²³⁵U and would probably have isotopic abundances similar to natural uranium. Accordingly, any extraneous uranium contribution to the units will have a large proportion of ²³⁵U and ²³⁸U relative to ²³⁴U. In contrast, the U-233 Spike has lower relative abundances of ²³⁵U and ²³⁸U, making the $n(^{235}U)/n(^{233}U)$ and $n(^{238}U)/n$ (^{233}U) ratios a more sensitive indicator of contamination than the *n* $(^{234}\text{U})/n(^{233}\text{U})$ ratio. Yet, statistically significant unit-to-unit viability is not observed for these isotope amount ratios. Based on this observation, it is unlikely that the measurement variability for the $n(^{234}\text{U})/n(^{233}\text{U})$ ratio represents a real difference in the uranium isotopic composition from unit-to-unit. A potential explanation is that the observed $n(^{234}U)/n$ (²³³U) variability is associated with the ratio-specific procedure used for this measurement. For instance, each of the solutions analyzed for the 3 units have slightly different dilution factors but the same ²³³UH⁺ formation rate was applied to the $n(^{234}U)/n(^{233}U)$ measurements data. If the concentration of uranium in the analysis solution had a direct effect on the uranium hydride formation rate, this could have created a systematic unit-to-unit difference in the 234 U data that would not be observed in the 235 U, 236 U, or the 238 U data.

The verification data from this project and published data for the ²³³U starting material are sufficient to demonstrate reproducibility, as defined in the VIM [32], for the U-233 Spike attribute values. The 6 modified Davies and Gray titration measurements of the ²³³U Master solution were used to establish the reference value for molality of uranium in the U-233 Spike stock solution. The IDMS measurements results confirm the reference value within measurement uncertainties but are systematically lower. The IDMS measurements performed on the Master solution have a relative expanded uncertainty of 0.17 % but differ from the reference value by only -0.058 %. The IDMS measurement made directly on the Stock solution indicate values ranging from -0.03 % to -0.18 % lower than the reference value. Bias for the IDMS results is most pronounced in samples prepared with the 2016 U Reverse Spike. This spike was prepared 1 year before the IDMS measurements were made and the solution was stored as a bulk solution in a Teflon bottle. The observed bias could be due to an increase in the concentration of uranium in the reverse-spike resulting from evaporative losses from the bottle over the course of 1 year. This is also consistent with the observation that IDMS results for the 2017 U Reverse Spike, prepared at the time of project activities, are more consistent with the reference value.

The isotopic composition of the ²³³U starting material was measured before and after purification for reference material production. Then, 3 replicate measurements were made on each of 3 units of the U-233 Spike. Within uncertainties, the isotopic ratio data for these measurement campaigns are consistent with the reference values. These values were also compared to a published isotopic composition of the ²³³U starting material that was measured using a substantially different analytical technique (i.e. thermal ionization mass spectrometry). The *n* (²³⁴U)/*n*(²³³U), *n*(²³⁵U)/*n*(²³³U), and *n*(²³⁸U)/*n*(²³³U) ratios derived from the published data are indistinguishable from the characterized

Table 5

Uncertainty evaluation for the molality of uranium in the²³³U Stock solution. Uncertainty evaluation including all the significant components contributing to the combined standard uncertainty for the characterized molality of uranium in the Stock solution for the U-233 Spike. Assessment Type "A" denotes evaluation by statistical methods; "B" denotes evaluation by other methods. A coverage factor (*k*) of 2 was applied to the combined standard uncertainty to obtain an expanded uncertainty with an approximately 95 % confidence level.

Uncertainty Component	Description	Assessment Type	Relative standard uncertainty (%) of component
N _{Var}	Standard uncertainty of multiple modified Davies and Gray measurements	А	0.010
δ_{Dil}	Combined standard uncertainty of dilution factor for the Stock solution	В	0.001
δ_{TEF}	Combined standard uncertainty of Titrant Equivalency Factor	В	0.021
W _{CRM}	Combined standard uncertainty of CRM 112-A calibrant for the TEF	В	0.005
M _{Titration}	Combined standard uncertainties for sample and titrant masses	В	0.005
N _{Blnk}	Estimated standard uncertainty for titration blank measurements	В	0.013
N_U	Relative combined standa (%)	rd uncertainty	0.028
	Relative expanded uncert	ainty (%)	0.057

Table 6

Uncertainty evaluation for uranium isotope amount ratios of the U-233 Spike. Significant uncertainty components contributing to the combined standard uncertainty for the characterized uranium isotope amount ratios of the U-233 Spike. Assessment Type "A" denotes evaluation by statistical methods; "B" denotes evaluation by other methods. A coverage factor (*k*) of 2 was applied to the combined standard uncertainties to obtain expanded uncertainties with an approximately 95 % confidence level.

Uncertainty	Description	Assessment Type	Relative standard uncertainty (%) of contributing components			
Component			$n(^{234}U)/n(^{233}U)$	$n(^{235}\text{U})/n(^{233}\text{U})$	$n(^{236}\text{U})/n(^{233}\text{U})$	$n(^{238}U)/n(^{233}U)$
R _{VarW}	Standard uncertainty of the data set or within-unit measurement variability	А	0.11	0.52	0.30	2.8
R _{VarB}	Standard uncertainty of between-unit measurement variability	A	0.60	-	-	-
δ_{Blnk}	Standard uncertainty of instrument uranium blank correction	В	0.00	0.32	0.33	4.3
δ_{CRM}	Standard uncertainty derived from certificate values for mass spectrometry calibration CRM	В	0.05	0.05	0.05	0.05
δ_{IC}	Estimated standard uncertainty of Ion Counter-Faraday intercalibration for mass spectrometry	В	0.41	0.47	0.41	0.33
δ_{UH+}	Estimated standard uncertainty of ²³³ U hydride correction.	В	0.40	-	-	-
(R_{ii})	Relative combined standard uncertainty (%)		0.84	0.77	0.61	5.1
	Relative expanded uncertainty (%)		1.7	1.5	1.2	10.2

values but the $n(^{236}\text{U})/n(^{233}\text{U})$ ratio is 5% lower than the value measured in this study. Although no explanation for the observed difference has been identified, it is notable that ^{236}U is the lowest abundance isotope measured by mass spectrometry for this project and is, therefore, very sensitive to a variety of factors such as contamination, background corrections, and dark noise corrections. No independent indication of problems with the measurements was recognized and the results for $n(^{236}\text{U})/n(^{233}\text{U})$ ratio have been particularly consistent for the MC-ICP-MS measurements. Due to these observations, the more conservative isotope amount ratios measured for this study will be utilized for the reference material value.

To establish the traceability for the characterized attributes of the U-233 Spike, it is necessary to demonstrate that "the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty" [32]. The attributes characterized for this reference material are the 233 U amount per sample unit and the $n(^{234}\text{U})/n(^{233}\text{U})$, $n(^{235}\text{U})/n(^{233}\text{U})$, $n(^{236}\text{U})/n(^{233}\text{U})$, and n $(^{238}\text{U})/n(^{233}\text{U})$ isotope amount ratios. These reference values can be tied directly to the mole through calibrations using CRMs from the NBL Program Office (the Department of Energy office maintaining nuclear material standards for the United States). The MC-ICP-MS measurements of uranium isotope amount ratios were corrected for mass bias using the CRM U010 uranium isotopic reference material which was also used to perform detector intercalibrations. The amount of uranium per unit was determined based on modified Davies and Gray titrations performed on subsamples of the Master solution; the quantitative dilution factor for the Stock solution; and the measured mass of solution dispensed to the individual units. All masses for sample preparation, sample aliquots for analysis, dispensed titrant solution, and individual sample units were measured on calibrated balances that were checked before and after project activities using certified weight sets. The titrimetric assay method for this project incorporated a calibration for the mass of a potassium dichromate solution that was necessary to titrate a known amount of the uranium metal assay standard CRM 112-A. This factor was used to calculate the amount of uranium titrated in each analyzed sample of Master solution. The quantitative dilution factor for the Stock solution allows the amount of uranium dispensed to each unit to be traceably calculated and the isotope amount fraction of ²³³U, as determined from the traceable isotope amount ratio measurements, was used to define the moles of ²³³U per unit.

4.2. Uncertainty evaluation for uranium amount and isotope amount ratios

Uncertainty models for the molality of uranium in the reference material Stock solution and for uranium isotope amount ratios were developed in accordance with the requirements of the ISO Guide for the Expression of Uncertainty in Measurement [33] and NIST Technical Note 1297 [34]. The GUM Workbench software (version 2.4.1, Metrodata, Grenzach-Wyhlen, Germany) was used to calculate the reference values and uncertainties.

The combined standard uncertainty for the molality of uranium (N_{II}) in the Stock solution is dominated by the uncertainties for the titrant equivalency factor (δ_{TEF}); the titration blanks for the measurements (N_{Blnk}) ; and the measurement variability (N_{Var}) (Table 5). The combined standard uncertainty for the CRM 112-A uranium metal standard used to calibrate the TEF (W_{CRM}) and the combined uncertainty for mass of titrant and sample $(M_{Titration})$ also contributed to the overall uncertainty. The dilution factor (δ_{Dil}) for preparation of the Stock solution resulted in a minimal contribution to the overall uncertainty and the contribution from the molar mass of CRM 112-A was insignificant (<0.001 % relative standard uncertainty). To calculate uncertainties for unit-specific amounts, the uncertainty for the isotope amount fraction of $^{233}\!\mathrm{U}$ and the mass of Stock solution distributed to each reference material unit were combined with the uncertainty for the molality of the Stock solution. The relative combined standard uncertainty for the mass of dispensed solution is small (0.01 %) and the relative uncertainty for 233 U isotope amount fraction is trivial (0.00025 %). The resulting relative expanded uncertainties for amount of ²³³U in each reference material unit are between 0.058 % and 0.059 %, depending on the uncertainty for the mass of a specific unit.

The reference values for the U-233 Spike uranium isotope amount ratios (R_{ij}) were calculated as the mean value of measurements performed for 3 sample units. The combined standard uncertainties for the uranium isotope amount ratios (Table 6) are dominated by uncertainty components for measurement variability (R_{Var}) (for the n (²³⁴U)/n (²³³U) ratio this includes both within and between-unit variability as derived from ANOVA); the uncertainty estimates for the Ion Counter-Faraday intercalibrations (δ_{IC}); and the correction for uranium instrumental blank (δ_{Blnk}). The combined standard uncertainty for the uranium isotopic composition of CRM U010 used for mass bias correction also



Fig. 4. Curves representing modelled uncertainties for isotope amount ratios from a 1% ²³⁵U enriched material corrected for spike contributions from different ²³³U reference materials. The curves represent the expanded uncertainties for isotope amount ratios recovered from samples spiked with molar proportions of ²³³U spike-to-sample ranging from 0.1 to 10.

contributed to the overall measurement uncertainty. For the $n (^{234}U)/n (^{233}U)$ ratio, the uncertainty on the $^{233}UH^+$ hydride correction was another major contributor to the combined standard uncertainty.

4.3. Improvements for simultaneous uranium amount and isotope amount ratio measurements

A reasonable estimate for the uncertainty of amount measurements by IDMS can be made by adding, in quadrature, the relative standard uncertainties for the masses of the sample and spike, the measured target isotope amount ratio for the IDMS mixture, the isotopic compositions of the sample, and the "known" isotopic composition and molality of the spike [1]. Although any of these components can contribute significantly to the measurement uncertainty, it is frequently the uncertainty of the isotope amount ratio measurements for an IDMS mixture and/or the sample that dominate. The ²³³U CRMs commonly used for IDMS and the U-233 Spike described here, are highly enriched (> 0.98 $n(^{233}\text{U})/n$ (U)) and have relatively low uncertainties for amount or molality of uranium (< 0.2 % relative expanded uncertainty). Therefore, carefully executed IDMS measurements with any of these spikes should yield

accurate values with relatively low uncertainties for amount of uranium across a wide range of sample isotopic compositions and spike-to-sample ratios [35,36]. The primary advantage of a very highly enriched ²³³U reference material is an improved ability to recover accurate and precise isotopic composition data from a spiked uranium sample.

To assess potential measurement improvements from the U-233 Spike, uncertainty modelling was performed for the available ²³³U CRMs and the U-233 Spike. Synthetic isotope amount ratio data for uranium was generated for mixed IDMS solutions of each ²³³U reference material and 3 different "unknown" U materials with ²³⁵U enrichments of 1 %, 4.5 %, and 20 %. The certified isotopic compositions of CRMs U010, U045 [37] and U200 [38] were used as sample compositions for generating the synthetic data. These compositions were combined with the ²³³U reference materials in molar proportions ranging from 0.1 to 10. Spike-corrected $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$, and $n(^{236}\text{U})/n$ (²³⁸U) isotope amount ratios (R_{ijCorr}) were calculated using a simplified correction algorithm (Eq. (1)). The synthetic $n(^{234}\text{U})/n(^{233}\text{U})$, $n(^{235}\text{U})/n$ (²³³U), $n(^{236}\text{U})/n(^{233}\text{U})$ ratios (R_{ikMeas}) and $n(^{238}\text{U})/n$ (²³³U) ratio (R_{jkMeas}) were input to an uncertainty modelling program (GUM Workbench) along with the appropriate uranium isotope amount fractions (N) from the ²³³U spike CRM certificates and from this study.

$$R_{ijCorr} = \left(R_{ikMeas} - \frac{N_i}{N_k}\right) \div \left(R_{jkMeas} - \frac{N_j}{N_k}\right)$$
(1)

The goal of the model was to assess uncertainty improvements that could be realized by use of the U-233 Spike, so it was assumed that the "unknowns" had no ²³³U present and that all of the synthetic isotope amount ratios had a small relative expanded uncertainty of 0.1 %. Fig. 4 shows the plotted result for the 1% enriched model. The U-233 Spike resulted in significant improvements for the uncertainty of recovered *n* $(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ ratios throughout the modelled range of spike-to-sample. For the $n(^{234}U)/n(^{238}U)$ ratio, these improvements ranged from a factor of approximately 2 for a 0.1 spike-to-sample ratio to more than a factor of 8 for a spike-to-sample ratio of 10. The observed improvements are even more substantial for the $n(^{236}\text{U})/n$ (²³⁸U) isotope amount ratios (from a factor of 3 to greater than 100). The potential improvements in recovered $n(^{235}U)/n(^{238}U)$ isotope amount ratios for the CRM 111 and CRM 111-A spikes, however, are not realized until spike-to-sample proportions exceeded 2. For the 4.5 % and 20 %enriched materials, the benefits of the U-233 Spike are still evident but are occur at slightly higher spike-to-sample ratios due to larger relative proportions of ²³⁴U, ²³⁵U, and ²³⁶U in these materials (Appendex B, Fig. B1).

5. Conclusion

A new highly-enriched ²³³U isotopic spike has been prepared and characterized for IDMS analyses of uranium. The ²³³U molality measurements for the solutions used to produce the U-233 Spike units are consistent, traceable, and reproducible. The uranium isotope amount ratio characterization measurements verify the highly-enriched nature of the ²³³U material and indicate that the solution dispensed to the reference material units was homogeneous. Relative to other widely used ²³³U reference materials, the U-233 Spike will allow for significantly lower uncertainties in spike-corrected isotopic data, particularly for minor isotope amount ratios of low-enriched materials. Accordingly, this reference material will be a valuable analytical tool for highly reliable measurements performed on trace level uranium samples such as those encountered in nuclear safeguards and nuclear forensics.³

³ This material was developed primarily for nuclear safeguard and nuclear forensic analyses and can be made available to users on a case by case basis. Please contact the corresponding author for more information.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Isotope Dilution Mass Spectrometry Data

United States Department of Energy was instrumental to the successful completion of this project. Funding for the characterization work at LLNL (release number: LLNL-JRNL-814535) and ORNL and project coordination activities at NIST was provided by the United States Department of Homeland Security. The starting material for this project was made available through a project funded by the NNSA.

IDMS Analysis sample data and results. Analysis data for IDMS verification measurements for molality of uranium in the 233 U Stock solution. Stock Solution Mass Equivalent is the calculated mass of Stock solution corresponding to the mass of the Master solution or diluted Stock solution aliquot that was spiked for the IDMS measurement. These calculated values are based on quantitatively determined dilution or factors. The dilution factor and expanded uncertainty for the production of the Stock solution from the Master solution is 50.15280 ± 0.00073 . The dilution factors for the Stock solution to produce sample aliquots for #U004, U044, and U160 are 3.03394 ± 0.00073 , 2.91254 ± 0.00072 ; and 2.95623 ± 0.00088 , respectively. All mass values are corrected for air buoyancy based on ambient laboratory conditions. Uncertainty values represent expanded uncertainties. See text for additional details.

Analysis Sample	Reverse IDMS Spike	IDMS Sample Mass (g)	Stock Solution Mass Equivalent (g)	Reverse Spike Solution Mass (g)	Measured Isotope Amount Ratio n (²³⁸ U)/ n (²³³ U)	Stock Solution Molality of U $(\mu mol g^{-1})$
Master 1	2017 U	0.48877 ± 0.00051	24.513 ± 0.025	0.48318 ± 0.00051	3.7548 ± 0.0075	0.7995 ± 0.0015
Master 2		0.76512 ± 0.00051	38.373 ± 0.025	0.89751 ± 0.00051	4.4557 ± 0.0066	0.7994 ± 0.0012
U004-1	2016 U	0.36351 ± 0.00051	$\textbf{0.11981} \pm \textbf{0.00017}$	0.47120 ± 0.00051	55.99 ± 0.11	0.7987 ± 0.0016
U004-2		0.44779 ± 0.00051	$\textbf{0.14759} \pm \textbf{0.00017}$	0.59683 ± 0.00051	57.566 ± 0.083	0.7988 ± 0.0012
U004-3		0.58907 ± 0.00051	0.19416 ± 0.00017	0.42814 ± 0.00051	31.393 ± 0.045	0.7988 ± 0.0012
U044-6		0.37234 ± 0.00051	$\textbf{0.12784} \pm \textbf{0.00018}$	0.46470 ± 0.00051	51.76 ± 0.10	0.7986 ± 0.0016
U044-7		0.46855 ± 0.00051	$\textbf{0.16087} \pm \textbf{0.00018}$	0.57701 ± 0.00051	51.052 ± 0.074	0.7990 ± 0.0012
U044-8		0.71828 ± 0.00051	$\textbf{0.24662} \pm \textbf{0.00018}$	0.52260 ± 0.00052	30.139 ± 0.045	0.7996 ± 0.0012
U044-9		0.89784 ± 0.00051	0.30827 ± 0.00019	0.57791 ± 0.00051	26.679 ± 0.038	0.7991 ± 0.0012
U044-10		1.16252 ± 0.00051	0.39914 ± 0.00020	0.56320 ± 0.00051	20.083 ± 0.029	0.7990 ± 0.0012
U044-11	2017 U	0.49630 ± 0.00051	$\textit{0.17040} \pm \textit{0.00018}$	7.00915 ± 0.00053	0.6529 ± 0.0010	0.7998 ± 0.0017
U044-12		0.44764 ± 0.00051	$\textit{0.15370} \pm \textit{0.00018}$	12.36502 ± 0.00058	1.2772 ± 0.0019	0.7996 ± 0.0018
U044-13		0.40047 ± 0.00051	0.13750 ± 0.00018	18.95319 ± 0.00067	2.1904 ± 0.0034	0.7989 ± 0.0018
U160-1	2016 U	0.33915 ± 0.00051	$\textit{0.11472} \pm \textit{0.00017}$	0.50573 ± 0.00051	62.782 ± 0.094	0.7985 ± 0.0013
U160-2		0.54497 ± 0.00051	$\textit{0.18435} \pm \textit{0.00018}$	0.55706 ± 0.00051	43.040 ± 0.075	0.7984 ± 0.0014
U160-3		0.71678 ± 0.00051	0.24246 ± 0.00019	0.70919 ± 0.00051	41.642 ± 0.069	0.7988 ± 0.0014

Appendix B. Uncertainty modelling results for spike corrected isotope amount ratios



Fig. B1. Curves representing modelled uncertainties for isotope amount ratios from 4.5 % to 20 % ²³⁵U enriched materials corrected for spike contributions from different ²³³U reference materials. The curves represent the expanded uncertainties for isotope amount ratios recovered from samples spiked with molar proportions of ²³³U spike-to-sample ranging from 0.1 to 10.

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