Qualification and Initial Characterization of a High-Purity ^{233}U Spike for use in Uranium Analyses

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Abstract:

Several high-purity ^{233}U items from the repository had been rescued and identified for use in uranium isotopic analyses to support a broad variety of applications in nuclear safeguards, non-proliferation, and nuclear forensics. By preserving and maintaining the supply chain of ^{233}U materials of different pedigree for use as source materials for certified reference materials (CRMs) it is ensured that the safeguards community has the tools needed for high quality analytical measurements of uranium elemental and isotopic amount contents by mass spectrometry. One of the items identified as a source material for a high-purity CRM had been characterized for the uranium isotope-amount ratios using thermal ionization mass spectrometry (TIMS). Additional verification measurements on this material using quadrupole inductively coupled plasma mass spectrometry (ICPMS) had also been performed. The comparison of the ICPMS uranium isotope-amount ratios with the TIMS data, with much smaller uncertainties, provided validation of the mass spectrometric measurement practices using the ICPMS instrument. ICPMS is the measurement method proposed to be used for the initial screening of the purity of all items in the rescue campaign.

1. Introduction

Oak Ridge National Laboratory (ORNL) had taken the leadership role in identifying and rescuing, from downblending, precious ^{233}U enriched material in its storage repository for certification as reference materials in support of uranium analysis by various analytical techniques for safeguards and non-proliferation measurements including nuclear forensics. The synthetic ^{233}U isotope is an end product of reactor processes starting with the ^{232}Th target material. High purity ^{233}U materials have several uses: i) comparative spike material in uranium amount content measurement techniques using isotope dilution mass spectrometry (IDMS), ii) production path studies in development of nuclear forensic signatures, iii) radiation signature training devices and standards, iv) power reactor fuel (LFTR), and v) treatment of cancer (^{233}U progeny). Compared to certified reference material (CRM) 111-A [1], presently used as a spike material for isotope dilution mass spectrometry, available from New Brunswick Laboratory (NBL) of the U.S. Department of Energy (DOE), some of the ^{233}U items in storage at ORNL have higher purity. Higher purity spike materials would make it possible to analyze smaller quantities of samples for uranium amount content and reduce the quantities of hazardous waste materials sent to storage facilities.

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Three different sub-samples from one of the high-purity ^{233}U material were characterized for the uranium isotope-amount ratios using TRITON thermal ionization mass spectrometer (TIMS) instrument. The sub-samples analyzed by TIMS came from the first large batch of ^{233}U material that was identified as a source material for CRM production. Additionally, isotope-amount ratios were obtained using Quad ICPMS instrument at ORNL. This initial characterization study is presented here.

2. Materials & Methods

2.1 Sample Preparation

Rescued items are processed in a glovebox laboratory located in the Radiochemical and Engineering Development Center at ORNL. A new glovebox train dedicated to only these rescue efforts is used to process each item. Items are processed one at a time starting with the highest purity items first and working in order of purity to the lower purity materials. Maintaining purity of each item during handling and processing is extremely important so as not to compromise the quality of the material available to the scientific community. Tasks such as opening the various sealed containers and performing sample chemistry routines in a glovebox are well thought out and planned to prevent not only cross-contamination between batches but also to prevent the introduction of uranium from ubiquitous external sources such as reagents, labware, and the glovebox environment. The glovebox train was designed to include a “dry” box in which all physical manipulations to the items would be accomplished and a separate “wet” box for all wet chemical operations. Before opening of the sealed containers with the rescued items, the outside surfaces of the containers are cleaned and swiped to monitor the uranium contamination levels. Once the material is removed from the container all weighings take place in the “dry” box including the separation of the aliquots to be digested for the verification measurements in the “wet” box. When the material is transferred into the “wet” box it is done so using all new containers and vessels. Only high purity reagents and acids are used for the chemical processes and bulk digestions are performed in quartz vessels which are leached and cleaned prior to use. Prior to the start of the processing of each item, the boxes are wiped down and smeared for uranium backgrounds.

For the dissolution of the high purity item characterized here, the larger “chunks” of oxide were first manually sized and then all of the material was weighed together. The oxide batch was then added slowly to a warm (100ºC) solution of 11M HNO_3. After approximately an hour at temperature an orange tint and cloudiness was observed in the solution. Additional acid was added and the hotplate temperature was raised to 150ºC. After 4 hours, the solution was noted to be a uniform “clear” bright yellow indicating a complete dissolution. The final solution was diluted to a known volume in a volumetric flask. From this solution an aliquot equal to 6 grams of U-233 was removed by weight for use in CRM production campaigns.

Three sub-samples were removed from the 6 gram solution and shipped to NBL for the characterization study described here. Each sub-sample had a concentration of ~0.5 mg/mL total uranium.

2.2 Thermal Ionization Mass Spectrometry

Characterization of the uranium isotope-amount ratios in the high-purity ^{233}U material used two TIMS measurement techniques: Total Evaporation (TE) and Conventional. Both techniques employed zone-refined Re in the double-filament configuration. Details on the analytical techniques are published elsewhere [2-5] and will not be repeated here. Prior to use, the Re filaments were preconditioned by heating in vacuum, at ~4.6 A for 30 minutes. Preconditioning reduces the U backgrounds, removes the organic surface contaminants, and facilitates the conversion of the uranyl nitrate solution into a refractory oxide (UO_3 or U_3O_8). The sample drying procedures consisted of evaporating μL-sized drops of uranyl nitrate deposited on the filament surface by passing a current of ~1 A for two minutes followed by 1.5 A and 2 A for 10 s each.

Filament heating routine during TE analyses included the following steps: a) the ionization filament current is ramped up to about 5 to 5.3 A (corresponding to a temperature of about ~1800°C and to a ^{187}Re signal of ~200 to 400 mV on the Faraday), b) the ^{187}Re ion beam is focused and peak-centered, c) the sample loaded evaporation filament is heated in a controlled manner such that about 50 to 200 mV summed signal intensity (^{233}U signal intensity for the characterization sample and sum of the “major” isotopes ^{235}U and ^{238}U for the CRM standards) is measured on the Faraday, d) the uranium ion beam is focused and peak centered, e) data acquisition begins and the evaporation filament is heated, under computer control, to yield a pre-defined summed uranium signal intensity, and f) data acquisition and evaporation filament heating is continued until the summed uranium ion signal intensity drop below a pre-defined lower limit (typically about 100 mV) as the sample is exhausted [2,5]. The filament heating routine in Conventional analyses is similar, except for step c, where a summed uranium signal intensity of ~4000 mV is used for focusing and peak centering. Another difference of the Conventional analyses compared to TE is that in Conventional analysis data acquisition stops once a specified number of cycles are complete. In other words, the sample is not analyzed to exhaustion during the Conventional analysis.

2.2.1 Major Ratio Measurements by TE technique using TRITON

TE is well established analytical technique for major isotope-amount ratio measurements of uranium and plutonium [2, 6]. The mass bias correction at the n(^{235}U)/n(^{238}U) major isotope ratio during TE analysis was evaluated using four aliquots of CRM U630 [7] (standards used for estimation of the mass bias correction in TE analyses are known as comparator standards). The TRITON TE turret also included four aliquots of CRM U500 [8] as quality control (QC) standards. The average mass bias correction factor from the comparator standard analyses was used to correct the major isotope ratio of the characterization sub-sample aliquots as explained in Mathew et al. [2].

The ^{233}U characterization sub-sample aliquots were analyzed on a TRITON instrument for the n(^{233}U/^{238}U) major ratio. Sample loads for TE analysis consisted of 0.5 μg of U dispensed onto preconditioned Re filament and dried according to the filament drying routine described in the previous section. The TE analyses were run using a 15 V summed (^{233}U signal intensity for the characterization sample and sum of the "major" isotopes - ^{235}U and ^{238}U, for comparator and QC CRMs) ion signal intensity. The cup configuration used for the TE analysis is given in Table 1. TRITON TE measurements consisted of consecutive 1-second integrations until the sample was exhausted [2]. During TE analyses the isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U are all measured simultaneously. Note that the ^{235}U abundances in the ^{233}U characterization samples were measured on the secondary electron multiplier (SEM) equipped with an energy filter (retarding potential quadrupole – RPQ).

Table 1 here

2.2.2 Conventional Measurements using TRITON instruments

The conventional analysis technique performs corrections for peak-tailing using peak tail intensity measurements on either side of the isotope of interest. The peak-tailing corrections are performed on a cycle-per-cycle basis. The mass bias effects at the minor isotopes are also corrected on a cycle-per-cycle basis using the major ratio measured in that cycle. However, unlike TE/MTE analysis, the sample is not analyzed to exhaustion. Hence, the major ratio data from conventional analysis is biased compared to those from TE/MTE. Because the residual bias in the major ratio data from conventional analysis varies significantly from filament-to-filament, this ratio is used only for estimation of the mass bias effects - on a cycle-per-cycle basis – at the minor isotope ratios and are not used for generating reportable data.

Three sub-samples from the high-purity ^{233}U material were analyzed for uranium minor isotope-amount ratios by the conventional technique using TRITON instrument. The Conventional turret on the TRITON instrument used the cup configuration and measurement steps shown in Table 2. These included ^{234}U and ^{236}U abundance measurements as well as background measurements at these isotopes using an ion-counter (SEM).

Table 2 here

Sample loads for Conventional analysis consisted of 5 μg of U dispensed onto preconditioned Re filaments and dried according to the drying routine described earlier. The Conventional analyses were performed at 15 V summed ion signal intensity.

For Conventional analysis, two aliquots of CRM U030-A were used as QC standards. During Conventional analyses, the mass bias correction at the minor isotope ratios were estimated by a comparison of the measured n(^{235}U)/n(^{238}U) isotope-amount ratio in each measurement cycle with the certified ratio and scaling this correction factor appropriately to the other isotope ratios.

2.3 Verification Measurements using ICP-MS

Uranium isotopics for this high-purity ^{233}U item were also measured at ORNL using a single detector quadrupole ICPMS, Thermo X-Series II. The ORNL ICPMS isotopic measurements are used to validate the higher precision and accuracy TIMS data from NBL. This comparison also provided a verification of the mass spectrometry procedure and practices at ORNL. For all items in the rescue campaign, ORNL intends to use ICPMS measurements to verify the purity of the items in the rescue campaign. The Thermo X-Series II instrument was tuned and optimized according to manufacturer procedures and the performance verified using the built-in specifications within the software. All uranium masses measured were kept within the pulse-counting mode of the detector. Corrections for uranium hydride (233U-1H) at mass 234 were accomplished using a correction factor obtained by measuring hydride generation at mass 239 using a natural uranium standard purchased from a commercial distributor. A typical hydride correction factor obtained from three internal replicates of a 238/239 measurement taken within the same run sequence of the unknown samples was used to calculate the hydride correction at mass 234 due to ^{233}U.

3. Results

3.1 The n(^{233}U)/n(^{238}U) major ratio measurements using TRITON

Four aliquots from each of the three sub-samples were analyzed by TE. Consistency in the TE analyses were evaluated by: mass bias correction factor, run duration, and the percent relative standard deviation (%RSD) of the major ratio of the comparator CRM. These parameters are listed in Table 3. Samples on the TRITON TE turrets ran expected durations considering the sample size (0.5 µg uranium) and analysis signal intensity (15 V summed intensity). The mass bias correction factors on each turret were small (close to 1.000) and the variability (1 standard deviation) of the comparator $^{235}U/^{238}U$ ratios for each turret is considerably lower than the international target values (ITVs) for precision of 0.05 % associated with TIMS analysis of HEU (high enriched uranium) material [9] (the ITVs associated with U isotopic analyses of HEU are more stringent than for other materials like LEU - low enriched uranium, NU - normal uranium, or DU - depleted uranium).

Table 3 here

Accuracy statistics on CRMs analyzed as QC standards during the TE analysis are shown in Table 3. Note that the accuracies achieved on the QC standards are similar to or better than the ITVs for accuracy of 0.05 % associated with TIMS analysis of HEU material [9]. Table 3 summarizes the uranium isotope amount ratio data in ^{233}U characterization samples using TE analytical technique. Average $n(^{233}U)/n(^{238}U)$ ratios and the relative standard uncertainties for each sub-sample are indicated.

The minor isotope-amount ratios from TE experiments are prone to biases due to the inability to correct for peak-tailing effects during the analysis [1, 5] as TE is essentially a static analytical technique in that the magnetic field remains constant throughout the course of the data acquisition. The relative magnitude of the “peak tail” at a mass 1 u below the ion beam mass is referred to as “abundance sensitivity”. The abundance sensitivity of TIMS instruments using Faraday cups is typically several ppm [6, 10]. On modern multi-collector TIMS/ICPMS instruments equipped with energy filters (such as the retarding potential quadrupole (RPQ) on TRITON and NEPTUNE) the abundance sensitivity is improved to ppb level [6, 10].

Recently TE analytical technique had been modified to address the peak-tailing correction quantitatively using the dynamic target intensity concept. The resulting analytical technique - modified total evaporation (MTE) – uses larger sample loads and have yielded good minor isotope ratios without compromising the quality of the major isotope ratio data [6, 11-14].

3.2 Minor ratio measurements by conventional method using TRITON

Two aliquots each from sub-samples #1 and #3 and three aliquots from sub-sample #2 were analyzed by the Conventional technique. Table 4 summarizes the uranium isotope-amount ratio data of the high-purity ^{233}U material using Conventional analytical technique. Note that accuracy and precision ITVs associated with minor U isotope-amount ratio data by TIMS are not available [9].

Table 4 here

3.3 Isotopic abundance measurements using ICPMS

Table 5 shows the uranium isotopic abundances measured using the single detector quadrupole ICPMS. These results have been corrected for hydride interferences at mass 234 as described above. The hydride correction factor was determined to be 4.80E-05 ± 0.53E-05 based on measurements in triplicates of the 238U and mass 239 (238U+1H) measurements.

Table 5 here

4. Discussion

Figure 1 (top panel) summarizes the n(^{233}U)/n(^{238}U) major isotope ratio measurements in the high-purity ^{233}U material. Note that the ^{235}U isotope abundance of this material is so low that it was measured on the ion counter. The error bars represent the standard error of the replicate measurements (four aliquots from each of the three sub-samples were analyzed by TE). The characterized value of the n(^{233}U)/n(^{238}U) ratio is indicated. For comparison, expanded uncertainty in the isotope-amount ratio (see section below for details) is also indicated.

Figure 1 here

The high-purity ^{233}U characterization samples present some unique opportunity for evaluating the peak-tailing corrections due to the distinct isotopic abundance pattern of this material. The magnitude of the peak-tail corrections can be assessed for each minor isotope-amount ratio through a comparison of the TE data with the characterized values from Conventional analyses. These comparisons will be useful for evaluating peak-tail corrections in material with extreme isotope-amount ratios, especially because the signal intensities for both analytical techniques were similar.

Figure 1 (bottom panel) summarizes the n(^{234}U)/n(^{238}U) minor isotope ratio in the high-purity ^{233}U material. TE data as well as characterized data using Conventional are shown. Figure 2 summarizes the n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) ratios in the ^{233}U material. Standard uncertainties as represented by the precision of the replicate analysis (error bars on each data point) as well as expanded uncertainties in the characterized isotope-amount ratios (dashed lines) are indicated (see section below for details on uncertainty estimations for the isotope ratios). Only data from the Conventional analysis technique is used for the characterization of the minor isotope-amount ratios. TE data is shown for comparison purposes. Note that in all cases, the minor isotope-amount ratio data from TE technique are biased high.

Figure 2 here

The n(^{234}U)/n(^{238}U) isotope-amount ratio from TE analytical technique is biased by ~3.55 % (± 0.48 %) compared to the Conventional data. The n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) ratios obtained by TE are biased, respectively, by 5.43 % (± 0.87 %) and 26 % (± 11 %) compared to the characterized values. The magnitudes of the biases are ~2 ppm at ^{234}U and 0.5 ppm at ^{235}U and ^{236}U.

4.1 Uncertainties in the uranium isotope-amount ratios

The uncertainties in the isotope-amount ratios are calculated following the JCGM 100:2008, “Evaluation of measurement data – Guide to the expression of Uncertainty in Measurement” [15] using the GUM Workbench software developed by Metrodata (R) [16]. The measurement uncertainties include all recognized significant Type-A and Type-B evaluated sources of uncertainty [17].

Table 7 provides a description of the quantities contributing to the uncertainties in the isotope-amount ratios measured by a TIMS instrument. Input values for these quantities had been estimated using the data obtained during this characterization work and professional judgment based on experience on the analytical equipment and measurement methodology.

Uncertainty in the major isotope-amount ratio n(^{233}U)/n(^{238}U) is evaluated as follows:

$$R_{38} = R_{38TE} * \delta_{Cert} * \delta_{CFVar} \quad (1)$$

Table 6 here

The uncertainty components are explained in Table 6. Table 7 shows that the uncertainty in the major ratio is dominated by the precision of the TE data (R_{38TE}) contributing 49 % and the uncertainty in the certified *n*(^{235}U)/*n*(^{238}U) major ratio of the comparator CRM (δ_{Cert}), contributing ~32 %.

Uncertainties in the minor isotope-amount ratios are evaluated using the following:

$$R_{48} = R_{48Conv} * \delta_{R38} * - \delta_{bkgd234} \quad (2)$$

$$R_{58} = R_{58Conv} * \delta_{R38} + \delta_{SEMCals} - \delta_{bkgd235} \quad (3)$$

$$R_{68} = R_{68Conv} * \delta_{R38} + \delta_{SEMCals} - \delta_{bkgd236} \quad (4)$$

Table 7 shows that whereas the n(^{234}U)/n(^{238}U) and n(^{235}U)/n(^{238}U) isotope-amount ratio uncertainties are dominated by the precision of the conventional data (respectively contributing 67 % and 61 % of the uncertainties in the characterized isotope ratios), uncertainty in the n(^{236}U)/n(^{238}U) ratio is dominated by uncertainties in the calibration factors associated with the SEM. Considering that the signal intensities of isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U are all small, with ^{236}U signal intensity being the smallest, the uncertainty budgets are not surprising.

Table 7 here

Several uncertainty components were not explicitly included in the model equations for estimation of uncertainties in the isotope-amount ratios. The variability associated with amplifier baseline and gain calibrations are confounded in the observed variability of the replicate isotope ratio measurements.

Conclusions

A high-purity ^{233}U material had been identified as a source material for standards for use in isotopic analyses of uranium. Initial characterization of the uranium isotope-amount ratios in this high-purity ^{233}U material shows that the material is of higher purity than CRM 111-A which is currently being used as a spike for IDMS. Two TIMS analytical techniques: i) total evaporation technique and ii) Conventional analysis using the TRITON instrument were employed for the study. Through a comparison of the minor isotope-amount ratios in this high purity 233U material it had been estimated that the bias due to peak-tailing is ~2 ppm at ^{234}U and ~0.5 ppm at ^{235}U and ^{236}U. The TIMS characterization data had been validated by additional measurements using quadrupole ICPMS.

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Figure Captions:

Figure 1: Uranium major isotope-amount ratio (top panel) in sub-samples of high-purity ^{233}U material identified as source material for Forensic RM standards. The n(^{233}U)/n(^{238}U) isotope-amount ratio as well as precision of the replicate measurements (as standard uncertainty) are shown. GUM compliant expanded uncertainties are shown (dashed lines in Figure) for comparison (see text for details of the uncertainty calculations). The n(^{234}U)/n(^{238}U) minor isotope-amount ratio (bottom panel) in high-purity ^{233}U characterization sample. Data from both TE and Conventional analytical techniques and their standard uncertainties are indicated.

Figure 2: Uranium n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{235}U) minor isotope-amount ratios in sub-samples of ^{233}U material analyzed for characterization purposes. The isotope-amount ratios n(^{235}U)/n(^{238}U) (top panel) and n(^{236}U)/n(^{238}U) (bottom panel) in each sub-sample and their standard uncertainties are shown. Note that similar to the minor isotope-amount ratio n(^{234}U)/n(^{238}U), the TE data are biased compared to those from Conventional analyses. Dashed lines in all panels correspond to GUM compliant expanded uncertainties.

Table Captions:

Table 1: Cup Configuration for TE analysis using TRITON
Table 2: Cup Configuration for Conventional analysis using TRITON
Table 3: Accuracy statistics on CRMs analyzed by TE
Table 4: Summary data for high-purity ^{233}U material
Table 5: Verification measurements using ICPMS
Table 6: Uncertainty components used in GUM calculations
Table 7: Uncertainty budgets for characterized isotope-amount ratios

Table 1: Cup Configuration for TE analysis using TRITON

Scan (line)	Cup L3	Cup L2	Cup L1	Center Cup/SEM	Cup H1	Cup H2	Cup H3
1		^{233}U	^{234}U	^{235}U	^{236}U	^{237}	^{238}U

Table 2: Cup Configuration for Conventional analysis using TRITON

Scan (line)	Cup L2	Cup L1	Center Cup/SEM	Cup H1	Cup H2	Cup H3	Integration Time (s)
1	^{233}U	^{234}U	^{235}U	^{236}U	237	^{238}U	16.77
2	232.55	233.55	234.55	235.55	236.55	237.55	8.39
3	233.55	234.55	235.55	236.55	237.55	238.55	8.39
4	232	^{233}U	^{234}U	^{235}U	^{236}U	237	8.39
5	^{234}U	^{235}U	^{236}U	237	^{238}U	239	16.77
6	233.55	234.55	235.55	236.55	237.55	238.55	8.39
7	234.55	235.55	236.55	237.55	238.55	239.55	8.39

[1] *The main integration steps are steps 2, 5, and 6. Steps 3 and 4 as well as 7 and 8 are used for peak-tailing corrections performed offline.*

Table 3: Accuracy statistics on CRMs analyzed by TE

CRM	Certified n(^{238}U)/n(^{235}U)	Rel. Uncertainty Certified ratio (%)	%RD
QA Turret, CF = 1.000116[†], #-integrations = 1274, %RSD (comparator = 0.0076) [‡]			
U500	0.9997	0.14	≡ 0.0
(N = 5)	± 0.0014		
U010	0.010140	0.10	- 0.0073
(N = 4)	± 0.000010		
U030-A	0.031367	0.053	0.0216
(N = 3)	± 0.000017		
U045	0.047310	0.053	0.0289
(N = 4)	± 0.000025		
U630	1.8067	0.065	- 0.0095
(N = 4)	± 0.0012		
Characteriz. Turret, CF = 1.000297[†], #-integrations = 1916, %RSD (comparator = 0.0255) [‡]			
U630	1.8067	0.065	≡ 0.0
(N = 4)	± 0.0012		
U500	0.9997	0.14	-0.0013
(N = 4)	± 0.0014		

[§] *N represents the number of replicate analysis*

† *CF is the ratio of the measured ^{235}U/^{238}U ratio for the comparator and the certificate ratio, and represents the extent of mass fractionation observed on the turret. For TE, CF is close to 1.0, indicating small mass bias effects.*

[‡] Repeatability of the comparator ^{235}U/^{238}U ratio on each turret.

Table 4: Summary data for the high-purity ^{233}U material

Method	Sub-sample §	Isotope amount ratio			
		$n(^{233}\text{U})/n(^{238}\text{U})^{\dagger}$	$n(^{234}\text{U})/n(^{238}\text{U})^{\ddagger}$	$n(^{235}\text{U})/n(^{238}\text{U})^{\ddagger}$	$n(^{236}\text{U})/n(^{238}\text{U})^{\ddagger}$
TE	# 1 (N = 4)	19710 ± 19	1.2809 ± 0.0058	0.1962 ± 0.0016	0.0462 ± 0.0034
	# 2 (N = 4)	19726 ± 13	1.2883 ± 0.0029	0.1980 ± 0.0006	0.0509 ± 0.0012
	# 4 (N = 4)	19725 ± 11	1.2764 ± 0.0074	0.1947 ± 0.0019	0.0424 ± 0.0032
	Average	**19720.1** **± 8.0**	**1.2818** **± 0.0033**	**0.19632** **± 0.00087**	**0.0465** **± 0.0018**
Conv.	# 1 (N = 2)	§	1.24248 ± 0.00019	0.18476 ± 0.00123	0.03734 ± 0.00016
	# 2 (N = 3)	§	1.23744 ± 0.00214	0.18710 ± 0.00115	0.03718 ± 0.00085
	# 3 (N = 2)	§	1.23391 ± 0.00255	0.18635 ± 0.00074	0.03651 ± 0.00067
	Average		**1.23789** **± 0.00166**	**0.18622** **± 0.00067**	**0.03703** **± 0.00038**

§ *N represents the number of replicate analysis for each CRM*

† *Average ratios and standard uncertainties are indicated*

†† *The n(^{234}U)/n(^{238}U), n(^{235}U)/n(^{238}U), and n(^{236}U)/n(^{238}U) data from TE are biased high due to the inability to correct for peak-tailing (see text for detailed discussion).*

§ *Conventional data are corrected for peak-tailing and for mass bias effects on a cycle-per-cycle basis. The mass bias corrections are based on the n(233U)/n(238U) ratios in each measurement cycle. Hence, these ratios are not reported in this Table.*

Table 5: Verification measurements using ICPMS

Isotope abundance (atom percent)†				
^{233}U	**^{234}U**	**^{235}U**	**^{236}U**	**^{238}U**
99.9869 ± 0.0100	0.0061 ± 0.0010	0.0009 ± 0.0003	0.0002 ± 0.0001	0.0059 ± 0.0010
		%RDs from TIMS data		
-0.0006 ±0.01	-3 ±16	-5 ±32	6 ±53	16 ±20

† *The ICPMS ^{234}U abundances are corrected for interferences due to the 233U-hydride (see text). Uncertainties shown for the ICPMS data represent GUM compliant estimates based on instrument/method capability as measured using traceable QC standards.*

Table 6: Uncertainty components used in GUM calculations

Quantity	Description	Evaluated As
R_{38}	Characterized $n(^{233}U)/n(^{238}U)$ ratio	Measurand
R_{48}	Characterized $n(^{234}U)/n(^{238}U)$ ratio	Measurand
R_{58}	Characterized $n(^{235}U)/n(^{238}U)$ ratio	Measurand
R_{68}	Characterized $n(^{236}U)/n(^{238}U)$ ratio	Measurand
R_{38TE}	Measured $n(^{233}U)/n(^{238}U)$ ratios from TE	Type A, Direct Observation, N = 12
δ_{Cert}	Relative uncertainty in the certified $n(^{235}U)/n(^{238}U)$ ratio of comparator	Type B, Normal, exp. uncertainty of 0.065 % (k = 2)
δ_{CFVar}	Variability in the mass bias correction factor (repeatability of CRM U630 data on TE turret)	Type B, Normal, exp. uncertainty of 0.0255 % (k = 1)
R_{48Conv}	Measured $n(^{234}U)/n(^{235}U)$ ratio from conventional	Type A, Direct Observation, N = 7
δ_{R38}	Relative uncertainty in the $n(^{233}U)/n(^{238}U)$ ratio used for estimation of the mass bias at $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$, and $n(^{236}U)/n(^{238}U)$ minor ratios.	Type B, Normal, exp. uncertainty of 0.06 % (k = 1)
$\delta_{bkgd234}$	Uncertainty in the peak-tailing correction at 234 u	Type B, Normal, exp. uncertainty of 0.0009 (k = 1) equal to observed variability at 234
R_{58Conv}	Measured $n(^{235}U)/n(^{235}U)$ ratio from conventional	Type A, Direct Observation, N = 7
$\delta_{bkgd235}$	Uncertainty in the peak-tailing correction at 235 u	Type B, Normal, exp. uncertainty of 8×10^{-6} (k = 1) equal to observed variability at 235
R_{68Conv}	Measured $n(^{236}U)/n(^{235}U)$ ratio from conventional	Type A, Direct Observation, N = 7
$\delta_{bkgd236}$	Uncertainty in the peak-tailing correction at 236 u	Type B, Normal, exp. uncertainty of 6×10^{-6} (k = 1) equal to observed variability at 236
$\delta_{SEMCals}$	Uncertainty associated with SEM characteristics (linearity, yield, dark-noise)	Type B, Rectangular, Half width of limits = 0.0009

Table 7: Uncertainty budgets for characterized isotope-amount ratios

Quantity	Value	Std. uncertainty (u_c)	ν_{eff}	Distribution	c	Contribution (%)
R_{38}	19720.1	11.4	40			
R_{38TE}	19720.13	0.041 % (rel.)	11	normal	1.0	49.2
δ_{Cert}	1.0	0.032 % (rel.)	50	normal	20000	31.5
δ_{CFVar}	1.0	0.026 % (rel.)	50	normal	20000	19.4
R_{48}	1.23789	0.00203	13			
R_{48Conv}	1.23789	0.13 % (rel.)	6	normal	1.0	66.8
δ_{R38}	1.0	0.060 % (rel.)	50	normal	1.2	13.4
$\delta_{bkgd234}$	0.0	0.00090	50	normal	-1.0	19.7
R_{58}	0.186219	0.000852	16			
R_{58Conv}	0.186219	0.36 % (rel.)	6	normal	1.0	61.0
$\delta_{bkgd235}$	0.0	0.0000080	50	normal	-1.0	0.0
δ_{R38}	1.0	0.060 % (rel.)	50	normal	0.19	1.7
$\delta_{SEMCals}$	0.0	0.00052	∞	rectangular	1.0	37.2
R_{68}	0.037034	0.000643	49			
R_{68Conv}	0.037034	1.0 % (rel.)	6	normal	1.0	34.7
$\delta_{bkgd236}$	0.0	0.0000060	50	normal	-1.0	0.0
δ_{R38}	1.0	0.060 % (rel.)	50	normal	0.037	0.1
$\delta_{SEMCals}$	0.0	0.00052	∞	rectangular	1.0	65.2

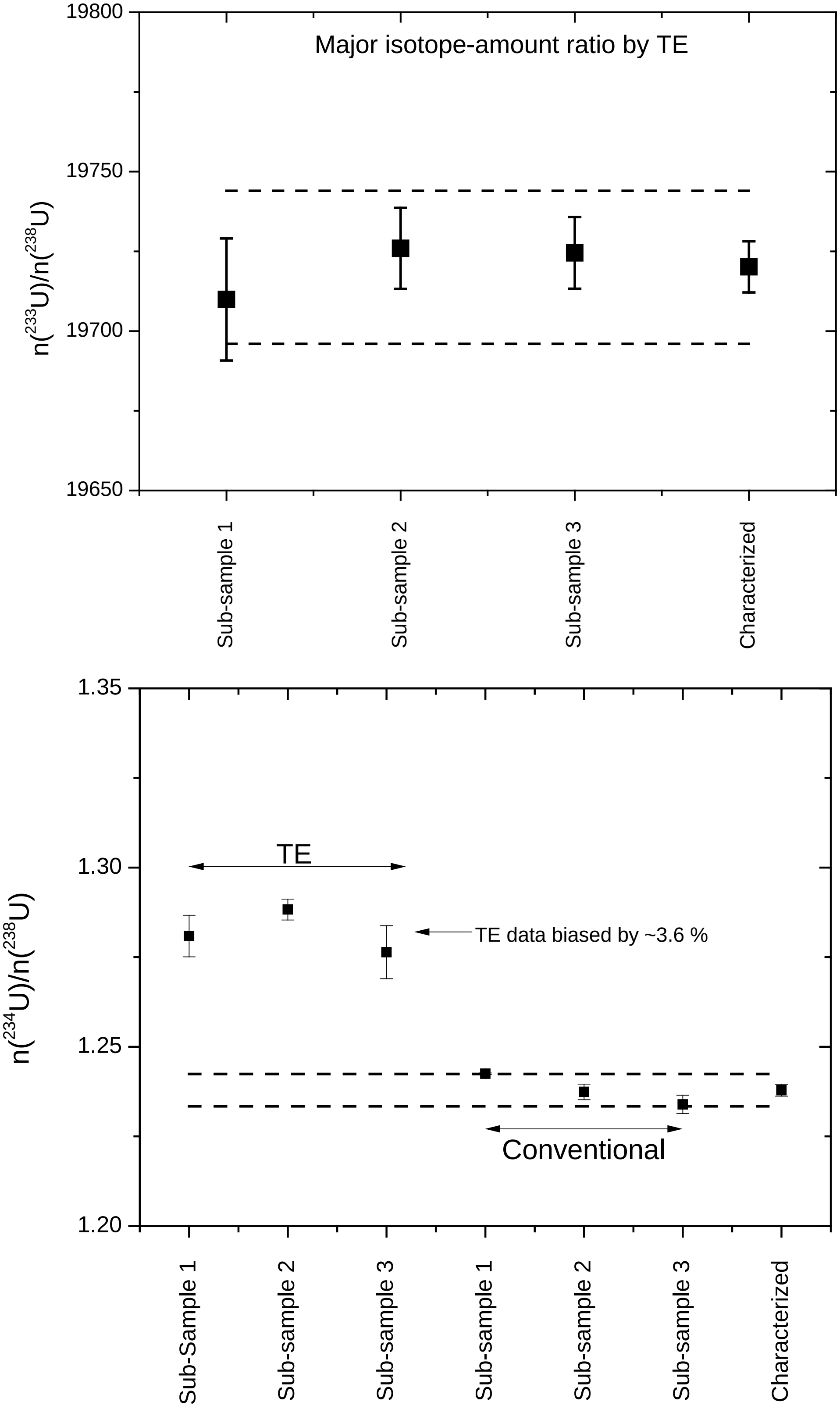

Figure 1: Mathew et al.

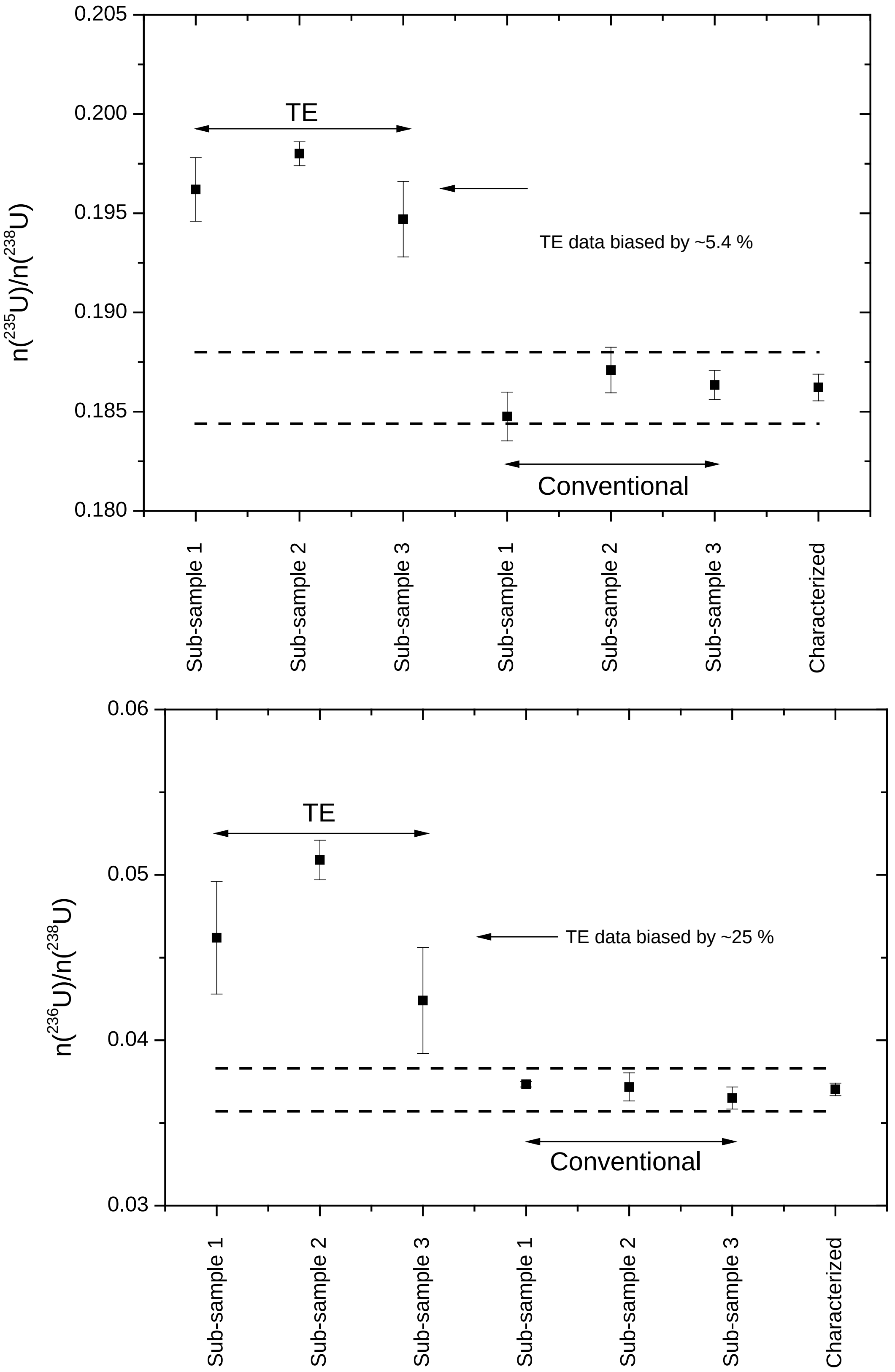

Figure 2: Mathew et al.