

# Uncertainties achievable for uranium isotope-amount ratios: estimates based on the precision and accuracy of recent characterization measurements

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Received: 15 September 2014 / Published online: 20 December 2014  
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**Abstract** Certified reference materials (CRMs) recently characterized by the NBL for isotope-amount ratios are: (i) CRM 112-A, Uranium (normal) Metal Assay and Isotopic Standard, (ii) CRM 115, Uranium (depleted) Metal Assay and Isotopic Standard, and (iii) CRM 116-A, Uranium (enriched) Metal Assay and Isotopic Standard. NBL also completed re-characterization of the isotope-amount ratios in CRM 125-A, Uranium (UO<sub>2</sub>) Pellet Assay, Isotopic, and Radio-chronometric Standard. Three different TIMS analytical techniques were employed for the characterization analyses. The total evaporation technique was used for the major isotope-amount ratio measurement, the modified total evaporation technique was used for both the major and minor isotope-amount ratios, and minor isotope-amount ratios were also measured using a Conventional technique. Uncertainties for the characterization studies were calculated from the combined TIMS data sets following the ISO Guide to the expression of uncertainty in measurement. The uncertainty components for the isotope-amount ratio values are discussed.

**Keywords** Uranium · Certified reference materials · Thermal ionization mass spectrometry · Traceability · Uncertainties · ISO-GUM

## Introduction

Certified reference materials (CRMs) with amount contents and isotopic abundances that are traceable to International System of Units (S.I.) are used by nuclear analytical laboratories to: (i) develop and validate new analytical methods, ensuring traceable results at a working level, (ii) calibrate and test measurement systems, (iii) assure that analytical methods are producing results at acceptable performance levels, (iv) assure adequacy and integrity of quality control programs, (v) serve as test materials in inter-laboratory comparisons and proficiency tests, and (vi) develop working standards [1, 2]. In other words, CRMs are an integral part of calibration and performance assessment, as well as being necessary for quality assurance and quality control of nuclear measurement processes and systems. Use of CRMs for calibration establishes traceability, which is an unbroken chain of measurement comparisons to the nationally accepted reference base (e.g., from the end user to the S.I. units). Traceability enhances the comparability of analytical results from different measurement techniques and is imperative to assure the accuracy of analytical measurements and establishing confidence in the measurement process. From a nuclear safeguards perspective, having validated and traceable measurements is fundamental to material control and accountability as it provides increased material loss detection sensitivity.

The Department of Energy's (DOE) New Brunswick Laboratory is the U. S. certifying authority for assay and isotopic standards, including uranium and plutonium, used in the nuclear fuel cycle. Recent characterization studies at NBL included certification of the uranium isotope-amount ratios in three uranium metal assay standards [3, 4, 7, 8] (of depleted, natural, and high-enriched isotopic compositions)

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and re-certification of the uranium isotope-amount ratios in an oxide pellet assay and isotopic standard [5, 6]. To minimize the potential for systematic biases these uranium isotopic characterization studies incorporated a number of TIMS analytical techniques and different TIMS instruments (THERMOFINNIGAN TRITON and modified MAT261 instruments). The precision and accuracy of the CRMs used as QC standards in the recent characterization and re-characterization measurements are summarized to estimate uncertainties achievable for uranium isotope-amount ratios using modern TIMS instruments.

## Experimental

Details about the mass spectrometry measurement techniques as well as analytical details specific to the CRM characterization studies are available elsewhere [3–8]. For brevity, those details are not repeated here. The general analytical approach has been that data from MTE and TE techniques were combined for characterization of the major isotope-amount ratio whereas data from both MTE and conventional technique were combined for characterization of the minor isotope-amount ratios. By using multiple techniques and, when possible, multiple instruments, the advantages of the various techniques can be leveraged, the disadvantages avoided, and potential for systematic biases associated with a method or instrument minimized.

Total evaporation (TE) is an established analytical method for the measurement of uranium and plutonium isotopic abundances [9–11] using TIMS instruments. For the major isotope-amount ratios, this technique yields data with relatively small biases due to instrumental fractionation and results that are highly reproducible. Modified

total evaporation (MTE) for the TRITON TIMS instrument has been developed to exploit the TE principle for obtaining state-of-the-art (in terms of accuracy and precision) major isotope-amount ratio data while improving the quality of the  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  minor ratios by incorporating real time measurement of background intensities thus allowing for the peak-tail corrections [12]. Due to the superior performance of the measurement technique for U and Pu isotope-amount ratio determinations, MTE had been extensively used for routine analyses of safeguards samples [1, 12, 13] and in characterization of NBL CRMs [3–5, 7]. MTE analyses are considerably longer in duration and are typically performed at higher signal intensities than TE analyses. Accordingly, the sample loads for MTE analyses are larger than those used in TE analyses by a factor of 5–10 but the increased measurement time and signal allow for significant improvements in the precision and accuracy of the minor ratio measurements. Richter et al. [12] provides a detailed description of the MTE analytical technique.

## Results and discussion

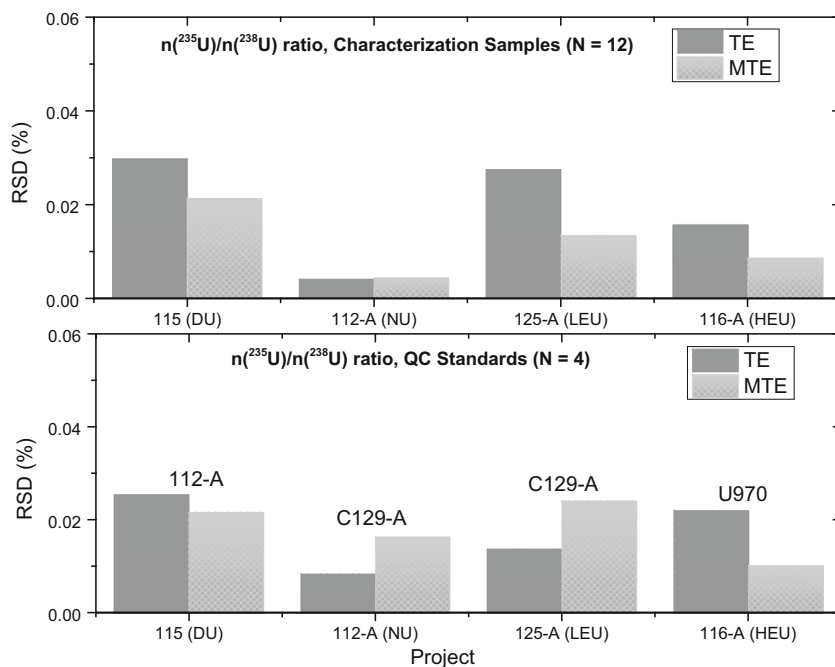
For the  $n(^{235}\text{U})/n(^{238}\text{U})$  major isotope-amount ratio, Table 1 shows that the precision of the characterization measurements (relative standard deviations, as a percent—%RSD) are comparable to those of the QC standards. The characterization samples had a precision of 0.0156 (%RSD) whereas the QC CRMs yielded a %RSD of 0.0177. Figure 1 shows the %RSDs of the major ratio measurements of the characterization samples (top panel) and of the QC standards (bottom panel). As the QC CRMs used in the characterization analyses have both major and

**Table 1** Summary of the major isotope  $^{235}\text{U}/^{238}\text{U}$  ratios in CRMs investigated here using TE and MTE

Project	Method	%RSD (Charact. sample)	%RSD (QC standard)	%RD (QC standard)	Combined uncertainty
115 (DU)	TE (3 turrets)	0.0297 ( $N = 10\text{--}11$ )	0.0254 ( $N = 3\text{--}5$ )	−0.0132	0.0287
	MTE (5 turrets)	0.0213 ( $N = 6\text{--}11$ )	0.0217 ( $N = 3\text{--}5$ )	−0.0218	0.0308
112-A (NU)	TE (3 turrets)	0.0041 ( $N = 12$ )	0.0084 ( $N = 2\text{--}3$ )	−0.0007	0.0085
	MTE (3 turrets)	0.0044 ( $N = 11\text{--}12$ )	0.0163 ( $N = 2\text{--}3$ )	0.0345	0.0382
125-A (LEU)	TE (3 turrets)	0.0274 ( $N = 6\text{--}12$ )	0.0137 ( $N = 3$ )	−0.0139	0.0195
	MTE (2 turrets)	0.0134 ( $N = 6\text{--}11$ )	0.0241 ( $N = 2\text{--}3$ )	−0.0202	0.0314
116-A (HEU)	TE (6 turrets)	0.0156 ( $N = 6\text{--}11$ )	0.0220 ( $N = 2\text{--}3$ )	−0.0311, 0.0089*	0.0381, 0.0238*
	MTE (3 turrets)	0.0086 ( $N = 10$ )	0.0102 ( $N = 4\text{--}5$ )	−0.0533, −0.0133*	0.0543, 0.0168*
Average		0.0156	0.0177	−0.0050	0.0184
GUM compliant modeled expanded uncertainties (95 % C.L., $k = 2.37$ )					0.025
Improvement compared to uncertainties for U CRMs					Factor of 3–7

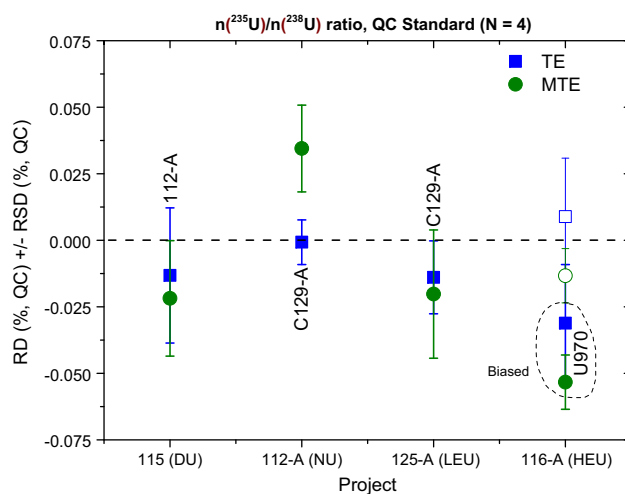
\* Bias of about 0.04 % in the major ratio of the QC standard is observed in both TE and MTE analyses. The biased values as well as bias removed values are shown for comparison purposes

**Fig. 1** Average precision (relative standard deviations expressed as a percent) of the major ratio data on characterization samples (*top*) and QC standards (*bottom*). Data from multiple turrets each with ~12 characterization aliquots and 3–4 QC aliquots are combined. The two analytical techniques TE and MTE are shown separately



minor isotope-amount ratios that are traceable to S.I. units, the accuracy achieved in the analytical effort can also be estimated. Table 1 shows the relative deviations (as a percent, %RD) of the major ratios of the QC standards from the certified ratios. For the major isotope-amount ratio, the %RD value of the QC CRM U970 used in the characterization of CRM 116-A exhibits a systematic bias of ~0.04 % in both TE and MTE analytical techniques. Although this value is within CRM uncertainty, the observed bias is substantially greater than that normally observed in QC measurements and is probably indicative of an issue with the CRM certificate value. Using the bias corrected value for CRM U970, an average %RD of -0.0050 % is calculated for all the major ratio data from QC standards. Table 1 shows that for all QC standards, the %RSDs and %RDs of the  $n(^{235}\text{U})/n(^{238}\text{U})$  major ratio are below 0.05 %, the precision and bias International Target Values (ITVs) for TIMS measurement [14] of HEU material. Table 1 also shows that the major ratio %RSDs and %RDs of the two analytical techniques TE and MTE are comparable. Figure 2 shows a plot of the precision and accuracy statistics on the major isotope-amount ratios of the QC CRMs. Both biased (filled symbols) and bias corrected (open symbols) data are shown for the U970 (QC CRM used in the characterization analyses of CRM 116-A).

Table 2 shows a summary of the precision and accuracy statistics on the minor  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope-amount ratios. Summary statistics on characterization samples and QC CRMs are shown separately. Figure 3 shows



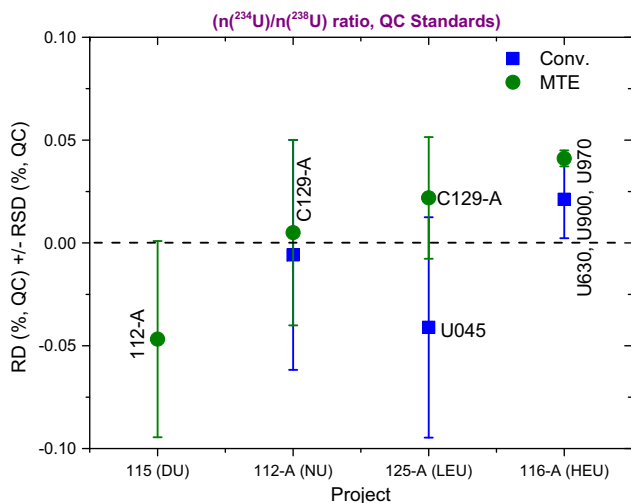
**Fig. 2** Relative deviations (as a percent) of the measured major ratio of the QC standards from the certified values. Uncertainties shown represent the repeatability of the measurements (%RSDs). For CRM U970 (QC standard in CRM 116-A characterization) both TE and MTE data indicate a bias. Both measured data (*filled symbols*) as well as bias corrected values (*open symbols*) are shown for CRM U970

a summary plot of the %RDs of the  $n(^{234}\text{U})/n(^{238}\text{U})$  ratios in the QC standards analyzed during the characterization analyses described here. The %RSDs of the QC analyses are shown as the uncertainties of the %RD values.

Uncertainties in the uranium isotope abundance ratios were calculated following the ISO guidelines for the expression of uncertainties in measurements (GUM, [15]) using the Workbench software developed by Metrodata

**Table 2** Summary of the minor isotope  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  ratios in CRMs investigated here using TE and MTE

Project	Method	Isotope-amount ratio	%RSD (Charact. sample)	%RSD (QC standard)	%RD (QC standard)	Combined QC uncertainty
115 (DU)	MTE (5 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.2576 ( $N = 6-11$ )	0.0477 ( $N = 3-5$ )	-0.0468	0.0668
		$n(^{236}\text{U})/n(^{238}\text{U})$	0.1790	0.3566	0.1649	0.3929
112-A (NU)	MTE (3 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0435 ( $N = 11-12$ )	0.0451 ( $N = 2-3$ )	0.0050	0.0454
		$n(^{236}\text{U})/n(^{238}\text{U})$		0.6941	0.6066	0.9218
	Conv. (3 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0904 ( $N = 12$ )	0.0559 ( $N = 3$ )	-0.0058	0.0562
		$n(^{236}\text{U})/n(^{238}\text{U})$		0.7362	-0.4240	0.8496
125-A (LEU)	MTE (2 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0547 ( $N = 6-11$ )	0.0296 ( $N = 2-3$ )	0.0219	0.0368
		$n(^{236}\text{U})/n(^{238}\text{U})$	0.1195	0.0796	1.165	1.1678
	Conv. (1 turret)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0618 ( $N = 9$ )	0.0536 ( $N = 3$ )	-0.0411	0.0675
		$n(^{236}\text{U})/n(^{238}\text{U})$	0.1458	0.1225	0.0276	0.1256
116-A (HEU)	MTE (3 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.00032 ( $N = 10$ )	0.0039 ( $N = 4-5$ )	0.0411	0.0413
		$n(^{236}\text{U})/n(^{238}\text{U})$	0.0024	0.0097	0.0592	0.0600
	Conv. (4 turrets)	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0055 ( $N = 8-16$ )	0.0165 ( $N = 3$ )	0.0212	0.0269
		$n(^{236}\text{U})/n(^{238}\text{U})$	0.0024	0.0214	0.0013	0.0214
GUM compliant modeled expanded uncertainties $n(^{234}\text{U})/n(^{238}\text{U})$ ratio (95 % C.L. $k = 2.65$ )						0.10
GUM compliant modeled expanded uncertainties $n(^{236}\text{U})/n(^{238}\text{U})$ ratio (95 % C.L. $k = 2.65$ )						0.10
Improvement compared to certified uncertainties in U CRMs						2–40

**Fig. 3** Relative deviations (expressed as a percent) of the measured QC standard  $n(^{234}\text{U})/n(^{238}\text{U})$  minor ratio from the certified values. Uncertainties shown represent the repeatability of the measurements (%RSDs)

[16]. Burger et al. [17] provides a detailed discussion of the various components that contributes to the uncertainties in the isotope-amount ratio measurements using TIMS and ICPMS instruments. When uncertainties in the isotope-amount ratios are calculated according to the ISO GUM, it is possible that some minor uncertainty components are double-counted as a result of the difficulty in separating out all the uncertainty components that influence the measurements from one another. The alternative of leaving out a significant uncertainty component that is already

incorporated in one of the confounded factors would be inconsistent with the goal of representative but conservative uncertainty estimation. Hence, the modeled uncertainties following ISO GUM guidelines tend to be larger than those obtained from a simple combination of the accuracy and precision of the QC data. This is so because one or more of the uncertainty components explicitly included as contribution in the uncertainty models are confounded in the uncertainty estimations based on the QC data. Therefore, the combined uncertainty estimate from QC data can be considered a lower limit to the uncertainties that are achievable using state-of-the-art MC-TIMS instruments.

The following uncertainty calculations assume state-of-the-art precision and accuracy in the isotope-amount ratio measurements. The major isotope-amount ratio and the minor isotope-amount ratios are treated separately as there are some differences in the components contributing to the overall uncertainty. For the major ratio measurement using TIMS, the following sources of uncertainties are important: the variability of the replicate measurements (Type A) of the sample and comparator aliquots and, to a much larger extent, the Type B uncertainty associated with the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio of the CRM used to estimate mass bias effects in the mass spectrometer [3–7, 11, 17]. For both  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  minor isotope-amount ratio measurements using the Faraday detector, major sources of uncertainties are: (i) repeatability of the  $n(^{234}\text{U})/n(^{238}\text{U})$  or  $n(^{236}\text{U})/n(^{238}\text{U})$  measurements, (ii) variability in the peak-tail corrections (implemented off-line on a cycle-per-cycle

basis), and (iii) uncertainty in the mass bias correction. As stated earlier, note that for the minor isotope-amount ratios, the mass bias correction is based on internal normalization using the major ratios. Thus, the variability in the major ratio data during the course of the analytical technique is an estimate of the uncertainty in the mass bias correction at the minor isotope-amount ratios. With the exception of the peak-tailing correction, which varies from one sample to the next due to differences in the relative abundances of the major isotopes, the minor ratio uncertainty components and their relative contribution to the uncertainty budget are similar for both  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$ . For trace isotope-amount ratio measurements that involve the ion counter [secondary electron multipliers (SEMs) on the TRITON TIMS instrument] additional uncertainty sources like the variability in the dark noise and the yield calibrations (Faraday/SEM inter-calibrations) must be considered in addition to the uncertainties in the peak-tailing corrections. The availability of the energy-filter (retarding potential quadrupole or RPQ) in the TRITON makes the peak-tail contributions less significant (even though not completely avoided) in the ion counting measurements. Note that the modeled expanded uncertainties are equivalent to 95 % confidence intervals for the measurands and that the GUM workbench software appropriately determines the coverage factors for the standard uncertainties (based on the degrees of freedom of the input quantities) to estimate expanded uncertainties at this level of confidence.

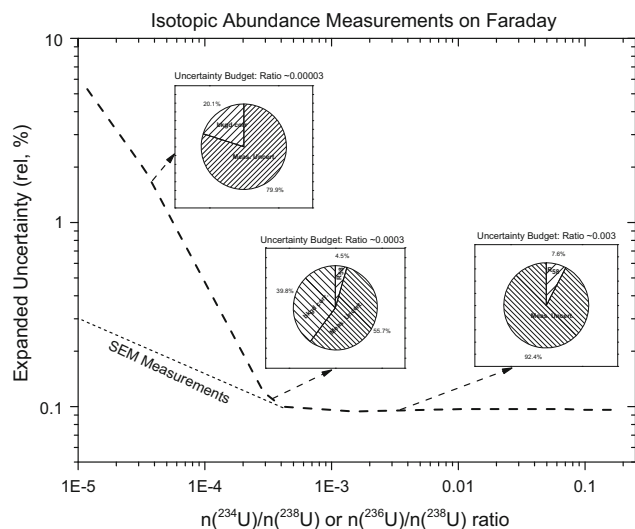
The precision and accuracy of the QC data, when combined, yields combined uncertainty of 0.0184 % for the

$n(^{235}\text{U})/n(^{238}\text{U})$  major ratio measurements by TE and MTE. This uncertainty estimate using QC data is comparable to the modeled uncertainty of 0.025 % for the major isotope-amount ratio using the ISO GUM models described above. The modeled major ratio uncertainties are lower than the certified uncertainties in NBL CRMs by a factor of 2–7. This uncertainty estimates using QC (or modeled ISO GUM uncertainty) represent uncertainties that are achievable in TIMS analyses using instruments currently available to the nuclear safeguards community. For the  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  minor isotope-amount ratios, combined uncertainty of  $\sim 0.1$  is obtained in both the model calculations following ISO GUM and by combining the accuracy and precision statistics of the QC CRMs. Figure 4 shows a plot of the modelled minor ratio uncertainties as a function of the ratio itself. These minor ratio uncertainties are lower than the certified uncertainties of the NBL CRMs by factor of 2–40. For both major and minor isotope-amount ratios the magnitudes of improvements in the uncertainties are consistent with what Buerger et al. predicted based on a “marriage” of the NBL and IRMM isotopic standards [18].

### Conclusions

Recent characterization studies of the uranium isotope-amount ratios in three uranium metal standards (of depleted, natural, and high-enriched isotopic compositions) and re-characterization of the uranium oxide pellet assay and isotopic standard are summarized to estimate uncertainties achievable for these measurements using modern TIMS instruments. Based on these measurements we conclude that:

- For uranium in the NU, LEU, and HEU enrichment categories, precision (%RSD) and accuracy (%RD) of the  $n(^{235}\text{U})/n(^{238}\text{U})$  major ratio data of the QC data are  $<0.05$ . The precision of the characterization samples are similar to those of the QC standards.
- Combining the accuracy and precision of the QC data, estimates of the uncertainties achievable for uranium isotope-amount ratio measurements using modern MC-TIMS instruments are made. The modeled uncertainties are lower than the certified uncertainties of NBL CRMs by factors of 2–8. Similar improvements in uncertainties are achievable for the minor isotope-amount ratio measurements, as well.
- Uncertainties calculated following ISO GUM principles are consistent with the uncertainty estimates made using the QC standard data for both major and minor isotope-amount ratios.



**Fig. 4** Modeled uncertainties (relative, as a percent) in the minor isotope ( $n(^{234}\text{U})/n(^{238}\text{U})$  or  $n(^{236}\text{U})/n(^{238}\text{U})$ ) ratios as a function of the value of the ratio. Uncertainty budgets for three ratio values 0.003, 0.0003, and 0.00003 are shown to demonstrate the interplay between the uncertainty contributions. Modeled uncertainties in the minor isotope-amount ratio using ion-counting (secondary electron multiplier) are shown for comparison

**Acknowledgments** We acknowledge discussions with NBL colleagues B. Srinivasan, M. Soriano, A. Hasozbek, G. O’Connor, and R.

Thomas as well as with IRMM colleague S. Richter on mass spectrometry and uncertainty related topics. Comments from two anonymous reviewers are appreciated. The nuclear safeguards community had lost a great champion and a visionary leader in the untimely death of Dr. Stefan Buerger (Safeguards Analytical Laboratory, IAEA). His passion for the advancement of science was unsurpassed. He had been a source of inspiration for the authors and we dedicate this paper to his memory.

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