Implementation of Guide to the expression of Uncertainty in Measurement (GUM) to multi-collector TIMS uranium isotope ratio metrology

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ABSTRACT

The application of the GUM (Guide to the expression of Uncertainty in Measurement) to calculate standard uncertainties for routine uranium isotope mass spectrometry measurements for nuclear safeguards and nuclear metrology is introduced. The benefit of this approach is an improved coherency and transparency of the uncertainty calculation, which should include contributions from all potentially significant sources of uncertainty to the mass spectrometric measurement result. The GUM approach puts the responsibility for quantifying the uncertainty on the analyst who makes the measurements and not with the user of the data. The uncertainty budget also serves to provide a feedback to the analyst. It identifies the dominant components of the measurement uncertainty and allows for better understanding, management, and improvement of the measurement process. Detailed examples of uncertainty calculations are presented for the most common types of uranium isotope measurements by multi-collector thermal ionization mass spectrometry (TIMS), e.g., total evaporation, conventional Faraday cup measurements using internal normalization, and combined measurements using a secondary electron multiplier and Faraday cups. Various sources of uncertainty common to multi-collector TIMS, such as baseline noise, peak-tailing effects, peak flatness, detector inter-calibration, and detector linearity response are discussed with respect to the determination of their uncertainty contribution and their influence on the results. Different approaches are explained with their advantages and disadvantages.

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1. Introduction

The New Brunswick Laboratory (NBL) and the Institute for Reference Materials and Measurements (IRMM) are metrology laboratories which, over the past decades, have performed high-precision high-accuracy multi-collector thermal ionization mass spectrometry (TIMS) measurements of actinide materials such as uranium and plutonium. Both facilities are responsible for the certification of U and Pu isotope reference materials of the highest metrological quality within their geographical areas (U.S. and the EU, respectively) and have contributed to the development of sophisticated mass spectrometric analytical techniques. As a result, both facilities have invested considerable effort toward evaluating uncertainties associated with actinide isotopic ratio measurements and are frequently tasked with the evaluation of data generated by other facilities. Within the analytical community, a lack of consistency for estimation of isotopic measurement uncertainty, as well as the frequent underestimation of measurement uncertainty,

has been observed. This lack of consistency can have the effect of making it difficult or impossible to perform realistic comparisons of measurement results. Wellum and Berglund (2002) [39] previously presented a description on implementing GUM to nuclear safeguards measurements using isotope dilution mass spectrometry. The detailed discussion of measurement uncertainty evaluation presented here will further aid other facilities and analysts in performing rigorous measurement uncertainty evaluations. Although this paper focuses on the special case for U isotope ratio multi-collector TIMS measurements, the principles are directly applicable to Pu TIMS measurements and broadly applicable to a wide range of isotopic analyses and a variety of mass spectrometric instruments.

The GUM guide [16] recommends a standardized approach to expressing uncertainty across the whole spectrum of measurements. Just as the use of the International System of Units (SI) brings coherence to measurements the International Organization for Standardization (ISO) Guide to the expression of Uncertainty in Measurement (GUM) represents a standardized way of expressing uncertainty in measurements. One of the merits is that an uncertainty budget evolves from the GUM approach, providing feedback to the analyst. The budget identifies the dominant components of the combined standard uncertainty (u_c) for the measurand and allows for better understanding and improvement of the

Fig. 1. Smallest relative uncertainties ($k = 2$, about 95% level of confidence) – per atomic mass unit – of certified isotope ratios; all certified reference materials worldwide as of year 2008.

measurement process. Furthermore, the GUM approach enhances transparency in the uncertainty calculations. Consequently, most of the national metrology institutes and regional metrology organizations in the world have adopted the ISO Guide [17,1,3,35].

The GUM approach has been applied to several different analytical procedures for isotope ratio measurements, radiometric dating, and impurity (trace element) analysis of nuclear materials. These measurements have been made for purposes that include nuclear safeguard analysis, nuclear forensic analysis, and bioassay as well as fuel cycle and metrology related studies. For example, the GUM approach to uncertainty has been applied to: uranium isotopic compositions analyzed using gas source mass spectrometry (GSMS), MC-TIMS, or sector-field inductively coupled plasma mass spectrometer (ICP-MS) [26,27,29,37,24,31]; age-dating of plutonium materials using sector-field ICP-MS [22] and MC-TIMS [38]; and determination of impurities and trace element signatures in uranium matrices measured using quadrupole, isotope dilution multi-collector ICP-MS, and various other methods [23,7,5]. The GUM approach has also been adopted for evaluation of measurement uncertainty in certification of uranium and plutonium reference materials, e.g., using GSMS and MC-TIMS for re-certifying the series IRMM-183 though -187 [30] for the minor ratios n(U-234)/n(U-238) and n(U-236)/n(U-238), the production of large size dried uranium–plutonium spike IRMM-1027f [34], the certification of plutonium and uranium isotope ratio reference materials NBL CRM 126-A, CRM 129-A [9], and CRM U045 [10], or the certification of NIST SRM 4324b (U-232 solution) [20] and NIST SRM 4338a (Pu-240 solution) [21].

In this paper, we will present a concise review of the GUM approach and will apply the GUM to multi-collector thermal ionization mass spectrometry (MC-TIMS) as used by New Brunswick Laboratory and the Institute for Reference Materials and Measurements in uranium metrology. Multi-collector TIMS is the primary method being used at NBL and IRMM for the production and certification of isotope ratio reference materials traceable to the International System of Units (SI Units). It should be noted that virtually all of the issues and principles presented for uranium analyses are directly applicable to plutonium as well.

1.1. A concise review of the GUM approach

GUM recommends a standardized approach to expressing uncertainty in measurement and tries to clarify common misusage

of terms. In the GUM approach, uncertainty is described as the dispersion of the values that can reasonably be attributed to the measurand (quantity of interest), whereas the word error refers to the difference between the measurand and a reference value which is considered to represent the "true" value. In contrast to classical error analysis, GUM does not separate between random component and systematic component. The GUM approach requires that the measurand is corrected for all recognized significant systematic effects and that an uncertainty is assigned to each of the applied corrections [16,17]. The uncertainties for the corrections are treated as random variables with a state-of-the-knowledge probability distribution (usually normal distribution or rectangular distribution). It is noted here that a correction applied to the measurand may not change the numerical value, but the associated uncertainty of the correction can be large. All uncertainty components are combined using the law of propagation of uncertainties, resulting in one combined standard uncertainty (u_c) value that can reasonably be attributed to the measurement. Section 8 of the ISO Guide presents the procedure for calculating uncertainty of the measurand (or measurands) as a step-by-step approach, which is summarized below [16,17]. Note that although the GUM uncertainty approach is fairly straight forward, some of the mathematical manipulations (e.g., partial derivatives) that are necessary to perform the uncertainty evaluations can be challenging. A variety of commercially or freely available software packages have been developed that can assist in this task.

Step 1: The relationship between the measurand Y and the input quantities X_i on which Y depends is expressed mathematically: $Y = f(X_1, X_2, \ldots, X_N)$. The function f is called the measurement function [4]. The terms measurement equation or model function are also used. Simply put, the measurement function is a mathematical formula that shows how all the necessary quantities are combined to obtain the desired measurement result. Significant components of uncertainty may include inexact values of constants and other parameters used in the function f, variations in the repeated observations of the measurand, approximations and assumptions incorporated in the measurement procedure, imperfect knowledge of the effects of environmental conditions on the measurement, finite instrument resolution or discrimination thresholds, and non-representative sampling. This also includes inexact values of measurement standards and reference materials: "Often, measuring instruments and systems are adjusted or calibrated using measurement standards and reference materials

to eliminate systematic effects; however, the uncertainties associated with these standards and materials must still be taken into account" [16]. This uncertainty component is of great importance for high-precision and accuracy isotope ratio analysis because it is frequently the case that the uncertainties associated with a measurement will be limited by the stated uncertainties of certified reference materials. This is illustrated in Fig. 1, which shows a survey of commercially available (worldwide) certified isotope ratio reference materials (as of year 2008). For the majority of chemical elements there is no reference material available that is certified for isotope ratios. Best accuracies achievable in isotope ratio measurement traceable to the SI, as indicated in Fig. 1, are about 0.01% through 0.3% (relative) per atomic mass unit. (Per atomic mass unit means that the relative uncertainty is divided by the difference in atomic mass between the two isotopes of interest.) Only for a few selected elements (i.e., Si, S, U, and Pu) are reference materials available with isotope ratio uncertainties of <0.01% (relative, $k = 2$, 95% level of confidence) per atomic mass unit.

Step 2: Determine the estimated value x_i for all input quantities X_i. The values associated with Step 2 represent the variables in the measurement function derived in Step 1. Estimates of input values for these variables may be obtained from single or repeated observations, judgment based on experience, or from external sources for input quantities associated with reference materials, calibration standards, or reference data from handbooks.

Step 3: The standard uncertainty $u(x_i)$ of each input estimate x_i is evaluated. The standard uncertainty is evaluated as "Type A" if the input estimate is obtained from statistical analysis of a series of observations and as "Type B" if the input estimate is obtained by other means. It is not uncommon that the standard uncertainties of the input quantities for a particular function represent a mix of Type A and Type B evaluations.

The standard uncertainty for a Type A evaluation is calculated as the standard deviation of the mean of a series of observations (this may include standard deviation from the fit of a calibration curve or a characteristic standard deviation from a control chart). If only a limited number of observations are available the "pooled estimate of standard deviation" can be used to provide a more robust estimate for a Type A evaluation for the measurement system [12]. The standard uncertainty for a Type B evaluation is based upon "professional judgement" using all available information, e.g., scientific publications, external sources, calibration certificates, manufacturer's quoted uncertainty bounds for a measuring instrument, historical agreement among independent laboratories, result of theoretical computations, and judgment based on experience. Type B evaluation may also be needed when the cost of collecting statistical data may be too high or a particular factor in question was not known to affect the measurement process until after the measurements were made.

Step 4: The covariances (i.e., correlation coefficient matrix) associated with any input estimates that are correlated are evaluated (see step 6 and chapter 5.2 [16] for more details). The nature of TIMS measurements (i.e., ratios of relative signal intensities) is such that calculated values such as isotope ratios and relative abundances will not be independent of one another. Accordingly, an evaluation of covariance is a necessary step to avoid inappropriate magnification or minimization of calculated measurement uncertainties.

Step 5: The result of the measurement (i.e., the estimate y of the measurand Y) using the functional relationship f and the estimates of the input quantities obtained in step 2 is performed. Thus, the estimate is $y = f(x_1, x_2, \ldots, x_N)$.

Step 6: The combined standard uncertainty $u_c(y)$ of the measurement result y from the standard uncertainties and covariances, i.e., correlation coefficients associated with the input estimates is

calculated. The law of propagation of uncertainties is used to calculate the combined standard uncertainty; see chapter 5.2 [16] for more details.

Step 7: An expanded uncertainty $U(y)$ can be expressed. It is calculated by multiplying the combined standard uncertainty $u_c(y)$ by a coverage factor k, typically in the range 2–3. The coverage factor is selected on the basis of level of confidence required of the interval. The result of the measurement is then conveniently expressed as: $Y = y \pm U$. The coverage factor necessary to yield a chosen level of confidence (e.g., 90%, 95%, or 99%) can be determined from the student-t distribution and the calculated effective degrees of freedom (using the Welch-Satterthwaite formula; see Appendix G [16]). For large effective degrees of freedom, a level of confidence of 95.45% corresponds to a coverage factor of $k = 2.00$ and 99.73% to $k = 3.00$.

Step 8: The result of the measurement together with its combined standard uncertainty or expanded uncertainty (and coverage factor) are reported with their associated units. An uncertainty budget should be provided. The ISO GUM guide states: "When reporting the result of a measurement and its uncertainty, it is preferable to err on the side of providing too much information rather than too little."; one should ask "Have I provided enough information in a sufficiently clear manner that my results [i.e., value of measurand and uncertainty] can be updated in the future if new information or data become available." [16].

2. Experimental

2.1. Multi-collector thermal ionization mass spectrometry

The implementation of GUM to multi-collector thermal ionization mass spectrometry reported in this work is based on work that was performed at NBL and IRMM over several years. At both facilities two different series of multi-collector TIMS instruments have been in use during this period. These include Thermo Fisher Scientific Triton instruments and the Triton's predecessor, the Finnigan MAT262. The uncertainty evaluation outlined below, however, should be directly applicable to any multi-collector TIMS instrument.

The primary sources of uncertainty in multi-collector TIMS uranium isotope ratio metrology include the Type A evaluation from measuring the isotope ratios of the sample of interest, the Type A evaluation from measuring the certified isotope ratio of the reference material used for mass fractionation correction (comparator), and the Type B evaluation of the certified isotope ratio for the reference material (comparator). Further sources of uncertainty may include uncertainties from background corrections (e.g., atomic or molecular interferences at the isotope masses of interest), Faraday cup baseline and gain variability, abundance sensitivity corrections, relative Faraday Cup efficiencies, and uncertainties from secondary electron multiplier (SEM) yield and non-linearity calibrations. These uncertainty components contribute in different proportions within the different analytical procedures, i.e., total evaporation, conventional analysis with internal normalization, or FC-SEM combined analysis. The case of multiple ion counting (MIC) is not presented here. The following sections discuss in detail the uncertainty evaluations for the three different mass spectrometry procedures listed.

3. Results and discussion

3.1. Total evaporation (TE)

The case is considered where the atom ratios of a sample are measured for multiple replicates using static Faraday cup multi-

collector TIMS and the total evaporation method [6,13,29]. Static analysis means, that the same isotopes are collected in the same Faraday cups throughout the analyses, thus the sector-field magnet is operating at a constant field setting throughout the course of the measurement. For each TE measurement of an unknown sample (or reference materials for mass fractionation and QC purposes) the current to the filament is regulated to achieve a reasonably constant ion current intensity throughout the measurement duration until the sample material loaded onto the filament is completely consumed. As described in detail in Richter and Goldberg [29], the total evaporation technique has the benefit of minimizing mass fractionation effects, which also improves the repeatability of replicate measurements. In the literature [6,13], the total evaporation technique has sometimes been described as an "accurate" method, in the sense that the total evaporation of the sample material from the filament would lead to a detection of all ions from the sample by the Faraday cups. This would automatically result in a measured isotope ratio which equals the actual ratio of atoms in the sample; the desired accurate result. But this assumption is questionable because only a small fraction (<1%) of the atoms evaporated from the filament actually reach the detectors due to the low ionization efficiency of U and due to less-than-100% transmission of the ion source optics. The change and drift of the isotope ratios due to the isotope mass fractionation during the measurement time, in combination with possible changes in the ion source focusing and transmission, can cause measurable deviations of total evaporation result from the true value. Therefore, an external fractionation correction using a reference material, measured repeatedly under similar conditions as the samples, is recommended [29]. In order to provide assurance that the assumption of working under "similar" conditions is valid, a second reference material should be measured for quality control (QC) purposes. This is frequently referred to as a QC sample.

The variability (or drift) of an isotope ratio can be significant over the entire duration of a measurement due to the effects of isotope fractionation, e.g., on the order of 0.5–1.0% for a n(U-235)/n(U-238) ratio. Total evaporation measurements represent ratios of signal intensities integrated over the entire duration of an analysis run. So it is not meaningful (and would be an overestimation) to assign an uncertainty related to the internal variability/drift during the course of a single measurement. The uncertainty of the reported result should rather be calculated from the repeatability of a series of measurements of the same sample (or reference material under similar conditions, as discussed below). The repeatability (standard deviation) of replicate U measurements using the total evaporation technique can be on the order of 0.03–0.01%, which is roughly a factor 10–30 lower than the drift/variability from the fractionation.

The primary sources of measurement uncertainty associated with TE or any static Faraday cup multi-collector measurement are measurement variability, gain and baseline variability, background corrections, mass bias (i.e., mass fractionation) corrections, and possibly Faraday cup efficiency inter-calibrations. Each of these factors will be discussed below.

3.1.1. Measurement variability (repeatability)

Measurement variability is a Type A evaluation component that is incorporated into an uncertainty evaluation as the standard uncertainty associated with the mean of a measured value. Some of this variability might stem from slightly different geometrical shapes and chemical and physical composition of the filaments and every sample will experience a slightly different pressure environment. However, the distribution of data from replicate measurements of a sample material analyzed using the same preparation and evaluation methods should capture theses effects as well as the effects from counting statistics and baseline and gain variability (see below). As discussed above, a "pooled estimate

of standard deviation" can be used to estimate the measurement uncertainty if only a few replicate are analyzed. All too frequently, an analyst will use the standard uncertainty derived from the many measurement cycles collected for a single sample filament (internal standard deviation). These values are typically unsatisfactory for uncertainty evaluation, because only the variability associated with a single measurement is represented so other factors that influence mass fractionation and measurement variability are not included in the estimation of the uncertainties.

3.1.2. Gain and baseline variability

Modern multi-collector TIMS instruments have calibration routines that measure the performance of signal amplification associated with the electronics for Faraday cups (gain) and the level of electronic noise (baseline). The variability of the mean value for these systematic corrections can be evaluated using long term trends or results from instrument electronic test routines. These values tend to vary randomly around some mean value. Typically, the instrument software automatically corrects raw data for baseline and gain. In practice, a separate uncertainty value for gain and baseline does not have to be applied. When replicate measurements are made on a sample, baseline and gain variability will be confounded in the variability of the measurement results. To account for baseline and gain variability separately would, essentially, be double counting the gain and baseline variability. If, however, uncertainty sources associated with gain and/or baseline corrections existed beyond the observed variability in the measurement data then a separate uncertainty factor can be added. The uncertainty can be incorporated into the uncertainty evaluation by adding a multiplicative δ-factor (gain) with a value of 1 and a standard uncertainty reflecting the variability of the gain, and by subtracting a δ-factor (baseline) with a value of 0 and a standard uncertainty representing the variability of the baseline.

3.1.3. Background, interference, and peak-tailing corrections

Background, atomic and molecular interferences, and peak tailing are sources of uncertainty that can be particularly significant for isotope ratio measurements that encompass a large dynamic range. Isobaric interferences (i.e., atomic and molecular) can be due to molecular species formed during an analysis (for example ReO_3 can form ions with masses of 233 u and 235 u) or from "blank" contribution to the analysis signal (TIMS filaments, particularly Re filaments, have a certain level of U contamination that adds to the measured uranium signal of U-238 and potentially other isotopes). Less than perfect transmission of an ion beam through a mass spectrometer results in some of the ions having altered trajectories or losing energy (e.g., ions colliding with residual gas molecules, scattering on edges of beam defining apertures) which will consequently result in a detected signal at a different position in the mass spectrum (typically at lower mass side of the major peak) [40]. The tail of the higher mass ions can, in extreme cases, completely overlap neighboring isotopes in the mass spectrum. The relative magnitude of the resulting "peak tail" at a mass 1 u off of the ion beam mass (taken on the low mass side) is referred to as "abundance sensitivity". The abundance sensitivity in modern TIMS instruments using Faraday cups is typically at the several ppm level [40]. This can be dramatically improved in instruments equipped with energy filters (ppb level) such as a retarding potential quadrupole (RPQ).

Isobaric interferences and peak-tailing contributions typically result in systematic effects (biases) and may sometimes be difficult to quantify. For extreme ratios, the dominant component of the combined standard uncertainty typically stems from the background and peak-tailing corrections. The magnitude and associated uncertainty (variability) of interferences can be assessed by taking the mean of replicate analyses of blank samples and using the observed variability in the interferences to determine a stan-

dard uncertainty. Contributions from peak tailing are commonly estimated by taking the mean of background signals (tailing signal) measured at half-mass locations bracketing the signal peak of interest (i.e., the signal to be corrected for tailing effects). For instance, the tailing contribution to the U-236 ion beam signal can be assessed by measuring the ion beam intensities at about 235.5 u and 236.5 u. It has long been recognized that this method of correction tends to result in a systematic overcorrection of the measurement data, but a consistently superior method for performing a peak tail correction has not been reported [8,36,11]. Although the variability of the peak tail correction will be captured by the replicate measurements incorporated into the analysis routine, an uncertainty still should be estimated to account for the poorly constrained bias that results from the peak tail correction.

Although the background from interferences and peak tailing are typically determined separately, both are subtracted from the raw data on a per-cycle (or per-analysis) basis so the uncertainties associated with the corrections could be combined into a single δ-factor (δ_{Bkgd}), or, alternatively, into separate factors (e.g., $\delta_{Interference}$ and $\delta_{PeakTailing}$). Because the background correction is applied as a difference, for the purpose of the uncertainty evaluation, δ_{Bkgd} or $\delta_{Interference}$ and $\delta_{PeakTailing}$ can be incorporated into the measurement function as an additive term (or subtractive). The value of the δ_{Bkgd} (or $\delta_{Interference}$ and $\delta_{PeakTailing}$) should be zero with a conservative estimate for the uncertainty attached to δ_{Bkgd} (or $\delta_{Interference}$ and $\delta_{PeakTailing}$).

3.1.4. Mass bias correction

Mass bias correction (i.e., mass fractionation) applied to U data are normally determined by repeated measurements of a comparator which is a material with well-characterized isotopic composition (preferably a certified reference material). The difference of the measured value to the certified value is assumed to be primarily due to the mass related isotopic fractionation. The correction factor, for example calculated using linear, power, or exponential functions (also referred to as "linear law", "power law" or "exponential law"), is then consequently applied to the samples and QC samples. The measurement uncertainty in the mass bias correction represent two components that are not captured elsewhere in the uncertainty analysis. These are the Type A evaluation associated with repeated comparator measurements and the Type B evaluation for the certified isotopic value used to determine the correction factor (e.g., uncertainty of the certified value obtained from the certificate). The incorporation of the uncertainty related to the mass fractionation correction is discussed in the example below in more detail.

3.1.5. Faraday cup efficiencies

The relative efficiency of the Faraday cups to each other for detecting the same ion signal is referred to here as Faraday cup efficiency. Bayne et al. [2] performed experiments to assess Faraday cup efficiency of a multi-collector TIMS instrument by peak shifting isotopes of Re-187, U-238, and Pu-239 between cups to determine relative efficiencies. Their results were somewhat inconsistent and

for U and Re the relative differences between cups were normally less than 0.05%. A multi-collector Faraday cup efficiency study at NBL indicated even smaller efficiency differences [18]. But the cup efficiencies should be evaluated for each instrument to validate this assessment. It should be noted that for measurements of comparators used to determine the mass bias, the resulting mass correction factor is a combination of mass bias effects and of cup efficiency effects. Consequently, the mass bias correction also incorporates a cup efficiency correction if the same cup configuration is used for the measurement of the comparator ratio and the measurement of the sample ratio. Given this fact and the comparably small magnitude of the correction, a correction factor and an associated uncertainty for cup efficiency are frequently not incorporated into measurement evaluation.

3.1.6. Measurement function

As an example of how the various uncertainty components are incorporated into a measurement uncertainty evaluation, the TE procedure will be presented here for uranium isotope ratio analysis (i.e., $n(U-234)/n(U-238)$, $n(U-235)/n(U-238)$, and $n(U-236)/n(U-238)$). This procedure can be easily adapted to plutonium isotope ratio analyses by renaming the mathematical terms for the uranium isotopes in the below given equations with plutonium isotopes. Additional isotopes (e.g., U-233) can easily be included in the evaluation if needed by adding new terms to the equations.

The analysis of a sample turret loaded with a number, N_C, of filaments (i.e., aliquots) of a comparator material for mass fractionation correction (i.e., a suitable reference material with certified isotope ratio) and a number, N_S, of filaments (i.e., aliquots) of the unknown sample is considered. Comparator and unknown sample should have the same sample size and chemical as well as similar isotopic composition. The filaments (both comparators and unknowns) are randomly distributed on the sample turret. The three measurands in this case are the mass fractionation corrected atom ratios $n(U-234)/n(U-238)$, $n(U-235)/n(U-238)$, and $n(U-236)/n(U-238)$ of the unknown sample (i.e., $R_{S,234/238}$, $R_{S,235/238}$, and $R_{S,236/238}$, respectively). They are calculated from the measured ratios ($R_{S,234/238meas}$, $R_{S,235/238meas}$, and $R_{S,236/238meas}$, respectively) and the corresponding fractionation factors ($CF_{234/238}$, $CF_{235/238}$, and $CF_{236/238}$ respectively) using the measurement functions (linear law for mass fractionation correction):

$$R_{S,234/238} = R_{S,234/238\,meas}/CF_{234/238} - \delta_{Bkgd} \tag{1a}$$

$$R_{S,235/238} = R_{S,235/238\,meas}/CF_{235/238} - \delta_{Bkgd} \tag{1b}$$

$$R_{S,236/238} = R_{S,236/238\,meas}/CF_{236/238} - \delta_{Bkgd} \tag{1c}$$

The mass fractionation correction factors ($CF_{234/238}$, $CF_{235/238}$, and $CF_{236/238}$) are calculated from the measured comparator ratio $n(U-235)/n(U-238)$ ($R_{C,235/238meas}$) and the certified comparator ratio ($R_{C,235/238cert}$) using the linear law (other laws can be utilized if necessary, e.g., exponential law or power law [14]):

$$CF_{234/238} = 1 + \frac{(238-234)}{(238-235)} \cdot \left(\frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} - 1 \right) = 1 + \frac{4}{3} \cdot \left(\frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} - 1 \right) \tag{2a}$$

$$CF_{235/238} = 1 + \frac{(238-235)}{(238-235)} \cdot \left(\frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} - 1 \right) = \frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} \tag{2b}$$

$$CF_{236/238} = 1 + \frac{(238-236)}{(238-235)} \cdot \left(\frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} - 1 \right) = 1 + \frac{2}{3} \cdot \left(\frac{R_{C,235/238\,meas}}{R_{C,235/238\,cert}} - 1 \right) \tag{2c}$$

Using the above given Eqs. (2a)–(2c), it can be seen that the uncertainty of the certified value of the $n(U-235)/n(U-238)$ ($R_{C,235/238cert}$) will be propagated in a way that its influence increases when calculating the $n(U-234)/n(U-238)$ ratio (divided

by a difference of 238 u − 235 u = 3 atomic mass units but multiplied by a difference of 238 u − 234 u = 4 atomic mass units) and decreases when calculating the n(U-236)/n(U-238) ratio (divided by a difference of 3 atomic mass units but multiplied by a difference of 238 u − 236 u = 2 atomic mass units). Thus, uncertainties in some measured isotope ratios (e.g., n(U-236)/n(U-238)) could become smaller than the uncertainty of the certified value itself used for normalization (e.g., n(U-235)/n(U-238)). This is particularly apparent where the mass difference of the measured ratios is significantly different from the mass difference of the normalization ratio (e.g., n(Pu-240)/n(Pu-239) internal normalization versus n(Pu-242)/n(Pu-239) sample ratio; or vice versa). Calibration of an instrument using a certified reference material provides measurement traceability for TIMS, so it is not possible to specify that the instrument is any more accurate than the uncertainty with which the certified value of the CRM is established. In fact, if analyses of a CRM indicate that no mass bias correction is necessary, the uncertainty of the calibration CRM would still have to be incorporated into the measurement uncertainty due to the fact that it represents the minimum resolution at which instrument bias can be observe. One alternative approach is to replace the mass fractionation factors $CF_{234/238}$, $CF_{235/238}$, and $CF_{236/238}$ in Eqs. (1a)–(1c) by $\delta CF_{234/238}$, $\delta CF_{235/238}$, and $\delta CF_{236/238}$, respectively. The values for $\delta CF_{234/238}$, $\delta CF_{235/238}$, and $\delta CF_{236/238}$ are calculated according to Eqs. (2a)–(2c), respectively, and used as input quantities in Eqs. (1a)–(1c). But for the standard uncertainties of $\delta CF_{234/238}$, $\delta CF_{235/238}$, and $\delta CF_{236/238}$ in Eqs. (1a)–(1c) the standard uncertainty of $CF_{235/238}$ is used instead of propagating according to Eqs. (2a)–(2c). According to Eq. (2b), the standard uncertainty of $CF_{235/238}$ is calculated by the standard uncertainty of $R_{C,235/238cert}$ (from the certificate) plus an uncertainty term that represents the repeatability of $R_{C,235/238meas}$. In this way, the uncertainty of the mass fractionation correction $CF_{235/238}$ is applied directly to all ratios. Note that this can, on the other hand, lead to an underestimation of the uncertainty of the n(U-234)/n(U-236) ratio. Both approaches will be illustrated in the numerical examples in this and the following sections.

To maintain simplicity in the uncertainty calculation, the raw data (summed intensities of each isotope) are corrected by the instrument software or manually for any potential contributions (e.g., background, atomic or molecular interferences at the isotope masses of interest, Faraday cup baseline and gain) as deemed necessary by the analyst. The values of the measured isotope ratios $R_{S,234/238meas}$ through $R_{S,236/238meas}$ and $R_{C,235/238meas}$ are then calculated from the corrected raw data. The ratios are then used as input quantities in the measurement functions (Eqs. (1a)–(1c) and (2a)–(2c)). In this case, a single factor (δ_{Bkgd}) can be added to the measurement function, as given in Eqs. (1a)–(1c), to account for the uncertainty stemming from the background contributions, peak tailing, Faraday cup baseline and gain variability, etc. Alternatively, multiple terms can be added instead of a single term to subdivide these contributions into individual terms if needed, e.g., δ_{Bkgd}, $\delta_{PeakTailing}$, $\delta_{FCbasline}$, etc. This utilization of δ-factors [12] for incorporation of certain uncertainty components with small deviations to the measurement function provides simplicity for the purpose of the uncertainty evaluation. In this case, the correction factor δ_{Bkgd} (or multiple factors if needed) has a value of zero (because the corrections are made to the raw data), but is assigned a standard uncertainty that corresponds to the standard uncertainty associated with the background correction. It may be derived from measured data for the correction factor δ_{Bkgd} (Type A) or derived from expert judgment (Type B). A different term can be used in each of the three Eqs. (1a)–(1c) (e.g., $\delta_{Bkgd234}$, $\delta_{Bkgd235}$, and $\delta_{Bkgd236}$) in case the magnitude of background correction to the different isotopes is different or to avoid correlation effects. Note that due to the nature of total evaporation, no half-mass background measurements can be performed without interrupting the

total evaporation analysis. Therefore, systematic contributions, for example from peak tailing, can potentially bias the isotope ratio results. If the abundance sensitivity is well known, the raw intensity data can be corrected for the peak tailing. Another approach would be to perform an external tailing correction by measuring an additional reference material with a similar value for the isotope ratio in question. An associated uncertainty can be assigned to this correction (Type A or Type B) and included in the measurement functions (Eqs. (1a)–(1c)) by adding an additional term similar to δ_{Bkgd}.

For uncertainty evaluation purposes a quality control sample can be treated as an additional unknown sample.

3.1.7. Example

A number of $N_C = 4$ filaments (i.e., aliquots) for the comparator and $N_S = 6$ filaments for the unknown sample are measured. In this case, NBL CRM U500 was used as comparator. A QC sample is not discussed in this example but can easily be added by treating it as an additional sample. Sample signals were acquired at comparably high ion beam intensities (e.g., 6 V summed intensity), thus background contribution (e.g., interferences and instrument noise, typically less than 20 μV) can be considered as negligible. In this example, we use the approach where the correction factors $CF_{234/238}$, $CF_{235/238}$, and $CF_{236/238}$ in Eqs. (1a)–(1c) are substituted by $\delta CF_{234/238}$, $\delta CF_{235/238}$, and $\delta CF_{236/238}$, respectively, all of which will have the relative uncertainty determined for $CF_{235/238}$ assigned to it, as described above. The numerical values of the measured isotope ratios to be considered in this example are listed in Table 1.

The three measurands to be evaluated are the mass fractionation corrected isotope ratios $R_{S,234/238}$, $R_{S,235/238}$, and $R_{S,236/238}$ of the unknown sample. $R_{S,234/238meas}$, $R_{S,235/238meas}$, $R_{S,236/238meas}$, and $R_{C,235/238meas}$ are measured input quantities and are thus statistically derived (Type A). Their estimates are given by the arithmetic mean: $N_S = 6$ observations (i.e., aliquots) for the unknown sample; thus $R_{S,234/238meas} = 0.0116625$, $R_{S,235/238meas} = 1.5103856$, and $R_{S,236/238meas} = 0.00202440$. The estimate for the value of the comparator $R_{C,235/238meas}$ (NBL CRM U500) is given by the arithmetic mean of the $N_C = 4$ observations; thus $R_{C,235/238meas} = 1.0003161$. Input quantity $R_{C,235/238cert}$ is 0.999698 with an expanded uncertainty of $U(R_{C,235/238cert}) = 0.0014$ (Type B, $k = 2$, normal distribution), which is derived from the NBL CRM U500 certificate using the uncertainties for the absolute abundances of 0.1% for both isotopes. Hence, the mass fractionation correction factors can be calculated: $CF_{234/238} = \delta CF_{234/238} = 1.000822$, $CF_{235/238} = \delta CF_{235/238} = 1.000616$, and $CF_{236/238} = \delta CF_{236/238} = 1.000411$ with a combined standard uncertainty $u_c(CF_{235/238}) = 0.000703$ (degrees of freedom $\nu_{eff} = 50$). Thus, the standard uncertainties for $\delta CF_{234/238}$, $\delta CF_{235/238}$, and $\delta CF_{236/238}$ are $u(\delta CF_{234/238}) = u(\delta CF_{235/238}) = u(\delta CF_{236/238}) = u_c(CF_{235/238}) = 0.000703$. For comparison, the combined standard uncertainties for $CF_{234/238}$ and $CF_{236/238}$ are $u_c(CF_{234/238}) = 0.000937$ ($\nu_{eff} = 50$) and $u_c(CF_{236/238}) = 0.000468$ ($\nu_{eff} = 50$), respectively, using the approach of directly propagating the uncertainties. The mass fractionation corrected ratios can now be calculated. The background correction to the measured data itself is estimated to be negligible, thus $\delta_{Bkgd} = 0$, but a conservative estimate of the standard uncertainty of $u(\delta_{Bkgd}) = 15\,\mu V/6\,V = 0.0000025$ is made and accounted for as standard uncertainty of δ_{Bkgd}. Peak tailing of U-235 and U-238 contribute to the peaks of the minor isotopes (U-234 and U-236). For the purpose of this example it is assumed (e.g., from measurement of the abundance sensitivity) that the contribution of U-235 to U-234 is 5 ppm and of U-238 to U-234 is negligible; the contribution of U-238 to U-236 is 3 ppm and U-235 to U-236 negligible. Therefore, a term $\delta_{PeakTailing234}$ and $\delta_{PeakTailing236}$ is added to the measurement function for $R_{S,234/238}$ and $R_{S,236/238}$

Table 1

Total evaporation example: measured uranium isotope ratios n(U-234)/n(U-238), n(U-235)/n(U-238), and n(U-236)/n(U-238) (atom ratios) for 4 comparator filaments and 6 sample filaments loaded on one turret.

Filament	n(U-234)/n(U-238)	n(U-235)/n(U-238)	n(U-236)/n(U-238)
Comparator (aliquot 1)		1.0001656	
Unknown sample (aliquot 1)	0.0116659	1.5103080	0.00201910
Unknown sample (aliquot 2)	0.0116640	1.5104500	0.00202622
Comparator (aliquot 2)		1.0004102	
Unknown sample (aliquot 3)	0.0116589	1.5103801	0.00202420
Unknown sample (aliquot 4)	0.0116703	1.5104151	0.00203031
Comparator (aliquot 3)		1.0003688	
Unknown sample (aliquot 5)	0.0116742	1.5103522	0.00202588
Unknown sample (aliquot 6)	0.0116417	1.5104085	0.00202070
Comparator (aliquot 4)		1.0003199	

respectively, with values zero (insignificant correction to or manual correction of raw data) and a conservative estimate for the standard uncertainties equal to 100% of the peak-tailing contribution, i.e., $u(\delta_{PeakTailing234}) = 5 \times 10^{-6} \cdot R_{S,235/238meas} = 0.0000076$ and $u(\delta_{PeakTailing236}) = 3 \times 10^{-6}$. This yields for the mass fractionation corrected ratios $R_{S,234/238} = 0.0116529$, $R_{S,235/238} = 1.50946$, and $R_{S,236/238} = 0.00202357$ with combined standard uncertainties $u_c(R_{S,234/238}) = 0.0000124$ ($\nu_{eff} = 92$), $u_c(R_{S,235/238}) = 0.00106$ ($\nu_{eff} = 50$), and $u_c(R_{S,236/238}) = 0.00000447$ ($\nu_{eff} = 100$), respectively. Hence, the expanded uncertainties are $U(R_{S,234/238}) = 0.000025$ ($k = 2.00$), $U(R_{S,235/238}) = 0.0021$ ($k = 2.00$), and $U(R_{S,236/238}) = 0.0000089$ ($k = 2.00$), respectively, for a coverage factor k equal to 95.45% level of confidence.

The uncertainty budgets for the three measurands of the sample are listed in Table 2. As can be seen, the background contribution and peak-tailing contribution increase with decreasing isotope abundance, as expected. It is most pronounced for the n(U-236)/n(U-238) ratio, which has the smallest abundance. The uncertainty arising from the mass fractionation correction (i.e., $\delta CF_{234/238}$ and $\delta CF_{235/238}$) is the dominant contributor to the expanded uncertainty of the isotope ratios n(U-234)/n(U-238) and n(U-235)/n(U-238), which is frequently the case in high-precision isotope ratio analysis.

3.2. Conventional Faraday cup analysis with internal normalization

The case is considered where the minor atom ratios n(U-234)/n(U-238) and n(U-236)/n(U-238) of an unknown sample are measured in multiple replicates using static Faraday cup multi-collector mass spectrometry and internal normalization. For internal normalization, the known major isotope ratio n(U-235)/n(U-238) of the sample is used to correct the mass fractionation of the n(U-234)/n(U-238) and n(U-236)/n(U-238) isotope ratios. It is assumed that the major isotope ratio n(U-235)/n(U-238) of the unknown sample was determined previously, e.g., using total evaporation, or is known by other means. Additional isotopes (e.g., U-233) can easily be included in the evaluation if needed by adding new terms to the equations given below. The uncertainty evaluation for this analysis method is very similar to the TE case with the exception of the uncertainty components associated with the mass bias correction. For internal normalization, the mass bias correction is essentially applied in real time using the known major ratio.

The analysis of a sample turret loaded with a number of N filaments (i.e., aliquots) of the unknown sample is considered. The two measurands in this case are the mass fractionation corrected n(U-234)/n(U-238) and n(U-236)/n(U-238) atom ratios of the sample ($R_{S,234/238}$ and $R_{S,236/238}$, respectively). They are calculated from the measured ratios ($R_{S,234/238meas}$ and $R_{S,236/238meas}$) and the corresponding mass fractionation correction factor ($CF_{234/238}$ and $CF_{236/238}$, respectively) using the measurement functions (lin-

ear law for mass fractionation correction) as given in Eqs. (1a) and (1c), respectively.

The mass fractionation correction factors ($CF_{234/238}$ and $CF_{236/238}$) are calculated from the measured n(U-235)/n(U-238) normalization ratio of the sample ($R_{S,235/238meas}$) and the known value of that ratio ($R_{S,235/238}$) using (see notes in the total evaporation section on other correction laws):

$$CF_{234/238} = 1 + \frac{(238 - 234)}{(238 - 235)} \cdot \left(\frac{R_{S,235/238\,meas}}{R_{S,235/238}} - 1 \right)$$

$$= 1 + \frac{4}{5} \cdot \left(\frac{R_{S,235/238\,meas}}{R_{S,235/238}} - 1 \right) \quad (3a)$$

$$CF_{236/238} = 1 + \frac{(238 - 236)}{(238 - 235)} \cdot \left(\frac{R_{S,235/238\,meas}}{R_{S,235/238}} - 1 \right)$$

$$= 1 + \frac{2}{3} \cdot \left(\frac{R_{S,235/238\,meas}}{R_{S,235/238}} - 1 \right) \quad (3b)$$

The term δ_{Bkgd} accounts for uncertainties arising from potential background contributions (e.g., atomic or molecular interferences at the isotope masses of interest), and additional terms may be added for Faraday cup baseline and gain variability, peak-tailing contributions, etc.; see above section on total evaporation for more details. Also, see note in above section on total evaporation regarding the propagation of the uncertainty of the reference value (here normalization ratio).

For uncertainty evaluation purposes a quality control sample can be treated as an additional unknown sample.

3.2.1. Example

A number of $N = 2$ filaments (i.e., aliquots) for the unknown sample are measured. The known value for the major isotope ratio n(U-235)/n(U-238) of the sample is $R_{S,235/238} = 1.5095$ with an expanded uncertainty of $U = 0.0017$ (Type B, normal distribution, $k = 2.13$), which will be used for the internal normalization. Because only a small number ($N = 2$) of repeat observations (aliquots) are obtained for the unknown sample, it is necessary to establish an estimate of the measurement repeatability. For example, a "pooled estimate of standard deviation" s_p is used for the measured ratios $R_{S,234/238meas}$ through $R_{S,236/238meas}$. A previous evaluation of the variability of isotope ratio measurements for similar samples (QA data with 30 data points) gives a pooled estimate of standard deviation of $s_p = 0.0000058$ for n(U-234)/n(U-238), 0.00020 for n(U-235)/n(U-238), and 0.0000050 for n(U-236)/n(U-238) (degrees of freedom $\nu = 30 - 1 = 29$). Here, for the purpose of this numerical example, we use the approach where the correction factors $CF_{234/238}$ and $CF_{236/238}$ in Eqs. (1a) and (1c) are not substituted by $\delta CF_{234/238}$ and $\delta CF_{236/238}$, respectively, but propagated using Eqs. (3a) and (3b) (see discussion in TE section). The numerical values

Table 2
Total evaporation example: Uncertainty budgets for the three measurands $R_{S,234/238}$, $R_{S,235/238}$, and $R_{S,236/238}$ of the unknown sample. "ν_{eff}" denotes effective degrees of freedom, "c" denotes sensitivity coefficient.

Quantity	Value	Standard uncertainty (u_c)	ν_{eff}	Distribution	c	Contribution
$R_{S,234/238}$:						
$R_{S,234/238meas}$	0.01166250	0.00000468	5	normal	1.0	14.3%
$\delta CF_{234/238}$	1.000822	0.000703	50	normal	−0.012	43.8%
δ_{Bkgd}	0.0	2.50×10^{-6}	50	normal	1.0	4.1%
$\delta_{PeakTailing234}$	0.0	7.6×10^{-6}	50	normal	1.0	37.8%
$R_{S,235/238}$:						
$R_{S,235/238meas}$	1.5103856	0.0000206	5	normal	1.0	0.0%
$\delta CF_{235/238}$	1.000616	0.000703	50	normal	−1.5	100%
δ_{Bkgd}	0.0	2.50×10^{-6}	50	normal	1.0	0.0%
$R_{S,236/238}$:						
$R_{S,236/238meas}$	0.00202440	0.00000166	5	normal	1.0	13.7%
$\delta CF_{236/238}$	1.000411	0.000703	50	normal	−0.002	10.1%
δ_{Bkgd}	0.0	2.50×10^{-6}	50	normal	1.0	31.2%
$\delta_{PeakTailing236}$	0.0	3.0×10^{-6}	50	normal	1.0	45.0%

of the measured isotope ratios to be considered in this example are listed in Table 3.

The two measurands to be evaluated are the mass fractionation corrected isotope ratios $R_{S,234/238}$ and $R_{S,236/238}$ of the unknown sample. $R_{S,234/238meas}$, $R_{S,235/238meas}$ and $R_{S,236/238meas}$ are measured input quantities (observations) and are thus statistically derived (Type A). Their estimates are given by the arithmetic mean of the $N = 2$ observations (i.e., aliquots); thus $R_{S,234/238meas} = 0.0116645$, $R_{S,235/238meas} = 1.510403$, and $R_{S,236/238meas} = 0.00202316$. Hence, the mass fractionation correction factors can be calculated: $CF_{234/238} = 1.000797$ and $CF_{236/238} = 1.000399$ with combined standard uncertainties of $u_c(CF_{234/238}) = 0.000716$ (degrees of freedom $\nu_{eff} = 52$) and $u_c(CF_{236/238}) = 0.000358$ ($\nu_{eff} = 52$). The mass fractionation corrected ratios can now be calculated. The background correction to the measured data itself is estimated to be negligible, thus $\delta_{Bkgd} = 0$, but a conservative estimate of the standard uncertainty of $u(\delta_{Bkgd}) = 15\,\mu V/6\,V = 0.0000025$ is made and accounted for as standard uncertainty of δ_{Bkgd}. Peak tailing of U-235 and U-238 contribute to the peaks of the minor isotopes (U-234 and U-236). For the purpose of this example it is assumed (e.g., from measurements of the abundance sensitivity) that the contribution of U-235 to U-234 is 5 ppm and of U-238 to U-234 is negligible; the contribution of U-238 to U-236 is 3 ppm and U-235 to U-236 negligible. Therefore, a term $\delta_{PeakTailing234}$ and $\delta_{PeakTailing236}$ is added to the measurement function for $R_{S,234/238}$ and $R_{S,236/238}$ respectively, with values zero (manual correction to the raw data) and a conservative estimate for the standard uncertainties equal to 100% of the peak-tailing contribution, i.e., $u(\delta_{PeakTailing234}) = 5 \times 10^{-6} \cdot R_{S,235/238meas} = 0.0000076$ and $u(\delta_{PeakTailing236}) = 3 \times 10^{-6} = 0.0000030$. This yields for the mass fractionation corrected ratios $R_{S,234/238} = 0.011655$ and $R_{S,236/238} = 0.0020224$ with combined standard uncertainties $u_c(R_{S,234/238}) = 0.0000122$ ($\nu_{eff} = 130$) and $u_c(R_{S,236/238}) = 0.00000533$ ($\nu_{eff} = 100$), respectively. Hence, the expanded uncertainties are $U(R_{S,234/238}) = 0.000024$ ($k = 2.00$) and $U(R_{S,236/238}) = 0.000011$ ($k = 2.00$), respectively, for a coverage factor k equal to 95.45% level of confidence.

The uncertainty budgets for the three measurands are listed in Table 4. The uncertainty arising from the internal normalization (i.e., mass fractionation correction using $R_{S,235/238meas}$ and $R_{S,235/238}$) is the dominant contributor to the expanded uncertainty of the isotope ratio $n(U-234)/n(U-238)$, whereas the variability of the $n(U-236)/n(U-238)$ measurements is the major contributor to the $n(U-236)/n(U-238)$ expanded uncertainty. Background contribution for U-236 and peak-tailing contribution for both minor isotopes are significant, as might be expected.

3.3. Combined Faraday cup and secondary electron multiplier analysis with internal normalization

Due to the limited dynamic range of Faraday cup (FC) detectors, many measurements require the use of more than one detector type for determining the full isotopic composition of an element of interest. This is, for instance, of particular interest for uranium and the determination of minor isotopes such as U-234 or U-236 in depleted, natural, or low enriched samples. Frequently, multi-collector instruments will include subsidiary detector(s) for measurement of low-abundance isotopes. A discrete dynode secondary electron multiplier (SEM) is one of the more frequently used high-sensitivity detectors. Other detectors commonly in use are continuous dynode SEMs and Daly detectors [40]. Although the following discussion is primarily focused on discrete dynode SEMs many of the principles are directly applicable to other high-sensitivity detector types.

As with Faraday cup multi-collector analyses, combined FC-SEM analyses have the advantage of simultaneously measuring all target isotopes of the element of interest; effectively eliminating components of uncertainty that arise from signal drift during a dynamic analysis (e.g., single collector peak jumping). Combined FC-SEM analyses have all of the uncertainty components previously described for conventional MC-TIMS analysis. These include uncertainty components such as Faraday cup baseline and gain variability, variability from repeated observations, and calibration material uncertainty (i.e., certified values of reference materials). For combined FC-SEM analyses, the uncertainties that arise from the use of different detector types also need to be specifically addressed and incorporated. These include uncertainties associated with SEM dark noise, Faraday cup versus SEM detector inter-calibration, and SEM detector non-linearity. Furthermore, the level of the extreme ratios typically measured using combined FC-SEM techniques can result in magnification of the

Table 3
Internal normalization example: measured uranium atom ratios $n(U-234)/n(U-238)$, $n(U-235)/n(U-238)$, and $n(U-236)/n(U-238)$ for 2 sample filaments loaded on one turret.

Filament	$n(U-234)/n(U-238)$	$n(U-235)/n(U-238)$	$n(U-236)/n(U-238)$
Unknown sample (aliquot 1)	0.0116649	1.5103901	0.00201910
Unknown sample (aliquot 2)	0.0116640	1.5104151	0.00202722

Table 4
Internal normalization example: Uncertainty budgets for the two measurands $R_{S,234/238}$ and $R_{S,236/238}$ of the unknown sample. "ν_{eff}" denotes effective degrees of freedom, "c" denotes sensitivity coefficient.

Quantity	Value	Standard uncertainty (u_c)	ν_{eff}	Distribution	c	Contribution
$R_{S,234/238}$:						
$R_{S,234/238meas}$	0.01166445	0.00000403	30	normal	1.0	10.8%
$R_{S,235/238meas}$	1.510403	0.000139	30	normal	−0.010	1.4%
$R_{S,235/238}$	1.509500	0.000798	50	normal	0.010	45.1%
δ_{Bkgd}	0.0	2.5×10^{-6}	50	normal	1.0	4.2%
$\delta_{PeakTailing234}$	0.0	7.6×10^{-6}	50	normal	1.0	38.6%
$R_{S,236/238}$:						
$R_{S,236/238meas}$	0.00202316	0.00000355	30	normal	1.0	44.5%
$R_{S,235/238meas}$	1.510403	0.000139	30	normal	−0.0009	0%
$R_{S,235/238}$	1.509500	0.000798	50	normal	0.0009	1.8%
δ_{Bkgd}	0.0	2.5×10^{-6}	50	normal	1.0	22.0%
$\delta_{PeakTailing236}$	0.0	3.0×10^{-6}	50	normal	1.0	31.7%

influence of uncertainty components such as those arising from isobaric and molecular interference and from peak tailing. All of these components are associated with measurement bias and, therefore, must be addressed explicitly because they will not be captured statistically by combining many measurement cycles nor addressed by making multiple discrete measurements of the same material. The uncertainties for background, dark noise, collector inter-calibration, and detector non-linearity are primarily due to an uncertainty in the absolute magnitude of the correction rather than random variability associated with the correction. So, even though each of the corrections are applied to raw data or individual measurement cycles, no large number of repeated observations (e.g., many measurement cycles) will reduce the magnitude of the uncertainty associated with these factors (this is not true for special cases associated with detector inter-calibration, see below). These uncertainty components should be incorporated into the evaluation of the measurements in an identical manner regardless of whether the various corrections are performed by commercial instrument software or manually by an analyst subsequent to measurement.

To maintain simplicity in the uncertainty calculation, the uncertainty components specific to FC-SEM multi-collector analyses can be incorporated by adding additional terms to the measurement function as outlined in the previous two sections (δ-factors). The corrections are applied to the raw measurement data or to the values for each measurement cycle. A δ-factor term is added to the measurement function as dictated by the manner in which the corrections were applied to the raw data representing the relative uncertainties associated with the corrections. For example, commercial software for multi-collector instruments often apply the corrections to the data automatically. Accordingly, it is necessary to include δ-factors to the measurement function so that the components of uncertainty associated with these corrections are incorporated into the combined standard uncertainty of the measurand. Table 5 gives a list of δ-factors that may need to be considered. For a combined FC-SEM isotope ratio analysis, the measurement function for a minor isotope ratio measurement, e.g., U-234, using the major ratio $n(\text{U-235})/n(\text{U-238})$ for internal normalization is given by Eqs. (4a) and (4b). Here, the minor isotope $n(\text{U-234})/n(\text{U-238})$ ($R_{S,234/238meas}$) is measured with the SEM on isotope U-234 and one FC on isotope U-238, whereas the major isotope ratio $n(\text{U-235})/n(\text{U-238})$ ($R_{S,235/238meas}$) is measured using Faraday cups. The δ-factors specific to the SEM are added:

$$R_{S,234/238} = R_{S,234/238\,meas}/CF_{234/238} \cdot \delta_{Yield} \cdot \delta_{LDT}$$
$$-\delta_{Bkgd} - \delta_{DN} \tag{4a}$$

$$CF_{234/238} = 1 + \frac{(238-234)}{(238-235)} \cdot \left(\frac{R_{S,235/238\,meas}}{R_{S,235/238}} - 1 \right) \tag{4b}$$

For the uncertainty associated with detector non-linearity/dead-time (δ_{LDT}) and detector inter-calibration (δ_{Yield}) the δ-factor (typically multiplicative terms) will have a value of 1 (raw data as already corrected manually or by the instrument software) with the standard uncertainty of the δ-factors representing the relative uncertainty associated with the particular component. For dark noise (δ_{DN}) and background (δ_{Bkgd}) the δ-factors are additive terms (or subtractions) and, therefore, have a value of zero (raw data already corrected manually or by the instrument software) with the absolute magnitude of the correction applied to the measured value as a conservative estimate for the uncertainties of the δ-factors. Outlined below are more detailed discussions of the determination and application of potentially significant FC-SEM multi-collector measurement uncertainty contributions.

3.3.1. Dark noise correction (δ_{DN})

Dark noise (dark current) is a signal registered by a pulse-counting detector system in the absence of any ion beam. The magnitude of dark noise can be assessed by observing long integrations on the SEM with the ion source isolated from the analyzer and detector systems of the mass spectrometer. Commercial instruments frequently have specific programs for measuring dark noise. Due to the fact that dark noise is typically very low for most newer SEM (certainly smaller than 1 count per second (cps) in pulse counting mode but typically in the range of 0.1–0.01 cps) and has a large variability (low counting statistics), a standard uncertainty that represents 100% of the measured dark noise may be used for the δ_{DN} term. This can be regarded as a conservative estimate, but the contribution of this uncertainty component to the overall uncertainty of the measurement is, for all but the most extreme measurements, inconsequential.

Table 5
Shown are various components of uncertainty that are of potential significance for combined Faraday cup (FC) and secondary electron multiplier (SEM) detector analyses.

Uncertainty components for FC-SEM measurements	Symbol	Value	Recommended standard uncertainty
Dark noise	δ_{DN}	0	magnitude of correction itself
FC-SEM inter-calibration correction factor	δ_{Yield}	1	relative standard deviation of calibration(s)
SEM detector linearity and dead-time correction factor	δ_{LDT}	1	relative standard deviation of calibration measurements
Background correction/contribution	δ_{Bkgd}	0	magnitude of correction itself or some fraction thereof

A dark noise correction to the raw data is made by subtracting the measured dark noise from the total measured signal. Accordingly, the δ-factor for dark noise (δ_{DN}) is incorporated in the measurement function, Eq. (4a), by subtraction. For instance, the value of the standard uncertainty of the term δ_{DN} applied to a $n(\text{U-}234)/n(\text{U-}238)$ ratio measured by FC-SEM multi-collector analysis can be calculated by taking the quotient of the uncertainty in the measured dark noise to the mean ion beam intensity for U-238 throughout the measurement(s). Note that the values of the SEM and the FC signals have to be expressed in the same units (e.g., in counts per second or in Volt).

3.3.2. SEM efficiency calibration (yield calibration, δ_{Yield})

FC-SEM inter-calibrations, which are also called yield calibrations, are normally performed by alternately measuring a stable ion beam (e.g., a Re beam from the sample ionization filament or a beam of the most suitable isotope in the element being measured) in a Faraday cup and the SEM. A number of replicate integrations typically at an ion beam signal of 3–5 mV (equal to about 2×10^5–3×10^5 cps) are performed resulting in a mean SEM efficiency factor (values close to 1, typically expressed in percent, e.g., 97%) and an observed variability of this factor (e.g., standard deviation of the mean or standard uncertainty). This standard uncertainty can be used directly for the inter-calibration δ-factor (δ_{Yield}) and will also include the baseline uncertainty of the Faraday cup used in this procedure, which is significant due to the low signal (only few millivolts) on the Faraday cup. This method of estimating uncertainty is often sufficient but has two major weaknesses in that the observed uncertainty primarily represents variability due to measurement statistics and signal drift and fails to encompass detector efficiency changes that might occur on the time scale of an actual multi-collector analysis. A more robust method for estimating uncertainty for δ_{Yield} would be to measure the FC-SEM inter-calibration repeatedly over the course of a measurement campaign. For instance, over the course of a days work, an inter-calibration can be performed before each measurement that utilizes the FC-SEM combination. The standard deviation of these measured efficiency factors probes the reproducibility and might represent a more reasonable estimate for uncertainty of any individual inter-calibration. Note that this is only true if the operating parameters of the SEM (e.g., operating voltage) are not changed over the course of the measurements, because changing the SEM operating voltage will result in a systematic change of the SEM efficiency as well. The FC-SEM inter-calibration correction (efficiency factor) is applied to measured SEM data in a multiplicative way (division). So, for the purpose of the uncertainty evaluation, δ_{Yield} can also be included in the measurement function, Eq. (4a), in a multiplicative way.

An SEM efficiency calibration can also be performed on a per-mass cycle basis if a dynamic analysis method is used instead of a static analysis. For this method of SEM efficiency calibration, one uranium isotope of a suitable size is measured both using the SEM and a Faraday cup for each mass cycle throughout the measurement [29]. The advantage of this method is that biases associated with short term drift in SEM efficiency will be avoided and uncertainty associated with variability of the inter-calibration will be captured in the distribution of the measured values. Accordingly, a dynamic measurement that incorporates a per-cycle FC-SEM inter-calibration significantly reduces the uncertainty of the SEM efficiency factor if a sufficiently large number of cycles are observed. In this case, a δ_{Yield} does not need to be incorporated into the measurements uncertainty calculation.

3.3.3. SEM non-linearity calibration (δ_{LDT})

Non-linearity in the response of SEM detectors is a result of a combination of dead-time effects and of other SEM non-linear responses including memory effects and afterpulsing, which are only partially understood. These effects are, to some extent, proportional to signal intensity but can have opposing results. Where dead-time causes a progressive decrease of detection efficiency as ion beam intensity increases, other SEM detector behavior has been observed to result in signal magnification [25,28,15]. Although it is possible to measure the electronic ("true") dead-time on an SEM [25] it is typically not possible or necessary to resolve all the competing non-linear effects. Accordingly, if a detector non-linearity correction is applied to the data which combine all non-linearity effects into a single value with an associated uncertainty, then individual correction terms with their individual associated uncertainties are not needed. Also, discrepancies between dead-time values measured electronically and measured using isotope ratios have been observed, as well as negative dead times, which are caused by a combination of dead-time and other non-linear effects, which may include afterpulsing [28,25]. Hence, a single functionality that describes the observed non-linearity behavior, i.e., all combined effects, will circumvent this issue.

The magnitude of a detector non-linearity correction should be derived from measurements performed on the particular detector of interest. Richter et al. [28,32] and Hoffmann et al. [15] outline procedures for characterizing SEM detector non-linearity, but there is no unanimous recommendation for determining an uncertainty associated with these corrections. Non-linearity correction factors are generally determined by regressing a curve through the results of a series of isotope ratio measurements performed on samples with known ratios (e.g., reference materials) at intensities that range across the SEM dynamic range. The equation for the curve is then used to determine a correction factor for signal intensities of interest. One way of estimating uncertainty for the correction factor (i.e., relative uncertainty for δ_{LDT}) is to apply the correction factor to the data used to generate the curve (e.g., reference materials), normalize the data to accepted/certified values, and then use the dispersion of the normalized values to calculate the standard uncertainty associated with the non-linearity correction. Although this method will capture potential variability associated with the calculated correction factor, this variability may be dominated by unrelated components associated with the measurement (i.e., counting statistics, signal drift). This dispersion of the normalized values also does not constitute the complete uncertainty of δ_{LDT}, because the (potentially dominating) contribution from the uncertainty of the accepted/certified values, has to be taken into account [32]. Furthermore, this method incorporates an implicit assumption that detector non-linearity does not drift substantially. Although it may prove impractical due to resource limitations, a superior uncertainty evaluation would be to perform a series of detector linearity measurement campaigns over a relatively short period (perhaps 1 month). The standard uncertainty of the correction factor can then be calculated from the variability of a single data set corrected by each of the individual determinations of the detector linearity. Calculating a non-linearity correction uncertainty by this method assures that the uncertainty accounts for any temporal drift in detector non-linearity as well.

Like the detector inter-calibration, the non-linearity correction is applied by taking the product (or quotient) of the measured SEM signal with the determined correction factor. Therefore, for the purpose of the uncertainty evaluation δ_{LDT} can be incorporated in the measurement function, Eq. (4a), in a multiplicative way.

It should be noted that recent improvements in SEM detector technology might have effectively eliminated (at a standard uncertainty level of <0.05%) non-linearity effects not related to "true" dead-time [32]. If the previously documented non-linearity effects have been eliminated in newer detectors, the electronic

Table 6
Combined FC-SEM example: measured uranium atom ratios n(U-236)/n(U-238) for 6 sample filaments.

Filament	n(U-236)/n(U-238)
Sample (aliquot 1)	0.0000114074
Sample (aliquot 2)	0.0000114102
Sample (aliquot 3)	0.0000114030
Sample (aliquot 4)	0.0000114026
Sample (aliquot 5)	0.0000114015
Sample (aliquot 6)	0.0000114033

dead-time and associated uncertainty can be determined using pulse-to-pulse timing measurements [25,32] or, with usually smaller uncertainties, using suitable isotope reference materials [32].

3.3.4. Background corrections (δ_{Bkgd})
See discussion on background corrections in the TE section.

3.3.5. Peak flatness factor ($\delta_{SEM-Flatness}$)
In case of a frequent use of an SEM, its characteristics can change over time, e.g., the efficiency (see Section 3.3.2. SEM efficiency calibration), peak-shape, and peak flatness can deteriorate. The peak shape can also depend on the ion source focusing and is therefore, to a certain degree, unpredictable during automatic measurement sequences where the ion beam focusing is performed periodically. Also, the drift of the mass calibration in combination with poor peak shapes can cause biases to isotope ratio measurements. This can be taken into account for the uncertainty budget by introducing a SEM peak flatness factor $\delta_{SEM-Flatness}$ with a value of zero (if additive) or a value of one (if multiplicative) and a standard uncertainty determined from peak shape investigations.

3.3.6. Example
As an example for a combined SEM-Faraday cup measurement, a verification measurement of the reference material IRMM-075/2 with a n(U-236)/n(U-238) isotope ratio of 10^{-5} is presented. The IRMM-075/1-6 series is a set of reference materials with n(U-236)/n(U-238) ranging between 10^{-9} and 10^{-4}, prepared gravimetrically by mixing of enriched U-236 (>99.96%) and natural U [33]. The n(U-235)/n(U-238) major isotope ratio is measured separately by UF$_6$ gas source mass spectrometry and used here for internal mass fractionation correction. The n(U-234)/n(U-238) and n(U-236)/n(U-238) ratios are measured by TIMS (n(U-234)/n(U-238) for the purpose of SEM yield calibration), U-234 is detected by a Faraday cup, U-236 is detected using an SEM in ion counting mode. A number of $N = 6$ filaments (i.e., aliquots) for n(U-236)/n(U-238) are measured ($R_{S,236/238meas}$); the numerical values to be considered in this example are listed in Table 6. The SEM is equipped with an energy filter (RPQ) to improve the abundance sensitivity. Isotope U-234 is held at an intensity of approx. 2 mV on the Faraday cup, which is equipped with an amplifier with a 10^{12} Ω resistor to improve the signal-to-noise ratio. The signal on the FC for U-238 is therefore about 36 V. For the mass fractionation correction factor (CF) (determined by UF$_6$ mass spectrometry) a value of effectively 1.0000 is used with and relative combined standard uncertainty of $u_c = 0.025\%$ ($k = 1$). The SEM-FC inter-calibration was performed internally using the U-234 signal by switching the beam between FC and SEM on a cycle-to-cycle basis. This results in a relative uncertainty of $u = 0.05\%$ ($k = 1$) with $\delta_{Yield} = 1$. For the SEM linearity factor $\delta_{LDT} = 1$ a relative standard uncertainty of $u = 0.05\%$ ($k = 1$) is used as well, stemming from linearity tests performed using reference materials with certified minor isotope abundances (e.g., IRMM-074 series). A background contribution of about 1 cps at mass U-236 results in a standard uncertainty of $u = 5 \times 10^{-10}$ ($k = 1$) for $\delta_{Bkgd} = 0$ (U-238 ion signal of 36 V = 2.2×10^9 cps). A SEM peak flatness factor of $\delta_{SEM-Flatness} = 1$ is applied with relative standard uncertainty

of $u = 0.03\%$ ($k = 1$), accounting for uncertainties from peak shape flatness of the SEM. It is taken into account twice: once for the U-236 measurements using the SEM and once for measurements of U-234 for the SEM yield calibration.

The result for the n(U-236)/n(U-238) isotope ratio (measurand $R_{S,236/238}$) including the budget is listed in Table 7; it is $1.1405(22) \times 10^{-5}$. Note that the expanded uncertainty ($k = 2$) is the result of this numerical example; a slightly different calculation was performed by [33]. For comparison, this is in good agreement with the result obtained in a conventional Faraday cup measurement of $1.1414(28) \times 10^{-5}$ and the certified value $1.14160(40) \times 10^{-5}$ obtained from the gravimetrical mass metrology (calculations not discussed in his example). Note that the uncertainty components from the SEM-FAR inter-calibration, the SEM linearity, and the SEM peak flatness factor are significant in this case. Their δ-values do not depend on the ion beam intensity of U-236 and therefore do not depend on the value of the n(U-236)/n(U-238) ratio. Thus, for n(U-236)/n(U-238) ratios larger than 10^{-5}, this combined SEM-Faraday cup method would not provide smaller uncertainties. Instead, conventional Faraday cup measurements provide smaller uncertainties due to the better signal-to-noise ratio using FC. On the other hand, for n(U-236)/n(U-238) ratios below 10^{-5} Faraday measurements without SEM are not advantageous any more because of the small U-236 signal on the FC. Instead, combined SEM-Faraday cup measurements are recommended using SEM for U-236 detection. With decreasing U-236 count rates and n(U-236)/n(U-238) ratios, the counting statistics (represented by the repeatability of the internally corrected measurement results for n(U-236)/n(U-238)) and the background become the dominant source of uncertainty.

3.4. Calculation of percent atom and weight abundances and atomic weight

The percent atom abundances (AtP$_{234}$, AtP$_{235}$, AtP$_{236}$, and AtP$_{238}$, in unit percent), percent weight abundances (WtP$_{234}$, WtP$_{235}$, WtP$_{236}$, and WtP$_{238}$, in unit percent), and atomic weight (AtW) can be calculated from the measured isotope ratios using well known mathematical relationships. They are presented here exemplary for the four uranium isotopes U-234, U-235, U-236, and U-238. The equations can easily be modified to include further isotopes (e.g., U-233) or uranium replaced by plutonium (or a different element)

$$\text{AtP}_{23x} = 100 \times \frac{R_{S,23x/238}}{(R_{S,234/238} + R_{S,235/238} + R_{S,236/238} + 1)} \quad \{x = 4, 5, 6\}$$

$$\text{AtP}_{238} = 100 \times \frac{1}{(R_{S,234/238} + R_{S,235/238} + R_{S,236/238} + 1)}$$

$$\text{AtW} = (\text{AtP}_{234} \cdot \text{AtM}_{234} + \text{AtP}_{235} \cdot \text{AtM}_{235} + \text{AtP}_{236} \cdot \text{AtM}_{236} + \text{AtP}_{238} \cdot \text{AtM}_{238})/100$$

$$\text{WtP}_{23x} = \text{AtP}_{23x} \cdot \text{AtM}_{23x}/\text{AtW} \quad \{x = 4, 5, 6, 8\}$$

The (relative) atomic masses AtM$_{234}$, AtM$_{235}$, AtM$_{236}$, and AtM$_{238}$ of the four isotopes are tabulated. It is noted here that, when calculating the combined standard uncertainties (and expanded uncertainties) of these quantities, the correlation coefficients cannot be neglected and have to be taken into account. This is because the isotope ratios (quantities $R_{S,234/238}$, $R_{S,235/238}$, and $R_{S,236/238}$) typically introduce significant correlations. This is of particular concern when performing the reversed calculation, i.e., when calculating isotope ratios from the known percent atom or weight abundances (see for example Meija and Mester [19]).

Table 7
Combined FC-SEM example: Uncertainty budget for the measurand $R_{S,236/238}$. "ν_{eff}" denotes effective degrees of freedom, "c" denotes sensitivity coefficient.

Quantity	Value	Standard uncertainty (u_c)	ν_{eff}	Distribution	c	Contribution
$R_{S,236/238,\text{meas}}$	1.140467×10^{-5}	0.000138×10^{-5}	5	normal	1.0	1.6%
δ_{Yield}	1.000000	0.000500	50	normal	11×10^{-6}	27.6%
δ_{LDT}	1.000000	0.000500	50	normal	11×10^{-6}	27.6%
$\delta_{\text{Peak-Flatness}}$	1.000000	0.000600	50	normal	11×10^{-6}	39.8%
δ_{Bkgd236}	0.0	5×10^{-10}	50	normal	1.0	0.2%
δ_{DN}	0.0	7.2×10^{-12}	50	normal	1.0	0.0%
$CF_{235/238}$	1.000000	0.000250	50	normal	-7.6×10^{-6}	3.1%

4. Conclusion

In the measurement sciences, a statement of uncertainty is an integral part of a measurement result. Due to its merits, ISO GUM is a beneficial approach to uncertainty in measurement. It improves the transparency of the uncertainty calculation, i.e., the calculation can be reproduced by others. GUM does not separate between random component and systematic component. Instead, they are treated in a consistent logical way, which results in one combined standard uncertainty value for the measurand. A result of the GUM uncertainty evaluation is the availability of an uncertainty budget, which provides a feedback to the analyst. It shows the relative contributions of each incorporated uncertainty component to the combined standard uncertainty and, therefore, allows better understanding, managing, and improving the measurement process. The total evaporation example and the conventional Faraday cup example clearly pointed out the importance of incorporating the uncertainty of reference materials used for mass fractionation correction in TIMS isotope ratio measurements. In high-accuracy and high-precision measurements the certified values with their associated uncertainties typically constitute the dominant source of uncertainty. For combined FC-SEM measurements, a variety of uncertainty sources will need to be considered. The lower the signal intensity on the SEM the more significant some of these uncertainty sources will become. The resulting uncertainty budget provides here a particularly helpful inside into the relative contributions and which sources need to be better controlled to improve the analytical results.

A discussion of the limitations of GUM should not be neglected at this point. One of the limitations is that the combined standard uncertainty of the measurand (and thus the expanded uncertainty) may be a poor approximation if the measurement function is nonlinear. In that case, higher order terms in the Taylor series expansion of the law of propagation of uncertainty can be included [16]. Also, the GUM does not provide a probability distribution for the measurand. It is assumed that the distribution is approximately normal. These limitations of the GUM led to the development of Supplement 1 to the GUM, which discusses the use of Monte Carlo simulation for that purpose (see Kacker et al. (2007) [17] for a more detailed discussion).

It seems appropriate to conclude this discussion on implementing GUM to TIMS isotope ratio analysis with a statement so pivotal to evaluation of uncertainty in all scientific endeavors where measurements are preformed: "Although this Guide [i.e., ISO GUM] provides a framework for assessing uncertainty, it cannot substitute for critical thinking, intellectual honesty, and professional skill. The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of the measurement. The quality and utility of the uncertainty quoted for the result of a measurement therefore ultimately depend on the understanding, critical analysis, and integrity of those who contribute to the assignment of its value." [16].

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