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# Total evaporation method for uranium isotope-amount ratio measurements

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Total evaporation (TE) is an analysis technique for the measurement of uranium isotopic abundance ratios using thermal ionization mass spectrometry (TIMS). A small mass dependent bias observed in this analytical technique is determined by an external correction factor using well characterized standards (most often certified reference materials, CRMs). The technique had been demonstrated to be highly precise and accurate for major isotope-amount ratio measurements of uranium and plutonium. We compare the performance of the TE analytical technique for uranium isotope ratio measurements on two TIMS instruments (TRITON and MAT261) using well characterized CRMs from NBL and investigate the dependence of the instrumental mass bias on the amount of sample analyzed. It is concluded that the mass bias during a TIMS uranium isotopic analysis by TE is independent of the amount of material analyzed. Unlike the major ratio, minor isotope ratio measurements by TE are biased high due to peak-tailing from the major isotopes. The biases in the minor isotope ratio data using TE are evaluated using well characterized NBL CRMs.

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## 1 Introduction

Uranium isotope-amount ratio measurements within different stages of the nuclear fuel cycle – mining operations, conversion and enrichment process, fuel element fabrication, power plant operations and spent fuel storage, reprocessing, and waste management operations – are required for cradle-to-grave safeguards of the fissile $^{235}$U under national and/or international regulations.[1] Isotopic abundance ratios of solid, liquid, or gaseous materials using a variety of analytical techniques including ICP-QMS, ICP-MS, TIMS, and GSMS are used to monitor/control the complex processes associated with the nuclear fuel cycle.[2] Total Evaporation (TE) is a well established analytical technique for isotope amount-ratio measurements of several elements,[3–7] including uranium, using thermal ionization mass spectrometry (TIMS).

Uranium has four naturally occurring, long-lived isotopes: $^{234}$U, $^{235}$U, $^{236}$U, and $^{238}$U. In addition, non-naturally occurring $^{233}$U isotope may also be present at trace abundance levels in materials associated with the nuclear fuel cycle (for example through the decay of $^{237}$Np). The relative abundances of isotopes $^{235}$U and $^{238}$U are the highest, and these are often referred to as major isotopes whereas $^{234}$U and $^{236}$U are referred to as minor isotopes due to their low abundances. In natural samples the presence of the minor isotope $^{236}$U is at relative abundances of $\sim 10^{-11}$.[8] Detection of isotopic abundances at these levels requires advanced mass spectrometry techniques like accelerated mass spectrometry. Note that the presence and abundance of $^{236}$U in a sample is a reliable indicator of the presence of reprocessed material.

The measured n($^{235}$U)/n($^{238}$U) isotope-amount ratios in a nuclear analytical laboratory can vary in a wide range from $\sim$0.00725 (natural uranium) to about 0.03 to 0.05 (typical enrichments for fuel in nuclear power reactors). This ratio can be as high as >10.3 for material originating from nuclear weapons.[9] For routine measurements of the major isotope ratios of uranium and plutonium, TE is a method of choice[7] as mass dependent fractionation effects are minimized due to the principle underlying this method.[10–13] TE analytical technique also has the advantage that it can be used over the whole range of isotopic compositions typical for nuclear materials measured at nuclear analytical laboratories,[14] with good precision and accuracy.

In the present study, we compare the performance of the TE analytical technique for uranium isotope-amount ratio measurements on two TIMS (TRITON and MAT261) instruments using well characterized CRMs from New Brunswick Laboratory (NBL) and investigate the dependence of the instrumental mass bias on the amount of sample analyzed.

## 2 Material and methods

Within this paper "sample" is used to represent any sample, CRM or other working standard that is used for instrument calibration and/or estimation of the correction factors associated with TIMS isotopic measurements. It has to be ensured that environmental or laboratory contamination does not

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influence the samples during their pre-analysis processing or during mass spectrometric measurements. For uranium isotope-amount ratio measurements, such steps include the use of pre-cleaned Teflon or quartz beakers and sample containers, use of ultra high purity acids and water in the preparation of the solutions for mass spectrometric analyses, and careful design of sample handling to eliminate potential cross-contamination.[15]

Isobaric interferences at uranium atomic masses are reduced through the use of pre-cleaned (degassed) zone refined rhenium filaments for TE analyses. Pre-cleaning of the filaments before loading uranium samples on them is another step aimed at reducing molecular and isobaric interferences in TIMS measurements. Pre-cleaning also helps to obtain consistent loads (similar sized drops) of the sample on the filaments. Tungsten or tantalum filaments are also used for TIMS analyses using TE. Note that the purity of the filament material need to be confirmed for each batch of filaments as variations between filament batches from the same manufacturer had been observed.

Uranium samples for TIMS analyses are prepared as purified nitrate solutions with similar concentrations. Typically μL-sized drops of the samples are placed near the center of the filament ribbon and the sample drying is accomplished by passing a current through the filament. The current is adjusted such that it is sufficient to dry the uranium nitrate droplet loaded on the filament without boiling. All sample solutions are dried following a consistent filament heating routine (same filament currents and same duration of time for which currents are passed though the filament during the sample drying). This drying procedure converts the uranyl nitrate into a refractory uranium oxide (*e.g.* $UO_3$ or $U_3O_8$) on the filament surface.

### 2.1 Mass spectrometry

Traditionally, TE analyses employ a double-filament configuration, where the sample of interest is deposited onto one of the two filaments. The sample-loaded filament (evaporation filament) with the filament surface containing the sample is placed in close proximity to another filament (ionization filament, without the sample). In the final configuration in which samples are analyzed by the TIMS instrument, the spacing between the evaporation and ionization filaments is approximately 1 mm. The filaments are heated independently of each other by passing electrical current through them.

The steps involved in the TE analyses of a uranium sample using rhenium double filaments are: (i) the current on the ionization filament is brought to a value sufficient to take the temperature in the immediate vicinity of the evaporation filament to ~1800 °C (typically a current of about 5–5.3 A on the ionization filament), (ii) the $^{187}Re$ signal (about 200 to 500 mV) is used for ion source focusing and peak-centering, (iii) a uranium ion signal sufficient for ion source focusing and peak-centering (typically about 50 to 200 mV) is brought up by controlled heating of the evaporation filament, (iv) following focusing and peak-centering of the uranium ion beam signal, data acquisition begins under computer control to yield a predefined summed ion signal intensity, and (v) data acquisition and evaporation filament heating is continued until the uranium ion signal intensities drop below a pre-defined lower limit as the sample is exhausted. The filament heating steps are aimed to collect most of the data at a constant summed intensity.

In TE analyses using TIMS instruments, the speed of signal regulation is a critical parameter for a steady sample evaporation process. Classical TE methods use the data system to read the ion signal and the difference of this ion signal from a predefined target intensity is used to determine the increment in which the filament is heated. For the MAT261 instrument, SPECTROMAT® had developed a hardware-driven DTE (direct total evaporation) method that uses an analog regulator in the filament power supply with direct feedback of the detector intensity.[16] During DTE analyses, only target values are set by the data system initially. The filament heating and sample evaporation process is then carried out by the hardware. The data system just monitors, collects, and calculates the data. Due to the nature of electronic regulation the ion signal is kept stable for the duration of the run (±3% in TE *vs.* ±0.2% in DTE) until the whole sample is consumed. For the MAT261 instrument, the DTE method had led to an improvement in the precision and accuracy of the uranium major isotope-amount ratio measurements.[16]

Two TIMS instruments, a TRITON multi-collector instrument from ThermoFisher Scientific® and a MAT261 instrument with SPECTROMAT® hardware and software upgrades, were used for the analyses presented here. The TE (or DTE, in the case of MAT261) measurements consisted of consecutive integrations of 1 second and 8 second durations, for the TRITON and MAT261 instruments, respectively.

Only data generated by qualified analysts on instruments that are qualified on the TE analytical technique for uranium isotopic analyses are included in the present study. Results for a total of 22 turrets are evaluated (data from two analysts each on two TIMS instruments are included). Of the 13 turrets analyzed by the TE analytical technique on the TRITON instrument, seven are quality assurance (QA) turrets. QA turrets are routinely analyzed before/during the course of measurement efforts to ensure that the instrument performance is within the historical limits established by analytical results on CRMs. Eight of the nine turrets from the MAT261 instrument, included in the present study are QA turrets. TE analyses included in the present evaluation are performed with uranium sample loads of 0.2 μg, 0.5 μg, and 1.0 μg on the TRITON instrument, and with 0.2 μg and 0.25 μg on the modified MAT261 instrument.

TE analyses are typically a Faraday only measurement as the emphasis of this analytical technique is on obtaining good major ratio data and in most materials analyzed in nuclear laboratories the abundances of both $^{235}U$ and $^{238}U$ are sufficient for detection using the Faraday cups. For both MAT261 and TRITON instruments, measurements presented here are Faraday only measurements. If not limited by sample amount a Faraday only measurement is the method of choice with the best external precision[17] as uncertainties arising from inter-calibration of detectors and non-linearity of the SEM detector are avoided.[18,19]

## 3 Results and discussion

On the TRITON instrument, the TE analyses presented here were run at summed ($^{235}U + ^{238}U$) signal intensities in the range of 6 V to 15 V. On the MAT261 instrument, the TE analyses were run at summed uranium isotope signal intensities in the range of 4 V to 6 V to accommodate the smaller dynamic range of the faraday detectors (10 V for the MAT261 instrument *vs.* 50 V for the TRITON instrument). During TE analysis, all of the isotopes $^{234}U$, $^{235}U$, $^{236}U$, and $^{238}U$ are measured simultaneously using static Faraday cup multi-collector TIMS (the cup configuration used for the TRITON instrument is shown in Table 1. A similar configuration is used for the MAT261 instrument). Static analyses means that the ion beam intensities from the same isotope is collected in the same Faraday cup throughout the course of the analyses. Hence the TIMS sector magnetic field is operating at a constant field setting throughout the TE measurement. Isotopic ratios are then determined by dividing the integrated signal intensities of $^{234}U$, $^{235}U$, $^{236}U$, and $^{238}U$.

### 3.1 Isotope release profiles and isotope-ratio profiles

Typical isotope abundance profiles for two uranium samples, measured by the TE analytical technique using the TRITON instrument, are shown in Fig. 1a and 2a. TE data shown in Fig. 1a were carried out at a summed ($^{235}U + ^{238}U$) signal intensity of 6 V (CRM U630, sample load = 0.2 μg) while that shown in Fig. 2a were carried out at a summed ($^{235}U + ^{238}U$) signal intensity of 15 V (CRM U010, sample load = 1 μg). Fig. 1b and 2b show the corresponding $n(^{235}U)/n(^{238}U)$ isotope-amount ratio profiles. The integrated $n(^{235}U)/n(^{238}U)$ ratio (sum total of all data acquired $[n(^{235}U)/n(^{238}U)]_{SUMI}$ in Fig. 1b and 2b) as well as the isotope ratio measured in each individual data acquisition cycle ($[n(^{235}U)/n(^{238}U)]_{cycle}$ in Fig. 1b and 2b) are indicated. The certified value of the isotope-amount ratio is shown by the dashed line. For both CRMs U630 and U010 the integrated isotope-amount ratios are only marginally higher than the certified values of the CRMs. The $[n(^{235}U)/n(^{238}U)]_{SUMI}/[n(^{235}U)/n(^{238}U)]_{certified}$ ratio represents the mass bias correction for the major ratio $n(^{235}U)/n(^{238}U)$. Note that the isotope abundance profiles (Fig. 1a and 2a) as well as the isotope ratio profiles (Fig. 1b and 2b) are similar even though the analysis intensities as well as the enrichment of the $^{235}U$ isotope are very different.

The isotopic abundance profiles and isotope-amount ratio profiles from the MAT261 instrument are similar to those discussed above (see ref. 16 for typical profiles). On the MAT261 instrument, the implementation of the DTE technique, had significantly improved the stability of the isotopic abundance profiles and the resulting isotopic ratio profiles.

**Table 1** Cup-configuration used for TE analyses on the TRITON. Except for the integration time, configuration used by the MAT261 is similar

| Scan | Cup L2 | Cup L1 | Center cup | Cup H1 | Cup H2 | Cup H3 | Integration time (s) |
|---|---|---|---|---|---|---|---|
| 1 | $^{233}U$ | $^{234}U$ | $^{235}U$ | $^{236}U$ | 237 | $^{238}U$ | 1.049 |

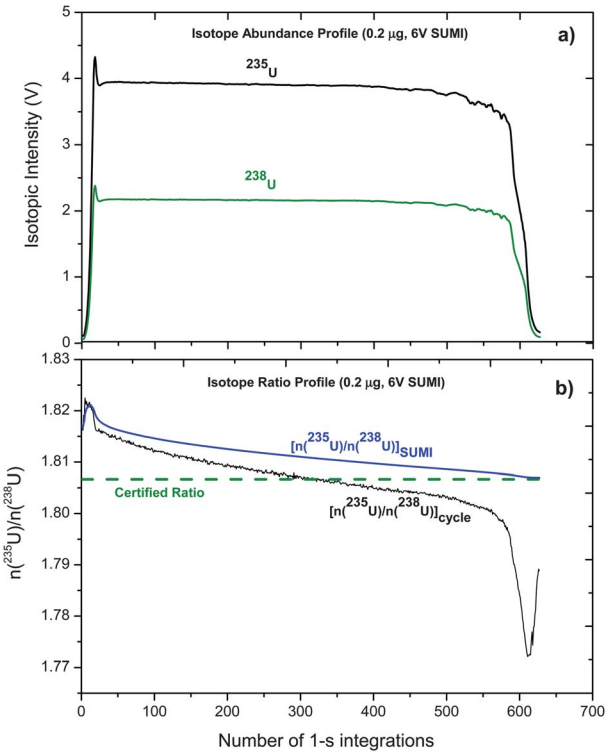


**Fig. 1** The $^{235}U$ and $^{238}U$ isotope abundance profiles (a) and $n(^{235}U)/n(^{238}U)$ isotope-amount ratio profile (b) in TE analyses of CRM U630. Amount of U loaded is 0.2 μg and analysis intensity (sum of the $^{235}U$ and $^{238}U$ intensities) is 6 V.

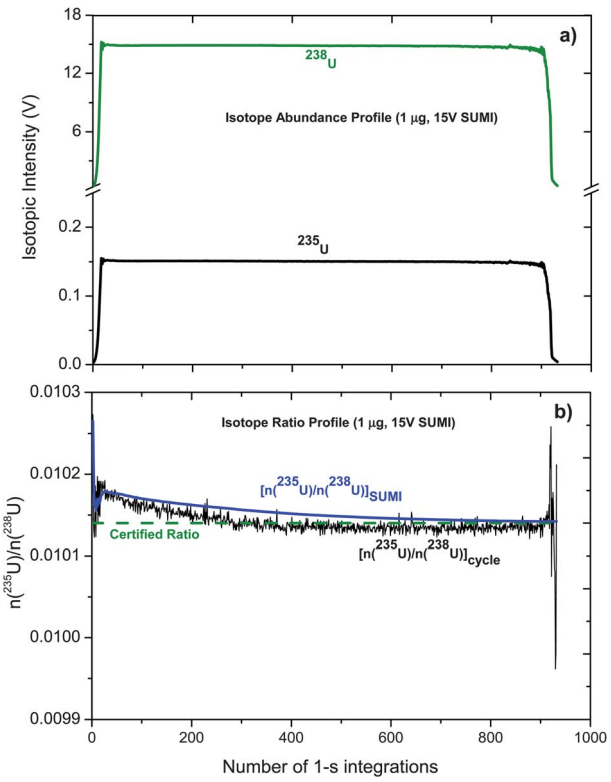


**Fig. 2** The $^{235}U$ and $^{238}U$ isotope abundance profiles (a) and $n(^{235}U)/n(^{238}U)$ isotope-amount ratio profile (b) in TE analyses of CRM U010. Amount of U loaded is1.0 μg and analysis intensity (sum of the $^{235}U$ and $^{238}U$ intensities) is 15 V.

Fig. 3 shows few features distinct from the 'normal' profiles observed in TE analyses (the release characteristics shown in Fig. 1 and 2 constitute 'normal' TE features). Towards the end of the TE analyses, the evaporation filament current is increased in larger increments, to maintain the pre-defined target ion signal intensity. As a result of this large heating step, excursions to higher intensities towards the end of the TE run, like that seen in Fig. 3a are sometimes observed. These excursions do not influence the integrated ratios as long as the limits for saturation of the Faraday detectors are not approached or exceeded (10 V for the MAT261 instrument and 50 V for the TRITON instrument). Additionally, the isotopic abundance profiles might also show oscillations (similar to those shown in Fig. 3a) for the full duration or part of the TE analysis routine. These oscillations have no significant influence on the isotopic ratio data as all isotopes are influenced to the same extent. Occasionally electronic spikes are evident in the release profile of the isotopic abundances (Fig. 3a). One spike is present in the isotope abundance release profile shown in Fig. 3a. The $[n(^{235}U)/n(^{238}U)]_{SUMI}$ ratio that includes the spike is significantly different from the $[n(^{235}U)/n(^{238}U)]_{certified}$ ratio. However, once the cycle with the spike is excluded from the sum total intensities, the $[n(^{235}U)/n(^{238}U)]_{corrSUMI}$ ratio becomes close to the certified ratio. The spike corrected $[n(^{235}U)/n(^{238}U)]_{corrSUMI}$ ratio is also consistent with what is expected from TE analyses (Fig. 3b). The isotopic abundance profile and ratio profile from TE must be evaluated to see if spikes attributable to electronic noise are present. As the spikes can be positive or negative, the integrated ratios can be positively or negatively biased. Note that minor isotope ratios can also be influenced by the presence of the spikes.

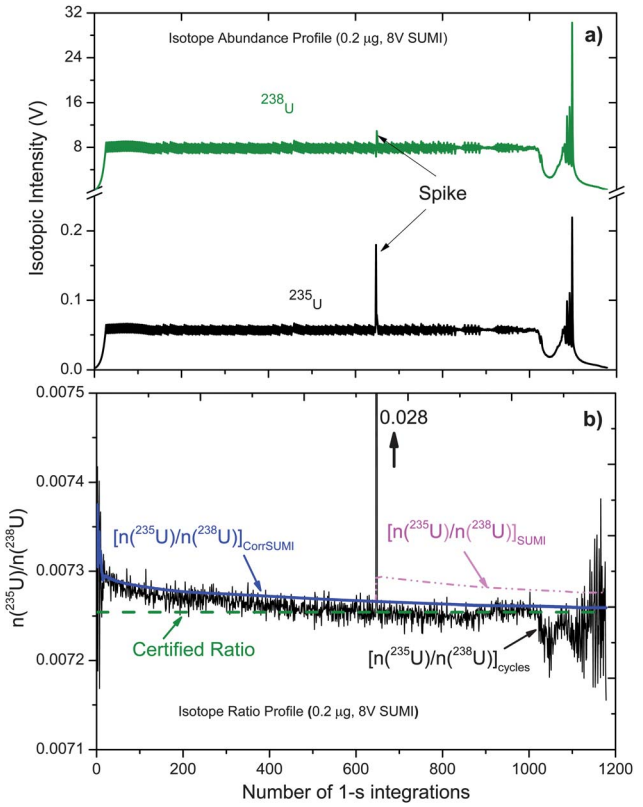


**Fig. 3** The $^{235}U$ and $^{238}U$ isotope abundance profiles (a) and $n(^{235}U)/n(^{238}U)$ isotope-amount ratio profile (b) in TE analyses of CRM C112-A. Amount of U loaded is 0.2 µg and analysis intensity (sum of the $^{235}U$ and $^{238}U$ intensities) is 8 V. One electronic spike is present (the measured ratio in the cycle influenced by the spike is – 0.028 – indicated).

### 3.2 Mass bias in TE

In uranium isotope-amount ratio analyses by TE, multiple replicates of a well characterized CRM are analyzed to estimate the magnitude of the mass bias correction in the $n(^{235}U)/n(^{238}U)$ isotope ratio. Factors that might influence the mass bias correction for a specific analysis (among others) are: (i) ambient pressure in the ion source region of the TIMS instrument, (ii) uniformity of the thickness of the ionization filament ribbon, (iii) consistency in the loading of the sample/standard, (iv) consistency in the spacing between the ionization and evaporation filaments, (v) cleanliness of the ion source, (vi) reproducibility of the source lens voltages for best focus conditions between different samples on the sample wheel, (vii) temperature fluctuations in the laboratory, and (viii) stability of the sector magnetic field. As these factors change on a day-to-day basis, the mass bias correction is estimated on a per turret basis.

The mass bias correction factor (CF) for each uranium isotopic ratio is calculated from the average measured $n(^{235}U)/n(^{238}U)$ ratio of the comparator CRM on the turret as follows:

$$\mathrm{CF}\left(\frac{n(^{235}U)}{n(^{238}U)}\right) = \frac{\text{average measured}\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{\text{summary ratio of comparator}}}{\text{certified}\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{\text{ratio of comparator}}} \quad (1)$$

$$\mathrm{CF}\left(\frac{n(^{234}U)}{n(^{238}U)}\right) = 1 + 4\left(\frac{\mathrm{CF}\left(\frac{n(^{235}U)}{n(^{238}U)}\right) - 1}{3}\right) \quad (2)$$

$$\mathrm{CF}\left(\frac{n(^{236}U)}{n(^{238}U)}\right) = 1 + 2\left(\frac{\mathrm{CF}\left(\frac{n(^{235}U)}{n(^{238}U)}\right) - 1}{3}\right) \quad (3)$$

Mass bias corrected isotope-amount ratios in the sample are calculated from the measured summary ratios as:

$$\frac{n(^{234}U)}{n(^{238}U)} = \left(\frac{n(^{234}U)}{n(^{238}U)}\right)_{\text{summary ratio}} \div \mathrm{CF}\left(\frac{n(^{234}U)}{n(^{238}U)}\right) \quad (4)$$

$$\frac{n(^{235}U)}{n(^{238}U)} = \left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{\text{summary ratio}} \div \mathrm{CF}\left(\frac{n(^{235}U)}{n(^{238}U)}\right) \quad (5)$$

$$\frac{n(^{236}U)}{n(^{238}U)} = \left(\frac{n(^{236}U)}{n(^{238}U)}\right)_{\text{summary ratio}} \div \mathrm{CF}\left(\frac{n(^{236}U)}{n(^{238}U)}\right) \quad (6)$$

Fig. 4a shows the mass bias correction factors estimated from the $n(^{235}U)/n(^{238}U)$ ratios of the comparator CRMs as a

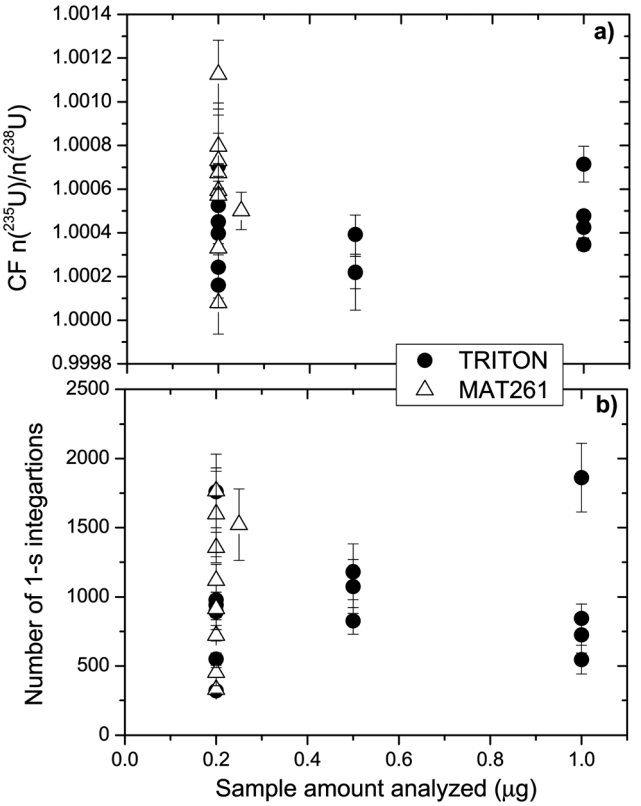


**Fig. 4** Mass bias correction factor as a function of amount of uranium analyzed (a). (b) shows the number 1 s integrations as a function of amount of uranium analyzed (filled circles represent TRITON data and open triangles represent MAT261 data).

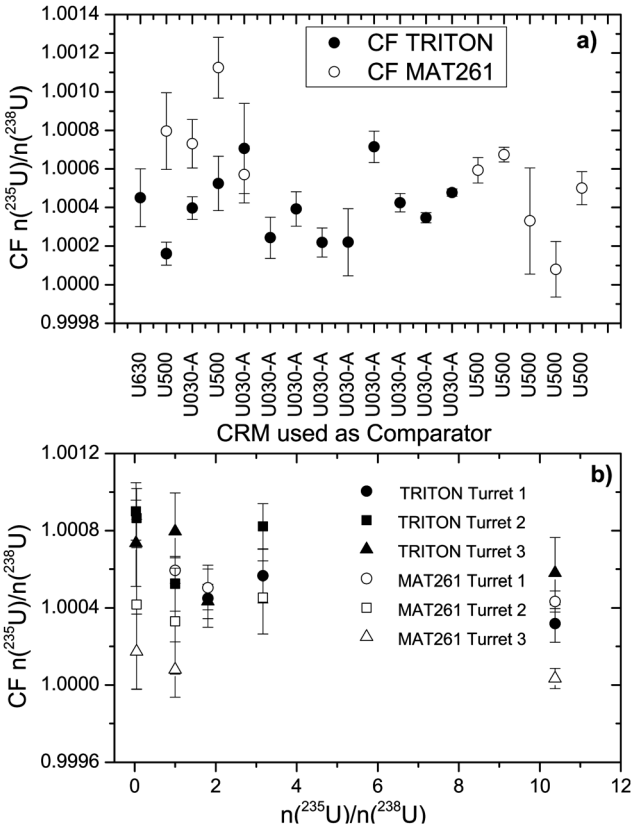


**Fig. 5** Comparison of the mass bias correction factor in different comparator CRMs (a – TRITON data is indicated by filled circles and MAT261 data is indicated by empty circles). Comparison of the independent estimates for the mass bias correction factor on the same turret using different CRMs (b) (uncertainties shown are relative standard uncertainties estimated based on variability of the replicate measurements).

function of the amount of uranium analyzed. Fig. 4a shows that mass bias correction is independent of the amount of uranium analyzed. Error bars shown in Fig. 4a represent the precision of the comparator measurements on the turret (relative standard uncertainties, expressed as a percent). Fig. 4b shows the number of 1 s integrations in the TE analyses as a function amount of uranium analyzed. Note that, for the MAT261 instrument, duration of the integrations is 8 s compared to 1.049 s for the TRITON instrument. Therefore, the number of cycles from the MAT261 data is multiplied by 8 to obtain the data shown in Fig. 4b. Fig. 4b shows that the number of cycles is independent of the amount of uranium analyzed. Note that the 0.5 and 1 μg samples had been analyzed at higher summed ion intensities than the 0.2 μg samples.

Fig. 5a compares the observed mass bias correction factors for the two instruments. TRITON data is indicated by filled circles and MAT261 data is indicated by open circles. Turret-to-turret differences in the mass bias correction factor are evident for both instruments. Due to the turret-to-turret difference in the mass bias correction, it is important that the mass bias correction factor is determined on a per turret basis. Additionally, several replicates of the comparator CRM (preferably five to six) must be analyzed on each turret to fully capture all potential variations in the mass bias during TE analyses.

For QA turrets included in the present evaluation, it is possible to independently estimate the mass bias correction factor from each of the CRMs analyzed on the turret. Fig. 5b shows a comparison of the mass bias correction factor estimated from different CRMs on the same turret. CRMs analyzed on three turrets each using the TRITON instrument and the MAT261 instruments are compared in Fig. 5b. Error bars shown in Fig. 5 correspond to standard uncertainties (relative standard uncertainties) estimated from the variability in the replicate measurements of the $n(^{235}U)/n(^{238}U)$ isotope ratios of each CRM on the same turret. All CRMs analyzed on the same turret, with $n(^{235}U)/n(^{238}U)$ ratios in the range of 0.00725 to 10.37, yield mass bias correction factors that are consistent with one another (within the standard uncertainties of the replicate measurements on the turret). This is expected, as the mass bias effect is an instrumental artifact expressed by a linear correction factor that is mass dependent. An important implication of the similarity of the mass bias corrections from CRMs with different enrichments is that it will be possible to recertify the whole suite existing NBL isotopic CRMs with uncertainties much smaller than the certified uncertainties of these standards using a well-characterized gravimetric mix with isotope-amount ratios that can be traced to the International System of Units (SI) and with uncertainties smaller than the analytical precision of the TIMS instruments.

 

### 3.3 Accuracy and precision of the uranium isotope ratios using TE

Measurement parameters that can be used as quantitative estimates for evaluating TE run conditions are: (i) mass bias correction factor for each turret, (ii) average run duration of the samples on a turret, and (iii) the precision (relative standard deviation, expressed as a percent – %RSD) of the mass bias corrected major ratio value for the comparator CRM. These parameters are quantifiable indicators of consistency in turret run characteristics. Table 2 lists these measurement parameters for all turrets included in the present evaluation. Table 2 shows that (i) all turrets ran expected durations considering the sample size and analysis signal intensity, (ii) the mass bias correction factors are small ($\leq$1.001) as usually observed in TE experiments, and (iii) the internal precision, as represented by the relative standard uncertainty (expressed in percent) of all $n(^{235}U)/n(^{238}U)$ ratio measurements of the comparator, are lower than 0.03% for both instruments (%RSDs < 0.05 are considered acceptable for TE experiments, where at least three to four replicate analyses are available). Table 2 shows that, on an average, the mass bias correction factor for the TRITON instrument is somewhat smaller than that for the MAT261 instrument. Table 2 and Fig. 5a also shows that the TRITON performance in terms of the variability in the mass bias correction factor is superior compared to that of the MAT261 instrument (%RSD of 0.0175 for TRITON *vs.* 0.0294 for MAT261).

**Table 2** Measurement parameters representative of the quality of TE runs

| Instrument | Sample load (μg U) | Comparator CRM | SUMI (V) | Number of integrations[a] | CF $n(^{235}U)/n(^{238}U)$ |
|---|---|---|---|---|---|
| TRITON | 0.2 | U630 | 6 | 891 | 1.000450 |
| | 0.2 | U500 | 6 | 978 | 1.000161 |
| | 0.2 | U030-A | 6 | 549 | 1.000397 |
| | 1.0 | U030-A | 15 | 545 | 1.000715 |
| | 1.0 | U030-A | 15 | 844 | 1.000425 |
| | 1.0 | U030-A | 15 | 724 | 1.000346 |
| | 1.0 | U030-A | 15 | 1862 | 1.000477 |
| | 0.2 | U500 | 6 | 1760 | 1.000525 |
| | 0.2 | U030-A | 8 | 942 | 1.000706 |
| | 0.5 | U030-A | 15 | 826 | 1.000392 |
| | 0.2 | U030-A | 8 | 320 | 1.000243 |
| | 0.5 | U030-A | 15 | 1181 | 1.000219 |
| | 0.5 | U030-A | 15 | 1075 | 1.000220 |
| | | **Average** | **11.2** | **961** | **1.000406** |
| | | **Std dev** | | | **0.000175** |
| | | **%RSD** | | | **0.0175** |
| MAT261 | 0.2 | U500 | 5 | 221 | 1.000797 |
| | 0.2 | U030-A | 5 | 169 | 1.001125 |
| | 0.2 | U030-A | 5 | 200 | 1.000731 |
| | 0.2 | U500 | 5 | 140 | 1.000593 |
| | 0.2 | U030-A | 6 | 114 | 1.000571 |
| | 0.2 | U500 | 6 | 56 | 1.000331 |
| | 0.2 | U500 | 6 | 41 | 1.000675 |
| | 0.2 | U500 | 5 | 90 | 1.000080 |
| | 0.25 | U500 | 5 | 190 | 1.000500 |
| | | **Average** | **5.3** | **136** | **1.000600** |
| | | **Std dev** | | | **0.000294** |
| | | **%RSD** | | | **0.0294** |

[a] Number of 1.049 s integrations for TRITON and 8 s integrations for MAT261.

Table 3 shows the average isotopic ratios (mass bias corrected) in each CRM/sample analyzed on a turret using the TRITON instrument and Table 4 shows corresponding data for the MAT261 instrument. The precision (relative standard uncertainty of the replicate aliquots on the turret, expressed as a percent) of the major ratio measurements by TE on both instruments are also shown in Tables 3 and 4. A comparison of Tables 3 and 4 shows that similar precisions were achieved on both instruments, for uranium major isotope ratio measurements. Hence, data for the same CRM from both instruments are combined to estimate the precision typically achieved by the TE analytical method. Precision (%RSE) of ~0.01 to 0.02% is achieved in uranium isotopic analyses using TE. Table 5 shows that the %RSE for the major ratio measurements is in the range 0.0069% to 0.0183%, with most CRMs yielding %RSE of ~0.01%. Since the data used for this evaluation include multiple instruments, multiple analysts, and data collected over a relatively long period of time, the precision estimate of ~0.01% for the $n(^{235}U)/n(^{238}U)$ isotope ratio is a conservative estimate for the precision reasonably achievable in uranium isotopic measurements by TE.

The accuracy (relative deviation of the measured ratios from the certified values, expressed as a percent) of the major and minor ratio measurements on each turret using TE analytical method are summarized in Table 3 for the TRITON instrument and in Table 4 for the MAT261 instrument. For the $n(^{235}U)/n(^{238}U)$ ratio, %RD values in the range $\pm$0.05% are obtained on both instruments using the TE analytical technique. Accuracy (%RDs) achieved on different CRMs by combining the data on different turrets is shown in Table 5. Typical accuracy (%RDs) of about $\pm$0.02% is achieved for the $n(^{235}U)/n(^{238}U)$ ratio of CRMs. Fig. 6 shows the %RDs of the $n(^{235}U)/n(^{238}U)$ isotopic ratios from the certified ratios (summary data shown in Table 6 is shown). The uncertainties shown in Fig. 6 correspond to the average value of the standard uncertainties representing the precision of the major ratio measurements on each turret. Fig. 6 and Table 5 show that the major ratio measurements for most CRMs (with the exception of U010) are consistent with certificate values within ~0.02%. The U010 data presented in this evaluation supports the value proposed for the $n(^{235}U)/n(^{238}U)$ ratio of this CRM by ref. 10 and 17.

Although the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope-amount ratios are all determined in TE measurements, the minor ratios from TE experiments are not used for generating reportable measurements. This is due to a persistent but variable bias (associated with major isotope peak tailing) in minor ratio data that, due to the nature of TE analysis, can only be corrected for using an assumed abundance correction with an associated high-uncertainty. Magnitude of the observed bias at minor isotope ratio data is discussed below.

The relative deviations of the minor ratio measurements from the certified values are shown in Fig. 7. Fig. 7a shows the relative deviations (%RDs) of the $n(^{234}U)/n(^{238}U)$ ratio and

**Table 3** Summary of the QC data from TRITON instrument included in the present evaluation[a]

| | Turret average | | | %RD ± %RSE | | |
|---|---|---|---|---|---|---|
| CRM | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ |
| **Turret 1, 18 Nov 2009, 0.2 μg, 6 V SUMI, Analyst A** | | | | | | |
| U750 ($N = 5$) | 0.0249224 | 3.1664937 | 0.0105253 | 0.1483 ± 0.0209 | 0.0116 ± 0.0140 | 0.2446 ± 0.0102 |
| U900 ($N = 5$) | 0.0895461 | 10.374342 | 0.0383133 | 0.0931 ± 0.0123 | −0.0131 ± 0.0097 | 0.1073 ± 0.0434 |
| **Turret 2, 17 Feb 2010, 0.2 μg, 6 V SUMI, Analyst A** | | | | | | |
| U030-A ($N = 4$) | 0.0002873 | 0.0313728 | 0.0000127 | 0.2576 ± 0.0348 | 0.0199 ± 0.0113 | 105.1 ± 12.7 |
| U900 ($N = 3$) | 0.0898010 | 10.374458 | 0.0383672 | 0.3781 ± 0.2587 | −0.0120 ± 0.0135 | 0.2481 ± 0.0813 |
| U010 ($N = 4$) | 0.0000577 | 0.010140 | 0.0000944 | 5.4161 ± 3.1236 | −0.0033 ± 0.0069 | 37.2 ± 13.4 |
| U630 ($N = 4$) | 0.0176701 | 1.8061717 | 0.0274627 | 0.1100 ± 0.1080 | −0.0281 ± 0.0053 | 0.0737 ± 0.0276 |
| **Turret 3, 9 Mar 2010, 0.2 μg, 6 V SUMI, Analyst A** | | | | | | |
| U010 ($N = 5$) | 0.0000548 | 0.0101355 | 0.0000730 | 0.2669 ± 0.2434 | −0.0448 ± 0.0034 | 6.13 ± 1.84 |
| U045 ($N = 5$) | 0.0004068 | 0.0473060 | 0.0002921 | 0.2427 ± 0.0311 | −0.0086 ± 0.0044 | 0.7877 ± 0.5741 |
| C129-A ($N = 4$) | 0.0000544 | 0.0072619 | 0.0000036 | 1.9611 ± 0.2322 | 0.0065 ± 0.0062 | |
| **Turret 4, 18 May 2010, 1.0 μg, 15 V SUMI, Analyst A** | | | | | | |
| C129-A ($N = 5$) | 0.0000545 | 0.0072608 | 0.0000022 | 2.2081 ± 0.1776 | −0.0078 ± 0.0036 | |
| U010 ($N = 4$) | 0.0000554 | 0.0101338 | 0.0000718 | 1.2290 ± 0.2000 | −0.0611 ± 0.0111 | 4.38 ± 0.53 |
| U005-A ($N = 5$) | 0.0000362 | 0.0050900 | 0.0000140 | 5.7472 ± 2.3068 | 0.0008 ± 0.0131 | 18.01 ± 1.85 |
| **Turret 5, 19 May 2010, 1.0 μg, 15 V SUMI, Analyst A** | | | | | | |
| C129-A ($N = 2$) | 0.0000532 | 0.0072618 | — | −0.234 ± 0.234 | 0.0053 ± 0.0025 | — |
| Sample ($N = 12$) | 0.0000531 | 0.0072545 | — | 0.4506 ± 0.2103 | 0.0034 ± 0.0010 | — |
| **Turret 6, 25 May 2010, 1.0 μg, 15 V SUMI, Analyst A** | | | | | | |
| C129-A ($N = 3$) | 0.0000536 | 0.0072617 | — | 0.541 ± 1.150 | 0.0046 ± 0.0085 | — |
| Sample ($N = 12$) | 0.0000533 | 0.0072543 | — | 0.8914 ± 0.6050 | 0.0003 ± 0.0014 | — |
| **Turret 7, 27 May 2010, 1.0 μg, 15 V SUMI, Analyst A** | | | | | | |
| C129-A ($N = 2$) | 0.0000543 | 0.0072606 | — | 1.7160 ± 0.2578 | −0.0113 ± 0.0046 | — |
| Sample ($N = 12$) | 0.0000539 | 0.0072539 | — | 1.9188 ± 0.1998 | −0.0052 ± 0.0011 | — |
| **Turret 8, 10 Aug 2010, 0.2 μg, 6 V SUMI, Analyst A** | | | | | | |
| U750 ($N = 4$) | 0.0249344 | 3.1670666 | 0.0105228 | 0.1965 ± 0.0074 | 0.0297 ± 0.0119 | 0.2211 ± 0.0359 |
| U045 ($N = 4$) | 0.0004094 | 0.0473262 | 0.0002952 | 0.8843 ± 0.3346 | 0.0340 ± 0.0154 | 1.8507 ± 0.4156 |
| U030-A ($N = 5$) | 0.0002882 | 0.0313784 | 0.0000094 | 0.5437 ± 0.4136 | 0.0375 ± 0.0149 | 51.80 ± 12.76 |
| **Turret 9, 26 Aug 2011, 0.2 μg, 8 V SUMI, Analyst A** | | | | | | |
| U010 ($N = 5$) | 0.0000560 | 0.0101358 | 0.0000839 | 2.32 ± 1.80 | −0.0412 ± 0.0193 | 21.9 ± 10.1 |
| C112-A ($N = 5$) | 0.0000543 | 0.0072533 | — | 2.78 ± 1.07 | −0.0138 ± 0.0178 | — |
| U045 ($N = 5$) | 0.0004069 | 0.0472964 | 0.0002906 | 0.2752 ± 0.2312 | −0.0290 ± 0.0103 | 0.2749 ± 0.0235 |
| **Turret 10, 22 Sep 2011, 0.5 μg, 15 V SUMI, Analyst A** | | | | | | |
| C112-A ($N = 4$) | 0.0000536 | 0.0072555 | — | 1.431 ± 0.245 | 0.0166 ± 0.0314 | — |
| Sample ($N = 10$) | 0.0000084 | 0.0020343 | 0.0000331 | 11.42 ± 1.58 | 0.0276 ± 0.0064 | 2.70 ± 0.88 |
| **Turret 11, 20 Dec 2011, 0.2 μg, 8 V SUMI, Analyst A** | | | | | | |
| U045 ($N = 7$) | 0.0004056 | 0.0473186 | 0.0002948 | −0.0430 ± 0.0331 | 0.0180 ± 0.0097 | 1.7088 ± 0.2518 |
| C129-A ($N = 7$) | 0.0000536 | 0.0072639 | — | 0.1951 ± 0.1133 | 0.0341 ± 0.0093 | — |
| **Turret 12, 14 Jul 2011, 0.5 μg, 15 V SUMI, Analyst B** | | | | | | |
| C112-A ($N = 5$) | 0.0000534 | 0.0072518 | — | 1.104 ± 0.918 | −0.0348 ± 0.0041 | — |
| Sample ($N = 10$) | 0.0000084 | 0.0020340 | 0.0000350 | 11.09 ± 8.30 | 0.0145 ± 0.0153 | 8.57 ± 4.85 |
| **Turret 13, 15 Jul 2011, 0.5 μg, 15 V SUMI, Analyst B** | | | | | | |
| C112-A ($N = 3$) | 0.0000533 | 0.0072527 | — | 0.9021 ± 0.0625 | −0.0220 ± 0.0024 | — |
| Sample ($N = 11$) | 0.0000081 | 0.0020342 | 0.0000330 | 7.59 ± 0.64 | 0.0267 ± 0.0058 | 2.50 ± 0.69 |

[a] $N$ represents number of replicate analyses included in the average ratios shown.

**Table 4** Summary of the QC data from MAT261 instrument included in the present evaluation[a]

| | Turret average | | | %RD ± %RSE | | |
|---|---|---|---|---|---|---|
| CRM | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ |
| **Turret 1, 2 Nov 2010, 0.2 μg, 5 V SUMI, Analyst A** | | | | | | |
| U900 ($N = 3$) | 0.0895719 | 10.3734619 | 0.0383184 | 0.1219 ± 0.0420 | −0.0216 ± 0.0184 | 0.1206 ± 0.0192 |
| U630 ($N = 3$) | 0.0176584 | 1.8060241 | 0.0274446 | 0.0439 ± 0.0268 | −0.0362 ± 0.0089 | 0.0077 ± 0.0107 |
| U030-A ($N = 3$) | 0.0002882 | 0.0313647 | 0.0000084 | 0.5561 ± 0.1401 | −0.0061 ± 0.0223 | 35.6 ± 8.6 |
| **Turret 2, 15 Jun 2011, 0.2 μg, 6 V SUMI, Analyst A** | | | | | | |
| U010 ($N = 4$) | 0.0000543 | 0.0101370 | 0.0000704 | −0.697 ± 3.655 | −0.0296 ± 0.0125 | 2.358 ± 0.927 |
| U045 ($N = 4$) | 0.0004059 | 0.0473175 | 0.0002903 | 0.0348 ± 0.2533 | 0.0156 ± 0.0219 | 0.1578 ± 0.6764 |
| **Turret 3, 12 Jan 2012, 0.2 μg, 5 V SUMI, Analyst A** | | | | | | |
| U045 ($N = 3$) | 0.0004066 | 0.0473034 | 0.0002922 | 0.1981 ± 0.6474 | −0.0142 ± 0.0068 | 0.8365 ± 1.1757 |
| C125-A ($N = 4$) | 0.0003920 | 0.0422973 | 0.0000047 | 0.5175 ± 0.2322 | −0.0218 ± 0.0081 | 52.6 ± 11.1 |
| **Turret 4, 23 Jan 2012, 0.2 μg, 5 V SUMI, Analyst A** | | | | | | |
| U900 ($N = 4$) | 0.0895205 | 10.3740517 | 0.0382805 | 0.0644 ± 0.0057 | −0.0159 ± 0.0055 | 0.0218 ± 0.0183 |
| U630 ($N = 3$) | 0.0176592 | 1.8065202 | 0.0274443 | 0.0484 ± 0.0259 | −0.0088 ± 0.0115 | 0.0067 ± 0.0140 |
| **Turret 5, 31 Aug 2011, 0.2 μg, 5 V SUMI, Analyst C** | | | | | | |
| U010 ($N = 4$) | 0.0000552 | 0.0101362 | 0.0000712 | 0.9591 ± 0.7694 | −0.0376 ± 0.0059 | 3.5217 ± 0.9248 |
| C112-A ($N = 3$) | 0.0000522 | 0.0072529 | — | −1.24 ± 1.54 | −0.0189 ± 0.0389 | — |
| **Turret 6, 1 Sep 2011, 0.2 μg, 6 V SUMI, Analyst C** | | | | | | |
| U750 ($N = 4$) | 0.0249109 | 3.1665158 | 0.0105207 | 0.1021 ± 0.0211 | 0.0123 ± 0.0189 | 0.2013 ± 0.0229 |
| U045 ($N = 4$) | 0.0004073 | 0.0473142 | 0.0002914 | 0.3624 ± 0.2835 | 0.0087 ± 0.0441 | 0.5644 ± 0.2548 |
| **Turret 7, 26 Sep 2011, 0.2 μg, 5 V SUMI, Analyst C** | | | | | | |
| U900 ($N = 4$) | 0.0895097 | 10.3752237 | 0.0382782 | 0.0524 ± 0.0351 | −0.0046 ± 0.0052 | 0.0156 ± 0.0224 |
| U045 ($N = 4$) | 0.0004077 | 0.0473145 | 0.0002918 | 0.4637 ± 0.1552 | 0.0093 ± 0.0194 | 0.7020 ± 0.3258 |
| **Turret 8, 30 Nov 2011, 0.2 μg, 6 V SUMI, Analyst C** | | | | | | |
| U900 ($N = 4$) | 0.0895722 | 10.3748522 | 0.0382996 | 0.1223 ± 0.0235 | −0.0082 ± 0.0072 | 0.0715 ± 0.0383 |
| U045 ($N = 4$) | 0.0004074 | 0.0473341 | 0.0002901 | 0.4026 ± 0.5316 | 0.0507 ± 0.0079 | 0.1016 ± 1.0447 |
| **Turret 9, 13 Jan 2012, 0.25 μg, 5 V SUMI, Analyst C** | | | | | | |
| C112-A ($N = 2$) | 0.0000537 | 0.0072535 | — | 1.65 ± 1.39 | −0.0114 ± 0.0152 | — |
| C149 ($N = 2$) | 0.1912716 | 17.5019860 | 0.0743657 | 0.1223 ± 0.0235 | −0.0082 ± 0.0072 | 0.0715 ± 0.0383 |
| Sample ($N = 2$) | 0.0314861 | 2.8836720 | 0.0122092 | ± 0.0129 | ± 0.0235 | ± 0.0725 |
| Sample ($N = 2$) | 0.0433967 | 3.9738032 | 0.0168597 | ± 0.0061 | ± 0.0044 | ± 0.0062 |

[a] $N$ represents the number of replicate analyses included in the average ratio shown.

**Table 5** Combined summary of the QC CRM data on both instruments. Relative deviation of the measured ratios from certified values and the relative standard uncertainties are shown for each CRM that was included in the present study[a]

| | Average for CRM | | | %RD ± %RSE | | |
|---|---|---|---|---|---|---|
| CRM | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ | $n(^{234}U)/n(^{238}U)$ | $n(^{235}U)/n(^{238}U)$ | $n(^{236}U)/n(^{238}U)$ |
| U900 ($N = 5$) | 0.0895869 | 10.3743983 | 0.0383095 | 0.1011 ± 0.0231 | −0.0126 ± 0.0110 | 0.0975 ± 0.0431 |
| U750 ($N = 3$) | 0.0249226 | 3.1666920 | 0.0105229 | 0.1490 ± 0.0177 | 0.0178 ± 0.0152 | 0.2223 ± 0.0252 |
| U630 ($N = 3$) | 0.0176626 | 1.8062387 | 0.0274506 | 0.0815 ± 0.0647 | −0.0244 ± 0.0089 | 0.0294 ± 0.0189 |
| U045 ($N = 9$) | 0.0004071 | 0.0473145 | 0.0002920 | 0.44 ± 0.25 | 0.0094 ± 0.0193 | 1.06 ± 0.62 |
| C125-A ($N = 1$) | 0.0003920 | 0.0422973 | 0.0000047 | 0.52 ± 0.23 | −0.0218 ± 0.0081 | 52.6 ± 11.1 |
| U030-A ($N = 2$) | 0.0002879 | 0.0313720 | 0.0000102 | 0.45 ± 0.25 | 0.0171 ± 0.0168 | 64.2 ± 11.5 |
| U010 ($N = 5$) | 0.0000557 | 0.0101365 | 0.0000772 | 2.59 ± 1.64 | −0.0362 ± 0.0112 | 12.6 ± 6.9 |
| C129-A ($N = 6$) | 0.0000539 | 0.0072618 | 0.0000026 | 1.10 ± 0.57 | 0.0052 ± 0.0088 | — |
| C112-A ($N = 6$) | 0.0000534 | 0.0072533 | — | 1.47 ± 0.83 | −0.0141 ± 0.0226 | — |
| U005-A ($N = 1$) | 0.0000362 | 0.0050900 | 0.0000140 | 5.75 ± 2.31 | 0.0008 ± 0.0131 | 18.01 ± 1.85 |

[a] $N$ represents the number of turrets included in the average ratio shown (each turret had multiple replicates of the CRM).

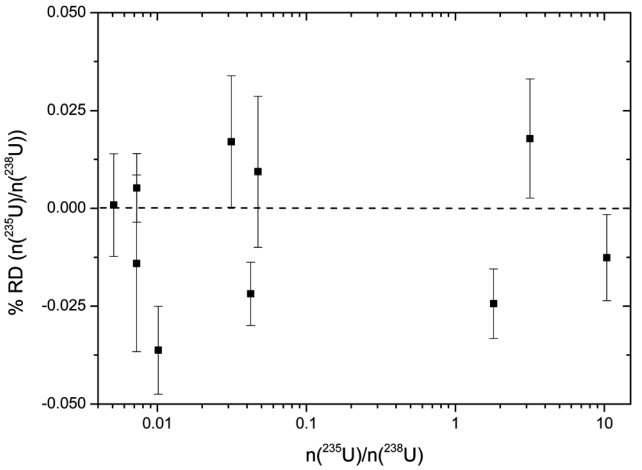


**Fig. 6** Relative deviations (expressed as a percent) of the $n(^{235}U)/n(^{238}U)$ ratio from the certified values of this ratio. Uncertainties shown are relative standard uncertainties indicating agreement of the replicate measurement.

Fig. 7b shows the relative deviations (%RDs) of the $n(^{236}U)/n(^{238}U)$ ratio from the certified values. Both ratios are biased high due to peak-tailing effects from the major isotopes. For CRMs U900, U750, and U630, the $n(^{234}U)/n(^{238}U)$ data using TE analytical technique are biased by $\sim 0.10 \pm 0.06$ (%RD ± %RSE) to $\sim 0.15 \pm 0.06$ (%RD ± %RSE) compared to the certified values. For CRMs U045, C125-A, and U030-A the magnitude of the bias at $n(^{234}U)/n(^{238}U)$ is $\sim 0.50 \pm 0.25$ (%RD ± %RSE) and for CRMs U010, C129-A, C112-A, and U005-A the $n(^{234}U)/n(^{238}U)$ ratio using TE technique can be biased by $\sim 1 \pm 0.8$ (%RD ± %RSE) to $\sim 6.0 \pm 2.3$ (%RD ± %RSE).

The $n(^{236}U)/n(^{238}U)$ ratios of CRMs U900, U750, and U630 using TE analytical technique are biased by up to $\sim 0.22 \pm 0.04$ (%RD ± %RSE). The $n(^{236}U)/n(^{238}U)$ ratio in CRM U045 using TE is biased high by $\sim 1.0 \pm 0.6$ (%RD ± %RSE). For CRMs C125-A, U030-A, U010, and U005-A the $n(^{236}U)/n(^{238}U)$ ratio using TE can be biased by up to $64 \pm 12$ (%RD ± %RSE).

The recognition that the minor ratio data using the TE analytical technique are biased and subsequent efforts to rectify this situation had led to the development of the modified total evaporation (MTE) technique.[20] This technique had led to significant improvement in the precision and accuracy of the minor ratio measurements without compromising the quality of the major ratio measurements.[21–23] Precision and accuracy of uranium major isotope ratio data obtained using the MTE technique are similar to the precision and accuracy of the TE analytical technique[20–23] as the underlying principle is the same. For the $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ minor isotope ratio measurements using MTE precision and accuracy that are an order of magnitude better than those of the TE technique are obtained.

### 3.4 Uncertainties in uranium isotope-amount ratios using TE

The uncertainties in the isotope-amount ratios obtained using the TE analytical technique (see ref. 13 for a detailed discussion of uncertainty calculations applicable to isotopic measurements using TIMS) are calculated following the recommendations in JCGM 100:2008, "Evaluation of measurement data – Guide to the expression of Uncertainty in Measurement"[24] using the GUM Workbench software developed by Metrodata®.[25] In the uncertainty calculations presented here, the following sources of uncertainties were included: (i) variability in the uranium isotope ratio measurements as represented by the %RSE of the repeat measurement of the sample, (ii) uncertainties in the $n(^{235}U)/n(^{238}U)$ certified ratio of the comparator, (iii) variability in the mass bias correction factor within the turret as represented by the %RSE of the comparator measurements on each turret. The model equation used for calculation of the uncertainties in the major ratio is shown below.

$$\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{sample} = \left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{corrected} \delta \left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{certified} \delta \left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{CF} \quad (7)$$

where $\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{corrected}$ is the mass bias corrected major ratio of the sample, $\delta\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{certified}$ is the relative uncertainty of the certified major ratio of the comparator, $\delta\left(\frac{n(^{235}U)}{n(^{238}U)}\right)_{CF}$ is the precision of major ratio measurement of the comparator.

Uncertainty calculations show that all three sources of uncertainties considered above are important and depending on the precision of the sample and of the comparator measurements on a turret, the uncertainty budgets would vary among these sources. The average standard uncertainty in

**Table 6** Expanded uncertainties in the $n(^{235}U)/n(^{238}U)$ isotope ratios for different uncertainties in the comparator standard and for different precisions of the major ratio measurements using TE

| $n(^{235}U)/n(^{238}U)_{sample}$ relative uncertainty (%) | Uncertainty of the $n(^{235}U)/n(^{238}U)_{comparator}$ isotope-amount ratio | | |
|---|---|---|---|
| | 0.015%[a] | 0.053%[a] | 0.10%[a] |
| 0.01 | 0.038 (27.9, 15.7, 56.4) | 0.063 (10, 70, 20.1) | 0.11 (3.6, 89.2, 7.2) |
| 0.02 | 0.051 (60.8, 8.6, 30.7) | 0.072 (30.7, 53.9, 15.5) | 0.11 (13.6, 79.9, 6.4) |
| 0.05 | 0.11 (90.7, 2.0, 7.3) | 0.12 (73.4, 20.6, 5.9) | 0.14 (48.1,48.1, 3.9) |

[a] Entries in parentheses indicate percent contributions to the final uncertainty from (i) assumed variability in the sample measurements (column 1), (ii) from uncertainty in the comparator $n(^{235}U)/n(^{238}U)$ ratio, and (iii) from variability in the mass bias correction (the average standard uncertainty in the TRITON mass bias correction factor is adopted).

 

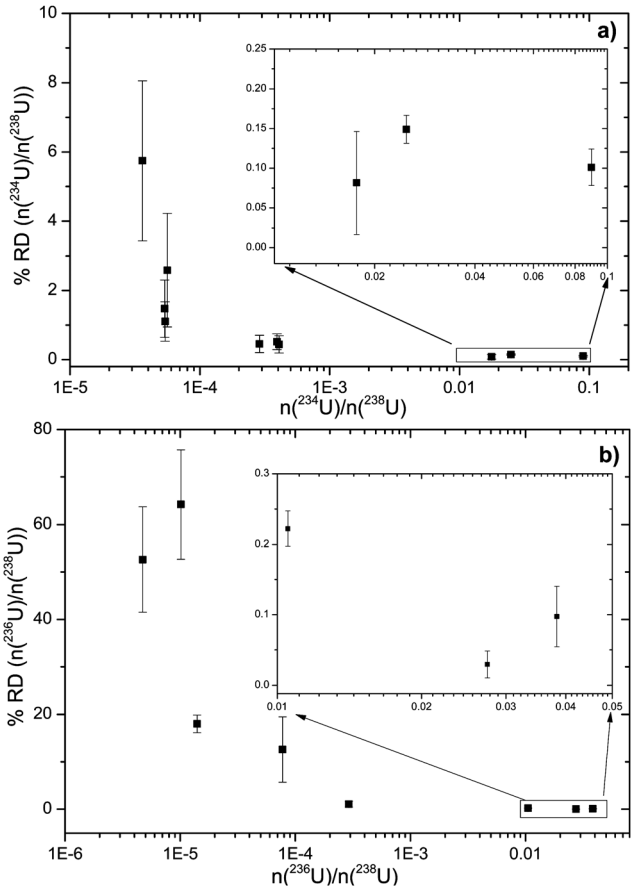


**Fig. 7** Relative deviations (expressed as a percent) of the $n(^{234}U)/n(^{238}U)$ (a) and $n(^{236}U)/n(^{238}U)$ (b) isotope-amount ratios from the certified values. Insets show an enlargement of the area indicated. Minor isotope ratios from TE are biased high as corrections due to peak-tailing from the major isotopes are not performed (these data have also been corrected for mass bias effects).

the mass bias correction factor for the TRITON instrument (= 0.000142, average %RSE of CF $n(^{235}U)/n(^{238}U)$ value shown in Fig. 4a for the TRITON) is used for the following calculations. Uncertainty calculations were made for three different uncertainties in the $n(^{235}U)/n(^{238}U)$ major ratio of the comparator standard (expanded uncertainties at the 95% confidence level of 0.015%, 0.053%, and 0.10% with a coverage factor of $k = 2$ were assumed for the certified major ratio of the comparator standard) and for three different precisions in the sample measurements (%RSEs of 0.01%, 0.02%, and 0.05% were assumed for the $n(^{235}U)/n(^{238}U)$ ratio measurements of the sample). Table 6 summarizes the uncertainty calculations for $n(^{235}U)/n(^{238}U)$ major ratio data using TE analytical technique. Contributions to the uncertainty budget from variability of the sample measurements, from certified uncertainty of the comparator major ratio, and from variability in the mass bias correction estimate are indicated in Table 6.

Uncertainty estimations presented here show that for all NBL CRMs reported here, the certified uncertainties are conservative compared to the current analytical techniques used by nuclear analytical laboratories. For the $n(^{235}U)/n(^{238}U)$ ratios of most NBL CRMs (except U010) %RD ± %RSE values better than 0.024 ± 0.023 are achieved. The $n(^{235}U)/n(^{238}U)$ ratio of CRM U010 show clear evidence for a bias of about −0.0362 ± 0.0112 (%RD ± %RSE) compared to the certified value (consistent with earlier conclusions by ref. 10 and 17).

## 4 Conclusions

Through a comparison of the uranium isotope-amount ratio measurements on two TIMS instruments (TRITON and MAT261) using total evaporation (TE) analytical technique, we conclude that:

- Mass dependent bias in TE analyses is independent of the amount of sample used for TIMS isotopic analyses.
- The mass bias correction factor shows turret-to-turret variation (hence it is necessary to analyze multiple replicates of a well-characterized standard as comparator to capture the variability in the mass bias correction).
- The mass bias correction factors obtained from different CRMs analyzed on the same turret are consistent with one another, showing that within turret variation is insignificant.
- Both TRITON and MAT261 instruments used in the present study provide an internal precision better than 0.01% for the $n(^{235}U)/n(^{238}U)$ major ratio measurements using TE.
- Bias in the minor isotope ratios, $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$, are present in the TE data for these isotopic ratios due to tailing from the major isotope peaks.
- Total evaporation is a powerful technique for uranium major isotope-amount ratio measurements.

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