



# Uranium and plutonium analysis of nuclear material samples by multi-collector thermal ionisation mass spectrometry: Quality control, measurement uncertainty, and metrological traceability

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## ABSTRACT

Metrological studies and recent improvements in multi-collector thermal ionisation mass spectrometry (MC-TIMS) of uranium and plutonium in bulk nuclear material samples are presented with a focus on nuclear safeguards. Using total evaporation and modified total evaporation methods, experimental data are presented for isotope ratio measurements in routine mode spanning a range of almost ten orders of magnitude, with  $n(\text{U-236})/n(\text{U-238})$  measurements as low as a few parts per billion. Based upon these data, measurement reproducibility, associated measurement uncertainties with comparison to International Target Values (ITV), an upper limit of the instrumental uranium memory effect and of the hydride formation, and process and instrumental blank levels are examined. A comparison of measurement performance between the latest and previous generation of instruments for the total evaporation method is conducted. In addition, the implementation of a quality control procedure including control charts is presented and, in this context, commercially available U or Pu certified reference materials for isotope ratio and isotope dilution mass spectrometry are surveyed. The implementation of the Guide to the expression of Uncertainty in Measurement (GUM) is discussed for the modified total evaporation method. To address the importance of metrological traceability of measurement results to the SI units, the agreement between the certified values of two independently produced series of uranium certified reference materials (CRMs) – NBL and IRMM U series – is probed. Using IRMM CRMs as calibration standards, a new set of values for selected NBL U series CRMs is presented with expanded uncertainties of about 0.035% for major isotope ratios and at an order of magnitude of 0.1–0.5% for minor ratios.

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## 1. Introduction

Multi-collector sector-field mass spectrometers are well established and indispensable analytical tools in isotope ratio and isotope dilution analysis. Due to the precision (measurement repeatability) attainable with state-of-the-art multi-collector thermal ionisation mass spectrometry (MC-TIMS) instruments and comparatively few molecular and polyatomic interferences, MC-TIMS is still considered a benchmark technique for isotope ratio analysis of elements like Sr, Nd, U, and Pu [1–12]. However, multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) [13–16] has recently shown significant instrumental and procedural

improvements. As such, MC-TIMS and, more recently, MC-ICPMS are employed in many fields of research and scientific endeavours including isotope geochemistry, cosmochronology, nuclear fuel cycle research, study of fossil nuclear reactors, environmental monitoring, forensics, and archaeological research [3,17–25,16]. It also includes the study of atomic and nuclear properties as well as metrology [26,27,6,28].

More recent applications are nuclear safeguards and nuclear forensics where the isotopic signature of uranium and plutonium plays a crucial role [29–32,53,33]. In nuclear safeguards, isotopic information is closely examined in the verification of a State's declared nuclear material and activities, and in the detection of undeclared nuclear material and activities. In nuclear forensics investigation, it is one of the clues helping to attribute unknown nuclear material to a person or place, for example in a case of nuclear smuggling or in unravelling a nuclear crime scene. It is part of a tool-box of analytical methods that can

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reveal tell-tale signatures inherent to samples, including age-dating [34–37], trace-impurity signatures [38–41], or geolocation information [42,43,39,44].

Multi-collector thermal ionisation mass spectrometry [45–48,9–12] has been the ‘working-horse’ for reliable and robust use in routine operation at the IAEA for decades to provide high quality analytical results for samples collected by nuclear safeguards inspectors from facilities all over the world. MC-TIMS plays a key role at the European Commission On-Site Laboratory at Sellafield [49], and is the benchmark technique at the Agency’s On-Site Laboratory (IAEA-OSL) at the Rokkasho Reprocessing Plant [50]. MC-TIMS instruments are also used at research institutions and nuclear facilities worldwide [51,30,52–55,82,9,10,56], notably for the certification of reference materials for uranium and plutonium [57,11,80] demonstrating state-of-the-art measurement precision and accuracy.

Some of the reasons why multi-collector TIMS is favour for U and Pu analysis are: a comparatively stable ion beam can be produced; the mass fractionation per mass unit is on the order 0.01%/u or less (“u” denotes the atomic mass unit) using the total evaporation method (herein or [58,5,11]); measurement sequences are fully automated; any hydride formation, for example  $^{235}\text{UH}$  overlapping with U-236, is insignificant for isotope ratio measurements of  $n(\text{U-236})/n(\text{U-238})$  at a part per billion level ( $10^{-9}$ ) (see below); potentially interfering molecules and polyatomic species can be burned off during the filament heating; even sequential U and Pu analysis may be performed on mixed U/Pu samples on the same filament [9,83]. And most noteworthy, due to the fact that U and Pu MC-TIMS measurement procedures are sufficiently understood, measurement uncertainties according to GUM principles have been reported in the literature by several groups [48,81,59,57]. Ionisation efficiency-enhancing techniques for low level U and Pu analysis, often involving more time-consuming sample preparation though, have been developed for TIMS including filament carburisation, resin bead loading, and cavity ion source [60–63,9,64,56,77] to match or in cases even surpassing MC-ICPMS overall efficiencies. It needs to be mentioned that matrix effects like organic components and various elements can significantly quench the ionisation efficiency of U and Pu in TIMS.

In this work, using the total evaporation (TE) and the modified total evaporation (MTE) analytical methods, we perform several metrological studies to assess measurement reproducibility and uncertainties, an upper limit of the instrumental uranium memory effect, an upper limit of the uranium hydride formation, process and instrumental blank levels, and comparing latest generation and previous generation of instruments. In addition, we present the implementation of a quality control procedure and the Guide to the expression of Uncertainty in Measurement (GUM) for the MTE method. Furthermore, we address metrological traceability by probing the agreement between the certified values of two independently produced series of certified reference materials (NBL and IRMM uranium series).

## 2. Experimental

### 2.1. Multi-collector thermal ionisation mass spectrometers

Within this work, at the IAEA Department of Safeguards’ Nuclear Material Laboratory (IAEA-NML), a Thermo Fisher Scientific Triton multi-collector thermal ionisation mass spectrometer and a previous generation Finnigan MAT-262 (referred to as ‘MAT-4’) are employed. Selected data of two other MAT instruments previously operated at IAEA-NML but since decommissioned, a MAT-262 (referred to as ‘MAT-3’) and a MAT-261 (referred to as ‘MAT-2’), will be presented for comparison as well; their hardware being

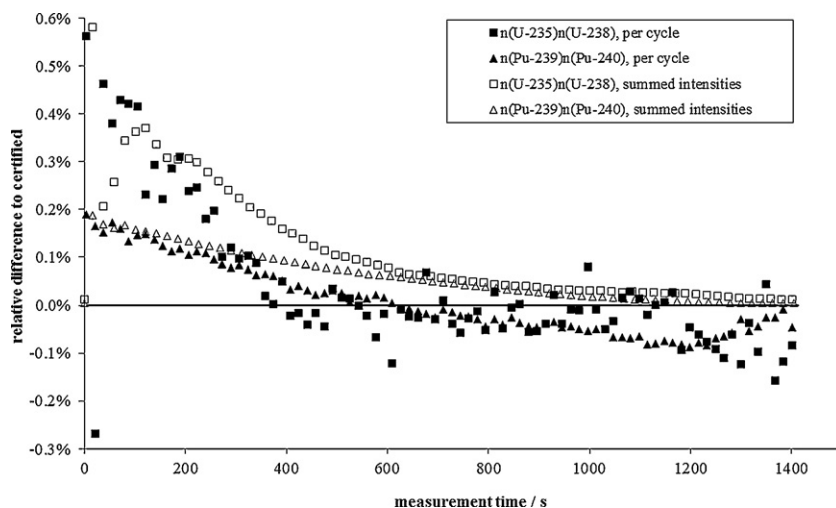
comparable to that of MAT-4. Both instruments, MAT-4 and Triton, are equipped with a multi-collector Faraday cup array with 7 and 9 Faraday cups with a maximum signal voltage of up to 10 V and 50 V, respectively. The Triton is additionally equipped with two  $10^{12}$  Ohm resistors connected to those Faraday cups used for U-234 and U-236 ion detection to improve the signal-to-noise ratio. Furthermore, the MAT-4 and the Triton have an axial secondary electron multiplier (SEM) with energy filter (called retarding potential quadrupole RPQ on the Triton) installed to improve abundance sensitivity for SEM measurements. The sample wheels (aka sample turrets) of the Triton and MAT-4 have up to 21 and 13 filament positions, respectively. Double filament assemblies are used. The vacuum inside the flight tube and ion source housing of the Triton during measurement is usually in the range of  $10^{-9}$  mbar and  $10^{-7}$  mbar, respectively. Both instruments are used for isotope ratio and isotope dilution measurements using TE protocols. The Triton is additionally employed for MTE measurements of uranium.

### 2.2. Sample preparation and filament loading

The analysis of U and Pu isotope ratios as well as U and Pu isotope dilution measurements is conducted for nuclear material samples including oxides, metals, alloys, yellowcakes, uranium ores, and hydrolysed uranium hexafluoride. The samples are dissolved and diluted to the appropriate concentration in nitric acid having a molar concentration of about 1–3 M. In case of isotope dilution, samples are spiked at the beginning of the chemical preparation typically using a U-233 spike (e.g., NBL CRM 111-A or NBS 995) or in certain cases a U-235 spike (e.g., NBL CRM 116) for U analysis, and typically a Pu-242 spike (various suppliers) or in some cases a Pu-239 spike (e.g., CEA CETAMA MP2) for Pu analysis. Uranium ores, yellowcakes, and alloy samples may require a chemical purification to remove impurities and interfering elements and to pre-concentrate the element of interest. For this purpose, column separation (e.g., trioctylphosphine oxide (TOPO) or UTEVA resin) are employed. More details will be presented in a separate publication. After chemical preparation, the sample solutions in nitric acid are drop-loaded with a pipette onto tungsten filaments (ThermoFisher Scientific, or Geradts GmbH, Germany). For total evaporation measurements on the Triton and MAT-4, a volume of typically 1  $\mu\text{L}$  is loaded with analyte amounts in the range of 50–100 ng for Pu and about 500 ng for U per filament. For modified total evaporation (MTE) measurements (see below), typically a volume of 2.5  $\mu\text{L}$  is loaded with an analyte amount in the range of 2500 ng of U. This five-fold increase in amount of U loaded for MTE analysis as compared to TE (about 500 ng) is made to improve the signal to noise ratio for minor isotope determination and respectively peak-tailing measurements which is the main focusing in MTE. The drops loaded onto the W filaments are dried by applying a current of 1 A for 300 s and 2.4 A for 60 s for U samples. For Pu it is 1 A for 300 s, 2.0 A for 300 s, and 2.5 A for 50 s. A double filament assembly is used with rhenium as the ionisation filament (ThermoFisher Scientific, or Geradts GmbH, Germany).

### 2.3. Total evaporation measurement of uranium and plutonium

The total evaporation (TE) protocol in combination with MC-TIMS has been used for decades for the analysis of isotopic composition of uranium and plutonium [45–48]. Briefly, the analyte ion signal is stabilized at a defined target intensity (summed voltage of all isotopes in the respective Faraday cups) by keeping the ionisation filament at a constant current but regulating the evaporator filament current. The ion signals of all isotopes are measured using the multi-collector until exhaustion (i.e., total evaporation of the analyte); the magnetic field (i.e., static measurement) and focus settings are not changed throughout the duration of the analysis



**Fig. 1.** Mass fractionation curve of a typical uranium (IRMM-184) and a typical plutonium (NBL CRM 137) total evaporation measurement using Triton MC-TIMS. The solid squares and solid triangles represent  $n(\text{U-235})/n(\text{U-238})$  and  $n(\text{Pu-239})/n(\text{Pu-240})$  ratios on a per cycle basis, respectively; light squares and triangles are the  $n(\text{U-235})/n(\text{U-238})$  and  $n(\text{Pu-239})/n(\text{Pu-240})$  ratios calculated from the summed intensities accumulated up to that point, respectively. The solid line indicates the certified value.

of one sample filament. The isotope ratios can then be calculated from the integrated (i.e., summed) intensities. The advantage of TE is that the effect of mass fractionation between the lighter isotope (e.g., U-235) and heavier isotope (e.g., U-238) that progresses within the duration of an analysis is averaged out to a large degree due to total evaporation of the sample, meaning the entire history of the mass fractionation is summed. An example of a typical mass fractionation curve for a U TE analysis  $n(\text{U-235})/n(\text{U-238})$  and Pu TE analysis  $n(\text{Pu-239})/n(\text{Pu-240})$  is illustrated in Fig. 1; with lighter isotopes being evaporated and ionised at the beginning of the analysis more efficiently compared to heavier isotopes. The effect is less pronounced for Pu compared to U. Although the effect of the mass fractionation (difference to certified value) is reduced by averaging when using total evaporation, however, it is not entirely cancelled out. This is because not one hundred percent of the analyte atoms loaded on a filament are detected as ions because the overall efficiency (ratio of ions detected to atoms loaded) is typically significantly less than 1% for U and Pu (summarized in [9]). It is self-evident (see Fig. 1) that the result of an isotope ratio analysis can be significantly biased if only a part of the fractionation curve is measured and summed; for example, a bias of up to 0.4% was observed herein if only a tenth of the sample is consumed and the measurement stopped at that point.

Using multi-collector Faraday cup arrays permits the simultaneous detection of all isotopes of interest (U-233, U-234, U-235, U-236, and U-238 for U; or Pu-238, Pu-239, Pu-240, Pu-241, Pu-242, and Pu-244 for Pu). Hence, inevitable drifts in the U or Pu ion signal over the duration of a sample analysis stemming from fluctuations in the evaporation and ionisation of the analyte from the filament is mitigated.

The disadvantage of the TE protocol is that measurements of background and peak tailing contributions cannot be performed in situ due to the nature of static measurements. This is particularly crucial for the determination for minor isotopes, e.g., U-234 and U-236, for which the TE method needs to be modified, the so-called modified total evaporation [11] method (see below). An additional requirement is that the results need to be checked for signal spikes which can be caused by high voltage arcing. Signal spikes can significantly bias results.

In this work, the main isotopes of interest are U-233 through U-238 and Pu-238 through Pu-244, with a focus on the major isotope ratios using TE (i.e.,  $n(\text{U-235})/n(\text{U-238})$  and  $n(\text{Pu-240})/n(\text{Pu-239})$ ),

and the minor and major uranium isotope ratios using modified total evaporation (MTE). Pu-238 measurements are corroborated by alpha-spectrometry due to potential U-238 interference which cannot be resolved from Pu-238 when using commercially available single-collector MC-TIMS instruments with resolution in the range of  $R = 500$  (at 10% height and U-238 mass range).

### 2.3.1. Triton uranium and plutonium TE measurement

A Triton TE measurement sequence consists of up to 21 filament positions to be analysed with at least two filament positions loaded with a mass fractionation standard of the same element and two loaded with a different quality control standard, leaving as much as 17 positions to be filled with samples analysed in multiple replicates. The measurement sequence is performed automatically using the Triton control software, often overnight. The measurement time per sample filament is about half an hour. An amplifier gain calibration is performed at the start of the sequence. The same method is employed for the measurement of all sample filaments: first, the ionisation filament current is increased to a target Re-187 ion signal of about 100 mV and an ion beam focus and peak centring (i.e., mass calibration) is performed. The established focus and mass calibration setting using the Re-187 signal of the ionisation filament will ensure that the settings are tuned sufficiently for uranium detection as well. Next, the evaporation filament is heated to a target U or Pu ion signal of 100 mV to perform an ion beam focusing and peak centring using the U-238 or Pu-239 signal, respectively. Afterwards, the evaporation filament current is increased up to a summed U or Pu signal of 0.5 V. The data acquisition starts as soon as the summed U or Pu intensity is 0.5 V (evaporation filament current about 2.0–2.5 A for U and about for 1.5–2.0 A Pu), the ion signal is stabilized at a summed U or Pu target intensity of 10 V by regulating the evaporation filament current, and acquisition stops as soon as it drops below 0.5 V (evaporation filament current well above 5 A). An amplifier baseline calibration is performed automatically before the analysis of each filament. The Faraday cup configurations for U and Pu are listed in Table 1. Two  $10^{12}$  Ohm resistors are used to improve the signal-to-noise ratio.

### 2.3.2. MAT-262 uranium and plutonium TE measurement

A MAT-262 TE measurement sequence consists of up to 13 filament positions to be analysed with at least two filament positions loaded with a mass fractionation standard of the same element

**Table 1**

Cup configurations used for total evaporation (TE) of U and Pu using Triton or MAT-4, and for modified total evaporation (MTE) measurements using Triton.

Faraday cup	Triton U TE and U MTE	Triton Pu TE	MAT-4 U TE	MAT-4 Pu TE
L3	U-233	Pu-238		Pu-238
L2	U-234 <sup>a</sup>	Pu-239	U-233	Pu-239
L1	U-235	Pu-240	U-234	Pu-240
C	U-236 <sup>a</sup>	Pu-241 <sup>a</sup>	U-235	Pu-241
H1	237.05 u	Pu-242	U-236	Pu-242
H2	U-238	243.05 u		
H3		Pu-244	U-238	Pu-244

<sup>a</sup> 10<sup>12</sup> Ohm resistor.

and one loaded with a different quality control standard, leaving as much as 10 positions to be filled with samples analysed in multiple replicates. The measurement sequence is performed automatically using in-house control software, typically one turret during the working day, a second turret overnight. The measurement time per sample filament is about half an hour. The same method is used for the measurement of all filament positions: first, the ionisation filament current is increased to a target current in the range of 6 A (equal to at least 100 mV Re-187 which needs to be determined for each batch of filaments). Next, the evaporation filament is heated up to achieve a U or Pu ion signal of about 20 mV. Then, an ion beam focusing and peak centring using the U-238 or Pu-239 signal, respectively, is performed. At this point the data acquisition starts while the evaporation current is ramped up and subsequently regulated to stabilize the ion signal at a summed U or Pu target intensity of about 6 V. Acquisition stops as soon as it drops below 100 mV (evaporation filament current well above 5 A). An amplifier gain calibration is performed weekly. The Faraday cup configurations for U and Pu are listed in Table 1.

#### 2.4. Modified total evaporation measurement of uranium

In the modified total evaporation (MTE) method [48,11], the total evaporation of a sample is interrupted at defined intervals to measure the background and peak-tailing contributions to be used to perform in situ corrections of these two effects. A yield calibration of the secondary electron multiplier (SEM), which is used to measure low-abundance isotopes, is also conducted throughout the duration of a modified total evaporation analysis. Here, a Triton MTE measurement sequence consists of up to 21 filament positions to be analysed. A typical sequence consists of five filament positions loaded with a mass fractionation standard of the same element and four loaded with a different quality control (QC) standard, leaving 12 positions to be filled with four samples analysed in triplicates. The number of mass fractionation standards may be changed as needed, but reducing the number from five to four or even less will increase the uncertainty on the mass fractionation correction which will increase in particular the uncertainty on the major ratio  $n(\text{U-235})/n(\text{U-238})$  of the samples. Because samples are usually measured in triplicates, the QC standard is also measured in triplicates with one additional filament (thus total of four) in case one filament measurement is lost (e.g., broken filament during analysis). The measurement sequence is typically performed automatically overnight. The measurement time per sample filament is about 1 h. An amplifier gain calibration is performed at the start of the sequence; an amplifier baseline calibration before and during the analysis of each filament. The same method is used for the measurement of all filament positions: first, the ionisation filament current is increased to a target Re-187 ion signal of about 200 mV and an ion beam focus and peak centring (i.e., mass calibration) is performed. Next, the evaporation filament is heated to a target summed U ion signal of 500 mV to perform an ion beam focusing and peak centring using the U-238 signal. Afterwards, the

evaporation filament current is increased up to a summed U signal of 2 V. The data acquisition starts as soon as the summed U intensity is 2 V (filament current about 2.5–3.0 A), the ion signal is step-wise increased to a summed U target intensity of 20 V and increased further using the 'dynamic target intensity concept' [11]. Acquisition stops as soon as it drops below 2 V (evaporation filament current > 5.5 A). A summed intensity of 0.5 V for start and end of the data acquisition as used in TE can be used for MTE as well, but applying 2 V yields an increased signal-to-noise ratio advantageous for minor isotope determination. The Faraday cup configuration for U MTE is listed in Table 1. Peak-tailing at low and high mass sides are measured at masses  $-0.35$  u and  $+0.35$  u off the peak, respectively. The in situ SEM calibration is performed using the U-234 isotope by switching between Faraday cup and SEM on a cycle-by-cycle basis. The two 10<sup>12</sup> Ohm resistors are used for L2 (i.e., U-234) and centre Faraday cup (i.e., U-236).

##### 2.4.1. Study of U-233 and U-236 blank levels, memory effects, uranium hydride formation, nitric acid matrix effect

The MTE protocol as described above was utilized for all experiments. For the measurements of the  $n(\text{U-233})/n(\text{U-238})$  ratio by MTE, the isotope U-236 with respective masses for peak-tailing correction were substituted with isotope U-233 and respective masses  $232.7$  u =  $233.05$  u  $- 0.35$  u and  $233.4$  u =  $233.05$  u +  $0.35$  u. No other changes were made to the MTE protocol for U-233 measurements. NBL CRM 112-A is utilized which has a certificate-stated upper limit of 5 parts per billion for  $n(\text{U-233})/n(\text{U-238})$  and  $n(\text{U-236})/n(\text{U-238})$  ratios. To assess whether there is a significant nitric acid matrix effect as a function of molarity, four different solutions of NBL CRM 112-A in nitric acid form of molarity of 0.1 M, 0.3 M, 1 M, and 3 M, were prepared and measured.

### 3. Results and discussion

#### 3.1. Certified reference materials, measurement performance, and quality control

##### 3.1.1. Availability and utilization of uranium and plutonium certified isotope reference materials

The validation of analytical methods, the continuous monitoring of measurement performance, the estimation of associated measurement uncertainties and establishing metrological traceability, hence, certified reference materials (CRMs) are a pivotal ingredient. In case of uranium and plutonium isotope ratio and isotope dilution analysis, CRMs need to be certified for uranium and/or plutonium isotopic composition and uranium and/or plutonium amount concentration, respectively. A survey of selected isotope CRMs commercially available from the main CRM producers is summarized in Tables S1 and S2 (supplementary information) [73,76,78] for U and Pu, respectively. As can be noted, a large set of uranium CRMs is available with the major ratio  $n(\text{U-235})/n(\text{U-238})$  covering a wide range from depleted uranium to 97% enriched. For minor isotopes, for example U-236, CRMs are available with ratio  $n(\text{U-236})/n(\text{U-238})$  as low as  $1 \times 10^{-9}$ . And uranium CRMs are offered in various chemical forms, but most of them are uranium oxides or nitric acid solutions. The choice of plutonium CRMs, on the other hand, is notably more limited. There are only a few CRMs certified for Pu-244, and the range of isotopic composition for the major ratio  $n(\text{Pu-240})/n(\text{Pu-239})$  is comparatively small. Many of the CRMs are in dried nitrate form.

In general, the available U and Pu CRMs permit a suitable matching of standards with samples typically encountered in nuclear safeguards analysis with respect to isotopic composition of the major isotope ratios and, in many cases, of the minor ratios. A lack of certified  $n(\text{U-233})/n(\text{U-238})$  ratios in the part per million range

or lower is apparent though; where U-233 is measured, for example, as an indicator for the Th-232(n, $\gamma$ )U-233 reaction. With respect to chemical form, a varied mix of samples is being analysed: ores, concentrates, oxides, fluorides, metals, alloys, fuel materials. CRMs of different matrices are of value for validating and monitoring chemical sample preparation procedures.

The measurement precision and measurement accuracy of both instruments are continuously being monitored using a representative selection of CRMs listed above. For the measurement of depleted, natural, and low enriched uranium samples, the certified reference materials NBL U005-A, 112-A, U030-A, and U100 as well as IRMM-184 through IRMM-187 are utilized; for high-enriched samples the CRMs NBL U200, U500, and U930 are mainly used. To monitor U-236 measurement performance, IRMM-075(1–5) is employed. For Pu analysis, certified reference materials NBL 128, 136, 137, 138, and 144 are predominantly used.

### 3.1.2. Measurement performance

The analytical methods used on both TIMS instruments, Triton and MAT-4, are tuned for achieving suitable sample throughput. In 2010, a total of about 3400 sample filaments were analysed on the Triton using U TE, Pu TE, and U MTE, and a total of about 2100 sample filaments were analysed on the MAT-4 by U TE and Pu TE. This includes measurements of samples and standards and various control samples such as blanks. The measurement time per filament position using Triton U TE or Pu TE is about 0.5 h with typically less than 12 h in total for a sequence of up to 21 filament positions; for MAT-4 it is about 0.5 h as well with typically less than 7 h in total for a sequence of up to 13 filament positions. For MTE measurements using the Triton, the measurement time per filament position is about 1 h with typically less than 24 h in total for a sequence of up to 21 filament positions.

The analyte amount loaded per filament is, to some extent, dictated by the sensitivity achievable by TIMS in routine operation with high sample throughput. The sensitivity (overall efficiency, i.e., ions detected per atoms loaded) for both instruments is in the range of 0.005% for U analysis and about 0.03% for Pu. No additives for ionisation enhancement (e.g., carbon) are applied to reduce sample preparation time, minimize uranium blanks and potential molecular interferences.

A summary of the precision (measurement reproducibility expressed as relative standard deviation) and accuracy (bias expressed as relative difference to the certified value) established from QC measurements is illustrated in Fig. 2. Each data point represents an average of several QC measurements (typically  $n > 20$ , in many cases  $> 50$ ) of a given CRM using Triton TE or MTE. The measurements for each CRM were made over a time period of typically several months to up to 1 year within the period 2010–2011, and performed by two or more analysts. Ratios  $n(\text{U-234})/n(\text{U-238})$  through  $n(\text{U-236})/n(\text{U-238})$  are plotted for U CRMs and  $n(\text{Pu-240})/n(\text{Pu-239})$ ,  $n(\text{Pu-242})/n(\text{Pu-239})$ , and  $n(\text{Pu-244})/n(\text{Pu-239})$  for Pu CRMs. Pu-238 and Pu-241 is not plotted due to U-238 and Am-241 interference, respectively, where Am-241 originates from Pu-241 decay. TE QC data are plotted as measured without correction of mass fractionation, peak-tailing, instrumental blank or interferences. MTE QC data were corrected for all recognised significant effects. The respective International Target Values (ITVs) are plotted as well. The ITVs “represent estimates of the ‘state of the practice’ which should be achievable under routine measurement conditions” [75] by analytical laboratories performing nuclear safeguards measurements. Note that there are ITVs only for a selected number of measurands. For example, there are none for the minor uranium isotope ratios.

As can be seen from Fig. 2, essentially all data points plotted are well below respective ITV limits, sometimes with a margin of up to one order of magnitude. The only exception is the

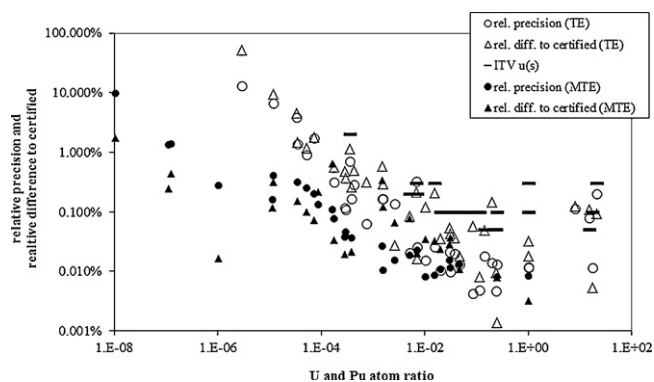


Fig. 2. Relative precision and relative difference to certified value calculated from QC data of various U and Pu certified reference materials using Triton MC-TIMS. Each data point represents an average of several TE or MTE QC measurements using Triton made over a time period of typically several months to up to 1 year performed by two or more analysts. The ITV limits for the maximum allowed difference (e.g., to certified value), called ITV u(s), are plotted as well (horizontal bars).

measurement of ratio  $n(\text{Pu-240})/n(\text{Pu-239}) \approx 15.1$  of NBL CRM 144, where the observed relative difference to the certified value is about twice as much as the respective ITV. This deviation was observed on other TIMS instruments as well (for example at above-mentioned TIMS instruments at IAEA-OSL, or [65]) and might hint at an issue with the certification of CRM 144. It is self-evident that the accuracy of the MTE results, particularly for the minor isotopes, is superior to the TE results. This is because peak-tailing effects, which are the predominant source of systematic errors for minor isotopes, are determined in situ and allow for an accurate and precise correction. Moreover, the precision and the deviation from certified value of MTE measurements of U-236 at part per million level or below is vastly improved by using a SEM instead of a FC detector as well as by the in situ calibration of the SEM which is implemented in the MTE protocol [11]. It is worth mentioning that the isotope ratios plotted in Fig. 2 cover a range of almost ten orders of magnitude. The measurement range, for example for U analysis using MTE, is at least eight orders of magnitude with measurements of  $n(\text{U-236})/n(\text{U-238}) = 1 \times 10^{-8}$  (IRMM-075/5) being on the low-end side and  $n(\text{U-235})/n(\text{U-238}) = 1$  (NBL U500) being on the high-end side. This is made possible by combining ion counting with Faraday cup detectors which can, in the case of Triton, measure up to 50 V signal intensity ( $10^{11}$  Ohm resistor, hence in the range of  $10^{-10}$  A) on the Faraday cups and as low as about one count per second (equivalent to  $10^{-19}$  A) on the SEM.

### 3.1.3. Comparison between latest generation and previous generation MC-TIMS, and TE versus MTE

Comparing measurement performance of the latest generation of MC-TIMS (here Triton) and the previous generation (here MAT-262), a significant gain in measurement reproducibility (expressed as relative standard deviation) of a factor of three, in some cases more than one order of magnitude, can be reported when using the TE method with identical loading procedures and same sample sizes (see Table 2). Similar results to those reported here for the MAT-262 (referred to as ‘MAT-4’) have been achieved on a second MAT-262 instrument (referred to as ‘MAT-3’) and a MAT-261 (referred to as ‘MAT-2’) previously operated at IAEA-NML but since decommissioned (selected data are presented as well). Also, comparable results to those reported here for the Triton are reported using two Triton instruments operated at IAEA-OSL (data not presented here; see [50]). QC results for selected uranium CRMs (depleted uranium NBL U005-A, low-enriched U030-A, and high-enriched U500) are summarized in Table 2. The measurements for each CRM were made over a time period of typically several months

**Table 2**

QC results for selected uranium CRMs comparing MAT, Triton U TE, and Triton U MTE for major isotope ratio  $n(\text{U-235})/n(\text{U-238})$  analysis. The measurements for each CRM were made over a time period of typically several months to up to 1 year, and performed by two or more analysts, with 'n' denoting the number of QC points. Note that the sample amount used for MTE measurement is about five times that of TE.

Method	Certified value (exp. uncertainty, $k = 2$ )	Relative standard deviation	Relative difference to certified value	n
<b>NBL CRM U005-A</b>				
MAT-262 TE (MAT-4)	0.0050900(15)	0.11%	0.12%	27
MAT-262 TE (MAT-3)		0.11%	0.13%	57
Triton TE		0.021%	0.083%	76
Triton MTE		0.018%	0.076%	18
<b>NBL CRM U030-A</b>				
MAT-262 TE (MAT-4)	0.031367(31)	0.032%	0.047%	43
MAT-262 TE (MAT-3)		0.044%	0.051%	75
MAT-261 TE (MAT-2)		0.046%	-0.042%	71
Triton TE		0.010%	0.043%	80
Triton MTE		0.012%	0.036%	15
<b>NBL CRM U500</b>				
MAT-262 TE (MAT-4)	0.9997(10)	0.049%	0.009%	19
MAT-262 TE (MAT-3)		0.054%	0.015%	36
MAT-261 TE (MAT-2)		0.034%	-0.065%	26
Triton TE		0.012%	0.018%	47
Triton MTE		0.008%	0.003%	9

to up to 1 year within the period 2010–2011 (period 2008–2009 for MAT-3 and 2002–2003 for MAT-2), and performed by two or more analysts. Compared are MAT U TE, Triton U TE, and Triton U MTE for major isotope ratio  $n(\text{U-235})/n(\text{U-238})$ . Although the TE data are not corrected for mass fractionation, blanks, and peak-tailing as in MTE, these three effects are small (mass fractionation and peak-tailing in the range of 0.01%) to insignificant (blanks) for the discussed  $n(\text{U-235})/n(\text{U-238})$  ratios. Note that the sample amount used for MTE measurement is about 5 times that of TE. As can be seen from Table 2, the relative standard deviations for the Triton are, in many cases, significantly smaller when compared to the respective relative difference to the certified value. Nonetheless, the relative differences to the certified value are all within the certificate-stated uncertainty of the respective CRM. It simply highlights the superior measurement repeatability/reproducibility obtainable with state-of-the-art MC-TIMS instruments and considering the fact that some CRMs have been certified several decades ago.

### 3.1.4. Quality control charts

For quality control purpose, the performance of the instruments is monitored on a day to day basis by plotting isotope ratio results of CRM measurements in Shewhart control charts. CRM results of isotope ratio measurements are checked against certified values and against control and warning limits as well as for signal spikes and summed total signal intensity (overall efficiency). Pu analyses are decay corrected. Additionally, critical parameters like SEM yield and dark noise, vacuum readings, amplifier gain and baseline, amplifier temperature, and mass calibration are tracked if applicable.

An example of a Triton MTE control chart is illustrated in Fig. 3 with QC measurements  $n(\text{U-236})/n(\text{U-238})$  of IRMM-075/5 plotted. The QC data ( $n = 77$ ) represent the time period mid 2010 through mid 2011, acquired by two operators. The certified value (uncertainty of certified value too small to scale) and upper and lower control limits (CLs) and warning limits (WLs) are plotted as well. Here, the WL and CL were set equal to the associated measurement uncertainty of a single replicate measurement ( $n = 1$ ) expressed as expanded uncertainty  $k = 2$  (about 94.45%) and  $k = 3$  (about 99.73%), respectively, according to GUM principles. Hence, the control chart with plotted WLs and CLs visually tracks whether a QC measurement is in agreement or disagreement with the certified value within an expanded uncertainty of  $k = 2$  and/or  $k = 3$ , respectively. Furthermore, it illustrates trends and drifts over time, indicating whether the analytical procedure might be subjected to changes in

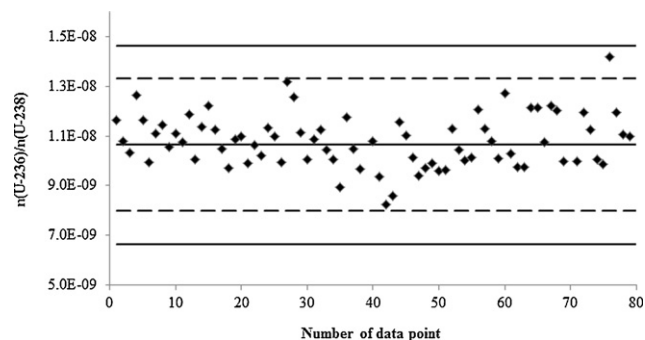
the measurement performance. As this example shows (Fig. 3), the QC points visually show no major trends or drifts (e.g., oscillations, upwards or downwards trends).

There are different recommendations on how to calculate the warning and control limits. Often, 2-sigma (about 95%) and 3-sigma (about 99.7%) standard deviations are used, respectively, or 95% and 99% limits. Here, WL and CL are calculated based upon GUM uncertainty calculations with the WL being equal to the expanded uncertainty ( $k = 2$ , for large effective degrees of freedom) and the CL equal 3/2 times the WL, hence  $k = 3$ . At a minimum, when it comes to safeguards nuclear material measurements, they need to be in compliance with the ITV requirements [75].

### 3.1.5. Monitoring of U-233 and U-236 blank levels and contamination during sample preparation

The instrumental limit of detection for  $n(\text{U-236})/n(\text{U-238})$  analysis using MTE as utilized in this work is in the range of two to three parts per billion, for  $n(\text{U-233})/n(\text{U-238})$  analysis below 5 parts per billion. This is monitored using NBL 112-A showing that no U-233 and U-236 are detected in NBL 112-A at a level of not more than 5 and 3 parts per billion, respectively. For comparisons, a certified ratio  $n(\text{U-236})/n(\text{U-238})$  of about  $1 \times 10^{-8}$  (IRMM-075/5), which is a factor of about 5 above the limit of detection, can be quantified accurately within an expanded uncertainty ( $k = 2$ ) of about 22% (see below).

The chemical blank introduced by sample preparation (e.g., acid dissolution, drying and evaporation, potentially column chemistry)



**Fig. 3.** A Triton MTE control chart tracking  $n(\text{U-236})/n(\text{U-238})$  measurements (black squares) of IRMM-075/5; time period of about one year, acquired by two operators. The centre line signifies the certified value, the outer lines represent the upper and lower control limits (solid lines) and warning limits (dashed lines).

is monitored using NBL 112-A as well by processing the standard in the same way or a comparable way as the samples. Even when performing an ion exchange column separation step, it is possible to maintain a U-236 blank level of less than 5 parts per billion, though contamination during chemical sample preparation at a level of more than 10 parts per billion has been observed, for example, due to handling samples or standards with high U-236 content (e.g., NBL U500, IRMM-3100). The issue is even more pronounced when it comes to U-233 due to handling of U-233 spikes used in IDMS analysis.

### 3.1.6. Memory effects

Instrumental memory effects in Triton TIMS MTE analysis as utilized in this work have been assessed by employing U-236 as a monitor. Several different samples with a comparatively high  $n(\text{U-236})/n(\text{U-238})$  ratio of as much as  $2 \times 10^{-3}$  were analysed with each sample measurement flowed by a CRM measurement of IRMM-184 or CRM 112-A with a certificate-stated ratio  $n(\text{U-236})/n(\text{U-238})$  of about  $1 \times 10^{-7}$  or  $<5 \times 10^{-9}$ , respectively. No significant bias in the measured ratio of IRMM-184 and CRM 112-A at a level of  $<3 \times 10^{-9}$  was observed. This yields an upper limit for the carry-over from the previous sample measurement (i.e., memory effect) of  $<1.5 \times 10^{-6}$ .

### 3.1.7. Uranium hydride formation

An upper limit for the hydride formation  $^{235}\text{UH}$  was assessed using natural uranium CRM 112-A. No significant signal above  $n(\text{U-236})/n(\text{U-238}) < 3 \times 10^{-9}$  was detected ( $n > 100$  analyses). Hence, an upper limit of  $n(\text{U-236})/n(\text{U-235}) = n(^{235}\text{UH})/n(\text{U-235}) < 4 \times 10^{-7}$  for the hydride formation ratio  $\text{UH}/\text{U}$  can be estimated. A value of about 0.00725 for the certified ratio  $n(\text{U-235})/n(\text{U-238})$  of CRM 112-A is used in the calculation. The determined upper limit for the hydride formation is essentially an insignificant contributor to the measurement uncertainty, and is also insignificant when compared to the uranium hydride formation typically observed in ICMS with solution-based sample introduction, which is on the order of  $10^{-4}$ – $10^{-6}$  (summarized in [66]).

## 3.2. Measurement uncertainty

As the measured value and its unit are integral parts of a measurement result, so is a statement of the associated measurement uncertainty. It provides confidence in the measured value, allows judgement on significance of differences between measurement results, permits assessing the capability of a measurement procedure, and is an integral part of quality assurance and to establish traceability to a reference, e.g., SI units. Herein, the associated measurement uncertainties are evaluated according to GUM principles [71,74] and using the GUM Workbench software [84]. The GUM approach represents a standardized way of expressing uncertainty, and has been adopted by most of the national metrology institutes in the world; it is regarded as state-of-the-art approach to Uncertainty in Measurement [67,68]. For uranium and plutonium total evaporation multi-collector Faraday TIMS analysis, the following sources of uncertainties are assessed: (1) mass fractionation and the certified value of the standard used for mass fractionation correction, (2) measurement repeatability of the mass fractionation standard and of the sample, (3) atomic and molecular interferences and TIMS loading blank, (4) peak tailing, (5) Faraday cup amplifier gain and baseline (6) relative Faraday cup yield and Faraday cup non-linearity; see [57] for more details. Additional sources of uncertainty in uranium modified total evaporation analysis are: (7) SEM dark noise, (8) SEM non-linearity, and (9) yield of SEM versus Faraday cup. Each source of uncertainty is briefly discussed below. In uranium TIMS analysis as utilized in this work, no significant hydride formation or memory effect is observed (see above).

- (1) The mass fractionation correction factor is established by measuring a mass fractionation standard of the same element, typically in multiple replicates (i.e., multiple filaments) per sample wheel. The average of the measured values is ratioed to the certified value yielding the mass fractionation correction factor [48,57,11]. Using the linear law, the correction is applied to all ratios of interest. Typically, a significant source of uncertainty in determination of major ratios is the certificate-stated uncertainty of the isotope ratio of the standard used for mass fractionation correction (see Tables S1 and S2 (supplementary information) for certificate-stated uncertainties). It needs to be accounted for to establish traceability to the SI units.
- (2) In case each standard and/or sample is analysed in multiple replicates, the measurement repeatability may be established from these replicate analyses. Otherwise, the measurement repeatability may be derived from pooled estimate of standard deviation [74] estimated from suitably matched QC standard (see Table 2 listing examples of values of (relative) standard deviations of QC measurements which are used to derived pooled estimate of standard deviation). The measurement repeatability is usually a significant contributor to the measurement uncertainty.
- (3) Atomic and molecular interferences as well as TIMS loading blanks are monitored, for example, using NBL CRM 112-A for U-236 and U-233, or by measuring Pu-242 and U-233 spikes to determine major isotope blanks. No significant interferences for the major U and Pu isotope ratios in TIMS can be reported here for samples that are appropriately chemically purified prior to analysis. A signal of about 2 cps on U-236 at 20 V summed U present using SEM detector, potentially stemming from interferences or blanks. A correction is made and a conservative uncertainty of 100% ( $k=2$ ) of the correction is applied, resulting in a limit in  $n(\text{U-236})/n(\text{U-238})$  detection using MTE of about  $2 \times 10^{-9}$  at 20 V summed U signal.
- (4) For minor isotope ratio measurements, peak-tailing effects can be the predominate source of uncertainty, for major isotope ratio determination the peak-tailing effects are usually insignificant. Using MTE, the peak-tailing is determined in situ on a block-by-block basis for each sample measurement [11]. For example, for Triton Faraday cup measurements of a natural uranium sample using the MTE protocol, the standard uncertainty associated with the correction of the peak-tailing of U-235 and U-238 to the signal intensity of mass U-234 (extrapolated from off-peak measurements at mass 233.7 u and 234.4 u) is about  $2 \times 10^{-7}$  ( $k=1$ ). For U-236 determination using SEM with RPQ, the standard uncertainty associated with the correction of the peak-tailing of U-235 and U-238 to the signal intensity of mass U-236 (extrapolated from measurements at mass 235.7 u and 236.4 u) is about  $3 \times 10^{-10}$  ( $k=1$ ). This needs to be accounted for in U-234 and U-236 minor isotope ratio measurements. In TE analysis, usually only major isotope ratios are of interest, hence no significant peak-tailing correction it needed except for extreme ratios. If minor isotope ratios need to be derived from TE analyses, the peak-tailing correction may be estimated from QC measurement (pooled estimated). This, of course, carries a larger uncertainty compared to MTE as the correction factors for TE are not determined in situ as in MTE.
- (5) Faraday cup amplifier gain and baseline correction and associated uncertainties are usually comparatively small. The repeatability of the baseline calibration is, in the case of Triton using  $10^{11}$  Ohm resistors, on the order of 0.010 mV ( $k=1$ ), insignificant for major isotope ratio analysis. The variability of the amplifier gain calibration is, in the case of Triton using  $10^{11}$  Ohm and  $10^{12}$  Ohm resistors, about 0.001–0.002% and

- about 0.003%, respectively, which is an insignificant contribution to the combined standard uncertainty as well.
- (6) By performing multi-collector Faraday cup analyses using a suite of U and Pu CRMs with a large range of isotope ratios (see Table S1 and S2, supplementary information), no significant non-linearity effects (to the extent of the uncertainty of the CRMs used) can be reported for the latest-generation Faraday cups used on the Triton up to 50 V signal intensity. The relative Faraday cup yield, i.e., the relative difference in ion detection response for the individual Faraday cups, is observed to have no significant deviation (within uncertainties) from linearity for the Triton.
  - (7) The SEM dark noise is on the order of a few counts per minute (less than or equal to 0.1 cps), an insignificant correction in all events even in  $10^{-9}$  ratio measurements.
  - (8) Analytical approaches to assess the ion counting detector non-linearity and dead-time for TIMS measurements, in particular for uranium, have been reviewed by Richter et al. [69]. For measurements at low count rates (up to a few thousand counts per second) using ion detectors, the uncertainty stemming from non-linearity and dead-time correction is usually small to insignificant. At higher count rates the uncertainty can be on the order of 0.05% ( $k=1$ ) or more [69,57,11] depending on the analytical approach and CRMs used to establish the non-linearity and dead-time correction.
  - (9) Using MTE, the yield of the SEM with RPQ versus Faraday cup is determined in situ on a block-by-block basis for each sample measurement [11] using the U-234 signal which can be measured on the SEM and on a Faraday cup. On the Triton using a  $10^{11}$  Ohm resistor, 1 mV signal on a FC is equal to 62,500 cps on the SEM. The relative yield is typically >0.9, depending on the setting of the SEM voltage. The uncertainty is determined based on these in situ measurements, which is on the order of 0.25% ( $k=1$ ) for a single measurement of a natural U sample (U-234 about 55 pm), slightly better for enriched samples with increased U-234 content. It can be a major source of uncertainty for  $n(\text{U-236})/n(\text{U-238})$  determination depending on the ratio.

A summary of typical measurement uncertainties (expanded uncertainties, approx. 95% CL) associated with TE and MTE analysis of U and Pu isotope ratios is presented in Table 3. The major contributors to the uncertainty budget are listed as well with their percentages of contribution. It is apparent that for major isotope ratio analysis, the uncertainty of the certified value of the CRM used for mass fractionation correction is the major source of uncertainty.

### 3.3. Metrological traceability

Metrological traceability to the International System of Units (SI units) is a “property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty” [72]. In isotope ratio or isotope dilution measurements, the relevant SI units are the unit mol and the unit kilogram. The above quoted “related to a reference” to which the results are traceable to is the certified reference material (CRM) used to calibrate the mass spectrometer, for example, the CRM used for mass fractionation correction or the spike used for isotope dilution. The CRM itself is supposed to be traceable to the relevant national standard (as stated on the certificate) which itself is supposed to be traceable to the SI unit as a certified reference material is “accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities” [72].

To the greatest degree possible, certified reference materials used for calibration (mass fractionation correction) and for QC

purposes are matched with the samples in: element, elemental concentration, isotopic composition, and chemical composition (e.g., matrix). With respect to matching analyte concentration, the QC measurements and control charts are established for a certain analyte concentration (about 500 ng for U and 100 ng for Pu for TE analysis per filament, and about 2500 ng for U MTE analysis) and the sample concentration is adjusted accordingly.

With respect to matching isotopic composition, as discussed above (Section 3.1) a large set of uranium and to some extent plutonium isotope CRMs are available from different suppliers to cover a wide range of isotopic compositions for major as well as for minor isotope ratios. A calibration of the instrument, hence traceability of the analytical results, can be established. For this, at least two different CRMs are analysed (usually in multiple replicates, i.e., multiple filament positions) within one measurement sequence, i.e., on one sample wheel. All analyses of one of the CRMs are used to perform the calibration, i.e., to calculate the mass fractionation factor or to verify that the mass fractionation factor is identical to unity within associated uncertainties. The second and all other CRMs are employed for QC to monitor the accuracy of the calibration and the measurement precision. The results are plotted as QC data points in control charts (see Section 3.1). It shall be noted here that for the instrument generations used in this work, particularly for the Triton MC-TIMS, no significant non-linearity effects in isotope ratio measurements have been observed when using the Faraday cup detectors. For example, no significant deviation from certified is observed when CRMs with NU composition are used to calibrate for HEU samples.

Matching the chemical composition, on the other hand, remains a challenge. This is because samples of quite different chemical composition are analysed, including metals, plutonium and uranium oxides (e.g.,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2$ ,  $\text{UO}_4$ ), uranium–fluorine compounds (e.g.,  $\text{UF}_6$ ,  $\text{UF}_4$ ,  $\text{UO}_2\text{F}_2$ ), yellowcakes, uranium ores, alloys (e.g., U–Zr or U–Al alloys), nitrate solutions and slurries. Only a limited number of isotope CRMs with more challenging matrices like yellowcakes are available (see Table S2), and virtually none for alloys or uranium ores. This is particularly the case when analysing U due to the frequency of U samples with complex matrices; it is less of a concern for Pu because many of the samples are oxides. Thus, the following discussion is limited to U samples. Often, those samples with more complex matrices like U–Al and U–Zr alloys, yellowcakes and ore samples are purified using ion exchange chemistry to separate the analyte from the matrix. Removing interfering elements stemming from the matrix is necessary to minimize atomic and molecular interferences, to mitigate quenching of the ionisation efficiency of U, for example due to refractory elements, and to minimize any matrix effects on the mass fractionation of U. To ensure that the chemical preparation and purification does not alter the isotopic composition of U, for example, due to introduction of blanks, the performance needs to be evaluated. For this purpose, various CRMs and standards including uranium oxides, yellowcakes, and ores were analysed with and without column separation using TOPO and/or UTEVA resin. No significant change in the  $n(\text{U-234})/n(\text{U-238})$  and  $n(\text{U-235})/n(\text{U-238})$  ratios were detected when comparing with and without a separation step; results will be published elsewhere. Once purified, the sample in nitric acid solution can be matched with CRMs in nitric acid solution.

#### 3.3.1. Nitric acid matrix effect

Depending on the CRM used and chemical procedures employed, the molarity of the nitric acid solution may not always be an exact match between CRMs and samples. NBL CRM 112-A solutions in 0.1 M through 3 M nitric acid were measured to assess whether the molarity causes a matrix effect that produces significant changes in the isotope ratios during TIMS measurements, e.g., due to changes in the mass fractionation. No significant



**Table 3**  
Typical measurement uncertainties (expanded uncertainty with coverage factor, approx. 95% CL) of TE or MTE analyses of U and Pu isotope ratios using Triton MC-TIMS; “mass fractionation” lists which CRM is used for mass fractionation correction, the major source of uncertainty and its percent contribution to the uncertainty budget are listed as well; meas. rep.: measurement repeatability; certified value CRM: certified value of the CRM used for mass fractionation correction.

Sample	Approx. atom amount ratio	Method	Mass fractionation	Expanded uncertainty (relative)	Coverage factor	Major source of uncertainty/contribution
<b><math>n(\text{U-234})/n(\text{U-238})</math></b>						
Depleted U	0.000034	MTE, triplicates	IRMM-184	0.87%	2.13	Peak tailing/74%
Natural U	0.000055			0.58%	2.11	Peak tailing/68%
Enriched U	0.00018			0.18%	2.09	Peak tailing/63%
<b><math>n(\text{U-235})/n(\text{U-238})</math></b>						
Depleted U	0.0051	TE, duplicates	IRMM-184	0.067%	2.00	Meas. rep./45%
Natural U	0.0073			0.066%	2.00	Meas. rep./61%
Low enriched U	0.047		IRMM-187	0.039%	2.00	Certified value CRM/57%
High enriched U	0.25		NBL U200	0.11%	2.00	Certified value CRM/95%
Natural U	0.0073	MTE, triplicates	IRMM-184	0.043%	2.00	Certified value CRM/49%
<b><math>n(\text{U-236})/n(\text{U-238})</math>; having natural uranium <math>n(\text{U-235})/n(\text{U-238})</math> ratio</b>						
'Natural U'	$7 \times 10^{-5}$	MTE, triplicates	IRMM-184	0.40%	2.07	SEM yield/57%
	$1 \times 10^{-7}$			2.3%	2.00	Meas. rep./50%
	$1 \times 10^{-8}$			22%	2.00	Background/74%
<b><math>n(\text{Pu-240})/n(\text{Pu-239})</math></b>						
Low burn-up	0.06	TE, duplicates	NBL 138	0.13%	2.00	Certified value CRM/99%
High burn up	0.43		NBL 137	0.12%	2.00	
Isotope dilution (Pu-242 spiked)	About 1		NBL 128	0.035%	2.00	Certified value CRM/55%

difference from certified and no trend as a function of the molarity was observed (number of replicate measurements about  $n = 20$  for each molarity). The largest relative difference to certified being 0.045% and 0.003% for ratios  $n(\text{U-234})/n(\text{U-238})$  and  $n(\text{U-235})/n(\text{U-238})$ , respectively, which are within certificate-stated uncertainties by a factor of more than three and ten, respectively, and are similar to the respective measurement repeatability.

### 3.3.2. Agreement between two independently produced series of uranium certified reference materials: NBL U series and IRMM-18x series

It is self-evident that the certified values of certified reference materials (CRMs) traceable to the SI units and produced by different national or even international metrological laboratories need to be consistent with each other within stated measurement uncertainties. Otherwise, calibrations of analytical instruments performed with respective CRMs may yield results not in agreement within associated uncertainties. Needless to say that such a disagreement would question the metrological traceability of respective analytical results. In the case of uranium isotope ratio measurements, the main suppliers for CRMs are the U.S. DOE New Brunswick Laboratory (NBL) and the EC JRC Institute for Reference Materials and Measurements (IRMM). Agreement between NBL's uranium series and IRMM's uranium series is therefore of interest regarding the statement of traceability of uranium isotope ratio measurements, measurement results which may influence decision-making on a national or international level as in the case in nuclear safeguards or nuclear forensics investigations.

For this purpose, the certified reference materials IRMM-184 (natural uranium) and IRMM-187 (5% enriched U-235) were measured against various NBL U series CRMs ranging from depleted uranium and natural U (CRM U005-A and 112-A) to low-enriched and high enriched U (CRM U030-A, U200, and CRM U500). IRMM's U Series (IRMM-183, -184, -185, -186, and -187) ranging from depleted (-183) through low enriched (-187) have already been measured against each other and agree within certificate-stated uncertainties, and with other IRMM CRMs like IRMM-3636; see for example [70,11,12].

Here, IRMM and NBL CRMs were measured in the same sequence and either IRMM-184 or -187 was used to correct the NBL CRM measurements for mass fractionation and the difference to NBL certified values calculated. No significant difference was identified between using IRMM-184 or IRMM-187 for correction of mass fractionation.

The results for both are therefore combined. The measured mean values and the differences (relative in percent) between the IRMM CRMs and the selected NBL U Series CRMs are listed in Table 4.

MTE was utilized for this purpose due to its superior measurement precision. The contribution to the expanded uncertainty of the relative difference as listed in Table 4 stemming from the MTE method itself is small. In almost all cases it is <10%, whereas the uncertainties of the certified values of the CRMs are the largest contributors (typically >90%). As a consequence, the relative differences with associated expanded uncertainties are a direct comparison of IRMM certified values versus NBL certified values within certificate-stated uncertainties. Additionally, the TE method in a 'high intensity mode' (1500 ng of U loads per filament, 20 V summed target U signal) was successfully applied to corroborate the MTE major isotope ratio results and are listed in Table 4 as well (index "HITE"). Note that IRMM-184 or -187 was used as mass fractionation standard, thus the uncertainties on the measured mean values of the major ratios are determined by the uncertainty of the certified value of IRMM-184 or -187, which is about 0.03%. The number of replicate measurements is about  $n = 10$ , in cases much more (distributed on multiple sample turrets).

With the exception of NBL CRM U005-A, an agreement within stated uncertainties between IRMM versus NBL can be confirmed, for major as well as for minor isotope ratios. For NBL CRM U005-A, the differences on the  $n(\text{U-235})/n(\text{U-238})$  and  $n(\text{U-236})/n(\text{U-238})$  isotope ratios do not agree within respective uncertainties with NBL certified values, whereas the  $n(\text{U-234})/n(\text{U-238})$  ratio does agree. All results presented herein including CRM U005-A agree when compared to Richter and Goldberg [48] published values for the NBL U Series. Furthermore, the relative differences on minor isotope ratios are significantly smaller when compared to Richter and Goldberg [48] (not listed in Table 4) instead of NBL certified. Note that for NBL CRM U030-A only an upper limit is stated on the NBL certificate for ratio  $n(\text{U-236})/n(\text{U-238})$  [79]; the results reported here agree with Richter and Goldberg [48] published value. Note further that for NBL CRM 112-A only an upper limit of  $<5 \times 10^{-9}$  is stated for ratios  $n(\text{U-233})/n(\text{U-238})$  and  $n(\text{U-236})/n(\text{U-238})$  on the NBL certificate [80] which both can be confirmed here at a limit of  $<3 \times 10^{-9}$ . The relative differences for NBL CRMs U200 and U500 major isotope ratios are equal to or less than 0.01%. This indicates that the certificate-stated uncertainties (0.10%) are potentially overestimated hinting at certified ratios that are established

**Table 4**

Mean values (atom amount ratios) and expanded uncertainties (about 95% CL) of selected NBL certified reference materials using IRMM-184 or IRMM-187 for mass fractionation correction determined using MTE or high intensity TE (index: "HITE").

Quantity	Mean value (expanded uncertainty)	Coverage factor	Relative difference to certified value $\pm$ expanded uncertainty
<b>NBL CRM U005-A</b>			
R <sub>234/238</sub>	0.00003423(11)	2.11	(0.2 $\pm$ 2.1) %
R <sub>235/238</sub>	0.0050935(18)	2.00	(0.069 $\pm$ 0.046) %
R <sub>235/238</sub> HITE	0.0050935(18)	2.00	(0.069 $\pm$ 0.046) %
R <sub>236/238</sub>	0.000012011(70)	2.14	(1.3 $\pm$ 1.0) %
<b>NBL CRM 112-A</b>			
R <sub>233/238</sub>	<5 $\times$ 10 <sup>-9</sup>		
R <sub>234/238</sub>	0.000052849(41)	2.06	(0.01 $\pm$ 0.17) %
R <sub>235/238</sub>	0.0072542(23)	2.00	(-0.001 $\pm$ 0.064) %
R <sub>235/238</sub> HITE	0.0072552(26)	2.00	(0.013 $\pm$ 0.065) %
R <sub>236/238</sub>	<3 $\times$ 10 <sup>-9</sup>		
<b>NBL CRM U030-A</b>			
R <sub>234/238</sub>	0.00028719(15)	2.00	(0.21 $\pm$ 0.22) %
R <sub>235/238</sub>	0.031376(10)	2.00	(0.031 $\pm$ 0.062) %
R <sub>235/238</sub> HITE	0.031380(10)	2.00	(0.044 $\pm$ 0.062) %
R <sub>236/238</sub>	0.000006257(35)	2.18	Only an upper limit is certified
<b>NBL CRM U200</b>			
R <sub>234/238</sub>	0.00156620(69)	2.00	(0.12 $\pm$ 0.25) %
R <sub>235/238</sub>	0.251235(81)	2.00	(-0.01 $\pm$ 0.11) %
R <sub>236/238</sub>	0.0026549(23)	2.16	(-0.06 $\pm$ 0.30) %
<b>NBL CRM U500</b>			
R <sub>234/238</sub>	0.0104259(45)	2.00	(0.03 $\pm$ 0.19) %
R <sub>235/238</sub>	0.99973(33)	2.00	(0.00 $\pm$ 0.11) %
R <sub>236/238</sub>	0.0015238(24)	2.18	(0.33 $\pm$ 0.44) %

to a degree much more accurate than the certificate-stated uncertainties imply.

#### 4. Conclusion

Multi-collector thermal ionisation mass spectrometry is still in many applications the most precise and accurate technique commercially available for isotope ratio analysis of microgram and nanogram sized samples of uranium and plutonium, usually conducted using a (modified) total evaporation protocol. It therefore continues to be the benchmark technique for this analytical task in the nuclear community. The precision and accuracy is due to minimal molecular and atomic interferences, comparatively stable ion signals, decade-long experience in the TIMS analytical techniques, minimal memory effects, insignificant hydride formation, and an overall robust and reliable technology proven for routine operation with several thousand sample filaments being analysed per instrument per year. Due to the fact that total evaporation MC-TIMS protocols are usually well understood and data evaluation schemes comparatively simple, a modelling of the associated measurement uncertainties according to GUM principles is routinely performed. In essentially all cases, International Target Values can be met with a substantial margin, sometimes up to one order of magnitude.

Comparing the latest generation and previous generation of MC-TIMS instruments (here Thermo Fisher Triton and Finnigan MAT 262, respectively), it is apparent that there has been a gain of up to an order of magnitude in precision of actinide isotope ratio measurements due to improvements in instrument design. With the introduction of the modified total evaporation protocol, more recently, a significant improvement in accuracy of U minor isotope measurement could be demonstrated covering a dynamic range of at least eight orders of magnitude in routine operation.

A pivotal ingredient in performing accurate and traceable measurements is the availability and quality of certified reference materials. The demonstrated consistency of the certified values of IRMM's U series and NBL's U series highlights the quality of both independently produced set of uranium CRMs, and provides confidence in the metrological traceability of respective results. Using IRMM CRMs as calibration standards, a new set of values for NBL U series CRMs is presented with expanded uncertainties ( $k=2$ , equal

to about 95%) of about 0.035% for major isotope ratios and at an order of magnitude of 0.1–0.5% for minor ratios. The results indicate that the certificate-stated uncertainties of some NBL CRMs, most notably the HEU standards, are potentially too conservative and that the certified values are established with a much better accuracy than the certificate-stated uncertainties imply.

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#### Appendix A. Supplementary data

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