



Demonstrating the metrological compatibility of uranium isotope amount ratio measurement results obtained by GSMS, TIMS and MC-ICPMS techniques

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ABSTRACT

The metrological compatibility of $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurement results obtained by gas source mass spectrometry (GSMS), thermal ionisation mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) techniques in a set of low-enriched uranium samples is demonstrated in this study. The impact of the correlation between certified isotope reference materials on the metrological compatibility of measured isotope amount ratios is also discussed. The metrological concepts defined in the VIM 3rd edition and the measurement uncertainty evaluation according to the BIPM-GUM guide was thoroughly applied in this work.

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1. Introduction

Uranium isotope composition must be accurately known to comply with the requirements of different fields such as geochronology [1], nuclear fuel characterisation [2], nuclear material safeguards [3], nuclear forensics [4], environmental monitoring [5] and health monitoring [6]. There are several techniques to measure uranium isotope amount ratios: optical spectrometry, alpha and gamma spectrometry, fission counting, neutron activation and mass spectrometry [7]. Some of them are destructive and some non-destructive. All have advantages and disadvantages as analytical techniques.

The most traditional technique to measure uranium isotope amount ratios is destructive assay applying mass spectrometry. There are several mass spectrometric techniques that can be applied reflecting combinations of different types of ion sources, mass analysers and ion detectors [8]. Among these different mass spectrometric techniques, GSMS and TIMS, because of their high measurement repeatability and accuracy, are regarded as the most reliable for measuring uranium isotope amount ratios [9]. Addition-

ally, multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) has recently joined this select group [10].

Uranium samples can be delivered to nuclear analytical laboratories either in solid, liquid or gas forms, which is no big deal, since there are chemical procedures to convert the received samples into any of these forms.

When samples are in the form of uranium hexafluoride (UF_6), a highly volatile and reactive compound processed in isotope enrichment facilities, GSMS technique can be selected. Sample preparation basically consists in removing the volatile compounds usually present in UF_6 , mainly HF, because it disturbs the measurement process. The required sample amount is of the order of milligrams of UF_6 . Sample throughput is low because the measurement procedure can require the use of two certified isotopic reference materials (CIRMs) for each sample. The big disadvantage of this technique relies on the fact that the mass spectrometer can just measure UF_6 samples [11].

When samples are in the form of uranium oxide (UO_2 , UO_3 or U_3O_8), TIMS technique can be applied after the dissolution of the oxide with nitric acid to generate uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$), which is deposited into metal filaments. Sample preparation basically consists in removing the existing fluorine ions. Just few nanograms of uranium are needed to carry out the measurement procedure. Sample throughput is considerably higher in this technique since five

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to ten samples can be analysed daily. A big advantage of this technique is the ability to analyse other chemical elements, provided they have first ionisation potential lower than 7.5 eV [12].

Finally, when samples are in the liquid form, MC-ICPMS technique can be readily applied, because solutions are directly introduced in the inductively coupled plasma (ICP) of the ion source of the instrument. Sample preparation is straightforward and just few nanograms of uranium are needed. Sample throughput is the highest of the described techniques, with the ability to process up to twenty samples per day. This technique can also be applied to most of the elements of the periodic table, which is clearly one of the reasons for its widespread use in modern analytical laboratories [13]. Additionally, when samples are in the solid form, a laser ablation device can be coupled to the MC-ICPMS and used to vaporize the samples in an argon atmosphere at normal pressure. Thus, the sample preparation step is avoided, the risk of sample contamination is reduced and the water vapour introduced in the plasma with liquid solutions is eliminated [14]. The strategy devised to measure the isotope amount ratios using the referred techniques will be described along the text.

The aim of this study is to demonstrate the metrological compatibility of the $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratios measurement results provided by GSMS, TIMS and MC-ICPMS techniques in a set of low-enriched samples and to investigate the impact of correlation between certified isotope reference materials on the metrological compatibility of the measured isotope amount ratios. This work is very important because in a later stage the obtained measurement results will be composed to calculate the isotopic composition of samples to be used as certified isotopic reference materials by several nuclear analytical laboratories. The use of these materials will enable the establishment of the metrological traceability of measurement results to the International System of Units (SI) and will help to provide accurate isotope amount ratios.

2. Metrological concepts

The goal of this study can just be achieved with the help of metrology, the science of measurement and its application, including all theoretical and practical aspects of measurement. Thus, all the metrological concepts and terms applied here were taken from the latest VIM edition [15].

The concept of the metrological compatibility, in particular, replaces the traditional “staying within the error” statement largely used in the past. Two measurement results will be considered metrologically compatible if they are traceable to the same unit or reference and if the value of their difference is smaller or equal to a multiple k of the standard uncertainty of the difference. In this work the value of k is 2. Therefore, to check whether two isotope ratio measurement results R_a and R_b are compatible, a multiple k of the uncertainty of the difference ($k \times u(\Delta)$) must be compared with the absolute value of the difference ($|\Delta|$) itself, as described in the equations below.

$$\Delta = R_a - R_b \quad (1)$$

$$u(\Delta) = \sqrt{u(R_a)^2 + u(R_b)^2 - 2 \times r(R_a, R_b) \times u(R_a) \times u(R_b)} \quad (2)$$

$$|\Delta| \leq k \times u(\Delta) \quad (3)$$

where R_a is the isotope amount ratio provided by technique a ; $u(R_a)$ the standard combined uncertainty associated with isotope ratio R_a ; R_b the isotope amount ratio provided by technique b ; $u(R_b)$ the standard combined uncertainty associated with isotope ratio R_b ; Δ the difference between R_a and R_b ; $r(R_a, R_b)$ the correlation coefficient between R_a and R_b ; $u(\Delta)$ the standard combined uncertainty of the difference; and k is the coverage factor equal to 2.

Thus, the evaluation of the measurement uncertainty is very important in the assessment of the metrological compatibility between measurement results. The recommendations of the BIPM-GUM guide [16] were fully complied with in this work and a special software package was used to facilitate the necessary calculations [17].

3. Experimental

3.1. Reagents and samples

Four samples produced at the CTMSP facility (São Paulo, Brazil) in the form of uranium hexafluoride (UF_6), ranging from approximately 0.5 to 3.5 wt% of ^{235}U , were selected for this study. They come from batches of parent materials that were submitted to purification and homogenisation processes required to produce isotope reference materials.

The CIRMs used for the calibration of the mass spectrometers were prepared by the Institute for Reference Materials and Measurement (IRMM) [18]. Their $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratios were measured using gravimetric mixtures of highly enriched uranium oxides, which provides metrological traceability to the SI [19].

Samples and CIRMs were hydrolysed by the addition of 18 MΩ cm high purity deionised water provided by a Milli Q Plus purification system (Millipore, Bedford, MA, USA). The resulting uranyl fluoride (UO_2F_2) solution were then converted to uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) by the addition of Suprapur nitric acid (Merck, Darmstadt, Germany) and evaporated to dryness. Finally, the solutions were made up to the concentrations required by each mass spectrometry technique to be employed, as presented in Table 1, by the addition of 1 M nitric acid.

The certified isotope amount ratios of the CIRMs used in this work are listed in Table 2.

3.2. Instrumentation

The mass spectrometers and associated measurement procedures applied as follows. All measurements were performed at the IRMM laboratories [18].

3.2.1. GSMS instrumentation

The gas source instrument used in this study was the MAT 511, an electron impact mass spectrometer manufactured by Varian MAT (Bremen, Germany). It is equipped with a 90° curvature, 23.5 cm radius, 3650 G magnetic sector analyser. It has two fixed Faraday collectors with $3.0 \times 10^{10} \Omega$ resistors positioned to measure the $^{235}\text{UF}_5^+$ and $^{238}\text{UF}_5^+$ ion-beam intensities and therefore the ratio of the two major uranium isotopes in UF_6 . Also it has a sensitivity of 9.6×10^{-10} A, mass resolution of 358 at 10% peak height and a sample consumption of 2.84 mg/h of UF_6 .

3.2.2. GSMS measurement procedure

The measurement procedure applied here was based on the double standard method [20], which relies on the bracketing of the sample by two CIRMs. The first CIRM must have an $n(^{235}\text{U})/n(^{238}\text{U})$ isotopic ratio slightly higher and the second CIRM, an $n(^{235}\text{U})/n(^{238}\text{U})$ isotopic ratio slightly lower than that of the sample.

The measurement sequence was executed in two sequential blocks [21]. In the first, the sequence was: sample-CRM1-sample. In the second block, the sequence was: sample-CRM2-sample. A mass discrimination correction factor was determined in each measurement sequence. Both correction factors and the isotope ratio values of the CIRMs were used to calculate the corrected isotope ratio for the sample. The advantage of the double standard method is that

Table 1
Certified isotope reference materials and concentrations used.

Technique	Sample	CIRMs used	Chemical form	Concentration of U
GSMS	B.1	IRMM 071, 021	UF ₆	–
	B.2	IRMM 071, 2079	UF ₆	–
	B.3	IRMM 295, 2408	UF ₆	–
	B.4	IRMM 2411, 295	UF ₆	–
TIMS	B.1 to B.4	IRMM 184	UO ₂ (NO ₃) ₂	5.0 mg U/mL
MC-ICPMS	B.1	IRMM 071	UO ₂ (NO ₃) ₂	1.0 mg U/mL
	B.2	IRMM 071	UO ₂ (NO ₃) ₂	1.0 mg U/mL
	B.3	IRMM 295, 2408	UO ₂ (NO ₃) ₂	1.0 mg U/mL
	B.4	IRMM 2411	UO ₂ (NO ₃) ₂	1.0 mg U/mL

Table 2
Certified isotope reference materials used and their isotope amount ratios. The expanded uncertainties are presented in brackets, include a coverage factor equal to 2 and apply to the two last digits.

CIRMs	$n(^{234}\text{U})/n(^{238}\text{U})$	$n(^{235}\text{U})/n(^{238}\text{U})$	$n(^{236}\text{U})/n(^{238}\text{U})$
IRMM 021	0.000 025 245 (80)	0.004 403 6 (21)	0.000 000 044 5 (44)
IRMM 2079	0.000 053 58 (32)	0.007 150 5 (24)	0.000 012 6 (27)
IRMM 071	0.000 053 4 (20)	0.007 262 3 (16)	0.000 000 20 (20)
IRMM 2408	0.000 198 5 (18)	0.019 733 3 (52)	0.001 984 (20)
IRMM 184	0.000 053 138 (32)	0.007 262 3 (22)	0.000 000 124 46 (17)
IRMM 295	0.000 292 8 (41)	0.030 771 1 (51)	0.000 034 0 (21)
IRMM 2411	0.000 406 8 (57)	0.040 621 1 (83)	0.004 062 (10)

any possible procedural effect (especially memory) and instrumental effects (drifts and non-linearity) are cancelled out.

3.2.3. TIMS instrumentation

The thermal ionisation instrument used was the Triton, a state-of-the-art multi-collector spectrometer manufactured by Thermo Fischer Scientific (Bremen, Germany). It is equipped with a sample magazine for twenty-one filaments, 90° magnetic sector analyser, dynamic zoom optics and nine Faraday collectors, each one associated with its own signal amplifier. For small signals it also has a secondary electron multiplier (SEM) device in connection with a retarded potential quadrupole (RPQ), an energy filter used to reduce undesired peak tails and thus improve the abundance sensitivity.

3.2.4. TIMS measurement procedure

The zone-refined rhenium filaments used in this work were previously degassed at 5 A for 20 min in a high vacuum bake-out unit. A sample drop of 1.0 µL containing 5.0 µg of uranium was deposited onto each filament. They were then dried at 0.5 A for 5 min, 1.0 A for 1 min and 1.5 A for 10 s. A set of these filaments was then assembled in the instrument magazine. The measurements were carried out using the modified total evaporation method (MTE) [22] in the static mode for all isotope ratios higher than 10⁻⁴. This method is designed to both minimise the overall fractionation effect and improve the precision compared with the traditional technique in which only part of the sample was used for data acquisition.

Each analysis comprised 40–60 blocks of measurements of 5 mass cycles with an integration time of 32 s. Measurements were carried out mostly at an intensity of 10 V until the sample on the filament was exhausted. The data acquisition was interrupted regularly to perform focusing, peak centering and Faraday background measurements.

Both sample and CIRMs were processed using the same operational parameters. The mass discrimination effect was corrected using external calibration. In this approach, several filaments loaded with CIRMs are measured and the mean mass discrimination correction factor obtained is applied to correct the observed isotope ratio of all sample filaments.

For the isotope ratios lower than 10⁻⁴, there was a need to work with higher intensities; therefore the high intensity method (HI) was used [22]. The basic differences relative to MTE method is that

the sample size was twice as big, and the measurements were carried out at 30 V intensity for the ²³⁸U ion beam, which corresponds to a 3.0 × 10⁻¹⁰ A ion current. For the HI method, the measured values of the minor ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ were normalized using the corrected results for the major ratio $n(^{235}\text{U})/n(^{238}\text{U})$ obtained from the MTE method.

3.2.5. MC-ICPMS instrumentation

The MC-ICP mass spectrometer used in this study was the Nu Plasma, a multiple collector, double focusing sector field ICPMS manufactured by Nu Instruments (Wrexham, North Wales, U.K.). It is equipped with a fixed array of twelve Faraday collectors plus three ion counters. The central ion counter is associated with a RPQ. Two zoom lenses are assembled between the magnet and the collector plane, which allows a precise peak overlap in all configurations. The instrumental parameters used are presented at Table 3.

3.2.6. MC-ICPMS measurement procedure

A static multi-collector measurement scheme using just two Faraday cups was used for the determination of the uranium major isotope ratio. The analysis comprised three blocks of ten measurements and one mass cycle with integration time of 10 s.

The measurement sequence applied was the following: blank-CRM1-rinse-blank-sample-rinse-blank-CRM2-rinse. The electronic noise of the Faraday detectors was measured by deflecting the ion beam at the electrostatic analyser (ESA). Then procedural blank samples were measured on the peak to allow the determination of the instrumental background. Both electronic and instrumental backgrounds were subtracted from the sample and CIRMs signal intensities. Finally the mass discrimination effect was corrected by the bracketing method, which applies the mean of the mass discrimination correction factors obtained from the measurement of the two CIRMs.

A dynamic multi-collector measurement scheme was used for the determination of the uranium minor isotope ratios. The analysis comprised three blocks of ten measurements and five mass cycles with integration time of 5 s each. The measurement sequence was the same as the one used for the static multi-collector measurements. The mass discrimination effect was corrected by internal calibration using an exponential law. The measurement procedure adopted is described in detail elsewhere [23].

Table 3
MC-ICPMS instrumental parameters.

<i>ICP ion source</i>	
RF generator frequency (MHz)	27.12
Cooling gas	Argon
Forward RF power (W)	1300
Reflected RF power (W)	0
Cooling gas flowrate (L/min)	13
Auxiliary gas flowrate (L/min)	0.75
Nebuliser flowrate (L/min)	0.68
Sample uptake ($\mu\text{L}/\text{min}$)	100
<i>Interface</i>	
Cones	Ni
Spray chamber	Jacketed cinnabar
Nebuliser	Micro-concentric
<i>Ion optics</i>	
Acceleration voltage (V)	4021
Extraction potential (V)	2000
Resolution	300
Sensitivity ($\text{V}/\mu\text{g g}^{-1}$)	11
<i>Energy filter setting</i>	
Decelerator (V)	4010
Focus (V)	3525
<i>Ion counter</i>	
Voltage	2000
<i>Acquisition</i>	
Number of blocks	3
Cycles per block	10
Integration time (s)	10
Magnetic delay (s)	2

4. Results and discussion

The following strategy was adopted to measure the isotope amount ratios in the samples: first the major ratio, $n(^{235}\text{U})/n(^{238}\text{U})$; then the minors $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$.

4.1. Measurement of uranium major isotope amount ratios

The $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratio was measured in each of the four samples. The obtained results were in the range of 10^{-2} to 10^{-3} , as presented in Table 4.

The values presented in Table 4 reveal that the lowest values for measurement uncertainty were always provided by GSMS. It is exactly for this reason that this technique was selected to certify the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio of the future isotopic reference materials.

To check the metrological compatibility between the measurement results for each sample, the mathematical tests described in Eqs. (1)–(3) were applied to all pairs of isotope amount ratios presented in Table 4.

4.2. The problem of correlation between input quantities

The calculation of the difference between isotope amount ratios (Δ) was straightforward but the calculation of the standard uncertainty ($u(\Delta)$) raised the issue of a possible correlation between the measured isotope ratios. If they are correlated, a serious limitation

would be present, because there is a reduction in the uncertainty of the difference (as can be seen in Eq. (2)), which would compromise the comparison between the isotope ratio values.

There are two possible cases of correlation between the input quantities. The isotope ratios R_a and R_b were measured using the same CIRMs or the certified values of the CIRMs used in their measurement process, despite being labelled differently, were correlated due to the route selected by the producer in their preparation and certification process.

The first case was applicable for all four samples measured by GSMS and MC-ICPMS techniques. The correlation coefficients ($r(R_a, R_b)$) were calculated [24] to lie in the range of 0.12–0.62. To evaluate the significance of these figures, further calculations were carried out to determine the change in the standard uncertainty of the difference ($u(\Delta)$) compared to the case where this type of correlation was absent, as in the situation where completely different CIRMs were used. The results are presented in Table 5.

The data presented in Table 5 shows that the absence of correlation, via the use of the different CIRMs in both measurements, would increase the uncertainty of the difference by up to 32% of the actual value. These values can make a significant difference in many real comparisons. The use of the same CIRM effectively sharpens the comparison between the two measurements results because the effects of the reference materials are cancelled out, highlighting the potential of each technique and measurement procedure employed. Unfortunately the second case of correlation could not be calculated because there are no data on possible correlations in the IRMM reference material's certificates.

Nevertheless, because there are strong indications these materials are correlated, a simulation was carried out to assess the influence of correlation on the standard uncertainty of the difference.

Correlation coefficients varying from 0.0 (CIRMs used are independent or uncorrelated) to 1.0 (CIRMs used are fully correlated) were assumed and a multiple k of the standard uncertainty of the difference ($k \times u(\Delta)$) was calculated and compared to the absolute value of the difference of isotope ratios ($|\Delta|$). If the former is equal or larger than the latter value, then they have passed the test and the two measured isotope ratios can be considered as metrologically compatible.

All measurement results related to samples B.1 and B.2 passed the test irrespective of the degree of the correlation between the values of the reference materials. However, several failures were detected for samples B.3 and B.4, as shown in Table 6, for higher correlation coefficients. For instance, measurement results pro-

Table 5

Change in the expanded uncertainty of the difference of isotope ratios measured by GSMS and MC-ICPMS techniques in case different CIRMs were used in the measurements.

Sample	$r(R_a, R_b)$ Same CIRM	$r(R_a, R_b)$ Different CIRM	$u(\Delta)$ Change %
B.1	0.12	0	7
B.2	0.47	0	21
B.3	0.59	0	32
B.4	0.62	0	30

Table 4

$n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratios measured by GSMS, TIMS and MC-ICPMS techniques. The expanded uncertainties are presented in brackets, include a coverage factor equal to 2 and apply to the two last digits.

Sample	$n(^{235}\text{U})/n(^{238}\text{U})$ GSMS	$n(^{235}\text{U})/n(^{238}\text{U})$ TIMS	$n(^{235}\text{U})/n(^{238}\text{U})$ MC-ICPMS
B.1	0.005 354 7 (17)	0.005 355 1 (18)	0.005 353 8 (23)
B.2	0.007 254 3 (16)	0.007 253 7 (27)	0.007 252 0 (34)
B.3	0.024 232 0 (42)	0.024 225 3 (86)	0.024 235 6 (63)
B.4	0.035 469 8 (47)	0.035 469 (12)	0.035 476 5 (87)

Table 6
Absolute differences between $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratios ($|\Delta|$) and a multiple of the standard uncertainties ($k \times u(\Delta)$) obtained for each sample. Different correlation coefficients between the reference materials ($r(R_{\text{CRM1}}, R_{\text{CRM2}})$) were assumed while calculating the correlation between the isotope ratios ($r(R_a, R_b)$).

Sample	Techniques	$r(R_{\text{CRM1}}, R_{\text{CRM2}})$	$r(R_a, R_b)$	$ \Delta $	$k \times u(\Delta)$	Test result
B.3	GSMS–TIMS	0.0	0.00	6.7×10^{-6}	9.6×10^{-6}	OK
		0.2	0.21	6.7×10^{-6}	8.8×10^{-6}	OK
		0.4	0.39	6.7×10^{-6}	8.0×10^{-6}	OK
		0.6	0.56	6.7×10^{-6}	7.2×10^{-6}	OK
		0.8	0.71	6.7×10^{-6}	6.2×10^{-6}	Fail
		1.0	0.85	6.7×10^{-6}	4.9×10^{-6}	Fail
	GSMS–ICPMS	0.0	0.59	3.6×10^{-6}	5.1×10^{-6}	OK
		1.0	0.72	3.6×10^{-6}	5.0×10^{-6}	OK
	ICPMS–TIMS	0.0	0.00	1.0×10^{-5}	1.1×10^{-5}	OK
		0.2	0.14	1.0×10^{-5}	1.0×10^{-5}	OK
		0.4	0.27	1.0×10^{-5}	9.4×10^{-6}	Fail
		0.6	0.39	1.0×10^{-5}	8.7×10^{-6}	Fail
		0.8	0.50	1.0×10^{-5}	7.9×10^{-6}	Fail
		1.0	0.61	1.0×10^{-5}	7.1×10^{-6}	Fail
	B.4	GSMS–TIMS	0.0	0.00	1.0×10^{-6}	1.3×10^{-5}
1.0			0.86	1.2×10^{-6}	7.5×10^{-6}	OK
GSMS–ICPMS		0.0	0.62	6.7×10^{-6}	6.9×10^{-6}	OK
		0.2	0.67	6.7×10^{-6}	6.5×10^{-6}	Fail
		0.4	0.71	6.7×10^{-6}	6.2×10^{-6}	Fail
		0.6	0.75	6.7×10^{-6}	5.8×10^{-6}	Fail
		0.8	0.79	6.7×10^{-6}	5.4×10^{-6}	Fail
		1.0	0.83	6.7×10^{-6}	4.9×10^{-6}	Fail
ICPMS–TIMS		0.0	0.00	8.0×10^{-6}	1.5×10^{-5}	OK
		1.0	0.72	8.0×10^{-6}	8.5×10^{-6}	OK

vided by GSMS and TIMS on sample B.3 are only metrologically compatible provided the correlation coefficient between the CIRMS used is lower than 0.8.

Correlation is therefore a very critical issue for the comparison of uranium major isotope ratio measurement results and shows up especially when highly precise measurements are performed. In these cases, the certified values of the CIRMS used are the dominant components in the uncertainty budget so that any possible correlation requires detailed investigation. Correlation is also a matter of high concern in inter-laboratory comparison (ILC) programs because they are based on the comparison between the participant's measurement result and the certified value of the sample. In this particular case, both of the described ways where correlation can occur are possible, which will certainly raise doubts regarding the agreement or disagreement of the participant's measurement result.

The measurement uncertainty estimation process allowed the sources of uncertainty and their contribution to the standard combined uncertainty associated with the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio measured by each technique to be identified. The results obtained for sample B.2 are presented in Table 7.

The values presented in Table 7 show that the dominant component for GSMS was the uncertainty associated with the isotope ratio of the reference materials used in the measurement procedure. Its contribution amounted to 97.4% of the uncertainty budget. The small contribution of the measurement repeatability is due to the use of the electron impact ion source, a device that produces very stable ion-beams, with large ion-current intensities and small spread of ion kinetic energy. Sample and standard gas are introduced in the ion source in a very reproducible way; as a result,

Table 7
Contribution of the uncertainty components to the standard combined uncertainty associated with the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratios measured by GSMS, TIMS and MC-ICPMS for sample B.2.

Uncertainty components	GSMS %	TIMS %	MC-ICPMS %
Reference material	97.4	66.5	22.2
Measurement repeatability	2.7	33.5	66.6
Blank correction	0.0	0.0	11.2

isotope ratio measurements with a relative standard deviation (RSD%) as low as 0.012% could be obtained.

The uncertainty associated with the isotope ratio of the reference materials used were also the dominant component for TIMS, contributing 66.5% of the uncertainty budget while measurement repeatability contributed 33.5%. In thermal ionisation, there is an unavoidable change in the evaporation and ionisation conditions during the course of each measurement and also a variable response between filaments. However, because the overall fractionation effects are minimised in the total evaporation technique, isotope ratio measurements with RSDs of about 0.025% were achieved.

A completely different profile was noticed for MC-ICPMS, where the dominant component in the uncertainty budget was the measurement repeatability, with a contribution of 66.6%. Isotope ratios were measured with a RSD of 0.060%, the highest value among these techniques. This is mainly attributed to plasma flickering. It is worth noting that the contribution of the blank correction was 11.2%, which means that the uncertainty would certainly be underestimated if this hadn't been carried out.

The values presented in Table 7 suggest that the better the measurement repeatability (lower RSD%) in a given mass spectrometry technique, the larger will be the contribution of the reference material to the standard combined uncertainty associated with the isotope ratio. Therefore the proper selection of the isotope reference materials is crucial in these techniques.

4.3. Measurement of uranium minor isotope amount ratios

The minor isotope amount ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ are important characteristics of nuclear materials and have to be measured with as low an uncertainty as possible. The $n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratio measured by MC-ICPMS and TIMS were in the range of 10^{-4} to 10^{-5} as shown in Table 8.

Because the GSMS instrument used has only two fixed Faraday cups, dedicated to the measurement of the major isotopes, the measurement of the minor uranium isotope ratios could not be carried out on this instrument.

The mathematical test previously described was also applied to the values presented in Table 8 and the conclusion was that the $n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratios are metrologically compat-

Table 8

$n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratios measured by MC-ICPMS and TIMS. The expanded uncertainties are presented in brackets, include a coverage factor equal to 2 and apply to the two last digits. The absolute differences between isotope ratios $|\Delta|$ and a multiple of the standard uncertainties ($k \times u(\Delta)$) are presented for each sample.

Sample	$n(^{234}\text{U})/n(^{238}\text{U})$ MC-ICPMS	$n(^{234}\text{U})/n(^{238}\text{U})$ TIMS	$ \Delta $	$k \times u(\Delta)$
B.1	$3.582 (12) \times 10^{-5}$	$3.581 2 (45) \times 10^{-5}$	7.17×10^{-9}	1.26×10^{-7}
B.2	$5.67 (20) \times 10^{-5}$	$5.658 1 (41) \times 10^{-5}$	1.20×10^{-7}	2.03×10^{-7}
B.3	$2.092 6 (82) \times 10^{-4}$	$2.092 8 (13) \times 10^{-4}$	1.79×10^{-8}	8.27×10^{-7}
B.4	$3.331 (14) \times 10^{-4}$	$3.327 1 (18) \times 10^{-4}$	4.05×10^{-7}	1.38×10^{-6}

Table 9

Contribution of the uncertainty components to the standard combined uncertainty associated with the $n(^{234}\text{U})/n(^{238}\text{U})$ isotope ratios measured by TIMS and MC-ICPMS for sample B.2.

Uncertainty components	TIMS %	MC-ICPMS %
Measurement repeatability	50.6	70.3
Reference material	49.4	0.7
Ion counter dead-time correction	–	28.6
Background subtraction	–	0.4

ible. The measurement uncertainties provided by TIMS, however, were always lower than those from MC-ICPMS.

The contribution of different components to the standard combined uncertainty associated with the $n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratio for sample B.2 is presented in Table 9.

There is an approximately equal contribution of uncertainty from measurement repeatability and reference materials as shown in the uncertainty budget for the TIMS measurements. A significant difference in the size of the uncertainty from repeated measurements is found compared to the equivalent measurements obtained for the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratios presented in Table 7. This fact is explained by the smaller ion-beam intensity generated by the low ^{234}U abundance in the sample.

Measurement repeatability is the dominant uncertainty component for MC-ICPMS, followed by the uncertainty arising from the ion counter dead-time correction. The greater number of components in the MC-ICPMS uncertainty budget is a clear indication of the complexity of this technique.

The $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratios measured by MC-ICPMS and TIMS are listed in Table 10.

The measured isotope amount ratios of these samples were in the range of 10^{-4} down to 10^{-8} , the lowest verified in this study. The mathematical test described in Eqs. (1)–(3) indicated that the measurement results for samples B.1, B.3 and B.4 are metrologically compatible but a real discrepancy was detected for sample B.2. Measurements for this sample were repeated and its uncertainties were recalculated but the discrepancy was confirmed. The ^{236}U abundance in sample B.2 was the lowest of all of the samples and the conclusion is that a source of uncertainty for one or both of these measurement techniques was not fully evaluated. This is not surprising considering the difficulty in measuring the ion intensity of such a low abundance isotope.

The contribution of different components to the standard combined uncertainty associated with the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio for sample B.2 is presented in Table 11.

Table 10

$n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratios measured by MC-ICPMS and TIMS. The expanded uncertainties are presented in brackets, include a coverage factor equal to 2 and apply to the two last digits. The absolute differences between isotope ratios $|\Delta|$ and a multiple of the standard uncertainties ($k \times u(\Delta)$) are presented for each sample.

Sample	$n(^{236}\text{U})/n(^{238}\text{U})$ MC-ICPMS	$n(^{236}\text{U})/n(^{238}\text{U})$ TIMS	$ \Delta $	$k \times u(\Delta)$
B.1	$1.158 10^{-6} (24)$	$1.148 0 10^{-6} (32)$	1.04×10^{-8}	1.23×10^{-8}
B.2	$4.68 10^{-8} (94)$	$3.213 3 10^{-8} (89)$	1.47×10^{-8}	9.37×10^{-9}
B.3	$1.15 10^{-7} (22)$	$1.140 8 10^{-7} (31)$	4.65×10^{-10}	2.18×10^{-8}
B.4	$3.885 10^{-4} (16)$	$3.881 0 10^{-4} (11)$	3.77×10^{-7}	1.56×10^{-6}

The uncertainty estimation of the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio is complicated by the existence of serious interferences, arising firstly from the large $^{238}\text{U}^+$ peak, which causes a tailing effect over the small neighbouring $^{236}\text{U}^+$ peak and also the presence of the $^{235}\text{UH}^+$ peak in the case of the MC-ICPMS. Correction for these interferences and the adequate estimation of the associated measurement uncertainties is a challenge, especially for very low isotope abundance.

Significant deviations between measurements carried out on very low abundant isotopes have been previously found. The results from REIMEP 18, an inter-laboratory comparison campaign organised by IRMM [25] for instance, showed a large spread in the measurements of ratios at about 3.0×10^{-8} . A similar spread was also detected in the CCQM-P48, a pilot study organised by IRMM on behalf of the Comité Consultatif pour la Quantité de Matière (CCQM) [26]. On the other hand, measurements performed with TIMS in synthetic isotope mixtures in the ratios of 10^{-4} to 10^{-8} showed excellent agreement with the prepared values [27]. This shows that reliable measurements can be carried out even at these low values. It is clear, however, that the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio is a very difficult measurand.

Finally, the impact of correlation in the comparison of minor isotope ratio measurement results was deemed as negligible. There are two reasons for this fact: first, different CIRMs were actually used in these measurements, which eliminated one of the possible cases of correlation. Second, the CIRMs used just had a marginal contribution to the uncertainty budget of the measurements carried out by MC-ICPMS and its contribution to TIMS measurements were much less pronounced than in major isotope ratio measurements. Thus, even if the CIRMs used were fully correlated, the uncertainty of the difference remained more than 10 times larger than the difference of the isotope ratios.

Table 11

Contribution of the components to the standard combined uncertainty associated with the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope ratios measured by TIMS and MC-ICPMS for sample B.2.

Uncertainty components	TIMS %	MC-ICPMS %
Measurement repeatability	84.96	26.7
Reference material	0.40	0.0
Ion counter dead-time correction	14.7	0.0
Blank correction	–	0.0
Peak tailing subtraction from ^{238}U	–	15.6
Hydride subtraction	–	57.7

5. Conclusions

The metrological compatibility of the $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurement results provided by different mass spectrometry techniques were successfully demonstrated in this study. The measurement results of the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratios revealed the existence of a high degree of equivalence between the investigated techniques. It is important to stress that despite many developments in other techniques, GSMS is still the most reliable for uranium because it always provided results associated with the lowest measurement uncertainties. It was, however, only applicable to the major uranium isotopes in this work.

The measurement results of the $n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratios provided by TIMS and MC-ICPMS also revealed a high degree of equivalence. But in this case, the results of TIMS were associated with lower measurement uncertainties.

The measurement results of the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratio by TIMS and MC-ICPMS revealed the existence of good degree of equivalence for samples B.1, B.3 and B.4 and one real discrepancy, in sample B.2, attributed to the extremely low ^{236}U abundance in the sample. The measurement of such a low ratio required all the resources of the instrumentation as well as the skill of the analysts. This is indeed a very difficult measurand.

This work also raised the issue of correlation of the certified isotope reference materials used in the measurement process, investigating its impact on the comparison of the measurement results provided by different mass spectrometric techniques. Because this kind of comparison lies at the very heart of international inter-laboratory comparison programs, producers of reference materials must carry on detailed investigations and publish all the relevant data to enable this kind of comparisons to be thoroughly meaningful.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

References

- [1] J.R. De Laeter, Applications of Inorganic Mass Spectrometry, John Wiley & Sons, Inc., NY, 2001.
- [2] Standard test methods for chemical, mass spectrometric and spectrochemical analysis of uranium dioxide, powders and pellets, American Society for Testing Materials ASTM C 696-99, 2009 Annual Book of ASTM Standards, vol. 12.01, Philadelphia, USA.
- [3] E. Kuhn, R. Binner, H. Aigner, U. Blohm-Hieber, K. Mayer, S. Guardini, C. Pietri, B. Rappinger, B. Mitterrand, J. Reed, O. Mafrá-Guidicini, S. Deron, International Target Values 2000 for Measuring Uncertainties in Safeguarding Nuclear Materials, International Atomic Energy Agency, Report STR-327, Vienna, Austria, 2001.
- [4] K. Mayer, M. Wallenius, I. Ray, Nuclear forensics—a methodology providing clues on the origin of illicitly trafficked nuclear materials, *Analyst* 130 (2005) 433–441.
- [5] J. Environ. Radioactiv., Special Issue on Tokai-mura Nuclear Criticality Accident in Japan, 50 (2000).
- [6] J.W. Ejniak, T.I. Todorov, F.G. Mullick, K. Squibb, M.A. McDiarmid, J.A. Centeno, Uranium analysis in urine by inductively coupled plasma dynamic reaction cell mass spectrometry, *Anal. Bioanal. Chem.* 382 (2005) 73–79.
- [7] C.D. Tabor, Mass Spectrometry for Uranium Isotopic Measurements, Review Series, Number 5, International Atomic Energy Agency (IAEA), Vienna, Austria, 1960.
- [8] J.S. Becker, Inorganic Mass Spectrometry: Principles and Applications, John Wiley & Sons, Inc., UK, 2008.
- [9] I.T. Platzner, Modern Isotope Ratio Mass Spectrometry, John Wiley & Sons, Chichester, West Sussex, UK, 1997.
- [10] J.S. Becker, Recent developments in isotope analysis by advanced mass spectrometry techniques, *J. Anal. Atom. Spectrom.* 20 (2005) 1173–1184.
- [11] O. Pereira de Oliveira Junior, W. De Bolle, A.M. Alonso, H. Kühn, S. Richter, R. Wellum, A new set of uranium isotope reference materials for the improvement of the nuclear safeguards in South America, in: Symposium on Safeguards and Nuclear Materials Management, ESARDA 29th Annual Meeting, Aix en Provence, France, 22–24 May, 2007.
- [12] D.H. Smith, Thermal ionization mass spectrometry, in: C.M. Barshick, D.C. Duckworth, D. Smith (Eds.), Inorganic Mass Spectrometry—Fundamentals and Applications, Marcel Dekker, New York, NY, USA, 2000.
- [13] A. Halliday, J.N. Christensen, D. Lee, C.M. Hall, X. Luo, M. Rehkämper, Multiple collector inductively coupled mass spectrometry, in: C.M. Barshick, D.C. Duckworth, D. Smith (Eds.), Inorganic Mass Spectrometry—Fundamentals and Applications, Marcel Dekker, New York, NY, USA, 2000.
- [14] J.S. Becker, State-of-the art and progress in precise and accurate isotope ratio measurements by ICPMS and LA-ICP-MS, *J. Anal. Atom. Spectrom.* 17 (2002) 1172–1185.
- [15] International Vocabulary of Metrology—Basic and General Concepts and Associated Terms (VIM), 3rd ed., Joint Committee for Guides in Metrology (JCGM200:2008), Bureau International des Poids et Mesures (BIPM), 2008.
- [16] Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement, Joint Committee for Guides in Metrology (JCGM100:2008), Bureau International des Poids et Mesures (BIPM), 2008.
- [17] GUM Workbench, The Software Tool for the Expression of Uncertainty in Measurement, Metrodata, Germany, <http://www.metrodata.de>.
- [18] Institute for Reference Materials and Measurements (IRMM), Joint Research Center (JRC), European Commission (EC), Geel, Belgium, <http://www.irmm.jrc.be>.
- [19] K.J.R. Rosman, R. Lycke, R. Damen, R. Werz, F. Hendrickx, L. Traas, P. De Bièvre, The preparation and use of synthetic isotope mixtures for testing mass spectrometers, *Int. J. Mass Spectrom. Ion Process.* 79 (1987) 61.
- [20] C.J. Roden, Uranium isotopic composition by the double standard interpolative mass spectrometric method, in: Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, TID-7029, 2nd ed., Office of Information Services, U.S. Atomic Energy Commission, Washington, DC, USA, 1972.
- [21] G. Müschenborn, W. De Bolle, ($^{235}\text{U})/(^{238}\text{U})$ isotope ratio measurements on double collector UF_6 mass spectrometers, Internal Report CBNM-MS-R-74-83, August 1983.
- [22] S. Richter, S.A. Goldberg, Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry, *Int. J. Mass Spectrom.* 229 (2003) 181.
- [23] C.R. Quétel, J. Diemer, Different isotope ratio measurement applications for different types of ICP-MS: comparative study of the performance capabilities and limitations, in: P. De Groot (Ed.), Handbook of Stable Isotope Analytical Techniques, vol. 1, Elsevier, Amsterdam, 2004, pp. 821–834.
- [24] R. Kessel, M. Berglund, P. Taylor, R. Wellum, How to treat correlation in the uncertainty budget when combining results from different measurements, *Advanced Mathematical Tools in Metrology*, vol. 5, in: Series on Advances in Mathematics for Applied Sciences, vol.57, World Scientific, Singapore, 2001, p. 232.
- [25] S. Richter, A. Alonso, J. Truyens, A. Verbruggen, R. Wellum, Evaluating the status of uranium isotope ratio measurements using an inter-laboratory comparison campaign, *Int. J. Mass Spectrom.* 264 (2007) 184.
- [26] C.R. Quétel, N. Lévêque, W. De Bolle, E. Ponzevera, Uranium isotope ratio measurements in simulated biological/environmental materials, CCQM-P48, Metrologia, 2007, vol. 44, Tech. Suppl., 08010, <http://www.iop.org/EJ/abstract/0026-1394/44/1A/08010/>.
- [27] S. Richter, A. Alonso, W. De Bolle, H. Kühn, A. Verbruggen, R. Wellum, P.D.P. Taylor, Preparation and certification of synthetic uranium isotope mixtures with $^{236}\text{U}/^{238}\text{U}$ ratios of 10^{-6} , 10^{-7} , 10^{-8} , *J. Anal. Atom. Spectrom.* 20 (2005) 1381–1385.