Evaluation of the $n(^{235}U)/n(^{238}U)$ isotope ratio measurements in a set of uranium samples by thermal ionization mass spectrometry

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Abstract

The measurement of $n(^{235}U)/n(^{238}U)$ isotope amount ratio in a set of representative uranium samples with enrichment levels ranging from 0.5 to 20.0 wt.% of ^{235}U was carried out by thermal ionization mass spectrometry using the traditional and the total evaporation methods. The uncertainties of the measurement results were evaluated according to the recommendations of the ISO guide to the expression of uncertainty in measurement. They were then compared to the requirements of the IAEA international target values for measurement uncertainties in safeguarding nuclear materials.
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1. Introduction

Thermal ionization mass spectrometry (TIMS) is regarded as one of the most precise and accurate techniques for isotope amount ratio measurements. It has long been used for the determination of isotope composition and when isotope dilution is applied, the concentration of uranium samples.

However, the measured isotope ratios always deviate from the isotope ratios of the sample. The reason for this deviation is mainly due the mass discrimination effect [1], which takes place in the sample evaporation, but also in the extraction, transmission and ion detection processes. The lighter isotopes are preferentially evaporated and extracted compared with the heavier isotopes of the element. This phenomenon is temperature dependent and is a function of mass [2].

As it is experimentally extremely difficult to assess the contribution of each source of mass discrimination individu-ally, the overall effect is accounted for using a single factor as defined below [3]

$$K = K_{evap} \times K_{extr} \times K_{trans} \times K_{det} \tag{1}$$

where K is the overall mass discrimination factor, K_{evap}, K_{extr}, K_{trans} and K_{det} are the mass discrimination factors related to the evaporation, ion extraction, ion transmission and ion detection processes, respectively.

The approach to correct the mass discrimination effect using a set of isotope reference materials (IRMs) having different certified isotope amount ratios is based on the following equation [4]:

$$K_i = R_i/r_i \tag{2}$$

where K_i is the mass discrimination factor, R_i the certified isotope amount ratio for the IRM and r_i the measured isotope amount ratio for the IRM used.

In practice, the average value for several IRM samples processed is calculated and then applied to correct the samples

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analyzed, as described below

$$K_{av} = \sum_{i=1}^{i=n} K_i/n \qquad (3)$$

$$R_c = K_{av} \times r_s \qquad (4)$$

where K_{av} is the average mass discrimination factor, R_c the corrected isotope amount ratio for the sample and r_s the measured isotope amount ratio for the sample.

Uranium isotope amount ratio measurements are usually carried out in TIMS using either the traditional or the total evaporation method. The difference between these methods is that the former just uses a small part of the sample and the latter uses the entire sample deposited onto the filament.

In the classical or traditional method, the isotope ratio is changing during the measurement due to the preferential evaporation of lighter isotopes [1]. The measurement is performed in just a limited period of the sample evaporation and all parameters such as sample size, chemical form, filament material and temperature, heating pattern and analysis time should be tightly controlled to reproduce the same fractionation behaviour. This is an important condition for applying the K-factor obtained from measurements of the reference materials to correct the measurements of the sample in a proper way [2,3].

The total evaporation method first introduced by Romkowski [5] combined the total evaporation of the sample with multiple ion collection and simultaneous integration of the ion signal from each isotope. Thus, this method is based on idea that if all atoms present in the sample are evaporated, ionised and collected, no bias should be introduced in the measurement.

In further developments of the total evaporation method, $n(^{235}U)/n(^{238}U)$ isotope amount ratio measurement results were reported in which small deviations from certified values were found in the range of 0.01–0.04% [6]. It was claimed that the method was insensitive to sample size and drying procedures and, above all, did not require the use of IRMs to correct for the mass discrimination effect.

The influence of the experimental parameters was also investigated and it was shown that the method could be used even for very small samples sizes (1 ng), that the sample drying procedure did not exert a great influence but more than 30 scans was really needed to get accurate measurement results [7].

Finally, recognizing the presence of a small residual bias in very precise measurements, with relative standard deviation (R.S.D.) below 0.01%, a modification of the classical total evaporation method has been proposed, applying a correction factor for the residual mass discrimination effect [8]. The causes of this residual mass discrimination were reported to be the time-dependent drift in isotope ratios in combination with changes in the ionization efficiency and ion transmission during the measurement.

Besides TIMS, several other mass spectrometry techniques can perform reliable uranium isotope ratio measurements with precisions in the range of 0.50–0.01% [9]. For instance, laser ionization mass spectrometry (LIMS), resonance ionization mass spectrometry (RIMS), glow discharge mass spectrometry (GDMS), spark source mass spectrometry (SSMS), secondary ion mass spectrometry (SIMS), gas source mass spectrometry (GSMS) and inductively coupled plasma mass spectrometry (ICPMS) [10]. In spite of that, TIMS, GSMS and ICPMS techniques are recognized to provide measurements results with the highest precision [11].

The GSMS technique relies in the very efficient electron impact ion source, which enables $n(^{235}U)/n(^{238}U)$ isotope amount ratio measurements with precisions of less than 0.01% [11]. However, just samples in the form of gas can be introduced in the inlet system. This is the case of uranium hexafluoride (UF_6), the compound used in the uranium isotope enrichment process.

The ICPMS technique, which relies on instruments having an ICP ion source, has presented a great instrumental development in the last two decades with the utilization of different sample introduction, ion separation and ion detector systems [12]. A study compared the performance of three important instrument configurations [13] and showed that the simplest instrument version, the quadrupole inductively coupled plasma mass spectrometer (ICP-QMS), provided measurements results with precisions in the range of 0.10–0.35%, the magnetic analyser single collector instrument (HR-ICPMS) precisions values around 0.05% and the multi collector instrument (MC-ICPMS) precision values around 0.02%.

Analytical laboratories worldwide are now being asked to be accredited as an impartial demonstration to the public that they carry on their tasks accordingly. Many accreditation bodies use the ISO 17025 standard [14] for the accreditation process of calibration and testing laboratories. In this standard there is a requirement for applying a procedure to evaluate the uncertainty of measurement.

Therefore, the first goal of this work is to measure the $n(^{235}U)/n(^{238}U)$ isotope amount ratio in a set of samples by TIMS using the traditional and the total evaporation methods. The evaluation of the measurement uncertainties will be carried out using the ISO GUM [15], as required by ISO 17025. The second goal is to verify the compliance with the requirements of the international target values for measurement uncertainties (ITV 2000) [16], as set up by the nuclear materials safeguards authority, the international atomic energy agency (IAEA).

2. Experimental

2.1. Instrumentation

Isotope amount ratios were measured using a thermal ionization mass spectrometer model MAT 262 manufactured by Finnigan MAT (Bremen, Germany). The sample magazine

has 13 positions where the rhenium double filaments were assembled. A set of electrostatic lenses is used to extract and collimate the ions accelerated at a 10 kV voltage. The instrument has a 90° magnetic sector with 23 cm radius with asymmetric and extended geometry design that gives a mass dispersion of 64 cm radius sector. The multi-collector system is assembled with six Faraday cups coupled to a $10^{11}\,\Omega$ resistor each. The $^{235}U^+$ and $^{238}U^+$ ion-beams were collected simultaneously in the static configuration mode. Although a secondary electron multiplier (SEM) is also available in the instrument for ion counting measurements, it was not used in this work. The mass range is from 1 to 280 u, the mass resolution $(m/\Delta m)$ is higher than 500 at 10% valley definition and the abundance sensitivity is 2.0×10^{-6} at 237 u. The data acquisition uses HP Basic software running in a Microsoft Windows platform.

2.2. Materials

Isotope reference materials IRMM 183, 184, 185, 186 and 187 produced by the European Commission Institute for Reference Materials and Measurements (EC-JRC-IRMM, Geel, Belgium) were used to measure the mass discrimination effect in the spectrometer during the sample analyses.

A set of samples ranging from 0.5 to 20.0 wt.% of ^{235}U originally in the form of uranium hexafluoride (UF$_6$) were first analyzed by gas source mass spectrometry (GSMS). They were then converted to uranyl nitrate (UO$_2$(NO$_3$)$_2$) to allow the measurements by TIMS.

Samples and isotope reference materials were prepared in 1 M HNO$_3$ at the concentration of 5.0 μg/μL for the traditional and 0.20 μg/μL for the total evaporation method. As an aliquot of 1.0 μL was loaded onto the filaments, approximately 5.0 μg of uranium was deposited for the traditional method and 0.2 μg for the total evaporation method.

2.3. Procedure

The filaments used in this work were made of zone-refined rhenium because of the high ionization efficiency and very low uranium background featured by this material. They were previously degassed under high vacuum for 3 h.

A set of five filaments was assembled in the filament-loading device. Then a sample drop (1.0 μL) was carefully deposited onto the filaments and the heating current was set in three consecutive steps: 0.5 A for a period of 300 s, 1.0 A for 60 s and 1.5 A for 10 s. In this way the deposited (UO$_2$(NO$_3$)$_2$) sample was converted into UO$_3$, a much more refractory compound that only evaporates at a higher temperature.

The analysis of each sample started with the typical calibration routines for the instrument comprising magnet mass, baseline and amplifier gain calibration. The baseline was measured at 233.5 u.

For the traditional method, an electric current was set to the ionization filament to generate for $^{187}Re^+$ approximately a

Table 1
Experimental parameters used in the TIMS measurements

Parameter	Method applied	
	Traditional	Total evaporation
Number of blocks	10	1
Number of scans per block	5	50
Integration time (s)	8	4
Delay time (s)	4	4
Sample size (μg)	5	0.2

100 mV signal intensity required for focusing and peak centering routines. The temperature in this filament was kept constant at about 2000 °C throughout the measurement process to provide a stable ionization condition. Then a current of 1.5–2.0 A was carefully and slowly set for the evaporation filament to generate a 5.0 V signal intensity for $^{238}U^+$. After some stabilization time, routines for focusing, peak centering, zeroing and drift checks were carried out without changing the filaments currents.

For the total evaporation method, the same procedure was applied to the ionization filament. But for the evaporation filament, the current was initially set to around 1.0 A to generate a small signal intensity for $^{238}U^+$. The current was then increased carefully to generate a signal necessary for focusing and peak centering routines, typically about 100 mV. Then the measurement started and the $^{238}U^+$ signal intensity soon reached about 7.0 V, a value that provided a good signal to noise ratio without any possible problem of amplifier saturation. The evaporation current was constantly increased to keep this intensity level throughout the measurement process. The analysis ended when the intensities fell below the preset value of 10 mV, when the sample on the filament was extinguished.

The experimental parameters used in this work are presented in Table 1.

The multi-collector system in TIMS always measured the signal intensities for all uranium isotopes, which allowed several ratios to be automatically calculated. Nevertheless this work was just focused in the $n(^{235}U)/n(^{238}U)$ isotope amount ratio because this is the value of major concern for the safeguards of nuclear material and consequently for the ITV 2000 document. The measurement of $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope amount ratios is more complex and require several corrections to provide accurate measurement results. For this reason, an experimental work using different mass spectrometers and monitoring all uranium isotope ratios was carried out recently and the data will be published soon.

3. Results and discussion

The uncertainty of all measurement results was evaluated according to the recommendations of the ISO GUM, which

has been adopted in many fields of the measuring science including the chemical measurement.

This new approach recognises that the uncertainty of a measurement result is composed by several components that can be grouped in two categories: those evaluated by statistical methods (Type A) and those evaluated by other means (Type B). It was very common practice in the past to report the uncertainty of a measurement as just the repeatability of many observations (Type A), which in many cases led to small but unrealistic uncertainty values.

The ISO GUM also requires the statement of a mathematical model for the measurement to transform the set of repeated observations into a measurement result. Other quantities that can influence the result can be included in this model. In this work, the evaluation of the uncertainty was carried out in practice with the help of the dedicated software GUM Workbench Pro 2.3.6. [17].

For the traditional method, 24 filaments containing the reference materials IRMM 183–187 were processed, which enabled the determination of the K-factor according to Eqs. (2) and (3). The uncertainty of the K-factor considered both the uncertainty of the IRMs and the uncertainty of the measured isotope amount ratio. Thus the average mass discrimination factor (K_t) was calculated as 0.99765 ± 0.00079 (0.080%, $k = 2$). The standard deviation (S.D.), standard com-

bined uncertainty (u_c) and the expanded uncertainty (U) of this experimental data were calculated according to the ISO GUM and are presented in Table 2.

For the total evaporation method, 42 filaments containing the reference materials IRMM 183–187 were processed and following the same procedure applied to the traditional method, the average mass discrimination factor (K_{av}) was calculated as 0.99971 ± 0.00018 (0.018%, $k = 2$).

In order to provide a comparison of performances, the K-factors experimentally obtained are presented in Fig. 1 for traditional and in Fig. 2 for the total evaporation method.

Based on the data and figures presented, it is clear that the average mass discrimination factor provided by the total evaporation has a lower relative uncertainty value (0.018%) than that provided by the traditional method (0.080%).

The application of the correction for the mass discrimination effect in the traditional method was carried out by means of Eq. (4). The average of six isotope ratio measurements for each sample was multiplied by the average mass discrimination factor (K_t) as presented in Table 3.

In this work the GSMS technique was selected to provide the reference values for the $n(^{235}U)/n(^{238}U)$ isotope amount ratios based on two facts. First, it is the technique, which provides the measurement results with the smaller uncertainties, as it will be shown below. Second, the reliability of this

Table 2
IRMM isotope reference materials used, certified, measured isotope amount ratio measurements and calculated K factors for TIMS using the traditional method

Number	IRMM	Certified isotope ratio $n(^{235}U)/n(^{238}U)$	Measured isotope ratio $n(^{235}U)/n(^{238}U)$	K
1	184	0.0072623 (11)	0.0072887 (44)	0.99638
2	185	0.0200552 (30)	0.020055 (12)	1.00001
3	186	0.0307711 (46)	0.030836 (19)	0.99790
4	187	0.0473250 (70)	0.047468 (28)	0.99699
5	183	0.00321570 (80)	0.0032306 (19)	0.99539
6	184	0.0072623 (11)	0.0072770 (44)	0.99798
7	184	0.0072623 (11)	0.0072740 (44)	0.99839
8	185	0.0200552 (30)	0.020087 (12)	0.99844
9	184	0.0072623 (11)	0.0072784 (44)	0.99778
10	185	0.0200552 (30)	0.020135 (12)	0.99604
11	185	0.0200552 (30)	0.020065 (12)	0.99951
12	186	0.0307711 (46)	0.030939 (19)	0.99459
13	187	0.0473250 (70)	0.047293 (28)	1.00068
14	187	0.0473250 (70)	0.047533 (29)	0.99562
15	187	0.0473250 (70)	0.047486 (28)	0.99661
16	187	0.0473250 (70)	0.047637 (29)	0.99345
17	186	0.0307711 (46)	0.030840 (19)	0.99777
18	187	0.0473250 (70)	0.047313 (28)	1.00025
19	185	0.0200552 (60)	0.020057 (12)	0.99991
20	187	0.0473250 (70)	0.047355 (28)	0.99937
21	187	0.0473250 (70)	0.047535 (29)	0.99558
22	186	0.0307711 (46)	0.030800 (18)	0.99908
23	186	0.0307711 (92)	0.030790 (18)	0.99939
24	187	0.0473250 (70)	0.047493 (28)	0.99646
Average				0.99765
S.D.				0.00195
u_c ($k = 1$)				0.00040
U ($k = 2$)				0.00079
U (%)				0.080

The combined standard uncertainties (u_c) are presented in parenthesis ($k = 1$). The expanded uncertainty (U) was calculated using $k = 2$.
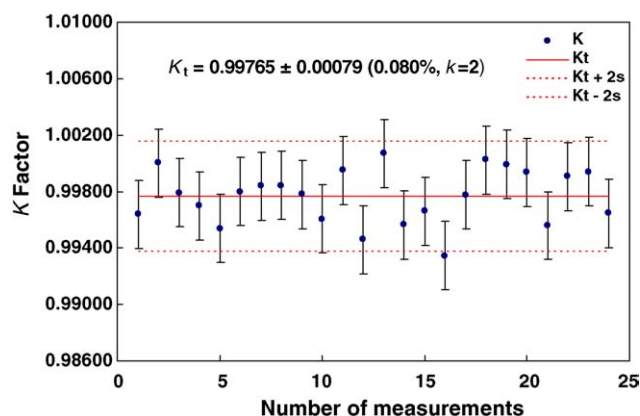
Fig. 1. Mass discrimination factor plus expanded uncertainty ($k = 2$) for the measurements carried out by TIMS using the traditional method.
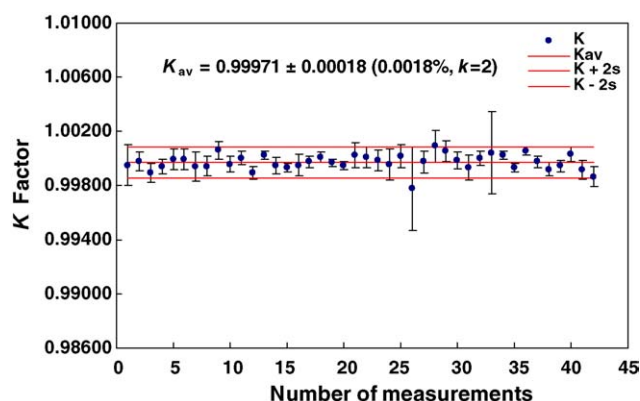

Fig. 2. Mass discrimination factor plus expanded uncertainty ($k = 2$) for the measurements carried out by TIMS using the total evaporation method.

measurement has been demonstrated in several international inter-comparison programmes involving the most important nuclear laboratories around the world [19,20].

The reference values provided by GSMS and the results provided by both TIMS methods are presented in Table 4.

Table 3
Measured isotope amount ratios, average mass discrimination factor (K_t) and corrected isotope amount ratio for sample 4 using TIMS with the traditional method

Number	Measured ratio $n(^{235}U)/n(^{238}U)$	K_t	Corrected ratio $n(^{235}U)/n(^{238}U)$
1	0.035530 (43)	0.99765 (40)	
2	0.035495 (43)		
3	0.035497 (43)		
4	0.035518 (43)		
5	0.035532 (43)		
6	0.035598 (43)		
Average	0.035529		0.035445
S.D.	0.000038		
u_c ($k = 1$)	0.000015		0.000021
U ($k = 2$)			0.000042

The combined standard uncertainties (u_c) are presented in parenthesis ($k = 1$) and the expanded uncertainty (U) is calculated with $k = 2$.
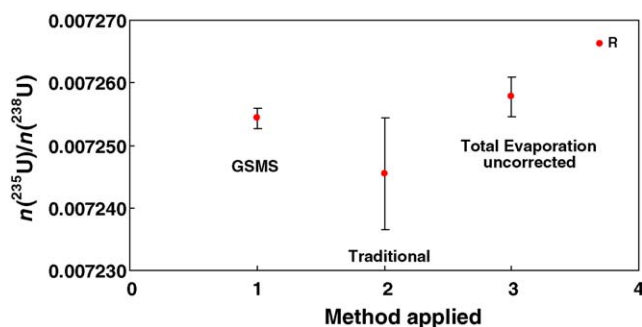

Fig. 3. Isotope amount ratio plus expanded uncertainties ($k = 2$) provided by GSMS, TIMS traditional and uncorrected total evaporation methods for sample 2.

The values in parenthesis represent the combined standard uncertainties (u_c) ($k = 1$) and apply to the last digits of the measurement results. It is important to note that the isotope amount ratio values presented in Table 4 are the average of six measurement results for the GSMS and both TIMS methods.

In order to verify the existence of a deviation, the relative difference between the reference values provided by GSMS and each TIMS method was calculated and expressed as percentage. The expanded uncertainty ($k = 2$) of the deviation is indicated in parenthesis and apply to the last digits of the results.

Some important observations can be made from the data presented in Table 4. The first one is that all the three methods provided comparable measurement results within their stated uncertainties.

However, the GSMS method always provided results with the lowest standard combined uncertainty (u_c). The second observation is that the total evaporation method without correction for mass discrimination provided measurement results with uncertainties two to three times smaller than the traditional method. Examples of measurement results from these three techniques are given in Figs. 3 and 4.

The measurement results for both the traditional and the total evaporation methods showed no evidence of a deviation
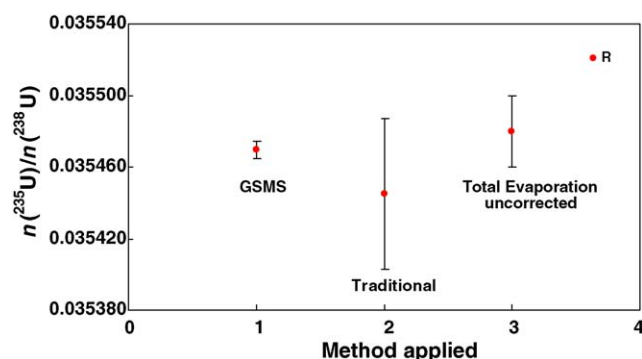

Fig. 4. Isotope amount ratio plus expanded uncertainties ($k = 2$) provided by GSMS, TIMS traditional and uncorrected total evaporation methods for sample 4.

Table 4

Measurement results for the $n(^{235}U)/n(^{238}U)$ isotope amount ratio provided by GSMS and TIMS using the traditional (corrected) and the total evaporation methods (data not corrected for mass discrimination) and its standard combined uncertainties (u_c)

Sample	GSMS $n(^{235}U)/n(^{238}U)$ (reference values)	TIMS $n(^{235}U)/n(^{238}U)$ (traditional method)	Deviation, % ($k = 2$)	TIMS $n(^{235}U)/n(^{238}U)$ (total evaporation)	Deviation, % ($k = 2$)
1	0.00535473 (85)	0.0053481 (35)	0.12 (13)	0.00535598 (92)	−0.023 (47)
2	0.00725430 (80)	0.0072454 (45)	0.12 (13)	0.0072577 (16)	−0.047 (49)
3	0.0242320 (21)	0.024222 (13)	0.04 (11)	0.0242344 (55)	−0.010 (49)
4	0.0354698 (24)	0.035445 (21)	0.07 (12)	0.035480 (10)	−0.029 (59)
5	0.25442 (14)	0.25423 (18)	0.07 (18)	0.254279 (96)	0.056 (133)

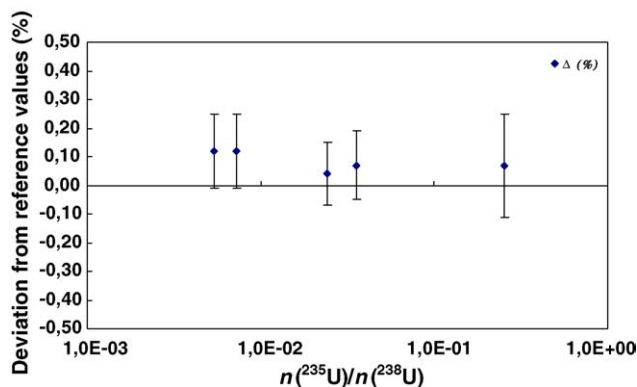The deviation from reference values provided by GSMS is presented with their expanded uncertainties in parenthesis ($k = 2$).

Fig. 5. Deviation from reference values plus expanded uncertainties ($k = 2$) for TIMS traditional method for the five samples of the set.

Fig. 7. Deviation from reference values plus expanded uncertainties ($k = 2$) for TIMS total evaporation method after the mass discrimination correction for the five samples of the set.

from reference values. The uncertainty of the deviation was always larger the deviation value itself, as can also be seen in Table 4 and in Figs. 5 and 6.

Nevertheless, the average mass discrimination value obtained using the total evaporation method ($K_{av} = 0.99971 \pm 0.00018$) revealed that there was still a small residual mass discrimination effect. A correction was applied by means of Eq. (4) and the final results are presented in Table 5.

The results presented in Table 5 shows that the correction applied only slightly changed the isotope amount ratio values and its standard combined uncertainties. The values of uncertainties increased for all samples as one more cor-
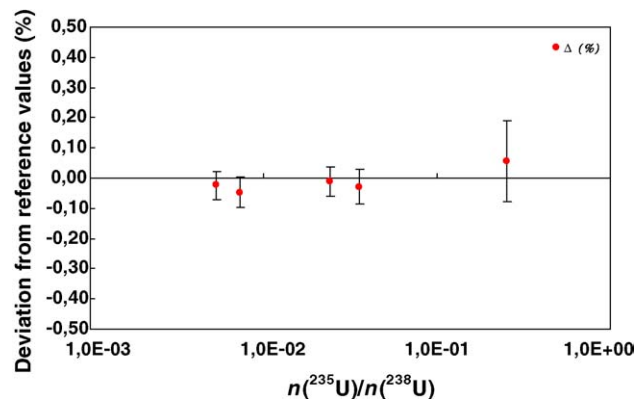

Fig. 6. Deviation from reference values plus expanded uncertainties ($k = 2$) for TIMS total evaporation method before the mass discrimination correction for the five samples of the set.
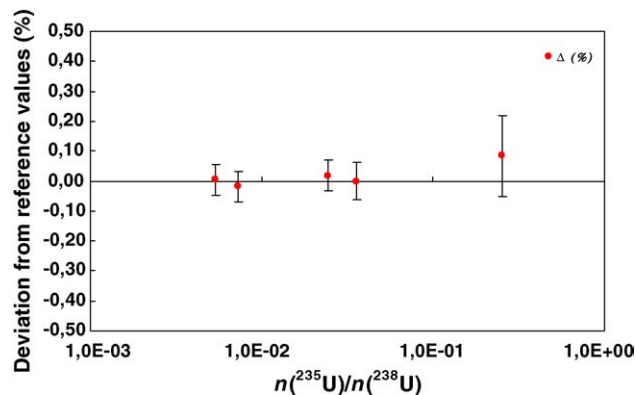
rection operation was added to the uncertainty budget of the samples. Finally it shows that the deviation values remained insignificant within the stated uncertainties.

The application of such correction did not change significantly the measurement results, as it can be easily checked comparing Figs. 6 and 7. But since a bias was detected in the measurements of the reference materials IRMM 183–187, it has to be corrected and the measurement uncertainty revaluated as it was done in this work.

Thus in the light of the current knowledge there is no hint of other additional effects that could have been affecting the measurements carried out using the total evaporation method. Therefore the mathematical model proposed here is believed to represent well the real measurement process.

It is of great interest to see if the uncertainty values for the methods described meet the requirements of the international safeguards system managed by the IAEA. The ITV 2000 lists several analytical techniques used in nuclear safeguards as well as its target uncertainties. This document was first published in 1983 last updated in 2001 [16].

The target values are defined as measurement uncertainties to be considered in judging the reliability of analytical techniques to be applied in safeguarding nuclear fissile materials. They are very important to the analyst because they present a goal to be reached in routine measurements. Thus the analytical instrumentation and the procedures selected must allow the achievement of the "target measurement uncertainty", as this concept is now being expressed [18].

Table 5
Measurement results for the $n(^{235}U)/n(^{238}U)$ isotope amount ratio provided by GSMS and TIMS using total evaporation method with uncorrected and corrected data for the mass discrimination

Sample	GSMS $n(^{235}U)/n(^{238}U)$ (reference values)	TIMS $n(^{235}U)/n(^{238}U)$ (total evaporation, uncorrected data)	Deviation, % ($k=2$)	TIMS $n(^{235}U)/n(^{238}U)$ (total evaporation, corrected data)	Deviation, % ($k=2$)
1	0.00535473 (85)	0.00535598 (92)	−0.023 (47)	0.0053544 (10)	0.005 (51)
2	0.00725430 (80)	0.0072577 (16)	−0.047 (49)	0.0072556 (17)	−0.018 (52)
3	0.0242320 (21)	0.0242344 (55)	−0.010 (49)	0.0242273 (59)	0.019 (52)
4	0.0354698 (24)	0.035480 (10)	−0.029 (59)	0.035470 (10)	0.000 (61)
5	0.25442 (14)	0.254279 (96)	0.056 (133)	0.254205 (98)	0.085 (134)

The deviation from reference values provided by GSMS is presented with their expanded uncertainties in parenthesis ($k=2$).

Table 6
Requirements for standard uncertainties in the ITV 2000 document

Material	^{235}U abundance	Standard uncertainty		
		Systematic, u_s (%)	Random, u_r (%)	Combined, u_c (%)
Depleted uranium	<0.3 wt.% ^{235}U	0.5	0.5	0.71
U	0.3% < ^{235}U < 1%	0.2	0.2	0.28
Low enriched uranium	1% < ^{235}U < 20%	0.1	0.1	0.14
High enriched uranium	>20 wt.% ^{235}U	0.05	0.05	0.07

Table 7
ITV 2000 requirements for combined standard uncertainties (u_c) and the values determined using TIMS traditional and the total evaporation methods with data corrected for mass discrimination

^{235}U abundance	ITV 2000, u_c (%)	Traditional, u_c (%)	Total evaporation, u_c (%)
0.3% < ^{235}U < 1%	0.28	0.06	0.02
1% < ^{235}U < 20%	0.14	0.05–0.07	0.02–0.04

The uncertainty requirements for uranium measurements carried out by TIMS are defined in the ITV 2000 according to the ^{235}U abundance range of the sample as presented in Table 6.

The IAEA safeguards document is developed in such a way to preserve the use of terms like systematic (u_s) and random (u_r) components of the uncertainty, although this terminology is avoided in the ISO GUM. It is stated in ITV 2000 that the combination of these two components results in a value equivalent to the combined standard uncertainty (u_c) as defined by the referred guide. It also allows the inclusion of an uncertainty component related to the sampling process, which has not been done in this work.

The measurement results presented in Tables 4 and 5 were expressed as isotope amount ratios and were converted to isotope abundances for comparison with the ITV values. The comparison between the experimentally determined combined standard uncertainties produced by the traditional and the total evaporation methods and the safeguards requirements as given in ITV 2000 are presented in Table 7.

The data presented in Table 7 clearly demonstrates that both methods described in this work comply with the IAEA safeguards requirements. Provided full adherence to the written instructions is observed, the quoted measurement uncertainties for nuclear materials can be easily achieved. This also means that the analytical instrumentation and procedures used are fit to the declared purpose.

As there were no samples in the set with abundances lower than 0.3% and higher than 20.0 wt.%, no conclusions could be drawn for these categories. Nevertheless it seems reasonable to expect that the requirements can also be easily met.

Finally the ISO GUM makes a recommendation concerning the expression of the uncertainty associated to a measurement result. The uncertainty value must be presented as expanded uncertainty (U) which is obtained by multiplying the combined standard uncertainty (u_c) by a coverage factor (k), usually 2. Therefore the final measurement results for the $n(^{235}U)/n(^{238}U)$ isotope amount ratio provided by TIMS using the traditional and the total evaporation method are presented in Table 8. The values in parenthesis are expanded uncertainties (U) ($k=2$) and applies to the last digits of the

Table 8
Final results for the $n(^{235}U)/n(^{238}U)$ isotope amount ratio provided by TIMS using traditional and total evaporation methods both with data corrected for mass discrimination

Sample	TIMS $n(^{235}U)/n(^{238}U)$ (traditional, corrected data)	U, % ($k=2$)	TIMS, $n(^{235}U)/n(^{238}U)$ (total evaporation, corrected data)	U, % ($k=2$)
1	0.0053481 (69)	0.13	0.0053544 (21)	0.039
2	0.0072454 (89)	0.12	0.0072556 (34)	0.047
3	0.024222 (26)	0.11	0.0242273 (12)	0.049
4	0.035445 (42)	0.12	0.035470 (21)	0.059
5	0.25423 (35)	0.14	0.254205 (20)	0.077

The values of the expanded uncertainties (U) are in parenthesis ($k=2$).

measurement results. The relative expanded uncertainties values ($U\%$) are also presented.

4. Conclusions

This study confirmed the fact that $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurements using thermal ionization mass spectrometry can be performed accurately using either the traditional or the total evaporation methods described in this work.

Measurements carried out using the traditional method provided isotope amount ratios with relative expanded uncertainties in the range of 0.11–0.14% and with the total evaporation method uncertainties in the range of 0.039–0.077% for samples having 0.50–20.0 wt.% of ^{235}U. The measured isotope amount ratios of both methods were corrected for the mass discrimination effect.

A mass discrimination effect could still be detected in the total evaporation measurements but it was much less pronounced than that found when the traditional method was employed.

The total evaporation method proved to be a more reliable analytical method because it consistently provided isotope ratio measurements results with combined standard uncertainties two to three times lower than the traditional method.

Finally it was concluded that the isotope ratio measurements performed by thermal ionization mass spectrometry using both the traditional and the total evaporation methods comply with the requirements expressed by the IAEA nuclear safeguards system for depleted, natural and low-enriched materials.

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References

[1] J.R. De Laeter, Mass Spectrom. Rev. 7 (1988) 71.
[2] E.L. Garner, L.A. Machlan, W.R. Shields, Standard Reference Materials: Uranium Isotopic Standard Reference Materials, National Bureau of Standards, NBS Special Publication 260-27, Department of Commerce, Washington DC, USA, 1971.
[3] D.H. Smith, in: C.M. Barshick, D.C. Duckworth, D.H. Smith (Eds.), Inorganic Mass Spectrometry: Fundamentals and Applications, Marcel Dekker, Inc., New York, USA, 2000, pp. 1–27.
[4] P. De Bièvre, in: N.R. Daly (Ed.), Advances in Mass Spectrometry, vol. 7A, The Institute of Petroleum, London, UK, 1978, pp. 395–447.
[5] M. Romkowski, S. Franzini, L. Koch, Proceedings of the Eighth Annual ESARDA Symposium, London, UK, 1987.
[6] E.L. Callis, R.M. Abernathy, Int. J. Mass Spectrom. 103 (1991) 93.
[7] R. Fiedler, Int. J. Mass Spectrom. 146–147 (1995) 91.
[8] S. Richter, S.A. Goldberg, Int. J. Mass Spectrom. 229 (2003) 181.
[9] J.S. Becker, J. Anal. Atom. Spectrom. 17 (2002) 1172.
[10] J.S. Becker, H.J. Dietze, Int. J. Mass Spectrom. 197 (2000) 1.
[11] I.T. Platzner (Ed.), Modern Isotope Ratio Mass Spectrometry, Willey, Chichester, UK, 1997, pp. 363–377.
[12] J.W. Olesik, in: C.M. Barshick, D.C. Duckworth, D.H. Smith (Eds.), Inorganic Mass Spectrometry: Fundamentals, Applications, Marcel Dekker, Inc., New York, USA, 2000, pp. 67–158.
[13] C.R. Quétel, J. Diemer, in: P.A. De Groot (Ed.), Handbook of Stable Isotope Analytical Techniques, vol. 1, Elsevier, Amsterdam, 2004, pp. 727–745.
[14] General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC 17025, Geneva, Switzerland, 1999.
[15] Guide to the Expression of Uncertainty in Measurements, 2nd ed., International Organization for Standardization, Geneva, Switzerland, 1995.
[16] E. Kuhn, R. Binner, H. Aigner et al., International Target Values 2000 for Measuring Uncertainties in Safeguarding Nuclear Materials, International Atomic Energy Agency, Report STR-327, Vienna, Austria, 2001.
[17] GUM Workbench, Metrodata, Germany, http://www.metrodata.de.
[18] P. De Bièvre, Accred. Qual. Assur. 9 (2004) 589.
[19] K. Mayer, W. De Bolle, A. Alonso, M. Blanco, P. De Bièvre, REIMEP uranium hexafluoride. II. Results, evaluation and discussion, in: Proceedings of the 17th Annual ESARDA Symposium, Aachen, Germany, 9–11 May, 1995, pp. 459–467.
[20] A. Alonso, W. De Bolle, A. Verbrugen, R. Wellum, REIMEP 15 uranium isotopic ratios and abundances, Internal Report EUR 19828 (EN), 2001.