International Journal of Mass Spectrometry 299 (2011) 120–124

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

IRMM-3100a: A new certified isotopic reference material with equal abundances of ^{233}U, ^{235}U, ^{236}U and ^{238}U

S. Richter[a,*], A. Alonso-Munoz[a], Y. Aregbe[a], R. Eykens[a], U. Jacobsson[a], H. Kuehn[a], A. Verbruggen[a], R. Wellum[a], S. Bürger[b], S. Boulyga[b], J. Poths[b]

[a] Institute for Reference Materials and Measurements (IRMM), JRC-EU Retieseweg 111, 2440 Geel, Belgium
[b] Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), A-1400 Vienna, Austria

ARTICLE INFO

Article history:
Received 18 August 2010
Received in revised form
29 September 2010
Accepted 29 September 2010
Available online 8 October 2010

Keywords:
Uranium
Isotope ratio
Reference material
Thermal ionization mass spectrometry

ABSTRACT

The new so-called Quad-IRM ("Quadruple Isotope Reference Material") was prepared from highly enriched ^{233}U, ^{235}U, ^{236}U and ^{238}U isotopic materials using an optimized combination of gravimetrical mixing and mass spectrometry. Within the mixing process the isotope ratios were adjusted to about $n(^{233}\mathrm{U})/n(^{235}\mathrm{U})/n(^{236}\mathrm{U})/n(^{238}\mathrm{U}) = 1/1/1/1$ and certified with expanded relative uncertainties of 0.0054% per mass unit (coverage factor $k = 2$). This new isotope reference material is ideal for verifying the inter-calibration of multi-detector systems in isotope mass spectrometry.

The certified $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio of IRMM-3100a was derived from the mass metrology data of the gravimetrical mixing of highly enriched ^{233}U and ^{236}U materials. It was verified by thermal ionization mass spectrometry (TIMS) measurements using the classical total evaporation (TE) and modified total evaporation (MTE) methods. The $n(^{234}\mathrm{U})/n(^{236}\mathrm{U})$, $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios were then determined by TIMS using the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio for internal normalization and using a multi-dynamic measurement procedure in order to circumvent any possible influence and uncertainties from Faraday cup efficiencies and amplifier gain factors. The certified $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios were additionally verified using the classical and modified total evaporation methods using two TIMS instruments at IRMM and one TIMS instrument at IAEA-SGAS. The verification data can be regarded as results obtained at three independent instruments at two different nuclear safeguards laboratories.

1. Introduction

There is a well recognized need for certified isotopic reference materials of uranium in nuclear safeguards and forensics analysis as well as in other associated scientific disciplines. The measurement of uranium by mass spectrometry is a special challenge because of the comparably wide dynamic range of the isotope abundances typically found in nature as well as in uranium undergoing isotopic changes within the nuclear fuel cycle. For nuclear safeguards and forensics purposes high precision isotopic measurements are needed. The accuracy, reliability, and traceability of such measurements depend heavily on suitable isotope reference materials. The reference materials programme at IRMM was started in the 1980s with the preparation of the IRMM-072 series [1,2]. The IRMM-072 series was prepared from purified, enriched uranium isotopic materials: ^{233}U, ^{235}U and ^{238}U. The set was designed in particular for the evaluation of mass-spectrometer linearity. After the supplies of the original IRMM-072 material became exhausted the replacement series IRMM-074 was prepared and certified in 2005 [3].

In 2007 the new "double spike" isotope reference material, IRMM-3636, followed [4], which is a synthetic reference material produced by gravimetrically mixing a highly enriched (99.96%) spike of ^{233}U with a highly enriched (99.97%) spike of ^{236}U. The double spike IRMM-3636 is an isotope mixture with a certified $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio close to unity with a relative expanded uncertainty of 0.016% (coverage factor $k = 2$). The double spike IRMM-3636 is ideal for high precision measurements of $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ ratios in samples with small ^{236}U abundance, e.g., for natural samples. The advantage of using a $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ double spike lies in the possibility of performing an internal correction for mass fractionation and/or instrumental mass bias effects rather than an external correction using an additional standard measured under, presumably, similar conditions. The IRMM-3636 double spike has already been used widely for investigating fractionation effects and variations observed for uranium samples in nature [5].

Another gravimetrically prepared reference material, the so-called "Quad-IRM" ("Quadruple Isotope Reference Mate-

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* Corresponding author at: Institute for Reference Materials and Measurements (IRMM), IM Unit, JRC-EU Retieseweg 111, 2440 Geel, Belgium. Tel.: +32 14 571701; fax: +32 14 571548.
E-mail address: stephan.richter@ec.europa.eu (S. Richter).

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doi:10.1016/j.ijms.2010.09.034

rial") IRMM-3100a, was prepared utilizing the same ^{233}U and ^{236}U materials as used for IRMM-3636 in combination with additional highly enriched components of ^{235}U and ^{238}U. The isotopic composition was adjusted to be close to $n(^{233}\text{U})/n(^{235}\text{U})/n(^{236}\text{U})/n(^{238}\text{U}) = 1/1/1/1$ in order to make this reference material suitable for verifying the inter-calibration of Faraday multi-collectors or multiple ion-counting detectors in TIMS and MC-ICP-MS instruments.

In the past only very few reference materials similar to IRMM-3100a have been prepared, e.g., the "Khlopin standard", which is used at the IAEA as a quality control sample, for instance for checking Faraday cup efficiencies during routine safeguards measurements. However, because the supplies of this material are almost exhausted and the uncertainties were considered too large, the preparation of a new reference material with similar isotopic composition and lower uncertainties was proposed by the IAEA and asked for by the community. The IAEA provided the highly enriched ^{236}U material needed for this project.

In this paper the preparation, certification and verification of the original "Quad-IRM" mixture IRMM-3101 and a 10-fold dilution of it, labelled IRMM-3100a, is described. The application of the new material for isotope mass spectrometry, in particular for quality control in nuclear safeguards measurements, is also discussed.

2. Preparation and verification of IRMM-3101 and IRMM-3100a

The unique characteristics of IRMM-3100a are the high isotopic enrichment of the ^{233}U, ^{235}U, ^{236}U and ^{238}U isotopic starting materials and the specific preparation technique. The original so-called "Quad-IRM"-mixture, labelled IRMM-3101, was made gravimetrically by dissolving weighable amounts of highly enriched oxides and mixing the resulting solutions in the desired proportions gravimetrically. Prior to mixing, the ^{233}U, ^{235}U, ^{236}U and ^{238}U starting materials were purified using the same reagents and procedures, which involved anion exchange in nitric acid medium, cation exchange in HNO_3/THF and precipitation as peroxide. The purified ^{233}U, ^{235}U, ^{236}U and ^{238}U starting materials were calcined under identical conditions of temperature and humidity in order to form U_3O_8 and to ensure that all enriched materials reach the same stoichiometry. The purified and calcined ^{233}U, ^{235}U, ^{236}U and ^{238}U oxides were weighed and dissolved in nitric acid and the solutions were then mixed gravimetrically resulting in the Quad-IRM, IRMM-3101. The isotopic composition of IRMM 3101 was calculated based on the weights of the ^{233}U, ^{235}U, ^{236}U and ^{238}U oxides with correction for the measured impurity levels, the weights of the subsequent solutions, and the isotopic compositions of the four components measured by TIMS. Because of the high isotopic enrichments of the starting materials, the uncertainties of their isotopic compositions measured by TIMS did not contribute significantly to the calculation of the isotope ratios of the Quad-IRM. The original Quad-IRM mixture IRMM-3101 was prepared with an uranium concentration of 1 mg/g. The diluted IRMM-3100a has an uranium concentration of 0.1 mg/g; it is stored and provided to customers in ampoules of quartz glass in 1 mL units. After dilution of IRMM-3101 into IRMM-3100a additional verification measurements were performed, as described further below. Only the diluted IRMM-3100a is available for purchase from IRMM; the original IRMM-3101 is exhausted.

Originally the intention was to certify all isotope ratios based on gravimetrically mixing of the ^{233}U, ^{235}U, ^{236}U and ^{238}U starting materials in a 1/1/1/1 proportion. However, a different approach was followed which promised to provided even smaller uncertainties for the $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ ratios of IRMM-3101 and IRMM-3100a.

Just prior to the preparation of IRMM-3101, the same highly enriched ^{233}U and ^{236}U starting solutions were also used to prepare the double spike IRMM-3636, for which the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio has been verified successfully at a level of 0.003(22)% (coverage factor $k = 2$) for the relative deviation from the certified value [4]. This measurement was done by thermal ionization mass spectrometry (TIMS) using the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of 1.00026(15) of the IRMM-074 reference material [3] for internal normalization. Therefore, as the properties of the starting materials have been proven to be under control, it can be assumed that the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio for the Quad-IRM IRMM-3101 should be certified by the value calculated from the gravimetrical mixing of ^{233}U and ^{236}U as well. The major contributors to the final uncertainty of this gravimetrical $n(^{233}\text{U})/n(^{236}\text{U})$ isotope ratio identified during the preparation of IRMM-3101 were the uncertainties from the weighings of the mixture, uncertainties on the isotopic composition of the starting solutions of ^{233}U and ^{236}U, the chemical impurities and the stoichiometry. The uncertainties were calculated according to the principles described in "Guide to the Expression of Uncertainty in Measurements ("GUM", [6]) and using the GUM Workbench software [7], in a similar way as for the IRMM-074 series [3] and for IRMM-3636 [4]. The calculated value for the $n(^{233}\text{U})/n(^{236}\text{U})$ isotope ratio is 1.01990 with a relative expanded uncertainty of 0.016% ($k = 2$). This relative expanded uncertainty is equal to the uncertainty of the IRMM-3636 double spike [4], not surprising, because they were prepared using same techniques and similar amounts of the same starting materials.

Verification measurements for the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio were performed using two Thermo Fisher Scientific TRITON multi-collector TIMS instruments at IRMM and one TRITON TIMS instrument at IAEA-SGAS, using two different methods: the "classical" total evaporation method (TE) and the "modified total evaporation" method (MTE) [8,9]. The reference material IRMM-074/10 [3] was used for external calibration at IRMM. At IAEA-SGAS the reference material IRMM-072/15 [1] was used. The results from IAEA-SGAS were re-normalized to IRMM-074/10 to allow for all verification measurements to be traceable to the same reference material for better comparison. To enable this re-normalization, comparative measurements of IRMM-074/10 and IRMM-072/15 using the $n(^{233}\text{U})/n(^{236}\text{U})$ double spike IRMM-3636 were performed at IRMM.

The results of the verification measurements for the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio of IRMM-3101 and IRMM-3100a are presented in Fig. 1a. The agreement within stated uncertainties ($k = 2$) of the measured ratios with the calculated value based on gravimetrical data is apparent for both the original material IRMM-3101 and the diluted material IRMM-3100a. As a conclusion, the gravimetrically calculated $n(^{233}\text{U})/n(^{236}\text{U})$ isotope ratio was verified independently at two different laboratories using two different analytical methods and three different TIMS instruments, providing a high degree of confidence for its use for the certification of the IRMM-3101 and IRMM-3100a materials.

Using this certified $n(^{233}\text{U})/n(^{236}\text{U})$ ratio for internal normalization, the remaining $n(^{234}\text{U})/n(^{236}\text{U})$, $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ ratios were then determined by TIMS using a multi-dynamic measurement procedure, similar to that described in [8] allowing to circumvent possible influences and uncertainties from Faraday cup efficiencies and amplifier gain factors. For the $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ ratios the uncertainties are dominated by the uncertainty contribution from the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio used for the internal normalization. Also for the $n(^{234}\text{U})/n(^{236}\text{U})$ ratio, multi-dynamic measurement data were acquired and used for certification. However, the $n(^{234}\text{U})/n(^{236}\text{U})$ ratio of about 0.00038 is too small to be used for the purpose of a detector inter-calibration. The uncertainty of the $n(^{234}\text{U})/n(^{236}\text{U})$

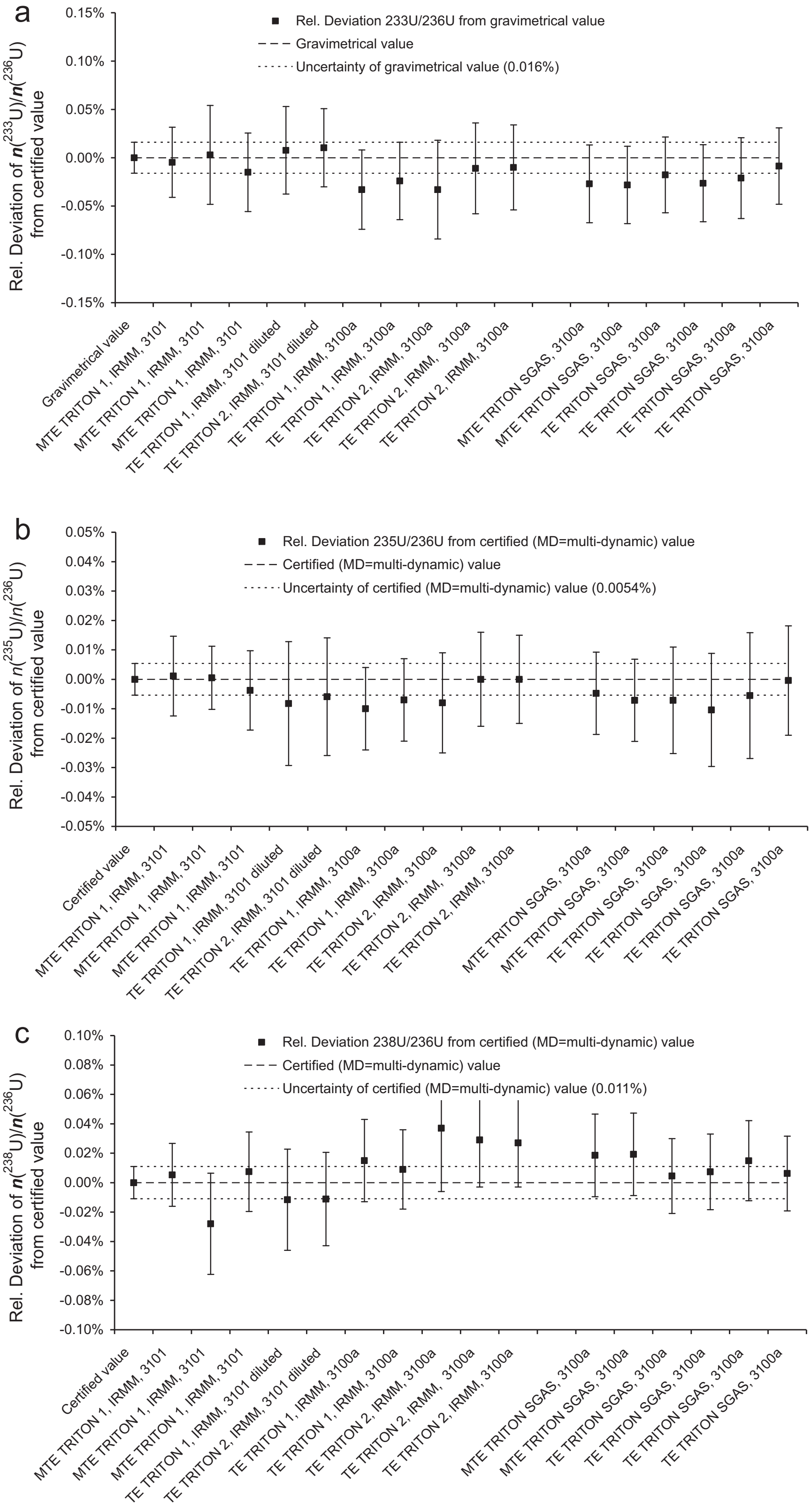

Fig. 1. (a–c) Various verification measurements for the certified isotopic composition of IRMM-3101 and IRMM-3100a by multi-collector TIMS. The certified $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio is determined gravimetrically, the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios are determined using the multi-dynamic procedure on TRITON 1 at IRMM, see text. TE: "classical total evaporation" method; MTE: "modified total evaporation" method.

ratio of about 0.5% is dominated by the Faraday amplifier noise, which results in a comparably poor repeatability for measurements at this abundance. The certified isotopic ratios for IRMM-3101 and IRMM-3100a are given in Table 1.

Because the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio is taken from the gravimetrical mixing of the ^{233}U and ^{236}U starting materials it has an uncertainty of 0.016% (coverage factor $k = 2$), equal to the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio of the double spike IRMM-3636 [3], which was prepared using

Table 1
Certified isotopic ratios for IRMM-3101 and IRMM-3100a.

	Method of certification	Certified ratio (expanded uncertainty, $k = 2$)
$n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$	Gravimetrically	1.01990(16)
$n(^{234}\mathrm{U})/n(^{236}\mathrm{U})$	TIMS TRITON 1, multi-dynamic	0.0003837(20)
$n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$	TIMS TRITON 1, multi-dynamic	1.004354(54)
$n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$	TIMS TRITON 1, multi-dynamic	0.98798(11)
$n(^{234}\mathrm{U})/n(^{233}\mathrm{U})$	Derived from above given ratios	0.0003762(20)
$n(^{235}\mathrm{U})/n(^{233}\mathrm{U})$	Derived from above given ratios	0.98476(11)
$n(^{236}\mathrm{U})/n(^{233}\mathrm{U})$	Derived from above given ratios	0.98049(16)
$n(^{238}\mathrm{U})/n(^{233}\mathrm{U})$	Derived from above given ratios	0.96870(26)
$n(^{233}\mathrm{U})/n(^{235}\mathrm{U})$	Derived from above given ratios	1.01548(11)
$n(^{234}\mathrm{U})/n(^{235}\mathrm{U})$	Derived from above given ratios	0.000382 0(20)
$n(^{236}\mathrm{U})/n(^{235}\mathrm{U})$	Derived from above given ratios	0.995664(53)
$n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$	Derived from above given ratios	0.98370(16)
$n(^{233}\mathrm{U})/n(^{238}\mathrm{U})$	Derived from above given ratios	1.03231(28)
$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$	Derived from above given ratios	0.0003884(20)
$n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$	Derived from above given ratios	1.01657(16)
$n(^{238}\mathrm{U})/n(^{238}\mathrm{U})$	Derived from above given ratios	1.01216(11)

similar quantities of the same starting solutions of ^{233}U and ^{236}U. Similar uncertainties had to be expected for the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios if the gravimetrical proportions of the ^{235}U and ^{238}U starting materials were used for the certification. On the other hand, the uncertainties for the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios obtained by TIMS in multi-dynamic mode and using the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio for normalization are smaller: they are 0.0054% ($k = 2$) for the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ ratio and 0.011% ($k = 2$) for the $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratio, both corresponding to an uncertainty of about 0.0054% per mass unit. This is due to the smaller mass differences for these ratios compared to the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio. Therefore, gravimetry with multi-dynamic mass spectrometry appears to be an optimal combination of methodology for the certification of the IRMM-3101 and IRMM-3100a and provided the smallest achievable uncertainties. Within the multi-dynamic measurement procedure [8] the linear fractionation law is automatically applied. However, as part of this work, differences between the various fractionation laws were investigated and found to be at the 10^{-6} (parts per million) level and can, therefore, be considered insignificant.

Within the verification measurements for the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio by TIMS, data for the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios were acquired using the TE and MTE methods on two TRITON TIMS instruments at IRMM and one instrument at IAEA-SGAS. As shown in Fig. 1b and c, they all agree within stated measurement uncertainties ($k = 2$) with the certified ratios obtained in multi-dynamic mode on the TRITON 1 as listed in Table 1. However, the multi-dynamic ratios from TRITON 1 at IRMM are used for the certification because of their independency on Faraday cup efficiencies and Faraday cup amplifier gains. The verification measurement data obtained using the two TRITON instruments at IRMM and one at IAEA-SGAS, however, can be regarded as results coming from three independent instruments with unknown detector efficiencies. Since no significant deviations were observed between the verification data obtained using these three instruments and the certified ratios, it can be concluded that all three TIMS instruments, at least at present, do not suffer from problems related to detector efficiencies at a level of uncertainty associated with the IRMM-3101 and IRMM-3100a. On the other hand, it has been reported in the literature that Faraday detector efficiencies of frequently used TIMS or ICPMS instruments can change over time [10,11]. This makes the IRMM-3100a very useful tool for checking the detector inter-calibration.

3. Application of IRMM-3101 and IRMM-3100a

The main reason for IRMM-3100a having the four isotopes ^{233}U, ^{235}U, ^{236}U, and ^{238}U with a 1/1/1/1 ratio is to use it for the verification of the Faraday cup inter-calibration of multi-collector systems or detector yields of ion counters, preferably at a level of about 0.01% or better, which is of interest in quality control (QC) in nuclear safeguards and nuclear forensics analysis and related fields. Although Faraday cup amplifiers can be inter-calibrated using a constant electric current source with a relative precision at the 10^{-6}–10^{-5} level, the accuracy of multi-collector instruments also depends on the actual ion detection efficiency of the cups themselves, the so-called cup efficiencies. Cup efficiencies can be verified with high precision, i.e., better than 0.005%, by peak-jumping measurements using high and stable ion beams, or even at a precision level of few ppm (ppm = part per million, 10^{-6}) by multi-dynamic measurements in various configurations [8,12] but for routine checks at a level of about 0.01% for quality control, the use of the IRMM-3100a is advantageous and less time-consuming.

Due to the unavoidable mass fractionation effects in the ion source, even for total evaporation measurements, a mass fractionation correction needs to be performed [8,9]. But any external correction using a standard, as required for TE and MTE measurements, is associated with uncertainties at the level of typically 0.04% or more (depending on the quality of reference materials available), which is insufficient for checking the Faraday cup inter-calibration at a level of about 0.01%. Thus, as a first step at least one pair of Faraday cups has to be inter-calibrated by some other suitable type of measurement, e.g., a peak-jumping measurement using a stable and intense uranium ion beam. In a second step the IRMM-3100a material can be applied by measuring the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio using the previously inter-calibrated pair of cups and then internally normalizing the results for the $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ ratios, which can then be used to inter-calibrate the 2 cups used to detect ^{235}U and ^{238}U. This then has to be continued iteratively using different cup configurations until all cups of the multi-collector array are evaluated for there efficiency.

In addition, the IRMM-3100a can be used to inter-calibrate and simultaneously check peak shapes of multiple ion counting (MIC) detector systems in TIMS and MC-ICP-MS instruments. As a further application, this four isotope reference material IRMM-3100a seems to be ideal for studying and better monitoring of instrumental mass bias effects in both TIMS and ICPMS instruments.

4. Conclusions

The methodology and techniques acquired in the preparation of several earlier series of synthetic mixtures were applied successfully for the preparation of the new (original) Quad-IRM

IRMM-3101 and its 10-fold dilution IRMM-3100a, with the isotope ratios adjusted to about $n(^{233}\mathrm{U})/n(^{235}\mathrm{U})/n(^{236}\mathrm{U})/n(^{238}\mathrm{U}) = 1/1/1/1$ and with relative expanded uncertainties of about 0.0054% per mass unit (coverage factor $k = 2$). The certified $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ isotope ratio was calculated based on the gravimetrical data and successfully verified by measurements from three TIMS instruments at two different laboratories using total evaporation and modified total evaporation. The remaining isotope ratios $n(^{234}\mathrm{U})/n(^{236}\mathrm{U})$, $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ were certified by TIMS utilizing a multi-dynamic mode with the $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio as internal mass fractionation correction. These ratios were confirmed by verification measurements as well.

This new isotope reference material IRMM-3100a is ideal for the verification of the inter-calibration of Faraday-multi-collectors or multiple ion counting detectors in TIMS and MC-ICP-MS instruments. It is furthermore a convenient reference material for checking detector peak shapes and alignment in various multi-collector systems on a routine basis and can additionally serve as quality control sample for routine safeguards measurements.

References

[1] K.J.R. Rosman, W. Lycke, R. Damen, R. Werz, F. Hendrickx, L. Traas, P. De Bìevre, Int. J. Mass Spectrom. 79 (1987) 61–71.

[2] W. Lycke, P. De Bièvre, A. Verbruggen, F. Hendrickx, K. Rosman, Fresenius Z. Anal. Chem. 331 (1988) 214–215.

[3] S. Richter, A. Alonso, Y. Aregbe, R. Eykens, F. Kehoe, H. Kühn, N. Kivel, A. Verbruggen, R. Wellum, P.D.P. Taylor, Int. J. Mass Spectrom. 281 (2009) 115–125.

[4] S. Richter, A. Alonso, R. Eykens, U. Jacobsson, H. Kühn, A. Verbruggen, Y. Aregbe, R. Wellum, E. Keegan, Int. J. Mass Spectrom. 269 (2008) 145–148.

[5] S. Weyer, A.D. Anbar, A. Gerdes, G.W. Gordon, T.J. Algeo, E.A. Boyle, Geochim. Cosmochim. Acta 72 (2008) 345–359.

[6] International Organisaton for Standardisation, Guide to the Expression of Uncertainty in Measurements, ISO, Geneva, Switzerland, 1993, ISBN 92-67-10188-9.

[7] GUM Workbench, Metrodata GmbH, www.metrodata.de.

[8] S. Richter, S.A. Goldberg, Int. J. Mass Spectrom. 229 (2003) 181–197.

[9] S. Richter, H. Kühn, Y. Aregbe, M. Hedberg, J. Horta-Domenech, K. Mayer, E. Zuleger, S. Bürger, S. Boulyga, A. Köpf, J. Poths, K. Matthew, Improvements for routine uranium isotope ratio measurements using the modified total evaporation method, J. Anal. At. Spectrom., 2011, submitted for publication.

[10] K.L. Ramakumar, R. Fiedler, Int. J. Mass Spectrom. 184 (1999) 109–118.

[11] C. Bayne, D. Donohue, R. Fiedler, Int. J. Mass Spectrom. 134 (1994) 169–182.

[12] A. Makishima, E. Nakamura, Isot. Geosci. Sect. 94 (1991) 105–110.