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Preparation and Certification of uranium QUAD isotopic reference materials IRMM-3100 and IRMM-3102

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Institute for Reference Materials and Measurements

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1 Abstract

Isotopic reference material IRMM-3101 was prepared by mixing of solutions from highly enriched 99.96% ^{233}U (IRMM-3630), 99.994% ^{235}U (IRMM-3650), 99.97% ^{236}U (IRMM-3660) and 99.99998% ^{238}U (IRMM-3680) in order to obtain an isotopic ratio $n(^{233}\text{U})/n(^{235}\text{U})/n(^{236}\text{U})/n(^{238}\text{U})$ close to unity. IRMM-3100 and IRMM-3102 were prepared from IRMM-3101 by gravimetrical dilution.

The certified isotope amount ratio[1] for ratio $n(^{233}\text{U})/n(^{236}\text{U})$ has been established by mass metrology and was verified by isotope mass spectrometry. The methodology used in the preparation and certification was similar to that of comparable uranium mixtures made in the past [1] [2]. The certified ratios $n(^{234}\text{U})/n(^{236}\text{U})$, $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ have been measured by TIMS in multi-dynamic mode and using the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio for internal normalization [3] [4].

The Isotopic Reference Materials IRMM-3100, IRMM-3101 and IRMM-3102 are part of a systematic IRMM programme to supply Isotopic Reference Materials of various isotopes at different concentrations. The Isotopic Reference Material is supplied in a polyethylene ampoule containing 1 mL of a 1 M nitric acid solution.

2 Introduction

Over the last 5 years, IRMM has been developing new sets of isotope reference materials based on proven methods of purifying and mixing highly enriched oxides. In the first stage, oxides of ^{233}U, ^{235}U, ^{236}U and ^{238}U were purified and solutions from each of these were established. From these four solutions a special 1:1:1:1 mixture was made, the QUAD isotopic reference material IRMM-3101 at a concentration of 1 mg U/g solution.

In this report the preparation and certification of a so-called "QUAD I(sotopic) R(eference) M(aterial)", a synthetic uranium isotope mixture produced by gravimetrical mixing of solutions of ^{233}U IRMM-3630), ^{235}U (IRMM-3650), ^{236}U (IRMM-3660) and ^{238}U (IRMM-3680) with $n(^{233}\text{U})/n(^{235}\text{U})/n(^{236}\text{U})/n(^{238}\text{U})$ isotope ratios close to unity and the smallest possible combined uncertainty is described.

For the certification of the QUAD IRM isotope ratios, the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio is calculated from the gravimetrical mixing of the $^{\mathbf{233}}$U and $^{\mathbf{236}}$U starting solutions. Both solutions were at the basis for the $^{\mathbf{233}}$U/$^{\mathbf{236}}$U-double spike IRMM-3636. The certified values of IRMM-3636 and therefore the calculated gravimetrical values of the starting materials were confirmed by verification measurements and reported [5][6]. The certified values and uncertainties for the $n(^{234}\text{U})/n(^{236}\text{U})$, $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ ratios of the QUAD IRM were obtained by TIMS in multi-dynamic mode, using the $n(^{233}\text{U})/n(^{236}\text{U})$ ratio for internal normalization.

The certification of the QUAD IRM was done with optimal choice of methodology - gravimetry combined with multi-dynamic measurements - and with smallest possible uncertainties.

The Quad Isotopic Reference Material will serve the following purposes:

- Verification of inter-calibration for Faraday-multi-collectors in TIMS- and MC-ICP-MS instruments.
- Verification or determination of inter-calibration factors for multiple ion counting systems in TIMS- and MC-ICP-MS instruments.
- Use as quality control sample for routine safeguards measurements.

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[1] Note: All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty calculated according to the ISO/BIPM guide. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI.

- Testing of 4 amplifiers simultaneously, e.g. for amplifier decay testing of Faraday-multi-collectors.

Following to the results of a recent customer survey the QUAD IRM will be available in three concentrations and will be a very much appreciated new synthetic uranium isotope reference material.

3 Design of IRMM-3100, 3101, 3102

The primary solution IRMM-3101 is designed such that the material consists of equivalent parts of four individual isotopes $n(^{233}U)/n(^{235}U)/n(^{236}U)/n(^{238}U)$ with a ratio of one. The starting materials, highly enriched 99.96% ^{233}U (IRMM-3630), 99.994% ^{235}U (IRMM-3650), 99.97% ^{236}U (IRMM-3660) and 99.99998% ^{238}U (IRMM-3680), were selected to prepare the primary QUAD IRM solution. A further 10-fold dilution of the primary mixture was made to prepare IRMM-3100; a 100-fold dilution of the primary mixture was made to prepare IRMM-3102.

The $n(^{233}U)/n(^{236}U)$ isotopic ratio of IRMM-3101 was calculated from the masses of the starting solutions mixed together and their respective isotopic compositions. Because of the very high enrichments of the starting materials, the contribution of the uncertainty from isotopic abundances to the combined uncertainty of the certified ratios and content of the mixture is small. The remaining isotope ratios were derived from the results of the TIMS measurements using $n(^{233}U)/n(^{236}U)$ as internal standard.

4 Certification of isotopic ratios in starting materials

The isotopic composition of the IRMM-3101 starting materials were measured using the (modified) total evaporation technique on the Triton TIMS [3][4]. By using a total evaporation technique the measurement is continued until the sample is exhausted. This is done in order to minimize mass fractionation effects for which nonetheless corrections were made.

The following measurements were made on the Triton TIMS:

- ^{233}U enriched material, IRMM-3630. Certified values are listed below in Table 1:

Table 1: Isotopic composition of highly enriched ^{233}U, Lot BC02153

Certified amount ratios	
$n(^{234}U)/n(^{233}U)$	0.000 359 21(47)
$n(^{235}U)/n(^{233}U)$	0.000 004 204 7(38)
$n(^{236}U)/n(^{233}U)$	0.000 000 025 36(19)
$n(^{238}U)/n(^{233}U)$	0.000 009 137(24)

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	99.962 756(47)	$m(^{233}U)/m(U)$	99.962 578(47)
$n(^{234}U)/n(U)$	0.035 908(47)	$m(^{234}U)/m(U)$	0.036 062(47)
$n(^{235}U)/n(U)$	0.000 420 31(38)	$m(^{235}U)/m(U)$	0.000 423 92(38)
$n(^{236}U)/n(U)$	0.000 002 535(19)	$m(^{236}U)/m(U)$	0.000 002 568(19)
$n(^{238}U)/n(U)$	0.000 913 4(24)	$m(^{238}U)/m(U)$	0.000 933 0(24)

The molar mass of the uranium is 233.040 040 8(60) $g \cdot mol^{-1}$

- ^{235}U enriched material, IRMM-3650. Certified values are below in Table 2.

Table 2: Isotopic composition highly enriched ^{235}U Lot BC02154

Certified amount ratios	
$n(^{234}U)/n(^{235}U)$	0.000 021 283(87)
$n(^{236}U)/n(^{235}U)$	0.000 042 28(19)
$n(^{238}U)/n(^{235}U)$	0.000 001 023 9(27)

amount fraction (·100)		mass fraction (·100)	
$n(^{234}U)/n(U)$	0.002 128 2(87)	$m(^{234}U)/m(U)$	0.002 119 1(87)
$n(^{235}U)/n(U)$	99.993 541(21)	$m(^{235}U)/m(U)$	99.993 531(21)
$n(^{236}U)/n(U)$	0.004 228(19)	$m(^{236}U)/m(U)$	0.004 246(19)
$n(^{238}U)/n(U)$	0.000 102 38(28)	$m(^{238}U)/m(U)$	0.000 103 69(28)

The molar mass of the uranium is 235.043 946 3(42) g·mol^{-1}

- ^{236}U enriched material, IRMM-3660. Certified values are listed below in Table 3.

Table 3: Isotopic composition of highly enriched ^{236}U, Lot BC02676

Certified amount ratios	
$n(^{233}U)/n(^{236}U)$	0.000 000 034 32(30)
$n(^{234}U)/n(^{236}U)$	0.000 000 001 222(82)
$n(^{235}U)/n(^{236}U)$	0.000 041 196(74)
$n(^{238}U)/n(^{236}U)$	0.000 225 50(38)

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	0.000 003 431(30)	$m(^{233}U)/m(U)$	0.000 003 387(29)
$n(^{234}U)/n(U)$	0.000 000 122 2(82)	$m(^{234}U)/m(U)$	0.000 000 121 1(81)
$n(^{235}U)/n(U)$	0.004 118 5(74)	$m(^{235}U)/m(U)$	0.004 101 0(74)
$n(^{236}U)/n(U)$	99.973 334(38)	$m(^{236}U)/m(U)$	99.973 160(39)
$n(^{238}U)/n(U)$	0.022 544(38)	$m(^{238}U)/m(U)$	0.022 735(38)

The molar mass of the uranium is 236.045 971 7(43) g·mol^{-1}

- ^{238}U enriched material IRMM-3650 Certified values are shown in Table 4:

Table 4: Isotopic composition highly enriched ^{238}U, Lot BC02155

Certified amount ratios	
$n(^{234}U)/n(^{238}U)$	0.000 000 005 41(12)
the $n(^{235}U)/n(^{238}U)$	0.000 000 507(14)
$n(^{236}U)/n(^{238}U)$	0.000 000 001 971(74)

amount fraction (·100)		mass fraction (·100)	
$n(^{234}U)/n(U)$	0.000 000 541(12)	$m(^{234}U)/m(U)$	0.000 000 532(12)
$n(^{235}U)/n(U)$	0.000 050 7(13)	$m(^{235}U)/m(U)$	0.000 050 0(13)
$n(^{236}U)/n(U)$	0.000 000 197 1(73)	$m(^{236}U)/m(U)$	0.000 000 195 4(73)
$n(^{238}U)/n(U)$	99.999 948 6(13)	$m(^{238}U)/m(U)$	99.999 949 3(13)

The molar mass of the uranium is 238.050 782 0(44) $g \cdot mol^{-1}$

5 Certification of IRMM-3101, 3100 and 3102

5.1 Verification of the $n(^{233}U)/n(^{236}U)$

Originally it was the intention to achieve a certification of all isotope ratios based on gravimetrically mixing of solutions of purified amounts of the $^{233}U_3O_8$, $^{235}U_3O_8$, $^{236}U_3O_8$ and $^{238}U_3O_8$ starting materials in a 1:1:1:1 proportion as in similar programs. Unfortunately because of anomalies at the level of <0.2%, in the uranium amount contents of the ^{235}U and ^{238}U starting materials, a different approach had to be followed.

The solutions made from $^{233}U_3O_8$ and $^{236}U_3O_8$, are also used to prepare the Double Spike IRMM-3636, for which the $n(^{233}U)/n(^{236}U)$ had been verified successfully by thermal ionization mass spectrometry (TIMS), [5][6]. Therefore, as the properties of the starting materials have proven to be correct, we assume that the $n(^{233}U)/n(^{236}U)$ ratio for the Quad-mixture IRMM-3101 should be as well in agreement with the value calculated from the gravimetrical mixing of $^{233}U_3O_8$ and $^{236}U_3O_8$. The abundances for the remaining isotopes ^{234}U, ^{235}U and ^{238}U could then be determined with high precision by TIMS, using the $n(^{233}U)/n(^{236}U)$ ratio for internal mass fractionation correction.

The major contributors to the final uncertainty of the $n(^{233}U)/n(^{236}U)$ isotope ratio identified during the preparation of IRMM-3101 were the uncertainties from weighings of the mixture, uncertainties on certified values of the starting solutions of ^{233}U and ^{236}U and the dilution of the mixture. Components of uncertainty from the properties of the initial base materials (uranium oxides) such as chemical impurities, stoichiometry and of the certified isotope amount contents of the starting solutions are already accounted for in the certified isotope content of the starting solutions of ^{233}U (IRMM-3630) and ^{236}U (IRMM-3660).

The effect of the impurities and the stoichiometry on the combined uncertainty of the certified $n(^{233}U)/n(^{236}U)$ isotope ratio in the mixture was evaluated by designing a mathematical model in the GUM Workbench. In the mixing model, the value of both variables was put at zero and a correlation factor of 0.8 was applied for both variables, the value for the uncertainties for both, impurities and stoichiometry, in this was set at 0.01%. The model for the starting materials included a value of 8 for the stoichiometry of the oxide and 100 ppm for the impurities both with an uncertainty of zero in order not have a double effect in the mixing.

Applying this model, the calculated value for the $n(^{233}U)/n(^{236}U)$ isotope ratio is 1.01990 with an uncertainty of 0.016%(k=2).

A verification measurement for this $n(^{233}U)/n(^{236}U)$ ratio was performed by TIMS, using two TRITON TIMS instruments at IRMM. On one of the instruments (TRITON 1) two slightly different methods were applied, the "classical" total evaporation technique (TE) and the "modified total evaporation technique" (MTE), as described in detail in WI-0149 of the IRMM quality system and in [3], [4. The reference material IRMM-3050 was used for external calibration.

The results of the verification measurements are presented in Figure 1; there is excellent agreement with the calculated value based on mass metrology. As a consequence, the $n(^{233}U)/n(^{236}U)$ isotope ratio can be used for the full certification of the Quad mixtures.

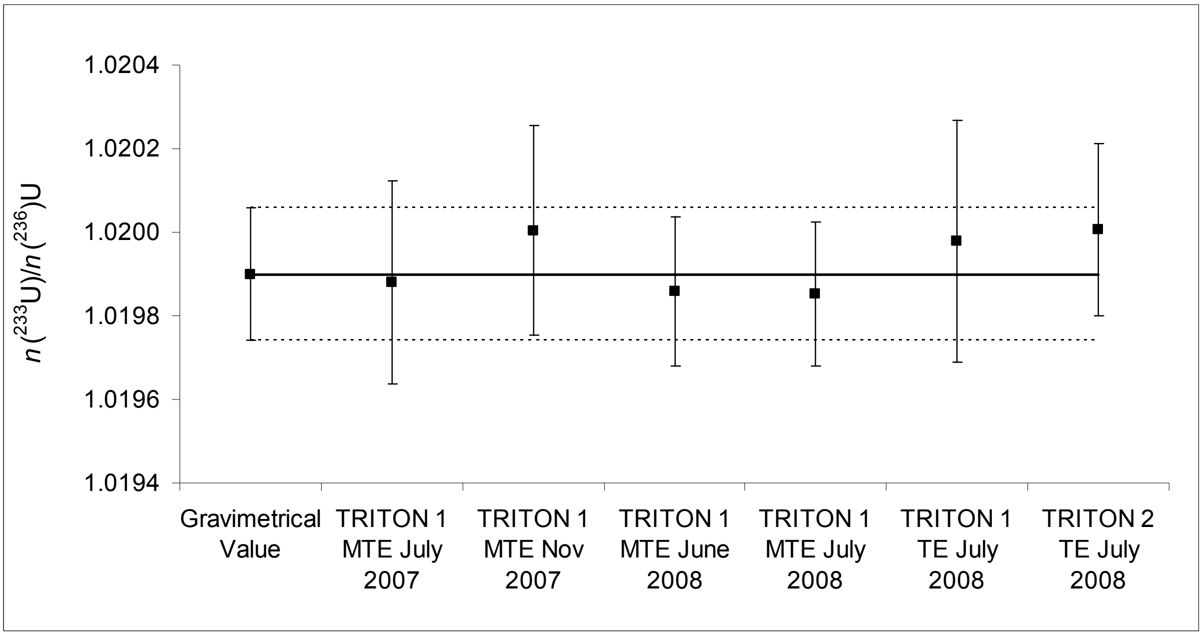

Figure 1: Verification measurements on $n(^{233}U)/n(^{236}U)$

5.2 Certification of $(^{234}U)/n(^{236}U)$, $(^{235}U)/n(^{236}U)$, $(^{238}U)/n(^{236}U)$

The remaining isotope ratios $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ were determined by thermal ionization mass spectrometry, using the $n(^{233}U)/n(^{236}U)$ ratio for internal mass fractionation correction. The measurements were performed in multi-dynamic mode, which eliminates influences of the measured ratios from Faraday cup detection efficiencies and Faraday cup amplifiers. The mathematical algorithms for the multi-dynamic mode are given in WI-0149, they already include the internal mass fractionation correction.

As a side-product from the verification of the $n(^{233}U)/n(^{236}U)$ ratio by TIMS, data for $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ ratios in TE mode on both the TRITON 1 TIMS and TRITON 2 TIMS and in MTE mode on the TRITON 1 TIMS have been acquired. As shown in Figure 2 and Figure 3, they agree well with the data obtained in multi-dynamic mode on the TRITON 1 TIMS. However, the multi-dynamic data from the TRITON 1 TIMS will be used for certification because of their independency on Faraday cup efficiencies and Faraday cup amplifier gains.

The data from the measurements in TE mode coming from the two TIMS instruments TRITON 1 and TRITON 2 can be regarded as results coming from 2 independent instruments with unknown detector efficiencies. No significant deviations were observed between the data in TE mode and in multi-dynamic mode, therefore it can be concluded that both TIMS instruments, at present, do not suffer from any problems related to detector efficiencies. From literature it is known that Faraday detector efficiencies of frequently used TIMS or ICPMS instruments can change over time. This makes the IRMM-3100 a very useful tool for checking the detector inter-calibration.

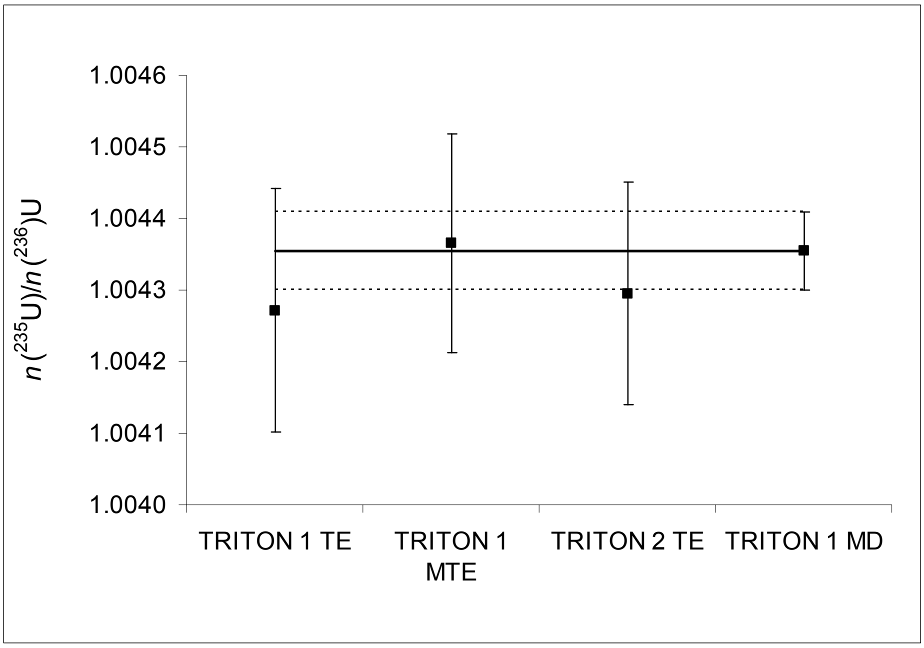

Figure 2: Verification measurements on $n(^{235}U)/n(^{236}U)$

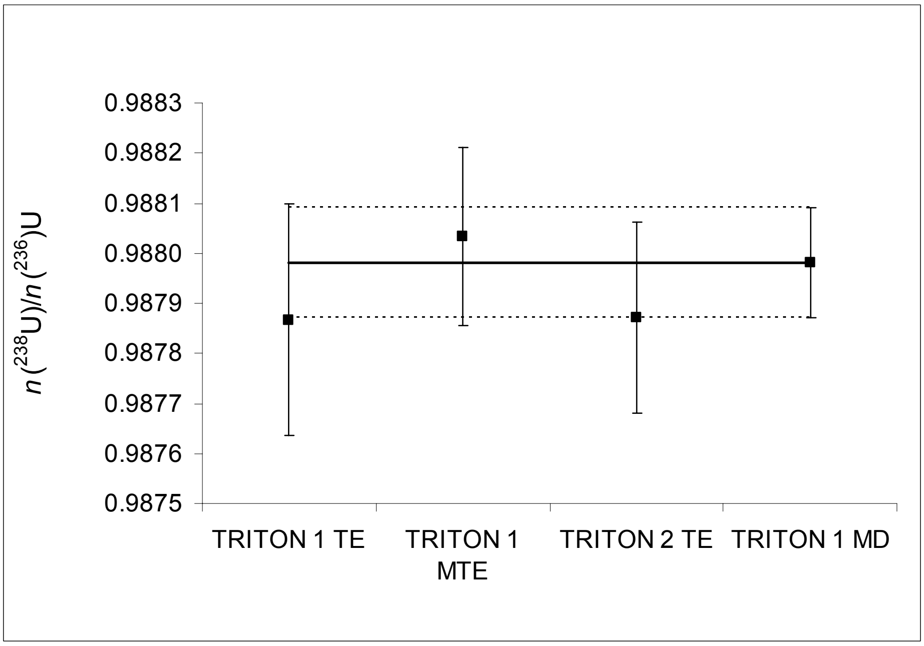

Figure 3: Verification measurements on $n(^{238}U)/n(^{236}U)$

For the $n(^{234}U)/n(^{236}U)$ ratio, multi-dynamic measurements data were acquired and used for certification. However, due to the low isotope abundance of ^{234}U the uncertainty of the $n(^{234}U)/n(^{236}U)$ ratio is dominated by the Faraday amplifier noise, which results in a poor repeatability for measurements of this ratio. Verification measurements for the $n(^{234}U)/n(^{236}U)$ ratio in TE mode were not meaningful due to the lack of tailing correction for adjacent isotope beams from ^{233}U and ^{235}U for this method.

5.3 Certification of IRMM-3100, 3101 and 3102

Certified values for the isotope amount ratios and uncertainties were calculated according to ISO/GUM recommendations [7] using the GUM Workbench [8] and are listed in Table 5.

The uncertainty budget shows for all ratios an almost 100% contribution from the $n(^{233}U)/n(^{236}U)$ ratio used for internal mass fractionation. The uncertainty budget for the $n(^{234}U)/n(^{236}U)$ ratio the uncertainty is dominated by Faraday collector noise.

Table 5: Isotopic composition of IRMM-3100, 3101 and 3102

Certified amount ratios	
$n(^{233}U)/n(^{236}U)$	1.019 90(16)
$n(^{234}U)/n(^{236}U)$	0.000 383 7(20)
$n(^{235}U)/n(^{236}U)$	1.004 354(54)
$n(^{238}U)/n(^{236}U)$	0.987 98(11)

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	25.417 3(34)	$m(^{233}U)/m(U)$	25.149 2(33)
$n(^{234}U)/n(U)$	0.009 562(50)	$m(^{234}U)/m(U)$	0.009 502(50)
$n(^{235}U)/n(U)$	25.029 89(64)	$m(^{235}U)/m(U)$	24.978 84(66)
$n(^{236}U)/n(U)$	24.921 37(69)	$m(^{236}U)/m(U)$	24.976 52(68)
$n(^{238}U)/n(U)$	24.621 9(33)	$m(^{238}U)/m(U)$	24.886 0(33)

The molar mass of the uranium is 235.524 36(17) $g \cdot mol^{-1}$

6 Ampouling of IRMM-3100 and 3102

Sampling of both batches IRMM-3100 and IRMM-3102 was carried out in a double section fume hood in the controlled area. The precleaned plastic vials were filled with 1 mL of solution by means of a 5 mL size dispenser. Each vial contained respectively about 100 µg (IRMM-3100) and 10 µg (IRMM-3102) total uranium. The fume hood was fitted with a new plastic interior. A part was used to set up flask and liquid dispenser. A sufficient number of clean plastic vials were brought into the controlled area from the clean lab, as well as dispensers and tubing. The area around and under the filling station was covered with a fresh layer of clean room wipes prior to ampuling.

The flask containing the Quad solutions to be processed was then opened. The dispenser was carefully fitted onto the flask, taking care to keep the ends of the tubing clean. One tube was then carefully inserted into the flask so that it reached the bottom of the flask. The other tubing was inserted into the vial. The required volume was then transferred from flask into vial with the dispenser. The vial was inspected that there was no solution on the top or outside and placed into a rack. From there the vial was closed with a screw cap, bagged into plastic bag and transferred to a safe for storage.

The same procedure was applied for the vialing of both IRMM-3100 and IRMM-3102. The concentrated solution IRMM-3101 was kept in a quartz flask for future use.

Table 6: Sequence of ampoule filling for IRMM-3100 and 3102

	Date	Number of ampoules sealed
3100	10-06-2008	303
3102	10-06-2008	102

7 Conclusions

The methodology and techniques acquired in the preparation of several series of synthetic mixtures have again been applied successfully for the preparation of the Quad isotopic reference material IRMM-3101 and of its dilutions IRMM-3100 and IRMM-3102.

The series have been prepared and certified values of the isotope amount ratio of $n(^{233}U)/n(^{236}U)$ has been calculated based on the weights of oxides and solutions and verified by the uncertainties of the mixing calculations and by independent TIMS measurements. The remaining isotope ratios $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ were determined by thermal ionization mass spectrometry used in a multi dynamic mode, using the $n(^{233}U)/n(^{236}U)$ ratio for internal mass fractionation correction.

The isotopic reference material IRMM-3100 and IRMM-3102 are commercially available from IRMM; the concentrated solution IRMM-3101 however will only be used for internal purposes and not be available externally.

8 References

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[6] Richter, S., A. Alonso, R. Eykens, U Jacobsson, H. Kühn, A. Verbruggen, Y. Aregbe, R. Wellum, E. Keegan, The Isotopic Composition of Natural Uranium Samples - Measurements using the new $n(^{233}U)/n(^{236}U)$ Double Spike IRMM-3636, International Journal of Mass Spectrometry 269 (2008) 145–148

[7] International Organisation for Standardisation, Guide to the Expression of Uncertainty in Measurements, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland 1993

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

Figure 4: Certificate IRMM-3100

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CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-3100

$n(^{233}U)/n(^{236}U)$:	**1.019 90(16)**
$n(^{234}U)/n(^{236}U)$:	**0.000 383 7(20)**
$n(^{235}U)/n(^{236}U)$:	**1.004 354(54)**
$n(^{238}U)/n(^{236}U)$:	**0.987 98(11)**

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	25.417 3(34)	$m(^{233}U)/m(U)$	25.149 2(33)
$n(^{234}U)/n(U)$	0.009 562(50)	$m(^{234}U)/m(U)$	0.009 502(50)
$n(^{235}U)/n(U)$	25.029 89(64)	$m(^{235}U)/m(U)$	24.978 84(66)
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$n(^{238}U)/n(U)$	24.621 9(33)	$m(^{238}U)/m(U)$	24.886 0(33)

The molar mass of the uranium in this sample is 235.524 36(17) $g \cdot mol^{-1}$

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against this Isotopic Reference Material will, therefore, also be traceable to the SI unit system.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement[1]. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland, 1993

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3. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

4. The atomic masses, used in the calculations, are[2]

^{233}U: 233.039 627 0(60) g·mol^{-1}
^{234}U: 234.040 944 7(44) g·mol^{-1}
^{235}U: 235.043 922 2(42) g·mol^{-1}
^{236}U: 236.045 561 0(42) g·mol^{-1}
^{238}U: 238.050 783 5(44) g·mol^{-1}

5. The Reference Material was prepared by metrological weighing of highly enriched uranium base materials and dissolution in HNO_3. Subsequently the solution was dispensed into individual units.

6. The Isotopic Reference Material IRMM-3100 is a dilution of IRMM-3101 and comes in a polyethylene vial containing about 0.43 µmol uranium in about 1 mL of a chemically stable 1 M nitric acid solution.

7. Values for molar isotope abundance ratios are valid for 1 July 2008.

8. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

9. Full details of the certification procedure can be found in the Preparation and Certification Report.[3]

10. Instruction for use:
    - The solution is provided in a plastic vial with screw cap.
    - The material is certified for isotopic ratios only; the concentration is approximate and can be expected to increase slowly with time due to diffusion of water through the plastic walls of the vial.
    - Particular care should be taken to avoid contamination of the solutions from other sources of uranium after opening the vial.
    - The isotopic certification is only valid at the time of delivery and if used frequently we advise replacing the vial for routine use at least on a yearly basis. The vial and remaining material should be disposed after use following local or national rules.

Chemical purification of the $^{233}U_3O_8$, $^{235}U_3O_8$, $^{236}U_3O_8$ and $^{238}U_3O_8$ starting materials was performed by R Eykens and F Kehoe.

[2] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[3] A. Verbruggen, R. Eykens, F. Kehoe, H. Kühn, U. Jacobsson, S. Richter, Y. Aregbe, Preparation and Certification of uranium QUAD isotopic reference materials IRMM-3100 and IRMM-3102, report EUR23543 EN

Weighing and preparation of the Isotopic Reference Material was performed by R Eykens. The dispensing, packing and labelling of this Isotopic Reference Material was accomplished by S Werelds, T Drooghmans, R Eykens and A Verbruggen.

Characterization of the enriched isotopes from which IRMM-3100 was prepared and verification measurements were performed by S Richter and H Kühn using thermal ionization mass spectrometry on samples prepared by F Kehoe and A Alonso Muñoz.

The certified $n(^{233}U)/n(^{236}U)$ ratio is calculated from the gravimetrical mixing of the ^{233}U and ^{236}U starting solutions. The $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ isotopic ratios were determined by S Richter and H Kühn using thermal ionization mass spectrometry. These measurements were performed in multi-dynamic mode, which eliminates influences of the measured ratios from Faraday cup detection efficiencies.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL October 2008	P Taylor Head Isotope Measurements Unit	Y Aregbe IRMM Safeguards Coordinator

Figure 5: Certificate IRMM-3102

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CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-3102

$n(^{233}U)/n(^{236}U)$:	**1.019 90(16)**
$n(^{234}U)/n(^{236}U)$:	**0.000 383 7(20)**
$n(^{235}U)/n(^{236}U)$:	**1.004 354(54)**
$n(^{238}U)/n(^{236}U)$:	**0.987 98(11)**

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	25.417 3(34)	$m(^{233}U)/m(U)$	25.149 2(33)
$n(^{234}U)/n(U)$	0.009 562(50)	$m(^{234}U)/m(U)$	0.009 502(50)
$n(^{235}U)/n(U)$	25.029 89(64)	$m(^{235}U)/m(U)$	24.978 84(66)
$n(^{236}U)/n(U)$	24.921 37(69)	$m(^{236}U)/m(U)$	24.976 52(68)
$n(^{238}U)/n(U)$	24.621 9(33)	$m(^{238}U)/m(U)$	24.886 0(33)

The molar mass of the uranium in this sample is 235.524 36(17) $g \cdot mol^{-1}$

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against this Isotopic Reference Material will, therefore, also be traceable to the SI unit system.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement[1]. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland, 1993

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3. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

4. The atomic masses, used in the calculations, are[2]

^{233}U: 233.039 627 0(60) g·mol^{-1}
^{234}U: 234.040 944 7(44) g·mol^{-1}
^{235}U: 235.043 922 2(42) g·mol^{-1}
^{236}U: 236.045 561 0(42) g·mol^{-1}
^{238}U: 238.050 783 5(44) g·mol^{-1}

5. The Reference Material was prepared by metrological weighing of highly enriched uranium base materials and dissolution in HNO_3. Subsequently the solution was dispensed into individual units.

6. The Isotopic Reference Material IRMM-3102 is a dilution of IRMM-3101 and comes in a polyethylene vial containing about 43 nmol uranium in about 1 mL of a chemically stable 1 M nitric acid solution.

7. Values for molar isotope abundance ratios are valid for 1 July 2008.

8. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

9. Full details of the certification procedure can be found in the Preparation and Certification Report.[3]

10. Instruction for use:
    - The solution is provided in a plastic vial with screw cap.
    - The material is certified for isotopic ratios only; the concentration is approximate and can be expected to increase slowly with time due to diffusion of water through the plastic walls of the vial.
    - Particular care should be taken to avoid contamination of the solutions from other sources of uranium after opening the vial.
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The certified $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ ratio is calculated from the gravimetrical mixing of the $^{233}\mathrm{U}$ and $^{236}\mathrm{U}$ starting solutions. The $n(^{234}\mathrm{U})/n(^{236}\mathrm{U})$, $n(^{235}\mathrm{U})/n(^{236}\mathrm{U})$ and $n(^{238}\mathrm{U})/n(^{236}\mathrm{U})$ isotopic ratios were determined by S Richter and H Kühn using thermal ionization mass spectrometry. These measurements were performed in multi-dynamic mode, which eliminates influences of the measured ratios from Faraday cup detection efficiencies.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

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Abstract

Isotopic reference material IRMM-3101 was prepared by mixing of solutions from highly enriched 99.96% ^{233}U (IRMM-3630), 99.994% ^{235}U (IRMM-3650), 99.97% ^{236}U (IRMM-3660) and 99.99998% ^{238}U (IRMM-3680) in order to obtain an isotopic ratio $n(^{233}U)/n(^{235}U)/n(^{236}U)/n(^{238}U)$ close to unity. IRMM-3100 and IRMM-3102 were prepared from IRMM-3101 by gravimetrical dilution.

The certified isotope amount ratio for ratio $n(^{233}U)/n(^{236}U)$ has been established by mass metrology and was verified by isotope mass spectrometry. The methodology used in the preparation and certification was similar to that of comparable uranium mixtures made in the past. The certified ratios $n(^{234}U)/n(^{236}U)$, $(^{235}U)/n(^{236}U)$ and $(^{238}U)/n(^{236}U)$ have been achieved by TIMS using the $n(^{233}U)/n(^{236}U)$ as internal standard.

Verification of the Quad isotopic reference material was performed on two independent TRITON by TIMS multidynamic measurements on Faraday collectors. The results agreed well with the certified values obtained from the mixing calculations.

The Isotopic Reference Materials IRMM-3100, IRMM-3101 and IRMM-3102 are part of a systematic IRMM programme to supply Isotopic Reference Materials of various isotopes at different concentrations. The Isotopic Reference Material is supplied in a polyethylene ampoule containing 1 mL of a 1 M nitric acid solution..

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