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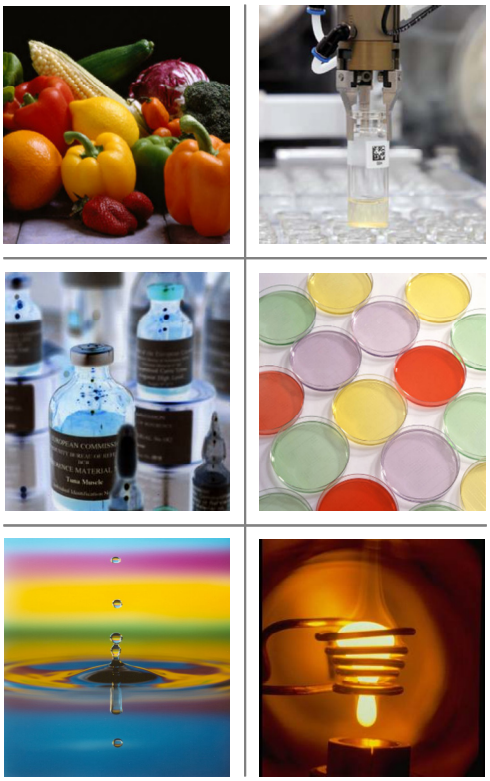
Preparation and Verification of QUAD Uranium Isotopic Reference Material IRMM-3100a

A. Verbruggen, R. Eykens, F. Kehoe, H. Kühn, U. Jacobsson, S. Richter, Y. Aregbe



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IRMM-3100a

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1 Introduction

Isotopic reference material IRMM-3100a was prepared by gravimetrical dilution of IRMM-3101. The primary solution IRMM-3101 was 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 certified isotope amount ratio[1] for ratio $n(^{233}U)/n(^{236}U)$ has been established by mass metrology and was verified by isotope mass spectrometry. The certified ratios $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ have been measured by TIMS in multi-dynamic mode and using the $n(^{233}U)/n(^{236}U)$ ratio for internal normalization. The preparation of IRMM-3101 is described elsewhere [1].

The Isotopic Reference Material IRMM-3100a is 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 quartz ampoule containing 1 mL of a 1 M nitric acid solution.

2 Design of IRMM-3100a

The primary solution IRMM-3101 was 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-3100a in 1 M nitric acid matrix. The uranium concentration is at the level of 0.1 mg U per g of solution, the isotopic composition is should be identical to the certified isotopic composition of IRMM-3100.

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, the remaining isotope ratios were derived from the results of the TIMS measurements using $n(^{233}U)/n(^{236}U)$ as internal standard. The certification of isotopic ratios in the starting materials and IRMM-3101 has been reported [1].

3 Verification of IRMM-3100a

Verification measurements were carried out using the TRITON TIMS and using the total evaporation procedure [3, 4].

For the mass fractionation correction two certified reference materials were used. The certified reference material IRMM-3636a has a $n(^{233}U)/n(^{236}U)$ ratio of $1.01906 \pm 0.016\%$, close to unity. IRMM-3636a (0.1 mg U/g) is a dilution of IRMM-3636 (1 mg U/g), a mixture of highly enriched ^{233}U and ^{236}U materials; the very same solutions were used within few days time also to prepare the original quad mixture IRMM-3101. Therefore IRMM-3636a is suitable standard for the verification measurement of IRMM-3100a.

As an additional standard, IRMM-074/10 with a $n(^{235}U)/n(^{238}U)$ ratio of $1.00026 \pm 0.015\%$ was used. The new reference material IRMM-3100a is a 1/10 dilution of IRMM-3101 and should therefore have the same isotopic composition. This was confirmed, as shown in Table 1 and Figure 1, by means of verification for the $n(^{233}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ ratios of IRMM-3100a, using IRMM-3636a and IRMM-074/10 as standards.

As a conclusion, the isotopic compositions of IRMM-3100a and the original quad mixture IRMM-3101 are in agreement.

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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 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.

Table 1: Verification measurements for IRMM-3100a

	Deviation of measured $n(^{233}U)/n(^{236}U)$ ratio from gravimetrical value	Uncertainty k=2	Augmented* Uncertainty, k=2
TE TRITON 1-Turret T091109	-0.033%	0.026%	0.042%
TE TRITON 1-Turret T091207	-0.024%	0.024%	0.041%
TE TRITON 2-Turret P100126	-0.033%	0.039%	0.051%
TE TRITON 2-Turret P100503	-0.011%	0.035%	0.048%
TE TRITON 2-Turret P100514	-0.010%	0.031%	0.045%

	Deviation of measured $n(^{235}U)/n(^{236}U)$ ratio from gravimetrical value	Uncertainty k=2	Augmented* Uncertainty, k=2
TE TRITON 1-Turret T091109	-0.010%	0.008%	0.014%
TE TRITON 1-Turret T091207	-0.007%	0.008%	0.014%
TE TRITON 2-Turret P100126	-0.008%	0.013%	0.017%
TE TRITON 2-Turret P100503	0.000%	0.012%	0.016%
TE TRITON 2-Turret P100514	0.000%	0.010%	0.015%

	Deviation of measured $n(^{238}U)/n(^{236}U)$ ratio from gravimetrical value	Uncertainty k=2	Augmented* Uncertainty, k=2
TE TRITON 1-Turret T091109	0.015%	0.017%	0.028%
TE TRITON 1-Turret T091207	0.009%	0.016%	0.027%
TE TRITON 2-Turret P100126	0.037%	0.036%	0.043%
TE TRITON 2-Turret P100503	0.029%	0.023%	0.032%
TE TRITON 2-Turret P100514	0.027%	0.020%	0.030%

TE = total evaporation method.

TRITON 1 and TRITON 2 are two TIMS instruments at IRMM.

*The uncertainties have been augmented by an additional relative uncertainty component associated to the external calibration of the TE method using a standard. This uncertainty contribution was quantified to be 0.032%, based on measurements of the gravimetrically prepared reference materials such as IRMM-074/10 and IRMM-3636a against each other [7].

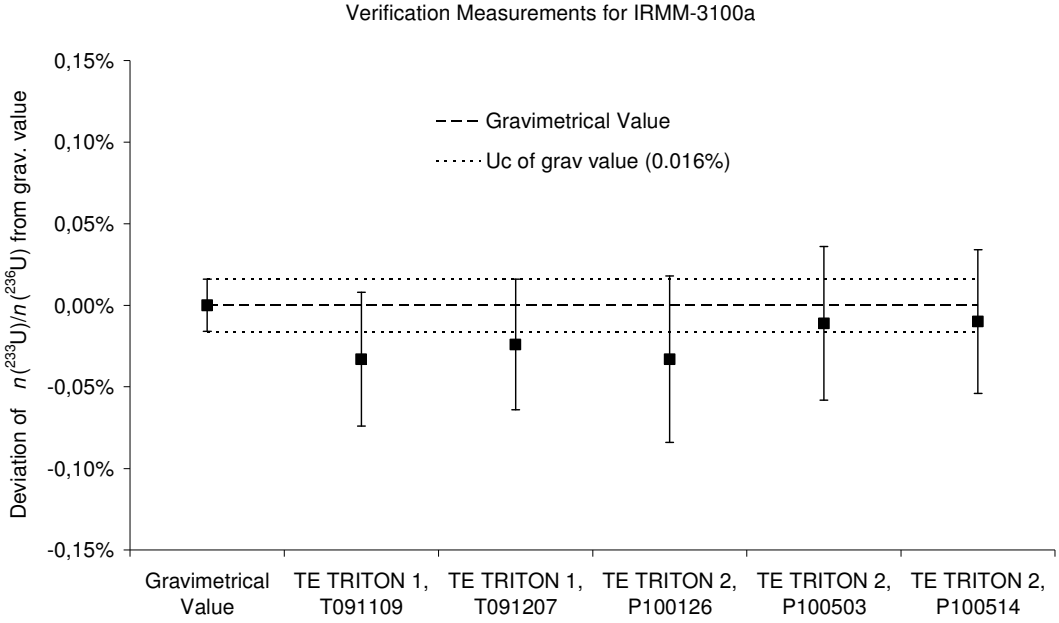

Figure 1: Verification measurements for the $n(^{233}U)/n(^{236}U)$ ratio of IRMM-3100a. Error bars represent uncertainties with a coverage factor $k = 2$.

4 Certification of IRMM-3100a

As confirmed by the verification measurements, IRMM-3100a and IRMM-3101 have the same isotopic composition. The certified values for the isotope amount ratios and uncertainties are published earlier [1] and were calculated according to ISO/GUM recommendations [8] using the GUM Workbench [9] as listed in Table 2.

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 for the $n(^{234}U)/n(^{236}U)$ ratio is dominated by Faraday collector noise.

Table 2: Isotopic composition of IRMM-3100a

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) $g \cdot mol^{-1}$

5 Ampouling of IRMM-3100a

Sampling of batch IRMM-3100a was carried out in a double section fume hood in the controlled area. The precleaned 2 mL quartz ampoules were filled with about 1 mL of solution by means of a 5 mL size dispenser. Each ampoule contained about 100 µg 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 quartz ampoules, dispensers and tubing were brought into the controlled area from the clean lab. 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 IRMM-3100a solution 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 the ampoule with the dispenser. The ampoule was inspected that there was no solution on the top or outside and placed into a rack.

From there it was put into a small PTFE holder and sealed using an oxygen-acetylene flame. After visual inspection the ampoule was placed into a rack to cool. This was done in a continuous process, with one ampoule being processed in less than a minute, on the average.

From earlier experiments and testing carried out during similar operations [8], the maximum possible contamination from environmental uranium during the preparation of the mother solutions, dilutions, ampoule filling and the sealing process is estimated to be about 26 pg uranium ($1.1 \cdot 10^{-6}$ mol). Possible contamination at this level of uranium with natural isotopic composition has no significant effect on the isotopic ratios of IRMM-3100a.

6 Conclusions

The preparation of IRMM-3100a has been successfully accomplished by dilution of IRMM-3101 a material prepared at IRMM to be used for production of the uranium QUAD series.

IRMM-3100a has been prepared and verification measurements were accomplished successfully. The certified values of the isotope amount ratio of $n(^{233}U)/n(^{236}U)$ have been calculated based on the masses 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.

Verification measurements for the certified isotopic composition of IRMM-3100a were performed successfully by the Safeguards Analytical Services (SGAS) of the International Atomic Energy Agency (IAEA) using thermal ionization mass spectrometry [10].

The isotopic reference material IRMM-3100a is commercially available from IRMM.

7 References

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[7] 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, drafted, to be published in 2010.

[8] International Organisation for Standardisation, Guide to the Expression of Uncertainty in Measurements, ISO/IEC Guide 98-3:2008, Geneva, Switzerland 2008.

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

[10] S Richter, A Alonso-Munoz, Y Aregbe, R Eykens, U Jacobsson, H. Kuehn, A Verbruggen, R Wellum, S Bürger, S Boulyga, J. Poths, IRMM-3100a: A New Certified Isotopic Reference Material with Equal Abundances of ^{233}U, ^{235}U, ^{236}U and ^{238}U, submitted to IJMS.

Figure 2: Draft Certificate IRMM-3100a

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CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-3100a

$n(^{233}U)/n(^{236}U)$:	**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)
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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. The certified values of this Isotopic Reference Material are metrologically traceable to the SI through gravimetrically prepared standards. Measurements calibrated with this Isotopic Reference Material can therefore provide SI-traceable results.

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.

[1] International Organisation for Standardisation, Guide to the Expression of Uncertainty in Measurements, ISO/IEC Guide 98-3:2008, Geneva, Switzerland 2008.

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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: 233.039 635 2(58) $g \cdot mol^{-1}$
^{234}U: 234.040 952 1(40) $g \cdot mol^{-1}$
^{235}U: 235.043 929 9(40) $g \cdot mol^{-1}$
^{236}U: 236.045 568 0(40) $g \cdot mol^{-1}$
^{238}U: 238.050 788 2(40) $g \cdot mol^{-1}$

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-3100a is a dilution of IRMM-3101 and comes in a flame sealed quartz ampoule containing about 0.22 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. This certificate is valid until July 2013; the validity may be extended after further tests on the stability of the spike material are carried out.

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 and a Technical Note.[3,4]

10. Instruction for use:
    - The material is certified for isotopic ratios only; the concentration is not certified.
    - Particular care should be taken to avoid contamination of the solutions from other sources of uranium after opening the vial.

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.

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[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 EUR 23543 EN, JRC 48379, ISBN 978-92-79-10326-1, ISSN 1018-5593.
[4] A. Verbruggen, R. Eykens, F. Kehoe, H. Kühn, U. Jacobsson, S. Richter, Y. Aregbe, Preparation and verification of uranium isotopic reference materials IRMM-3100a, Technical Note

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.

Characterisation of the enriched isotopes from which IRMM-3100a 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 the multi-dynamic mode, which eliminates influences of the measured ratios from Faraday cup detection efficiencies.

Verification measurements for the certified isotopic composition of IRMM-3100a were performed successfully by the Safeguards Analytical Services (SGAS) of the International Atomic Energy Agency (IAEA) using thermal ionization mass spectrometry[5].

The overall project coordination of this Isotopic Reference Material was performed by A.Verbruggen.

B-2440 GEEL
September 2010

H. Emons
Head Reference Materials Unit

[5] S Richter, A Alonso-Munoz, Y Aregbe, R Eykens, U Jacobsson, H. Kuehn, A Verbruggen, R Wellum, S Bürger, S Boulyga, J. Poths, IRMM-3100a: *A New Certified Isotopic Reference Material with Equal Abundances of ^{233}U, ^{235}U, ^{236}U and ^{238}U*, submitted to the International Journal of Mass Spectrometry.

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Abstract

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The certified isotope amount ratio[2] for ratio $n(^{233}U)/n(^{236}U)$ has been established by mass metrology and was verified by isotope mass spectrometry. The certified ratios $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ have been measured by TIMS in multi-dynamic mode and using the $n(^{233}U)/n(^{236}U)$ ratio for internal normalization. The preparation of IRMM-3101 is in full described elsewhere. [1]
The Isotopic Reference Material IRMM-3100a is 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 quartz ampoule containing 0.5 mL of a 1 M nitric acid solution.

[2] 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.

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