



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

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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 gravimetric mixing and mass spectrometry. Within the mixing process the isotope ratios were adjusted to about $n(^{233}\text{U})/n(^{235}\text{U})/n(^{236}\text{U})/n(^{238}\text{U}) = 1/1/1/1$ 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 $n(^{233}\text{U})/n(^{236}\text{U})$ ratio of IRMM-3100a was derived from the mass metrology data of the gravimetric 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 $n(^{234}\text{U})/n(^{236}\text{U})$, $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ ratios were then determined by TIMS using the $n(^{233}\text{U})/n(^{236}\text{U})$ 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 $n(^{235}\text{U})/n(^{236}\text{U})$ and $n(^{238}\text{U})/n(^{236}\text{U})$ 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.

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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 $n(^{233}\text{U})/n(^{236}\text{U})$ 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 $n(^{235}\text{U})/n(^{238}\text{U})$ ratios in samples with small ^{236}U abundance, e.g., for natural samples. The advantage of using a $n(^{233}\text{U})/n(^{236}\text{U})$ 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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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 gravimetric mixing of ^{233}U and ^{236}U as well. The major contributors to the final uncertainty of this gravimetric $n(^{233}\text{U})/n(^{236}\text{U})$ 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 gravimetric 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 $n(^{234}\text{U})/n(^{236}\text{U})$

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