European Commission

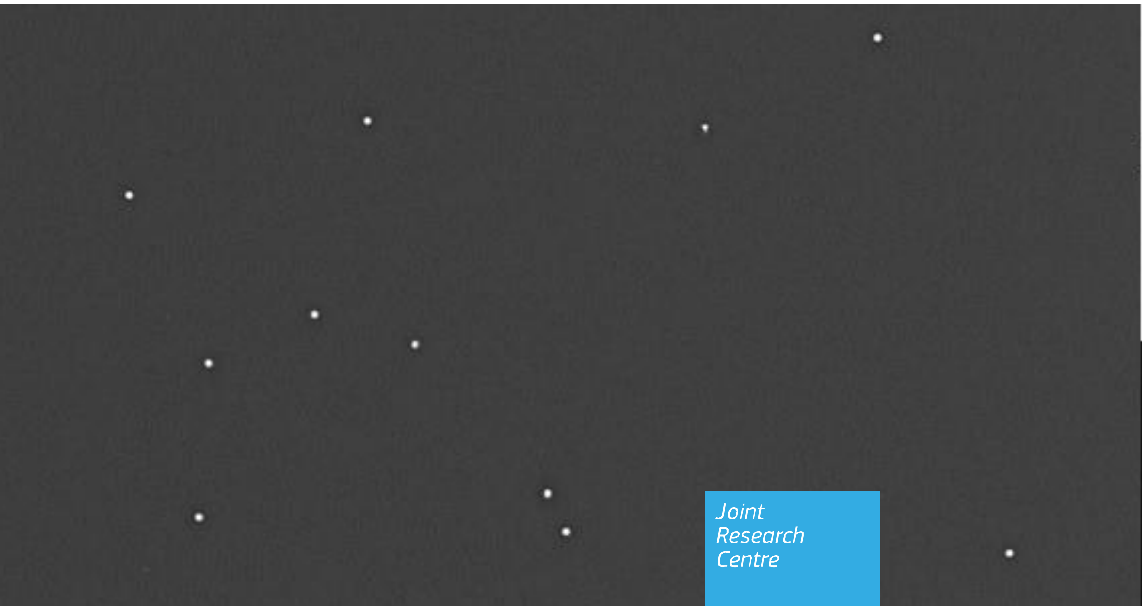
JRC REFERENCE MATERIALS REPORT

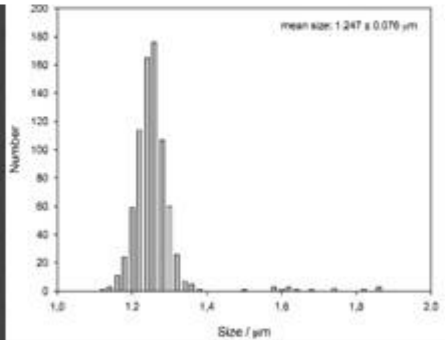
Preparation and Certification of the Uranium Oxide Micro Particle Reference Material IRMM-2331P

Certified for Isotope Ratios

J. Truyens, S. Neumeier, P. Kegler, M. Klinkenberg, M. Zoriy, S. Richter, Y. Aregbe

2021





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Contents

Foreword

The Directorate G "Nuclear Safety and Security", Unit G.2 "Standards for Nuclear Safety, Security and Safeguards" (SN3S) at the European Commission's Joint Research Centre in Geel, Belgium (formerly known as the "Institute for Reference Materials and Measurements", IRMM), provides a wide range of nuclear Certified Reference Materials to safeguards authorities and the nuclear industry.

This report describes the certification of the IRMM-2331P, a uranium micro particle reference material. The project was a collaboration between the Forschungszentrum Jülich (FZJ), Germany, and the Joint Research Centre's Unit G.2 "Standards for Nuclear Safety, Security and Safeguards" in Geel, Belgium.

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Abstract

This report describes the certification of IRMM-2331P, a uranium micro particle reference material. This certification project was a collaboration between the Forschungszentrum Jülich (FZJ), Germany, and the Joint Research Centre (JRC), Unit G.2 in Geel, Belgium.

The reference material was produced in compliance with ISO/IEC 17034:2016 [1] and certified in accordance with ISO Guide 35:2006 [2]. Uncertainties of the certified values were estimated in compliance with ISO/IEC Guide 98-3:2008 (the Guide to the Expression of Uncertainty in Measurement, GUM) [3]. In order to achieve "fit-for-purpose" isotope ratios for particle analysis, the base material IRMM-2330 was prepared by mixing of two uranium nitrate solutions, which were prepared by conversion of uranium hexafluoride (UF_6) materials. Certification of the uranium isotopic composition for the base material IRMM-2330 was performed directly by Thermal Ionisation Mass Spectrometry (TIMS) using the Modified Total Evaporation (MTE) method at JRC-G2, and the results were verified by TIMS/MTE measurements at the IAEA.

The production of the uranium particles was performed at the FZJ using a dedicated method based on spray-pyrolysis of droplets generated with a vibrating orifice aerosol generator (VOAG). Verification measurements of the base solution and 'process control measurements' on dissolved uranium particles were performed at the FZJ via Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) and the results agreed with the isotopic composition of the base solution IRMM-2330. This agreement permitted the certification of the isotopic composition for the particle reference material IRMM-2331P to be performed using the certified isotopic composition of the base material IRMM-2330.

The reference material is intended for the calibration of instruments and methods, quality control purposes, and the assessment of method performance for isotope mass spectrometry on uranium particles. As with any certified reference material, it can also be used for validation studies.

The following certified values and expanded uncertainties were assigned for isotope amount ratios, isotope amount fractions, isotope mass fractions, and molar mass for IRMM-2331P.

TRIURANIUM OCTOXIDE PARTICLE		
	Isotope amount ratio	
	Certified value [1)] [mol/mol]	Uncertainty [2)] [mol/mol]
$n(^{234}U)/n(^{238}U)$ $n(^{235}U)/n(^{238}U)$ $n(^{236}U)/n(^{238}U)$	0.00042156 0.051025 0.000062641	0.00000018 0.000015 0.000000087
	Isotope amount fraction	
	Certified value [3)] [mol/mol]	Uncertainty [2)] [mol/mol]
$n(^{234}U)/n(U)$ $n(^{235}U)/n(U)$ $n(^{236}U)/n(U)$ $n(^{238}U)/n(U)$	0.00040091 0.048526 0.000059572 0.951014	0.00000017 0.000013 0.000000083 0.000013
	Isotope mass fraction	
	Certified value [3) 4)] [g/g]	Uncertainty [2)] [g/g]
$m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	0.00039440 0.047942 0.000059107 0.951604	0.00000016 0.000013 0.000000083 0.000013
	Molar mass	
	Certified value [3) 4)] [g/mol]	Uncertainty [2)] [g/mol]
$M(U)$	237.903151	0.000041

1) The certified values are traceable to the International System of units (SI) via IRMM-074.

2) The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

3) These values are calculated using the isotope amount ratios and therefore traceable to the SI. The calculation of n(U), m(U) and M(U) includes the contributions from the isotopes ^{234}U, ^{235}U, ^{236}U and ^{238}U.

4) These values are calculated using the values for the atomic masses listed below from *Wang et al., The AME 2016 atomic mass evaluation, Chinese Physics C Vol. 41, No. 3 (2017) 030003:*

$M(^{234}U) = 234.0409504 \pm 0.0000024\ g{\cdot}mol^{-1}$ (k = 2)

$M(^{235}U) = 235.0439282 \pm 0.0000024\ g{\cdot}mol^{-1}$ (k = 2)

$M(^{236}U) = 236.0455662 \pm 0.0000024\ g{\cdot}mol^{-1}$ (k = 2)

$M(^{238}U) = 238.0507870 \pm 0.0000032\ g{\cdot}mol^{-1}$ (k = 2)

1 Introduction

1.1 Background

Environmental samples are used by national and international safeguards authorities to verify the absence of undeclared nuclear material and/or activities in nuclear facilities under safeguards [4, 5]. Nuclear security authorities also use environmental samples for evidence collection in cases of border interdictions of nuclear material, and seizures or discoveries of nuclear material in the public domain [6]. Environmental sampling makes use of pieces of cotton cloth, called swipes, to wipe surfaces of interest. The dust collected on these swipes may contain micrometer-sized particles of actinides or other elements of interest. The majority of environmental samples collected for safeguards purposes are taken from bulk handling facilities at the front end of the nuclear fuel cycle (e.g., uranium conversion plants, uranium enrichment plants and uranium fuel fabrication plants), therefore uranium particles are the most often investigated type of particle. In addition to the ^{235}U abundance in uranium particles, the minor isotope abundance ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ of uranium in particles may provide additional information to safeguards authorities about equipment or plant design and irradiation history, and may also help to evaluate mixing and decay scenarios. Major and minor uranium isotope ratios in environmental samples collected by inspectors are measured by the IAEA's Office of Safeguards Analytical Services (SGAS) in Seibersdorf, Austria and the IAEA's Network of Analytical Laboratories (NWAL) [7].

Considering the potential consequences of particle analyses in nuclear safeguards, these measurements are subjected to a rigorous quality management system. The reliability and comparability of measurement results of isotope ratios in uranium particles need to be guaranteed and monitored via the correct use of reference materials and quality tools. Laboratories involved in particle analysis have a continuous need for quality control reference materials at the particle level [8]. Therefore, a collaborative project was launched involving the European Commission's Joint Research Centre, Unit G.2 (JRC-Geel, Belgium) and the Forschungszentrum Jülich's Institute for Nuclear Waste Management and Reactor Safety (FZJ/IEK-6, Jülich GmbH, Germany) to produce monodispersed, spherical micrometre-sized uranium oxide particles.

One batch of monodispersed micrometre-sized uranium particles with a ^{235}U enrichment of approximately 3 % and a ^{236}U isotope amount fraction of about 3.0 x 10^{-5} was already certified as IRMM-2329P [9] in 2020. Prior to its release, the candidate reference material IRMM-2329P was the test item in the NUSIMEP-9 Nuclear Signatures Inter-laboratory Measurement Evaluation Programme [10]. Following the IRMM-2329P and the NUSIMEP-9 campaign, another batch of monodispersed micrometre-sized uranium particles with a ^{235}U enrichment of approximately 5 % and a ^{236}U isotope amount fraction of about 6.0 x 10^{-5} was produced by JRC-Geel and FZJ, called IRMM-2331P, which is the subject of this report.

1.2 Choice of the material

Following recommendations from the IAEA regarding the preferred isotopic compositions for particle reference materials, suitable uranium base solutions were prepared at JRC-G.2 in Geel for both IRMM-2329P and IRMM-2331P. This was achieved by mixing solutions of low-enriched uranium (LEU) materials derived from uranium hexafluoride (UF_6) from the JRC-G.2 stock of UF_6 materials. In the case of IRMM-2331P, two solutions derived from IRMM-029 (with about 4.5 % ^{235}U and 1 % ^{236}U) and a quality control material called EURA 2014-02T (with about 5 % ^{235}U and <5 x 10^{-6} abundance ^{236}U) were mixed. The mixing of the solutions was not performed strictly using the classical gravimetrical approach for which the accurate knowledge of the uranium concentrations and mixing proportions between the two solutions would have to be known. The applied mixing proportions were only based on estimates from the concentrations. Therefore the isotopic composition of the base solution mixture, called IRMM-2330, was directly characterised by TIMS using the standardised MTE (modified total evaporation) method [11, 12] and subsequently verified by an external laboratory (IAEA-SGAS), using the TIMS/MTE method as well.

The candidate reference material for certification, called IRMM-2331P, consists of spherical uranium oxide micro particles with a mean particle diameter in the micrometre-size range. The particles are characterised by a high degree of sphericity and a narrow particle size distribution. The average diameter in the micrometre-sized range was selected to reflect typical samples collected on nuclear safeguards swipe samples [8]. The particles are easily measurable by the current state-of-practice particle mass spectrometric techniques but also provide a challenge for state-of-the-art techniques to further reduce the measurement uncertainty.

The particles are distributed onto glass-like carbon disks, also called planchets, which allows the samples to be measured directly by various techniques (e.g. SIMS, LG-SIMS) but also allows the easy transfer of particles onto different substrates (e.g. by micromanipulation). The particles consist of triuranium octoxide (U_3O_8) which ensures that the chemical properties of the particles remain stable over a long period of time [13, 14,15].

Finally, the uranium isotope amount ratios in IRMM-2331P represent low-enriched uranium (LEU), with a $n(^{236}U)/n(U)$ isotopic abundance at the level of 6 x 10^{-5}, that can be measured by the commonly applied techniques.

1.3 Design of the certification project

The IRMM-2331P material has been produced and certified for the uranium isotope amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The IRMM-2331P uranium micro particles were produced at the Forschungszentrum Jülich from uranium solutions, prepared at JRC-G.2 in Geel by mixing uranium solutions derived from UF_6 certified reference materials.

Based on evaluation and control of environmental conditions and production processes, no change of the uranium isotope amount ratios from the solutions to the particles is expected during the production. However, the uranium isotope ratios in the base solution called IRMM-2330 were first measured for characterisation at JRC-G.2 using TIMS/MTE. Then, the isotopic composition was verified at IAEA-SGAS by TIMS/MTE. After the particle production at FZJ, the integrity of the uranium isotope ratios in the produced particles was verified by process control measurements on particles. The particles were leached back into a nitrate solution and subsequently measured using MC-ICPMS at FZJ. Due to this strategy, the typically used instruments designed for particle analysis such as LG-SIMS, LA-MC-ICPMS and FT-TIMS, for which this new reference material IRMM-2331P should be used as calibrant, were intentionally not involved in this certification project. Measuring the base solution IRMM-2330 as well as the (leached) particles IRMM-2331P both in the physical form of solutions and also using the same MC-ICPMS instrument guarantees the independency of this certification process from the instruments to be calibrated later-on. This strategy was already applied successfully for the certification of IRMM-2329P [9].

2 Participants

Project management and evaluation, processing of base solution and characterisation have been performed at the European Commission, Joint Research Centre, Directorate G – Nuclear Safety and Security, unit G.2 - Standards for Nuclear Safety, Security and Safeguards in Geel, Belgium.

The production of the particles and the preparation of particles on the glass-like carbon disks (processing) and the verification measurements of the isotopic composition for particles leached from the carbon disks using multi-collector ICP-MS system „Neptune/Plus“ were performed at Forschungszentrum Jülich GmbH in Jülich, Germany at the Institute for Energy and Climate Research, IEK-6: Nuclear Waste Management and Reactor Safety, and the Division of Safety and Radiation Protection, S-BA, respectively.

Within the context of the IRMM-2331P certification, the verification measurements for the uranium isotope ratios in the base solution IRMM-2330 were performed at the International Atomic Energy Agency, Office of Safeguards Analytical Services (SGAS), Nuclear Material Laboratory (NML) in Seibersdorf, Austria.

3 Material processing and process control

3.1 Origin of the starting material

The IRMM-2331P particles were produced from a base solution, the IRMM-2330. This solution was prepared at the JRC-G.2 by mixing solutions obtained by conversions from the UF_6 materials IRMM-029 and EURA 2014-02T, which are two uranium materials with certified uranium isotope amount ratios. The IRMM-2330 solution was characterised for the isotopic composition using TIMS/MTE [11, 12] and a certificate of a reference measurement was issued (Annex 1). It is noted that for the calculation of the isotope mass fractions and the molar mass on this measurement certificate a different (i.e. older) set of atomic masses was used in contrast to this certification (see details in section 6). The uncertainties of the certified ratios of IRMM-2330 include an additional component for the maximum possible inhomogeneity between different units of the material. This uncertainty component was already introduced and calculated during the certification of the uranium hexafluoride reference materials series IRMM-019-029, which was also performed using TIMS on uranyl nitrate solutions [16, 17].

In order to comply with the ISO 17034:2016 [1], for the certification of the isotopic composition of the IRMM-2330 solution, external verification measurements were performed at the IAEA-SGAS using the TIMS/MTE method. As shown in Table 1, the isotope ratios from the IAEA-SGAS were in good agreement with the values on the measurement certificate, which can therefore be used as certified values for the IRMM-2330 solution. The verification measurement results are compared with the certified values in Table 1.

Table 1. Results with expanded uncertainty (*k=2*) of the certified isotope ratios for IRMM-2330 solution and results of verification measurements performed by the IAEA-SGAS.

		$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Certification Measurement by JRC-G.2	TIMS/MTE (using IRMM-074, Annex 2, for mass bias correction)	0.00042156(18)	0.051025(15)	0.000062641(87)
Verification Measurements by IAEA-SGAS	TIMS/MTE (using IRMM-184, Annex 3, for mass bias correction), by IAEA	0.00042145(22)	0.051013(32)	0.00006271(27)

3.2 Processing

The flow scheme for the production of IRMM-2331P is as follows in Figure 1:

The IRMM-2330 base solution was prepared by mixing solutions of IRMM-029 with EURA 2014-02T as described above. All of the original materials were uranium hexafluoride (UF_6), which were converted to uranyl nitrate ($UO_2(NO_3)_2$) by hydrolysis of the gaseous UF_6 in diluted nitric acid, i.e.

$$\mathrm{UF_6 + 2HNO_3 + 2H_2O \rightarrow UO_2(NO_3)_2 + 6HF}$$

The $n(NO_3)/n(U)$ ratio of the solution was adjusted to around 10 using nitric acid (Suprapur®), which was required to convert the solutions to particles [14].

The prepared IRMM-2330 solution was shipped to FZJ, where the solutions were used to produce micrometre-sized triuranium octoxide (U_3O_8) particles. Detailed information about the particle production process is given in [13, 14 15, 18 and 19].

The IRMM-2330 solution was first diluted with ultra-pure water (18.2 MΩ·cm) and ethanol (Ethanol absolute for analysis EMSURE®, Merck KGaA, Germany) to a uranium content of around 125 $\mu g \cdot g^{-1}$ and a water to ethanol volume ratio around 1. This prepared solution was then fed into a vibrating orifice aerosol generator (VOAG, model 3450, TSI Inc., USA) at a volume flow rate of 2.59 $\mu L \cdot s^{-1}$. The VOAG was operated using a goldcoated orifice with a diameter of 20 µm oscillating with a frequency of 69 kHz. Under the given conditions, a liquid jet was formed, which broke up into monodisperse droplets.

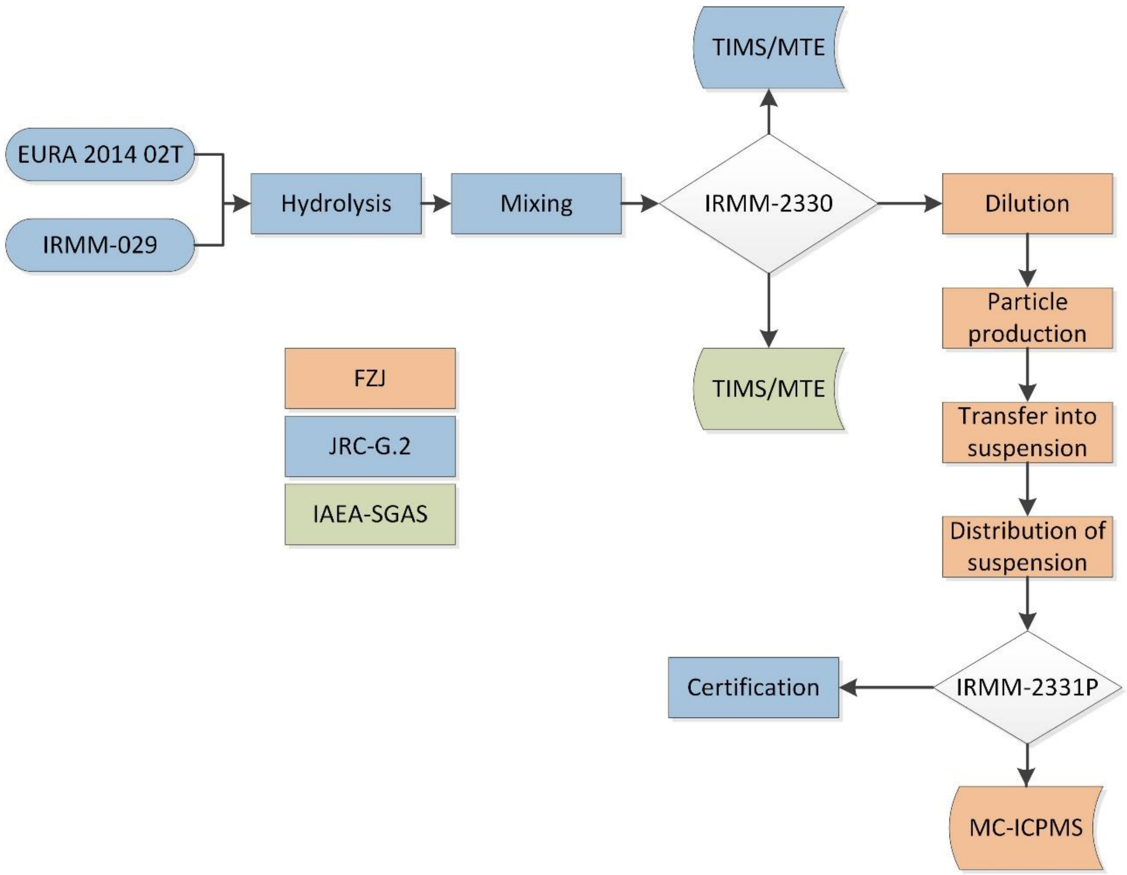
The generated droplets were carried with a pre-cleaned supply of compressed air through a drying column and a 200 mm long aerosol heater (Pressurized air heater, Dekati Ltd., Finland). The solvents (water and ethanol) within the droplets evaporated and resulted into formation of uranyl nitrate precursor particles. The aerosol heater was set to 500 °C, at which temperature the uranyl nitrate precursor particles were decomposed and partially reduced to solid triuranium octoxide micro particles.

After passing through the aerosol heater, the particle-bearing flow was passed through a 500 mm long air-cooled stretch. The particles were then extracted from the particle-bearing stream by means of a single-stage inertial impactor onto a 25.4 mm (1 inch) diameter quartz disk. Several quartz disks were produced over a course of two subsequent days. These quartz disks were transferred into an ethanol-filled bottle, which was ultra-sonicated to detach particles from the quartz disks into the ethanol. The stability of the produced particles in an ethanol suspension was previously demonstrated [14, 20].

Aliquots of the produced suspension were distributed by pipette onto 25 mm diameter glass-like carbon disks, which were gently heated to dryness to homogeneously deposit the particles onto the substrate. Before packing, the disks were shortly heated using a heating plate at 300 °C to evaporate all volatile residues.

Finally, 160 units of IRMM-2331P were produced using the procedure described above. This was achieved during one working day and the suspension was regularly agitated. Each IRMM-2331P unit contains about 15000-20000 monodisperse uranium particles of micrometre-sized diameter, distributed onto a 25 mm diameter glass-like carbon disk.

Figure 1. Flow-scheme of the production of uranium micro particles IRMM-2331P, starting from the two UF_6 materials IRMM-029 and EURA 2014-02T, towards the verification measurements and certification of the uranium isotope ratios.

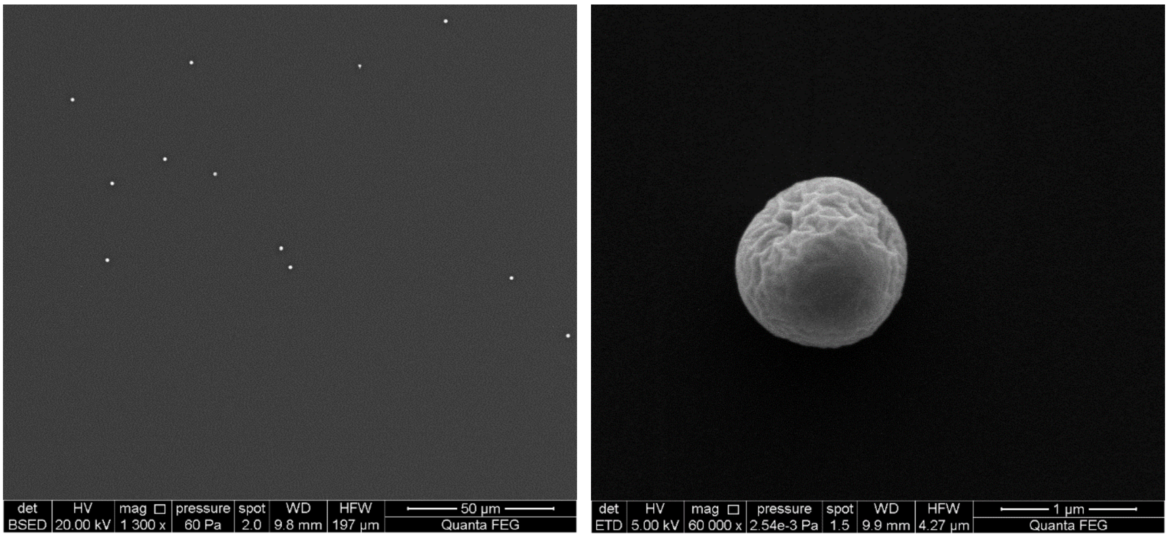


3.3 Process control of the IRMM-2331P particle production

Prior to the production of the particles from the diluted solutions, a test run was performed at FZJ using the intended solution and parameters. The produced particles were examined using a scanning electron microscope (SEM). Once the presence of spherical particles had been confirmed, the particle production started. During the production, an optical particle sizer (OPS, model 1110, TSI Inc., USA) provided an online measurement of the (estimated) particle count and particle size distribution.

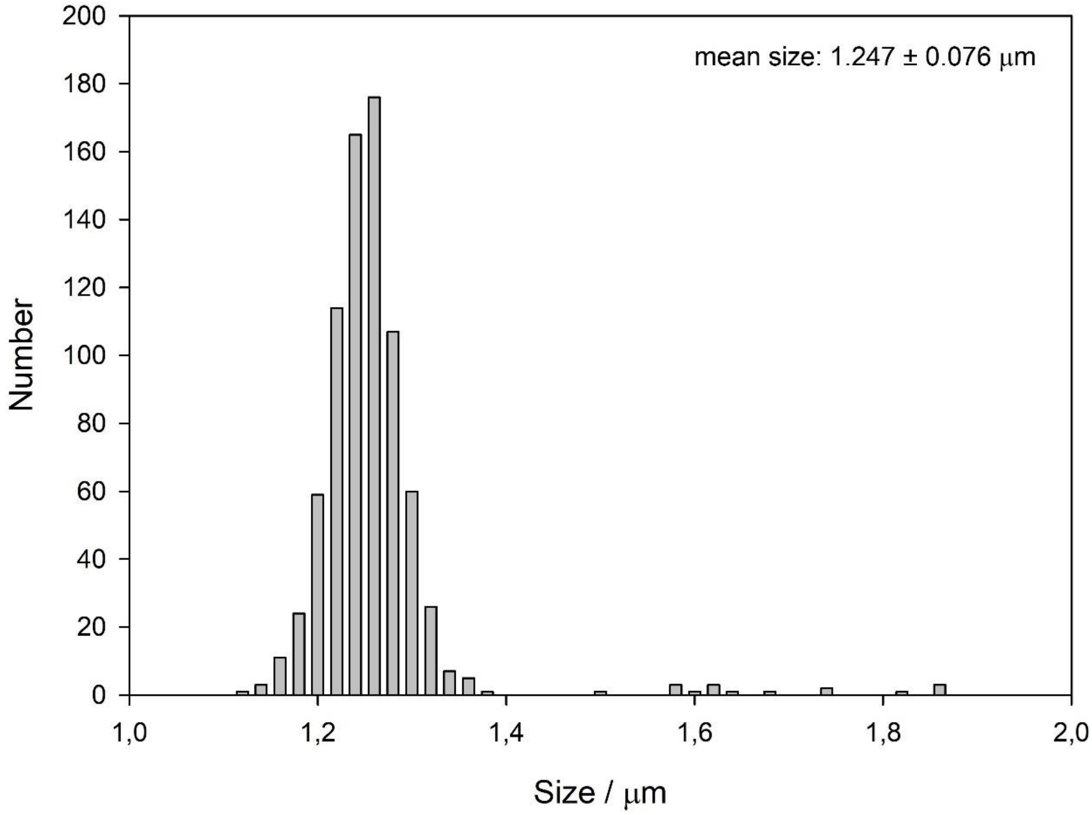
The final produced particles were investigated by SEM before dispersion over the glass-like carbon disks and after dispersion, four randomly selected samples were investigated by SEM to provide an estimate of the particle morphology, size distribution and the number of particles present on the samples.

Figure 2. SEM images of IRMM-2331P particles (taken at FZJ). The picture on the left gives an overview of the uranium particles present on section of the planchet. The picture on the right shows a single particle.



Based on these studies, it was found that each unit of IRMM-2331P contained approximately 15000-20000 particles. Although quantification of the particle size proved difficult, the particle diameters was found to range between 1 µm and 2 µm, with an average of 1.247 µm and a relative standard deviation of about 6 % for the most abundant population (indicative values for particle diameter and standard deviation, not certified).

Figure 3. Particle Size distribution for IRMM-2331P particles.



In addition to the main particle population, approximately 1.5 % of the particles have a diameter of about 1.6 µm which corresponds to twice the volume, of uranium oxide, compared to the main particle population. Such particles are likely produced by the fusion of two droplets or particles during the particle production [14].

4 Homogeneity

A key requirement for any reference material aliquoted into units is equivalence between those units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value, but it is not relevant if this variation between units is significant compared to the analytical variation. Consequently, ISO 17034 [1] requires reference material (RM) producers to quantify the between-unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the IRMM-2331P are valid for all produced units of the material, within the stated uncertainties.

As shown below in section 6.1 about the characterisation and process control measurements, the isotopic composition of the particles was verified to be in agreement with the certified composition of the solution, which is assumed to be homogeneous. Therefore, no between-unit homogeneity study for the uranium isotopic composition of the particles was deemed necessary.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus should be used in an analysis. Using sample sizes equal or above the minimum sample intake guarantees the certified value within its stated uncertainty.

Based on the thorough evaluation and control of environmental conditions during the production processes, the uranium isotopic composition can be considered homogeneous throughout the unit. Therefore the minimal sample intake is one particle.

5 Stability

Stability testing is necessary to establish the conditions for storage (long-term stability) as well as the conditions for dispatch of the materials to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C can be reached and stability under these conditions must be demonstrated, if the samples are to be transported without any additional cooling.

5.1 Short-term stability study

As the uranium isotopic composition is independent of the temperature, there is no impact from the transportation on the uranium isotopic composition. Therefore, no short-term stability study was performed for the uranium isotope amount ratios in the particles. The material can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability study

Data from the certification and monitoring program for various types of uranium CRMs such as the IRMM-2019-2029 and IRMM-019-029 series have demonstrated that the uranium isotopic composition remained stable over a timeframe of 30 years, and the relative uncertainty of the isotope amount ratios due to long-term stability for a shelf-life of 10 years can be considered negligible compared to the uncertainty due to the characterisation [16, 17]. Also, it is known that all uranium isotopes have the same physical properties, except for the half-life. As the half-lives[1] of ^{234}U ($245.5 \cdot 10^3$ a), ^{235}U ($704 \cdot 10^6$ a), ^{236}U ($23.43 \cdot 10^6$ a) and ^{238}U ($4.468 \cdot 10^9$ a) are much longer than the intended shelf life of the material, no significant effect due to radioactive decay is expected on the uranium isotope amount ratios. It can therefore be expected that the stability effects on the uranium isotope amount ratios are negligible. Therefore also for IRMM-2331P the shelf-life and the validity period of the certified values will be 10 years, similar to the IRMM-2019-2029 and IRMM-019-029 series. The IRMM-2331P will be placed under the regular stability monitoring program at JRC-G.2. The stability will be monitored using isotope ratios measurements performed using LG-SIMS at the IAEA.

[1] DDEP-BIPM (accessed: 22 February 2018) http://www.nucleide.org/DDEP_WG/DDEPdata.htm

6 Characterisation

The material characterisation is the process of determining the property value(s) of a reference material. The material characterisation was based on a primary isotope ratio method of measurement combined with a primary direct method (gravimetry) [21], and confirmed by an independent method. A primary method of measurement (also called "primary reference method" in the International Vocabulary of Metrology (VIM) [22]) is a method that does not require calibration with a standard of the same measurand and does not depend on a chemical reaction[2]. Such methods are of highest metrological order and often yield results with low uncertainties. However, it is nevertheless prudent to demonstrate absence of bias or gross errors by use of an independent method of lower metrological order.

6.1 Uranium isotope amount ratios in IRMM-2331P

The certification of the isotopic composition of the IRMM-2330 base solution was applied to the IRMM-2331P particle reference material after so-called "process control measurements" (PCM) had been performed successfully. The PCM were designed in a way to control the entire processing of the base solution, including the particle production and the process of dissolving the particles back into a nitrate solution for analysis.

The PCM measurements of the uranium isotope amount ratios in the IRMM-2331P particles were performed by MC-ICPMS at FZJ. There, the particles were leached from the sample planchets using highly concentrated nitric acid (65 %, 99.9999 % purity). For the leaching of the particles each planchet was placed on a clean and levelled surface. Then 200 µL of nitric acid was pipetted in two steps of each 100 µL on the surface on which the particles were placed. After 60 seconds dwell time the solution was transferred into a vial filled with 9.5 mL of milliQ water using a pipette. In a second step another 300 µL nitric acid was placed on the surface of the planchet in 3 steps of 100 µL each. Again after 60 seconds of dwell time the solution was pipetted from the planchet into the same vial. In total, a solution of 10 mL volume was produced with a dilution of 1:20. The solutions were further diluted by the operator of the MC-ICPMS laboratory at FZJ to the concentration appropriate for the measurements and in compliance with the standard operation procedure.

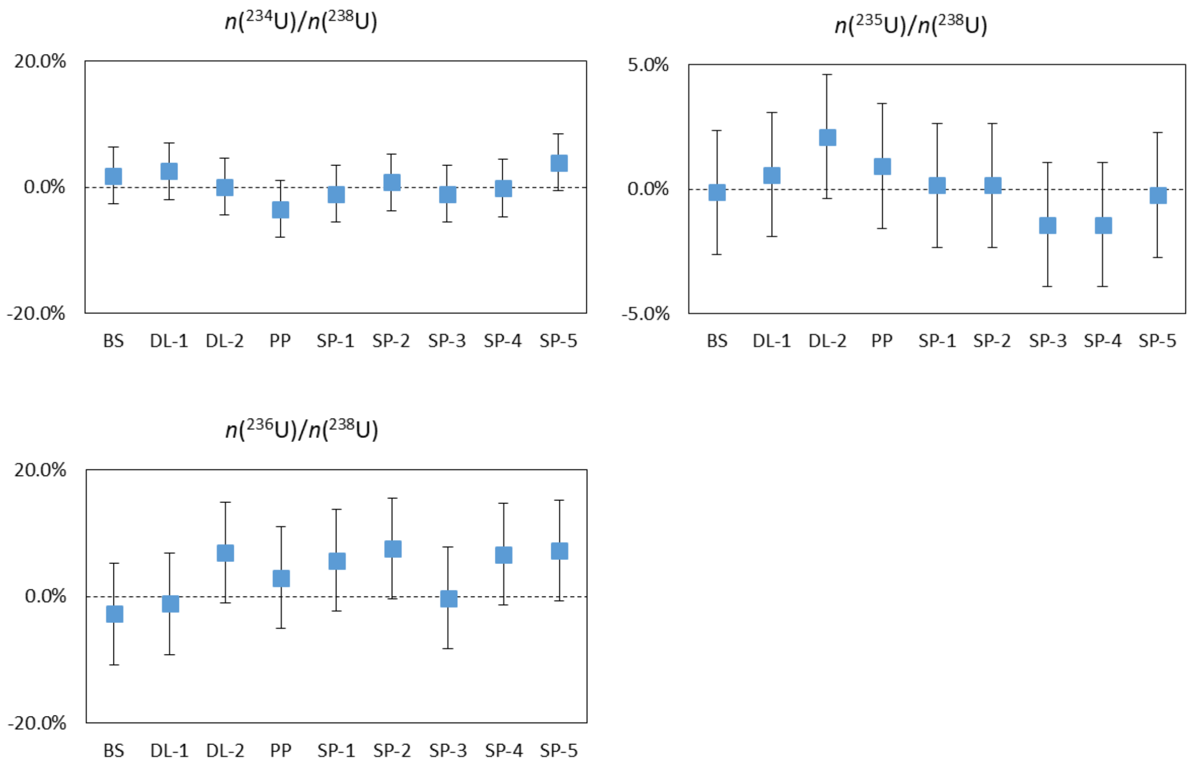
The base solution and the leaching solutions from five planchets of IRMM-2331P were analysed using a NEPTUNE MC-ICPMS at FZJ. The MC-ICPMS laboratory at FZJ is accredited according to ISO 17025 and is regularly participating in external inter-calibration campaigns. The certified reference material NBL CRM U-020 is used as standard for instrument calibration and NBL CRM U-350 for quality control. The measurement uncertainties include contributions from the sample preparation, possible cross contamination and most dominantly from the uncertainty of the measurement itself.

In addition to the PCM, the surfaces of blank planchets, used for both IRMM-2329P and IRMM-2331P, were analysed by leaching with HNO_3 with subsequent ICP-MS analysis at FZJ, and no uranium was found on the surfaces of the blank planchets [9].

The results of the PCM by MC-ICPMS on the base solution and the leached particles showed agreement with the certified values of the base solution as shown in Figure 4. It is recognized that the uncertainties for the PCM by MC-ICPMS are higher compared to those encountered during the certification measurements of the base solution using high precision TIMS/MTE method. This is due to the much smaller sample size of the particles samples leached from the planchets for MC-ICPMS measurements, compared to the sample filament loading for TIMS/MTE. However, no significant deviations were found in the PCM, which makes the particle reference material IRMM-2331P eligible for certification using the certified isotopic composition obtained for the base solution IRMM-2330.

[2] *A primary method is "a method having the highest metrological qualities, whose operation(s) can be completely described and understood and for which a complete uncertainty statement can be written in terms of SI units. A primary ratio method measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation*

Figure 4. Process Control Measurements for the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios. Legend: BS: base solution; DL-1 and Dl-2: diluted base solution (measured twice), PP: particles collected on a planchet directly after VOAG, prior to suspension step, leached from the planchet; SP-1-5: particles dispensed using suspension on 5 planchets, subsequently leached from the planchets.



7 Value assignment

Certified values are values that fulfil the highest standards of accuracy. The assigned uncertainties consist of uncertainties relating to characterisation, u_{char} (section 6) using the isotopic composition of the base solution IRMM-2330, potential within-unit and between-unit inhomogeneities, combined and expressed as u_{hom} (section 4.1), potential degradation during transport, u_{trn} (section 5.1), and potential degradation during storage, u_{lts} (section 5.2). These different contributions were combined to estimate the relative expanded uncertainty of the certified value (U_{CRM}) with a coverage factor k given as:

$$\boldsymbol{U_{\mathrm{CRM}}} = \boldsymbol{k} \cdot \sqrt{\boldsymbol{u}_{\mathbf{char}}^{2} + \boldsymbol{u}_{\mathbf{hom}}^{2} + \boldsymbol{u}_{\mathbf{trn}}^{2} + \boldsymbol{u}_{\mathbf{lts}}^{2}} \qquad \text{Equation 1}$$

As explained before, the uncertainties u_{hom}, u_{trn}, and u_{lts} are equal to zero, so only the uncertainties u_{char} are relevant for the determination of the expanded uncertainties. The uncertainty budgets for the isotope ratios are shown in Table 2.

Table 2. Uncertainty budgets for the characterized isotope ratios for IRMM-2331P, based on the TIMS/MTE measurements of base solution IRMM-2330.

	$n(^{235}\text{U})/n(^{238})\text{U}$	$n(^{234}\text{U})/n(^{238})\text{U}$	$n(^{236}\text{U})/n(^{238})\text{U}$
IRMM-074, certified $n(^{235}\text{U})/n(^{238})\text{U}$	26.5%	23.0%	0.5%
IRMM-074, measured $n(^{235}\text{U})/n(^{238})\text{U}$	9.0%	7.8%	0.2%
IRMM-2330, measured $n(^{235}\text{U})/n(^{238})\text{U}$	10.6%	9.2%	0.2%
IRMM-2330, measured $n(^{234}\text{U})/n(^{238})\text{U}$		2.8%	
IRMM-2330, measured $n(^{236}\text{U})/n(^{238})\text{U}$			31.7%
External uncertainty for MTE [11]	47.2%	40.9%	0.9%
Homogeneity contribution according to [9]	6.7%	16.4%	66.5%

7.1 Uranium isotope amount ratios, isotope amount fractions, isotope mass fractions and molar mass

The certified values of the uranium isotope ratios for IRMM-2331P were derived from the TIMS/MTE measurements in the IRMM-2330 solution, with confirmation by the TIMS/MTE verification measurements at IAEA-SGAS. The uranium isotope ratios in IRMM-2331P are given in mol·mol^{-1} below.

From the certified values for the uranium isotope ratios, the isotope amount fractions were derived by dividing the isotope amount ratios for the various isotopes by the sum of the isotope amount ratios:

$$\boldsymbol{n}(\,^{x}\mathbf{U})/\boldsymbol{n}(\mathbf{U}) = \frac{\boldsymbol{n}(\,^{x}\mathbf{U})/\boldsymbol{n}(^{238}\mathbf{U})}{\sum_{i=\{234;235;236;238\}}^{i} \boldsymbol{n}(\,^{i}\mathbf{U})/\boldsymbol{n}(^{238}\mathbf{U})} \qquad \text{Equation 2}$$

Moreover, the molar mass of the uranium was calculated by multiplication of the isotope amount fractions with the molar mass of the respective isotope:

$$\boldsymbol{M}(\mathbf{U}) = \sum_{i=\{234;235;236;238\}}^{i} \boldsymbol{n}(\,^{i}\mathbf{U})/\boldsymbol{n}(\mathbf{U}) \cdot \boldsymbol{M}(\,^{i}\mathbf{U}) \qquad \text{Equation 3}$$

For the re-calculation of the uranium molar mass, the molar mass of the individual isotopes of uranium (^{234}U, ^{235}U, ^{236}U and ^{238}U) have been taken from the most recent atomic mass evaluation (AME2016, 23]).

Finally, the isotope mass fractions for the different uranium isotopes were re-calculated by multiplication of the isotope amount fraction with the isotope molar mass, followed by division by the molar mass of the uranium:

$$\boldsymbol{m}(\,^{x}\mathbf{U})/\boldsymbol{m}(\mathbf{U}) = \frac{\boldsymbol{n}(\,^{x}\mathbf{U})/\boldsymbol{n}(\mathbf{U})\cdot\boldsymbol{M}(\,^{x}\mathbf{U})}{\boldsymbol{M}(\mathbf{U})} \qquad \text{Equation 4}$$

The certified and calculated derived values related to the uranium isotopic composition for IRMM-2331P are summarised in **Error! Reference source not found.**3.

Table 3. Certified and derived values and their uncertainties related to the uranium isotopic composition of IRMM-2331P.

	Certified values	U_{CRM} (1)	$U_{CRM,rel}$ (1)
$n(^{234}U)/n(^{238}U)$ [mol·mol^{-1}]	0.00042156	0.00000018	0.043 %
$n(^{235}U)/n(^{238}U)$ [mol·mol^{-1}]	0.051025	0.000015	0.029 %
$n(^{236}U)/n(^{238}U)$ [mol·mol^{-1}]	0.000062641	0.000000087	0.14 %
$n(^{234}U)/n(U)$ [mol·mol^{-1}]	0.00040091	0.00000017	0.042 %
$n(^{235}U)/n(U)$ [mol·mol^{-1}]	0.048526	0.000013	0.027 %
$n(^{236}U)/n(U)$ [mol·mol^{-1}]	0.000059572	0.000000083	0.14 %
$n(^{238}U)/n(U)$ [mol·mol^{-1}]	0.951014	0.000013	0.0014 %
$M(U)$ [g·mol^{-1}]	237.903151	0.000041	0.000017 %
$m(^{234}U)/m(U)$ [g·g^{-1}]	0.00039440	0.00000016	0.041 %
$m(^{235}U)/m(U)$ [g·g^{-1}]	0.047942	0.000013	0.027 %
$m(^{236}U)/m(U)$ [g·g^{-1}]	0.000059107	0.000000083	0.14 %
$m(^{238}U)/m(U)$ [g·g^{-1}]	0.951604	0.000013	0.0012 %

(1) Expanded (k = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

Traceability of the obtained results is based on the traceability of all relevant input factors. Instruments were verified and calibrated with tools ensuring traceability to the International System of units (SI).

The certified values for the uranium isotope amount ratios of IRMM-2331P are traceable to the International System of Units (SI) via the certified values of the certificate of the IRMM-074.

8.2 Commutability

Many measurement procedures include one or more steps which select specific analytes from the sample for the subsequent whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures is summarised in a concept called 'commutability of a reference material'. There are various definitions that define this concept. For instance, the CLSI Guideline C53-A [24] recommends the use of the following definition for the term commutability:

"The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and is therefore a crucial characteristic when applying different measurement methods. When the commutability of a CRM is not established, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

The IRMM-2331P uranium particles were produced from synthetic micro particles produced via a spray-pyrolysis procedure employing a thermal treatment to improve stability. The analytical behaviour will be the same as for typical uranium micro particles.

This reference material is tailor-made to be used by the nuclear safeguards community as calibrant, QC sample and reference material mainly for mass spectrometry analysis.

9 Instructions for use

9.1 Safety information

The IRMM-2331P contains low-level radioactive material in exempted quantities. The planchet should be handled with great care and by experienced personnel in a laboratory suitably equipped for the safe handling of low-level radioactive materials.

9.2 Storage conditions

The material should be stored in a dry environment at room temperature. A silica bag should be placed with the material to optimise its storage.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially for opened units.

9.3 Preparation and use of the material

Care should be taken to identify the particle bearing surface and to prevent any cross-contamination onto the sample surface. It is recommended to pay attention as to the correct side on which the particles are deposited when manipulating the planchet and placing it back into its case. The identification number of each planchet is engraved on the under side.

9.4 Minimum sample intake

The minimal sample intake of IRMM-2331P is 1 particle.

9.5 Use of the certified values

The main purpose of these materials is to assess method performance, i.e. for checking accuracy of analytical results and calibration. As any reference material, they can be used for establishing control charts or validation studies.

9.6 Use as a calibrant

The uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org).

When assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is summarised here [25]:

1. Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
2. Combine the measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2}$.
3. Calculate the expanded uncertainty (U_Δ) from the combined uncertainty (u_Δ) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %.
4. If $\Delta_{meas} \leq U_\Delta$ then no significant difference exists between the measurement result and the certified value, at a confidence level of approximately 95 %.

9.7 Use in quality control charts

The materials can be used for quality control charts. Using CRMs for quality control charts has the added value that a trueness assessment is built into the chart.

References

[1] ISO 17034:2016 General requirements for the competence of reference material producers.

[2] ISO Guide 35:2006 Reference materials – General and statistical principles for certification.

[3] ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM, 1995), International Organization for Standardization, Geneva, Switzerland, 2008

[4] International Atomic Energy Agency. Treaty on the non-proliferation of nuclear weapons, 22 April 1970.

[5] International Atomic Energy Agency. Model Protocol Additional to the Agreement(s) between State(s) and the International Atomic Energy Agency for the Application of Safeguards, September 1997COUNCIL

[6] COUNCIL REGULATION (EURATOM) No 1314/2013 on the Research and Training Programme of the European Atomic Energy Community

[7] International Atomic Energy Agency. The IAEA Safeguards Analytical Laboratories, October 2012.

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List of abbreviations and definitions

AP	Additional protocol
CRM	Certified reference material
CLSI	Clinical & Laboratory Standards Institute
EC	European Commission
ES	Environmental sampling
FT-TIMS	Fission track thermal ionisation mass spectrometry
FZJ	Forschungszentrum Jülich
IAEA	International Atomic Energy Agency
JRC	Joint Research Centre
k	Coverage factor
LA-MC-ICPMS	Laser Ablation multi-collector inductively coupled plasma mass spectrometry
LG-SIMS	Large-geometry secondary ion mass spectrometry
M	Molar mass
MC-ICPMS	Multi-collector inductively coupled plasma mass spectrometry
MTE	Modified total evaporation
NML	Nuclear Material Laboratory
NUSIMEP	Nuclear Signatures Inter-laboratory Measurement Evaluation Programme
NWAL	Network of analytical laboratories
OPS	Optical particle sizer
QC	Quality control
R	Isotope amount ratio
RM	Reference material
SGAS	Safeguards Analytical Services (belongs to the IAEA)
SEM	Scanning electron microscope
SI	International system of units
SIMS	Secondary ion mass spectrometry
TIMS	Thermal ionisation mass spectrometry
U	Expanded uncertainty
u	Standard uncertainty
VIM	International vocabulary on metrology
VOAG	Vibrating orifice aerosol generator

List of figures

List of tables

Annexes

Annex 1. Measurement Certificate for IRMM-2330.

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate G - Nuclear Safety and Security
Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (SN3S)

Certificate of Reference Measurement #3867

Customer	
Company/Institute	JRC
Division	Unit G.2
Address	Retieseweg 11 2440 Geel Belgium
Requestor	JRC-G.2

Sample Information	
Sample type	Uranium nitrate solution for particle production
Sample reference	IRMM-2330
Date of receipt of sample(s)	04/04/2017
JRC sample identification	27005
Condition of sample	Uranium nitrate solution, 2mg U / mL

Measurement Results

Analyte	Result	Unit	Method
$n(^{234}U)/n(^{238}U)$	0.00042156(18)	mol / mol	TIMS/MTE
$n(^{235}U)/n(^{238}U)$	0.051025(15)	mol / mol	TIMS/MTE
$n(^{236}U)/n(^{238}U)$	0.000062641(87)	mol / mol	TIMS/MTE

Derived Quantities

Molar Mass	237.903147(41)

Amount fraction (×100)		Mass fraction (×100)	
$n(^{234}U)/n(U)$	0.040091(17)	$m(^{234}U)/m(U)$	0.039440(16)
$n(^{235}U)/n(U)$	4.8526(13)	$m(^{235}U)/m(U)$	4.7942(13)
$n(^{236}U)/n(U)$	0.0059572(83)	$m(^{236}U)/m(U)$	0.0059107(83)
$n(^{238}U)/n(U)$	95.1014(13)	$m(^{238}U)/m(U)$	95.1604(13)

Uncertainties:
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[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. The traceability to SI is established through IRMM-074. Uncertainties include an extrapolated contribution for homogeneity, as described in[2].

Analytical measurement procedure:

- Sample preparation has been accomplished by J. Truyens
- Mass spectrometric measurements have been accomplished by S. Richter
- Analytical method/technique used : TIMS/MTE
- The atomic masses, used in the calculations, are[3]:
- The half-lives used in the calculations are: N/A
- The mass spectrometer was calibrated using IRMM-074
- Quality control samples used were IRMM-075/1 and IRMM-075/2

Date of analysis (dd/mm/yyyy)	27/04/2017
Date of internal analysis report (dd/mm/yyyy)	14/06/2017
Certification date normalised to (reference date)	27/04/2017 at 12:00 h

Backup Files and Raw Data
Folder: "G:\JRC.G.2\Nuclear Safeguards\Nuclear\Particles\Certification U Particle RM IRMM-2329-2330\TIMS MTE Measurements of Base Solutions IRMM-2329-2330"
Data Files: "T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls" "Calculation homogeneity extrapolation-2 - applied for IRMM-2329-2330.xls" "IRMM-2330.SMU"

Annexes
Copy of Internal Analysis Report (2 pages)

JRC G.2 Unit Head: Prof. Dr. W. Mondelaers

Signature and date:

22/06/17

References:
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3 G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nuclear Physics A 729(2003) 337-676

Annex 2. Certificate of IRMM-074 series

CERTIFICATE

ISOTOPIC REFERENCE MATERIAL IRMM-074

The Isotopic Reference Material IRMM-074 is a set of mixtures of uranium isotopes ^{233}U, ^{235}U and ^{238}U with molar ratios certified as follows:

Code Number	Molar Isotope Abundance Ratio		
	$n(^{233}U)/n(^{235}U)$ U = 0.025% (relative)	$n(^{233}U)/n(^{238}U)$ U = 0.025%(relative)	$n(^{235}U)/n(^{238}U)$ U = 0.015%(relative)
IRMM-074/1	1.026 85	1.027 11	1.000 254
IRMM-074/2	0.307 993	0.308 072	1.000 258
IRMM-074/3	0.010 228 8	0.010 231 4	1.000 259
IRMM-074/4	0.003 073 58	0.003 074 37	1.000 259
IRMM-074/5	0.001 030 61	0.001 030 88	1.000 259
IRMM-074/6	0.000 307 778	0.000 307 858	1.000 259
IRMM-074/7	0.000 102 603	0.000 102 629	1.000 259
IRMM-074/8	0.000 030 801 1	0.000 030 809 1	1.000 259
IRMM-074/9	0.000 008 158 7	0.000 008 160 8	1.000 259
IRMM-074/10	0.000 001 018 86	0.000 001 019 13	1.000 259

The Isotopic Reference Material is intended for the verification and correction of non-linearities of the entire mass spectrometer measurement system.

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 these Isotopic Reference Materials will, therefore, also be traceable to the SI unit system.

07/2006

2. The uncertainties as specified in the table can be considered as expanded uncertainties U where $k = 2$. The value of the standard uncertainty can therefore be derived: $u_c = U \cdot 0.5$
   The uncertainties given are supported by calculation of the combined uncertainty following the ISO/GUM recommendations[1] and are based on measured values of the isotopic enrichments, the weights of oxides and solutions, and of the impurity levels. The uncertainties were also confirmed through comparison measurements made on samples of IRMM-072, IRMM-199 and CRM-U-500 (DOE/NBL).

3. Values for molar isotope abundance ratios are valid for June 2005.

4. The Isotopic Reference Material IRMM-074 consists of a set of 10 units. Each unit consists of approximately 0.2 mg uranium as uranylnitrate in 2 mL 1 M nitric acid solution in a sealed quartz glass ampoule.

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

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

6. The vial should by opened with great care and by experienced personnel in a laboratory environment suitably equipped for the safehandling of radioactive materials.

7. Full details on the certification procedure can be found in the Certification Report EUR 22270 EN[3].

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

Weighing and preparation of the Isotopic Reference Material was performed by F Hendrickx and R Eykens. Characterization of the enriched isotopes from which the set was prepared and verification measurements on the mixtures, were performed by S Richter on samples prepared by F Kehoe and A Alonso Muñoz. The ampoulation of this Isotopic Reference Material was accomplished by G Van Baelen and A Verbruggen.

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	P Taylor	R Wellum
July 2006	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

[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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Annex 3. Certificate of IRMM-184

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and Safeguards Unit

CERTIFIED REFERENCE MATERIAL
IRMM – 184

CERTIFICATE OF ANALYSIS

Uranium in nitric acid solution		
	Isotope amount ratios	
	Certified value [1] [mol/mol]	Uncertainty [2] [mol/mol]
$n(^{233}U)/n(^{238}U)$	< 0.000000002	/
$n(^{234}U)/n(^{238}U)$	0.000053138	0.000000032
$n(^{235}U)/n(^{238}U)$	0.0072623	0.0000022
$n(^{236}U)/n(^{238}U)$	0.00000012446	0.00000000053

[1] The certified values are traceable to the International System of units (SI).

[2] The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

There is no minimum sample intake to be taken into account.

The certificate is valid for 3 years; the validity may be extended after further tests on the stability of the material are carried out.

The certificate is a revision of the original certificate of 1987, which was revised in 1993, 1999 and 2005.

Geel, September 2019

Signed: 18 SEP. 2019

Dr. Arjan Plompen
European Commission
Joint Research Centre
Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and Safeguards Unit
Retieseweg 111
B-2440 Geel, Belgium

The following values were assigned (continued):

	Isotopic mass fractions (·100)	
	Value [3] [g/g]	Uncertainty [4] [g/g]
$m(^{233}U)/m(U)$	< 0.0000002	/
$m(^{234}U)/m(U)$	0.0051868	0.0000032
$m(^{235}U)/m(U)$	0.71191	0.00021
$m(^{236}U)/m(U)$	0.000012253	0.000000052
$m(^{238}U)/m(U)$	99.28289	0.00021
	Isotopic amount fractions (·100)	
	Value [3] [mol/mol]	Uncertainty [4] [mol/mol]
$n(^{233}U)/n(U)$	< 0.0000002	/
$n(^{234}U)/n(U)$	0.0052752	0.0000032
$n(^{235}U)/n(U)$	0.72096	0.00021
$n(^{236}U)/n(U)$	0.000012356	0.000000052
$n(^{238}U)/n(U)$	99.27376	0.00022
	Molar mass	
	Value [3] [g/mol]	Uncertainty [4] [g/mol]
U	238.0288936	0.0000079

[3] The derived certified values are calculated from the certified uranium isotope amount ratios and the atomic masses according to G. Audi et al. (The 1993 atomic mass evaluation, Nuclear Physics, A565, 1-65, 1993).

[4] The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

DESCRIPTION OF THE MATERIAL

The IRMM-184 is a uranium isotopic Certified Reference Material (CRM) supplied with isotope amount ratios as certified above. IRMM-184 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of nitric acid solution. The concentration of nitric acid is 5 mol·L^{-1}.

ANALYTICAL METHODS USED FOR CERTIFICATION

The certified $n(^{235}U)/n(^{238}U)$ ratio was established by mass spectrometric measurements using the MAT511 mass spectrometer. The certified $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios were measured using the Triton thermal ionisation mass spectrometer.
Compared to the last revision in 2005, the uncertainties for the $n(^{236}U)/n(^{238}U)$ ratios were updated according to the recommendation from ASTM C1832, section 14.6.4, by adding a relative uncertainty contribution of 0.4 % ($k = 2$) for the use of the secondary electron multiplier for measuring ^{236}U.

SAFETY INFORMATION

The IRMM-184 contains radioactive material. The ampoules should be handled with great care and by experienced personnel in a laboratory suitably equipped for the safe handling of radioactive materials.

INSTRUCTIONS FOR USE AND INTENDED USE

The material is used for calibration of mass spectrometers.

STORAGE

The vials should be stored at + 18 °C ± 5 °C.
However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

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European Commission – Joint Research Centre
Directorate G – Nuclear Safety and Security
G.2 – Standards for Nuclear Safety, Security and Safeguards Unit
Retieseweg 111, B - 2440 Geel (Belgium)

Annex 4. Uranium isotopic composition in base solution IRMM-2330 and IRMM-2331P

IRMM-2330

Original folder: U:\Nuclear Safeguards\Nuclear\IRMM-2329P$_{\text{IRMM-2331P\textbackslash IRMM-2331P\textbackslash Characterization}}$ Original File: T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls

Model Equation:

$f_{233U} = R_{233/238U}/\Sigma R_U;$
$f_{234U} = R_{234/238U}/\Sigma R_U;$
$f_{235U} = R_{235/238U}/\Sigma R_U;$
$f_{236U} = R_{236/238U}/\Sigma R_U;$
$f_{238U} = 1/\Sigma R_U;$
$\Sigma R_U = R_{233/238U} + R_{234/238U} + R_{235/238U} + R_{236/238U} + 1;$

$M_U = M_{233U} \cdot f_{233U} + M_{234U} \cdot f_{234U} + M_{235U} \cdot f_{235U} + M_{236U} \cdot f_{236U} + M_{238U} \cdot f_{238U};$
$w_{233U} = f_{233U} \cdot M_{233U}/M_U;$
$w_{234U} = f_{234U} \cdot M_{234U}/M_U;$
$w_{235U} = f_{235U} \cdot M_{235U}/M_U;$
$w_{236U} = f_{236U} \cdot M_{236U}/M_U;$
$w_{238U} = f_{238U} \cdot M_{238U}/M_U;$

List of Quantities:

Quantity	Unit	Definition
$R_{233/238U}$		isotope amount ratio n_{233}/n_{238} of U
$R_{234/238U}$		isotope amount ratio n_{234}/n_{238} of U
$R_{235/238U}$		isotope amount ratio n_{235}/n_{238} of U
$R_{236/238U}$		isotope amount ratio n_{236}/n_{238} of U
M_U		molar mass of U
f_{233U}		isotope amount fraction of ^{233}U in U
f_{234U}		isotope amount fraction of ^{234}U in U
f_{235U}		isotope amount fraction of ^{235}U in U
f_{236U}		isotope amount fraction of ^{236}U in U
f_{238U}		isotope amount fraction of ^{238}U in U
w_{233U}		isotope mass fraction of ^{233}U in U
w_{234U}		isotope mass fraction of ^{234}U in U
w_{235U}		isotope mass fraction of ^{235}U in U
w_{236U}		isotope mass fraction of ^{236}U in U
w_{238U}		isotope mass fraction of ^{238}U in U
M_{233U}		atomic mass for ^{233}U
M_{234U}		atomic mass for ^{234}U
M_{235U}		atomic mass for ^{235}U
M_{236U}		atomic mass for ^{236}U
M_{238U}		atomic mass for ^{238}U

Quantity	Unit	Definition
ΣR_U		sum of isotope ratios for U

$R_{233/238U}$: Type B rectangular distribution
Value: 0
Halfwidth of Limits: 0

$R_{234/238U}$: Import from Excel
Filename: T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls
Worksheet: Summary-calc
Value Cell: C206 = $421.5611 \cdot 10^{-6}$
Standarduncertainty Cell: C207 = $87.9 \cdot 10^{-9}$
Degrees of Freedom Cell: 50 = Error

$R_{235/238U}$: Import from Excel
Filename: T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls
Worksheet: Summary-calc
Value Cell: B206 = 0.05102504
Standarduncertainty Cell: B207 = $7.43 \cdot 10^{-6}$
Degrees of Freedom Cell: 50 = Error

$R_{236/238U}$: Import from Excel
Filename: T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls
Worksheet: Summary-calc
Value Cell: D206 = $62.6410 \cdot 10^{-6}$
Standarduncertainty Cell: D207 = $43.7 \cdot 10^{-9}$
Degrees of Freedom Cell: 50 = Error

M_{233U}: Type B normal distribution
Value: 233.039627
Expanded Uncertainty: 0.000003
Coverage Factor: 1.0

The mass of the isotope is read from \\Sim_server\gumwork\wizards\ELTABLE.CSV.

M_{234U}: Type B normal distribution
Value: 234.0409504
Expanded Uncertainty: 0.0000024
Coverage Factor: 2

Wang et al., The AME 2016 atomic mass evaluation, Chinese Physics C Vol. 41, No. 3 (2017) 030003

M_{235U}: Type B normal distribution
Value: 235.0439282
Expanded Uncertainty: 0.0000024
Coverage Factor: 2.0

Wang et al., The AME 2016 atomic mass evaluation, Chinese Physics C Vol. 41, No. 3 (2017) 030003

M_{236U}: Type B normal distribution
Value: 236.0455662
Expanded Uncertainty: 0.0000024
Coverage Factor: 2

Wang et al., The AME 2016 atomic mass evaluation, Chinese Physics C Vol. 41, No. 3 (2017) 030003

M_{238U}: Type B normal distribution
Value: 238.0507870
Expanded Uncertainty: 0.0000032
Coverage Factor: 2

Wang et al., The AME 2016 atomic mass evaluation, Chinese Physics C Vol. 41, No. 3 (2017) 030003

Interim Results:

Quantity	Value	Standard Uncertainty
ΣR_U	1.05150924	$7.43 \cdot 10^{-6}$

Uncertainty Budgets:

M_U: molar mass of U

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$R_{233/238U}$	0.0	0.0	rectangular	0.0	0.0	0.0 %
$R_{234/238U}$	$421.5611 \cdot 10^{-6}$	$87.9 \cdot 10^{-9}$		-3.7	$-320 \cdot 10^{-9}$	0.0 %
$R_{235/238U}$	0.05102504	$7.43 \cdot 10^{-6}$		-2.7	$-20 \cdot 10^{-6}$	99.4 %
$R_{236/238U}$	$62.6410 \cdot 10^{-6}$	$43.7 \cdot 10^{-9}$		-1.8	$-77 \cdot 10^{-9}$	0.0 %
M_{233U}	233.03962700	$3.00 \cdot 10^{-6}$	normal	0.0	0.0	0.0 %
M_{234U}	234.04095040	$1.20 \cdot 10^{-6}$	normal	$400 \cdot 10^{-6}$	$480 \cdot 10^{-12}$	0.0 %
M_{235U}	235.04392820	$1.20 \cdot 10^{-6}$	normal	0.049	$58 \cdot 10^{-9}$	0.0 %
M_{236U}	236.04556620	$1.20 \cdot 10^{-6}$	normal	$60 \cdot 10^{-6}$	$71 \cdot 10^{-12}$	0.0 %
M_{238U}	238.05078700	$1.60 \cdot 10^{-6}$	normal	0.95	$1.5 \cdot 10^{-6}$	0.6 %
M_U	237.9031506	$20.3 \cdot 10^{-6}$				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
M_U	237.903151	$41 \cdot 10^{-6}$	2.00	manual
f_{234U}	$400.91 \cdot 10^{-6}$	$170 \cdot 10^{-9}$	2.00	manual
f_{235U}	0.048526	$13 \cdot 10^{-6}$	2.00	manual
f_{236U}	$59.572 \cdot 10^{-6}$	$83 \cdot 10^{-9}$	2.00	manual
f_{238U}	0.951014	$13 \cdot 10^{-6}$	2.00	manual
w_{234U}	$394.40 \cdot 10^{-6}$	$160 \cdot 10^{-9}$	2.00	manual
w_{235U}	0.047942	$13 \cdot 10^{-6}$	2.00	manual
w_{236U}	$59.107 \cdot 10^{-6}$	$83 \cdot 10^{-9}$	2.00	manual
w_{238U}	0.951604	$13 \cdot 10^{-6}$	2.00	manual

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