Certification of the First Uranium Oxide micro-particle reference materials for Nuclear Safety and Security, IRMM-2329P and IRMM-2331P

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Abstract

For nuclear safeguards purposes, two new uranium oxide micro-particle isotope reference materials were certified, IRMM-2329P and IRMM-2331P, with ^{235}U enrichments of 3% and 5%, and ^{236}U abundances of 30 $\mu g \cdot g^{-1}$and 60 $\mu g \cdot g^{-1}$, respectively. The isotopic compositions of the base materials were measured by TIMS. The production of the uranium oxide particles was achieved using a vibrating orifice aerosol generator (VOAG) and the particles deposited on carbon planchets. Process control verification measurements on dissolved uranium oxide particles were performed by MC-ICPMS. For IRMM-2329P also the uranium amount per particle was certified by TIMS/IDMS and verified by MC-ICPMS/IDMS.

Introduction

During the past decades, the European Commission's Joint Research Centre (EC-JRC) has supported safeguards activities of the International Atomic Energy Agency (IAEA) and the Euratom inspectorate. The IAEA Network of Analytical Laboratories (NWAL) for environmental sampling apply validated measurement methods for the analyses of 8environmental samples, which allows the IAEA to make credible safeguards conclusions. 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 [1].

The JRC unit G.2 (Standards for Nuclear Safety, Security and Safeguards), the FZJ (Forschungszentrum Jülich, Germany) and the IAEA-SGAS (Office of Safeguards Analytical Services, Seibersdorf, Austria) collaborated to produce and characterize micrometre-sized uranium oxide particles, which can be used as reference materials for nuclear safeguards purposes [2, 3]. Two micrometre-sized uranium oxide particle materials, called IRMM-2329P and IRMM-2331P, have been certified at JRC-G.2 in compliance with ISO 17034 [4] for the uranium isotopic composition; IRMM-2329P was additionally certified for the uranium amount per particle. The certification of the uranium amount per particle is useful to optimize sensitivity and transmission efficiency of LG-SIMS [5], FT-TIMS [6, 7] and laser ablation – multi collector - inductively coupled plasma mass spectrometry (LA-MC-ICPMS) [8, 9].

Preparation and certification of IRMM-2329P and IRMM-2331P, two uranium particle reference materials

In the framework of this collaborative project micrometresized uranium oxide (U3O8) particle materials were produced from a uranium base solution certified by JRC-G.2 for the uranium isotopic composition [2, 3]. Following the IAEA's recommendations, the particles were produced as a low enriched uranium (LEU) with ^{235}U relative isotopic abundances in the range of 3–5%, and ^{236}U relative isotopic abundances in the range of 30 $\mu g \cdot g^{-1}$ to 60 $\mu g \cdot g^{-1}$, to be detectable and at the same time challenging for most of the commonly applied techniques. The base solutions used for the production of the IRMM-2329P and IRMM-2331P uranium oxide particles were prepared by mixing uranium solutions converted from the UF6 isotopic reference materials IRMM-023 and IRMM-029 [10], and an in-house quality control material labelled 2014-02T, and characterizing the mixture solution for the isotopic composition using the modified total evaporation (MTE) method for TIMS [11]. The isotopic compositions of the base solutions were verified by MTE/TIMS at IAEA-SGAS.

For the particle production, a special processing set-up was designed at FZJ using a vibrating orifice aerosol generator (VOAG, model 3450, TSI Inc., USA) in order to generate droplets and a respective procedure was developed to stabilize and homogenize the particles [12]. For this purpose, the uranium solution was first diluted with ultra-pure water (18.2 MΩ cm) and ethanol (ethanol absolute for analysis EMSURE® ACS,ISO,Reag. Ph Eur, 1.00983, Supelco) towards a uranium content of around 125 $\mu g\ g^{-1}$, and a water to ethanol volume ratio around 1. The prepared feed solution was then fed into the VOAG at a volume flow rate of 2.59 $\mu L \cdot s^{-1}$. The VOAG was operated using a gold-coated orifice with a diameter of 20 µm oscillating with a frequency of 70 kHz. Under the given conditions, a liquid jet was formed, which is split by the vibrating orifice into monodisperse droplets. The generated droplets were carried with a precleaned supply of compressed air through a drying column, at which temperature the solvents (water and ethanol) evaporate and result into the formation of uranyl nitrate precursor particles, and a 200 mm long aerosol heater. The aerosol heater was set to 500 °C, to induce subsequently nitrate decomposition and partially transformation into solid U3O8 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 glassy carbon disk (PXG-3 S, Seishin Trading, Kobe, Japan).

Several carbon disks loaded with particles were produced over the course of two subsequent days. The carbon disks loaded with the particles were transferred into a pre-cleaned ethanol-filled bottle, which was ultra-sonicated to detach particles from the carbon disks into the ethanol. The stability of the produced particles in an ethanol suspension was previously demonstrated [13], and allows for the production of a large number of particle loaded glass-like carbon disks (referred to as units). Aliquots of the produced suspension were distributed using a pipette onto 25.4 mm diameter glass-like carbon disks, which were gently heated to dryness to deposit the particles onto the disks as homogeneously as possible. Before packing, the disks were shortly heated to evaporate all volatile residues.

For both IRMM-2329P and IRMM-2331P, more than 100 units were produced using the procedure described above. Each IRMM-2329P and IRMM-2331P unit contains about 15,000–20,000 monodisperse uranium oxide particles with a micrometre-sized diameter, distributed onto a 25.4 mm diameter glass-like carbon disk. Images of IRMM-2331P particles and the particle size distribution are shown in Figs. 1 and 2 below, the respective images for IRMM-2329P look similar.

The particle diameters were found to range between 1 and 2 µm, with an average of about 1.25 µm and a relative standard deviation of about 6% for the most abundant population. These values for particle diameter and its standard deviation are purely indicative and not certified. Figure 2 shows the particle size distribution of IRMM-2331P, which is similar to IRMM-2329P.

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 the uranium oxide compared to the main particle population. Such particles are likely produced by the fusion of two aerosol droplets before solvent evaporation.

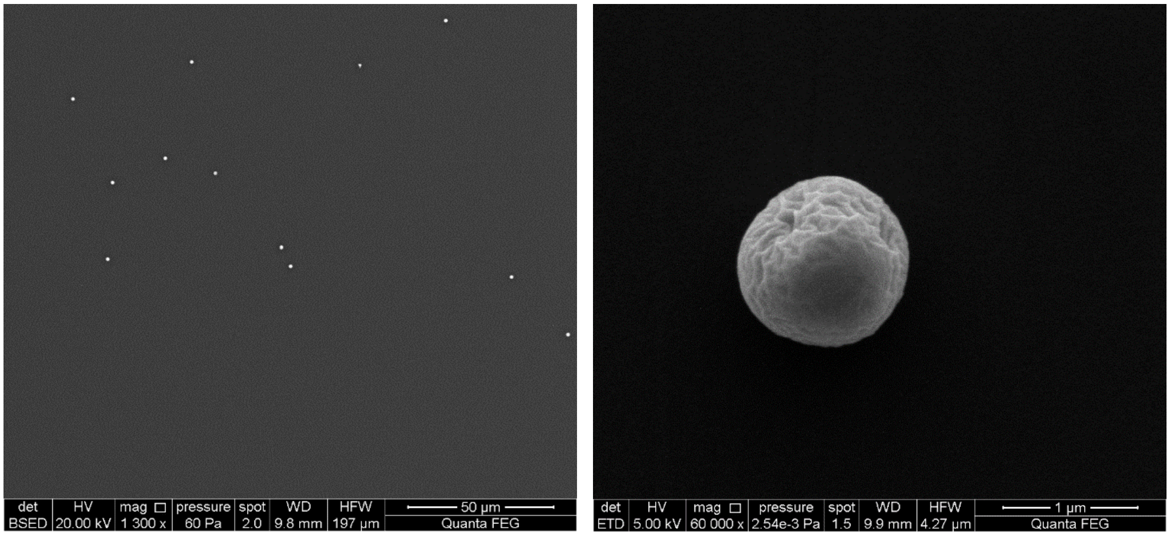

Figure 1. SEM images of IRMM-2331P particles (taken at FZJ). The picture on the left gives an overview of the uranium particles present on section of the planchet. The picture on the right shows a single particle.

In order to guarantee the isotopic integrity of the uranium isotope ratios from the solutions to the produced particles, so-called "process control measurements" (i.e. verification measurements) were carried out at the IAEA-SGAS and FZJ, respectively, for IRMM-2329P and IRM-2331P, in compliance with ISO 17,025 [14]. For this purpose, several disks were leached using nitric acid and the dissolved particles from the uranyl nitrate leaching solutions were measured by MC-ICPMS (Neptune Plus™, Thermo Scientific ™, Bremen, Germany). The measurement results for the leaching solutions were directly compared to the uranium isotopic composition measured in the original base solution during the same measurement sequence, together with respective quality control standards. Measuring these solutions during the same sequence is advantageous as all solutions are measured under the same measurement conditions, thus cancelling out effects that are dependent on the respective daily instrument optimization and performance (e.g. formation rate of interferences, mass bias correction, ion counter yields, hydride correction, etc.). The results of the process control measurements demonstrated clearly that the isotopic compositions of the base solutions were not altered during the entire particle production process. By following this strategy of process control measurements, the isotopic composition of the particles was measured on the same medium, i.e. on uranyl nitrate solutions, as the original mother solution. This has the advantage, that for the certification of IRMM-2329P and IRMM2331P, none of the particle specific techniques like LG-SIMS, FT-TIMS or LAMC- ICPMS, have been employed, for which these particle reference materials have been prepared to be used later-on, e.g. for calibration, validation, study of instrument specific fractionation effects, etc. The certification of this particle reference material is therefore independent of the characteristics of the typically applied particle analysis techniques. More details about the certification process can be found in the respective certification reports for IRMM-2329P [15] and IRMM-2331P [16]. The certified isotope ratios for IRMM2329P and IRMM-2331P are shown in Table 1.

Table 1: Certified isotope ratios for IRMM-2329P [15] and IRMM-2331P. [16]. All uncertainties are given with a coverage factor of k = 2.

	$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
IRMM-2329P	0.00034083(19)	0.033902(12)	0.00003021(12)
IRMM-2331P	0.00042156(18)	0.051025(15)	0.000062641(87)

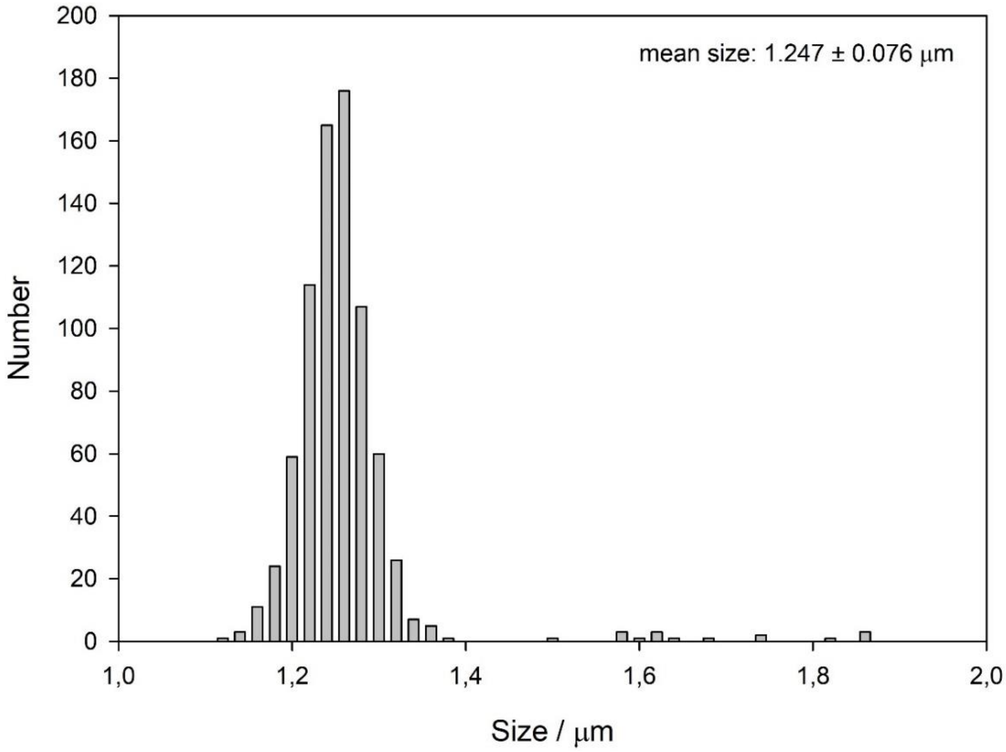

Figure 2: Particle Size distribution for IRMM-2331P particles.

Since the certification of IRMM-2329P and IRMM-2331P, these materials have been used as quality control materials (QC) at various NWAL laboratories, including IAEA-SGAS laboratory. The results for 41 micro-beam analyses of IRMM-2331P obtained between April 2021 and July 2021 on the Cameca-1280 LG-SIMS at the IAEA-SGAS instrument are shown in Figs. 3 to 5. The majority as well as the overall averages of LG-SIMS measurements are in agreement with the certified values.

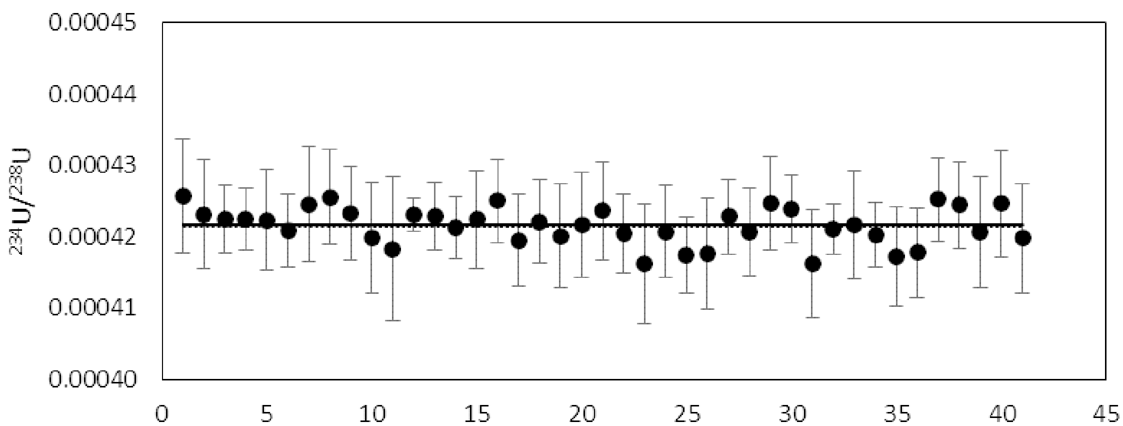

Figure 3: Quality Control (QC) measurements for the 234U/238U ratio for IRMM-2331P particles measured on the Cameca-1280 LG-SIMS at the IAEA-SGAS, recorded between April 2021 and July 2021. The certified ratios are indicated by solid lines, and their uncertainties by dashed lines. All uncertainties are given with a coverage factor of k = 2.

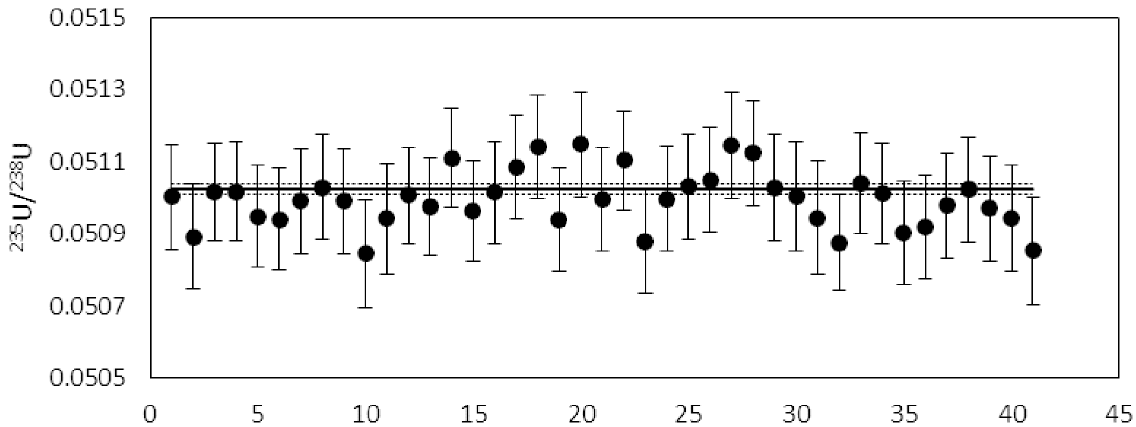

Figure 4: Quality Control (QC) measurements for the 235U/238U ratio for IRMM-2331P particles measured on the Cameca-1280 LG-SIMS at the IAEA-SGAS, recorded between April 2021 and July 2021. The certified ratios are indicated by solid lines, and their uncertainties by dashed lines. All uncertainties are given with a coverage factor of *k* = 2.

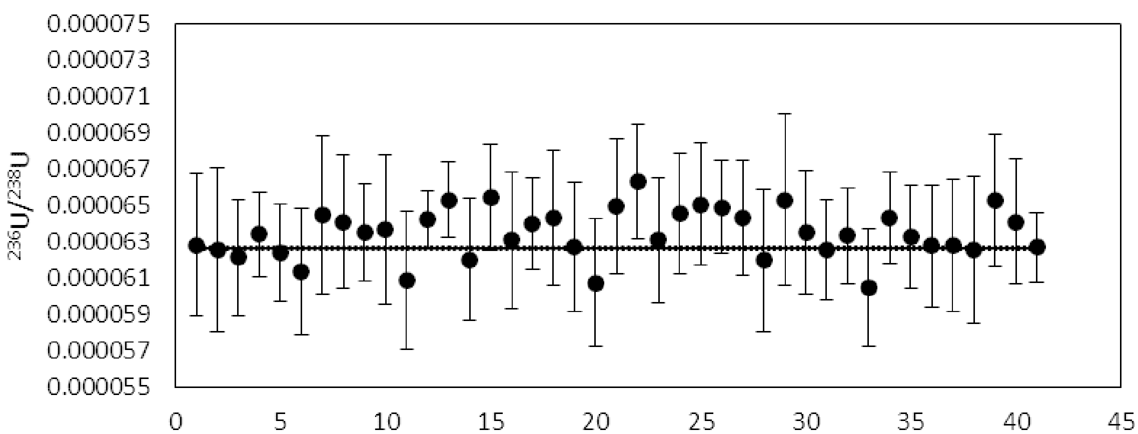

Figure 5: Quality Control (QC) measurements for the 236U/238U ratio for IRMM-2331P particles measured on the Cameca-1280 LG-SIMS at the IAEA-SGAS, recorded between April 2021 and July 2021. The certified ratios are indicated by solid lines, and their uncertainties by dashed lines. All uncertainties are given with a coverage factor of *k* = 2.

In addition to the certification of the uranium isotopic composition of the particles, in case of IRMM2329P the uranium amount content and mass per particle were certified at JRC-G.2 using isotope dilution TIMS [14], leading to a mass of uranium of (3.58 pg ± 0.64, *k* = 2) pg per particle. Verification measurements of the uranium mass per particle using MC-ICPMS were carried out at IAEA-SGAS [17], and confirmed the uranium mass per particle value that had been previously determined by ID-TIMS [15]. The certification of the uranium mass and amount content per particle is useful to determine and monitor the sensitivity and transmission of particle mass spectrometers like LG-SIMS, FT-TIMS and LAMC-ICPMS, as already demonstrated during the NUSIMEP-9 inter-laboratory comparison for uranium isotope amount ratios and uranium mass in uranium microparticles [18].

Conclusions

In a trilateral collaboration between JRC-G.2, FZJ and the IAEA-SGAS, the first commercially available particle reference materials of mono-disperse micrometre-sized uranium particles, IRMM-2329P and IRMM-2331P, have been produced and certified for the uranium isotopic composition, and in case of IRMM-2329P also for the uranium amount and mass per particle. These particle reference materials can be used as calibrant for particle specific instruments such as LG-SIMS, FT-TIMS or LAMC-ICPMS. They are specifically useful for the purpose of quality control, method validation, study of instrument specific fractionation effects and as conformity assessment tools. This is of particular interest to the IAEA-NWAL laboratories but also to other stakeholder and partner laboratories in various scientific areas specialised in uranium particle analysis. Each IRMM2329P and IRMM-2331P unit consists of roughly 15,000 monodisperse uranium oxide particles with a micrometre-sized diameter, distributed onto a 25.4 mm diameter glasslike carbon disk, and can be ordered via the Certified Reference Materials catalogue of the JRC (https://crm.jrc.ec.europa.eu/e/92/Catalogue-price-list-pdf).

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