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50 Years of uranium isotopic reference materials at JRC-Geel

S. Richter[1] · C. Hennessy[1] · J. Truyens[1] · U. Jacobsson[1] · C. Venchiarutti[1] · R. Bujak[1,2] · Y. Aregbe[1]

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Abstract
The history of uranium isotopic reference materials from JRC-Geel during the last 50 years is reviewed by presenting certification methods and relevant applications. The certified isotope ratios are traceable to the SI via gravimetrical preparation, either directly through gravimetrical mixing of highly enriched materials, or indirectly using existing gravimetrically prepared reference materials for calibration of mass spectrometers used for certification measurements. Due to developments of mass spectrometers and analytical methods, certification measurements have improved regarding precision, uncertainties and accuracy. This has led to a comprehensive set of uranium isotopic reference materials available for nuclear safety, security and the scientific community.

Keywords Uranium · Isotopes · Reference materials · Certification · Nuclear safeguards · Nuclear security

Introduction

During about the last 50 years [1–3], the Directorate G, "Nuclear Safety and Security", unit G.II.5 "Nuclear Data and Measurement Standards" at the European Commission's Joint Research Centre location in Geel, Belgium (formerly known as the "Institute for Reference Materials and Measurements", IRMM, and prior to that, "Central Bureau for Nuclear Measurements", CBNM), has been providing a wide range of nuclear Certified Reference Materials (CRMs) to the safeguards authorities and the nuclear industry. This is an obligation under the Euratom treaty signed in 1957, where the need for nuclear standards is explicitly mentioned, acknowledging their importance for all measurements of nuclear materials. It was emphasized that for accurate mass spectrometric measurements in nuclear material accountancy and nuclear safeguards, suitable CRMs are needed to calibrate instruments and validate measurement procedures. The unit JRC.G.II.5 is accredited by the Belgian accreditation body (BELAC) for reference measurements, the provision of nuclear CRMs and coordination of interlaboratory comparisons in compliance with the ISO standards ISO 17025 [4], ISO 17034 [5] and ISO 17043 [6].

For mass spectrometry in particular, CRMs produced using procedures that are as far as possible independent of mass spectrometric techniques, are needed. One way to achieve this is to use highly isotopically enriched base materials and mix them gravimetrically in suitable proportions to achieve the requested characteristic target values for the isotope ratios. This procedure has been applied for the preparation of isotope CRMs for uranium and plutonium for five decades by several institutions, like NIST, NBL (New Brunswick Laboratory, recently renamed the NBL Program Office) and JRC-Geel (IRMM, CBNM).

For example, in the 1980s the IRMM-072 series [7, 8] of isotope mixtures containing ^{233}U, ^{235}U and ^{238}U in various proportions was prepared. About 20 years later, the isotope mixing program was revived, and several additional isotopic CRMs were prepared and certified: the IRMM-073 [9], IRMM-074 [10] (similar to IRMM-072) and IRMM-075 series (^{236}U/^{238}U ratios ranging from 10^{-9} to 10^{-4}) [11], the IRMM-3636a/b double spikes (^{233}U/^{236}U ≈ 1) [12], the quad-spike IRMM-3100a [13], and in 2021 the IRMM-3000 and IRMM-3000a series of HEU (highly enriched uranium) solutions [14]. These CRMs can be called "gravimetrical", because they have isotopic compositions gravimetrically tailor-made for specific types of mass spectrometer

✉ S. Richter
stephan.richter@ec.europa.eu

1 European Commission, Joint Research Centre (JRC), Geel, Belgium

2 Present Address: Environmental Sample Laboratory, IAEA Laboratories, Office of Safeguards Analytical Services, Department of Safeguards, International Atomic Energy Agency, Seibersdorf, Austria

calibrations, e.g. for detector linearity, detector inter-calibration and mass fractionation correction, but they are not similar to samples commonly observed in the environment or the nuclear fuel cycle.

In parallel to the certification of the gravimetric mixtures, also uranium reference materials in the form of uranium hexafluoride (UF_6) and uranium nitrate solutions were certified, which rather mimic the isotopic compositions of samples encountered in a nuclear mass spectrometry laboratory, so they could be called "non-gravimetrical" reference materials. For example, in the 1970s–1990s, CRMs in the form of UF_6 as well as uranium nitrate solutions were prepared, such as the IRMM-019-027 and the IRMM-183-187 series, with ^{235}U enrichments (i.e. ^{235}U mass fractions) from 0.16 to 5.0%.

The IRMM-183-187 series of uranium solutions were originally known also as the EC 183-187 series, containing about 1 g of uranium in about 5 ml of 1 mol/l nitric acid solution per unit. The IRMM-183-187 series was prepared by dissolution from the original EC-171 series of uranium oxides (U_3O_8), consisting of the materials called EC-171/031, /071, /194, /295, /446, which are also used as γ-spectrometry standards. Small fractions from this oxide series EC-171 were also fluorinated into UF_6 gas, and then characterized for the $^{235}U/^{238}U$ ratio by GSMS (Gas Source Mass Spectrometry) against a set of 10 UF_6 internal standards, prepared by fluorination from gravimetrically prepared uranium oxide mixtures (see also "The IRMM-183-187 series" section). These fluorinated fractions of the EC-171 series played an important role as calibrants for GSMS measurements because they were also used for the certification of the IRMM-019 to IRMM-027 series of UF_6 reference materials, later extended to the IRMM-019-029 series. The IRMM-019-029 series was re-certified in 2014 [15] and 2018 [16] by conversion to uranium nitrate solutions and isotope analysis by the newly developed modified total evaporation (MTE, [17, 18]) method for TIMS (Thermal Ionization Mass Spectrometry), using new calibrants such as IRMM-074/10 and IRMM-3636a (see in "The IRMM-072, IRMM-073 and IRMM-074 series" and "The Double spike IRMM-3636" sections, resp.), which are only available in solution form. The uranium nitrate solutions prepared by conversion from the IRMM-019-029 series, the so-called IRMM-2019-2029 series, was certified as a new CRM series of uranium nitrate solutions in 2018 [16] using the TIMS/MTE method and extended towards IRMM-2030 with a ^{235}U enrichment of 6% [19] in 2021.

In this context, it has to be emphasized, that the above-mentioned TIMS/MTE method for measurements of uranium isotope ratios has provided significant improvements for certification measurements since 2003. This method was first developed at NBL (New Brunswick Laboratory) [17] and further improved in 2011 in a collaboration between JRC.G.II.5, JRC.G.II.8 (Karlsruhe/Germany), NBL and the IAEA-SGAS (International Atomic Energy Agency/Safeguards Analytical Services laboratories in Seibersdorf/Austria) [18]. The MTE method takes advantage of the total evaporation principle for an optimized control of the mass fractionation in combination with high precision measurement of all isotope ratios within a large dynamic range and with an internal correction for peak tailing interferences from the major isotopes ^{235}U and ^{238}U towards the minor isotopes ^{234}U and ^{236}U.

When the IRMM-183-187 series of uranium solutions was originally prepared by dissolution of the EC-171 series of oxides, the $^{235}U/^{238}U$ ratios were certified using the same values as obtained from the UF_6 measurements of their fluorinated fractions. The minor ratios of the IRMM-183-187 series were certified by TIMS already in the 1980s to 1990s, but at that time the uncertainties were much larger compared to uncertainties achievable by modern TIMS instruments and methods. The minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ were re-certified in 2004 [20] using the advantages in terms of precision provided by the new TRITON TIMS instrument from Thermo Fisher Scientific at JRC-G.II.5 in combination with the TIMS/MTE method [18]. The new results for the minor ratios were still normalized to the major ratios $^{235}U/^{238}U$ obtained by UF_6 GSMS in the 1990s. However, some of the uncertainties for the new minor ratios were underestimated in 2004 by only stating measurement precisions as uncertainties, without strictly following the Guide to the Expression of Uncertainty in Measurement (GUM) [21]. The uncertainties for the minor ratios were updated in 2019 following the recommendations from the ASTM C1832 [22] standard for TIMS/MTE measurements and in compliance with the GUM, in particular by adding a relative uncertainty contribution of 0.4% ($k=2$) for the use of a SEM (secondary electron multiplier) for measuring the $^{236}U/^{238}U$ ratio [18].

Nevertheless, not only for the minor but also for the major ratios, significant differences between new measurement results and the certified values were observed at the IAEA/SGAS and also at JRC-G.II.5. Therefore, in 2022 JRC.G.II.5 performed a complete re-characterization and re-certification of the IRMM-183-187 series [23]. Instead of UF_6 GSMS, the high-precision double spike method TIMS/DS [12] was used for re-measuring the major isotope ratios $^{235}U/^{238}U$. This method takes advantage of the internal normalization of all $^{235}U/^{238}U$ isotope ratios during the measurement using the $^{233}U/^{236}U$ isotope ratio of the double spike material IRMM-3636a, loaded and mixed on the centre of the same sample filaments. This leads to relative uncertainties of 0.016–0.017% (coverage factor $k=2$) for the corrected $^{235}U/^{238}U$ isotope ratios, dominated by the uncertainty of the $^{233}U/^{236}U$ ratio of the double spike material itself. The TIMS/MTE method was used for the determination of the minor isotope ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$, which were subsequently normalized using the major isotope ratios obtained by the double spike method.

For several of the above mentioned CRMs, the IAEA/SGAS laboratories were involved as a collaborator through the European Commission's support program to the IAEA, either by providing the ^{236}U base material for the double spike materials IRMM-3636a,b or by performing verification measurements, e.g. for IRMM-3100a, the IRMM-3000 and the IRMM-183-187 series.

The combination of the above-mentioned gravimetrical and non-gravimetrical uranium isotope reference materials provides a comprehensive set of uranium isotope reference materials, suited for calibration and quality control for a variety of instruments such as TIMS and MC-ICPMS (Inductively Coupled Plasma Mass Spectrometry), and several methods such as the standardized TIMS/TE (Total Evaporation, ASTM C1672 [24]), TIMS/MTE ([18] ASTM C1832 [22]) and TIMS/DS ([12], ASTM C1871 [25]). The certified isotope ratios for these isotope reference materials are traceable to the SI via gravimetrical preparation, either directly through gravimetrical mixing of highly enriched base materials, or indirectly, by using existing gravimetrically prepared reference materials for calibration of the mass spectrometers that are being used for the certification measurements of the non-gravimetrical reference materials.

For more recently certified CRMs, the certified values and their uncertainties were assigned following ISO 17034 [5] and the uncertainties calculated according to the GUM [21]. The compliance with ISO 17034 applies to all abovementioned CRMs, except for the earlier prepared IRMM-072, IRMM-073, IRMM-074 and IRMM-075 series and IRMM-3636a/b, for which no homogeneity and stability testing studies were performed. However, these earlier solution reference materials were stored in flame-sealed quartz ampoules, and no problems regarding homogeneity or long-term stability of the isotope ratios have been observed. Therefore these reference materials meet the physical requirements for certified reference materials as outlined in ISO 17034.

Uranium isotope reference materials have also been prepared and certified elsewhere, mainly at NIST (National Institute for Standards and Technology, USA) and later at NBL and the NBL program office. Similar preparation and certification techniques, similar instrumentation and measurement methods have been used. The well-known U-series of uranium solution isotopic reference materials was originally started by NIST and later continued and extended by NBL. Since 2001 several materials were certified, re-measured or re-certified using modern TIMS instrumentation and new methods such as the MTE method [17, 18]. In recent years additional materials were certified, such as CRM-115 (DU, depleted uranium metal) [26], CRM-112A (NU, natural uranium metal) [27], CRM-116A (HEU, highly enriched uranium metal) [28] and CRM-125A (LEU, UO_2 pellets) [29]. In addition, a small number of uranium isotopic reference materials is also offered by CETAMA (Commission d'ETAblissement des Méthodes d'Analyse) in France and the Khlopin Radium Institute in Russia.

In the following sections, each of the above-mentioned series of uranium isotopic CRMs certified at JRC.G.II.5 in Geel (including the former IRMM and CBNM) will be briefly described regarding the preparation of the materials, the certification and the verification of the isotope ratios. For each reference material series, the certified ratios will be presented in a separate table for a better distinction and understanding of the main characteristics, and some interesting applications of the CRMs will be described.

Gravimetrically prepared uranium isotope reference materials

The IRMM-072, IRMM-073 and IRMM-074 series

The IRMM-072 series was prepared and certified gravimetrically from purified, highly enriched uranium base materials of ^{233}U, ^{235}U and ^{238}U. The IRMM-072 series consists of 15 individual CRMs. In each of these the isotope ratio $^{235}U/^{238}U$ is held constant at a value close to unity and the $^{233}U/^{235}U$ isotope ratio varies in 15 steps across the series from approximately 1.0 down to 1.0×10^{-6}. The uranium concentration in IRMM-072 is about 1 mg U/ml for each unit, a convenient concentration for use in mass spectrometry laboratories. However, this series is no longer available.

In 2000, a part of the remaining material of the IRMM-072 series was diluted to make this material also available for use in environmental uranium mass spectrometry. The uranium concentration of the diluted series, the IRMM-073 series [9], is about 0.003 mg U/ml. The complete IRMM-073 series has a total activity of just under 1000 Bq, which both simplifies the shipment and suits applications at laboratories working in the environmental field. The certified isotope ratios of the IRMM-072 and IRMM-073 series are shown in Table 1.

Because of the usefulness and general popularity of the IRMM-072 series, it became clear some years later that a replacement would need to be produced and certified. The result of this effort was the preparation and certification of a new series, the IRMM-074 series [10]. The dynamic range of 1 to 10^{-6} was retained but fewer members in the set were deemed to be necessary. The original methods used for the IRMM-072 series were reused and, where necessary, adapted. Uranium materials with high

Table 1 Certified isotope ratios for the IRMM-072 [7, 8] and IRMM-073 [9] series

Material	Certified isotope ratios		
	$^{233}U/^{235}U$ IRMM-072 series: Rel. Unc. 0.030% of value IRMM-073 series: Rel. Unc. 0.036% of value	$^{233}U/^{238}U$ Rel. Unc. 0.030% of value	$^{235}U/^{238}U$ Unc. 0.00020
IRMM-072/073-1	1.00033	0.99136	0.99103
IRMM-072/073-2	0.69967	0.69385	0.99168
IRMM-072/073-3	0.49985	0.49591	0.99212
IRMM-072/073-4	0.29987	0.29763	0.99256
IRMM-072/073-5	0.100014	0.099313	0.99299
IRMM-072/073-6	0.050091	0.049746	0.99310
IRMM-072/073-7	0.019994	0.019857	0.99317
IRMM-072/073-8	0.010165	0.010095	0.99319
IRMM-072/073-9	0.0050000	0.0049660	0.99320
IRMM-072/073-10	0.0020012	0.0019876	0.99321
IRMM-072/073-11	0.00096892	0.00096234	0.99321
IRMM-072/073-12	0.00050088	0.00049748	0.99321
IRMM-072/073-13	0.00010182	0.00010113	0.99321
IRMM-072/073-14	0.000019996	0.000019860	0.99321
IRMM-072/073-15	0.0000019995	0.0000019859	0.99321

The uncertainties are given with a coverage factor of $k=2$

isotopic enrichments of 99.96%, 99.993% and 99.99995% for ^{233}U, ^{235}U and ^{238}U, respectively, were purified using identical procedures involving separation on anion and cation columns followed by a precipitation as peroxide. The oxides were calcined, to convert them to U_3O_8 simultaneously, in an oven installed in a glove box that provided a controlled low-humidity environment. The oxides of ^{235}U and ^{238}U were weighed and mixed with a ratio of $^{235}U/^{238}U = 1.0$ and then dissolved in nitric acid. The ^{233}U oxide was dissolved to form a separate solution with the same concentration, and from this primary solution three dilutions were made by weighing. A weighed amount of the $^{235}U/^{238}U$ solution and weighed amounts of the ^{233}U solutions were then mixed in various proportions in order to achieve $^{233}U/^{238}U$ isotope ratios varying from 1.0 to 1.0×10^{-6}. The preparation and mixing scheme for the IRMM-074 series, which also included the IRMM-075 series and the "double spike" IRMM-3636 as described in "The IRMM-075 series" and "The double spike IRMM-3636" sections below, is shown in Fig. 1.

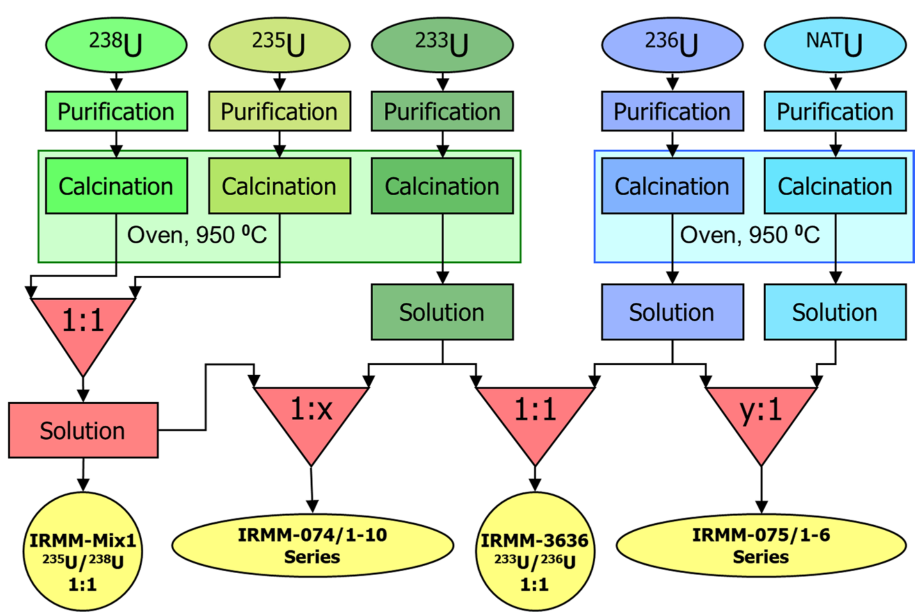

Fig. 1 Preparation and mixing scheme for the IRMM-074 series, including the IRMM-075 series and the "double spike" IRMM-3636 as described in 2.2 and 2.3 below. "x" is the varying mass fraction of ^{233}U added to IRMM-Mix1, the 1/1 mixture of ^{235}U and ^{238}U, for the IRMM-074 series. "y" is the varying mass fraction of ^{236}U added to the ^{NAT}U for the IRMM-075 series

The relative expanded uncertainties (with coverage factor $k = 2$) of the certified isotope ratios for the IRMM-074 series are 0.015% for the $^{235}U/^{238}U$ ratio and 0.025% for the ^{233}U ^{235}U and $^{233}U/^{238}U$ ratios, which constitutes an improvement compared to those of the predecessor IRMM-072 series. This quite low level of uncertainties is achievable due to the certification based on the gravimetry and is in some cases much lower than achievable by mass spectrometry. The uranium concentration is about 0.1 mg U/ml for each unit. The certified isotope ratios of the IRMM-074 series were verified by TIMS/MTE measurements. The certified isotope ratios are shown in Table 2.

The three IRMM-072/-073/-074 series are recommended for the investigation of mass spectrometer linearity, in particular for SEM detectors. The linearity response of a detector can be determined by measuring the $^{233}U/^{235}U$ or $^{233}U/^{238}U$ ratios across the IRMM-072/-073/-074 series, while the certified $^{235}U/^{238}U$ isotopic ratios close to unity allow an internal correction of the mass fractionation within the ion source of the mass spectrometer, as explained in detail for TIMS instruments in [7, 10] and for MC-ICPMS instruments in [30].

Regarding the linearity assessment of SEM detectors, several interesting conclusions were made. Both the SEM detector itself as well as the amplifier connected to it, can be affected by non-linear phenomena. If an SEM is operated in pulse counting mode for reducing the background noise, the pulse amplifier is always inherently non-linear due to the dead time effect. To investigate the linearity of the combined system of the SEM detector itself and the pulse counting system, first the dead time of the pulse counting system has to be determined independently from the SEM detector, e.g. using electronic equipment such as a double pulse generator with variable delay and an oscilloscope. Applying the resulting 'electronic' dead time value as a first estimate, a linearity test of the SEM detector itself can be performed by measuring certified reference materials from the IRMM-072/-073/-074 series. If this test confirms the linearity of the detector, a reliable and even SI traceable dead time value can be determined by performing a linear regression calculation on the dead-time-un-corrected measured isotope ratios for the certified reference materials. It was observed [30] that the resulting dead time values often disagree with the nominal values provided by the manufacturer, which can lead to significant biases in measurement results.

If linearity can be confirmed for a given SEM detector in good running condition (i.e. with a high voltage setting well within a counting plateau) using certified reference materials like the IRMM-072/-073/-074 series, the derived dead time correction value only depends on the pulse amplifier, and not on the SEM detector. Therefore, the dead time does also not depend on the ion flight path towards the SEM detector, and also not on the operation of an energy filter within the flight path. Another conclusion is the possibility to exchange the pulse amplifiers among each other versus the various detectors installed on a multi-collector mass spectrometer and thereby determine the (only pulse-amplifier-dependent) dead times using the best choices of detectors from the measurement point of view. This is called the "amplifier cross-over" principle [30].

The linearity of SEM detectors is a frequently discussed matter in the literature. A variety of SEM detectors and linearity related observations, and various ways to correct for non-linearity and for dead time effects have been introduced. However, if reliable results for isotope ratios are needed, the use of reference materials has been proven crucial to ensure the reliability and SI traceability of measurement results.

Table 2 Certified isotope ratios for the IRMM-074 [10] series

Material	Certified isotope ratios		
	$^{233}U/^{235}U$ Rel. Unc. 0.025% of value	$^{233}U/^{238}U$ Rel. Unc. 0.025% of value	$^{235}U/^{238}U$ Rel. Unc. 0.015%
IRMM-074-1	1.02685	1.02711	1.000254
IRMM-074-2	0.307993	0.308072	1.000258
IRMM-074-3	0.0102288	0.0102314	1.000259
IRMM-074-4	0.00307358	0.00307437	1.000259
IRMM-074-5	0.00103061	0.00103088	1.000259
IRMM-074-6	0.000307778	0.000307858	1.000259
IRMM-074-7	0.000102603	0.000102629	1.000259
IRMM-074-8	0.0000308011	0.0000308091	1.000259
IRMM-074-9	0.0000081587	0.0000081608	1.000259
IRMM-074-10	0.00000101886	0.00000101913	1.000259

The uncertainties are given with a coverage factor $k = 2$

The IRMM-075 series

IRMM-075 is a series of gravimetrically prepared isotope reference materials with $^{236}U/^{238}U$ isotope ratios varying from 10^{-4} to 10^{-9} [11]. This series is suitable for calibration and QC (Quality Control) of $^{236}U/^{238}U$ ratio measurements using various mass spectrometric techniques such as TIMS, MC-ICPMS, AMS (Accelerator Mass Spectrometry) and RIMS (Resonance Ionization Mass Spectrometry).

Natural uranium with a low ^{236}U isotope abundance determined by AMS and highly enriched ^{236}U characterized by TIMS were separately purified and simultaneously calcined (see preparation scheme in Fig. 1) using the methodology described for the IRMM-074 series [10]. Primary solutions of the same concentration were prepared by dissolving the oxides of highly enriched ^{236}U and ^{NAT}U. From the highly enriched ^{236}U solution a series of five dilutions was prepared gravimetrically. Weighed amounts of the dilutions of the highly enriched ^{236}U and weighed amounts of ^{NAT}U were gravimetrically mixed to form a set of $^{236}U/^{238}U$ mixtures at a concentration of about 1.0 mg U/ml. Verification measurements of the IRMM-075/1-6 series were performed by TIMS using Faraday collectors and SEM in combination with an energy filter for improved abundance sensitivity. The results agreed with the certified values obtained from the gravimetrical mixing calculations. The isotope ratios of the IRMM-075 series are shown in Table 3. Only the $^{236}U/^{238}U$ ratios of the IRMM-075 series were certified. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios are (almost) constant for the entire set but were not certified, because they could not be calculated independently from mass spectrometric results. They were determined by TIMS and UF_6 GSMS measurements, respectively, at JRC.G.II.5 and only added for information purposes in Table 3.

The IRMM-075 series is not only suited for calibration of $^{236}U/^{238}U$ measurements made by various mass spectrometric techniques, but also for QC purposes and for method validation. For example, at the JRC.G.II.5 mass spectrometry laboratory the IRMM-075 series was successfully used for the implementation of Faraday cup amplifiers with 10^{13} Ω resistors and the subsequent validation of changes to the TIMS/MTE method [31].

The use of 10^{13} Ω resistors provide an improved signal-to-noise ratio leading to smaller uncertainties for the measured ratios. However, they also require longer idle times prior to each data acquisition during the measurement to take the slower response of the 10^{13} Ω resistors into account. In Fig. 2, a QC chart for $^{236}U/^{238}U$ ratio measurements by TIMS/MTE of the gravimetrically prepared IRMM-075/1 [11] with a certified $^{236}U/^{238}U$ ratio of about 10^{-4} is shown. The internal precision and external reproducibility are obviously better and the uncertainties lower when 10^{13} Ω amplifiers are used, as explained in detail in [31]. The same applies to measurements of IRMM-075/2 with a certified value of $^{236}U/^{238}U$ of about 10^{-5}. As described in the ASTM standard document C1832-23[22] for the TIMS/MTE method, $^{236}U/^{238}U$ ratios at the level of 10^{-5} can be measured with uncertainties of about 0.2% by detecting ^{236}U by a Faraday cup equipped with a 10^{13} Ω resistor. This uncertainty is smaller than that obtained using an SEM detector. This is due to the fact that uncertainties arising from the inter-calibration of the SEM versus the Faraday cups, the SEM dead time correction, etc. cause an increase of the uncertainty for SME measurements towards a level of 0.4% (with coverage factor $k=2$).

Due to the lack of highly enriched ^{234}U materials, there are no gravimetrically prepared reference materials available with certified $^{234}U/^{238}U$ ratios. As one possible alternative, also being independent of mass spectrometry, natural samples in secular equilibrium for the ^{238}U to ^{234}U decay chain can be used as working reference materials with a $^{234}U/^{238}U$ ratio of 0.00005494 (15) calculated using the half live values for ^{234}U [32] and ^{238}U [33]. For certain geological formations such as calcites and well-preserved zircons, a closed system can be assumed as explained by Cheng et al. [34]. He determined a secular equilibrium value for $^{234}U/^{238}U$ of 0.000054970 (19) by MC-ICPMS using the IRMM-074 series for instrument calibration, which leads to an insignificant relative difference of 0.05 (27) % of the measured from the radiometric ratio. However, this independent confirmation for the mass spectrometric results using the radiometric ratio of the half-lives is given only at an uncertainty level of about 0.3%, which is a factor of about 10–20 higher than the uncertainties from gravimetrically prepared reference materials. This situation will improve if half-life values with lower uncertainties can be provided in the future, or if highly enriched ^{234}U materials for gravimetric mixing become available.

The double spike IRMM-3636

The double spike isotope reference material IRMM-3636 was prepared gravimetrically using highly enriched ^{233}U and ^{236}U base materials [12]. The $^{233}U/^{236}U$ ratio was adjusted to about 1:1 and certified with an expanded relative uncertainty of 0.016% (coverage factor $k=2$). The highly enriched ^{233}U and ^{236}U base materials were purified and calcined,

Table 3 Certified isotope ratios for the IRMM-075 [11] series

Material	Isotope abundance ratios		
	$^{236}U/^{238}U$, certified	$^{234}U/^{238}U$, TIMS, not certified	$^{235}U/^{238}U$, UF_6 GSMS, not certified
IRMM-075/1	1.04433 (37) × 10^{-4}	0.000053288 (37)	0.0072603 (36)
IRMM-075/2	1.14160 (40) × 10^{-5}	0.000053288 (37)	0.0072603 (36)
IRMM-075/3	1.04093 (36) × 10^{-6}	0.000053288 (37)	0.0072603 (36)
IRMM-075/4	1.13742 (40) × 10^{-7}	0.000053288 (37)	0.0072603 (36)
IRMM-075/5	1.06519 (75) × 10^{-8}	0.000053288 (37)	0.0072603 (36)
IRMM-075/6	1.0885 (63) × 10^{-9}	0.000053288 (37)	0.0072603 (36)

The uncertainties are given in parentheses for the last two digits with a coverage factor of $k=2$

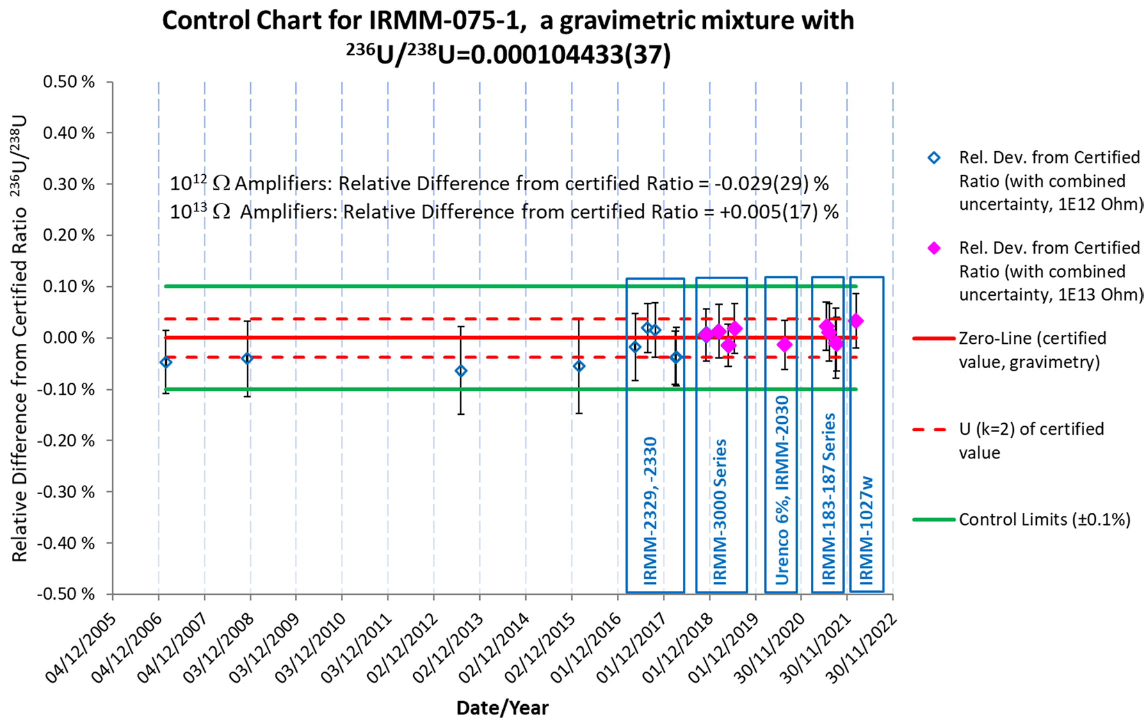

Fig. 2 QC chart for $^{236}U/^{238}U$ ratio measurements of the gravimetrically prepared IRMM-075/1 [11], $^{236}U/^{238}U = 0.000104433(37)$, using TIMS/MTE by JRC-Geel. The certification projects for which QC measurements were performed, are indicated. Uncertainties are given with coverage factor $k=2$

the oxides were dissolved and the solutions mixed using the procedures explained in detail in [10]. As indicated in the preparation and mixing scheme in Fig. 1, the ^{233}U, ^{235}U and ^{238}U base materials used for the IRMM-074 series were calcined not only using the same controlled conditions of temperature and humidity, but even calcined in the same oven simultaneously in order to ensure the same stoichiometry for the oxidized base materials prior to gravimetrical mixing. This applies as well for the ^{236}U and ^{NAT}U for the IRMM-075 series. In contrast to that, the ^{233}U and ^{236}U base materials for the double spike IRMM-3636 could not be calcined simultaneously, due to the design of the oven. However, the control of the conditions within the oven for calcination was sufficiently reproducible, as demonstrated by the result of the verification measurement by TIMS. The $^{233}U/^{236}U$ ratio of IRMM-3636 was directly measured in multi-dynamic mode versus the gravimetrically prepared $^{235}U/^{238}U$ mixture "IRMM-Mix1" used for the IRMM-074 series: the relative difference of 0.003(16) % between the measured and certified $^{233}U/^{236}U$ ratios was insignificant. This confirms the assumption of having indistinguishable stoichiometry values for the oxides of all enriched base materials of ^{233}U, ^{235}U, ^{236}U, ^{238}U and ^{NAT}U prior to gravimetric preparation of the mixtures. The certified isotope ratios and mass concentrations for IRMM-3636 and the two dilutions called IRMM-3636a and IRMM-3636b are presented in Table 4.

The main application of the double spike IRMM-3636 and its dilutions IRMM-3636a and IRMM-3636b is the high precision measurement of $^{235}U/^{238}U$ ratios in natural samples, for geochemical, cosmochemical and nuclear forensics applications. By mixing the $^{233}U/^{236}U$ double spike with the sample and applying an internal rather than an external mass

Table 4 Certified isotope ratios for IRMM-3636 and the two dilutions called IRMM-3636a and IRMM-3636b [12]

Material	Certified isotope ratios				Mass fraction (mg U/g solution)
	$^{233}U/^{236}U$	$^{234}U/^{236}U$	$^{235}U/^{236}U$	$^{238}U/^{236}U$	
IRMM-3636	1.01906 (16)	0.00036606 (48)	0.000045480 (74)	0.00023481 (38)	1.00304 (13)
IRMM-3636a	1.01906 (16)	0.00036606 (48)	0.000045480 (74)	0.00023481 (38)	0.100375 (13)
IRMM-3636b	1.01906 (16)	0.00036606 (48)	0.000045480 (74)	0.00023481 (38)	0.0052019 (13)

The uncertainties are given in parentheses for the last two digits with a coverage factor of $k=2$

fractionation correction, the $^{235}U/^{238}U$ ratio of a given sample can be determined with high relative precision, typically at a level of 0.0030–0.0050%. The uncertainties of the corrected ratios are dominated by the 0.016% relative uncertainty contribution of the $^{233}U/^{236}U$ ratio from the double spike itself, but for comparative measurements relative to a well-known consensus standard like NBL CRM-112A (also known as NIST SRM 960), this uncertainty contribution is not relevant. The $^{238}U/^{235}U$ ratio of NBL CRM-112A was determined using the double spike IRMM-3636a within an ILC (inter-laboratory comparison) to be 137.837(15) [35], in agreement with the new certified value from NBL [27]. This value replaced the earlier used consensus value of 137.88 with a relative difference of 0.03%.

For measurements of non-natural uranium samples, the isobaric interference with ^{236}U contained in the sample itself has to be determined and corrected for. Correction algorithms are presented in the ASTM C1871 standard document [25], along with a suggested upper limit of 5×10^{-4} for the $^{236}U/^{238}U$ ratio of the sample for double spike measurements. By respecting this limit, it was possible to apply the double spike method also for re-certification measurements of several DU (depleted uranium), NU (natural uranium) and LEU (low enriched uranium) isotope reference materials, such as IRMM-2021, IRMM-2022 and IRMM-2023 from the IRMM-2019-2030 series [16, 19], as well as the entire IRMM-183-187 series [23] (see Sects. "The IRMM-019-029 and IRMM-2019-2029 (2030) series" and "The IRMM-183-187 series").

As an additional application for DU, NU and LEU samples, the double spike IRMM-3636a was also used within the validation study for the ABACC-Cristallini sampling method for UF_6 [36] jointly with the IAEA/SGAS [37]. The ABACC-Cristallini sampling method uses a fluorothene P-10 tube, containing alumina pellets that absorb and hydrolyse the UF_6 directly during the sampling process using the crystalline water inside the pellet. This sampling device is less expensive and the uranium amount is lower and less reactive compared to the traditional sampling of UF_6 in stainless steel containers. In addition, since the sample is solid rather than volatile and chemically less reactive, the transport is cheaper and safer from a radiological protection point of view. Currently, the Cristallini sampling method is undergoing further validation at the IAEA in cooperation with operators of nuclear facilities handling UF_6 materials.

Due to the popularity of the double spike IRMM-3636 and the dilution IRMM-3636a, the stocks at JRC.G.II.5 are almost exhausted. Therefore, other available double spike materials should be used or successor reference materials for IRMM-3636 and IRMM-3636a be produced in the near future.

The "Quad-CRM" IRMM-3100a

The Quad-CRM ("Quadruple Certified Reference Material") was prepared from highly enriched ^{233}U, ^{235}U, ^{236}U and ^{238}U base materials using an optimized combination of gravimetrical mixing and mass spectrometry [13]. Within the mixing process the isotope ratios were adjusted to about $^{233}U/^{235}U/^{236}U/^{238}U = 1/1/1/1$ and certified with expanded relative uncertainties of 0.0054% per mass unit (coverage factor $k = 2$). The certified $^{233}U/^{236}U$ ratio of IRMM-3100a was derived from the gravimetrical mixing of highly enriched ^{233}U and ^{236}U materials after calcination to U_3O_8, in a similar way as for the double spike IRMM-3636 [12]. It was verified by TIMS measurements using the classical total evaporation (TIMS/TE, [24]) and the TIMS/MTE methods. Subsequently, the $^{234}U/^{236}U$, $^{235}U/^{236}U$ and $^{238}U/^{236}U$ ratios were determined by TIMS using the $^{233}U/^{236}U$ ratio for internal normalization and using a multi-dynamic measurement procedure to circumvent any influence and uncertainties from Faraday cup efficiencies and amplifier gain factors. The certified $^{234}U/^{236}U$, $^{235}U/^{236}U$ and $^{238}U/^{236}U$ ratios were additionally verified using the classical and modified total evaporation methods using two TIMS instruments at JRC.G.II.5 and one TIMS instrument at IAEA/SGAS.

The certification of the Quad-CRM IRMM-3000a was a joint project between JRC.G.II.5 and the IAEA/SGAS for replacing the so-called Khlopin standard reference material with a similar isotopic composition used at the IAEA/SGAS. This isotope reference material is ideal for verifying the inter-calibration of multi-detector systems in isotope mass spectrometry and for investigating potential changes in the efficiencies of Faraday cups depending on the usage. However, the IRMM-3100a has not become very popular with potential users, because with development of modern and technologically advanced mass spectrometers, testing of Faraday cup efficiencies has become less important. The certified isotope ratios for IRMM-3100a are presented in Table 5.

The IRMM-3000 series

The IRMM-3000 series is a set of five highly enriched uranium nitrate solution reference materials named IRMM-3020, IRMM-3035, IRMM-3050, IRMM-3075 and IRMM-3090, with the isotopic ratios $^{235}U/^{238}U$ varying from about 0.25–6.6, and the ^{235}U enrichments (i.e. the isotope mass fraction $^{235}U/U$) varying from about 20–90% [14]. The solutions were prepared by dissolving uranium oxide (U_3O_8) materials, which were prepared by gravimetrically mixing oxide base materials, highly enriched in ^{235}U and ^{238}U, in a similar way as used for the preparation of the IRMM-074, IRMM-075, IRMM-3636a,b

Table 5 Certified isotope ratios for IRMM-3100a [13]

Material	Certified isotope ratios			
	$^{233}U/^{236}U$	$^{234}U/^{236}U$	$^{235}U/^{236}U$	$^{238}U/^{236}U$
IRMM-3100a	1.01990 (16)	0.0003837 (20)	1.004354 (54)	0.98798 (11)

The uncertainties are given in parentheses for the last two digits with a coverage factor of $k=2$

series and the IRMM-3000a isotope reference materials [10–13]. However, due to the exhaustion of the previous highly enriched base material for the isotope ^{238}U, a different material had to be used for the IRMM-3000 series.

The $^{235}U/^{238}U$ isotope ratios of the IRMM-3000-series were calculated based on the weighing of the two base materials enriched in ^{235}U and ^{238}U and on the impurities of both, except for IRMM-3035 for which the $^{235}U/^{238}U$ ratio measured by TIMS/DS was used [12, 14]. The main contributions to the final uncertainties of the isotopic ratios are originating from the weighing uncertainties, the uncertainties of the measured isotope ratios and impurities in the two starting materials. The relative expanded uncertainties for the certified $^{235}U/^{238}U$ ratios range between 0.014 and 0.018%. The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios of the IRMM-3000 series were certified by TIMS/MTE and normalized to the $^{235}U/^{238}U$ ratio obtained by gravimetrical calculations.

Verification measurements for all isotope ratios were performed by the Oak Ridge National Laboratory (ORNL) and the IAEA-SGAS laboratories using several methods of mass spectrometry, such as TIMS/TE, TIMS/MTE and MC-ICPMS. The IRMM-3000 series is provided in flame-sealed quartz ampoules, containing 5 mg of uranium in about 1 ml of solution. There are also larger samples called IRMM-3020-5, IRMM-3075-5 and IRMM-3090-5 available in flame-sealed quartz ampoules, containing 25 mg uranium in about 5 ml of solution. Part of the IRMM-3000 series materials was also diluted by a factor of about 100. This is suitable for users who need smaller uranium amounts, e.g. for TIMS/TE or MC-ICPMS measurements. The IRMM-3000a series is provided in quartz ampoules containing 0.2 mg uranium in about 4 ml of solution and sealed with a screw cap. The certified isotope ratios of the IRMM-3000 series are shown in Table 6.

Table 6 Certified isotope ratios for the IRMM-3000 [14] series

Material	Certified isotope ratios		
	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
IRMM-3020	0.000004931 (35)	0.254264 (41)	0.000009805 (63)
IRMM-3035	0.000010699 (69)	0.548531 (89)	0.000021214 (86)
IRMM-3050	0.00001991 (13)	1.02359 (18)	0.00003969 (12)
IRMM-3075	0.00005473 (35)	2.81872 (44)	0.00010966 (20)
IRMM-3090	0.00012770 (83)	6.57731 (92)	0.00025642 (34)

The uncertainties are given in parentheses for the last two digits with a coverage factor of $k=2$

The IRMM-3000 series of HEU materials is ideal for investigating or verifying the linearity of the ^{235}U enrichment scale between 20 and 90% for various types of isotope mass spectrometers, such as TIMS/MTE, TIMS/DS, ICP, MC-ICPMS, with various detection systems and measurement methods. This is illustrated in Fig. 3, by using all the available verification measurements performed for the IRMM-3000 series by JRC.G.II.5 (TIMS/MTE and TIMS/DS), IAEA-SGAS (TIMS/MTE and MC-ICPMS) and ORNL (TIMS/MTE and MC-ICPMS) as an example.

As a conclusion regarding the application of the IRMM-3000 series for a variety of modern mass spectrometers and methods, the verification of $^{235}U/^{238}U$ ratios for the enrichment scale from 20 and 90% can be confirmed at a level of better than 0.025% for uncertainties and accuracy.

The verification of the enrichment scale has also been extended to uranium oxide micro-particles analyzed by LG-SIMS (Large Geometry Secondary Ion Mass Spectrometry). For this purpose, uranium oxide (U_3O_8) particles were recently generated from IRMM-3050 and IRMM-3090 solutions using a VOAG (vibrating orifice aerosol generator) at the Forschungszentrum Juelich (Juelich/Germany). Verification measurements were performed by LG-SIMS at the University of Heidelberg (Germany) and IAEA/SGAS and by MC-ICPMS at ORNL, and confirmed the isotopic composition of the FZJ-3050P and FZJ-3090P particles to be in agreement with the certified isotopic compositions of the IRMM-3050 and IRMM-3090 solutions [38]. Verification measurements for LEU particles by LG-SIMS have been described elsewhere [39].

It is worth mentioning in this context, that for ^{235}U enrichments below 20%, e.g. for DU, NU and LEU solution reference materials, the verification of the enrichment scale, at the same level for uncertainties and accuracy, has already been described elsewhere, e.g. for UF_6 GSMS instruments in [15] and for TIMS and MC-ICPMS measurements in [16, 19, 23].

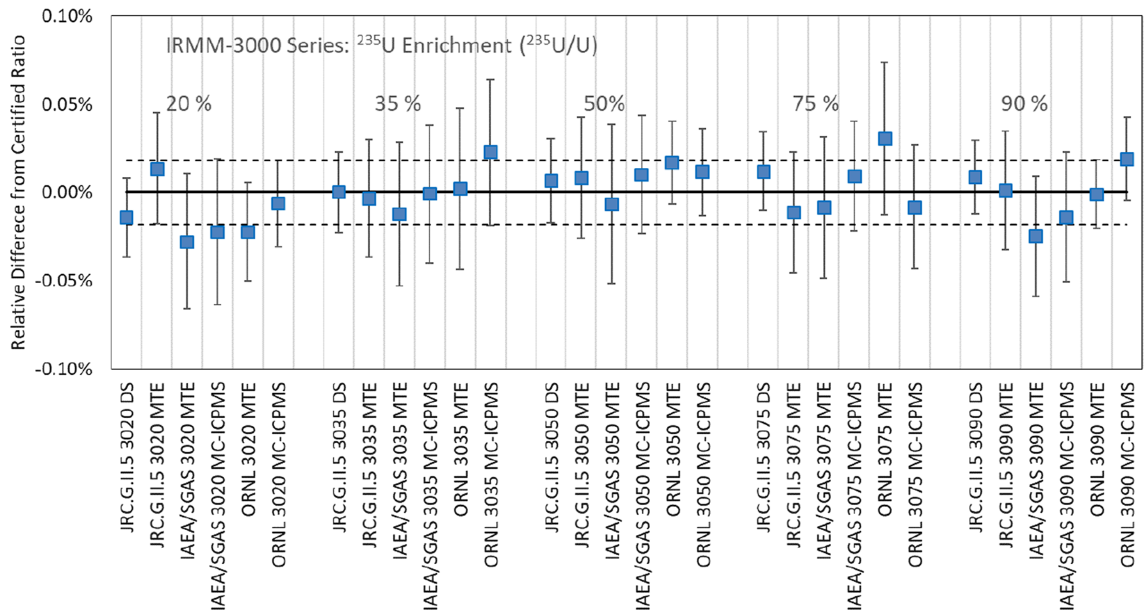

Fig. 3 Verification of ^{235}U enrichment scale, shown by relative differences between the measured $^{235}U/^{238}U$ ratios from the certified $^{235}U/^{238}U$ ratios of the IRMM-3000 series. Measurements were performed at JRC.G.II.5 (TIMS/DS and TIMS/MTE), IAEA-SGAS (TIMS/MTE and MC-ICPMS) and ORNL (TIMS/MTE and MC-ICPMS). Uncertainties are given with a coverage factor $k=2$

Non-gravimetrical uranium isotope reference materials

The IRMM-019-029 and IRMM-2019-2029 (2030) series

Apart from gravimetrically prepared reference materials, non-gravimetrical reference materials also play an important role for instrument calibration and QC. Within the following sections, non-gravimetrical reference materials are described which are similar to actual samples occurring in the nuclear fuel cycle, e.g. low enriched, natural and depleted samples, that are sent for verification measurements to nuclear safeguards mass spectrometry laboratories such as the IAEA/SGAS.

Isotopic measurements on uranium samples and preparation of reference materials at JRC.G.II.5 in Geel/Belgium (formerly IRMM, and formerly CBNM) started about 50 years ago, in 1972, when the MAT511 UF_6 GSMS (Varian MAT, Bremen, Germany) was installed in the mass spectrometry laboratory. The MAT511 was used successfully for about 40 years and was replaced in 2010 by the Uranus UF_6 GSMS from Thermo Fisher Scientific (Bremen, Germany), the successor of Finnigan MAT (earlier Varian MAT). In contrast to the MAT511, the Uranus GSMS also allows the measurement of the minor isotopes ^{234}U and ^{236}U using a Faraday cup multi-collector detection system, constructed in a similar way as the TRITON TIMS and NEPTUNE MC-ICPMS (Thermo Fisher Scientific).

For the best possible analytical performance, UF_6 GSMS measurements are preferentially performed using the double standard method, also called bracketing standard method, as described in earlier publications [40, 41], as well as the ASTM standard document C1429 [42]. The memory corrected double spike method (MCDS) was introduced for the Uranus GSMS in 2010 and explained in detail in [43].

The UF_6 GSMS measurements are known for the excellent level of the relative precision of about 0.003–0.005% for the major ratio $^{235}U/^{238}U$. This is due to the homogeneity of the gas sample introduced to a UF_6 GSMS and the reproducible isotope fractionation history during the measurement. This is in contrast to a solid sample dried on a TIMS filament, which becomes isotopically inhomogeneous during the measurement process, causing a less reproducible fractionation history. Therefore the reproducibility of TIMS measurements, even using the modern total evaporation principle, is a factor 5–10 inferior compared to UF_6 GSMS.

However, for the combined uncertainties for typical $^{235}U/^{238}U$ ratio measurements by GSMS the reproducibility is only a minor contribution. Most dominant uncertainty contributions are (at a similar level) the uncertainties of the two bracketing standards and the two observed types of memory effects. The memory effects are related to the alternating measurements of the sample and the bracketing standards in the same ion source chamber, and to the memory effect caused by adsorption of UF_6 on the inner walls of the inlet system.

The combined and expanded uncertainty for $^{235}U/^{238}U$ ratio measurements on the Uranus GSMS is between 0.050% and 0.075% ($k=2$), which is no longer smaller but larger compared to the TIMS/MTE method (0.025–0.050% [22]), and even larger compared to the TIMS/DS method (0.016%, [25]). This is an example showing the necessary distinction between repeatability and uncertainty, and how the proportions between uncertainty components for different instruments and methods have changed by the application of the Guide to the Expression of Uncertainty in Measurements [21].

The uncertainties for measurements of the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ by UF_6 GSMS are much larger compared to modern TIMS methods like TIMS/MTE as explained in [18, 43], in particular for $^{236}U/^{238}U$ ratios below 10^{-5}. From an uncertainty point of view, TIMS/MTE and MC-ICPMS have become the preferred methods for uranium isotopic analysis of uranium, but UF_6 GSMS is still preferred in facilities involved in UF_6 enrichment, where UF_6 is the most frequent chemical form of the samples to be analyzed.

The materials used for the preparation of the IRMM-019-029 series of UF_6 reference materials are described in Fig. 4. The $^{235}U/^{238}U$ ratios were certified by UF_6 GSMS using the MAT511 and the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios by TIMS. In 2014, the IRMM-019-029 series was recertified by TIMS/MTE and TIMS/DS measurements with smaller uncertainties obtained on converted samples [15]. In 2018 the uranium nitrate solution series IRMM-2019-2029 was also certified to be available for TIMS and MC-ICPMS users [16] and extended towards the IRMM-2030 solution with a ^{235}U enrichment of 6% in 2021 [19]. The certified isotope ratios of the IRMM-019-029 and the IRMM-2019-2030 series are shown in Table 7.

The IRMM-019-029 series is mainly used for calibration of GSMS instruments in laboratories involved in isotopic measurements of UF_6 samples in and from enrichment facilities. Due to the limited stock of primary reference materials

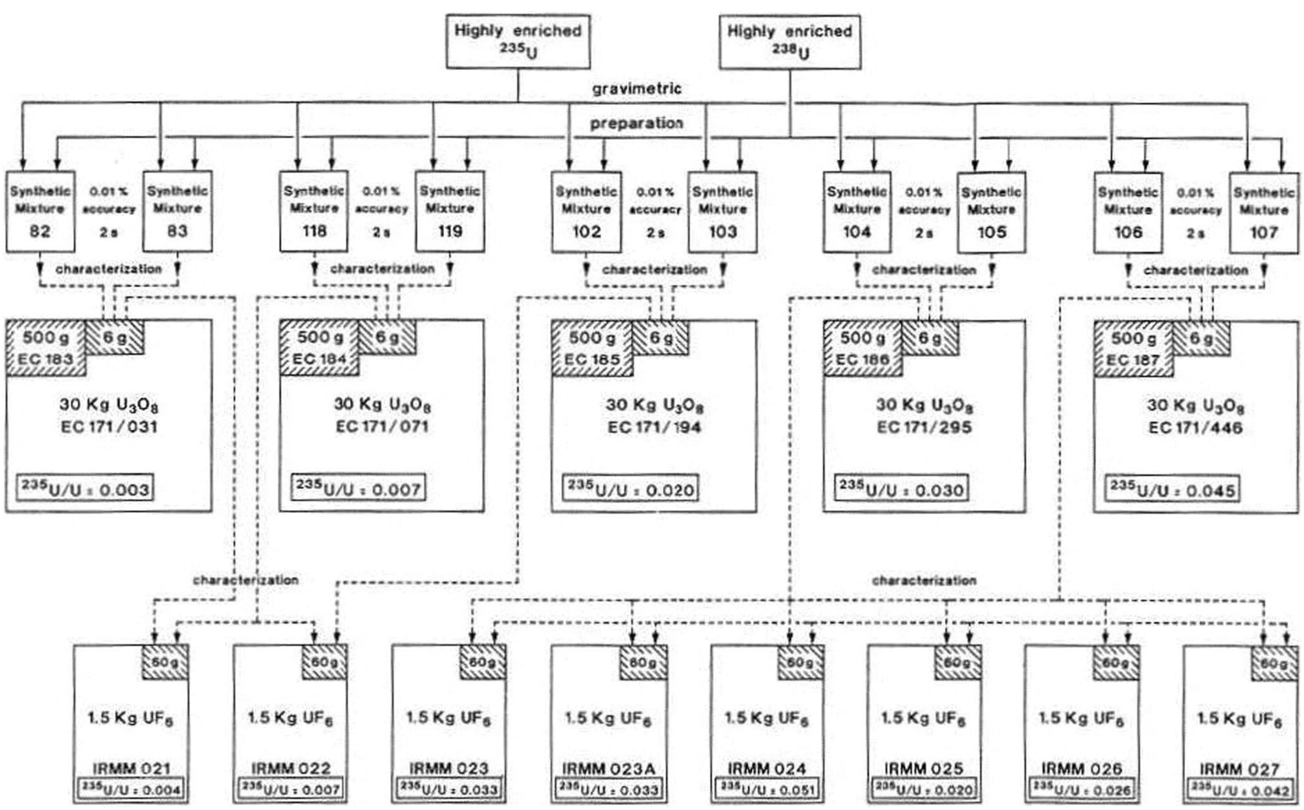

Fig. 4 The following materials were used in the preparation of the IRMM-019-029 and IRMM-183-187 series, from top to bottom: (a) Set of two base materials, "Highly enriched" in ^{235}U and ^{238}U. (b) Set of 10 gravimetrically prepared "Synthetic Mixtures" of enriched samples (from a), for which fluorinated subsamples were prepared. (c) EC-171 series (consisting of EC171/031, EC171/071, EC171/194, EC171/295 and EC171/446). A mass of 30 kg of oxides (U_3O_8) were available for each. For each of them also 6 g were fluorinated and characterised by UF_6 GSMS using the set of fluorinated 10 mixtures (from b). (d) EC183, EC184, EC185, EC186, EC187, also known as IRMM-183–IRMM-187 series, uranium nitrate solutions, prepared by dissolving 500 g for each of the IRMM-171 series materials (from c). (e) IRMM-021– IRMM-027 (later extended towards IRMM-019–IRMM-029), characterized by UF_6 GSMS using the fluorinated fractions of the IRMM-171 series (from c)

Table 7 Certified isotope ratios for the IRMM-019-029 and the IRMM-2019-2030 series [16, 19] series

Material	Certified isotope ratios		
	$^{234}U/^{238}U$ TIMS/MTE	$^{235}U/^{238}U$ TIMS/MTE, except (*): TIMS/DS	$^{236}U/^{238}U$ TIMS/MTE
IRMM-019/-2019	0.000006846 (31)	0.00167749 (48)	0.000036523 (85)
IRMM-020/-2020	0.000011923 (51)	0.00209571 (60)	0.00028615 (11)
IRMM-021/-2021	0.000024846 (76)	0.00440521 (71) (*)	0.00000002657 (78)
IRMM-022/-2022	0.000053275 (85)	0.0072562 (12) (*)	0.0000002415 (25)
IRMM-023/-2023	0.00033950 (11)	0.0338814 (54) (*)	0.0000001153 (17)
IRMM-024/-2024	0.00029075 (14)	0.053254 (15)	0.00051696 (13)
IRMM-025/-2025	0.000122452 (90)	0.0204356 (55)	0.000148386 (83)
IRMM-026/-2026	0.00014941 (10)	0.0256791 (75)	0.00020730 (11)
IRMM-027/-2027	0.00023159 (13)	0.041717 (12)	0.00038739 (11)
IRMM-028/-2028	0.00061041 (27)	0.037576 (12)	0.0051943 (11)
IRMM-029/-2029	0.00084444 (37)	0.044052 (13)	0.0105563 (22)
IRMM-2030	0.00052968 (23)	0.062659 (20)	0.000066513 (27)

The uncertainties are given in parentheses for the last two digits with a coverage factor of $k=2$

like the IRMM-019-029 series, enrichment facilities have also contracted JRC.G.II.5 to characterize and certify their in-house UF_6 working reference materials. Due to the better analytical performance, the certification is nowadays being performed using the TIMS/MTE rather than the UF_6 GSMS method. As a consequence of the analytical performance and small user group, the production of the Uranus UF_6 GSMS has been stopped by the manufacturer several years ago. For process control within enrichment facilities also quadrupole ICP-MS instruments with sufficient analytical performance are used, but for high precision isotopic analysis TIMS/MTE and MC-ICPMS on converted samples are nowadays preferred.

The IRMM-183-187 series

The materials used for the preparation of the IRMM-183-187 series of uranium solution reference materials are also described in Fig. 4. Originally, the $^{235}U/^{238}U$ ratios were characterized by UF_6 GSMS using the MAT511, and the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios characterized by a conventional TIMS method and normalized using the $^{235}U/^{238}U$ ratios. Due to the smaller achievable uncertainties, the $^{235}U/^{238}U$ ratios were re-certified using the TIMS/DS method in 2021, and the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios recertified by TIMS/MTE, normalized to the re-certified $^{235}U/^{238}U$ ratios obtained using TIMS/DS.

The revised certified isotope ratios of the IRMM-183-187 series are shown in Table 8.

Verification measurements for the isotopic composition for the IRMM-183-187 series were performed using the TIMS/MTE method by ORNL and the IAEA/SGAS. From the IAEA/SGAS, historical TIMS/MTE data acquired on three TRITON TIMS instruments within a time period from 2012 to 2021, were received. The re-certification of the IRMM-183-187 series was needed by customers, in particular by the IAEA/SGAS, where the IRMM-183-187 series is being used for instrument calibration and QC on a routine basis [44].

Uranium oxide particle reference materials

In addition to the forms of UF_6 gas and uranium nitrate solutions, uranium isotopic reference materials have also been produced in the form of mono-dispersed uranium oxide (U_3O_8) micro-particles [39]. The particle reference

Table 8 Certified isotope ratios for the IRMM-183-187 series [23]

Material	Certified isotope ratios		
	$^{234}U/^{238}U$ TIMS/MTE	$^{235}U/^{238}U$ TIMS/DS	$^{236}U/^{238}U$ TIMS/MTE
IRMM-183	0.000019814 (14)	0.00321826 (52)	0.000148492 (30)
IRMM-184	0.000053196 (16)	0.0072631 (11)	0.00000012410 (96)
IRMM-185	0.000179659 (39)	0.0200659 (32)	0.000002907 (12)
IRMM-186	0.000293966 (64)	0.0307894 (48)	0.000033388 (34)
IRMM-187	0.000387298 (91)	0.0473430 (75)	0.000072049 (38)

The uncertainties are given for the last two digits in parentheses with a coverage factor, $k=2$

materials IRMM-2329P [45] and IRMM-2331P [46] were generated from tailor made uranium nitrate solutions certified at JRC.G.II.5, for subsequent conversion into uranium particles using a VOAG (vibrating orifice aerosol generator), calcination into the U_3O_8 form and deposition on carbon planchets at the Forschungszentrum Juelich (Juelich/Germany). The IRMM-2329P uranium oxide particles were not only certified for the isotopic composition but also for the uranium mass per particle, which is about 4 pg. The particle diameter is about 1.3–1.4 µm. Prior to the certification, the IRMM-2329P particles deposited on carbon planchets were also used as test samples for the inter-laboratory comparison NUSIMEP-9 [47] among the NWAL (Network of Analytical Laboratories of the IAEA). The certified isotope ratios of the IRMM-2329P and IRMM-2331P are shown in Table 9.

As described in Sect. "The IRMM-3000 series", uranium particles have also been produced using the HEU solutions of the certified IRMM-3000 series, called FZJ-3050P and FZJ-3090P [38]. FZJ-3020P, FZJ-3035P and FZJ-3075P are requested to follow. Further uranium particles have recently been produced at FZJ using a certified uranium solution with a (so far) undisclosed isotopic composition from JRC.G.II.5, to be used for another inter-laboratory comparison among the NWAL in 2024.

Uranium spike reference materials

Apart from uranium isotopic reference materials certified only for the isotope ratios, reference materials certified for the isotope ratios and also the amount concentration or mass concentration have been prepared at JRC.G.II.5 and earlier at CBNM and IRMM [48], as well as at NBL and CEA. The purpose of these so-called spike isotopic reference materials is mainly to determine the amount concentration or mass concentration of an unknown sample using the Isotope Dilution Mass Spectrometry (IDMS) method, by weighing aliquots of the unknown sample and the spike, mixing them gravimetrically and measuring the isotopic composition of the mixture and the original (un-spiked) sample. Mathematical algorithms for IDMS measurements of uranium are presented in the ASTM standard document C1672 [24]. Uranium spike reference materials should usually be highly enriched in one isotope, like ^{233}U, ^{235}U or ^{236}U, which has in contrast a rather low abundance in the sample to be analyzed. Applications of the IDMS method for sample analysis for amount concentration or mass concentration, and the preparation of the necessary spike reference materials, either by gravimetrical mixing or the reverse IDMS method, have been described in the literature many times (e.g. [3, 49, 50]), and are beyond the scope of this publication.

Conclusions

The 50 year history of uranium isotopic reference materials at JRC.G.II.5 in Geel has been reflected in detail by presenting a variety of examples regarding their chemical and physical form, their ^{235}U enrichment, preparation, characterization, certification, verification, and their applications at JRC.G.II.5 as well as at customer laboratories. Following the mandate for nuclear standards included in the Euratom Treaty signed in 1957, and the establishment of the Joint Research Centre of the European Commission in the 1960s, the commissioning of the MAT511 UF_6 GSMS at JRC-Geel in 1972 was a major step for starting uranium isotope ratio measurements and subsequent preparation of suitable reference materials for instrument calibration and quality control. Among the many uranium materials produced and characterized, sometimes even mixed among each other and re-characterized, two series of DU, NU and LEU reference materials have emerged over the years, the IRMM-019-029 series of UF_6 reference materials and the IRMM-2019-2030 series of uranium nitrate solution reference materials. In addition, the IRMM-183-187 series of uranium nitrate solution reference materials continues to play a significant role and has been recertified recently, taking advantage of the significant instrumental and analytical developments over time.

The preparation of reference materials by gravimetrically mixing isotopically highly enriched uranium materials, e.g. of ^{233}U, ^{235}U, ^{236}U and ^{238}U, in suitable proportions, was developed in order to allow an independent calibration of mass spectrometers and provided traceability of the measured isotope ratios to the SI system. The gravimetrical principle was also applied to prepare several series of further uranium nitrate solution reference materials, such as the IRMM-072,-073,-074,-075 and the IRMM-3000 series, as well as the double spike IRMM-3636a,b and the Quad-CRM

Table 9 Certified isotope ratios for IRMM-2329P and IRMM-2331P [39]

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

The uncertainties are given of the two last digits in parentheses with a coverage factor, $k=2$

IRMM-3000a, which are tailor made for specific mass spectrometric applications and widely used.

In particular the IRMM-3000 series of HEU solution reference materials has gained special attention recently in the context of the discovery of uranium materials with ^{235}U enrichments of 60% and 84% in Iran [51, 52]. As a consequence, the IRMM-3000 series as well as the HEU oxide particles produced from this series at FZJ are crucial for mass spectrometer calibration and QC at the IAEA/SGAS and other network laboratories working with nuclear safeguards and combatting illicit trafficking of nuclear materials.

The IRMM-3636a,b double spike reference materials have become important not only for high precision ^{235}U/^{238}U measurements for certification projects, but also for geochemical and cosmochemical sciences. The popularity of the double spike reference material is also the reason for the low remaining stock available at JRC.G.II.5.

JRC nuclear reference materials are tailored to support Euratom and international safeguards but are equally suited for measurements in nuclear forensics and environmental sampling. They support EU policies beyond the nuclear applications by reaching out to earth sciences, geo-and cosmochemistry being an intrinsic component for research in these fields. Tools for accurate measurements are in addition an asset for industry in terms of competiveness, fairness and towards a circular economy. Concerning the future needs of nuclear isotopic reference materials, a new double spike might be the most important request from the geo-scientific community. The needs for the nuclear mass spectrometry and nuclear safeguards communities are regularly discussed among users and producers at special technical meetings at the IAEA and at the JRC.

One recently suggested new uranium isotopic reference material would be a HEU material with an extremely low ^{236}U/^{235}U ratio at the order of 10^{-8}–10^{-6}, needed to investigate the source of materials used for uranium enrichment towards HEU. In case of NU, a series with a wide range of ^{236}U/^{235}U ratios is already available, as shown by the IRMM-075 series [11]. Current challenges limiting the production of new types of nuclear reference materials, the recertification of expired or older materials are maintaining the required nuclear laboratory infrastructure, as well as shortages of highly enriched spike materials, equipment and budgetary and human resources.

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Data availability All data discussed in this publication are included in the above-mentioned references. Further information about reference materials provided by JRC.G.II.5 can be obtained via the online catalogue at https://crm.jrc.ec.europa.eu/e/92/Catalogue-price-list-pdf.

Declarations

Conflict of interest The authors declare the absence of any conflict of interest.

References

1. De Bievre P (1973) Atomic weights and isotopic abundances of the elements: a future concern for the analytical chemist. Z Anal Chem 264:365–371
2. Lamberty A, Emons H (2011) Reference materials: from CBNM to IRMM. Accred Qual Assur 16:393–398
3. De Bievre P, Debus GH (1965) Precision mass spectrometric isotope dilution analysis. Nucl Instrum Methods 32:224–228
4. ISO/IEC 17025:2017. General requirements for the competence of testing and calibration laboratories. https://www.iso.org/standard/66912.html Accessed 22 Sept 2023
5. ISO 17034:2016. General requirements for the competence of reference material producers. https://www.iso.org/standard/29357.html Accessed 22 Sept 2023
6. ISO/IEC 17043:2023. Conformity assessment—general requirements for the competence of proficiency testing providers. https://www.iso.org/standard/80864.html Accessed 22 Sept 2023
7. Rosman KJR, Lycke W, Damen R, Werz R, Hendrickx F, Traas L, De Bìevre P (1987) The preparation and use of synthetic isotope

mixtures for testing mass-spectrometers. Int J Mass Spectrom Ion Process 79:61–67
8. Lycke W, De Bièvre P, Verbruggen A, Hendrickx F, Rosman K (1988) A CBNM isotopic reference material set for testing linearity of isotope mass spectrometers (CBNM IRM 072/1-15). Fresenius Z Anal Chem 331:214–215
9. Held A, Van Baelen G, Hendrickx F, Taylor P, Verbruggen A, Wellum R (2002) IRMM-073 preparation—dilution and ampulation. Internal Report IRMM, GE/R/IM/22/02
10. Richter S, Alonso A, Aregbe Y, Eykens R, Kehoe F, Kühn H, Kivel N, Verbruggen A, Wellum R, Taylor PDP (2009) A new series of uranium isotope reference materials for investigating the linearity of secondary electron multipliers in isotope mass spectrometry. Int J Mass Spectrom 281:115–125
11. Richter S, Alonso A, Aregbe Y, Eykens R, Jacobsson U, Kehoe F, Kühn H, Verbruggen A, Wellum R (2010) Certification of a new series of gravimetrically prepared synthetic reference materials for $n(^{236}U)/n(^{238}U)$ isotope ratio measurements. In: Proceedings of the 11th international conference on accelerator mass spectrometry, Rome, Italy, Sept. 2008, Nuclear instruments and methods in physics research B, vol 268, pp 956–959
12. Richter S, Alonso A, Eykens R, Jacobsson U, Kühn H, Verbruggen A, Aregbe A, Wellum R, Keegan E (2008) The isotopic composition of natural uranium samples—measurements using the new $n(^{233}U)/n(^{236}U)$ double spike IRMM-3636. Int J Mass Spectrom 269:145–148
13. Richter S, Alonso, Aregbe A, Eykens R, Jacobsson U, Kuehn H, Verbruggen A, Wellum R, Bürger S, Boulyga S, Poths J (2011) IRMM-3100a: A new certified isotopic reference material with equal abundances of 233U, 235U, 236U and 238U. Int J Mass Spectrom 299:120–124
14. Richter S, Hennessy C, Venchiarutti C, Aregbe Y, Hexel C (2021) CERTIFICATION REPORT: "preparation and certification of highly enriched uranium nitrate solutions IRMM-3000 series. Publications Office of the European Union, Luxembourg. ISBN 978-92-76-38745-9. https://doi.org/10.2760/141638, JRC125513
15. Mialle S, Richter S, Truyens J, Hennessy C, Jacobsson U, Aregbe Y (2015) Certification of uranium hexafluoride reference materials for isotopic composition. J Radioanal Nucl Chem 305:255–266
16. Richter S, Venchiarutti C, Hennessy C, Jacobsson U, Bujak R, Truyens J, Aregbe Y (2018) Preparation and certification of the uranium nitrate solution reference materials series IRMM-2019 to IRMM-2029 for the isotopic composition. J Radioanal Nucl Chem 318:1359–1368
17. Richter S, Goldberg SA (2003) Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry. Int J Mass Spectrom 229:181–197
18. Richter S, Kühn H, Aregbe Y, Hedberg M, Horta-Domenech J, Mayer K, Zuleger E, Bürger S, Boulyga S, Köpf A, Poths J, Matthew K (2011) Improvements for routine uranium isotope ratio measurements using the modified total evaporation method. J Anal At Spectrom 26:550
19. Richter S, Hennessy C, Truyens J, Bujak R, Aregbe Y (2021) CERTIFICATION REPORT: "IRMM-2030: certification of a uranium nitrate solution reference material with a 235U "enrichment" (i.e. $n(^{235}U)/n(U)$) of 6 %", Publications Office of the European Union, Luxembourg, ISBN 978-92-76-40744-7. https://doi.org/10.2760/119345. JRC125991
20. Richter S, Alonso A, De Bolle W, Kühn H, Verbruggen A, Wellum R, Taylor PDP (2005) Re-certification of a series of uranium isotope reference materials, IRMM-183, IRMM-184, IRMM-185, IRMM-186 and IRMM-187. Int J Mass Spectrom 247:37–39
21. ISO/IEC Guide 98-3 (2008) Guide to the expression of uncertainty in measurement (GUM, 1995), International Organization for Standardization, Geneva, Switzerland
22. ASTM Standard Document C1832, available through the ASTM website: https://www.astm.org/c1832-23.html Accessed 22 Sept 2023
23. Richter S, Hennessy C, Jacobsson U, Aregbe Y, Hexel C (2022) CERTIFICATION REPORT: "re-certification of the IRMM-183-187 series of uranium nitrate solution reference materials. Publications Office of the European Union, Luxembourg. ISBN 978-92-76-52116-7. https://doi.org/10.2760/312568, JRC129154
24. ASTM Standard Document C1672, available through the ASTM website: https://www.astm.org/c1672-17.html Accessed 22 Sept 2023
25. ASTM Standard Document C1871, available through the ASTM website: https://www.astm.org/c1871-22.html. Accessed 22 Sept 2023
26. Mathew KJ, Singleton GL, Essex RM, Hasozbek A, Orlowicz G, Soriano M (2013) Characterization of uranium isotopic abundances in depleted uranium metal assay standard 115. J Radioanal Nucl Chem 296:435–440
27. Mathew KJ, Mason P, Voeks A, Narayanan U (2012) Uranium isotope abundance ratios in natural uranium metal certified reference material 112-A. Int J Mass Spectrom 315:8–14
28. Mathew KJ, Essex RM, Hasozbek A, Orlowicz G, Soriano M (2014) Uranium isotope-amount ratios in certified reference material 116-A—uranium (enriched) metal assay and isotopic standard. Int J Mass Spectrom 369:48–58
29. Kraiem M, Essex RM, Mathew KJ, Orlowicz GJ, Soriano MD (2013) Re-certification of the CRM 125-A UO_2 fuel pellet standard for uranium isotopic composition. Int J Mass Spectrom 352:37–43
30. Richter S, Konegger-Kappel S, Boulyga S, Stadelmann G, Koepf A, Siegmund H (2016) Linearity testing and dead-time determination for MC-ICP-MS ion counters using the IRMM-072 series of uranium isotope reference materials. J Anal At Spectrom 31:1647
31. Richter S (2019) Implementation of Faraday cup amplifiers with 10^{13} Ω resistors for TIMS measurements at JRC-G.2 in Geel. In: INMM annual meeting, Palm Desert, United States
32. Holden NE (1989) Total and spontaneous fission half-lives for uranium, plutonium, americium and curium nuclides. Pure Appl Chem 61:1483–1504
33. Jaffey AH, Flynn KF, Glendenin LE, Bentley WC, Essling AM (1971) Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U. Phys Rev C 4:1889–1906
34. Cheng H, Edwards RL, Chuan-Chou S, Polyak VJ, Asmerom Y, Woodhead J, Hellstrome J, Wang Y, Kong X, Spötl C, Wang X, Alexander EC Jr (2013) Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. Earth Planet Sci Lett 371–372:82–91
35. Richter S, Eykens R, Kühn H, Aregbe Y, Verbruggen A, Weyer S (2010) New average values for the $n(^{238}U)/n(^{235}U)$ isotope ratios of natural uranium standards. Int J Mass Spectrom 295:94–97
36. Galdoz E, Esteban A, Cristallini O, Perrotta J (2008) UF_6 sampling method using alumina. In: 49th INMM annual meeting, Nashville, United States
37. Richter S, Hiess J, Jacobsson U (2015) Validation of cristallini sampling method for UF_6 by high precision double-spike measurements. Publications Office of the European Union, Luxembourg. ISBN 978-92-79-63505-2. https://doi.org/10.2789/215269, JRC 103668
38. Neumeier S, Kegler P, Richter S, Hammerich S, Zoriy M, Hexel C, Manard B, Schmitt A, Trieloff M, Potts S, Bosbach D, Niemeyer I (2023) Production and analyses of uranium oxide microparticulate reference standards: current status and outlook. In: Proceedings of the INMM & ESARDA—joint annual meeting, Vienna/Austria

39. Richter, Truyens J, Venchiarutti C, Aregbe Y, Middendorp R, Neumeier S, Kegler P, Klinkenberg M, Zoriy M, Stadelmann G, Macsik Z, Koepf A, Sturm M, Konegger-Kappel S, Venzin A, Sangely L, Tanpraphan T (2023) Certification of the first uranium oxide micro-particle reference materials for nuclear safety and security, IRMM-2329P and IRMM-2331P. J Radioanal Nucl Chem 332:2809–2813
40. Müschenborn G, De Bolle B (1983) $^{235}U/^{238}U$ isotope ratio measurements on double collector UF_6 mass spectrometers. Internal report CBNM -MS-R-74-83
41. De Bolle B, Müschenborn G (1981) Small systematic errors of chemical origin in UF_6 isotope measurements during the conversion of UF_6 into UO_3 and the reconversion of UF_6 into UO_3. Int J Mass Spectrom 38:91–96
42. ASTM Standard Document C1429, available through the ASTM website: https://www.astm.org/c1429-21.html Accessed 22 Sept 2023
43. Richter S, Kühn H, Truyens J, Kraiem M, Aregbe Y (2013) Uranium hexafluoride (UF_6) gas source mass spectrometry for certification of reference materials and nuclear safeguards measurements at IRMM. J Anal At Spectrom 28:536
44. Richter S, Boulyga S, Sangely L, Aregbe Y (2022) Certification of new reference materials for uranium isotope analysis and their application at the IAEA. In: IAEA safeguards symposium, Vienna, Austria
45. Truyens J, Dürr M, Macsik Z, Middendorp R, Neumeier S, Richter S, Stadelmann G, Venchiarutti C, Aregbe Y (2020) CERTIFICATION REPORT: Preparation and certification of the uranium oxide micro particles IRMM-2329P. Publications Office of the European Union, Luxembourg. ISBN 978-92-76-09878-2. https://doi.org/10.2760/584367
46. Truyens, Neumeier S, Kegler P, Klinkenberg M, Zoriy M, Richter S, Aregbe Y (2021) CERTIFICATION REPORT: Preparation and certification of the uranium oxide micro particles IRMM-2331P. Publications Office of the European Union, Luxembourg. ISBN 978-92-76-31383-0. https://doi.org/10.2760/874191
47. Venchiarutti C, Richter S, Middendorp R, Aregbe Y (2019) NUSIMEP-9: uranium isotope amount ratios and uranium mass in uranium micro-particles. Publications Office of the European Union, Luxembourg. ISBN 978-92-76-09182-0. https://doi.org/10.2760/533028
48. Jakopič R, Toth K, Bauwens J, Buják R, Hennessy C, Kehoe F, Jacobsson U, Richter S, Aregbe A (2021) 30 years of IRMM-1027 reference materials for fissile material accountancy and control: development, production and characterisation. J Radioanal Nucl Chem 330:333–345
49. Heumann KG (1992) Isotope dilution mass spectrometry. Int J Mass Spectrom Ion Process 118–119:575–592
50. Venchiarutti C, Jakopič R, Richter S, Jacobsson U, Hennessy C, Aregbe Y (2017) CERTIFICATION REPORT, preparation and certification of a new batch of ^{242}Pu spike: IRMM-049e. Publications Office of the European Union, Luxembourg, 2017. ISBN 978-92-79-72279-0. https://doi.org/10.2760/115196
51. Grossi R, Alkhaldi C (2023) Iran's amassed enough material for 'several nuclear weapons', says IAEA Chief. Interview at CNN. https://edition.cnn.com/2023/01/25/middleeast/iran-nuclear-weapons-iaea-chief-intl/index.html Accessed 22 Sept 2023
52. Grossi R, Pourahmani A (2023) Near bomb-grade level uranium found in Iranian nuclear plant, says IAEA report. Interview at CNN. https://edition.cnn.com/2023/03/01/middleeast/iran-uranium-enrichment-iaea-intl/index.html Accessed 22 Sept 2023