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Preparation and certification of the uranium nitrate solution reference materials series IRMM-2019 to IRMM-2029 for the isotopic composition

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

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Abstract

The IRMM-2019-2029 series of uranium nitrate solutions was certified for the isotopic composition. The solutions were originally prepared for the certification of the IRMM-019-029 series of uranium hexafluoride (UF_6) materials in 2014, for which certification measurements were performed by thermal ionization mass spectrometry after conversion of UF_6 into uranyl nitrate solutions. Analyses were performed using the modified total evaporation method and for some materials with low ^{236}U abundances, the $n(^{235}U)/n(^{238}U)$ ratio was measured using a $n(^{233}U)/n(^{236}U)$ double spike. The integrity of the certified values after dilution and ampouling of the original solutions was checked through process control measurements.

Keywords Reference materials · Thermal ionization mass spectrometry · Nuclear safeguards · Uranium nitrate solution · Uranium hexafluoride

Introduction

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, Geel in Belgium (formerly known as the "Institute for Reference Materials and Measurements" (IRMM)), provides 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, where the need for isotopic standards is explicitly mentioned, acknowledging their importance for the measurements of nuclear materials. For accurate mass spectrometric measurements in nuclear material accountancy and nuclear safeguards, suitable CRMs are needed to validate measurement procedures and to calibrate instruments.

The IRMM-019 to IRMM-029 series of of uranium hexafluoride (UF_6) isotope reference materials was originally certified between 1984 and 1996. The series covers the enrichment range from depleted uranium (IRMM-019 to IRMM-021) via natural uranium (IRMM-022) to enriched uranium (IRMM-023 to IRMM-029). At that time, the relative expanded uncertainties (coverage factor $k = 2$) were in the 0.05–0.2% range for the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ and between 0.3 and 10% for the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The certification was achieved in several procedural steps, using the EC-171/031, /071, /194, /295, /446 series of uranium oxides, which were fluorinated into UF_6 gas, then calibrated by GSMS (Gas Source Mass Spectrometry) against special UF_6 internal standards prepared by fluorination of gravimetric uranium oxide mixtures. The widely used IRMM-183-187 series of certified uranium nitrate solutions was directly prepared from the original EC-171/031, /071, /194, /295, /446 series of uranium oxides, therefore the isotopic compositions are the same as the already calibrated fluorinated fractions. The fluorinated fractions from the IRMM-183-187 series were then used as calibrants for the certification of the isotopic composition of the IRMM-019-029 series of UF_6 materials.

In summary, this original certification project for the IRMM-019-029 series was a quite complicated process, which included numerous steps of sample conversions and mass spectrometric measurements, associated with

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

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

uncertainties that were most likely underestimated since at that time the certification did not include homogeneity and stability testing according to ISO 17034 [1] and the "Guide to the Expression of Uncertainty in Measurement " (GUM) [2] was not applied yet. Furthermore, some of the fluorides prepared from the EC-171 series are exhausted and no longer available for GSMS measurements at JRC-G.2.

Moreover, since the minor isotope ratios contain valuable information about the origin of the feed material used for commercial or possibly clandestine isotopic enrichment of UF_6, safeguards authorities now require more accurate and reliable measurements and reference materials with smaller measurement uncertainties. Therefore, in 2012–2014, the unit JRC-G.2 undertook the initiative to re-measure and re-certify this IRMM-019-029 series of UF_6 materials with emphasis on the minor isotope amount ratios in order to provide lower uncertainties on the certified values. The certified values for the isotopic composition and their uncertainties were assigned following ISO 17034 [1], ISO Guide 35 [3] and the Guide to the Expression of Uncertainty in Measurement [2].

This re-certification of the entire IRMM-019 to IRMM-029 series was also performed by using a new set of calibrants, which were gravimetrically prepared uranium nitrate solutions, in combination with recently developed new mass spectrometric measurement methods, in particular for thermal ionisation mass spectrometry (TIMS) [4, 5]. Following this strategy, JRC-G.2 re-certified the IRMM-019-029 series of UF_6 reference materials to be suitable for accountancy measurements of UF_6 for the major isotope ratios in compliance with the ITV-2010 values [6], and in addition provided certified values for the minor isotope amount ratios with smaller uncertainties than before.

In order to make the IRMM-019-029 series of re-certified UF_6 reference materials also available for TIMS and ICP-MS users, a follow-up project was started in 2016. The goal of this new certification project was to provide the remaining uranium nitrate solutions prepared for the certification of IRMM-019-029 series by TIMS as a set of new uranium nitrate solution reference materials, labelled as the IRMM-2019-2029 series. These remaining solutions were diluted to a concentration of about 2 mg U/g solution and dispensed in screw-cap quartz ampoules. This concentration level is deemed ideal for TIMS/MTE measurements, and the solutions can be further diluted by the users for TIMS/TE or MC-ICP-MS measurements. However, the integrity of the certified values for the isotopic composition from the processing of the original remaining uranium nitrate solutions from the IRMM-019-029 series towards their certification as the IRMM-2019-2029 series had to be checked. This was controlled by the so-called process control measurements (PCM), which were performed on three ampoules for each of the IRMM-2019-2029 series reference materials.

As a justification for this particular way of certification of the IRMM-2019-2029 series, the IRMM-019-029 series of UF_6 reference materials was actually not characterized on the UF_6 materials themselves but rather on the uranium nitrate solutions prepared from the UF_6 materials by hydrolysis and nitration, and subsequently analysed by TIMS [4, 5]. Both characterization and homogeneity studies were performed by TIMS directly on the uranium nitrate solutions, and the certified values calculated from those results. The certified values were subsequently confirmed by GSMS measurements of the original UF_6 materials as required by ISO 17034 [1]. As a conclusion, both the original UF_6 materials as well as the nitrate solutions prepared from them can be considered identical regarding their isotopic composition and could be certified with the same values. However, in 2014, certificates were only issued for the UF_6 materials of the IRMM-019-029 series, but not for the remaining uranium nitrate solutions.

The uranium nitrate solutions were further processed to make them more suitable for mass spectrometry applications and therefore, available for sale as reference materials for a wider range of laboratories within the nuclear community. The processing steps included a dilution by a factor of about 10 and dispensing into cleaned screw-cap quartz ampoules. These operations are not expected to cause any change in the isotopic composition of the materials, therefore new certification measurements (i.e. new characterisation and homogeneity assessments) were not deemed necessary. In order to guarantee the integrity of the assigned/certified values through the process, process control measurements were performed on the IRMM-2019-2029 series solutions. Within the project plan, it was stated that under the condition that the results of the process control measurements on the IRMM-2019-2029 series agree with the certified values for the IRMM-019-029 series, the same certified values will be assigned also to the IRMM-2019-2029 series.

Experimental

Sample processing

The original uranium nitrate solutions prepared for the IRMM-019-029 certification project in 2012 had a concentration of about 20 mg U/mL solution, the solution volumes were 50–100 mL and the acidity was 1M. However, since they were originally stored in glass vials closed only with plastic lids, it could not be excluded that the concentration might have increased over time due to the evaporation of liquid. Therefore these solutions were first transferred in 2014 into screw-cap quartz ampoules and stored for later use. In 2017 and 2018, in the frame of the certification of the IRMM-2019-2029 series, the solutions were transferred into 1L quartz flasks and gravimetrically diluted by a factor of about 8 by addition of ultrapure 1M HNO_3. The uranium concentrations for each solution were then determined by IDMS using the ^{235}U spike IRMM-054. The results for the uranium concentrations were between 10 and 30% higher than expected from the original concentration and the applied dilution factor, due to the evaporation, which may have occurred between the preparation in 2012 and the re-ampouling in 2014. In order to obtain the target concentration of 2 mg U/g solution (suitable for TIMS/MTE analysis), all solutions were further diluted within the quartz flasks by further adding ultrapure 1M HNO_3 under gravimetrical control. The final concentration of the U nitrate solutions can then be calculated based on the gravimetrical weighing and no additional IDMS measurements were deemed necessary.

From the 1L quartz flasks the solutions were directly transferred into new screw-cap quartz ampoules, which were cleaned using a procedure involving HNO_3 and deionized water. The cleanliness of the ampoules, the possible uranium contamination from the reagents (HNO_3 solution) used for dilutions and possible leaching of uranium from the quartz material of the ampoules were checked as well. Blank and leaching test measurements of HNO_3 solutions after a storage time of 2 years were performed on five cleaned screw-cap quartz ampoules by TIMS/IDMS using the low level ^{233}U spike IRMM-058, and the results showed negligible uranium concentrations.

The screw-cap quartz ampoules have also been checked for possible leak and good vacuum tightness by filling them with distilled water and putting them into a vacuum chamber. After pumping at a pressure of 10^{-6} mbar, no leakage from the tightly closed ampoules under vacuum was observed.

After the dispensing of the reference materials solutions, each ampoule contained about 5 mL of uranium nitrate solution in 1M HNO_3. Although the concentration in the IRMM-2019-2029 series materials is indicated as 2 mg U/g solution, these reference materials are not intended to be used as spikes for IDMS, since they are certified for the isotopic composition only.

Process control measurements

The process control measurements of the eleven materials of the IRMM-2019-2029 series were performed by TIMS (TRITON, Thermo Fischer Scientific) using the Modified Total Evaporation (MTE) method with the gravimetrically prepared IRMM-074/10 isotope reference material as calibrant. The MTE method was introduced in 2003 [7, 8] in particular to determine the minor isotope amount ratios with smaller measurement uncertainties than those achieved by traditional methods. The MTE method was standardized by ASTM-International as C1832-16 in 2016 [9]. Additionally for some materials such as IRMM-2021, IRMM-2022 and IRMM-2023 with $n(^{236}\text{U})/n(^{238}\text{U})$ ratios below 10^{-5}, the major isotope amount ratios were measured by the double spike method (DS) using IRMM-3636a, a mixture of highly enriched ^{233}U and ^{236}U with a ratio of $n(^{233}\text{U})/n(^{236}\text{U}) \approx 1$. This allows for an internal mass fractionation correction and therefore leads to lower measurement uncertainties on the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio [10, 11]. The double spike method (DS) was standardized by ASTM-International as C1871a-18 in 2018 [12]. In addition, the certified $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio of the calibrant IRMM-074/10 used for MTE measurements has been confirmed by the DS method at an accuracy level better than 0.002% [10, 12, 13] using the certified $n(^{233}\text{U})/n(^{236}\text{U})$ isotope ratio of IRMM-3636a. This effectively provides a close link between these two gravimetrically prepared calibrants.

For internal quality control (QC) purposes, solutions of the IRMM-075 series were measured by TIMS/MTE within the same sequences (i.e. on the same TIMS turrets) as the samples of IRMM-2019-2029. The IRMM-075 is a series of gravimetric mixtures characterised by major isotope amount ratios $n(^{235}\text{U})/n(^{238}\text{U})$ of about 0.007256 (close to natural uranium) with uncertainties of 0.05% ($k = 2$) and certified isotope amount ratios $n(^{236}\text{U})/n(^{238}\text{U})$ ranging between 10^{-9} and 10^{-4}, with uncertainties varying between 0.035 and 0.58% ($k = 2$) [14]. This series is suitable for quality control in particular for measurements of the $n(^{236}\text{U})/n(^{238}\text{U})$ isotope amount ratios for the IRMM-2019 to IRMM-2029 series, covering a wide dynamic range and requiring different types of detectors such as Faraday cups and a secondary electron multiplier (SEM) in combination with an energy filter to improve the abundance sensitivity. As a special QC sample for the double spike method, the close-to-natural certified reference material IRMM-184 was introduced into the same sequence as IRMM-2021, IRMM-2022 and IRMM-2023.

In addition to the internal quality control measurements, several external certified reference materials have been measured at JRC-G.2 within the recent few years, using the same MTE and DS methods with the same calibrants and similar measurement parameters and in compliance with the respective ASTM standards. For example, for the depleted uranium certified reference material NBL CRM 115 [15] and the highly enriched uranium certified reference material NBL CRM 116A [16] both certified by New Brunswick Laboratory (U.S. DOE), verification measurements were performed at JRC-G.2 using the MTE method [17, 18, respectively]. Furthermore, the re-certified

$n(^{235}U)/n(^{238})$ ratio of the natural uranium certified reference material NBL CRM 112A [19] was verified using the double spike (DS) method at JRC-G.2 and several other laboratories [11, 12].

Results and discussion

Process control measurements

No significant differences were found between the measurements results for all the ratios from the three ampoules of each solution of the IRMM-2019-2029 series. Therefore, these results were subsequently combined and only the averages evaluated and presented below. The process control measurements did not show any significant deviations from the certified isotopic ratios of IRMM-019-029, as shown below in Figs. 1, 2, 3 and 4. Expanded uncertainties are given with a coverage factor $k = 2$, with about equal proportions originating from the process control measurements and the certified values. For some of the minor ratios $n(^{236}U)/n(^{238}U)$, in particular for IRMM-021 and IRMM-075/5, the relative uncertainties were at the level of up to 12%, which was dominated by counting statistics at the quite low count rates detected for ^{236}U. However, the relative differences between the process control measurements and the certified values were much lower than their uncertainties, and therefore not significant. As a conclusion, the good agreement of the process control measurements with the certified values allows the certification of the isotopic composition in the solution reference material series IRMM-2019-2029 using the same certified values of the IRMM-019-029 series of UF_6 materials.

Additionally, several external certified reference materials, covering a wide range of isotope ratios and ^{235}U enrichments from 0.2 to 90%, were measured by TIMS at JRC G.2 and showed no significant deviations from their certified values (see Figs. 5, 6, 7). This serves as an additional confirmation for the reliability of the applied TIMS/MTE and TIMS/DS methods.

Verification of the long-term stability of the reference materials

In 2014, the stability study for the IRMM-019-029 series of UF_6 materials was carried out in two complimentary ways using historical data for IRMM-023 materials:

1. In 2009 measurements were already performed on IRMM-023 by TIMS using the double spike (DS) technique (for more details see [4, 5]) on several samples of freshly distilled UF_6, converted into uranyl nitrate solution. The review of all data showed that the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ did not change significantly between 2009 and 2013, covering a period of 4 years. However, since these measurements were not performed on a regular basis, they were not considered appropriate to be used for the long-term

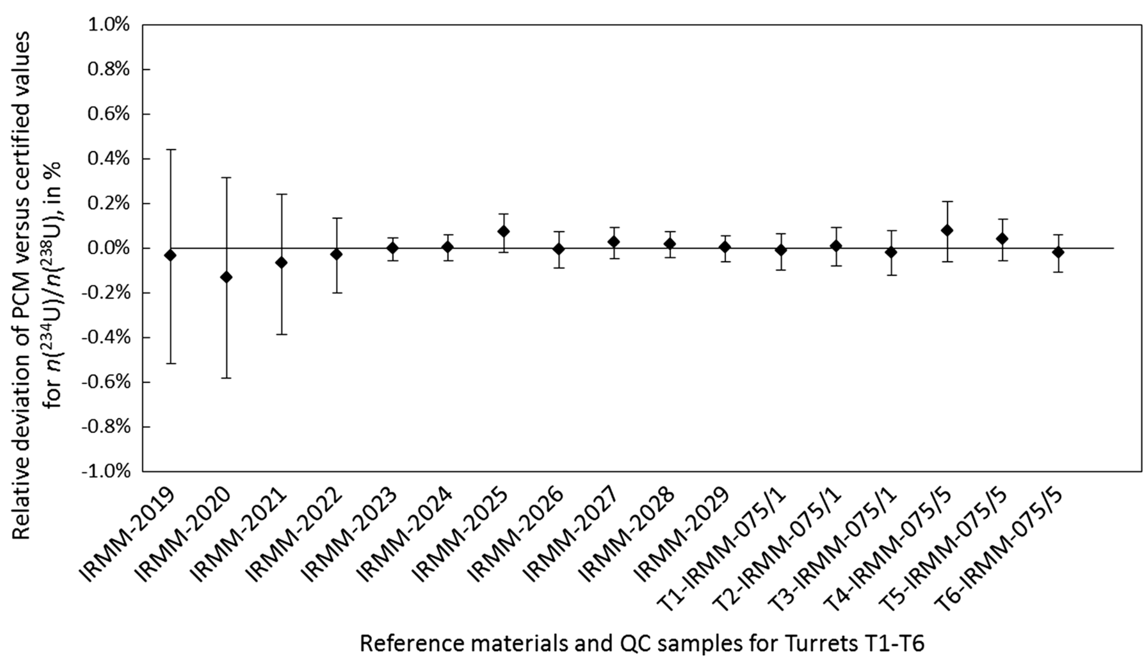

Fig. 1 Process control measurements (PCM) for $n(^{234}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 and IRMM-075/5 (with $n(^{234}U)/n(^{238}U) \cong 0.000053277(34)$) for MTE sequences (turrets) T1–T6. Expanded uncertainties are given with a coverage factor $k = 2$

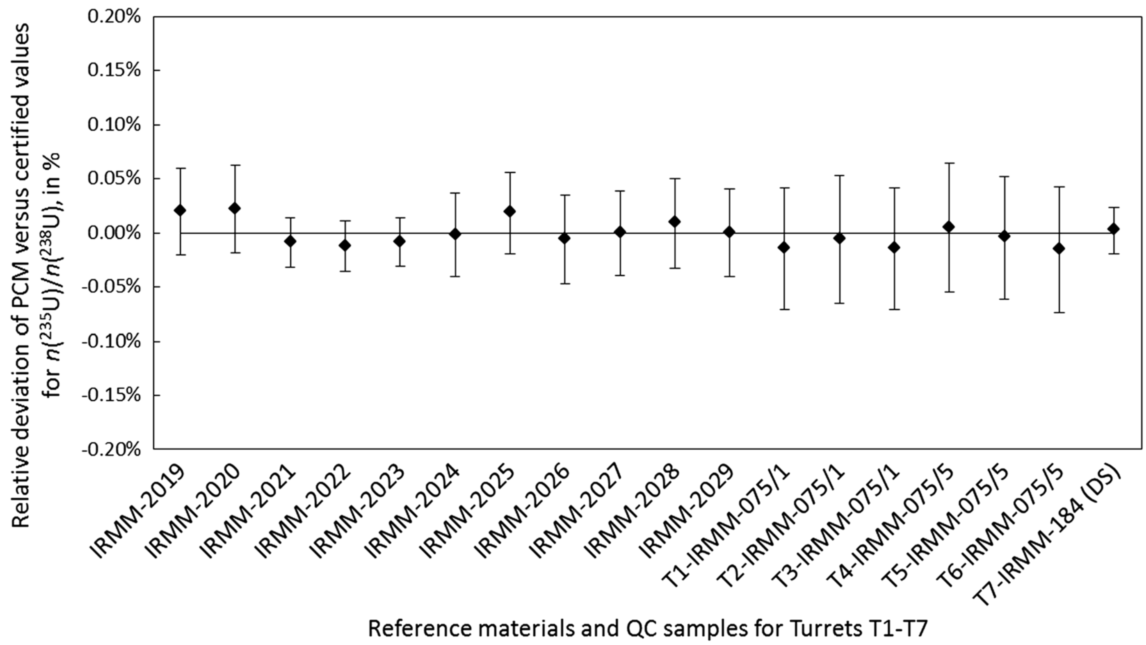

Fig. 2 Process control measurements (PCM) for $n(^{235}U)/n(^{238}U)$ for the IRMM-2019-2029 series, using the MTE method for IRMM-2019, IRMM-2020 and IRMM-2024-2029, and using the DS method for IRMM-2021-2023. Also shown are results for QC samples IRMM-075/1 and IRMM-075/5 (with $n(^{234}U)/n(^{238}U) \cong 0.0072603(36)$) for MTE sequences (turrets) T1–T6, in addition IRMM-184 as QC sample for the DS method for sequence (turret) T7. Expanded uncertainties are given with a coverage factor $k = 2$

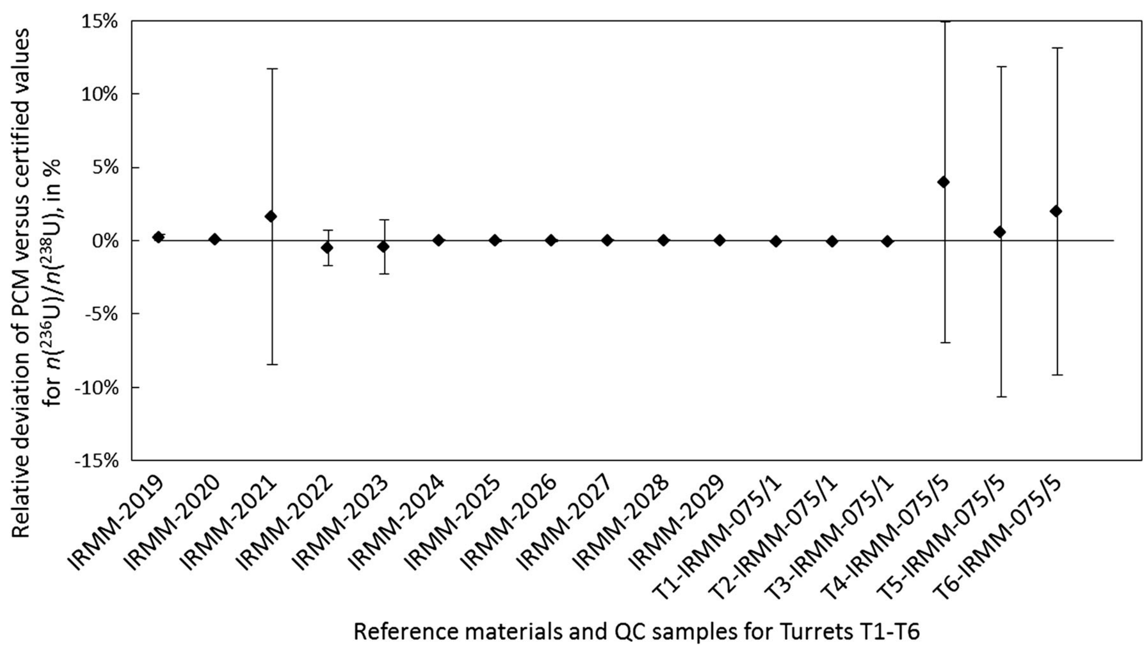

Fig. 3 Process control measurements (PCM) for $n(^{236}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 (with $n(^{236}U)/n(^{238}U) \cong 10^{-4}$) and IRMM-075/5 (with $n(^{236}U)/n(^{238}U) \cong 10^{-8}$) for MTE sequences (turrets) T1–T6, within a $\pm$ 15% range on the ordinate. Expanded uncertainties are given with a coverage factor $k = 2$

stability study in 2014. But in the meantime, in 2016 [13] as well as in 2018 for the process control measurements for the IRMM-2019-2029 series, additional measurements were performed on the solutions of IRMM-023 and IRMM-2023 by TIMS using the double spike technique.

2. The long-term stability study for the UF_6 materials IRMM-019-029 series was performed in 2014 using historical data from verification measurements by

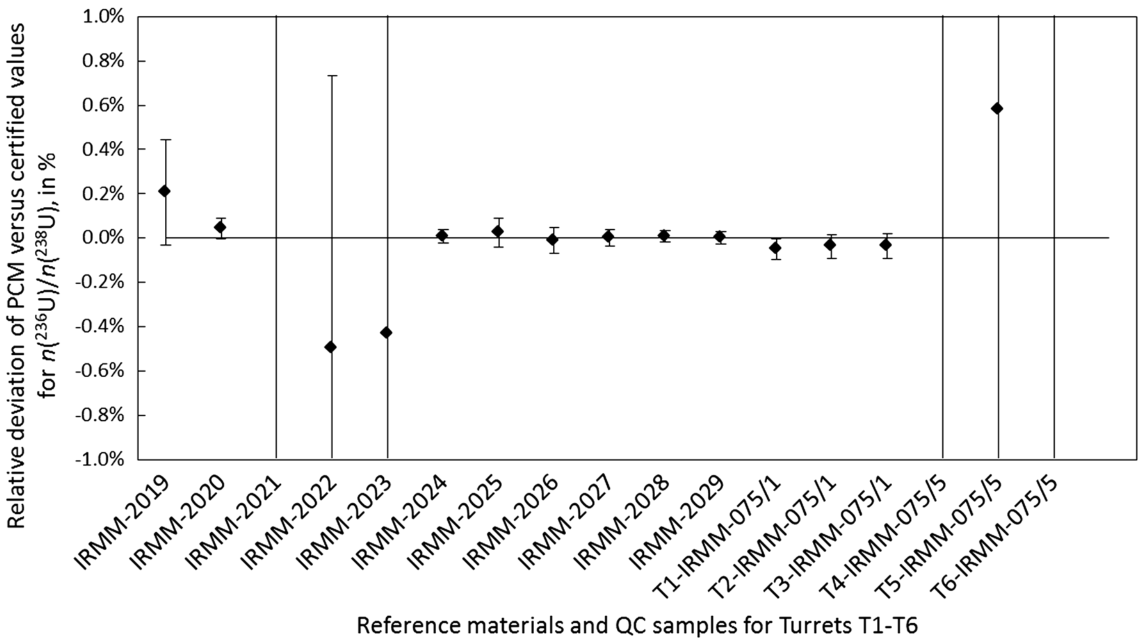

Fig. 4 Process control measurements (PCM) for $n(^{236}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 (with $n(^{236}U)/n(^{238}U) \cong 10^{-4}$) and IRMM-075/5 (with $n(^{236}U)/n(^{238}U) \cong 10^{-8}$) for MTE sequences (turrets) T1–T6, within a ± 1% range on the ordinate. Expanded uncertainties are given with a coverage factor $k = 2$

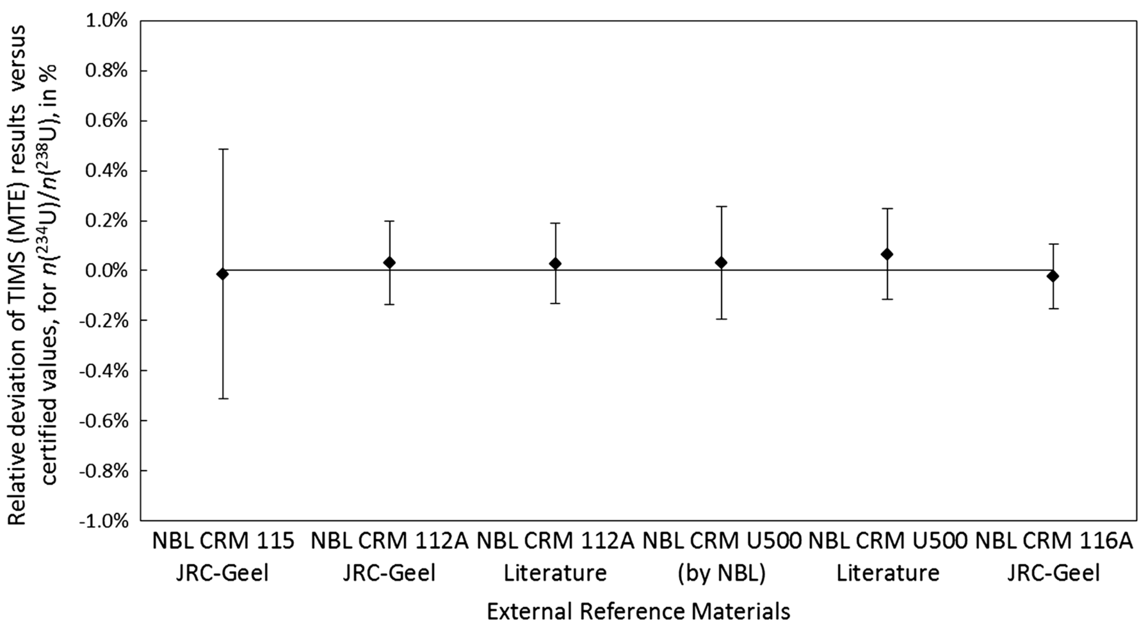

Fig. 5 Measurement results from JRC-Geel using the TIMS/MTE method for $n(^{234}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CR112A (close to natural U), NBL CRM U500 (50% enriched in ^{235}U) and NBL CRM 116A (90% enriched in ^{235}U). In addition results from the literature [7, 11, 20] are shown for comparison. Expanded uncertainties are given with a coverage factor $k = 2$

GSMS, which were performed on numerous ('daughter') ampoules prior to sale. These verification measurements of the daughter ampoules were done relative to the mother ampoule without the use of a reference material.

In order to study the long-term stability of the uranium nitrate solutions of the IRMM-2019-2029 series for the step 1 approach, all measurement data for IRMM-023 and IRMM-2023 by TIMS using the double spike method (DS) between 2009 and 2018 were combined, as shown in Fig. 8.

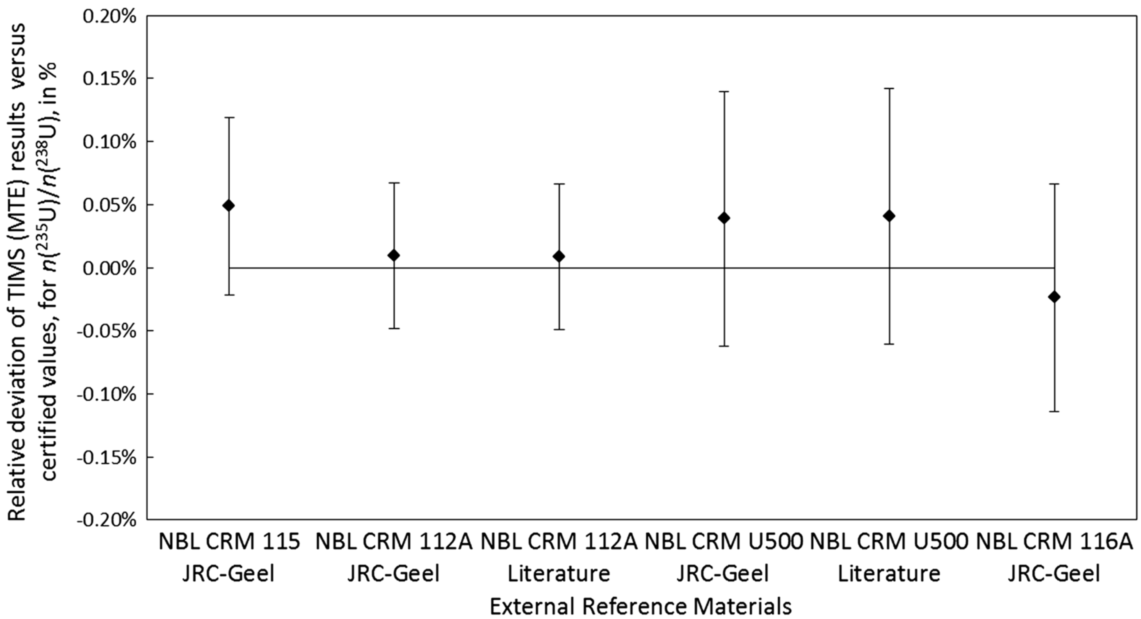

Fig. 6 Measurement results from JRC-Geel using the TIMS/MTE method for $n(^{235}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CR112A (close to natural U, measured using DS method), NBL CRM U500 (50% enriched in ^{235}U) and NBL CRM 116A (90% enriched in ^{235}U). In addition results from the literature [11, 20, 21] are shown for comparison. Expanded uncertainties are given with a coverage factor $k = 2$

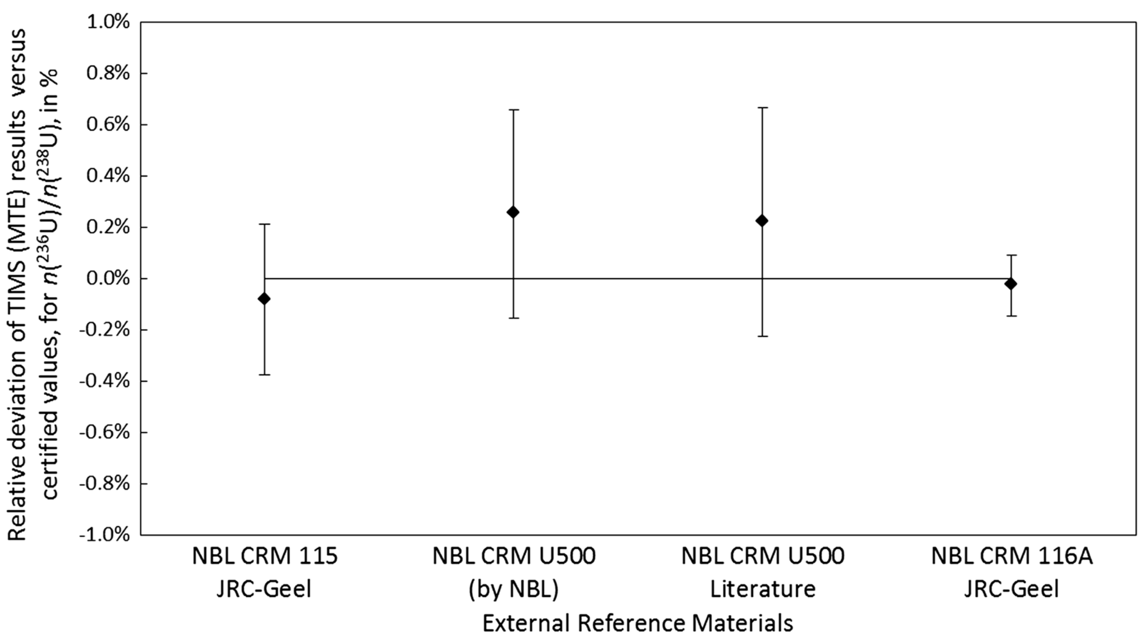

Fig. 7 Measurement results from JRC-Geel using the TIMS/MTE method for $n(^{236}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CRM U500 (50% enriched in ^{235}U) and NBL CRM 116A (90% enriched in ^{235}U). In addition results from the literature [7, 20] are shown for comparison. Note that the $n(^{236}U)/n(^{238}U)$ ratio for NBL CR112A (close to natural U) is below the detection limit of 6×10^{-10} [8] and therefore not shown here. Expanded uncertainties are given with a coverage factor $k = 2$

No outliers were observed at the 99% confidence level and the slope of the regression line was not significantly different from zero at the 95% confidence level. Therefore, this study shows that there is no significant variation between 2009 and 2018 on the major isotope amount ratio of IRMM-023/-2023 and also no significant trend. Consequently, and in compliance with ISO 17034 and ISO Guide 35, this can be used as a justification for assigning a 10-year validity time for the IRMM-2019-2029 solution reference materials, starting from 2018. This is the same

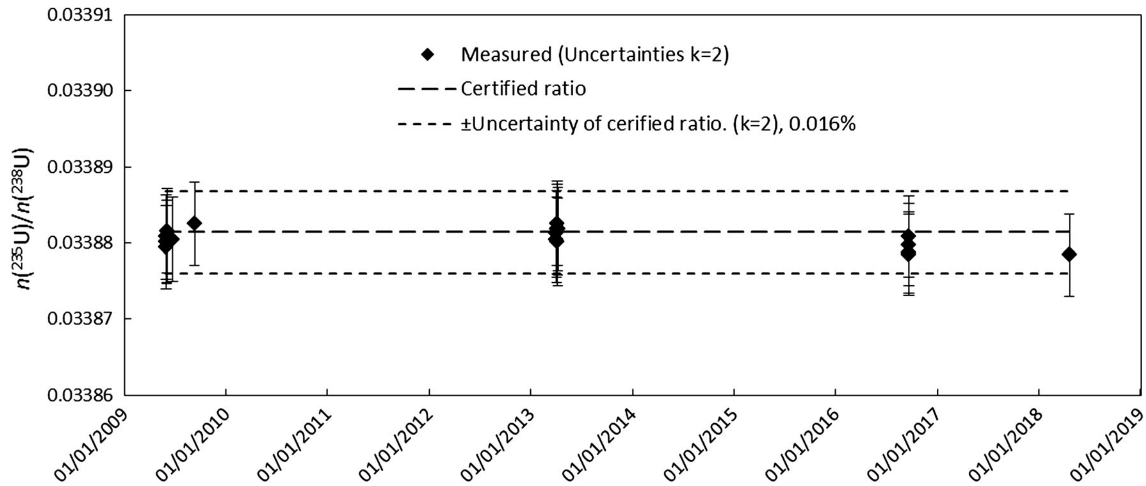

Fig. 8 TIMS-DS measurements (n = 19) for IRMM-023 and IRMM-2023 performed between 2009 and 2018. Expanded uncertainties are given with a coverage factor k = 2

Table 1 Certified values for the IRMM-019-029 and IRMM-2019-2029 series

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

The expanded uncertainties (k = 2) are given in parenthesis

validity time as previously assigned in 2014 to the UF_6 materials based on the long-term stability study according to the step 2 approach. During the 10-year validity time, post-certification measurements will be performed on a regular basis in order to verify and confirm the stability of the certified values, i.e. of the isotopic composition of the uranium nitrate solutions.

Revision of the certified values for the isotopic composition of the IRMM-019 to IRMM-029 series of UF_6 reference materials

In 2014, the isotopic composition of the IRMM-019-029 series of uranium hexafluoride (UF_6) reference materials was re-certified based on new characterisation measurements using newly developed TIMS methods [4, 5, 7, 8]. However, the rounding rules applied for the certified values and their uncertainties at that time were adopted from a different section within the JRC performing certification work on different types of materials. But later it was realized that for isotope mass spectrometry in the nuclear field the 2-digit rounding rule is usually preferred. In addition, since 2014, a new set of molar masses (AME 2016, [22]) used for the calculation of uranium isotope mass fractions has been published. Therefore, these two new elements (the 2 digit rounding rule and the new molar masses) were directly taken into account in the calculation and assignment of the final certified values for the IRMM-2019-2029 series. Similarly, the certified values and the uncertainties of the IRMM-019-029 series materials as published in 2014 were modified using the 2-digit rounding rule and the certified values and the uncertainties for the isotope mass fractions and molar masses were re-calculated using the new AME 2016 values [22].

Based on the recent successful verification of the certified isotope ratios for the IRMM-2019-2029 solutions during the process control measurements, the validity of the certificates for the IRMM-019-029 series UF_6 materials can also be extended for another 10 years, re-starting from 2018. Therefore, new certificates for the eleven UF_6 reference materials of the IRMM-019-029 series shall be issued in 2018.

The certified isotope ratios for the IRMM-019-029 and IRMM-2019-2029 series are presented in Table 1.

Conclusions

The certification process for the IRMM-2019-2029 series of uranium nitrate solution isotope reference materials as well as a revision of the IRMM-019-029 series of uranium hexafluoride isotope (UF_6) reference materials were performed at the JRC-Geel (JRC G.2 unit) in compliance with ISO 17034 [1]. The two series were certified in a manner to be SI traceable via a new set of calibrants in the form of gravimetrically prepared isotope reference materials like the IRMM-074 series and the IRMM-3636a double spike. The isotope ratio measurements were performed by TIMS using standardized methods such as the MTE method (ASTM C1832) and the double spike (DS) method (ASTM C1871a), and combined with quality control (QC) measurements of internal (IRMM-075 series) and external certified reference materials (NBL CRMs 112A, 115 and 116A). Finally, the same certified values for the isotopic composition were assigned for both series, IRMM-2019-2029 and the IRMM-019-029, the uranium nitrate solutions and the UF_6 materials, respectively. The combined expanded uncertainties for the two series were estimated using the "Guide to the Expression of Uncertainty in Measurement" (GUM) [2] and are generally lower than the uncertainties obtained in the initial certification of the IRMM-019-029 series, enabling more precise and accurate uranium isotope ratio measurements.

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