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CERTIFICATION REPORT

Preparation and Certification of the Uranium Nitrate Solution Series IRMM-2019-2029

Revision of the IRMM-019-029 Series of UF_6 Materials

Certified reference materials for the U isotopic composition

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Table of contents

Foreword

The Directorate G "Nuclear Safety and Security", Unit G.2 "Standards for Nuclear Safety, Security and Safeguards" (SN3S) at the European Commission's Joint Research Centre, 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 safeguards authorities and the nuclear industry.

This report describes the certification of the IRMM-2019-2029 series of uranium nitrate solution reference materials and the revision of the uranium hexafluoride (UF_6) reference materials series IRMM-019-029, both certified for the uranium isotopic composition.

Acknowledgments

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Abstract

This report describes the certification of the IRMM-2019-2029 series of uranium nitrate solution reference materials and the revision of the uranium hexafluoride (UF_6) reference materials series IRMM-019-029, both certified for the uranium isotopic composition. The certified values and their uncertainties were assigned following ISO 17034 [1], ISO Guide 35 [2] and the Guide to the Expression of Uncertainty in Measurement [3].

The IRMM-019-029 series of eleven uranium hexafluoride (UF_6) reference materials was originally produced and certified in the 1980's-1990's. For the first re-certification performed in 2014, the UF_6 materials were converted into eleven uranium nitrate solutions to perform the homogeneity and characterisation studies. These materials were characterised in compliance with ISO 17034 [1] by Thermal Ionisation Mass Spectrometry (TIMS), by taking advantage of newly established measurement procedures such as the Modified Total Evaporation (MTE) and Double Spike (DS) methods, and using a new set of certified uranium isotope reference materials, which were prepared by gravimetrical mixing of highly enriched ^{233}U, ^{235}U, ^{236}U and ^{238}U oxides or solutions. The results of the characterisation measurements were also confirmed by Gas Source Mass Spectrometry (GSMS) measurements using the original UF_6 gases [4, 5].

For the certification of the isotopic composition of the IRMM-2019-2029 series each of the remaining uranium nitrate solutions used for the certification of IRMM-019-029 was diluted using one molar nitric acid to a concentration of about 2 mg uranium per g solution and dispensed into cleaned screw-cap quartz ampoules. Each ampoule contains 5 ml of solution. Subsequently "process control measurements" (PCM) by TIMS using the MTE and DS methods were performed for three ampoules for each of the reference materials. The results for the isotopic composition from the process control measurements on these uranium nitrate solutions agreed well with the certified values for IRMM-019-029 series of UF_6 materials. Therefore no separate new characterisation and homogeneity studies were performed, and the certified values for IRMM-019-029 were assigned as well to the uranium solution reference material series IRMM-2019-2029.

Moreover, certified values for both the IRMM-019-029 series of UF_6 reference materials and the IRMM-2019-2029 series of uranium nitrate solution reference materials were established using new published values for the atomic masses and applying a 2-digit rounding rule.

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

The following values were assigned for both reference materials series IRMM-019-029 (UF_6) and IRMM-2019-2029 (U nitrate solutions):

	Isotope amount ratios	
	Certified values [mol/mol]	Uncertainty 3) [mol/mol]
IRMM-019/IRMM-2019 1)		
$n(^{234}U)/n(^{238}U)$	0.000006846	0.000000031
$n(^{235}U)/n(^{238}U)$	0.00167749	0.00000048
$n(^{236}U)/n(^{238}U)$	0.000036523	0.000000085
IRMM-020/IRMM-2020 1)		
$n(^{234}U)/n(^{238}U)$	0.000011923	0.000000051
$n(^{235}U)/n(^{238}U)$	0.00209571	0.00000060
$n(^{236}U)/n(^{238}U)$	0.00028615	0.00000011

IRMM-021/IRMM-2021[2)]		
$n(^{234}U)/n(^{238}U)$	0.000024846	0.000000076
$n(^{235}U)/n(^{238}U)$	0.00440521	0.00000071
$n(^{236}U)/n(^{238}U)$	0.00000002657	0.00000000078
IRMM-022/IRMM-2022[2)]		
$n(^{234}U)/n(^{238}U)$	0.000053275	0.000000085
$n(^{235}U)/n(^{238}U)$	0.0072562	0.0000012
$n(^{236}U)/n(^{238}U)$	0.0000002415	0.0000000025
IRMM-023/IRMM-2023[2)]		
$n(^{234}U)/n(^{238}U)$	0.00033950	0.00000011
$n(^{235}U)/n(^{238}U)$	0.0338814	0.0000054
$n(^{236}U)/n(^{238}U)$	0.0000001153	0.0000000017
IRMM-024/IRMM-2024[1)]		
$n(^{234}U)/n(^{238}U)$	0.00029075	0.00000014
$n(^{235}U)/n(^{238}U)$	0.053254	0.000015
$n(^{236}U)/n(^{238}U)$	0.00051696	0.00000013
IRMM-025/IRMM-2025[1)]		
$n(^{234}U)/n(^{238}U)$	0.000122452	0.000000090
$n(^{235}U)/n(^{238}U)$	0.0204356	0.0000055
$n(^{236}U)/n(^{238}U)$	0.000148386	0.000000083
IRMM-026/IRMM-2026[1)]		
$n(^{234}U)/n(^{238}U)$	0.00014941	0.00000010
$n(^{235}U)/n(^{238}U)$	0.0256791	0.0000075
$n(^{236}U)/n(^{238}U)$	0.00020730	0.00000011
IRMM-027/IRMM-2027[1)]		
$n(^{234}U)/n(^{238}U)$	0.00023159	0.00000013
$n(^{235}U)/n(^{238}U)$	0.041717	0.000012
$n(^{236}U)/n(^{238}U)$	0.00038739	0.00000011
IRMM-028/IRMM-2028[1)]		
$n(^{234}U)/n(^{238}U)$	0.00061041	0.00000027
$n(^{235}U)/n(^{238}U)$	0.037576	0.000012
$n(^{236}U)/n(^{238}U)$	0.0051943	0.0000011
IRMM-029/IRMM-2029[1)]		
$n(^{234}U)/n(^{238}U)$	0.00084444	0.00000037
$n(^{235}U)/n(^{238}U)$	0.044052	0.000013
$n(^{236}U)/n(^{238}U)$	0.0105563	0.0000022

[1)] The certified values are traceable to the International System of units (SI) via the values on the certificate of IRMM-074/10.

[2)] The certified values are traceable to the International System of units (SI) via the values on the certificate of IRMM-3636a.

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

	Isotope amount fraction (x 100)	
	Certified values [1)] [mol/mol]	Uncertainty [2)] [mol/mol]
IRMM-019/IRMM-2019		
$n(^{234}U)/n(U)$	0.0006834	0.0000031
$n(^{235}U)/n(U)$	0.167461	0.000048
$n(^{236}U)/n(U)$	0.0036460	0.0000085
$n(^{238}U)/n(U)$	99.828210	0.000049
IRMM-020/IRMM-2020		
$n(^{234}U)/n(U)$	0.0011895	0.0000050
$n(^{235}U)/n(U)$	0.209070	0.000060
$n(^{236}U)/n(U)$	0.028547	0.000011
$n(^{238}U)/n(U)$	99.761193	0.000061
IRMM-021/IRMM-2021		
$n(^{234}U)/n(U)$	0.0024736	0.0000076
$n(^{235}U)/n(U)$	0.438578	0.000071
$n(^{236}U)/n(U)$	0.000002645	0.000000077
$n(^{238}U)/n(U)$	99.558946	0.000071
IRMM-022/IRMM-2022		
$n(^{234}U)/n(U)$	0.0052889	0.0000084
$n(^{235}U)/n(U)$	0.72035	0.00012
$n(^{236}U)/n(U)$	0.00002397	0.00000025
$n(^{238}U)/n(U)$	99.27433	0.00012
IRMM-023/IRMM-2023		
$n(^{234}U)/n(U)$	0.032827	0.000010
$n(^{235}U)/n(U)$	3.27603	0.00051
$n(^{236}U)/n(U)$	0.00001115	0.00000016
$n(^{238}U)/n(U)$	96.69113	0.00051
IRMM-024/IRMM-2024		
$n(^{234}U)/n(U)$	0.027584	0.000013
$n(^{235}U)/n(U)$	5.0523	0.0014
$n(^{236}U)/n(U)$	0.049045	0.000012
$n(^{238}U)/n(U)$	94.8711	0.0014
IRMM-025/IRMM-2025		
$n(^{234}U)/n(U)$	0.0119968	0.0000088
$n(^{235}U)/n(U)$	2.00210	0.00053
$n(^{236}U)/n(U)$	0.0145375	0.0000081
$n(^{238}U)/n(U)$	97.97136	0.00053
IRMM-026/IRMM-2026		
$n(^{234}U)/n(U)$	0.014562	0.000010
$n(^{235}U)/n(U)$	2.50275	0.00071

$n(^{236}U)/n(U)$ $n(^{238}U)/n(U)$	0.020204 97.46249	0.000011 0.00071
IRMM-027/IRMM-2027 $n(^{234}U)/n(U)$ $n(^{235}U)/n(U)$ $n(^{236}U)/n(U)$ $n(^{238}U)/n(U)$	 0.022218 4.0023 0.037166 95.9383	 0.000012 0.0011 0.000011 0.0011
IRMM-028/IRMM-2028 $n(^{234}U)/n(U)$ $n(^{235}U)/n(U)$ $n(^{236}U)/n(U)$ $n(^{238}U)/n(U)$	 0.058503 3.6014 0.49783 95.8423	 0.000026 0.0011 0.00011 0.0011
IRMM-029/IRMM-2029 $n(^{234}U)/n(U)$ $n(^{235}U)/n(U)$ $n(^{236}U)/n(U)$ $n(^{238}U)/n(U)$	 0.080007 4.1737 1.00017 94.7461	 0.000035 0.0012 0.00021 0.0012

1) These values are derived from the certified isotope amount ratios (given in previous table) and are therefore traceable to the SI.

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

	Isotope mass fraction (x 100)	
	Certified values 1)2) [g/g]	Uncertainty 3) [g/g]
IRMM-019/IRMM-2019 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0006719 0.165349 0.0036154 99.830364	 0.0000031 0.000047 0.0000085 0.000048
IRMM-020/IRMM-2020 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0011695 0.206435 0.028307 99.764088	 0.0000050 0.000059 0.000011 0.000060
IRMM-021/IRMM-2021 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0024321 0.433062 0.000002623 99.564503	 0.0000075 0.000070 0.000000077 0.000070

IRMM-022/IRMM-2022 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0052003 0.71132 0.00002377 99.28346	 0.0000083 0.00011 0.00000025 0.00011
IRMM-023/IRMM-2023 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.032288 3.23601 0.00001106 96.73169	 0.000010 0.00050 0.00000016 0.00050
IRMM-024/IRMM-2024 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.027137 4.9917 0.048663 94.9325	 0.000013 0.0014 0.000012 0.0014
IRMM-025/IRMM-2025 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0117977 1.97732 0.0144188 97.99646	 0.0000086 0.00052 0.0000081 0.00052
IRMM-026/IRMM-2026 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.0143212 2.47193 0.020040 97.49371	 0.0000098 0.00070 0.000011 0.00070
IRMM-027/IRMM-2027 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.021855 3.9538 0.036871 95.9875	 0.000012 0.0011 0.000011 0.0011
IRMM-028/IRMM-2028 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.057546 3.5577 0.49389 95.8909	 0.000025 0.0011 0.00010 0.0011
IRMM-029/IRMM-2029 $m(^{234}U)/m(U)$ $m(^{235}U)/m(U)$ $m(^{236}U)/m(U)$ $m(^{238}U)/m(U)$	 0.078709 4.1236 0.99237 94.8054	 0.000034 0.0012 0.00021 0.0012

1) These values are calculated using the isotope amount ratios and they are therefore traceable to the SI.

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

M(^{234}U) = 234.0409504 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{235}U) = 235.0439282 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{236}U) = 236.0455662 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{238}U) = 238.0507870 ± 0.0000032 g·mol^{-1} (k = 2)

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

	Uranium molar mass	
	Certified values [1)2)] [g/mol]	Uncertainty [3)] [g/mol]
IRMM-019/IRMM-2019 M(U)	238.0456512	0.0000035
IRMM-020/IRMM-2020 M(U)	238.0438804	0.0000037
IRMM-021/IRMM-2021 M(U)	238.0375003	0.0000038
IRMM-022/IRMM-2022 M(U)	238.0289144	0.0000047
IRMM-023/IRMM-2023 M(U)	237.950965	0.000016
IRMM-024/IRMM-2024 M(U)	237.896783	0.000042
IRMM-025/IRMM-2025 M(U)	237.989814	0.000016
IRMM-026/IRMM-2026 M(U)	237.974544	0.000022
IRMM-027/IRMM-2027 M(U)	237.928808	0.000034
IRMM-028/IRMM-2028 M(U)	237.930170	0.000032
IRMM-029/IRMM-2029 M(U)	237.902026	0.000036

1) These values are calculated using the isotope amount ratios and they are therefore traceable to SI.

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

M(^{234}U) = 234.0409504 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{235}U) = 235.0439282 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{236}U) = 236.0455662 ± 0.0000024 g·mol^{-1} (k = 2)
M(^{238}U) = 238.0507870 ± 0.0000032 g·mol^{-1} (k = 2)

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

Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

1 Introduction

1.1 Background

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 safeguards authorities and the nuclear industry.

The IRMM-019-029 series of uranium hexafluoride (UF_6) isotope reference materials was originally certified between 1984 and 1996. 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 $n(^{236}U)/n(^{238}U)$. Since the minor isotope amount 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 it was decided in 2012 to re-characterise the entire IRMM-019-029 series by using a new set of calibrants which had become available since 2009 in the form of gravimetrically prepared uranium nitrate solutions, in combination with recently developed mass spectrometric measurement methods, in particular for Thermal Ionisation Mass Spectrometry (TIMS) [4, 5]. Following this strategy, in 2014 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 this series of re-certified reference materials IRMM-019-029 also available for TIMS and ICP-MS users, a follow-up project was started in 2016. The uranium nitrate solutions remaining from the characterisation of IRMM-019-029 series (UF_6) re-certification by TIMS were used as a set of new uranium nitrate solution reference materials to be certified according to ISO 17034 as the IRMM-2019-2029 series. For this purpose, these remaining solutions were diluted to a concentration of about 2 mg U per g solution and subsequently dispensed in screw-cap quartz ampoules. This concentration level was deemed suitable for TIMS/MTE measurements and solutions can be easily diluted by the users for TIMS/TE or MC-ICP-MS measurements. The processing of the original solutions left from the re-certification of the IRMM-019-029 series to their certification as the IRMM-2019-2029 series was controlled by so-called Process Control Measurements (PCM), performed on three ampoules for each of the eleven IRMM-2019-2029 reference materials. Within the project plan, it was stated that under the condition that the results of the process control measurements on the isotopic composition of the IRMM-2019-2029 series agree with the certified values for the IRMM-019-029 series, the same certified values and uncertainties for IRMM-019-029 series of UF_6 materials will be assigned to the IRMM-2019-2029 series of uranium nitrate solutions.

1.2 Choice of the material

In the 1980's-1990's, the certification measurements of the IRMM-019-029 series were performed by GSMS for the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ using the IRMM-171/031 - IRMM-171/446 series of reference materials as calibrants, and by TIMS for the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The IRMM-019-029 series was re-certified in 2014 using TIMS and a new set of calibrants in uranium nitrate solution form such as the IRMM-074 series and the IRMM-3636a double spike.

The IRMM-019 to IRMM-029 series covers the enrichment range from depleted uranium (IRMM-019 to IRMM-021) via natural uranium (IRMM-022) to low enriched uranium (IRMM-

023 to IRMM-029). The uranium nitrate solutions IRMM-2019-2029 were prepared by diluting and dispensing the remaining uranium nitrate solutions prepared for the certification of the IRMM-019-029 series into cleaned screw-cap ampoules.

1.3 Design of the project

In the frame of the certification of the IRMM-019-029 series of UF_6 reference materials in 2014, the characterisation study was not performed directly on the UF_6 materials themselves but on uranium nitrate solutions prepared from the UF_6 materials by hydrolysis and nitration, and subsequently analysed by TIMS [4, 5]. Both characterisation and homogeneity studies were performed directly on the U nitrate solutions by TIMS, and the certified values for isotopic composition calculated from the 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, the original UF_6 materials and the solutions prepared from them are in agreement regarding their isotopic composition and could be certified with the same values.

Consequently, as the assigned values for the isotopic composition of the IRMM-2019-2029 series (U nitrate solutions) were expected to be the same as the certified values for the IRMM-019-029 series of UF_6 reference materials, it was not necessary to perform any new measurements of the isotopic composition for characterisation, homogeneity or long-term stability for the certification of the uranium nitrate solution reference materials IRMM-2019-2029.

However, in 2014, certificates were only issued for the UF_6 materials IRMM-019-029, and not for the remaining U nitrate solutions. In 2017 and 2018, following the goal of certifying these remaining solutions, they were further processed to make them available for sale as reference materials. The processing steps included a dilution by a factor of about 10 and dispensing into cleaned screw-caps quartz ampoules. These processing steps (dilution and dispensing) are not expected to cause any change in the isotopic composition of the materials, therefore new certification measurements were not deemed necessary. However to guarantee the integrity of the assigned values through the process, process control measurements were performed on three ampoules for each of the eleven IRMM-2019-2029 series solutions.

The process control measurements of IRMM-2019 to IRMM-2029 were performed by TIMS (Triton, Thermo Fischer, Bremen, Germany) using the Modified Total Evaporation method (MTE) 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, and was standardized in 2015 by ASTM-International as C1832-16 [9]. Additionally for some materials such as IRMM-2021, IRMM-2022 and IRMM-2023 with low ^{236}U abundance, the major isotope amount ratios were measured using the double spike (DS) 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 method allows an internal mass fractionation correction and therefore leads to lower measurement uncertainties [10, 11]. The DS method was standardized by ASTM-International as C1871-18 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 was confirmed with the DS method at an accuracy level of better than 0.002% [10, 12, 13] by 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 quality control (QC) purposes, solutions of the IRMM-075 series were measured by TIMS within the same sequences (on the same sample turrets) as the IRMM-2019-2029 samples. The IRMM-075 series 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 relative 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 $n(^{236}U)/n(^{238}U)$ isotope amount ratios of the IRMM-2019-2029 series, covering a wide dynamic range and using 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 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 methods like MTE and DS 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 116-A [16] certified by New Brunswick Laboratory (U.S. DOE), verification measurements were performed at JRC-G.2 using the MTE method [17 and 18, respectively]. Furthermore, the re-certified $n(^{235}U)/n(^{238})$ ratio of the natural uranium certified reference material NBL CRM 112-A [19] was verified using the double spike (DS) method at JRC-G.2 and several other laboratories [11, 12].

2 Participants

Project management, evaluation and processing, were performed by 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". The Unit JRC-G.2 participates regularly in several uranium interlaboratory comparisons on uranium oxides and UF_6 materials, which are organised by the French "Commissariat à l'Energie Atomique et aux Energies Alternatives" (CEA) / "Commission d'ETablissement des Méthodes d'Analyses" (CETAMA), the US "Department of Energy (DOE) / New Brunswick Laboratory Program Office (NBL-PO)" and the International Atomic Energy Agency (IAEA).

3 Material processing and process control

3.1 Origin of the starting material

For the certification of the isotopic composition in the uranium nitrate solution reference material IRMM-2019-2029 series, the remaining uranium nitrate solutions prepared for the certification of the IRMM-019 to IRMM-029 series of UF_6 materials in 2014 [4, 5] were used as starting materials.

3.2 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. Since the material was 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 in a first step, 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 Isotope Dilution Mass Spectrometry (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 final 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. Although the new reference materials are only certified for their isotopic composition, it was deemed necessary to provide a reliable value of the uranium concentration for the customer.

From the 1L quartz flasks, the solutions were directly transferred into new screw-cap quartz ampoules. These ampoules were pre-cleaned using a procedure involving HNO_3 and de-ionized H_2O. 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 on HNO_3 solutions after a storage time of two years on five screw-cap quartz ampoules were performed by TIMS/IDMS using the low level ^{233}U spike IRMM-058. These measurement results showed negligible uranium amounts, and therefore any uranium contamination of the solutions can be ruled out.

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 in a vacuum chamber. After pumping at a pressure of about 10^{-6} mbar, no leakage from the tightly closed ampoules under vacuum was observed.

After the dispensing, each ampoule contained about 5 mL of uranium nitrate solution in 1M HNO_3. The indicative concentration value of 2 mg U /g solution is mentioned within the accompanying text in the certificates, but the solution reference materials are not considered suitable as spikes for IDMS, they are only certified for the isotopic composition. Table 1 below shows the reference material IDs/names, batch numbers, ^{235}U enrichments and the number of dispensed ampoules for the IRMM-2019-2029 series. The Figure 1 shows a set of photos taken during the dispensing actions.

Table 1: Inventory of the U nitrate solutions IRMM-2019-2029 series (available in 5 mL 1M HNO_3 screw-cap quartz ampoules).

Name of CRM	Batch Number (BC)	$n(^{235}U)/n(U)$, [%]	Number of Ampoules
IRMM-2019	00369D	0.17	80
IRMM-2020	01281C	0.21	80
IRMM-2021	00409C	0.44	71
IRMM-2022	00410C	0.72	115
IRMM-2023	00399D	3.27	115
IRMM-2024	00441E	5.05	102
IRMM-2025	01891C	2.00	89
IRMM-2026	01892C	2.50	62
IRMM-2027	01893C	4.00	93
IRMM-2028	02086C	3.60	58
IRMM-2029	02087C	4.17	68

Figure 1: Photos of the 1L quartz flasks, dispensers and screw-cap ampoules used during the processing of the IRMM-2019-2029 series.

3.3 Process control

Process control measurements were performed by TIMS using the same methods as for the certification of the UF_6 materials IRMM-019-029 series in 2012-2014 [4, 5]. For all eleven IRMM-2019-2029 materials, TIMS measurements using the MTE method were performed for the major ratios $n(^{235}U)/n(^{238}U)$ and the minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$, combined within the same sequences with QC measurements of IRMM-075/1 ($n(^{236}U)/n(^{238}U) \cong 10^{-4}$) and IRMM-075/5 ($n(^{236}U)/n(^{238}U) \cong 10^{-8}$). The uncertainties were in most cases at the same level as for the certification measurements of the IRMM-019-029 series in 2014 [4, 5] and described in detail in the publication [8] and the ASTM C1832-16 standard document for the MTE method [9].

In addition, for the major ratios $n(^{235}U)/n(^{238}U)$ for IRMM-2021, IRMM-2022 and IRMM-2023, TIMS measurements using the DS method (and the IRMM-3636a double spike) were performed within the same sequence as the QC sample IRMM-184. The uncertainties were at the same level as for the certification measurements of the IRMM-019-029 series in 2014

[4, 5] and described in the publications [10, 11] and the ASTM C1871a-18 standard document for the double spike (DS) method [12].

No significant differences were found between the measurements results for all the ratios from the three ampoules of each solution. Therefore these results were subsequently combined and only the averages evaluated and presented below. During all the process control measurements, no significant deviations from the certified ratios of IRMM-019-029 were found, as shown below in Figures 2-5 and Annex 1. 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. In the case of IRMM-2021, the uncertainty of the minor ratio $n(^{236}U)/n(^{238}U)$ was about three times higher compared to the certification measurements of IRMM-021 performed in 2014 [4, 5]. This is due to the higher number of replicate measurements at that time, which has a significant influence in cases where the uncertainty is dominated by counting statistics. 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.

Moreover, measurements of several external reference materials, covering a wide range of isotope ratios and ^{235}U enrichments from 0.2 %-90 %, showed no significant deviations from their certified values (see Figures 6-8). This serves as an additional confirmation for the reliability of the applied TIMS/MTE and TIMS/DS methods.

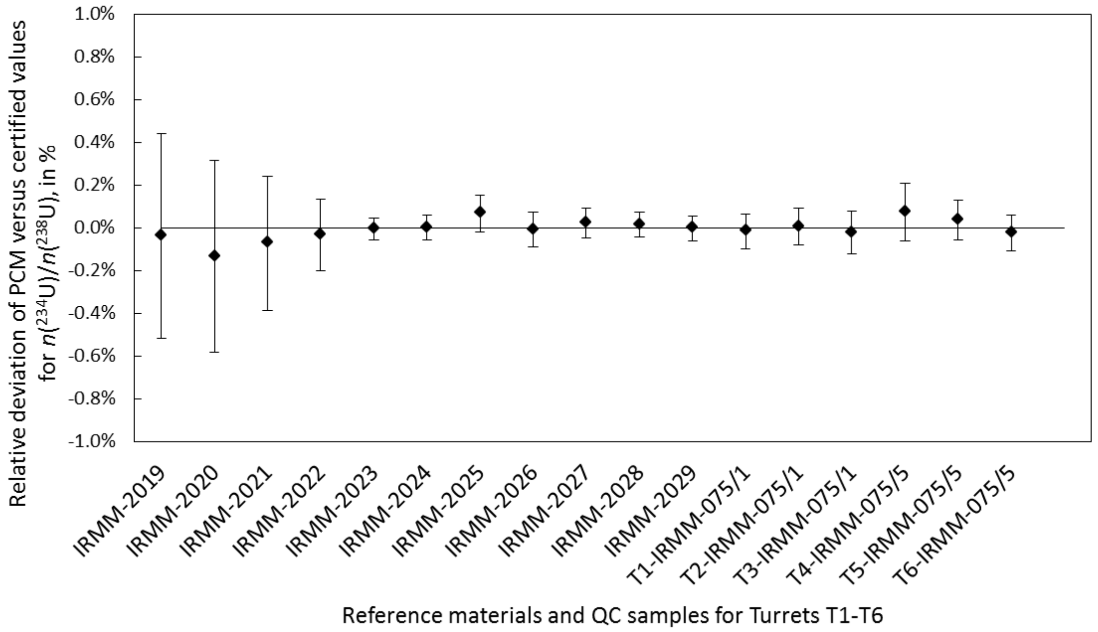

Figure 2: Process control measurements for $n(^{234}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 and IRMM-075/5 for MTE sequences (turrets) T1-T6. Expanded uncertainties are presented with a coverage factor k = 2.

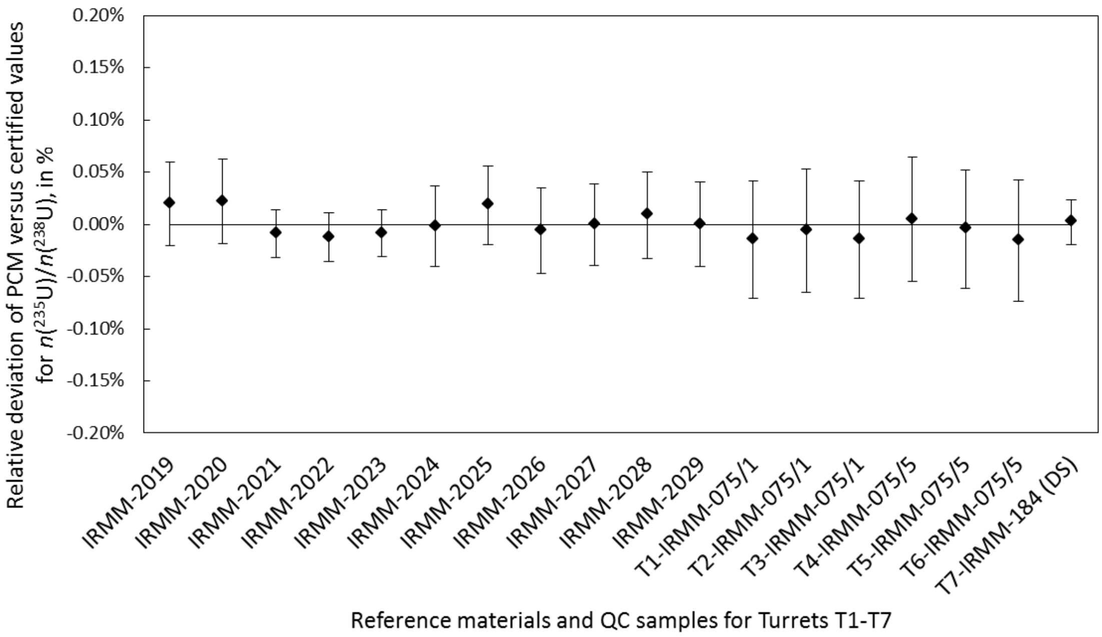

Figure 3: Process control measurements for $n(^{235}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 and IRMM-075/5 for MTE sequences (turrets) T1-T6, in addition IRMM-184 as QC sample for the DS method for sequence (turret) T7. Expanded uncertainties are presented with a coverage factor k = 2.

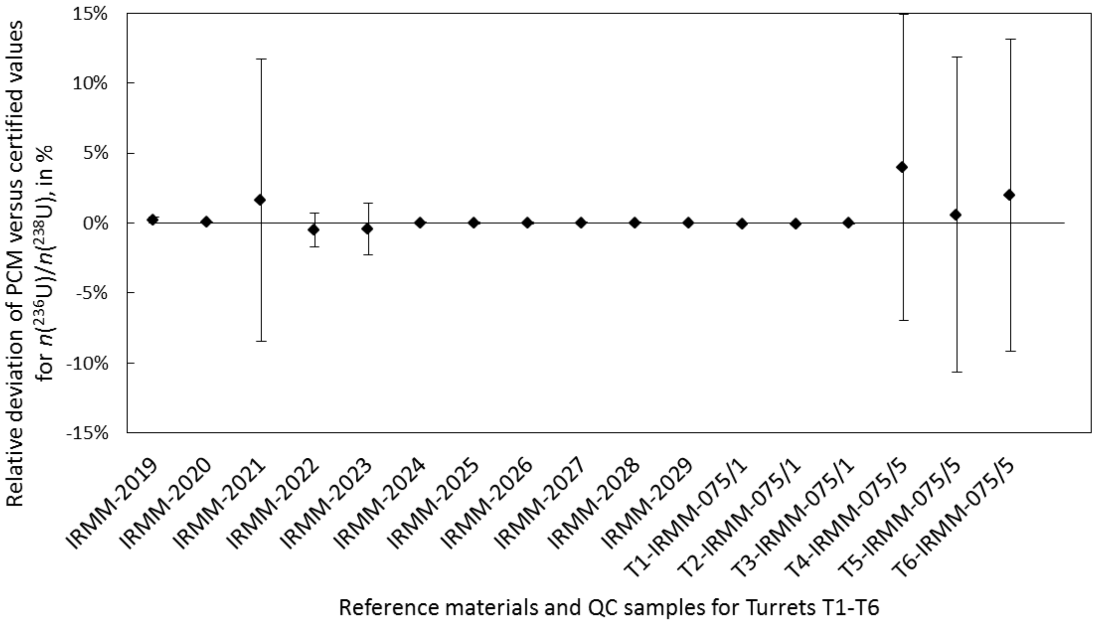

Figure 4: Process control measurements for $n(^{236}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 (with $n(^{236}U)/n(^{238}U) \cong 10^{-4}$) and IRMM-075/5 (with $n(^{236}U)/n(^{238}U) \cong 10^{-8}$) for MTE sequences (turrets) T1-T6, within a ±15 % range on the ordinate.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

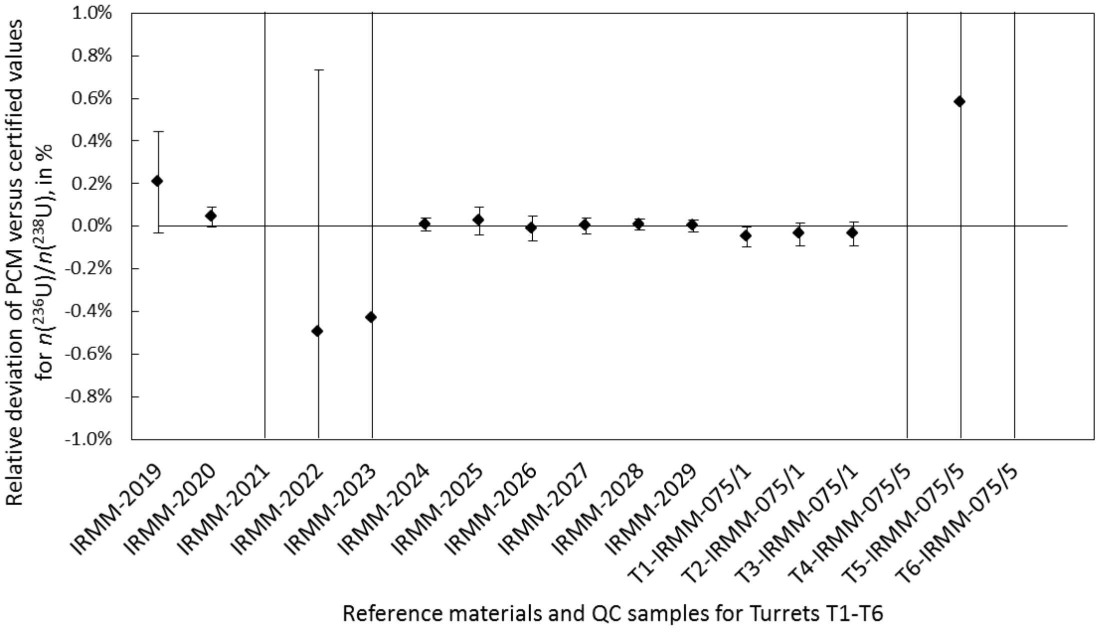

Figure 5: Process control measurements for $n(^{236}U)/n(^{238}U)$ for the IRMM-2019-2029 series, including QC samples IRMM-075/1 (with $n(^{236}U)/n(^{238}U) \cong 10^{-4}$) and IRMM-075/5 (with $n(^{236}U)/n(^{238}U) \cong 10^{-8}$) for MTE sequences (turrets) T1-T6, within a ±1 % range on the ordinate.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

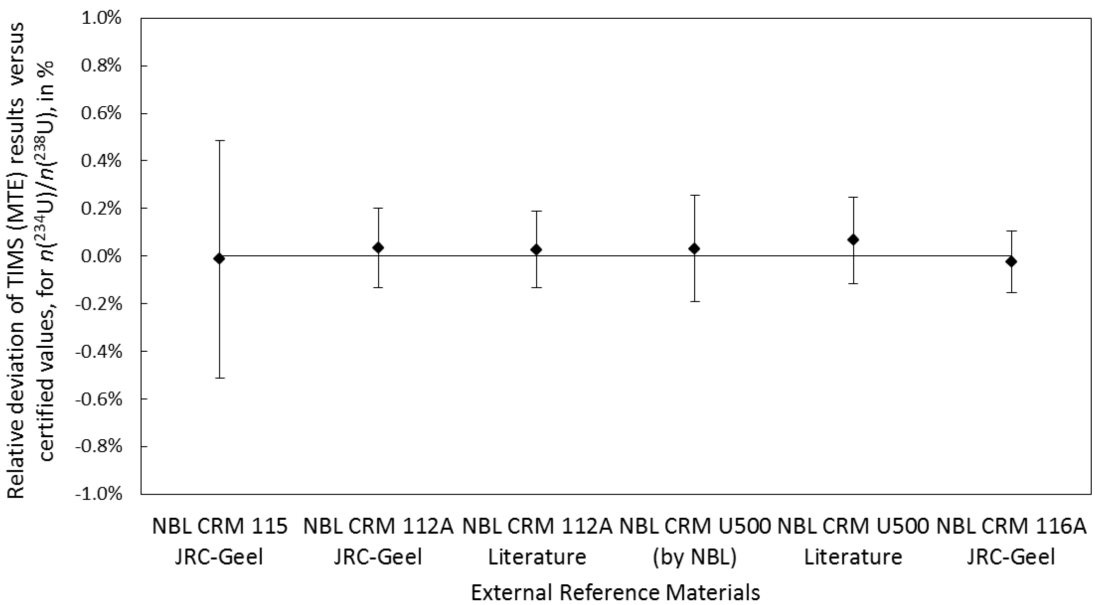

Figure 6: Measurement results from JRC-G.2 using the TIMS/MTE method for $n(^{234}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CRM 112-A (close to natural U), NBL CRM U500 (50 % enriched in ^{235}U) and NBL CRM 116-A (90 % enriched in ^{235}U). In addition results from the literature [7, 11, 20] are shown for comparison. Expanded uncertainties are presented with a coverage factor $k = 2$.

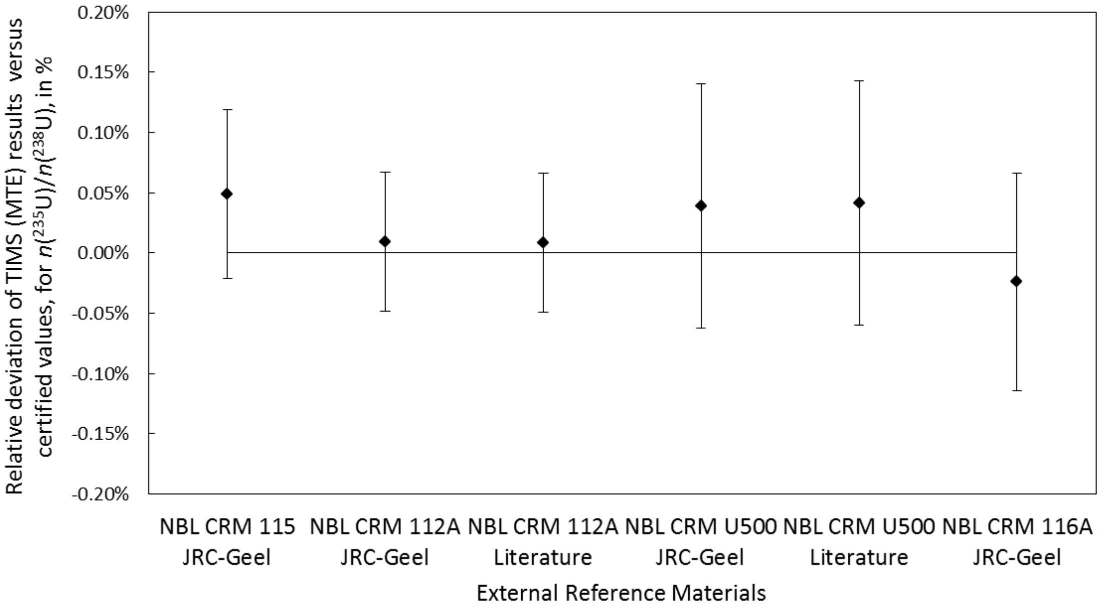

Figure 7: Measurement results from JRC-G2 using the TIMS/MTE method for $n(^{235}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CR112-A (close to natural U, measured using DS method), NBL CRM U500 (50 % enriched in ^{235}U) and NBL CRM 116-A (90 % enriched in ^{235}U). In addition results from the literature [11, 20, 21] are shown for comparison. Expanded uncertainties are presented with a coverage factor k = 2.

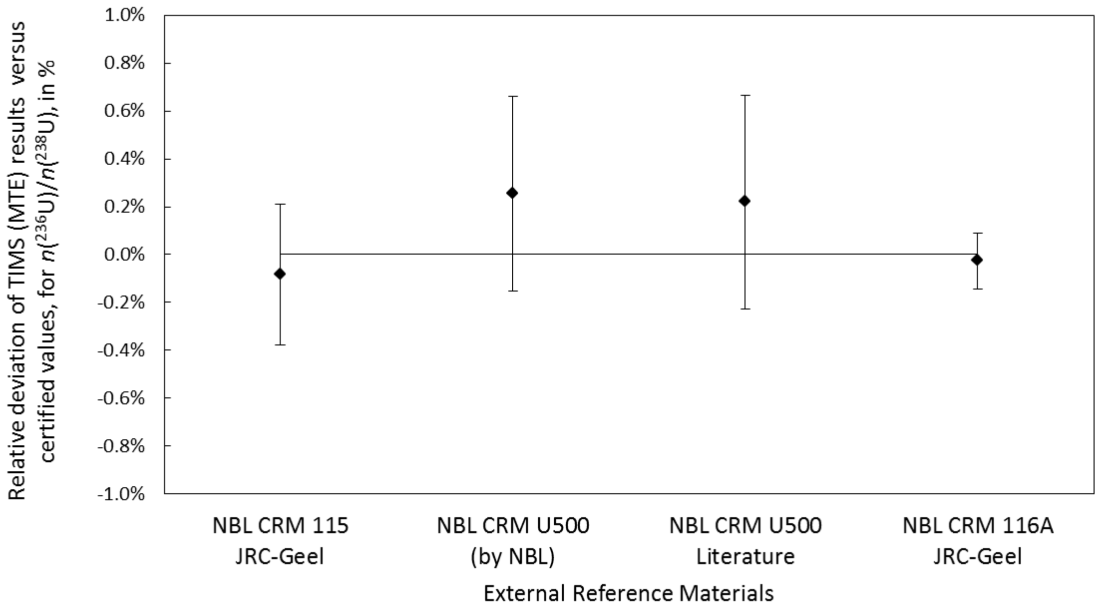

Figure 8: Measurement results from JRC-G.2 using the TIMS/MTE method for $n(^{236}U)/n(^{238}U)$ for external reference materials NBL CRM 115 (depleted in ^{235}U), NBL CRM U500 (50 % enriched in ^{235}U) and NBL CRM 116-A (90 % enriched in ^{235}U). In addition results from the literature [7, 20] are shown for comparison. Note that the $n(^{236}U)/n(^{238}U)$ ratio for NBL CR112-A (close to natural U) is below the detection limit of 6×10^{-10} [8] for the MTE method. Expanded uncertainties are presented with a coverage factor k = 2.

4 Stability

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability).

4.1 Short-term stability study

The IRMM-2019 to IRMM-2029 series consists of uranium nitrate solution isotope reference materials in 1M HNO_3 contained in tightly closed screw-cap quartz ampoules. Since the isotopic composition is independent of the temperature, there is no impact from transportation on the uranium isotopic composition. Therefore no short term stability study was performed and the materials can be dispatched without further precautions under ambient conditions.

4.2 Long-term stability study

In 2014, the long-term study was carried out for the IRMM-019-029 series of UF_6 materials in two complimentary steps using historical data for IRMM-023 materials stored at room temperature:

1. In 2009, measurements were 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 data summary showed that the certified major isotope amount ratio $n(^{235}U)/n(^{238}U)$ did not change significantly between 2009 and 2013 (the time when IRMM-023 was analysed), covering a period of four years. However, since these measurements were not performed on regular basis, they were not considered appropriate to be used for the long-term stability study in 2014. But in the meantime, in 2016 [13] as well as in 2018 for the process control measurements within this project, additional measurements were performed on the solutions of IRMM-023/-2023 by TIMS using the double spike technique.

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

For step 1, all data for IRMM-023 and IRMM-2023 measured between 2009 and 2018 by TIMS using the double spike method (DS) can be combined, as shown in Figure 9.

No outliers are observed at the 99 % confidence level and the slope is 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. This can be used as a justification for a validity time of 10 years starting from 2018 for the IRMM-2019-2029 solution reference materials. This is the same validity time as previously assigned to the UF_6 materials in 2014 based on the long-term stability study according to step 2 [4, 5].

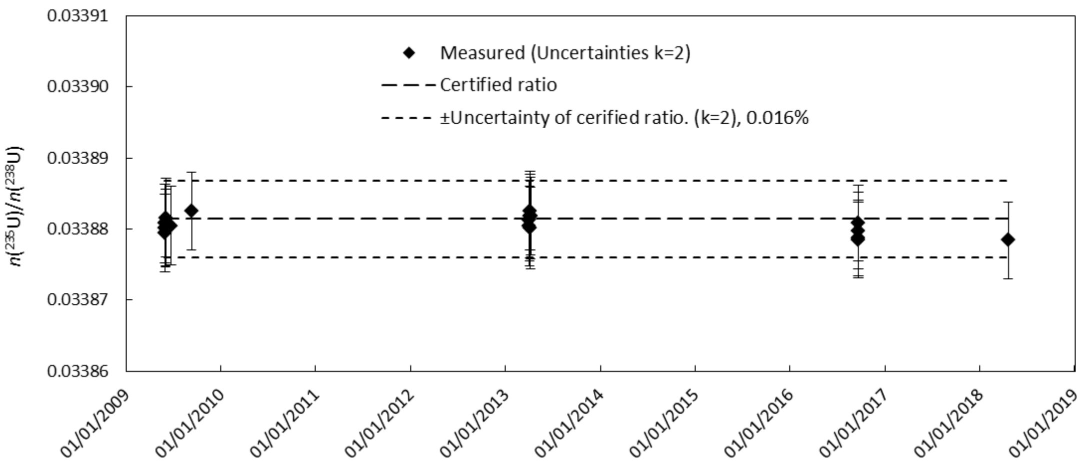

Figure 9: TIMS-DS measurements (19 measurement results) for the $n(^{235}U)/n(^{238}U)$ ratio on IRMM-023/-2023 performed between 2009 and 2018. Expanded uncertainties are given with a coverage factor of k = 2.

5 Value assignment

Following the conclusions from the process control measurements, the certified values and the uncertainties of the solution reference material series IRMM-2019-2029 materials have been assigned using the certified values for the IRMM-019-029 series of UF_6 materials, but re-calculated using the new AME 2016 values for molar masses [22] and applying the 2-digit rounding rule.

6 Metrological traceability

6.1 Metrological traceability

The certified values for IRMM-2021, IRMM-2022 and IRMM-2023 are traceable to the International System of units (SI) via the values on the certificate of the gravimetrically prepared IRMM-3636a. All the other materials are traceable to the SI via the values on the certificate of the gravimetrically prepared IRMM-074/10. In addition, the certified $n(^{235}U)/n(^{238}U)$ isotope ratio of IRMM-074/10 is also confirmed by DS measurements using the certified $n(^{233}U)/n(^{236}U)$ isotope ratio of IRMM-3636a [10, 12, 13], which effectively provides a link between these two gravimetrically prepared calibrants.

6.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific analytes or specific groups of analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CLSI Guideline C-53A [23] recommends the use of the following definition for the term commutability:

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

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

The IRMM-2019 to IRMM-2029 series is a set of uranium nitrate solution reference materials certified for uranium isotope amount ratios, isotope amount fraction, isotope mass fraction and uranium molar mass. These reference materials are tailor-made by JRC and are intended to serve as calibrants for isotope mass spectrometry measurements.

The agreement of results obtained for reference materials prepared by other providers than JRC ("external reference materials") using the same analytical methods, as presented in Figures 6-8 within section 3.3., is a good indication for the commutability of the IRMM-2019 to IRMM-2029 series of reference materials.

7 Instructions for use

7.1 Safety information

The IRMM-2019-IRMM-2029 series contains radioactive material stored in 5 mL 1M HNO_3 in screw-cap quartz ampoules. The ampoules should be handled with great care and by experienced personnel in a laboratory suitably equipped for the safe handling of radioactive materials.

7.2 Storage conditions

The materials shall be stored at room temperature.

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

7.3 Preparation and use of the material

This series of reference materials is for use as calibrant for isotope mass spectrometry measurements.

7.4 Use of the certified values

The main purpose of these materials is to be used as calibrant for isotope mass spectrometry techniques such as TIMS and ICP-MS. As any reference material, they can also be used for assessing the method performance (checking accuracy of analytical results/calibration), for quality control purpose or validation studies.

<u>Use as a calibrant</u>

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

<u>Comparing an analytical result with the certified value</u>

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result.

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

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

Use for quality control purposes

The certified values can be used for quality control charts. Different CRM-units will give the same result, because the results of the homogeneity testing was included in the uncertainties of the certified values.

8 Revision of the IRMM-019-029 series of uranium hexafluoride (UF_6) reference materials

In 2014, the isotopic composition of the IRMM-019-029 series of 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 it was realised that for isotope mass spectrometry in the nuclear field, the 2-digit rounding rule is usually preferred.

In addition, since the certification of the IRMM-019-029 series in 2014, a new set of molar masses (AME 2016, [22]) has been published.

Therefore, as it was done for the certified values of the IRMM-2019-2029 series, the certified values and the uncertainties of the IRMM-019-029 series materials have been modified using the 2-digit rounding rule and the certified values and the uncertainties for the isotope mass fractions and molar masses were 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 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.

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10 Abbreviations and Definitions used within this Report

ASTM	American Society for Testing and Materials (nowadays called ASTM-International)
CEA	Commissariat à l'Energie Atomique et aux Energies Alternatives, France
CETAMA	Commission d'établissement des méthodes d'analyses
CRM	Certified reference material
DOE	United States "Department of Energy"
DS	Double spike
EC	European Commission
EU	European Union
GSMS	Gas Source Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IRMM	Institute for Reference Materials and Measurements of the JRC (since 1st July, 2017 the nuclear part is represented by Unit G.2. within Directorate G of the JRC)
IAEA	International Atomic Energy Agency
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
MC-ICP-MS	Multi-Collector Inductively Coupled Plasma Mass Spectrometry
MTE	Modified Total Evaporation
PCM	Process Control Measurements
QC	Quality Control
SEM	Secondary Electron Multiplier
SI	International System of units
TIMS	Thermal Ionisation Mass Spectrometry

11 Annex-1: Results of Process Control Measurements

IRMM-2019, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.00167782	0.000006852	0.000036599
Uncertainty u (k=1)	0.00000024	0.000000006	0.000000009
Uncertainty U (k=2)	0.00000048	0.000000011	0.000000018
Rel. uncertainty (k=2)	0.029%	0.166%	0.049%
Certified value	0.00167749	0.000006846	0.000036523
Uncertainty k=2	0.00000048	0.000000031	0.000000085
Rel. uncertainty (k=2)	0.029%	0.453%	0.233%
Rel. diff. meas./cert.	0.020%	0.092%	0.21%
Unc. of rel. diff. (k=2)	0.041%	0.483%	0.24%

IRMM-2020, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.00209617	0.000011907	0.000286276
Uncertainty u (k=1)	0.00000030	0.000000008	0.000000037
Uncertainty U (k=2)	0.00000060	0.000000017	0.000000073
Rel. uncertainty (k=2)	0.028%	0.143%	0.026%
Certified value	0.00209571	0.000011923	0.00028615
Uncertainty k=2	0.00000060	0.000000051	0.00000011
Rel. uncertainty (k=2)	0.029%	0.428%	0.038%
Rel. diff. meas./cert.	0.022%	-0.136%	0.044%
Unc. of rel. diff. (k=2)	0.040%	0.450%	0.046%

IRMM-2021, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0044047	0.000024828	0.0000000270
Uncertainty u (k=1)	0.0000006	0.000000009	0.0000000013
Uncertainty U (k=2)	0.0000013	0.000000018	0.0000000026
Rel. uncertainty (k=2)	0.029%	0.074%	9.79%
Certified value	0.00440521	0.000024846	0.00000002657
Uncertainty k=2	0.00000071	0.000000076	0.00000000078
Rel. uncertainty (k=2)	0.016%	0.306%	2.936%
Rel. diff. meas./cert.	-0.011%	-0.073%	1.7%
Unc. of rel. diff. (k=2)	0.033%	0.314%	10.4%

IRMM-2022, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072558	0.000053257	0.0000002403
Uncertainty u (k=1)	0.0000011	0.000000013	0.0000000008
Uncertainty U (k=2)	0.0000023	0.000000027	0.0000000016
Rel. uncertainty (k=2)	0.032%	0.050%	0.648%
Certified value	0.0072562	0.000053275	0.0000002415
Uncertainty k=2	0.0000012	0.000000085	0.0000000025
Rel. uncertainty (k=2)	0.017%	0.160%	1.035%
Rel. diff. meas./cert.	-0.005%	-0.035%	-0.48%
Unc. of rel. diff. (k=2)	0.036%	0.167%	1.22%

IRMM-2023, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0338810	0.00033948	0.0000001148
Uncertainty u (k=1)	0.0000049	0.00000007	0.0000000007
Uncertainty U (k=2)	0.0000098	0.00000013	0.0000000013
Rel. uncertainty (k=2)	0.029%	0.039%	1.153%
Certified value	0.0338814	0.00033950	0.0000001153
Uncertainty k=2	0.0000054	0.00000011	0.0000000017
Rel. uncertainty (k=2)	0.016%	0.032%	1.474%
Rel. diff. meas./cert.	-0.001%	-0.007%	-0.47%
Unc. of rel. diff. (k=2)	0.033%	0.050%	1.86%

IRMM-2024, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.053253	0.00029075	0.000517000
Uncertainty u (k=1)	0.000007	0.00000005	0.000000047
Uncertainty U (k=2)	0.000014	0.00000010	0.000000094
Rel. uncertainty (k=2)	0.026%	0.035%	0.018%
Certified value	0.053254	0.00029075	0.00051696
Uncertainty k=2	0.000015	0.00000014	0.00000013
Rel. uncertainty (k=2)	0.028%	0.048%	0.025%
Rel. diff. meas./cert.	-0.002%	0.001%	0.008%
Unc. of rel. diff. (k=2)	0.038%	0.060%	0.031%

IRMM-2025, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0204394	0.000122535	0.000148423
Uncertainty u (k=1)	0.0000027	0.000000027	0.000000023
Uncertainty U (k=2)	0.0000054	0.000000055	0.000000046
Rel. uncertainty (k=2)	0.026%	0.045%	0.031%
Certified value	0.0204356	0.000122452	0.000148386
Uncertainty k=2	0.0000055	0.000000090	0.000000083
Rel. uncertainty (k=2)	0.027%	0.073%	0.056%
Rel. diff. meas./cert.	0.019%	0.068%	0.025%
Unc. of rel. diff. (k=2)	0.038%	0.086%	0.064%

IRMM-2026, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0256775	0.000149397	0.000207278
Uncertainty u (k=1)	0.0000037	0.000000035	0.000000026
Uncertainty U (k=2)	0.0000074	0.000000070	0.000000052
Rel. uncertainty (k=2)	0.029%	0.047%	0.025%
Certified value	0.0256791	0.00014941	0.00020730
Uncertainty k=2	0.0000075	0.00000010	0.00000011
Rel. uncertainty (k=2)	0.029%	0.067%	0.053%
Rel. diff. meas./cert.	-0.006%	-0.009%	-0.011%
Unc. of rel. diff. (k=2)	0.041%	0.082%	0.059%

IRMM-2027, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.041717	0.000231642	0.000387396
Uncertainty u (k=1)	0.000006	0.000000047	0.000000042
Uncertainty U (k=2)	0.000011	0.000000094	0.000000084
Rel. uncertainty (k=2)	0.027%	0.041%	0.022%
Certified value	0.041717	0.00023159	0.00038739
Uncertainty k=2	0.000012	0.00000013	0.00000011
Rel. uncertainty (k=2)	0.031%	0.056%	0.028%
Rel. diff. meas./cert.	0.000%	0.022%	0.001%
Unc. of rel. diff. (k=2)	0.041%	0.069%	0.036%

IRMM-2028, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0375794	0.00061050	0.00519471
Uncertainty u (k=1)	0.0000050	0.00000011	0.00000046
Uncertainty U (k=2)	0.0000099	0.00000022	0.00000092
Rel. uncertainty (k=2)	0.026%	0.035%	0.018%
Certified value	0.037576	0.00061041	0.0051943
Uncertainty k=2	0.000012	0.00000027	0.0000011
Rel. uncertainty (k=2)	0.032%	0.044%	0.021%
Rel. diff. meas./cert.	0.009%	0.014%	0.008%
Unc. of rel. diff. (k=2)	0.041%	0.057%	0.028%

IRMM-2029, MTE

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.044052	0.00084441	0.0105563
Uncertainty u (k=1)	0.000006	0.00000015	0.0000009
Uncertainty U (k=2)	0.000012	0.00000030	0.0000019
Rel. uncertainty (k=2)	0.027%	0.036%	0.018%
Certified value	0.044052	0.00084444	0.0105563
Uncertainty k=2	0.000013	0.00000037	0.0000022
Rel. uncertainty (k=2)	0.030%	0.044%	0.021%
Rel. diff. meas./cert.	0.001%	-0.004%	0.000%
Unc. of rel. diff. (k=2)	0.040%	0.057%	0.027%

IRMM-075-1, MTE (Turret 1)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072593	0.000053268	0.000104388
Uncertainty u (k=1)	0.0000009	0.000000013	0.000000016
Uncertainty U (k=2)	0.0000019	0.000000025	0.000000031
Rel. uncertainty (k=2)	0.025%	0.047%	0.030%
Certified value	0.0072603	0.000053277	0.000104438
Uncertainty k=2	0.0000036	0.000000034	0.000000037
Rel. uncertainty (k=2)	0.050%	0.065%	0.035%
Rel. diff. meas./cert.	-0.014%	-0.017%	-0.048%
Unc. of rel. diff. (k=2)	0.056%	0.080%	0.046%

IRMM-075-1, MTE (Turret 2)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072599	0.000053280	0.000104398
Uncertainty u (k=1)	0.0000011	0.000000015	0.000000020
Uncertainty U (k=2)	0.0000023	0.000000030	0.000000039
Rel. uncertainty (k=2)	0.031%	0.057%	0.038%
Certified value	0.0072603	0.000053277	0.000104438
Uncertainty k=2	0.0000036	0.000000034	0.000000037
Rel. uncertainty (k=2)	0.050%	0.065%	0.035%
Rel. diff. meas./cert.	-0.006%	0.005%	-0.038%
Unc. of rel. diff. (k=2)	0.059%	0.086%	0.052%

IRMM-075-1, MTE (Turret 3)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072593	0.000053264	0.000104400
Uncertainty u (k=1)	0.0000009	0.000000020	0.000000023
Uncertainty U (k=2)	0.0000019	0.000000041	0.000000046
Rel. uncertainty (k=2)	0.026%	0.076%	0.044%
Certified value	0.0072603	0.000053277	0.000104438
Uncertainty k=2	0.0000036	0.000000034	0.000000037
Rel. uncertainty (k=2)	0.050%	0.065%	0.035%
Rel. diff. meas./cert.	-0.014%	-0.024%	-0.036%
Unc. of rel. diff. (k=2)	0.056%	0.100%	0.056%

IRMM-075-5, MTE (Turret 4)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072606	0.000053316	0.00000001108
Uncertainty u (k=1)	0.0000012	0.000000031	0.00000000061
Uncertainty U (k=2)	0.0000024	0.000000062	0.00000000121
Rel. uncertainty (k=2)	0.033%	0.116%	10.9%
Certified value	0.0072603	0.000053277	0.000000011
Uncertainty k=2	0.0000036	0.000000034	0.000000000
Rel. uncertainty (k=2)	0.050%	0.065%	0.070%
Rel. diff. meas./cert.	0.005%	0.073%	4.0%
Unc. of rel. diff. (k=2)	0.060%	0.133%	11.4%

IRMM-075-5, MTE (Turret 5)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072600	0.000053296	0.00000001071
Uncertainty u (k=1)	0.0000010	0.000000018	0.00000000060
Uncertainty U (k=2)	0.0000019	0.000000036	0.00000000120
Rel. uncertainty (k=2)	0.026%	0.067%	11.2%
Certified value	0.0072603	0.000053277	0.000000011
Uncertainty k=2	0.0000036	0.000000034	0.000000000
Rel. uncertainty (k=2)	0.050%	0.065%	0.070%
Rel. diff. meas./cert.	-0.004%	0.036%	0.58%
Unc. of rel. diff. (k=2)	0.057%	0.093%	11.31%

IRMM-075-5, MTE (Turret 6)

	$n(^{235}U)/n(^{238}U)$	$n(^{234}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Measurement Result	0.0072592	0.000053264	0.0000000109
Uncertainty u (k=1)	0.0000011	0.000000014	0.0000000006
Uncertainty U (k=2)	0.0000022	0.000000028	0.0000000012
Rel. uncertainty (k=2)	0.030%	0.053%	11.177%
Certified value	0.0072603	0.000053277	0.000000011
Uncertainty k=2	0.0000036	0.000000034	0.000000000
Rel. uncertainty (k=2)	0.050%	0.065%	0.070%
Rel. diff. meas./cert.	-0.016%	-0.024%	2.0%
Unc. of rel. diff. (k=2)	0.058%	0.083%	11.4%

IRMM-2021 using TIMS/DS method:

	$n(^{235}U)/n(^{238}U)$
Average	0.00440483
SD	0.00000024
RSD	0.0054%
RSE	0.0024%
Uncertainty, k=2	0.00000072
Rel Uncertainty, k=2	0.016%
Certified Value	0.00440521
Uncertainty, k=2	0.00000071
Rel. Dev.	-0.009%
Uncertainty, k=2	0.023%

IRMM-2022 using TIMS/DS method:

	$n(^{235}U)/n(^{238}U)$
Average	0.00725531
SD	0.00000026
RSD	0.0036%
RSE	0.0016%
Uncertainty, k=2	0.000001
Rel Uncertainty, k=2	0.016%
Certified Value	0.0072562
Uncertainty, k=2	0.0000012
Rel. Dev.	-0.012%
Uncertainty, k=2	0.023%

IRMM-2023 using TIMS/DS method:

	$n(^{235}U)/n(^{238}U)$
Average	0.03387839
SD	0.00000062
RSD	0.0018%
RSE	0.0007%
Uncertainty, k=2	0.0000053
Rel Uncertainty, k=2	0.016%
Certified Value	0.0338814
Uncertainty, k=2	0.0000054
Rel. Dev.	-0.009%
Uncertainty, k=2	0.022%

<u>IRMM-074 (QC sample) using TIMS/DS method:</u>

	$n(^{235}U)/n(^{238}U)$
Average	0.00726323
SD	0.00000012
RSD	0.0016%
RSE	0.0008%
Uncertainty, k=2	0.000001
Rel Uncertainty, k=2	0.016%
"Known Value" [11]	0.0072631
Uncertainty of "Known value" [11], *k=2*	0.0000011
Rel. Dev. from "Known value" [11]	0.0023%
Uncertainty, k=2	0.021%
Certified Value	0.0072623
Uncertainty, k=2	0.0000022
Rel. Dev. from Certified Value	0.013%
Uncertainty, k=2	0.034%

12 Annex-2: Certificates for IRMM-074, IRMM-075, IRMM-184 and IRMM-3636a

CERTIFICATE

ISOTOPIC REFERENCE MATERIAL IRMM-074

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

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

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

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against these Isotopic Reference Materials will, therefore, also be traceable to the SI unit system.

07/2006

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

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

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

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

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

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

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

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

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

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL	P Taylor	R Wellum
July 2006	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993
[2] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Hendrickx, F. Kehoe, H. Kühn, S. Richter, G. Van Baelen, R.Wellum, Preparation and certification of IRMM-074, a new set of uranium isotope mixtures for calibration of mass spectrometers, Report EUR 22270 EN

CERTIFICATE

ISOTOPIC REFERENCE MATERIAL IRMM-075

The Isotopic Reference Material IRMM-075 is a set of mixtures of uranium isotopes ^{236}U and ^{nat}U with molar ratios certified as follows:

Code Number	Molar Isotope Abundance Ratio
	$n(^{236}U)/n(^{238}U)$
IRMM-075/1	$1.044\ 33(37) \cdot 10^{-4}$
IRMM-075/2	$1.141\ 60(40) \cdot 10^{-5}$
IRMM-075/3	$1.040\ 93(36) \cdot 10^{-6}$
IRMM-075/4	$1.137\ 42(40) \cdot 10^{-7}$
IRMM-075/5	$1.065\ 19(75) \cdot 10^{-8}$
IRMM-075/6	$1.088\ 5(63) \cdot 10^{-9}$

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

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against these Isotopic Reference Materials will, therefore, also be traceable to the SI unit system.
2. The uncertainties as specified in the table can be considered as expanded uncertainties U where $k = 2$. The value of the standard uncertainty can therefore be derived: $u_c = U \cdot 0.5$. The uncertainties given are supported by calculation of the combined uncertainty following the ISO/GUM recommendations[1] and are based on measured values of the isotopic enrichments, the weights of oxides and solutions, and of the impurity levels.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993

08/2007

3. Values for molar isotope abundance ratios are valid for 6 May 2006
4. The Isotopic Reference Material IRMM-075 consists of a set of 6 units. Each unit consists of approximately 1 mg uranium as uranyl nitrate in 1 mL 1 M nitric acid solution in a sealed quartz glass ampoule.
5. The atomic masses, used in the calculations, are[2]

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

6. The vial should by opened with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.
7. Full details on the certification procedure can be found in the Certification Report[3].

Chemical purification of the $^{236}U_3O_8$ and $^{nat}U_3O_8$ starting materials was performed by R Eykens and F Kehoe.

Weighing and preparation of the Isotopic Reference Material was performed by R Eykens. The ampoulation of this Isotopic Reference Material was accomplished by S Werelds, E Joos, M Peeters, R Eykens and A Verbruggen.

Characterization of the enriched isotopes from which the set was prepared and verification measurements on the mixtures were performed by S Richter on samples prepared by F Kehoe and A Alonso Muñoz.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL	P Taylor	Y Aregbe
August 2007	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

[2] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe, H. Kühn, S. Richter, R.Wellum, Y. Aregbe, Preparation and certification of IRMM-075, Report EUR …….. EN

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-184

$n(^{233}\mathrm{U})/n(^{238}\mathrm{U}) < 0.000\ 000\ 002$
$n(^{234}\mathrm{U})/n(^{238}\mathrm{U}) = 0.000\ 053\ 138(32)$
$n(^{235}\mathrm{U})/n(^{238}\mathrm{U}) = 0.007\ 262\ 3(22)$
$n(^{236}\mathrm{U})/n(^{238}\mathrm{U}) = 0.000\ 000\ 124\ 46(17)$

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}\mathrm{U})/n(\mathrm{U})$	< 0.000 000 2	$m(^{233}\mathrm{U})/m(\mathrm{U})$	< 0.000 000 2
$n(^{234}\mathrm{U})/n(\mathrm{U})$	0.005 275 2(32)	$m(^{234}\mathrm{U})/m(\mathrm{U})$	0.005 186 8(32)
$n(^{235}\mathrm{U})/n(\mathrm{U})$	0.720 96(21)	$m(^{235}\mathrm{U})/m(\mathrm{U})$	0.711 91(21)
$n(^{236}\mathrm{U})/n(\mathrm{U})$	0.000 012 356(17)	$m(^{236}\mathrm{U})/m(\mathrm{U})$	0.000 012 253(17)
$n(^{238}\mathrm{U})/n(\mathrm{U})$	99.273 76(22)	$m(^{238}\mathrm{U})/m(\mathrm{U})$	99.282 89(21)

The molar mass of the uranium in this sample is 238.028 893 6(79) $\mathrm{g \cdot mol^{-1}}$

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

2. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

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3. The Isotopic Reference Material IRMM-184 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of a chemically stable nitric acid solution. The molality is about 6 m HNO_3 (i.e. 6 mol HNO_3 kg^{-1} of solvent); the molarity is 5 M HNO_3 (i.e. 5 mol $HNO_3 \cdot L^{-1}$ of solution).

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safehandling of radioactive materials.

5. The atomic masses, used in the calculations, are[1]

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

Chemical preparation and ampoulation of this Isotopic Reference Material were accomplished by W Lycke and A Verbruggen.

Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by W De Bolle. TIMS re-measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter using the TRITON mass spectrometer. Sample ampoules were re-opened and sample solutions prepared for TIMS analysis by A Alonso[2]. A Verbruggen was responsible for the preparation and issuance of the certificate.

Metrological weighing required in the preparation was performed by F Hendrickx.

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December 1987	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

Revised July 1993
Revised June 1999
Revised March 2005

[1] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[2] Measurement certificate IM/MeaC/24/04-IRMM-184 of March 2005

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CERTIFICATE
SPIKE ISOTOPIC REFERENCE MATERIAL IRMM-3636a

$2.119\ 06(26) \cdot 10^{-7}$ mol (^{236}U) $\cdot$ g^{-1} (solution)

The Spike Isotopic Reference Material is supplied with an isotope amount content of ^{236}U certified as above.

The amounts of other uranium isotopes present are related to the ^{236}U content through the following certified amount ratios:

$n(^{233}U)/n(^{236}U)$:	1.019 06(16)
$n(^{234}U)/n(^{236}U)$:	0.000 366 06(48)
$n(^{235}U)/n(^{236}U)$:	0.000 045 480(74)
$n(^{238}U)/n(^{236}U)$:	0.000 234 81(38)

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	50.455 8(39)	$m(^{233}U)/m(U)$	50.135 5(39)
$n(^{234}U)/n(U)$	0.018 125(24)	$m(^{234}U)/m(U)$	0.018 087(24)
$n(^{235}U)/n(U)$	0.002 251 8(37)	$m(^{235}U)/m(U)$	0.002 256 8(37)
$n(^{236}U)/n(U)$	49.512 2(39)	$m(^{236}U)/m(U)$	49.832 4(39)
$n(^{238}U)/n(U)$	0.011 626(19)	$m(^{238}U)/m(U)$	0.011 801(19)

The molar mass of the uranium in this sample is 234.528 74(12) $g \cdot mol^{-1}$

From the certified values, the following amount content and mass fractions are derived:

$4.279\ 88(54) \cdot 10^{-7}$	mol (U) $\cdot$ g^{-1} (solution)
$2.159\ 45(35) \cdot 10^{-7}$	mol (^{233}U) $\cdot$ g^{-1} (solution)
$1.003\ 75(13) \cdot 10^{-4}$	g (U) $\cdot$ g^{-1} (solution)
$0.500\ 195(62) \cdot 10^{-5}$	g (^{236}U) $\cdot$ g^{-1} (solution)
$0.503\ 237(81) \cdot 10^{-5}$	g (^{233}U) $\cdot$ g^{-1} (solution)

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NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against this Isotopic Reference Material will, therefore, also be traceable to the SI unit system.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following ISO/GUM recommendations[1]. They are given in parentheses and include a coverage factor k=2. They apply to the last two digits of the value. The values certified are traceable to the SI.

3. This Reference Material was prepared by metrological dilution of IRMM-3636 which was prepared by metrological weighing of high enriched uranium base materials. and dissolution in HNO_3. Subsequently the diluted solution was dispensed into individual units.

4. Values for molar isotope abundance ratios are valid for 1 July 2007.

5. The Isotopic Reference Material IRMM-3636a comes in a flame-sealed quartz ampoule containing about 0.42 µmol uranium in about 1 mL of a chemically stable 1 M nitric acid solution.

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

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

7. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

8. Full details on the certification procedure can be found in the Certification Report EUR 23408 EN[3]

Chemical purification of the $^{236}U_3O_8$ and $^{233}U_3O_8$ starting materials was performed by R Eykens and F Kehoe.

Weighing and preparation of the Isotopic Reference Material was performed by R Eykens. The ampoulation of this Isotopic Reference Material was accomplished by S Werelds, M Peeters, R Eykens and A Verbruggen.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993
[2] G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nucl Phys A729(2003) 337-676.
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe, H. Kühn, S. Richter, Y. Aregbe, Preparation and certification of IRMM-3636 and 3636a, Report EUR 23408 EN

Characterization of the enriched isotopes from which IRMM-3636 was prepared and verification measurements were performed by S Richter and H Kühn on samples prepared by F Kehoe and A Alonso Muñoz.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL	P Taylor	Y Aregbe
May 2008	Head Isotope Measurements Unit	IRMM Safeguards Coordinator

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