Preparation and Certification of IRMM-075

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Table of Contents

1 Abstract

A set of 6 new synthetic mixtures with $n(^{236}U)/n(^{238}U)$ isotope ratios varying from 10^{-4} to 10^{-9} has been prepared and certified.

Natural uranium with low ^{236}U isotope abundance and enriched ^{236}U were both purified using well proven chemical methodology extensively tested in the preparation of other uranium synthetic mixtures such as IRMM-074. The purification involved separation on anion and cation columns followed by precipitation as peroxide. Manipulations were carried out in separate new glove-boxes to avoid cross contamination. The oxides were sintered into U_3O_8 in an oven installed in a glove-box with controlled humidity. Primary solutions of the same concentration were prepared by dissolving the oxides of ^{236}U and ^{nat}U. From the ^{236}U solution four dilutions were made by weighing. Weighed amounts of the dilutions of ^{236}U and weighed amounts of ^{nat}U were mixed to form a set of $^{236}U/^{238}U$ mixtures at a concentration of 1 mg $U \cdot g^{-1}$. The final solutions were dispensed into quartz ampoules which were subsequently flame sealed.

Verification of the mixtures IRMM-075/1-7 was performed by TRITON TIMS measurements using Faraday collectors and secondary electron multiplier in combination with an RPQ energy filter for improved abundance sensitivity. The results agreed well with the certified values obtained from the mixing calculations.

The uncertainties contributing to the final uncertainties of the isotopic ratios are the weighing errors, the measured impurities in each starting material, the stoichiometry of the oxides and the isotopic abundances of each. The method for the preparation and mixing are described and the certification and verification procedures are reported.

2 Introduction

The existence of varying isotopic compositions for natural uranium are very well known phenomena. In nature, the major isotopes are ^{235}U and ^{238}U, the minor isotopes with a low isotopic abundance are ^{234}U and ^{236}U. The abundance of ^{236}U covers a very wide range down to 10^{-11} in nature and 10^{-2} in a nuclear reactor. The measurement of the $n(^{236}U)/n(^{238}U)$ ratio proves to be an excellent tool for tracing of sources of material and is also recognised as providing information on the enrichment processes of uranium. This makes these measurements a valuable and important tool in nuclear safeguards.

The variety of isotopic compositions and the high dynamic range of the ratios require high specifications on the instrumentation used. For measurement of very low $n(^{236}U)/n(^{238}U)$ ratios it is recommendable to use a set of reference materials with $n(^{236}U)/n(^{238}U)$ ratios covering a wide range but specifically in the lower range below 10^{-5}.

Experience from Interlaboratory comparisons such as REIMEP and NUSIMEP showed very scattered results; it became clear that specific suitable isotopic reference materials were needed to calibrate the mass spectrometers and to maintain a rigid quality management system.

In this paper the preparation and certification of a set of 6 synthetic uranium isotope mixtures with $n(^{236}U)/n(^{238}U)$ isotope ratio ranging from 10^{-4} to 10^{-9} is described. It is demonstrated that the calculated $n(^{236}U)/n(^{238}U)$ ratios from mass metrology are in excellent agreement with the values obtained from the TIMS measurements.

3 Design of IRMM-075

IRMM-075 is designed such that each set consists of 6 individual isotope reference materials with $n(^{236}U)/n(^{238}U)$ ratio from 10^{-5} to 10^{-9}. Natural uranium with very low ^{236}U isotope abundance and highly enriched ^{236}U starting materials were selected to prepare the primary solutions. Four further dilutions of the ^{236}U primary solution were made following the preparation scheme shown in Figure 5.

The techniques of mixing oxides of enriched uranium isotopes as previously applied successfully for IRMM-072 and IRMM-074 have been used. The mixtures were made gravimetrically with the basic principle of dissolving weighable amounts of chemically in identical fashion purified, highly enriched oxides and mixing the solutions in the correct proportions, again gravimetrically. The critical points of the preparation were to ensure that:

- The enriched isotopes were handled in different glove-boxes completely isolated from the others to avoid cross-contamination (to maintain isotopic integrity).
- Similar chemical purification steps were used (and the same reagents) for each of the enriched isotopic uranium materials in parallel.
- The purified isotopes were dried and then sintered together under the same conditions in an oven built specifically for this purpose.
- The concentrations of the final solutions were defined at a concentration of 1 $mg \cdot g^{-1}$ to meet the demands of modern mass-spectrometers.
- A minimum weight of oxide > 100 mg for the starting material was needed to keep the uncertainties from the weighing procedure as low as possible.

4 Purification of uranium

The procedure for chemical purification of the uranium used in the preparation of IRMM-074 as extensively described elsewhere [1] was applied.

The purification of the uranium involved anion exchange in nitric acid medium, cation exchange in HNO_3/THF and precipitation as peroxide. Earlier experiments showed that this three step procedure gave an excellent level of purification.

The enriched isotopic uranium materials were purified using identical methods and chemicals, but in separate clean glove-boxes to avoid cross-contamination. For both enriched materials, new glove-boxes were installed to avoid cross-contamination or contamination from the environment.

The oxides were calcined at 920°C to arrive at a given stoichiometry in an oven. The individual oxides were sintered together in quartz crucibles held in a quartz housing to allow movement of air above the oxides but separating each material from the next. The purpose of this procedure was to form U_3O_8 and to ensure that both enriched materials have exactly the same stoichiometry.

The glove-box environment was completely controlled and the humidity in the glove-box and oven were kept at less than 30 ppm throughout the final sintering process.

The humidity was also controlled in the second section of the glove-box, in which two analytical balances were installed for weighing the oxides and the solutions. The set of weights were certified at IRMM against the IRMM kilogram. The relative uncertainty from weighing was kept lower than 0.01%

Although the impurities in both starting materials were not measured because of the limited amount of material available, the design of the purification cycle, as applied in parallel to the starting materials, allowed us to assume with confidence that each component has the same impurity amount, conservatively set at 100 ± 100 ppm in the certification of the final mixtures.

5 Certification of isotopic ratios in starting materials

The isotopic composition of the IRMM-075 starting materials (enriched ^{236}U and ^{nat}U materials) were measured using the (modified) total evaporation technique on the Triton TIMS [2][3]. By using a total evaporation technique the measurement is continued until the sample is exhausted. This is done in order to minimize mass fractionation effects for which nonetheless corrections were made.

The following measurements were made on the Triton TIMS:

- ^{236}U enriched material, LOT 02676, Turret T6502, on Triton TIMS. The sample loading was 5 microgram of U; 8 filaments were measured. Certified values are listed below in Table 1.

Table 1: Isotopic composition of highly enriched ^{236}U, Lot BC02676

Certified amount ratios	
$n(^{233}U)/n(^{236}U)$	0.000 000 034 32(30)
$n(^{234}U)/n(^{236}U)$	0.000 000 001 222(82)
$n(^{235}U)/n(^{236}U)$	0.000 041 196(74)
$n(^{238}U)/n(^{236}U)$	0.000 225 50(384)

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	0.000 003 431(30)	$m(^{233}U)/m(U)$	0.000 003 387(29)
$n(^{234}U)/n(U)$	0.000 000 122 2(82)	$m(^{234}U)/m(U)$	0.000 000 121 1(81)
$n(^{235}U)/n(U)$	0.004 118 5(74)	$m(^{235}U)/m(U)$	0.004 101 0(74)
$n(^{236}U)/n(U)$	99.973 334(38)	$m(^{236}U)/m(U)$	99.973 160(39)
$n(^{238}U)/n(U)$	0.022 544(38)	$m(^{238}U)/m(U)$	0.022 735(38)

The molar mass of the uranium is 236.045 971 7(43) g·mol^{-1}

- ^{nat}U enriched material, LOT 02063, INM-001466: Turret T6A30 on Triton TIMS. The sample loading was 5 microgram of U, 6 filaments were measured.
  - No ^{233}U was detected in the ^{nat}U sample: the acquired intensity at mass 233 were at background level. Therefore all $^{233}U/^{238}U$ ratios were set to zero.
  - AMS measurements carried out at the University of Vienna showed a value of $n(^{236}U)/n(^{238}U) = 5.20(63)\cdot10^{-11}$ mol/mol [4]
  - Certified values are shown in Table 2.

Table 2: Isotopic composition highly enriched ^{nat}U Lot BC02063

Certified amount ratios	
$n(^{234}U)/n(^{238}U)$	0.000 053 283(37)
$n(^{235}U)/n(^{238}U)$	0.007 260 3(36)
$n(^{236}U)/n(^{238}U)$	<0.000 000 000 5

amount fraction (·100)		mass fraction (·100)	
$n(^{234}U)/n(U)$	0.005 289 6(37)	$m(^{234}U)/m(U)$	0.005 201 0(36)
$n(^{235}U)/n(U)$	0.720 76(36)	$m(^{235}U)/m(U)$	0.711 72(35)
$n(^{236}U)/n(U)$	<0.000 000 05	$m(^{236}U)/m(U)$	<0.000 000 05
$n(^{238}U)/n(U)$	99.273 95(36)	$m(^{238}U)/m(U)$	99.283 08(36)

The molar mass of the uranium is 238.028 899(12) g·mol^{-1}

- IRMM-184 for the k-factor: Turret T6502 on Triton TIMS. Sample loading: 5 microgram of U, 5 filaments were measured.

  Mass fractionation correction for all $n(^{233}U)/n(^{236}U)$, $n(^{234}U)/n(^{236}U)$, $n(^{235}U)/n(^{236}U)$ and $n(^{238}U)/n(^{236}U)$ ratios has been done using a k-factor of K58 = 0.999 39+/- 0.000 31 (k=2) for 3 mass units. K-factors have been calculated based on K58 using the exponential fractionation law.

- For the ^{nat}U sample, within the original data spreadsheet all $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios were normalized internally using the (experimental value of the) $n(^{235}U)/n(^{238}U)$ result from Gas MS.

6 Preparation of solutions and mixtures

The series was produced by careful weighing of amounts of a solution containing ^{236}U and ^{nat}U. The 'mother' solution of ^{236}U was diluted consecutively to make 4 further solutions with lower concentrations of this isotope before mixing. A mixing schedule as shown in Figure 5 was designed which resulted in 6 solutions covering the range of ^{236}U ratios relative to ^{238}U from 10^{-4} to 10^{-9}.

7 Certification

The aim of the IRMM-075 mixing programme was to achieve isotopic mixtures with uncertainties equivalent to those of IRMM-074, i.e. 0.03% relative for $n(^{236}U)/n(^{238}U)$ for the ratios up to 10^{-7} (all uncertainties are expanded combined uncertainties, k=2). The basis for this certification was the calculation from the mixing of the enriched isotopes, as described in the report and the verification measurements carried out on the thermal ionisation mass spectrometer in direct comparison with three earlier prepared test synthetic mixtures [5].

7.1 Calculation of the ratios from the mixing equations

The isotope amount ratios of the individual units of the set were calculated according to GUM [6, 7] using the GUM Workbench.

Four main contributors to the final uncertainties of the isotopic ratios were recognised during the preparation of IRMM-075:

- Uncertainties from weighing: expanded uncertainties (k=2) between 0.012% and 0.031 % on the amount content of the mother solutions of ^{236}U and ^{nat}U and the dilutions of ^{236}U.
- Chemical impurities: based on an equal level of impurities for each of the starting materials as explained above, a value of 100 ppm ± 100 ppm was applied with 0.8 for correlation coefficient.
- Stoichiometry: caused by differences in stoichiometry between the oxides of the starting materials. For the U_3O_8 a value of 8 was assumed for the oxygen with an uncertainty of 0.01% with a rectangular distribution indicating the limit values for the stoichiometry. A correlation of 0.8 was applied in the calculations.
- Measurements of the individual isotopic amount ratios: expanded uncertainties (k=2) up to $2.5 \cdot 10^{-6}$ % on the molar mass of the individual starting materials were introduced.

The ratios calculated from the mixing procedure for $n(^{236}U)/n(^{238}U)$ are shown in Table 3 below. An uncertainty budget with the major components of uncertainty for IRMM-075/1-5 is given in, 8, 9, 10, 11 in the annex. The major component (99.7%) of uncertainty for IRMM-075/6 is the isotope abundance of ^{236}U therefore no uncertainty budget is provided.

Table 3: Calculated values for IRMM-075 set

	$n(^{236}U)/n(^{238}U)$
IRMM-075/1	1.044 33(29) $\cdot 10^{-4}$
IRMM-075/2	1.141 60(32) $\cdot 10^{-5}$
IRMM-075/3	1.040 93(31) $\cdot 10^{-6}$
IRMM-075/4	1.137 42(35) $\cdot 10^{-7}$
IRMM-075/5	1.065 19(72) $\cdot 10^{-8}$
IRMM-075/6	1.088 5(63) $\cdot 10^{-9}$

The expanded uncertainties in Table 3, calculated from the mixing of the isotopically enriched materials, lie within the uncertainties proposed for the certification of IRMM-075. The certificate values of IRMM-075 are therefore verified.

7.2 Effect of correlation coefficients for stoichiometry and impurities

The effects of the assumptions for the correlation coefficients for stoichiometry and impurities were modelled for both parameters and the results of this for IRMM-075/1 and IRMM/075/5 are shown in Figure 1 and Figure 2. For IRMM-075/6 which is certified at *Uc* = 0.58%, the effects are not significant.

7.2.1 Stoichiometry

The effect of the stoichiometry on the combined uncertainty on the $n(^{236}U)/n(^{238}U)$ ratio of the synthetic mixtures was evaluated by designing a mathematical model in the GUM Workbench [7]. In this model, the correlation factor of the stoichiometry (δ_{stoich}) between the values entered for the two uranium components was varied between 0 and 1 whereby the value of the stoichiometry for oxygen in U_3O_8 was kept constant at 8 (Fig. 1)

For each value of δ_{stoich}, the standard uncertainty on this oxygen stoichiometry factor was varied between 0.01% and 0.2% and the expanded uncertainty of the $n(^{236}U)/n(^{238}U)$ ratio was calculated.

All calculations were carried out for a impurity level set at 100 ± 100 ppm for the starting materials with a correlation factor of δ_{imp}= 0.8 .

The expanded uncertainty values for the $n(^{236}U)/n(^{238}U)$ ratio on the certificate are for IRMM-075/1 *Uc* = 0.035% and for IRMM-075/5 *Uc* = 0.070% for δ_{stoich}= 0.8. It can be seen in Figure 1 that these values of uncertainty can be achieved even for assumed relative uncertainties of the stoichiometry of 0.15% for IRMM-075/1 and of 0.1% for IRMM-075/5.

For both materials these values are much higher than the accepted realistic value of 0.01%.

The model clearly shows that the effect of the stoichiometry on the uncertainties of the certified values of $n(^{236}U)/n(^{238}U)$ on the two mixtures of the series is low. The assumption of a correlation coefficient of 0.8 appears to be completely acceptable.

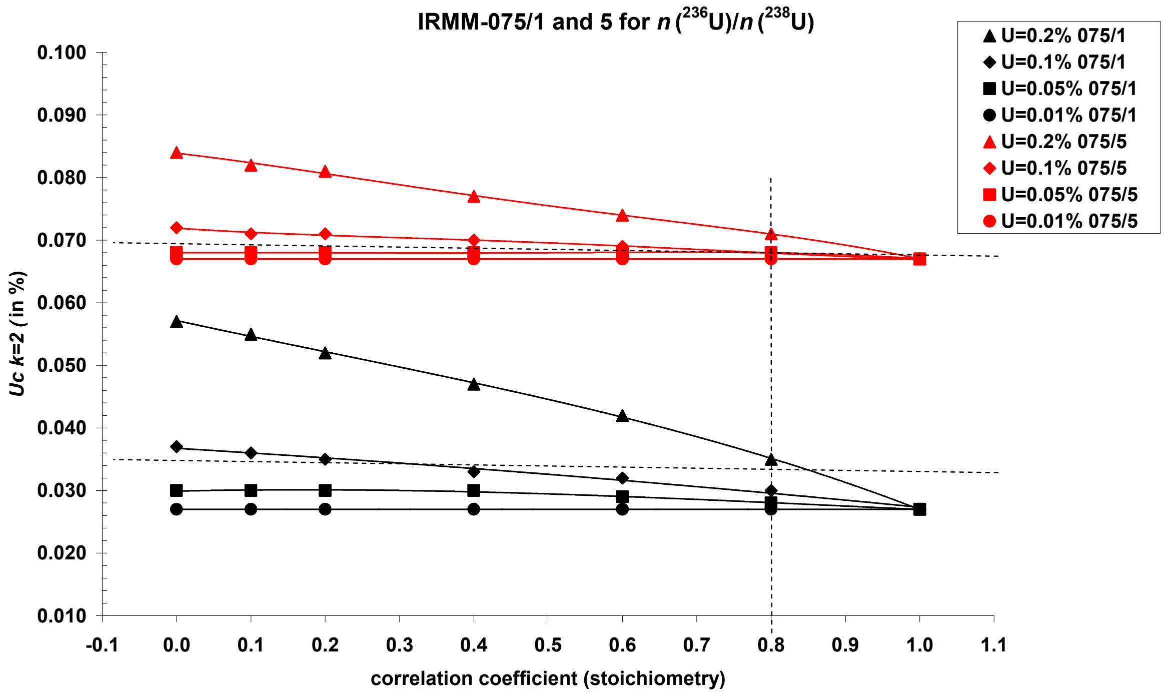

Figure 1: Stoichiometry correlation factor and total uncertainty on $n(^{236}U)/n(^{238}U)$ ratio

7.2.2 Impurities

In a similar manner the effect of the assumption of the correlation between the level of impurities of the starting uranium oxides on the combined uncertainty of the synthetic mixtures and also specifically on the $n(^{236}U)/n(^{238}U)$ ratio was evaluated by designing a mathematical model using the GUM Workbench [7]. In this model, the correlation factor on the impurities (δ_{imp}) was varied between 0 and 1 while the impurity level was set at 100 ppm.

For each δ_{imp}, the standard uncertainty on the total impurities was varied between 50 ppm and 200 ppm and the expanded uncertainty of the $n(^{236}U)/n(^{238}U)$ ratio was calculated.

All calculations were carried out for a stoichiometry of 8 ± 0.01% on the oxygen in U_3O_8 and with the correlation factor between the stoichiometry of the starting materials set at δ_{stoich}= 0.8.

It can be seen in Figure 2 that even with relative uncertainties of 200 ppm on the impurity for both IRMM-075/1 and IRMM-075/5, the expanded uncertainty values for the $n(^{236}U)/n(^{238}U)$ ratio are less than the respective certified values of 0.035% and 0.070% showing that the value of 100 ± 100 ppm used in making the certificate is conservative.

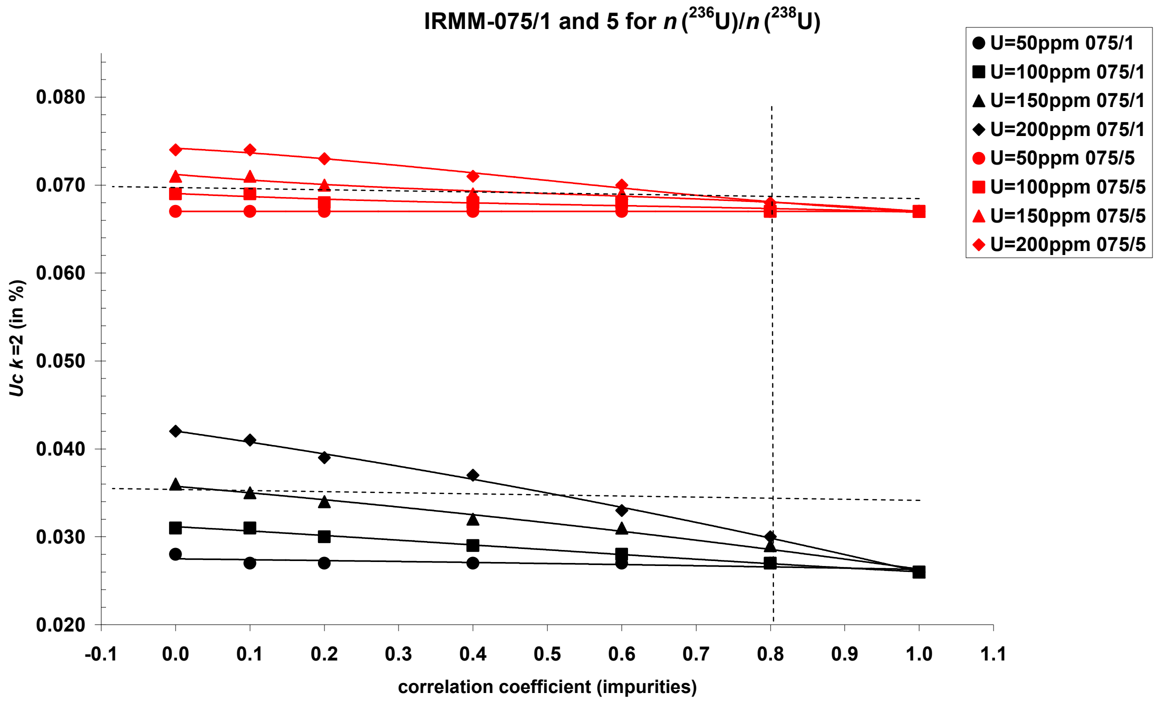

Figure 2: Impurities correlation factor and total uncertainty on $n(^{236}U/^{238}U)$ ratio

7.3 Certified values

The uncertainties as specified in Table 4 are relative expanded uncertainties U where $k = 2$ and given in percent. The value of the relative 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 [6] 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 the three synthetic test samples prepared earlier.

The certified ratios for $n(^{236}U)/n(^{238}U)$ are given below.

Table 4: Certified for IRMM-075 set

	$n(^{236}U)/n(^{238}U)$
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) $\cdot 10^{-9}$

8 IRMM-075 Ampouling

Ampouling was carried out in a double section fume hood in the controlled area. The ampoules were filled with 1 mL of solution (1 mg uranium) by means of a dispenser (5 or 10 mL).

The fume hood was fitted with a new plastic interior. In the left part of the fume hood the top part was not covered since it would get too hot when the ampoules were sealed. In the left part the burner for the flame sealing of the ampoules (acetylene/oxygen flame) was installed, surrounded by fireproof plates. The right part was used to set up flask and liquid dispenser. A sufficient number of clean ampoules were brought into the controlled area from the clean lab, as well as dispensers and tubing. The area around and under the filling station was covered with a fresh layer of clean room wipes every morning.

The flask containing the IRMM-075 solution to be processed was then opened. The dispenser was carefully fitted onto the flask, taking care to keep the ends of the tubing clean. One tube was then carefully inserted into the flask so that it reached the bottom of the flask. The other tubing was inserted into the ampoule. The required volume was then transferred from flask into ampoule with the dispenser. The ampoule was inspected that there was no solution in the neck and placed into a rack.

From there it was put into a small PTFE holder and sealed using an oxygen-acetylene flame. After visual inspection the ampoule was placed into a rack to cool. This was done in a continuous process, with one ampoule being processed in less than a minute, on the average. The sequence of filling is shown in Table 5 below.

From earlier experiments and testing carried out during similar operations [8], the maximum possible contamination from environmental uranium during the preparation of the mother solutions, dilutions, ampoule filling and the sealing process is estimated to be about 26 pg uranium ($1.1\cdot10^{-6}$ mol). Possible contamination at this level of uranium with natural isotopic composition has no significant effect on the isotopic ratios of the IRMM-075 solutions.

Table 5: Sequence of ampoule filling for IRMM-075

IRMM-075	Date	Number of ampoules sealed
6	15-02-2007	96
5	27-01-2007	91
4	28-01-2007	86
3	28-01-2007	86
2	16-02-2007	86
1	16-02-2007	97

9 Verification of certified values by comparison measurements

The calculated isotope ratios $n(^{236}U)/n(^{238}U)$ for each of the materials IRMM-075/1-7 were verified by isotopic measurements using a TRITON TIMS at IRMM. The TIMS measurement procedure is described in detail in [9]. All $n(^{236}U)/n(^{238}U)$ ratios higher or equal to $1\cdot10^{-5}$ (IRMM-075/1-2) were measured using Faraday collectors only, using current amplifiers which were equipped with $10^{12}\Omega$ resistors to improve the signal to noise ratio. All $n(^{236}U)/n(^{238}U)$ ratios below or equal to $1\cdot10^{-5}$ (IRMM-075/2-6) were measured using an SEM (secondary electron multiplier) for the detection of ^{236}U, in combination with an RPQ-energy filter for improved abundance sensitivity, which was inter-calibrated against the Faraday cups using the ^{234}U ion beam.

For quality control purposes a series of standards was measured under identical conditions. The following standards were used: IRMM-184 with a $n(^{236}U)/n(^{238}U)$ ratio of ca. $1.2 \cdot 10^{-7}$ and three materials from the test series consisting of BC 2691, BC 2692 and BC 2693 which have $n(^{236}U)/n(^{238}U)$ ratios of 10^{-7}, 10^{-8} and 10^{-6} respectively. As described in detail in [5], the test materials were synthetic mixtures as well, but the calculation of their $n(^{236}U)/n(^{238}U)$ ratios was solely done based on the $n(^{235}U)/n(^{238}U)$ ratios of the constituents measured by TIMS. They were analyzed for the $n(^{236}U)/n(^{238}U)$ ratio using the TIMS method as described above and in [9], the results showed excellent agreement with the calculated ratios, see Figure 3.

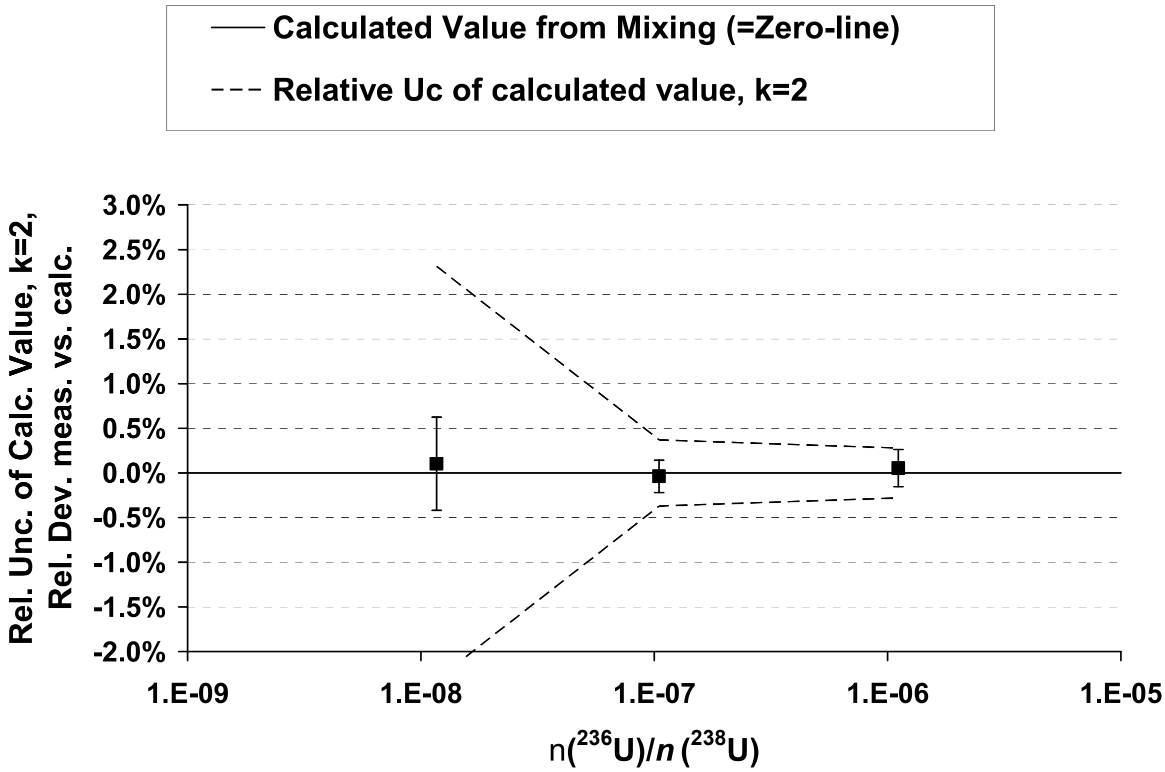

Figure 3: Comparison Triton TIMS and the calculated values of 3 synth.mixtures

Verification measurements for IRMM-075/1-6 were performed using the same TIMS method. For IRMM-075-2 with a $n(^{236}U)/n(^{238}U)$ ratio of about 10^{-5} measurements were performed using a Faraday cup as well as the SEM for the detection of ^{236}U. For IRMM-075/6 with $n(^{236}U)/n(^{238}U)$ ratios below 10^{-8} significant background interferences at about mass 236 amu hampered meaningful verification measurements. The results for the measurements of IRMM-075/1-5 are shown in Table 6 and Figure 4.

Table 6: Results for Verification Measurements of IRMM-075/1-5 using the TRITON TIMS

IRMM-075	Detector ^{236}U	$n(^{236}U)/n(^{238}U)$ certified	$n(^{236}U)/n(^{238}U)$ measured	Relative Difference	u_c, k=2 on Relative Difference
IRMM-075-1	FAR	0.000 104 433(37)	0.000 104 384(52)	-0.05%	0.06%
IRMM-075-2	FAR	0.000 011 416 0(40)	0.000 011 414(28)	-0.02%	0.25%
IRMM-075-2	SEM	0.000 011 416 0(40)	0.000 011 405(26)	-0.10%	0.23%
IRMM-075-3	SEM	0.000 001 040 93(36)	0.000 001 040 6(31)	-0.04%	0.30%
IRMM-075-4	SEM	0.000 000 113 742(40)	0.000 000 113 89(45)	0.13%	0.40%
IRMM-075-5	SEM	0.000 000 010 651 9(75)	0.000 000 010 59(15)	-0.58%	1.42%

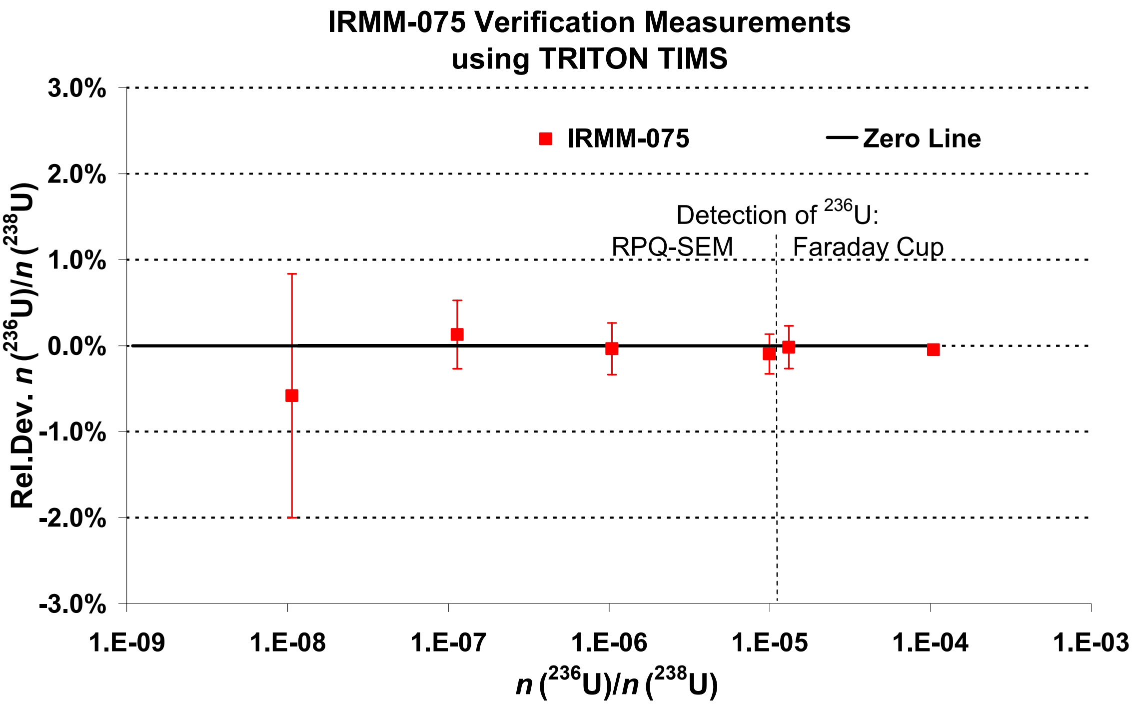

Figure 4: Comparison measured - certified $n(^{236}U)/n(^{238}U)$

As a conclusion the verification measurements using TIMS did not show any significant deviation from the certified $n(^{236}U)/n(^{238}U)$ ratios and were therefore successful. The new IRMM-075 series can be considered the primary reference material for the measurement of $n(^{236}U)/n(^{238}U)$ ratios within the range of 10^{-4} to 10^{-9}.

10 Conclusions

The methodology and techniques used in the preparation of synthetic mixtures IRMM-072 and recently IRMM-074 have been applied with success for the series IRMM-075.

The series has been prepared and certificate values of the isotopic ratio have been calculated based on the weights of oxides and solutions and verified by the uncertainties of the mixing calculations and by independent TIMS measurements.

A certificate is now being produced. As for the other series, it will again be important for verification measurements to be made by other laboratories to demonstrate an international validity for the reference material.

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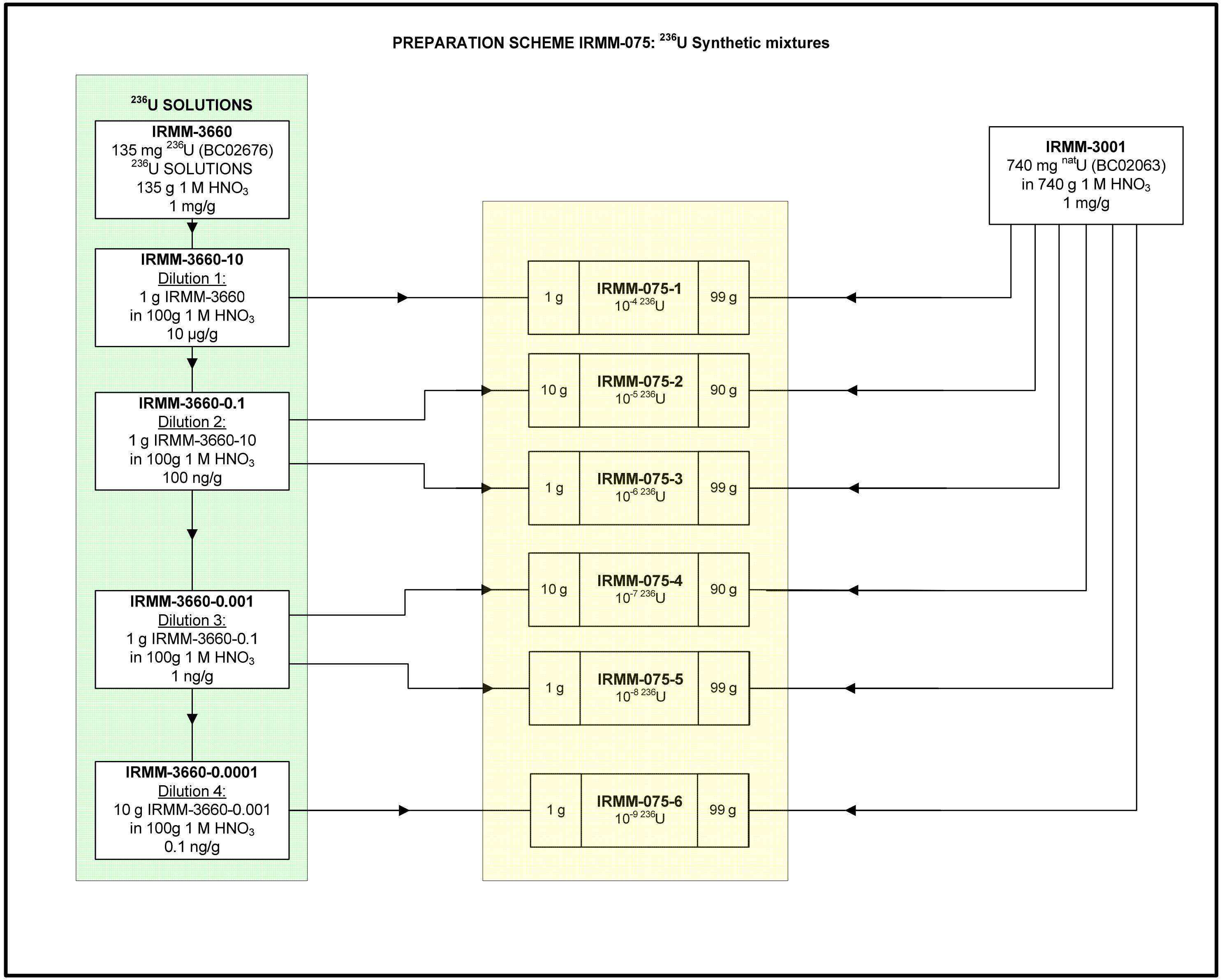

Figure 5: Preparation scheme

IRMM
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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

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

6. The vial should be 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[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 August 2007	Y Aregbe IRMM Safeguards Coordinator	P Taylor Head 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

Table 7: Uncertainty budget for $n(^{236}U)/n(^{238}U)$ in IRMM-075-1

Quantity	Description	Value	Standard Uncertainty	Index
f_{O236}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
f_{Onat}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
m_{U236O}	weight starting material	0.15897000 g	$1.73 \cdot 10^{-6}$ g	0.6 %
m_{UnatO}	weight starting material	0.87455400 g	$2.89 \cdot 10^{-6}$ g	0.0 %
δ_{U236O}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.6 %
δ_{UnatO}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.6 %
$m_{Sol3001}$	weight solutions for mix	742.3600 g	0.0115 g	1.3 %
$m_{Sol3660}$	weight solutions for mix	134.75800 g	$1.73 \cdot 10^{-3}$ g	0.9 %
$m_{Sol3660\text{-}10}$	weight solutions for mix	100.11700 g	$1.73 \cdot 10^{-3}$ g	1.6 %
$m_{3660\text{-}in\text{-}3660\text{-}10}$	weight solutions for mix	1.009300 g	$115 \cdot 10^{-6}$ g	70.0 %
$m_{Sol3660\text{-}10\_075/1}$	weight solutions for mix	1.0107000 g	$57.7 \cdot 10^{-6}$ g	17.5 %
$m_{3001\_075/1}$	weight solutions for mix	99.08600 g	$1.15 \cdot 10^{-3}$ g	0.7 %
$R_{236\backslash 238\_075/1}$	calculated 236/238 ratio	$104.4333 \cdot 10^{-6}$	$14.3 \cdot 10^{-9}$	

Table 8: Uncertainty budget for $n(^{236}U)/n(^{238}U)$ in IRMM-075-2

Quantity	Description	Value	Standard Uncertainty	Index
f_{O236}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
f_{Onat}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
m_{U236O}	weight starting material	0.15897000 g	$1.73 \cdot 10^{-6}$ g	0.6 %
m_{UnatO}	weight starting material	0.87455400 g	$2.89 \cdot 10^{-6}$ g	0.0 %
δ_{U236O}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.5 %
δ_{UnatO}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.5 %
$m_{Sol3001}$	weight solutions for mix	742.3600 g	0.0115 g	1.3 %
$m_{Sol3660}$	weight solutions for mix	134.75800 g	$1.73 \cdot 10^{-3}$ g	0.9 %
$m_{Sol3660\text{-}10}$	weight solutions for mix	100.11700 g	$1.73 \cdot 10^{-3}$ g	1.6 %
$m_{3660\text{-}in\text{-}3660\text{-}10}$	weight solutions for mix	1.009300 g	$115 \cdot 10^{-6}$ g	68.1 %
$m_{Sol3660\text{-}0,1}$	weight solutions for mix	100.10500 g	$1.73 \cdot 10^{-3}$ g	1.6 %
$m_{3660\text{-}10\text{-}in\text{-}3660\text{-}0,1}$	weight solutions for mix	1.0013000 g	$57.7 \cdot 10^{-6}$ g	17.3 %
$m_{Sol3660\text{-}0,1\_075/2}$	weight solutions for mix	10.037800 g	$115 \cdot 10^{-6}$ g	0.7 %
$m_{3001\_075/2}$	weight solutions for mix	90.04600 g	$1.15 \cdot 10^{-3}$ g	0.9 %
$R_{236\backslash 238\_075/2}$	calculated 236/238 ratio	$11.41598 \cdot 10^{-6}$	$1.58 \cdot 10^{-9}$	

Table 9: Uncertainty budget for $n(^{236}U)/n(^{238}U)$ in IRMM-075/3

Quantity	Description	Value	Standard Uncertainty	Index
f_{O236}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
f_{Onat}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
m_{U236O}	weight starting material	0.15897000 g	$1.73 \cdot 10^{-6}$ g	0.5 %
m_{UnatO}	weight starting material	0.87455400 g	$2.89 \cdot 10^{-6}$ g	0.0 %
δ_{U236O}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.0 %

Quantity	Description	Value	Standard Uncertainty	Index
δ_{UnatO}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	3.0 %
$m_{Sol3001}$	weight solutions for mix	742.3600 g	0.0115 g	1.1 %
$m_{Sol3660}$	weight solutions for mix	134.75800 g	$1.73 \cdot 10^{-3}$ g	0.7 %
$m_{Sol3660-10}$	weight solutions for mix	100.11700 g	$1.73 \cdot 10^{-3}$ g	1.3 %
$m_{3660-in-3660-10}$	weight solutions for mix	1.009300 g	$115 \cdot 10^{-6}$ g	58.6 %
$m_{Sol3660-0,1}$	weight solutions for mix	100.10500 g	$1.73 \cdot 10^{-3}$ g	1.3 %
$m_{3660-10-in-3660-0,1}$	weight solutions for mix	1.0013000 g	$57.7 \cdot 10^{-6}$ g	14.9 %
$m_{Sol3660-0,1\_075/3}$	weight solutions for mix	1.0074000 g	$57.7 \cdot 10^{-6}$ g	14.7 %
$m_{3001\_075/3}$	weight solutions for mix	99.11500 g	$1.15 \cdot 10^{-3}$ g	0.6 %
$R_{236\backslash 238\_075/3}$	calculated 236/238 ratio	$1.040930 \cdot 10^{-6}$	$156 \cdot 10^{-12}$	

Table 10: Uncertainty budget for $n(^{236}U)/n(^{238}U)$ in IRMM-075/4

Quantity	Description	Value	Standard Uncertainty	Index
f_{O236}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
f_{Onat}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
m_{U236O}	weight starting material	0.15897000 g	$1.73 \cdot 10^{-6}$ g	0.5 %
m_{UnatO}	weight starting material	0.87455400 g	$2.89 \cdot 10^{-6}$ g	0.0 %
δ_{U236O}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	2.8 %
δ_{UnatO}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	2.8 %
$m_{Sol3001}$	weight solutions for mix	742.3600 g	0.0115 g	1.0 %
$m_{Sol3660}$	weight solutions for mix	134.75800 g	$1.73 \cdot 10^{-3}$ g	0.7 %
$m_{Sol3660-10}$	weight solutions for mix	100.11700 g	$1.73 \cdot 10^{-3}$ g	1.3 %
$m_{3660-in-3660-10}$	weight solutions for mix	1.009300 g	$115 \cdot 10^{-6}$ g	55.4 %
$m_{Sol3660-0,1}$	weight solutions for mix	100.10500 g	$1.73 \cdot 10^{-3}$ g	1.3 %
$m_{3660-10-in-3660-0,1}$	weight solutions for mix	1.0013000 g	$57.7 \cdot 10^{-6}$ g	14.1 %
$m_{Sol3660-0,001}$	weight solutions for mix	100.23700 g	$1.73 \cdot 10^{-3}$ g	1.3 %
$m_{3660-0,1-in-3660-0,001}$	weight solutions for mix	1.0005000 g	$57.7 \cdot 10^{-6}$ g	14.1 %
$m_{Sol3660-0,001\_075/4}$	weight solutions for mix	10.020100 g	$115 \cdot 10^{-6}$ g	0.6 %
m3001_075/4	weight solutions for mix	90.09000 g	$1.15 \cdot 10^{-3}$ g	0.7 %
$f_{236-from-SMnat}$	isotope abundance ^{236}U	$51.60 \cdot 10^{-12}$	$3.13 \cdot 10^{-12}$	3.3 %
$R_{236\backslash 238\_075/4}$	calculated 236/238 ratio	$113.7418 \cdot 10^{-9}$	$17.5 \cdot 10^{-12}$	

Table 11: Uncertainty budget for $n(^{236}U)/n(^{238}U)$ in IRMM-075/5

Quantity	Description	Value	Standard Uncertainty	Index
f_{O236}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
f_{Onat}	stoichiometry	8.000000	$462 \cdot 10^{-6}$	0.0 %
m_{U236O}	weight starting material	0.15897000 g	$1.73 \cdot 10^{-6}$ g	0.1 %
m_{UnatO}	weight starting material	0.87455400 g	$2.89 \cdot 10^{-6}$ g	0.0 %
δ_{U236O}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	0.6 %
δ_{UnatO}	impurities	$100.0 \cdot 10^{-6}$	$57.7 \cdot 10^{-6}$	0.6 %

Quantity	Description	Value	Standard Uncertainty	Index
$m_{Sol3001}$	weight solutions for mix	742.3600 g	0.0115 g	0.2 %
$m_{Sol3660}$	weight solutions for mix	134.75800 g	$1.73 \cdot 10^{-3}$ g	0.1 %
$m_{Sol3660\text{-}10}$	weight solutions for mix	100.11700 g	$1.73 \cdot 10^{-3}$ g	0.3 %
$m_{3660\text{-}in\text{-}3660\text{-}10}$	weight solutions for mix	1.009300 g	$115 \cdot 10^{-6}$ g	11.5 %
$m_{Sol3660\text{-}0,1}$	weight solutions for mix	100.10500 g	$1.73 \cdot 10^{-3}$ g	0.3 %
$m_{3660\text{-}10\text{-}in\text{-}3660\text{-}0,1}$	weight solutions for mix	1.0013000 g	$57.7 \cdot 10^{-6}$ g	2.9 %
$m_{Sol3660\text{-}0,001}$	weight solutions for mix	100.23700 g	$1.73 \cdot 10^{-3}$ g	0.3 %
$m_{3660\text{-}0,1\text{-}in\text{-}3660\text{-}0,001}$	weight solutions for mix	1.0005000 g	$57.7 \cdot 10^{-6}$ g	2.9 %
$m_{Sol3660\text{-}0,001\_075/5}$	weight solutions for mix	1.0289000 g	$57.7 \cdot 10^{-6}$ g	2.8 %
m3001_075/5	weight solutions for mix	99.21900 g	$1.15 \cdot 10^{-3}$ g	0.1 %
$f_{236\text{-}from\text{-}SMnat}$	isotope abundance ^{236}U	$51.60 \cdot 10^{-12}$	$3.13 \cdot 10^{-12}$	77.4 %
$R_{236\backslash 238\_075/5}$	calculated 236/238 ratio	$10.65195 \cdot 10^{-9}$	$3.58 \cdot 10^{-12}$	

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Abstract

A set of 6 new synthetic mixtures with $n(^{236}U)/n(^{238}U)$ isotope ratios varying from 10^{-4} to 10^{-9} has been prepared and certified.

Natural uranium with low ^{236}U isotope abundance and enriched ^{236}U were both purified using well proven chemical methodology extensively tested in the preparation of other uranium synthetic mixtures such as IRMM-074. The purification involved separation on anion and cation columns followed by precipitation as peroxide. Manipulations were carried out in separate new glove-boxes to avoid cross contamination. The oxides were sintered into U_3O_8 in an oven installed in a glove-box with controlled humidity. Primary solutions of the same concentration were prepared by dissolving the oxides of ^{236}U and ^{nat}U. From the ^{236}U solution four dilutions were made by weighing. Weighed amounts of the dilutions of ^{236}U and weighed amounts of ^{nat}U were mixed to form a set of $n(^{236}U)/n(^{238}U)$ mixtures at a concentration of 1 mg $U \cdot g^{-1}$. The final solutions were dispensed into quartz ampoules which were subsequently flame sealed.

Verification of the mixtures IRMM-075/1-6 was performed by TRITON TIMS measurements using Faraday collectors and secondary electron multipliers in combination with an RPQ energy filter for improved abundance sensitivity. The results agreed well with the certified values obtained from the mixing calculations.

The uncertainties contributing to the final uncertainties of the isotopic ratios are the weighing errors, the measured impurities in each starting material, the stoichiometry of the oxides and the isotopic abundances of each. The method for the preparation and mixing is described and the certification and verification procedures are reported

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