JRC REFERENCE MATERIALS REPORT

Preparation and certification of IRMM-1000a (20 mg) and IRMM-1000b (50 mg)

Certified uranium reference material for the production date

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Abstract

This report describes the production and certification of IRMM-1000a and IRMM-1000b, uranium reference materials certified for the production date based on the ^{230}Th/^{234}U radiochronometer, which corresponds to the last chemical separation, i.e. the removal of any ^{230}Th from the material to the maximum extent achievable. The starting material was low-enriched uranium with a relative mass fraction, $m(^{235}U)/m(U)$ of 3.6 %. The targeted completeness for the last chemical separation of the ^{230}Th decay product from its parent nuclide ^{234}U was achieved. The certified production date was assigned following ISO Guide 34:2009. The between unit-homogeneity and the stability of the certified value were assessed in accordance with ISO Guide 35:2006.

The uncertainty of the certified value was estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and includes uncertainties related to characterisation, possible inhomogeneity and instability.

The material is mainly intended for calibration of methods, quality control, and assessment of method performance with isotope mass spectrometry and radiometry techniques. As any reference material, it can also be used for control charts or validation studies. The certified reference material is available in two sizes: 20 mg (IRMM-1000a) and 50 mg uranium (IRMM-1000b) as dried uranyl nitrate in screw-cap Teflon® (PFA) vials.

CERTIFICATION REPORT

Preparation and certification of IRMM-1000a (20 mg) and IRMM-1000b (50 mg)

Certified uranium reference material for the production date

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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.

Summary

This report describes the development and certification of IRMM-1000a and IRMM-1000b, a uranium reference material certified for the production date based on the ^{230}Th/^{234}U radiochronometer. The certified value was assigned following ISO Guide 34:2009 [1].

The starting material was low-enriched uranium with a relative mass fraction, $m(^{235}U)/m(U)$ of 3.6%. The chemical separation of the ^{230}Th decay product from its parent nuclide ^{234}U to the maximum extent of completeness was achieved. The certified production date was confirmed using the ^{230}Th/^{234}U radiochronometer, and corresponds to the last chemical separation, i.e. the removal of ^{230}Th from the material to the maximum extent achievable.

The between unit-homogeneity and the stability of the certified value were assessed in accordance with ISO Guide 35:2006 [2].

The material was characterised by taking into account the date and time elapsed of the last chemical and complete separation of ^{230}Th from ^{234}U.

The completeness of the separation was confirmed firstly by determining the U/Th separation factors and uranium recoveries using γ-ray spectrometry, and then by means of ICP-MS measurements using a ^{232}Th tracer. After sufficient ingrowth of thorium into the characterised uranium reference material, measurements of the ^{234}U and the ^{230}Th amount contents were carried out by isotope dilution mass spectrometry (IDMS) in compliance with ISO/IEC 17025:2005 [3]). Subsequently, the determined $n(^{230}Th)/n(^{234}U)$ was used in the calculation to confirm the certified production date.

The uncertainty of the certified value was estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4] and includes uncertainties related to characterisation, possible inhomogeneity and instability.

The material is intended for calibration of methods, quality control, and assessment of method performance with isotope mass spectrometry and radiometry techniques. As any reference material, it can also be used for control charts or validation studies. The certified reference material is available in two sizes: 20 mg (IRMM-1000a) and 50 mg uranium (IRMM-1000b) as dried uranyl nitrate in screw-cap Teflon® (PFA) vials. There is no minimum sample intake to be taken into account.

The following value was assigned to IRMM-1000a and IRMM-1000b:

IRMM-1000a/IRMM-1000b		
	Production date based on the $n(^{230}Th)/n(^{234}U)$ radiochronometer	
	Certified value	Uncertainty [4)] [day]
Production date [1)]	09/07/2012 (UTC) [2)] 2012-07-09Z [3)]	13
1) The production date is the date of the last chemical separation of ^{230}Th from ^{234}U in the uranium reference material.		
2) The certified value is expressed as a date dd/mm/yyyy, relative to the universal coordinated time (UTC).		
3) Here the certified value is expressed as a date yyyy-mm-ddZ according to ISO 8601.		
4) 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. It is based on the confirmation measurements and calculations using the radiochronometer and is traceable to the International System of units (SI).		

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Glossary

ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
c	Amount of substance concentration (mol L^{-1})
CI	Confidence interval
CLSI	Clinical and Laboratory Standards Institute
CRM	Certified reference material
EC	European Commission
GUM	Guide to the Expression of Uncertainty in Measurement
IAEA-SGAS	International Atomic Energy Agency - Safeguards Analytical Services
ICP-MS	Inductively coupled plasma-mass spectrometry
ID-TIMS	Isotope dilution Thermal Ionisation Mass Spectrometry
IDMS	Isotope dilution mass spectrometry
ILC	Inter-laboratory comparison
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
ITU	Institute for Transuranium Elements of the JRC
JRC	Joint Research Centre of the European Commission
k	Coverage factor
λ	Decay constant
M	Molar mass
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
rel	Index denoting relative figures (uncertainties etc.)
PFA	Perfluoroalkoxy alkane
RM	Reference material
RSD	Relative standard deviation
r^2	Coefficient of determination of the linear regression
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SD	Standard deviation
SF	Separation factor

SI	International System of Units
s_{meas}	Standard deviation of measurement data; an additional index "rel" is added as appropriate
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
$T_{1/2}$	Half-life of radionuclides in years
t	Time
t_{sl}	Proposed shelf-life
TEVA	TEtraValent Actinides
TIMS	Thermal Ionisation Mass Spectrometry
u	Standard uncertainty
U	Expanded uncertainty
u_{bb}^{*}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_c	Combined standard uncertainty; an additional index "rel" is added as appropriate
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate
u_{lts}	Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate
u_{Δ}	Combined standard uncertainty of measurement result and certified value
u_{meas}	Standard measurement uncertainty
VIM	Vocabulaire International de Métrologie – Concepts Fondamentaux et Généraux et Termes Associés (International Vocabulary of Metrology – Basic and General Concepts and Associated Terms) *[ISO/IEC Guide 99:2007]*
$\overline{x}$	Arithmetic mean
x_i	Results at a point of time i
α	Significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

Nuclear forensics is a relatively young discipline, which endeavors thorough interpretative and comparative (radio-) analytical methodologies to identify the possible origin and intended use of nuclear or other radioactive material intercepted from illicit trafficking. The parameters to be investigated are inherent to the material and range from isotopic composition, micro and macro-structures, and chemical impurities to decay products [5,6].

The elapsed time since the production of the material, commonly referred to as the "age" of the material, is an important investigation parameter. During the production, nuclear material is chemically purified from impurities, which includes the removal of radioactive decay products or daughter nuclides, thereby "zeroing" the initial amount of daughter nuclides in the nuclear material at the time of separation. Therefore, assuming that the parent–daughter separation was complete and allowing the ingrowth of the daughter nuclides in the sample, the elapsed time since the last separation (i.e. the age of the material) can be determined by measuring the parent-daughter ratio in the sample, according to the equations of radioactive decay [7,8].

Unlike other characteristic parameters, the age of the material, i.e. the time elapsed since the last chemical separation of the daughter nuclides from the mother radionuclide, does not require comparison samples or reference data for interpretation. It is a self-explaining parameter and supports without ambiguity the identification of the origin of unknown material or helps to verify the source of intercepted nuclear material (e.g. safeguarding shut-down or decommissioned facilities to detect if chemical separation operations recently occurred). However, up to now, no certified reference material existed for validation of measurement procedures to determine accurately the production date of a nuclear material. Age determination has been based so far on historical data, archives and on the determination of the aforementioned combined parameters for the characterisation of nuclear material.

As a consequence, the European Commission - Joint Research Centre Institute for Reference Materials and Measurements (JRC-IRMM) in Geel, Belgium and the European Commission - Joint Research Centre Institute for Transuranium Elements (JRC-ITU) in Karlsruhe, Germany joined efforts to produce the first uranium reference material certified for the production date based on the $n(^{230}\text{Th})/n(^{234}\text{U})$ radiochronometer in order to answer the emerging need expressed by communities involved in national or international nuclear forensics, security and safeguards programmes for such a reference material [9]. Reference materials are a prerequisite for method validation. Such validated methods in combination with correct propagation of uncertainties are required when characterising intercepted nuclear material, to establish its origin, and to identify perpetrators and their network as well as providing evidence to bring them to justice [9].

1.2 Choice of the material

The IRMM-1000a and IRMM-1000b were prepared at the JRC-ITU from a mixture of low-enriched uranium dioxide pellets of three different origins and different enrichments resulting in a relative mass fraction $m(^{235}\text{U})/m(\text{U})$ of 3.6 % in the final material. Low-enriched uranium was chosen as it is one of the most relevant nuclear forensic or safeguards sample materials. This material is exempt from transport regulation because of the low amount of fissile material, which facilitates the shipping of the final reference material. The mother solution used for the separation contained about 20 g of uranium in nitric acid ($c = 3$ mol·L^{-1}), from which an aliquot containing about 6 g of uranium was used to produce the reference material.

1.3 Design of the project

The target value of the uranium age-dating reference material is the date of production of the material based on the $n(^{230}\text{Th})/n(^{234}\text{U})$ radiochronometer, which corresponds to the date of the last chemical separation of these two radionuclides.

The production of the reference material was carried out at JRC-ITU and consisted of the preparation of the mother solution, four chemical separations by extraction chromatography in order to remove the radionuclide ^{230}Th from its parent ^{234}U, the aliquoting and evaporation of the purified solution The separation was monitored by γ-ray spectrometric measurements to estimate the U recoveries and the U/Th separation factor and also by means of a ^{232}Th tracer measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The production date of IRMM-1000a and IRMM-1000b corresponds to the date and the carefully recorded time of the last (fourth) separation. The individual units were prepared by dispensing the separated solution into Teflon® (PFA) vials with subsequent evaporation to dryness. Aliquots of the purified mother solution are available in two different unit sizes of 20 mg uranium for mass spectrometric methods and 50 mg uranium for radiometric methods, corresponding to IRMM-1000a and IRMM-1000b respectively.

Confirmation measurements, homogeneity and stability assessment were combined using IDMS analysis on selected vials.

2 Participants

Preparation and processing of the reference material as well as the measurements for homogeneity, stability and characterisation and the different chemical steps were carried out at the JRC-ITU.
The overall project management has been performed at the JRC-IRMM, including data evaluation for value assignment, homogeneity and stability studies.

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium
(accredited to ISO Guide 34 for production of certified reference materials [1], BELAC No. 268-RM)

European Commission, Joint Research Centre, Institute for Transuranium Elements (ITU), Karlsruhe, Germany
(accredited to ISO 17025:2005 for General requirements for the competence of testing and calibration laboratories [3], DAkkS, D-PL-19821-01-00, 2014)

3 Material processing and process control

3.1 Origin/Purity of the starting material

IRMM-1000a and IRMM-1000b were prepared from high-purity natural and low-enriched uranium dioxide pellets of three different origins available at JRC-ITU. The natural uranium originated from Sweden and the two slightly enriched uranium starting materials from Kazakhstan and Germany. This base material with a relative mass fraction $m(^{235}U)/m(U)$ of 3.6 % was stored at JRC-ITU. From the dissolved uranium dioxide a mother solution used for the separation was prepared. It contained about 20 g of uranium in nitric acid ($c = 3$ mol·L^{-1}). An aliquot of the mother solution containing about 6 g of uranium was used to produce the reference material.

3.2 Processing

Most of the instrumental methods and measurement procedures for the preparation and purification of a uranium reference material (by extraction chromatography) and associated γ- and ICP-MS measurements have been described in details in [10,11,12]. The determination of the production date based on the measured amount ratio of $n(^{230}Th)/n(^{234}U)$ in the sample in a uranium-based radiochronometry reference material is described as well in [12].

The acids and reagents used during the processing were high-purity (Suprapur® from Merck or sub-boiled), and all the labware was acid-cleaned before use.

The production of the IRMM-1000a and IRMM-1000b from the low enriched uranium nitrate mother solution (corresponding to 6 g of uranium) consisted of four chemical separation steps by chromatography with TEVA® Resin (Triskem International, Bruz, France) in order to completely remove thorium from uranium to the maximum extent achievable, as can be seen in Figure 1 [11,12]. These TEVA® Resin columns also contained a thin layer of silica gel on the top in order to allow removal of protactinium (^{231}Pa) from the uranium material [7], however there is no confirmed complete separation of the ^{231}Pa daughter. This means that if the ^{231}Pa removal would be complete, the $^{231}Pa/^{235}U$ radiochronometer could be used as well to determine the production date, which would agree then with the certified value of IRMM-1000a and IRMM-1000b.
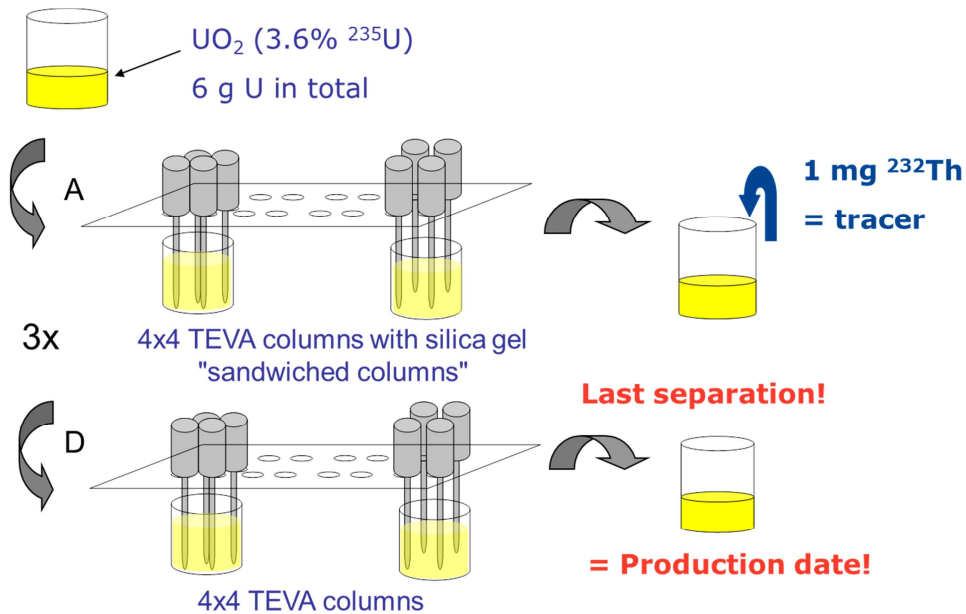
The efficiency of the thorium-uranium separation was monitored after each chemical separation by γ-ray spectrometric measurements to estimate the uranium recoveries (%) and the U/Th separation factor. The aim was to achieve a final cumulative U/Th separation factor (SF) better than 10^7 so that the residual ^{230}Th in the purified material would correspond to a bias of less than 6 hours [11]. After each γ-ray spectrometry measurement, the fractions obtained by the parallel separations were mixed together again into one solution. This solution was weighed, and re-measured by γ-ray spectrometry and subsequently evaporated overnight.

One chemical separation step of the uranium material required a full day of laboratory work; it included evaporation of the sample, subsequent dissolution and weighing, chromatographic separation (including a 3-hour elution of Th, see Annex 1) with intermediate γ-ray spectrometric measurements of the recovered fractions, and the final evaporation of the sample [11].

Before the second separation was performed, a natural ^{232}Th tracer (1 g of a SPEX CertiPrep with a total Th concentration of [1000 ± 5] µg·g^{-1}) was added to the solution in order to determine the residual thorium by ICP-MS in the reference material after the last chemical separation using isotope dilution. Then a third separation step was performed using the same analytical protocol as described above.

Finally, a fourth chemical separation was performed in order to achieve the maximum possible removal of thorium from the uranium. This defines the "production date", i.e. the

certified reference value of the material. The date of this last chemical separation was 9 July, 2012. The time of the separation was also recorded as 11:08 a.m. and corresponds to the median time between start and finish of the last chemical separation.

Figure 1: Four-step chemical separation of the thorium in the uranium starting material using TEVA resin to ensure efficient and complete Th removal from the uranium matrix

After this last separation and the subsequent γ-ray spectrometry measurements of the final solution, the solution was directly aliquoted into 161 pre-cleaned Teflon® PFA vials to obtain 108 units of IRMM-1000a containing approximately 20 mg of uranium each and 53 units of IRMM-1000b containing approximately 50 mg of uranium each. The aliquots were evaporated, capped, labelled, and put individually in Ziploc® bags (see evaporations and dispensing in Figure 2 and Figure 3) and stored at JRC-ITU prior to shipment to JRC-IRMM in June 2013.
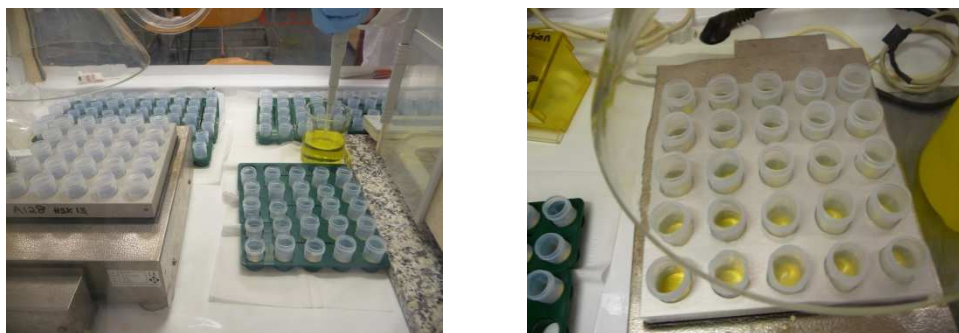
Figure 2: Pictures of the IRMM-1000a and IRMM-1000b units being aliquoted and evaporated in PFA vials

Figure 3: Pictures of the IRMM-1000b units as dried uranyl nitrate in PFA vials

3.3 Process control

As described in Section 3.2, in order to assess the completeness and efficiency of the U/Th separation, the separation factor and uranium recovery were determined by γ-ray spectrometry for each of the separation steps using the well-resolved γ-ray peaks of the short-lived ^{234}Th ($T_{1/2}$= 24.1 days, peak at 63.3 keV) and the ^{235}U (peak at 185.7 keV), respectively [11].

Table 1 summarises the uranium recovery results obtained from the different γ-measurements for each of the separation steps. The uranium recoveries were calculated using the γ-peak of ^{235}U and the separation factors using the γ-peak of ^{234}Th. The results in Table 1 prove that the 'target value' was reached, with an overall U recovery of 83.7 % ± 0.3 % (standard uncertainty) and a cumulative U/Th SF resulting from the four successive separations better than $(2.77 \pm 0.93) \cdot 10^7$ (standard uncertainty) attesting to the effective quantitative recovery of uranium in the reference material and the efficiency of the separation of Th in the uranium material.

The completeness of the removal of thorium from the initial uranium was further confirmed by ICP-MS measurements of the Th amount content using the ^{232}Th tracer that had been added to the uranium sample before the second chemical separation step. Based on this measurement, the final cumulative U/Th SF was found to be better than $(1.81 \pm 0.7) \cdot 10^7$ fulfilling the 'target value' of thorium mass fraction being less than 0.01 µg·g^{-1} uranium in the purified solution.

Table 1: Summary of the uranium recoveries and U/Th separation factors based on γ-ray spectrometric measurements of ^{235}U and ^{234}Th and on ICP-MS measurements of total Th (traced with ^{232}Th). Reported measurement uncertainties are standard uncertainties.

Separation steps	U recoveries (^{235}U) [a]	SF from U/Th [a]	SF from total Th [b]
1	95.0 ± 0.4 %	714 ± 126	714 ± 126 [c]
2	94.9 ± 0.4 %	22 ± 4	
3	96.2 ± 0.5 %	24 ± 4	25366 [d]
4	94.4 ± 0.4 %	75 ± 12	
Final	**83.7 ± 0.3 %**	**$(2.8 \pm 0.9) \cdot 10^7$**	**$(1.8 \pm 0.7) \cdot 10^7$**

[a] Based on γ-measurements of ^{235}U and ^{234}Th

[b] Based on ICP-MS measurements of Th isotopes (mainly ^{232}Th)

<superscript>c</superscript> Note that no separation factor can be calculated based on ^{232}Th for the first step since it is only introduced in the sample after this step. It is therefore assumed to be equal to the separation factor based on the γ-determination of the U/Th ratio

<superscript>d</superscript> This SF corresponds to the cumulative SF based on Th ICP-MS measurements for the 2nd - 4th separation steps

Other impurities in the final U material were measured as well at JRC-ITU and were found to be insignificant for the determination of the age.

Finally, the residual ^{230}Th mass fraction in the purified uranium material was expressed as an age of the material using the determined U/Th separation factors and the original Th/U ratio in the feed solution and gives a value of less than 1.3 hours (i.e. less than 80 min or 0.056 days, $k = 1$).

4   Homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value. In contrast to that, it is not relevant if this variation between units is significant compared to the analytical variation. Consequently, ISO Guide 34 requires Reference Material (RM) producers to quantify the between unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1   Between-unit homogeneity

The between-unit homogeneity was evaluated in October 2013 to ensure that the certified values of the CRM are valid for all 161 units of the material, within the stated uncertainty.

For the between-unit homogeneity test, the number of selected units corresponds to approximately the cubic root of the produced 108 units of 20 mg uranium and of the 53 units of the 50 mg uranium. Five units of 20 mg and five units of 50 mg uranium were therefore selected using a random stratified sampling scheme covering the whole batch.

The preparation and the chemical separation of the samples were carried out at the JRC-ITU. For the homogeneity assessment, both uranium and thorium amount contents were measured and the chemical separation described in section 3.2 and Annex 1 was used to recover as well the thorium fraction separated from the uranium matrix. Therefore, the analytical procedure was slightly modified to measure both thorium and uranium after Th-ingrowth in the selected IRMM-1000a and IRMM-1000b units.

The sample notations with the vial numbers of the 10 units selected for this homogeneity study are given below in the order of their chemical preparation (sequence for the weighing, aliquoting, separations):

20 mg uranium samples: A: 83 / B: 94/ C: 107/ D: 38/ E: 62

50 mg uranium samples: F: 154 / G: 131/ H: 125/ I: 124/ J: 119

The units of 20 mg and 50 mg uranium were dissolved in 2 mL and 5 mL concentrated nitric acid respectively, resulting in a U concentration of ~ 10 mg·mL^{-1} of total U and less than 10 pg of ^{230}Th per measured aliquot.

Then, aliquots from the 2 mL or 5 mL reference material samples were prepared in order to measure the uranium isotopes and amount concentrations by Isotope Dilution using Thermal

Ionisation Mass Spectrometry (ID-TIMS) and ICP-MS (ID-ICP-MS), and the thorium isotopes and amount concentrations by ICP-MS.

For the determination of the uranium isotopic composition, one aliquot per sample was prepared and measured by ID using a TIMS (MAT262, Thermo Fischer Scientific, Bremen, Germany) by the JRC-ITU Analytical Service (see Annex 2 for results). For the determination of the ^{234}U amount by isotope dilution mass spectrometry (IDMS), two aliquots from each of the ten selected units were prepared, one aliquot after addition of an in-house ^{233}U spike at 3.5 µg·g^{-1} (kept under weight control at JRC-ITU) and one unspiked aliquot. Procedural blanks were also prepared and measured together with the samples. All measurements were performed with the ICP-MS (Element 2, Thermo Fischer Scientific, Bremen, Germany).

For the determination of the thorium amount, 3 aliquots for each of the 5 units of 20 mg and 50 mg were prepared and spiked with the same natural ^{232}Th tracer as in the production of the reference material (i.e. SPEX CertiPrep with a total Th concentration of [1000 ± 5] µg·g^{-1}). Each thorium aliquot was prepared gravimetrically, using about 0.101 g of solution and 0.135 g of natural ^{232}Th spike (no spike was added to the blank and unspiked samples).

The thorium samples were therefore divided in 10 series (hereafter referred with letters from A to J) of 3 aliquots (with number 1-3). An unspiked sample (referred by number "4") was prepared with each series. Moreover, 8 procedural blanks (noted BL) and 3 replicates of the natural Th tracer (referred hereafter as Th#3) were also prepared (see Table 2).

Only one chemical separation using TEVA® Resin was required per aliquot, and the separation of the series of samples were carried out on the following dates and times:

- Series A to C and blanks 1-2, on 16 October, 2013 at 14:40 (the reference time given here corresponds to the median time between loading/start and finish times for the chemical separation)

- Series D to G and blanks 3-5, on 17 October, 2013 at 11:00

- Series H to J and blanks 6-8, on 17 October, 2013 at 14:50

The thorium fraction was eluted using 800 µL of a mixture of hydrofluoric acid c =0.02 mol·L^{-1} and nitric acid c = 0.02 mol·L^{-1} as described in [12] and Annex 1. The samples were then diluted in nitric acid and homogenised prior to the ICP-MS measurements using the Element 2.

As shown in Table 2 the sequence for the thorium analysis was as such that procedural blanks bracketed each measurement series in order to correct the amount contents in the samples. The unspiked samples were measured with each corresponding measurement series for the initial amount ratios $n(^{230}$Th$)/n(^{232}$Th$)$ and $n(^{234}$U$)/n(^{233}$U$)$. The detailed mass spectrometric parameters and corrections applied for the measurements of the $n(^{230}$Th$)/n(^{232}$Th$)$ and $n(^{234}$U$)/n(^{233}$U$)$ amount ratios are described in [10].

The ICP-MS measurements to determine the ^{230}Th amount were performed over three consecutive days as shown in Table 2. The uranium ICP-MS measurements had to be carried out a week later. However, day-to-day effects due to ingrowth of thorium are not likely to occur due to the long half-lives of uranium and thorium, $T_{1/2}$ = (245.5 ± 1.2)·10^3 a for ^{234}U and $T_{1/2}$= (75.38 ± 0.3)·10^3 a for ^{230}Th, k = 2, respectively [13].
The thorium measurements were carried out under repeatability conditions and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence (see Table 2).

Table 2: Sequences of the ICP-MS measurement of the thorium aliquots for the homogeneity study

Sequence 29/10/2013	Sequence 30/10/2013	Sequence 31/10/2013
BL6	BL8	BL5
I4 unspiked	J4 unspiked	G4 unspiked
I1	J1	G1
I2	J2	G2
I3	J3	G3
BL3	C4 unspiked	BL2
D4 unspiked	C1	A4 unspiked
D1	C2	A1
D2	C3	A2
D3	BL7	A3
BL1	H4 unspiked	BL4
B4 unspiked	H1	E4 unspiked
B4	H2	E1
B1	H3	E2
B2	F4 unspiked	E3
B3	F1	T#3-1
	F2	T#3-2
	F3	T#3-3

By combining the IDMS-TIMS with the ICP-MS results for the ^{234}U amount content and using the ICP-MS results for the ^{230}Th amount content, the $n(^{230}\text{Th})/n(^{234}\text{U})$ amount ratios were calculated for all 30 Th aliquots.

From these $n(^{230}\text{Th})/n(^{234}\text{U})$ amount ratios, the ages of the 10 selected units and their associated expanded uncertainties ($k = 2$) were calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM) [4] using the GUM Workbench Software [14] applying the following equation based on the radioactive decay [11]:

$$t = \frac{1}{\lambda_{234U}-\lambda_{230Th}} \times \ln\left(1-\frac{n(^{230}\text{Th})}{n(^{234}\text{U})} \times \frac{\lambda_{230Th}-\lambda_{234U}}{\lambda_{234U}}\right) \qquad \textbf{Equation 1}$$

Where t is the age of the uranium sample (in years), and λ_{234U} and λ_{230Th} are the respective decay constants of ^{234}U and ^{230}Th based on their half-lives [13] ($\lambda = \ln 2/T_{1/2}$).

The results of the homogeneity study for the 10 selected units are shown in Figure 4 in analytical sequence. The complete homogeneity results are shown in the Annex 3.

The ages reported in Figure 4 represent the elapsed time between the production of the reference material and the last chemical separation carried out for the homogeneity study. However, the chemical separations for all of the 10 selected units could not be carried out on the same day. Therefore, calculated ages for all selected units were normalised to the same reference date, i.e. the date of the separation of the first series (16 October, 2013 at 14:40 for series A). The known elapsed time between the production date of the material and the separation date is hereafter referred to as the "known age". As shown in Figure 4, good

agreement was obtained within uncertainties between the calculated ages per units, their average and the known age.
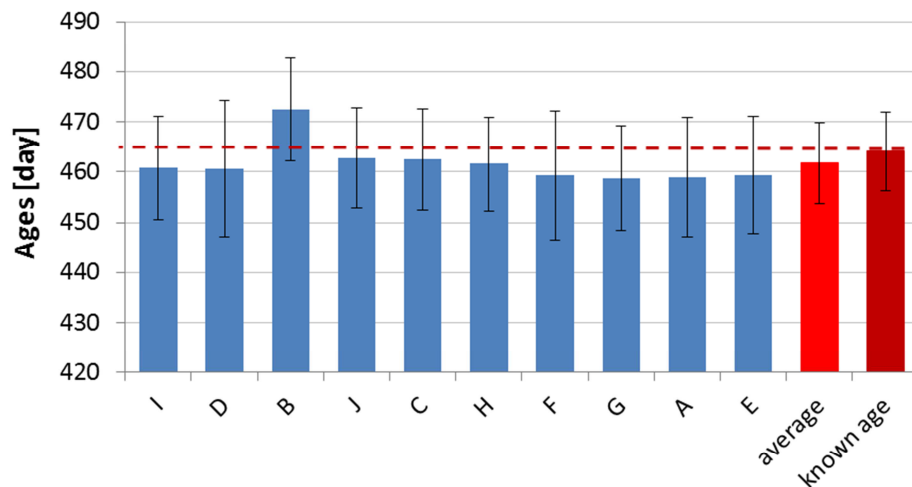
Figure 4 : Calculated ages obtained for the 10 units selected for the homogeneity study (blue), their average and the known age based on the reference value (last column and dashed line) with their expanded uncertainties ($k = 2$).

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends were visible in the filling sequence or the analytical sequence (Figure 5).
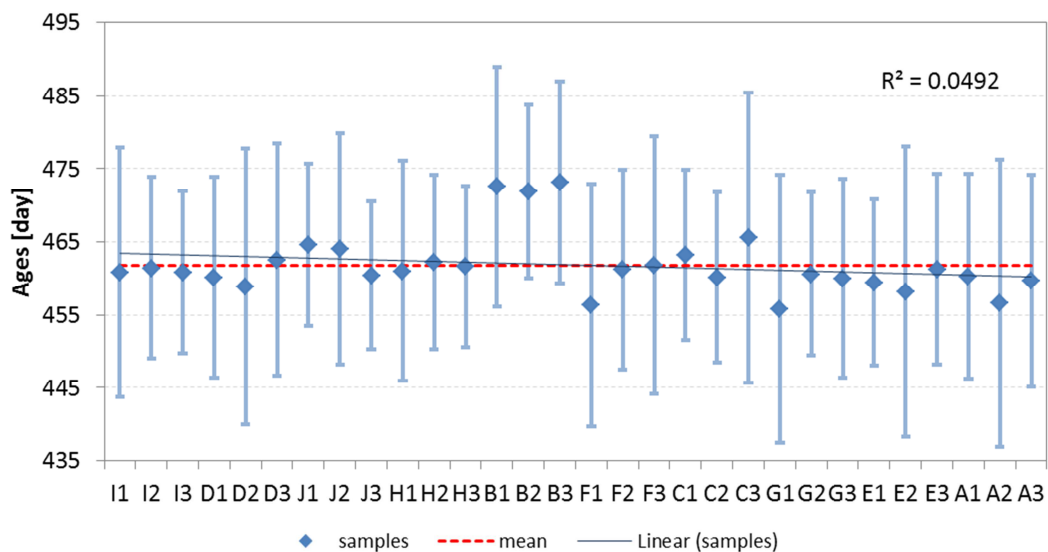
Figure 5: Calculated ages in analytical sequence order for the 30 aliquots (individual measurement points) and their average (dashed line) with expanded uncertainties ($k = 2$), respective regression line and correlation coefficient.

Quantification of between-unit inhomogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole unit [15]. Therefore, the data were checked for any significant difference in between-day means using one way-ANOVA on the samples in analytical sequence order as shown in Figure 5.

Evaluation by ANOVA requires unit means that follow at least unimodal distribution, and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of the statistical evaluations are given in Table 3.

Table 3: Results of the statistical evaluation of the homogeneity study of the ages based on $n(^{230}\text{Th})/n(^{234}\text{U})$

	Trends (before correction)		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
based on $n(^{230}\text{Th})/n(^{234}\text{U})$	no	no	Two	none	normal/ unimodal	normal/ unimodal

The dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Two outlying individual results, corresponding to two aliquots of the same unit (aliquots B1 and B3), were detected for the ages (Grubbs single and double test at $\alpha = 0.01$ on the unit mean and on the individual results respectively). These two aliquots showed higher age than the other samples (Figure 4), because of the higher ^{232}Th measured in the method blank used for the B aliquots than in the other method blanks, thereby leading to an overcorrection of the ^{232}Th signal in these aliquots and a high $^{230}\text{Th}/^{232}\text{Th}$ isotopic ratio. However since no technical reason for the outliers was found and all the results agree well within uncertainties, these two aliquots were not discarded as outliers. Therefore all the data were taken into account for the statistical analysis.

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean square within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [15]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\overline{y}}$$

Equation 2

$$s_{bb,rel} = \frac{\sqrt{\dfrac{MS_{between} - MS_{within}}{n}}}{\overline{y}}$$

Equation 3

$$u^*_{bb,rel} = \frac{\sqrt{\dfrac{MS_{within}}{n}}\sqrt[4]{\dfrac{2}{v_{MSwithin}}}}{\overline{y}}$$

Equation 4

| | MS_{within} | mean square within a unit from an ANOVA |
| MS_{within} | mean square within a unit from an ANOVA |

MS_{within} — mean square within a unit from an ANOVA

$MS_{between}$ — mean squares between-unit from an ANOVA

$\overline{y}$ — mean of all results of the homogeneity study

n — mean number of replicates per unit

$v_{MSwithin}$ — degrees of freedom of MS_{within}

The results of the evaluation of the between-unit variation are summarised in Table 4. The resulting values from the above equations were converted into relative uncertainties.

Table 4: Results of the homogeneity study

	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
based on $n(^{230}\text{Th})/n(^{234}\text{U})$	0.43	0.83	0.14	0.83

The homogeneity study showed no outlying unit means or trends in the filling sequence. An inhomogeneity ($u^*_{bb,rel}$) of maximum 0.14 % was found whereas the between-unit variation ($s_{bb,rel}$) was found to be of 0.83 %, and therefore above this limit to detect inhomogeneity. Therefore, the between-unit standard deviation can be used as estimate of u_{bb} and s_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

There is no minimum sample intake to be taken into account.

5 Stability

The IRMM-1000a and IRMM-1000b are uranium reference materials and consist of uranium isotopes and their decay-products. Consequently, the isotope amount ratios and amount contents in this reference material are unstable by nature following the law of radioactive decay, depending on the half-lives of these isotopes as given in [13,16]. However, the IRMM-1000a and IRMM-1000b are certified for the production date of this uranium reference material based on the $^{230}\text{Th}/^{234}\text{U}$ radiochronometer. Therefore, the certified value is not subject to any instability by itself, and stability testing was only used here to establish the reproducibility over time of the measurement procedure [17,18].

The short-term stability study was carried out together with the homogeneity study, whereas the long-term stability was investigated during a separate study (more than two years after the production of IRMM-1000a and IRMM-1000b).

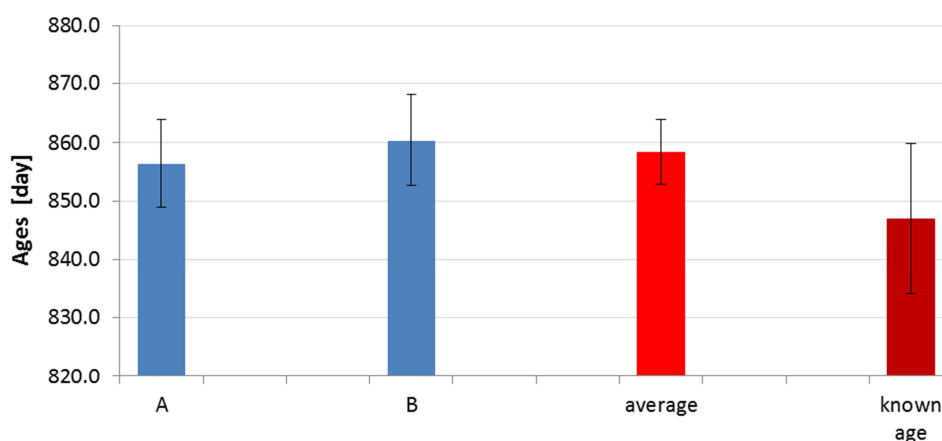## 5.1 Short-term stability study

The short-term stability assessment has been carried out in combination with the homogeneity assessment on the two sizes of IRMM-1000 units more than one year after their production and storage under ambient conditions. Therefore, this study encompasses

the effects on the reference value (i.e. date) inherent to the short-term stability since it has been carried out for beyond the time required for any regular transport of the CRM to its customer.

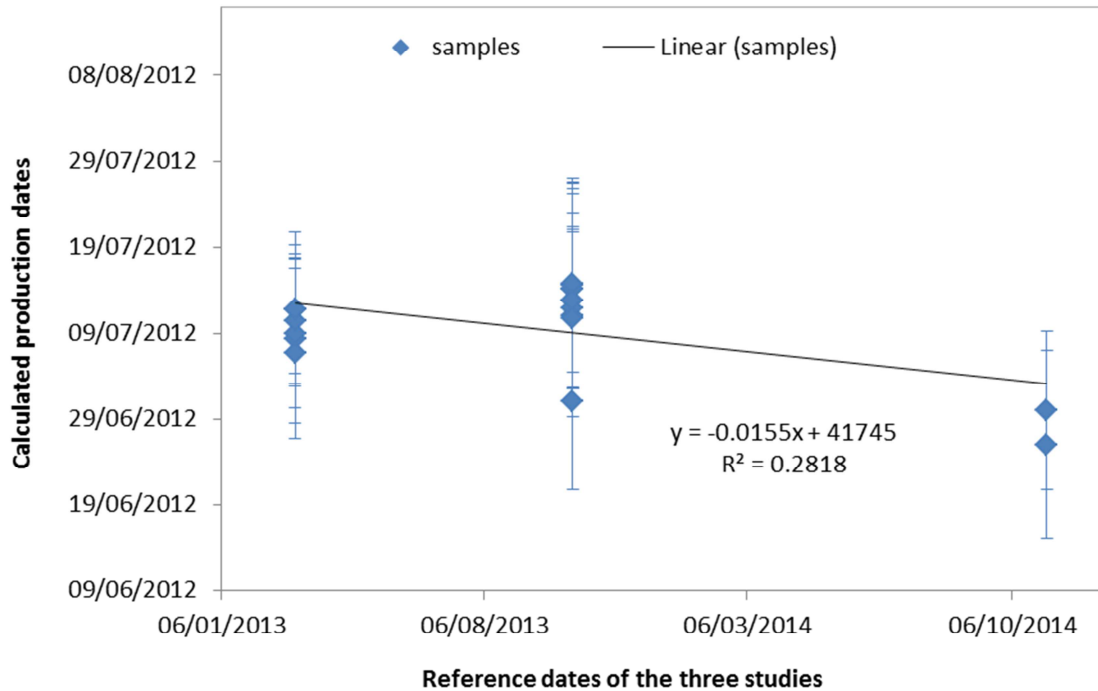## 5.2 Long-term stability study

The long-term stability study was carried out more than two years after the production of IRMM-1000a and IRMM-1000b, with the chemical separation taking place on 3 November, 2014 at 10:53 a.m.

Two 20 mg uranium samples (referred hereafter as A and B) were selected and analysed by ICP-MS at JRC-ITU following the same analytical procedure as described in Section 4.1, i.e. with three aliquots for the thorium analysis and two aliquot measurements for the uranium analysis. All the thorium aliquots were separated and measured with ICP-MS within one day and all the uranium aliquots were measured with ICP-MS the following day. Therefore, the measured ages for the samples did not need to be normalised to a common reference date and could be directly compared with each other and the known age. The age results and the average of the two samples in the long-term stability study are presented in Figure 6 and agree within uncertainties with the known age.

Figure 6: Measured ages for the 2 units selected for the long-term stability study (blue), their average (red) and the known age based on the reference value (dark red) with expanded uncertainties ($k = 2$).

Because of the number of samples (lower than 3) a conventional single and double Grubbs test at 99 % confidence level could not be performed to check for outliers. However, the straight line of the normal probability plot of the results of the long term stability measurements on the six aliquots showed that there were no outliers and therefore, all data were retained for statistical analysis.

Figure 7: Calculated production dates (N = 18) with their expanded uncertainties (*k* = 2) at the dates of the three studies: confirmation (see Section 6.2), homogeneity and long-term stability.

Furthermore, the data were plotted against the elapsed time between the confirmation (see Section 6.3) and the long-term stability studies, i.e. taking into account all the results from the different certification studies (see Annex 5) and linear regression lines of production dates versus time were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to storage conditions). The slope was not significantly different from zero on a 99 % confidence level at room temperature.

No technically unexplained outliers were observed and none of the trends was statistically significant on a 99 % confidence level at room temperature. The material can therefore be stored at room temperature.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be that there is no detectable degradation.

Uncertainties of stability during storage were estimated as described in [18]. For this approach, the uncertainty of the linear regression line with a slope of zero was calculated (see Figure 7). The uncertainty contribution u_{lts} was calculated as the product of the chosen shelf-life and the uncertainty of the regression lines as:

$$u_{lts} = \frac{SD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl}$$

Equation 5

SD   standard deviation of all results of the stability study

x_i	result at a point of time i (these are the following: 240.6 days, 464.6 days and 847.5 days)
$\bar{x}$	mean results for all time points (432.5 days)
t_{sl}	chosen shelf life (2 years or 732 days, at room temperature)

where u_{lts} is the stability during storage. This uncertainty contribution was estimated from samples stored at room temperature and describes the possible degradation during two years storage at room temperature.

The calculated u_{lts} for the production dates from the three studies over time demonstrated that the storage contribution was not negligible compared to the characterisation and homogeneity and had to be taken into account into the final uncertainty of the CRM with u_{lts} = 5.20 days for a two-year shelf-life.

As no significant degradation during dispatch was found, the material can be transported at ambient conditions without special precautions.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

6 Characterisation

The material characterisation is the process of determining the property value of a reference material.

The material characterisation was based on a primary method of measurement, confirmed by an independent method. A primary method of measurement, also called "primary reference method" in the International Vocabulary of Metrology (VIM) [19] is a method that does not require calibration with a standard of the same measurand and does not depend on a chemical reaction. Such methods are of highest metrological order and often yield results with low uncertainties. However, it is nevertheless prudent to demonstrate absence of bias or gross errors by use of an independent method of lower metrological order.

6.1 Method used

The method used for the production, confirmation, homogeneity and stability assessments is a validated analytical method, routinely used at JRC-ITU, Karlsruhe, and described in [10-12].

6.2 Confirmation study

Confirmation measurements were carried out on 6 March, 2013 at the JRC-ITU in compliance with ISO Guide 34 [1] after ingrowth of Th in the uranium reference material to assess if the measured age corresponded to the known production date. This confirmation step consisted of the analysis of six sets of randomly selected units of 20 mg out of the entire batch of produced units.

The six sets of randomly selected units of 20 mg were dissolved in 2 mL concentrated nitric acid respectively, resulting in a U concentration of ~ 10 mg·mL^{-1} of total U and about 1 pg of ^{230}Th per measured aliquot, seven months after the production of IRMM-1000. Subsequently, aliquots were prepared gravimetrically and by dilutions from the 2 mL dissolved samples in order to measure the uranium isotopes and amount concentrations by ID-TIMS and ICP-MS, and the thorium isotopes and amount concentrations by ICP-MS on an Element 2 instrument.

For the isotope dilution measurements, a ^{233}U spike (same as for the homogeneity study) was used to determine the uranium amount content in the uranium aliquots, and two aliquots were spiked with two different natural ^{232}Th spikes (noted Th#2 and Th#3) to determine the

thorium amount content. With each of the six sets (referred as A, B, C, D, E and F), a blank (using 2 mL concentrated nitric acid) and an unspiked sample were prepared as well. In total 36 samples were analysed for the thorium IDMS, numbered as follows: 1-Blank, 2-unspiked, 3-4 samples spiked with Th#2 and 5-6 spiked with Th#3.

Each sample was chemically separated using TEVA® Resin and measured using ICP-MS on the Element 2, following a similar protocol for the mass spectrometry measurements to the one used in the homogeneity study and described in Section 4.1.

As in the homogeneity study, all the ages were normalised to the same reference date, i.e. the date of the separation of the first series (6 March 2013, at 15:30 for series A) so that all ages can be compared. The calculated/measured production dates in dd/mm/yyyy are reported with their expanded uncertainties ($k = 2$) in Figure 8 and compared with the known production date of the reference material, i.e. 9 July, 2012.
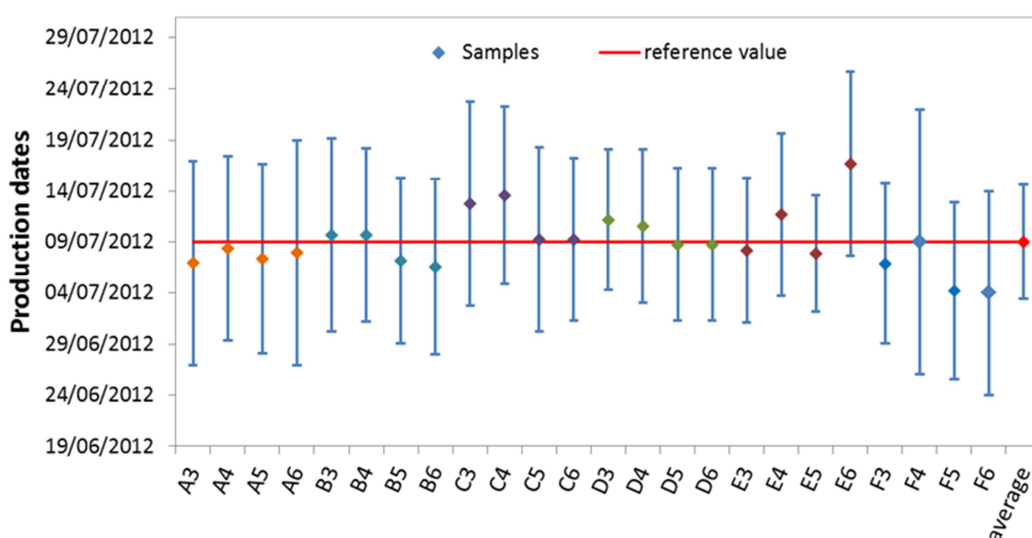
Figure 8: Production dates as calculated from the 'measured' ages for the 24 samples (diamond symbols) for the confirmation study, the reference value (red line) and their associated expanded uncertainties ($k = 2$). Diamond symbols are colour coded according sample set, A through F.

Figure 8 confirms that there is no significant difference between the calculated production dates per aliquot and single unit, their average and the known production date. The good agreement of the average of all the production dates with the reference value (as shown in Annex 4) confirms the completeness of the separation of the thorium from the uranium matrix during the production of the uranium reference material.

The combined standard uncertainty inherent to the production of the reference material includes:

- the uncertainty on the exact time of the last chemical separation; i.e. the uncertainty on the time interval necessary for the last separation of Th from the U material, which was estimated to be 1.5 hours (90 min or 0.063 days, $k = 1$) in order to account for the whole thorium elution time

- the uncertainty from the residual ^{230}Th in the reference material during its production, which could be translated into less than 0.056 days ($k = 1$).

The combined standard uncertainty for the characterisation is therefore 0.084 days ($k = 1$).

7 Value Assignment

Certified values are values that fulfil the highest standards of accuracy.

The certified value of IRMM-1000a and IRMM-1000b is the production date based on the ^{230}Th/^{234}U radiochronometer and was assigned as the date of the last chemical separation, i.e. when the radionuclide ^{230}Th was removed to the maximum extent achievable from its "parent radionuclide"- ^{234}U in the original uranium nitrate material (see Section 3.2). It is expressed as a date in dd/mm/yyyy (UTC) and its expanded uncertainty (*k=2*) is given in day. It is therefore identical for both IRMM-1000a and IRMM-1000b since both unit sizes were aliquoted from the same final solution. Full uncertainty budgets (Table 5) were established in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [4].

Finally, the assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 6.2), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and the uncertainty related to degradation during long-term storage, u_{lts} (Section 5.3).

These different contributions were combined to estimate the expanded uncertainty of the certified value (U_{CRM}) with a coverage factor *k* as:

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2}$$ **Equation 6**

- u_{char} was estimated as described in Section 6

- u_{bb} was estimated as described in Section 4.1

- u_{lts} was estimated as described in Section 5.3

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor *k* of 2 was applied, to obtain the expanded uncertainties.

The certified value and its uncertainty are summarised in Table 5.

Table 5: IRMM-1000a/IRMM-1000b certified value and its uncertainty contributions

IRMM-1000a IRMM-1000b	Certified value dd/mm/yyyy	u_{char} [a] [day]	u_{bb} [a] [day]	u_{lts} [a] [day]	U_{CRM} [b] [day]
Production date based on $n(^{230}$Th$)/n(^{234}$U$)$ radiochronometer	09/07/2012	0.084	3.88	5.20	13

[a] Standard uncertainties, not rounded

[b] Expanded and rounded uncertainty (*k = 2*)

8 Metrological traceability and commutability

8.1 Metrological traceability

The certified value is the production date of the uranium material based on the ^{230}Th/^{234}U radiochronometer, which corresponds to the date of the last chemical separation of ^{230}Th from ^{234}U in the uranium reference material. The uncertainty of the certified value is traceable to the International System of units (SI).

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific 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 [20] 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 an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, 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.

This reference material is tailor-made by JRC-IRMM and is intended to be used as a calibrant for age determination in uranium material, mainly by the nuclear forensics and safeguards communities.

9   Instructions for use

9.1   Safety information

The usual laboratory safety measures apply for the handling of radioactive/nuclear material.

9.2   Storage conditions

The materials shall be stored at room temperature.

The user is reminded to close the vial(s) immediately after taking the sample.

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 vials.

9.3   Preparation and use of the material

The IRMM-1000a and IRMM-1000b are intended to be used as a calibrant, using the reference value/production date of CRM and its uncertainty for age determination of uranium materials. There are no specific recommendations for the use or conditioning of this CRM.

9.4   Minimum sample intake

There is no minimum sample intake to be taken into account.

9.5   Use of the certified value

The main purpose of this material is to assess method performance, i.e. for checking accuracy of analytical results and calibration. As any reference material, it can also be used for control charts 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 (see also ERM Application Note 1, www.erm-crm.org [21]).

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 mean measured value and the certified value (Δ_{meas})

- Combine 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_Δ) 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

<u>Use for quality control purpose</u>

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

10 Acknowledgments

11 References

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[21]   Linsinger, T.P.J., ERM Application Note 1: Comparison of a measurement result with the certified value, www.erm-crm.org (last accessed on 14/05/2014).

Annexes

Annex 1 Protocol for U-Th separation on TEVA columns based on [11,12]

Annex 2 Results of IDMS-TIMS analysis of the uranium isotope ratios for the homogeneity test
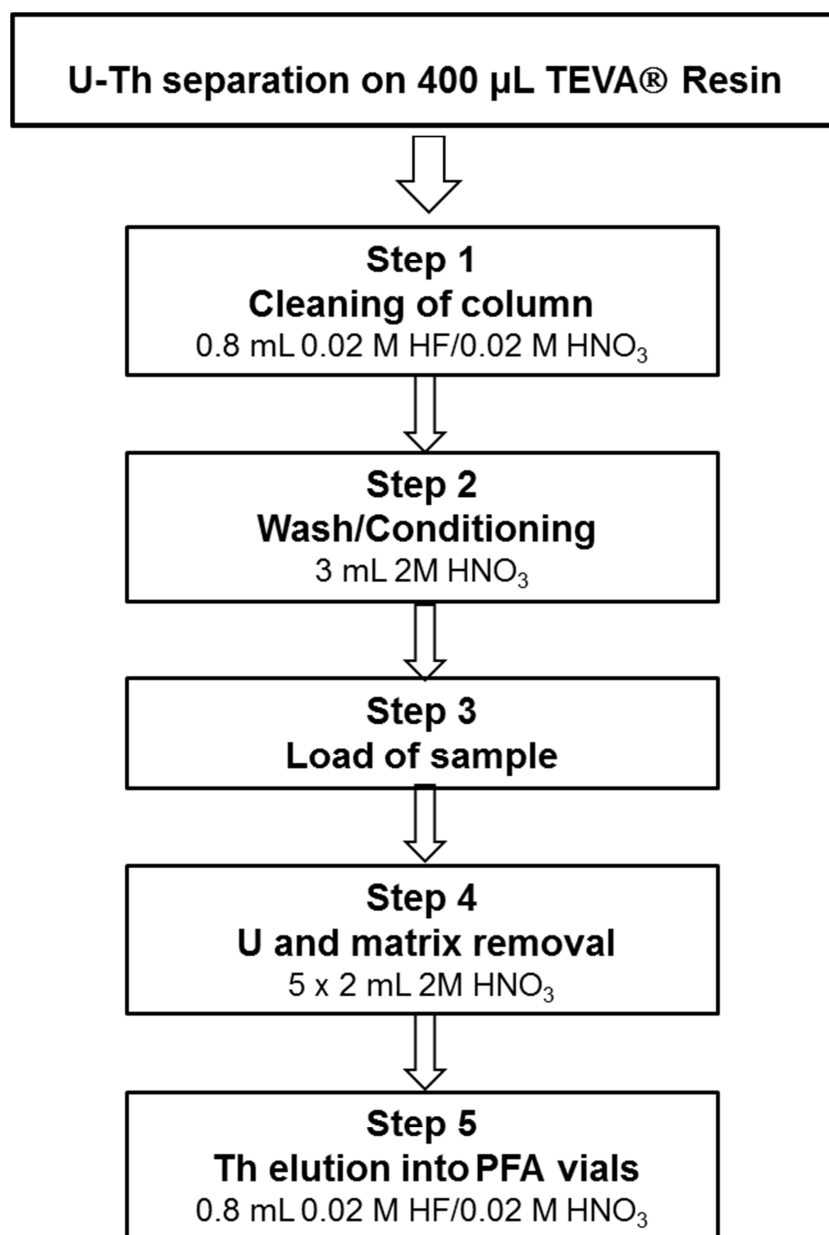
Annex 3 Homogeneity results for the ages [day] of the 30 samples (5 units of 20 mg uranium and 5 units of 50 mg uranium, with 3 aliquots per unit)

Annex 4 Results of the confirmation study on the 24 selected samples (six sets of randomly selected units of 20 mg uranium with four aliquots per set)

Annex 5 Measurement results used for the evaluation of the u_{lts} for the long-term stability study

Annex 1   Protocol for U-Th separation on TEVA® columns based on [11, 12]

U-Th separation on 400 µL TEVA® Resin

Step 1
Cleaning of column
0.8 mL 0.02 M HF/0.02 M HNO$_3$

Step 2
Wash/Conditioning
3 mL 2M HNO$_3$

Step 3
Load of sample

Step 4
U and matrix removal
5 x 2 mL 2M HNO$_3$

Step 5
Th elution into PFA vials
0.8 mL 0.02 M HF/0.02 M HNO$_3$

Note: During the production of the IRMM-1000a and IRMM-1000b units, the solution containing uranium (after step 4) was kept and purified by repeating steps 1-5 three other times. For the confirmation, homogeneity and stability assessments, a similar protocol, with some modifications of the amounts of samples and eluents used, was carried out only once per sample, yielding the recovery of the purified Th fraction after step 5 to be measured by ICP-MS.

Annex 2 Results of IDMS-TIMS analysis of the uranium isotope ratios for the homogeneity test

EUROPEAN COMMISSION
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Institute for Transuranium Elements
Nuclear Safeguards and Forensics

TMP0002/S5/R8
Issued on: 24/02/2014

Analysis Result

Request n° SG140004

1. Client and Sample Identification

Client	Firm/Organisation/Unit/Section	Project	Arrival Date	
			Request	Sample(s)
A. Nicholl	Institute for Transuranium Elements	700	27/01/2014	27/01/2014

Sample ID	Sample Type	Requested Analysis	Observations
Reimep22A			
Reimep22B			
Reimep22C			
Reimep22D			
Reimep22E	U nitrate solution	U isotopic composition	N.A.
Reimep22F			
Reimep22G			
Reimep22H			
Reimep22I			
Reimep22J			

2. Analyses Performed

Measurand	Method	Remarks
U isotopic composition	MTE[a] according with WI0397	N.A.

[a] Modified total evaporation

3. Results

All uncertainties are expanded uncertainties $U = k u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They include a coverage factor $k = 1$. The expressed uncertainties are relative uncertainties.

RESULTS ARE VALID WITHOUT SIGNATURE
Name: Hélène Schorlé   (Data Manager)

Date: 22/05/2014	Request: SG140004	Version: 1	Page 1 of 3

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JOINT RESEARCH CENTRE

Institute for Transuranium Elements
Nuclear Safeguards and Forensics

TMP0002/S5/R8
Issued on: 24/02/2014

Table 1. Uranium isotopic composition measured by MTE-TIMS

Sample ID	Isotope / Element	Mass fraction (Wt %)	Uncertainty [k=1, Rel. (%)]	Measurement date	Reference date
Reimep22A	U^{234}	0.028561	0.050	07/02/2014	N.A.
	U^{235}	3.6080	0.037		
	U^{236}	0.089860	0.028		
	U^{238}	96.274	0.021		
Reimep22B	U^{234}	0.028555	0.059	07/02/2014	N.A.
	U^{235}	3.6075	0.043		
	U^{236}	0.089850	0.034		
	U^{238}	96.274	0.021		
Reimep22C	U^{234}	0.028572	0.052	07/02/2014	N.A.
	U^{235}	3.6076	0.034		
	U^{236}	0.089872	0.026		
	U^{238}	96.274	0.021		
Reimep22D	U^{234}	0.028569	0.048	07/02/2014	N.A.
	U^{235}	3.6080	0.034		
	U^{236}	0.089883	0.027		
	U^{238}	96.274	0.021		
Reimep22E	U^{234}	0.028557	0.054	14/02/2014	N.A.
	U^{235}	3.6082	0.037		
	U^{236}	0.089864	0.029		
	U^{238}	96.273	0.021		
Reimep22F	U^{234}	0.028551	0.048	10/02/2014	N.A.
	U^{235}	3.6079	0.035		
	U^{236}	0.089867	0.026		
	U^{238}	96.274	0.021		
Reimep22G	U^{234}	0.028565	0.049	10/02/2014	N.A.
	U^{235}	3.6081	0.035		
	U^{236}	0.089878	0.029		
	U^{238}	96.273	0.021		
Reimep22H	U^{234}	0.028574	0.060	10/02/2014	N.A.
	U^{235}	3.6077	0.033		
	U^{236}	0.089874	0.028		
	U^{238}	96.274	0.021		
Reimep22I	U^{234}	0.028554	0.046	20/05/2014	N.A.
	U^{235}	3.6074	0.034		
	U^{236}	0.089844	0.028		
	U^{238}	96.274	0.021		
Reimep22J	U^{234}	0.028551	0.047	14/02/2014	N.A.
	U^{235}	3.6082	0.034		
	U^{236}	0.089871	0.026		
	U^{238}	96.273	0.021		

RESULTS ARE VALID WITHOUT SIGNATURE
Name: Hélène Schorlé   (Data Manager)

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Annex 3 Results for the ages [day] of the 30 samples (5 units of 20 mg uranium and 5 units of 50 mg uranium, with 3 aliquots per unit) in the homogeneity study

IRMM-1000	Ages [day]		
Selected Units	Aliquot 1	Aliquot 2	Aliquot 3
A	460.3	456.6	459.7
B	472.5	471.9	473.1
C	463.2	460.1	465.6
D	460.1	458.9	462.6
E	459.4	458.9	461.2
F	456.3	461.2	461.8
G	455.7	460.6	460.0
H	461.0	462.2	461.6
I	460.8	461.4	460.8
J	464.6	464.0	460.4
Mean	461.9		
Known age[a]	464.2		

[a] The known age is defined as the elapsed time between the production date of IRMM-1000a and IRMM-1000b (i.e. 9 July, 2012) and the reference date of the sample analysis for the homogeneity study (i.e. 16 October, 2013) as described in Section 4.1.

Annex 4 Results of the confirmation study on the 24 selected samples (six sets of randomly selected units of 20 mg uranium with four aliquots per set)

Aliquots	Ages [day]	U [day] k = 2	Production dates [dd/mm/yyyy]	U [day] k = 2
A3	242.0	10	07/07/2012	10
A4	240.6	9.0	08/07/2012	9.0
A5	241.6	9.3	07/07/2012	9.3
A6	241.0	11.0	08/07/2012	11.0
B3	239.3	9.5	09/07/2012	9.5
B4	239.3	8.5	09/07/2012	8.5
B5	241.8	8.1	07/07/2012	8.1
B6	242.4	8.6	06/07/2012	8.6
C3	236.2	10.0	12/07/2012	10.0
C4	235.4	8.7	13/07/2012	8.7
C5	239.7	9.0	09/07/2012	9.0
C6	239.7	8.0	09/07/2012	8.0
D3	237.8	6.9	11/07/2012	6.9
D4	238.4	7.5	10/07/2012	7.5
D5	240.2	7.5	08/07/2012	7.5
D6	240.2	7.5	08/07/2012	7.5
E3	240.8	7.1	08/07/2012	7.1
E4	237.3	8.0	11/07/2012	8.0
E5	241.1	5.7	07/07/2012	5.7
E6	232.3	9.0	16/07/2012	9.0
F3	242.1	7.8	06/07/2012	7.8
F4	240.0	13.0	09/07/2012	13
F5	244.8	8.7	04/07/2012	8.7
F6	245.0	10	04/07/2012	10.0
Mean	240.0	5.6[b]	09/07/2012	5.6[b]
Reference value	240.0[a]	0.17[c]	09/07/2012	0.17[c]

(a) The known age is here defined as the elapsed time between the production date of the IRMM-1000a (i.e. 9 July, 2012) and the reference date for the confirmation analysis (i.e. 6 March, 2013) as described in Section 6.2

(b) The uncertainties (in day) on the mean of the ages and production dates is calculated as 2·SD

(c) The uncertainty of the reference value (as known age or production date) reported in the table above corresponds to the known expanded uncertainty at the time of the confirmation study (i.e. on 6 March, 2013)

Annex 5 Measurement results used for the evaluation of the u_{lts} for the long-term stability study

Samples per studies	Production dates dd/mm/yyyy	U [day, *k = 2*]
A [a]	08/07/2012	9.8
B	08/07/2012	8.7
C	11/07/2012	8.9
D	10/07/2012	7.4
E	11/07/2012	7.5
F	06/07/2012	9.9
A [b]	14/07/2012	11.8
B	01/07/2012	10.3
C	11/07/2012	10.0
D	12/07/2012	13.6
E	14/07/2012	11.6
F	14/07/2012	12.7
G	14/07/2012	10.4
H	11/07/2012	9.4
I	12/07/2012	10.2
J	10/07/2012	9.9
A [c]	30/06/2012	9.2
B	26/06/2012	11.0
Mean	*09/07/2012*	*10.8* [d]

[a] Samples measured for the confirmation study on 6 March, 2013

[b] Samples measured for the homogeneity study on 16 October, 2013

[c] Samples measured for the long-term stability study on 3 November, 2014

[d] The expanded uncertainty (in day) on the mean of the production dates is calculated as $2 \cdot SD$

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