



A new series of uranium isotope reference materials for investigating the linearity of secondary electron multipliers in isotope mass spectrometry

S. Richter^{a,*}, A. Alonso^a, Y. Aregbe^a, R. Eykens^a, F. Kehoe^a, H. Kühn^a, N. Kivel^b,
A. Verbruggen^a, R. Wellum^a, P.D.P. Taylor^a

^a Institute for Reference Materials and Measurements, JRC-EU Retieseweg 111, 2440 Geel, Belgium

^b Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

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ABSTRACT

A new series of gravimetrically prepared uranium isotope reference materials, the so-called IRMM-074 series, with the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio held constant at unity and the $n(^{233}\text{U})/n(^{238}\text{U})$ isotope ratios varying from 1.0 to 10^{-6} has been prepared and certified. This series is suited for calibration of secondary electron multipliers used widely in isotope mass spectrometry, in particular for techniques such as thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICPMS), accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS). The new IRMM-074 was prepared as a replacement for the already exhausted IRMM-072 predecessor series.

Uranium materials with high isotopic enrichments of ^{233}U , ^{235}U and ^{238}U were purified using identical methods involving separation on anion and cation column followed by a precipitation as peroxide. The oxides were calcined to convert them to U_3O_8 simultaneously, in an oven installed in a glove-box that provided a controlled low-humidity environment. The oxides of ^{235}U and ^{238}U were weighed and mixed with a mole ratio $n(^{235}\text{U})/n(^{238}\text{U}) = 1.0$ and then dissolved. The ^{233}U oxide was dissolved to form a separate solution with the same concentration and from this primary solution three dilutions were made by weighing. A weighed amount of the $n(^{235}\text{U})/n(^{238}\text{U})$ solution and weighed amounts of the ^{233}U solutions were mixed in various proportions in order to achieve $n(^{233}\text{U})/n(^{238}\text{U})$ isotope ratios varying from 1.0 to 10^{-6} . The methods for the preparation, the mixing and the mixing calculations are described. The expanded uncertainties (coverage factor $k=2$) of the certified isotope ratios for the IRMM-074 series are 0.015% for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio and 0.025% for the $n(^{233}\text{U})/n(^{238}\text{U})$ ratios, which constitutes an improvement compared to those of the predecessor IRMM-072 series.

In addition, recent observations regarding the linearity response of secondary electron multipliers (SEMs) and suitable reference materials for investigating detector linearity are reviewed. Two measurement procedures for applying the IRMM-072 and IRMM-073 (diluted from the remaining fraction of IRMM-072) series as well as the new IRMM-074 series for assessing SEM linearity are suggested. The procedures are tailor-made for the specific instrumental characteristics of thermal ionization mass spectrometers (TIMS) and multiple-collector inductively coupled plasma mass spectrometers (MC-ICPMS) but can be adapted also for further types of isotope ratio mass spectrometers.

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1. Introduction

In isotope ratio mass spectrometry there is a recognized need for certified isotopic reference materials. In particular for nuclear safeguards, the elements of interest are uranium and plutonium. The measurement of uranium by mass spectrometry is a special challenge because of the very wide dynamic range of the isotope abundances typically found in nature as well as in samples

of the nuclear fuel cycle. During the recent years a programme has been carried out at IRMM to replace the series of certified isotopic reference materials (IRM), IRMM-072, which was prepared some 25 years ago and which has been shown to have the highest quality of certified isotope ratios [1,2]. IRMM-072 was prepared gravimetrically from purified, highly enriched uranium isotopic material of ^{233}U , ^{235}U and ^{238}U . The IRMM-072 series consisted of 15 individual IRMs; in each of these the isotopic ratio $n(^{235}\text{U})/n(^{238}\text{U})$ was held constant at a value close to unity and $n(^{233}\text{U})/n(^{235}\text{U})$ varied in 15 steps across the series from 1.0 to down to 1.0×10^{-6} . The U concentration in IRMM-072 was 1 mg U/mL of solution for each of the 15 samples of the entire set. That

* Corresponding author. Tel.: +32 14 571701; fax: +32 14 571863.

E-mail address: stephan.richter@ec.europa.eu (S. Richter).

was a concentration for easy use in mass spectrometry laboratories.

In 2002, part of the remaining material of IRMM-072 was diluted in order to make this material also available for use in environmental uranium mass spectrometry. The U concentration of the diluted series, the so-called IRMM-073 series [3], was adjusted to 0.003 mg U/mL. The entire set has a total activity just below 1000 Bq in order to facilitate application and shipment for laboratories working in environmental fields.

But because of the usefulness and general popularity of the IRMM-072 series, it became clear some years ago that a replacement would have to be made and certified. The original methods had to be rediscovered and where necessary adapted to present conditions. In particular the dynamic range of $1:10^{-6}$ was to be retained but fewer members in the set were deemed to be needed.

This paper describes the preparation and certification of a new series, the certified isotopic reference material 'IRMM-074'. The 2 series IRMM-073/-074 are to be used for the investigation of mass spectrometer linearity, in particular for SEM detectors. The linearity response of a detector can be determined by measuring the ratio $n(^{233}\text{U})/n(^{235}\text{U})$ across the IRMM-074 series, while the certified $n(^{235}\text{U})/n(^{238}\text{U})$ isotopic ratios allow an internal correction of the mass fractionation within the ion source of the mass spectrometer. This paper also reviews the major past observations regarding the linearity response of SEMs and furthermore suggests new procedures to assess and correct for possible non-linearity effects of secondary electron multipliers (SEMs) using the new IRMM-074 isotope reference material.

2. Linearity of secondary electron multipliers

Linearity of a detector such as an SEM is expressed by a linear relationship between the sample ion current hitting the SEM and the output signal, e.g., output count rate. For this linear relationship, the intercept represents the so-called dark count rate, which is the output count rate registered by the counting electronics in the case where there are no incident ions. The dark count rate has to be measured and corrected for and is usually small compared to the measured count rates. The slope of the linear relationship represents the relative efficiency of the SEM, which is the ratio between the measured count rate (corrected for dark noise) and the true rate of ions entering the SEM. If a SEM is truly linear, the relative efficiency, an inherent property of the SEM, is independent of the count rate applied to the SEM, and therefore any ratio of ion currents from different isotopes equals the ratio of the respective output count rates.

In order to perform linearity checks in isotope mass spectrometry, suitable IRMs are needed that have multiple isotopes differing in relative abundances by several orders of magnitude. An additional advantageous feature is to have two isotopes whose ratio is close to unity, which can be used for internal mass fractionation correction without being influenced by possible non-linearity effects. Due to their design the IRMM-072, IRMM-073 (diluted from a fraction of IRMM-072 [3]) and IRMM-074 series fulfil this requirement. They are particularly useful for linearity investigations of SEMs, which are widely used detectors in various fields of isotope mass spectrometry.

Due to the large range of applications and the strengthened requirements for precision and accuracy for isotope ratio measurements, both in nuclear safeguards and geological sciences, linearity investigations for SEMs have become a matter of increased concern within recent years.

As a starting point, the paper by Rosman et al. [1] in 1987 described the use of IRMM-072 for SEM linearity testing and presented how far from ideal the behaviour of SEMs can actually be. Significant deviations of up to 3% for the measured $n(^{233}\text{U})/n(^{235}\text{U})$

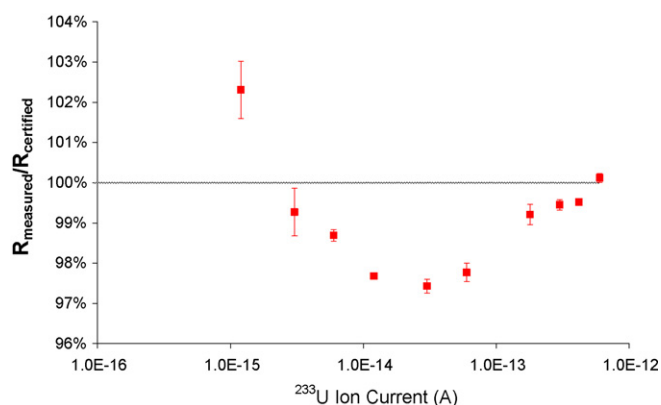


Fig. 1. Results of a linearity check using the IRMM-072 series, applied to a SEM operated in analogue mode.

ratios from the certified ones were observed, see Fig. 1. For this investigation the SEM was operated in analogue mode, which excludes the dead time of any pulse counting system to be responsible for the observation. Because this size of deviation is unlikely to be caused by a non-linearity of the amplifier electronics, it probably originated in the SEM detector itself.

Since sufficiently fast pulse amplifiers and pulse counting systems have become available, most SEMs are usually operated in the pulse counting mode (also called ion counting mode) rather than in analogue mode. The advantage of the pulse counting mode is the much lower background noise. But the observation made by Rosman et al [1] shows clearly that SEM detectors may exhibit their own non-linearity effects. Thus even for SEMs operated in ion counting mode non-linearity effects cannot be directly attributed to the dead time of the pulse amplifier or pulse counting electronics. The assumption, often made, that linearity testing of SEMs is equivalent with dead time determination has to be re-considered very carefully in each case.

Thus the linearity of an SEM operated in ion counting mode is dependent on the linearity of two components, firstly the SEM detector itself and secondly the pulse counting system. The mathematical dependence of the SEM efficiency on the input count rate might have different characteristics for these two components, e.g., the SEM itself could have a logarithmical characteristic (see below) whereby the pulse counting system always has a quite linear characteristics due to the dead time effect (in first order, for moderate count rates). A possibly third component, the dead time of the SEM itself is usually shorter (less than 10 ns) and therefore completely covered by the dead time of the pulse amplifier (20–70 ns), which is often fixed electronically to be more stable over time.

In order to investigate the combined system of the SEM itself and the pulse counting system, first the dead time of the pulse amplifier has to be determined independently from the SEM detector. This can be done for instance by applying artificial double pulses from a pulse generator to the input of the pulse counting system and increasing the delay time between the two input pulses until the second output pulse appears, using an oscilloscope to determine this. This dead time result can be used to apply a correction for mass spectrometric measurements using the SEM detector, and can then also allow possible existing residual non-linearities of the SEM detector to be observed. This kind of dead time determination using electronic means has also been discussed [4] and provides quite reliable results. A slight disadvantage of this method is given by the fact that the time reading on an oscilloscope cannot always be considered traceable to the SI system, whereas the dead time determination using SI-traceable isotopic reference materials provides SI-traceable correction parameters with usually smaller uncertainties.

The distinction between the dead time related non-linearity of the pulse counting system and a poorly understood additional component originating from the SEM detector itself was also emphasized by Cheng et al. [5]. Additionally Cheng et al. reported differences in the linearity behaviour between Al-dynode SEMs from ETP (ETP-SGE, 31 Hope Street, Ermington, NSW 2115) and Cu-Be-dynode MassCom (Norderoog 1, Bremen, Germany). The ETP multipliers showed a relatively enhanced counting efficiency for higher ion currents of up to 0.8%; the effect for MassCom SEMs is much smaller and more stable. But for SEMs from MassCom a mass-dependent fractionation of up to 0.09% per mass unit was also reported. The very detailed linearity investigations by Cheng et al. [5], based on thermal ionization mass spectrometry (TIMS) measurements, were applied to establish a consensus value for the $n(^{234}\text{U})/n(^{235}\text{U})$ ratio of NBL CRM 112A. A value for the $n(^{234}\text{U})/n(^{235}\text{U})$ ratio in secular equilibrium was presented as well, from which the commonly used value for the ^{234}U half-life was derived [5].

In 2001 at New Brunswick Laboratory (NBL, US DOE) an extensive study of non-linearity effects for SEMs was performed [6]. Using electronically determined values for the dead time of the pulse amplifier this component was corrected for, but for all 6 SEMs investigated in this study significant residual non-linearity effects were observed. Analyses of a certified uranium reference material (NBL U500, characterized by $^{234}\text{U}/^{235}\text{U}/^{236}\text{U}/^{238}\text{U} \approx 0.01/1/0.0015/1$) using SEMs in ion counting mode yielded deviations from linearity ranging up to 1.5% in the measured $n(^{234}\text{U})/n(^{235}\text{U})$ and $n(^{236}\text{U})/n(^{235}\text{U})$ ratios. The fact that the deviations from linearity were the same (within uncertainties) for these two different ratios (by a factor of about seven), led to the conclusion that the deviations are rather originating from the detection of the ^{235}U isotope in the denominator of these ratios. Therefore the deviation from linearity only occurs at those higher count rates, observed for the much more abundant ^{235}U isotope.

From the results for the 6 SEMs investigated at NBL [6] it was concluded that for count rate below a certain limit no deviations occur and consequently no correction was required. Beyond that rate, the output response of the SEM starts to increase linearly with the logarithm of the applied count rate, with slopes ranging between 0.2 and 1.0% per decade of the count rate for the SEMs investigated in this work. The so-called “RLR”-algorithm (“RLR” = restricted logarithmic rate effect) was established:

For $c_{\text{measured}} > c_{\text{limit}}$:

$$c_{\text{corrected}} = c_{\text{measured}} \{1 - m [\log(c_{\text{measured}}) - \log(c_{\text{limit}})]\}$$

For $c_{\text{measured}} = c_{\text{limit}}$: $c_{\text{corrected}} = c_{\text{measured}}$

The parameters varied between SEMs: c_{limit} ranged between 20,000 and 100,000 cps and the slope m ranged between 0.2 and 1.0%. The parameters were also found to change over the lifetime of the SEM and depend slightly on the operating voltage [6].

The RLR correction pattern was verified directly for the entire count rate range from 20,000 to 500,000 cps at IRMM as shown in Fig. 2. This is based on a series of peak-jumping measurement using a sample of IRMM-074/3 with a $n(^{233}\text{U})/n(^{235}\text{U})$ ratio of ca. 0.01, instead of using the similar $n(^{234}\text{U})/n(^{235}\text{U})$ ratio of NBL U500. A logarithmic deviation was observed only for count rates of ^{235}U higher than ca. $c_{\text{limit}} = 100,000$ cps, below this limit no deviation was found. It is obvious from Fig. 2 that the measured $n(^{233}\text{U})/n(^{235}\text{U})$ ratios, divided by certified value for $n(^{233}\text{U})/n(^{235}\text{U})$, decrease with the count rate of ^{235}U , which is corresponding to an increase in the efficiency for counting the more abundant denominator isotope ^{235}U .

The validity of the RLR correction pattern was confirmed by numerous further measurements at various laboratories. A com-

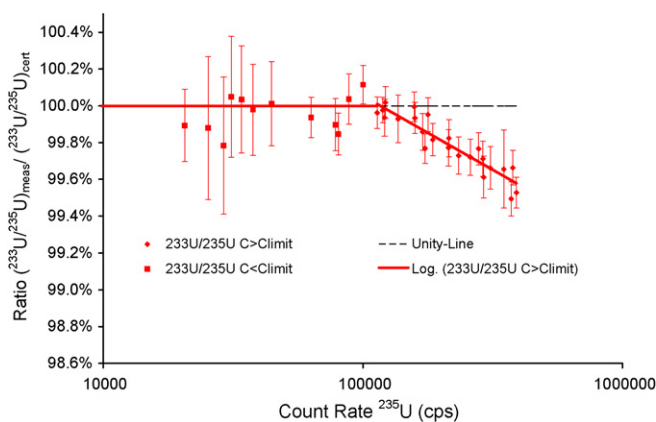


Fig. 2. The RLR (“restricted logarithmic rate effect”) correction pattern was verified directly for the entire count rate range from 20,000 to 500,000 cps. A series of peak-jumping measurements at different beam intensities was performed using a sample of IRMM-074/3 with a $n(^{233}\text{U})/n(^{235}\text{U})$ ratio of about 0.01. The measured $n(^{233}\text{U})/n(^{235}\text{U})$ ratios (divided by certified value for $n(^{233}\text{U})/n(^{235}\text{U})$ in this figure) decrease with the count rate of ^{235}U , which is corresponding to an increase in the efficiency for counting the more abundant denominator isotope ^{235}U . Therefore the SEM response is increasing logarithmically with the count rate, but only for count rates beyond a certain limiting count rate (c_{limit}) of ca. 100,000 cps.

parison of linearity correction patterns for more than 30 SEMs on TIMS instruments is shown in Fig. 3. SEMs from both ETP and MassCom were investigated, but no significant difference was found between the average parameters of them. But as reported already by Cheng et al. [5], the SEMs from ETP have a tendency of exhibiting slightly higher deviations from linearity, even reaching the lower percent range.

It is worth mentioning that the non-linearity is not expected to start sharply at certain count rate value, the response of the SEM can rather be assumed to be a smooth function of the count rate. However, it is difficult to investigate the possible curvature of this function due to limitations from counting statistics. The observed pattern can be conveniently modelled using a discrete nominal threshold. As a conclusion from Fig. 3 it is obvious that all SEMs, or at least the more than 30 SEMs reported here, exhibit a non-linearity pattern with two main characteristics:

1. The SEM response is only linear for count rates below a certain limiting count rate (c_{limit}).

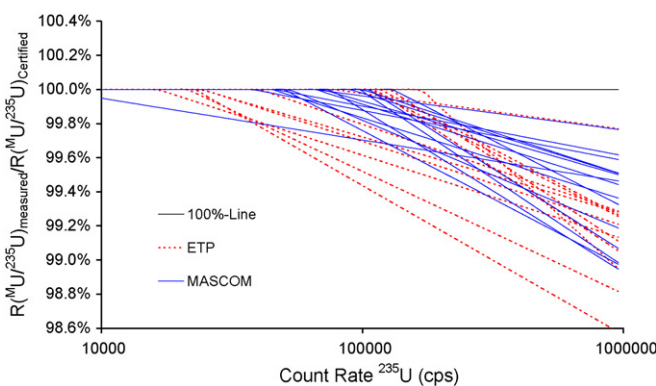


Fig. 3. Compilation of linearity correction patterns for more than 30 SEMs on TIMS instruments at various laboratories. The measured $n(^M\text{U})/n(^{235}\text{U})$ ratios are divided by certified value for $n(^M\text{U})/n(^{235}\text{U})$, where $M=233$ in case IRMM-072/-073/-074 was used, and $M=234$ in case where NBL U500 was used. All these materials are suitable for this purpose due to the fact that the $n(^{238}\text{U})/n(^{235}\text{U})$ ratio is close to unity. SEMs from both ETP (ETP-SGE, 31 Hope Street, Ermington, NSW 2115) and MassCom (Norderoog 1, Bremen, Germany) were investigated, but no significant difference was found between the average parameters of them.

2. The SEM response increases logarithmically with the count rate, but only for count rates beyond a certain limiting count rate (C_{limit}). The non-linear response results in relatively more pulses counted at higher beam intensities, as also reported by Hoffmann et al. [7]. This effect is opposite to the dead time effect from the pulse amplifier, by which relatively less pulses are counted with higher beam intensity. Therefore, in some cases with a small dead time, like e.g., 20 ns, and a large logarithmic slope, e.g., 1%, negative values for the dead time have been determined from isotope ratio measurements of standards, if the above-mentioned increase of the SEM efficiency was ignored [6].

This type of non-linear response is still not well understood. It was suggested in Refs. [6,7], that an increased ion beam intensity could cause a (logarithmically) increased overlap of successive electron pulses within the SEM, which then leads to increased pulse heights and therefore a slightly increased fraction of pulses exceeding the pulse amplifier threshold. But this assumption could not be verified directly and not described quantitatively. Therefore this type of SEM non-linearity pattern can only be examined empirically by doing isotope ratio measurements using well-known samples or certified standards.

In 2005, Hoffmann et al. [7] verified the SEM non-linearity pattern found at NBL [6] using an inductively coupled plasma mass spectrometer (MC-ICPMS) in peak-jumping mode for the first time (Fig. 2 in Ref. [7]). But Hoffmann et al. also suggested a so-called “multi-static” measurement procedure for MC-ICPMS instruments in order to circumvent the short-time instabilities of the plasma. As a result of investigations on two SEMs from ETP in 2005, Hoffmann et al. proposed the existence of two logarithmic components of non-linearity. The first starts at count rates as low as 10 cps with a slope of between about 0.3 and 1.1%, and above count rates of 10,000–100,000 cps a second component with a slope between 0.7 and 2.7% was observed. The second component was affecting a similar range of count rates as the logarithmic component described above [6], but with a larger slope. But the first component has only been observed on MC-ICPMS instruments so far. Hoffman et al. argue that this low count rate component is always existing but “masked” due to memory effects from the detection of a strong ^{235}U beam during peak-jumping (in Refs. [6,7]) or “multi-static” measurements (in Ref. [7]). Hoffmann et al. furthermore reported agreement of non-linearity patterns for different elements such as U and Th.

As an additional complication or a possible explanation for the first (low count rate) non-linearity component, Hoffmann et al. observed memory effects on the 2 SEMs from ETP installed on his MC-ICPMS instrument [7]. After applying a high intensity ^{235}U beam of more than 100,000 cps to the SEM as part of the “multi-static” measurement procedure, the measured $n(^{234}\text{U})/n(^{235}\text{U})$ ratios are elevated by about 1% for a duration of at least 20 s. After removing the ^{235}U from the “multi-static” measurement procedure, the first non-linearity component still remained, but with a different offset. The memory effect is suggested to be related to the operating temperature of the SEM and therefore related to an averaged beam intensity applied to the SEM. However, for this combination of SEMs from ETP and MC-ICPMS instruments, there seems to be a mixture of two non-linearity components and a memory effect, which require sophisticated corrections in order to obtain reliable measurements. Similar memory effects were observed for several SEMs from ETP mounted on TIMS instruments at IRMM and Thermo Fisher Scientific (Hannah-Kunath-Str.11, Bremen, Germany). Since new SEMs came on the market at that time (see below) these SEMs were not further investigated at IRMM and rather discarded. It is worth mentioning, that the first (low count rate) logarithmic non-linearity component has never been observed on TIMS instruments.

The observations of two different logarithmic components of SEM non-linearity on MC-ICPMS instruments were confirmed by Ball et al. [8] in 2007. However, the extent of the deviation from linearity was found to be smaller if no energy filter (called RPO on the NEPTUNE from Thermo Fisher Scientific) was applied to reduce tailing effects from ^{235}U and ^{238}U on ^{234}U . It became obvious that for inductively coupled plasma mass spectrometry (ICPMS) instruments an energy filter can have an influence on the SEM performance that applies to both the linearity and the transmission, the latter was found to be species-dependent as well. For TIMS instruments these phenomena have not been observed up to now.

A new generation of SEMs [9] was developed from a collaboration of Thermo Fisher Scientific with MasCom in 2006 and investigated by the NERC Isotope Geosciences Laboratory (British Geological Survey, Keyworth, Nottingham, NG12 5GG, United Kingdom). This SEM features several hardware differences to other SEM's: (1) superior peak-shape through modified first dynode geometry and (2) improved linearity and stability via lower operating voltage and modified last dynode electronics. The SEM was reported to be linear within 0.1% and required only the dead-time correction for the pulse amplifier, which was found not to be species specific from Pb to UO_2 . However, Condon et al. [10] reported small differences of dead times for different elements such as Pb and U and expressed the need for certified Pb standards with small uncertainties in order to investigate the linearity response of SEMs for Pb measurements, in a similar way as already possible for U using the IRMM-073/074 series.

Recently, the new SEM from Thermo Fisher Scientific and MasCom has been investigated for linearity at IRMM as well. On two TIMS instruments the SEMs were found to be linear within 0.1%. On both instruments the dead time of the combined system of SEM and pulse amplifier was found to agree with the nominal value of 20 ns for the dead time of the pulse amplifier. In order to obtain a SI-traceable value for the dead time of the combined detection system, the dead time was re-determined by measurements of certified isotope reference materials such as the IRMM-073/-074 series. As explained below, two procedures were used for the dead time determination, the so-called static and the so-called dynamic procedure.

3. Experimental Part A: preparation and certification of the IRMM-074 series of isotope reference materials

3.1. Design of the IRMM-074 isotopic reference material

IRMM-074 is designed such that each set has 10 individual IRMs; in each of these the isotopic ratio $n(^{235}\text{U})/n(^{238}\text{U})$ is held constant at a value close to unity and the isotopic ratio $n(^{233}\text{U})/n(^{235}\text{U})$ varies across the series from 1.0 to down to 1.0×10^{-6} .

Following the method previously applied successfully for the IRMM-072 series, the mixtures were made gravimetrically, by weighing purified, highly enriched oxides into solution and mixing the solutions in the correct proportions, again gravimetrically. The critical points of the preparation were to ensure that:

1. The starting materials were handled in different gloveboxes completely isolated from the others to avoid cross-contamination.
2. Identical chemical purification steps and aliquots of the same reagents were used for each of the starting materials in parallel.
3. The purified starting materials were dried and then calcined simultaneously under the same conditions in an oven built specifically for this purpose.
4. A minimum weight of oxide >100 mg for the starting material was needed to keep the relative uncertainties from the weighing procedure below 0.005%.

3.2. Purification and calcination of starting materials

The purification of the uranium involved anion exchange in nitric acid medium, cation exchange in HNO_3/THF and precipitation as peroxide. Earlier experiments described in Refs. [1,2] showed that this three step procedure gave an excellent level of purification. The impurities in the enriched isotopic materials were measured by spark-source mass spectrometry and by ICP-MS. Because of the limited amounts available for the ^{233}U and ^{238}U starting materials, samples were only taken from the ^{235}U starting material and a test batch of natural U which was also used to evaluate different purification methods. Impurity levels considerably lower than 100 ppm were achieved. Although the impurities could not be measured in all the starting materials because of the limited amount of material available, the design of the purification cycle, as applied in parallel to the starting materials, allowed to assume with a high degree of confidence that each component has the same impurity amount, conservatively set at 100 ± 100 ppm in the certification of the final mixtures. The starting materials were purified using identical methods and chemicals, but in separate clean glove-boxes to avoid cross-contamination or contamination from the environment.

The oxides of the starting materials were calcined at 920°C in a special oven. The individual oxides were calcined simultaneously 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 all three enriched materials have the same stoichiometry. The glove-box conditions were completely controlled and the humidity in the glove-box and oven were kept at less than 30 ppm throughout the final sintering process. The assumption of obtaining a sufficiently similar stoichiometry and impurity levels for different starting materials calcined under identical conditions within the oven, either done simultaneously or sequentially, was proven to be valid by a verification experiment performed for the $n(^{233}\text{U})/n(^{236}\text{U})$ -“double spike” IRMM-3636, which is described in detail in Ref. [11].

3.3. Preparation of solutions and mixtures

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 in-house kilogram. The relative uncertainty from weighing was kept lower than 0.005%.

The IRMM-074 series was produced by careful weighing of amounts of a solution containing ^{235}U and ^{238}U with a molar ratio 1:1 and a solution containing the ^{233}U . The ‘mother’ solution of ^{233}U was diluted consecutively to make three further solutions with lower concentrations of this isotope before mixing. In the first stage, ^{235}U and ^{238}U oxides were weighed and dissolved together in nitric acid to make a single solution. The ^{233}U oxide was dissolved separately to form a second solution. A mixing schedule as shown in Fig. 4 was designed.

IRMM-074 preparation scheme

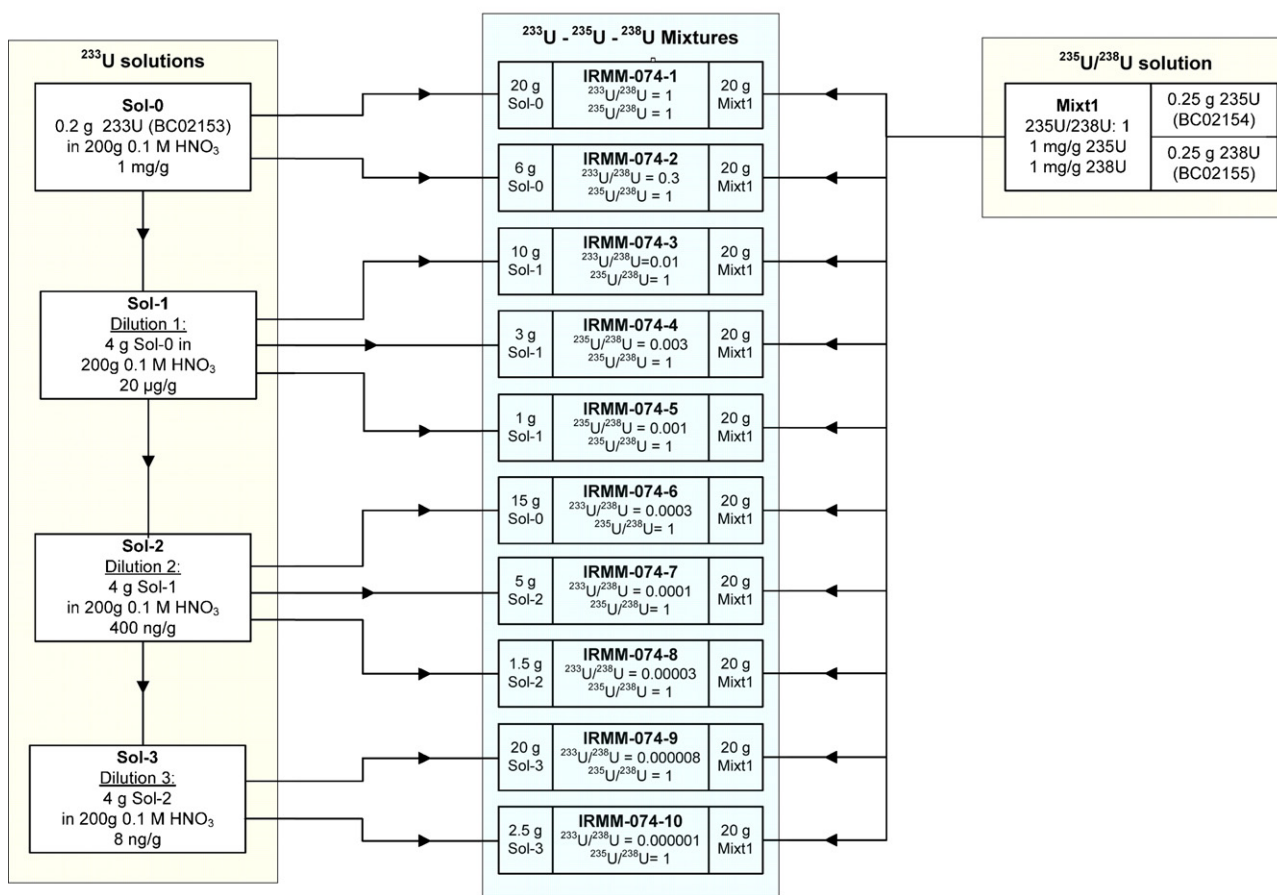


Fig. 4. Mixing schedule for preparation of IRMM-074 series. In the first stage, ^{235}U and ^{238}U oxides were weighed together and dissolved in nitric acid. The ^{233}U oxide was dissolved separately to form a ‘mother’ solution of ^{233}U , which was diluted consecutively to make three further solutions with lower concentrations of ^{233}U before mixing. By mixing the solution of the ^{235}U and ^{238}U oxides with the ^{233}U ‘mother’ solution and the various dilutions from it, 10 solutions covering the range of ^{233}U ratios relative to ^{235}U and ^{238}U from 1 to 10^{-6} were prepared.

Table 1
Isotopic compositions in atom ratios of the IRMM-074 starting materials enriched in ^{233}U , ^{235}U and ^{238}U .

	Enriched ^{233}U in %	Enriched ^{235}U in %	Enriched ^{238}U in %
$n(^{233}\text{U})/n(\text{U})$	99.962756 (47)	<10 ⁻⁷ (%)	<10 ⁻⁷ (%)
$n(^{234}\text{U})/n(\text{U})$	0.035908 (47)	0.0021282 (87)	0.000000541 (12)
$n(^{235}\text{U})/n(\text{U})$	0.00042031 (38)	99.993541 (21)	0.0000507 (13)
$n(^{236}\text{U})/n(\text{U})$	0.000002535 (19)	0.004228 (19)	0.000000197 1 (73)
$n(^{238}\text{U})/n(\text{U})$	0.0009134 (24)	0.00010238 (28)	99.9999486 (13)
Molar mass (g mol ⁻¹)	233.0400408 (60)	235.0439463 (42)	238.0507820 (44)

Measurements were performed using the (modified) total evaporation technique on the TRITON TIMS [12] in order to minimize mass fractionation effects. Within the ^{235}U and ^{238}U enriched starting materials no ^{233}U was detected, the $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{233}\text{U})/n(^{238}\text{U})$ ratios were <10⁻⁹, therefore the ^{233}U abundances are indicated as <10⁻⁷%.

3.4. Certification of isotopic ratios in starting materials

The isotopic compositions of the starting materials for IRMM-074, enriched in ^{233}U , ^{235}U and ^{238}U , were measured using the (modified) total evaporation technique on the TRITON TIMS as described in Ref. [12]; the results are given in Table 1. In any total evaporation technique the measurement is continued until the sample is exhausted. This is done in order to minimize mass fractionation effects.

The challenge for isotopic measurements of the ^{233}U , ^{235}U and ^{238}U enriched starting materials was given by the high enrichment of one (“major”) isotope relative to all the others (“minors”). The major isotope was measured using a Faraday cup using a considerably large ion beam current of e.g., 10⁻¹⁰ A, corresponding to signal of 10 V signal at the 10¹¹ Ω amplifier resistor. In some cases minor isotopes could be measured also on a Faraday cup but they were usually measured rather by a SEM due to their much lower relative abundance. The necessary inter-calibration between the Faraday cup (or Faraday multi-collector, internally calibrated using constant current source) and the ion counter has to be done continuously throughout the entire measurement time (“internal calibration”), preferentially using an ion beam of the same element (uranium) and of appropriate size. A suitable ion beam size is about 2–5 × 10⁻¹⁴ A (2–5 mV), equivalent to ca. 120.000–300.000 cps. For extremely highly enriched samples an ion beam of this size is not always available. This can cause significant problems, in the worst case the inter-calibration between the Faraday multi-collector and the ion counter can only be done once prior to the measurement, e.g., using the major isotope beam, but at a much lower intensity and therefore lower filament temperature. It is difficult to ensure that the inter-calibration factor remains the same after the sample is then further heated up to the final beam intensity and temperature needed for a reasonable measurement. Furthermore the inter-calibration factor may change or drift during the measurement time. Therefore it is important to have an ion beam of suitable size available which can be used for an internal inter-calibration.

If a 10 V signal is always applied for the major isotope, the situation for each of the three starting materials ^{233}U , ^{235}U and ^{238}U can be described as follows:

1. ^{233}U enriched starting material: fortunately the ^{234}U beam was about 3–4 mV, which was appropriate for an internal inter-calibration between the Faraday cups and the SEM ion counter.
2. ^{235}U enriched starting material: the ^{236}U beam was only about 0.4 mV, corresponding to \cong 24.000 cps, and the other minor isotope beams ^{234}U and ^{238}U were even lower. This ^{236}U beam was too low for an internal inter-calibration between Faraday cups and ion counter. Therefore a small aliquot of the ^{233}U enriched starting material was added to the sample solution of the ^{235}U starting material, with a ratio of ca. $n(^{233}\text{U})/n(^{235}\text{U}) \cong 1/2000$, in order to achieve a 5 mV signal for this “artificial” calibrating ^{233}U beam. The mixing ratio does not have to be adjusted and known very precisely ($\pm 20\%$ is sufficient), because the ^{233}U ion beam is only used to establish the link between the ion counter

and the Faraday cups. This technique provided more reliable $n(^{234}\text{U})/n(^{235}\text{U})$, $n(^{236}\text{U})/n(^{235}\text{U})$ and $n(^{238}\text{U})/n(^{235}\text{U})$ data, with the previously measured ^{234}U , ^{236}U and ^{238}U contributions from the ^{233}U enriched starting material being corrected for.

3. ^{238}U enriched starting material: Due to the high enrichment (ca. 99.99995% ^{238}U) none of the minor isotope ion beams was appropriate for an internal inter-calibration, even the ^{235}U “major” isotope count rate was only about 200 cps. Therefore a small aliquot of the ^{233}U enriched starting material was added to the sample solution of the ^{238}U starting material, with a ratio of ca. $n(^{233}\text{U})/n(^{238}\text{U}) \cong 1/2000$, in order to achieve a 5 mV signal for the “artificial” calibrating ^{233}U beam. This technique provided more reliable $n(^{235}\text{U})/n(^{238}\text{U})$ data, which is important for the certification of IRMM-074. However, the minor abundances of ^{234}U and ^{236}U were significantly interfered by contributions from the ^{233}U spike. Therefore the $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ ratios were determined in a separate measurement without using the ^{233}U enriched starting material for internal calibration.

3.5. Certification of IRMM-074

The aim of the IRMM-074 mixing programme was to achieve isotopic mixtures with uncertainties equivalent to those of IRMM-072, i.e., 0.02% relative for $n(^{235}\text{U})/n(^{238}\text{U})$ and 0.03% for $n(^{233}\text{U})/n(^{235}\text{U})$ and $n(^{233}\text{U})/n(^{238}\text{U})$ ratios. (All uncertainties in this paper are shown as expanded combined uncertainties, with coverage factor $k=2$). The basis for this certification was the calculation from the mixing of the enriched isotopes described here and the verification measurements carried out on a TIMS. The isotope amount ratios of the individual units of the set were calculated according to GUM [13] and using the GUM Workbench software [14]. Four main contributors to the final uncertainties of the isotopic ratios were recognized during the preparation of IRMM-074:

- Uncertainties from weighing: expanded uncertainties ($k=2$) ranging between 0.012 and 0.024% for the mixture of the ^{235}U and ^{238}U starting materials, for the amount content of the mother solutions of ^{233}U , and for the dilutions of ^{233}U .
- Chemical impurities: based on an equal level of impurities for each of the starting materials as explained above, a value of 100 ± 100 ppm was applied with 0.8 for correlation coefficient.
- Stoichiometry: caused by possibly remaining differences in stoichiometry between the oxides of the enriched isotopic material. 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 $2.6 \times 10^{-6}\%$ on the molar mass of the individual starting materials were introduced.

The IRMM-074 certified ratios for $n(^{233}\text{U})/n(^{235}\text{U})$, $n(^{233}\text{U})/n(^{238}\text{U})$ and $n(^{235}\text{U})/n(^{238}\text{U})$ are calculated from the mixing pro-

Table 2
Certified isotopic ratios for IRMM-074 series.

	$n(^{233}\text{U})/n(^{235}\text{U})$ $U = 0.025\%$	$n(^{233}\text{U})/n(^{238}\text{U})$ $U = 0.025\%$	$n(^{235}\text{U})/n(^{238}\text{U})$ $U = 0.015\%$
IRMM-074/1	1.02685	1.02711	1.000254
IRMM-074/2	0.307993	0.308072	1.000258
IRMM-074/3	0.0102288	0.0102314	1.000259
IRMM-074/4	0.00307358	0.00307437	1.000259
IRMM-074/5	0.00103061	0.00103088	1.000259
IRMM-074/6	0.000307778	0.000307858	1.000259
IRMM-074/7	0.000102603	0.000102629	1.000259
IRMM-074/8	0.0000308011	0.0000308091	1.000259
IRMM-074/9	0.0000081587	0.0000081608	1.000259
IRMM-074/10	0.00000101886	0.00000101913	1.000259

cedure and shown in Table 2. The uncertainties as specified in the table are relative expanded uncertainties U_c with coverage factor $k=2$ and given in percent. The uncertainties given are supported by calculation of the combined uncertainty following the ISO/GUM recommendations [13] and are based on measured values of the isotopic enrichments, the weights of oxides and solutions, and of the impurity levels. Expanded uncertainties are 0.025% for the $n(^{233}\text{U})/n(^{235}\text{U})$ and $n(^{233}\text{U})/n(^{238}\text{U})$ ratios and 0.015% for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios, which are slightly lower compared to the values of 0.025% and 0.015%, respectively, recorded for the predecessor series IRMM-072.

3.6. Verification of the IRMM-074 certified values by TIMS measurements

The verification measurements for the IRMM-074 reference materials were done in 2 steps. The first step consisted of measurements of the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio, the so-called “major” ratio, for the following materials: IRMM-072, IRMM-199, NBL U500, IRMM-074-1 and IRMM-074-Mix1. IRMM-074-Mix1 is the basic mixture of ^{235}U and ^{238}U , prepared prior to including any ^{233}U . This measurement series includes some of the worldwide most recognized reference materials with $n(^{235}\text{U})/n(^{238}\text{U})$ ratios close to unity and provides a link of them to the new reference material IRMM-074. The measurements were performed using the (modified) total evaporation technique on the TRITON TIMS [12]. The sample loading was 5 μg of U for all materials. IRMM-072-1 was used as a reference, thus the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of this so-called “comparator” IRMM-072-1 was used to determine the k -factor which is then used to perform an external mass fractionation correction on the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for all other materials.

According to Table 3, the results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for IRMM-199 and NBL U500, corrected for mass fractionation using IRMM-072-1, agree well with the certified values, showing that the employed method provides accurate data. Remarkably, the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of NBL U500 shows a relative difference of 0.04%. This difference is not significant because of the 0.11% uncertainty, which is mainly arising from the 0.1% uncertainty of the

Table 3
TIMS measurements of the $n(^{235}\text{U})/n(^{238}\text{U})$ so-called “major” isotope ratio for IRMM-072, IRMM-199, NBL U500, IRMM-074-1 and IRMM-074-Mix1, using the (modified) total evaporation technique [12].

	Measured $n(^{235}\text{U})/$ $n(^{238}\text{U})$	Certified $n(^{235}\text{U})/$ $n(^{238}\text{U})$	Rel. Dev from certified value
IRMM-072-1	*	0.99103 (20)	N/A
NBL U500	1.00009 (37)	0.9997 (10)	0.04 (11)%
IRMM-199	1.00018 (36)	1.00015 (20)	0.003 (42)%
IRMM-074-Mix1	1.00009 (43)	1.00026 (15)	-0.017 (44)%
IRMM-074-1	1.00022 (32)	1.00025 (15)	-0.003 (33)%

IRMM-072 was used as reference (“comparator”: * no result) for the mass fractionation correction.

Table 4
TIMS measurements of the $n(^{233}\text{U})/n(^{238}\text{U})$ ratios for IRMM-072-1, IRMM-199, IRMM-074-1, internally corrected for mass fractionation using the respective certified $n(^{235}\text{U})/n(^{238}\text{U})$ ratios.

	Measured $n(^{233}\text{U})/$ $n(^{238}\text{U})$	Certified $n(^{233}\text{U})/$ $n(^{238}\text{U})$	Rel. Dev from certified value
IRMM-072-1	0.99097 (33)	0.99114 (30)*	-0.016 (45)%
IRMM-199	0.99965 (33)	0.99978 (30)*	-0.013 (45)%
IRMM-074-1	1.02708 (26)	1.02711 (15)	-0.003 (29)%

*The certified $^{233}\text{U}/^{238}\text{U}$ values for IRMM-072-1 and IRMM-199 have been corrected for the α -decay of ^{233}U since their certification.

certified value. Among other improvements, use of this standard led to a small change in values and a two-fold decrease in uncertainties for the re-determinations of the equilibrium $n(^{234}\text{U})/n(^{238}\text{U})$ ratio and the ^{234}U half-life by Cheng et al. [15].

Furthermore the corrected $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for IRMM-074-1 and IRMM-074-Mix1 agree well with the certified values obtained from the mixture calculation (Table 2). This confirms that the mixing was done properly and the assumptions regarding the impurities and stoichiometry were valid. Based on the successful verification for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for both IRMM-074-1 and IRMM-074-Mix1 it can be concluded that the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of IRMM-074-Mix1 is not affected by adding any of the ^{233}U enriched solution to it, as expected from the low ^{235}U and ^{238}U abundances as shown in Table 1. This also implies that the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios of IRMM-074-2 to IRMM-074-10 are also not affected by the ^{233}U enriched solution and do not have to be verified by TIMS measurements separately.

As shown in Table 4, the measured $n(^{233}\text{U})/n(^{238}\text{U})$ ratios for IRMM-072, IRMM-199 and IRMM-074-1, which were internally corrected for mass fractionation using the respective certified $n(^{235}\text{U})/n(^{238}\text{U})$ ratios, agree well with the certified values for both IRMM-072-1 and IRMM-199, showing that the method employed and internal correction provides accurate data. Furthermore the measured $n(^{233}\text{U})/n(^{238}\text{U})$ ratio for IRMM-074-1 agrees well with the certified value obtained from the mixture calculation (Table 2). NBL U500 and IRMM-074-Mix1 do not contain ^{233}U .

Based on step 1, the calculated $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for IRMM-074-1 to IRMM-074-10 have been confirmed. Therefore, in step 2 the $n(^{233}\text{U})/n(^{235}\text{U})$ or $n(^{233}\text{U})/n(^{238}\text{U})$ ratios can be verified using the already confirmed $n(^{235}\text{U})/n(^{238}\text{U})$ ratios for internal mass fractionation correction. For the measurements of IRMM-074-1 to IRMM-074-7 only Faraday cups were used. The remaining ones, IRMM-074-8 to IRMM-074-10, had to be measured using the SEM ion counter for the detection of ^{233}U . Unfortunately, since there was no suitable uranium isotope beam available for an “internal” SEM/Faraday cup inter-calibration during the course of these measurements, this calibration had to be done “externally” using the ^{235}U beam at different sample conditions (lower sample filament temperature) prior to the measurement. This usually leads to a larger spread in the results and larger final uncertainties. However, as shown in Table 5, the $n(^{233}\text{U})/n(^{235}\text{U})$ ratios for IRMM-074-1 to IRMM-074-10 calculated from the mixing of the solutions are verified by the TIMS measurements.

3.7. Conclusions for the preparation and certification of IRMM-074

The well-proven techniques of purification, calcination and gravimetric mixing that were demonstrated successfully in the preparation of IRMM-072 have been re-employed for the new series, IRMM-074. After a successful verification of the certified isotope ratios by TIMS this series is available for use as isotopic reference material and the certified isotopic ratios, calculated based

Table 5
TIMS measurements of the $n(^{233}\text{U})/n(^{235}\text{U})$ ratio for IRMM-074-1 to IRMM-074-10.

	Corrected $n(^{233}\text{U})/n(^{235}\text{U})$	Certified $n(^{233}\text{U})/n(^{235}\text{U})$	Rel. Dev from certified value
IRMM-074-1	1.02682 (26)	1.02685 (25)	-0.003 (29)%
IRMM-074-2	0.307969 (62)	0.307993 (75)	-0.008 (25)%
IRMM-074-3	0.0102294 (24)	0.0102288 (25)	0.006 (28)%
IRMM-074-4	0.0030733 (10)	0.00307358 (75)	-0.010 (36)%
IRMM-074-5	0.00103062 (76)	0.00103061 (25)	0.001 (75)%
IRMM-074-6	0.00030780 (42)	0.000307858 (75)	0.003 (136)%
IRMM-074-7	0.00010269 (36)	0.000102603 (25)	0.082 (347)%
IRMM-074-8	0.00003077 (43)	0.0000308011 (75)	-0.11% ($\pm 1.40\%$)
IRMM-074-9	0.000008196 (43)	0.0000081587 (20)	0.46 (52)%
IRMM-074-10	0.000001013 (28)	0.00000101886 (25)	-0.61% ($\pm 2.7\%$)

The $n(^{233}\text{U})/n(^{235}\text{U})$ values for IRMM-074-1 are calculated based on the result for $n(^{233}\text{U})/n(^{238}\text{U})$ in Table 4.

on the weights of oxides and solutions, and their uncertainties are equivalent to the values for IRMM-072.

4. Experimental Part B: new procedures for using IRMM-073/-074 for investigating SEM linearity

In this section two procedures for the application of the IRMM-073/-074 series for SEM linearity testing and dead time determination are presented. The static procedure is suggested preferentially for MC-ICPMS instruments and the dynamic procedure for TIMS instruments.

4.1. Static procedure

This procedure is a suggestion for MC-ICPMS instruments. The ^{233}U within the IRMM-073/1-15 (or IRMM-074/1-10) series is measured at various intensity levels using the SEM, whereas the ^{235}U and ^{238}U isotopes are detected using a Faraday multi-collector at a uniform intensity level for each of the samples of the series. The inter-calibration of the SEM versus the Faraday multi-collector is in each case performed internally by the additional detection of ^{235}U in one Faraday cup. The mass cycle arrangement is shown in Table 6.

The isotope measurements usually consist of 5–10 blocks of 10 mass cycles. The entire static procedure consists of a series of measurements, in which the 2-step mass cycle arrangement in Table 6 has to be applied separately to the various samples of the IRMM-073/-074 series. By going through the IRMM-073/-074 series the ^{233}U intensity covers the entire range of count rates from ca. 400,000 cps down to a few 100 cps. For all measurements, the ^{235}U and ^{238}U intensity on the Faraday cups has to be kept a uniform level of about 6.4 mV, corresponding to about 400,000 cps on the SEM.

Using this mass cycle arrangement the efficiency of the SEM versus the Faraday multi-collector can be calculated as a ratio of ratios. Thereby only statically measured ratios are used, no dynamic (peak-jumping) ratios at all, which makes this procedure independent on plasma instabilities and therefore advantageous for ICPMS:

$$\left(\frac{^{233}\text{U}}{^{235}\text{U}}\right)_{\text{CAL}} = \left(\frac{^{233}\text{U}}{^{235}\text{U}}\right)_{\text{STEP 1}} \left[\left(\frac{(^{235}\text{U}/^{238}\text{U})_{\text{STEP 1}}}{(^{235}\text{U}/^{238}\text{U})_{\text{STEP 2}}} \right) \right] \quad (1)$$

The mass fractionation of the $n(^{233}\text{U})/n(^{235}\text{U})$ ratio is corrected internally using the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio measured using Faradays

cups in step 1:

$$\left(\frac{^{233}\text{U}}{^{235}\text{U}}\right)_{\text{CORR}} = \left(\frac{^{233}\text{U}}{^{235}\text{U}}\right)_{\text{CAL}} \left\{ \left[\left(\frac{(^{235}\text{U}/^{238}\text{U})_{\text{CERTIFIED}}}{(^{235}\text{U}/^{238}\text{U})_{\text{STEP 1}}} \right) \right] \times \frac{2}{3} - 1 \right\} \quad (2)$$

The principle of the static procedure is to possibly measure the dead time by detecting ^{233}U for different count rates, while the ^{235}U count rate is kept at a constant count rate with a constant dead time effect. The dead time of the entire SEM system can be calculated as the slope of a regression line, as shown in Fig. 5a and b, for which the quantity $\{n(^{233}\text{U})/n(^{235}\text{U})\}_{\text{meas}}/n(^{233}\text{U})/n(^{235}\text{U})_{\text{CERTIFIED}} - 1\}$ is plotted versus the count rate of ^{233}U . Fig. 5a represents measurements of IRMM-073/1-6 performed using a NEPTUNE MC-ICPMS at the Paul Scherrer Institut (PSI, Villingen, Switzerland) and Fig. 5b results from measurements using a TRITON TIMS at IRMM. The measurement with the highest count rate of ^{233}U is the result for the IRMM-073/1, which is a 1/1/1 mixture of $^{233}\text{U}/^{235}\text{U}/^{238}\text{U}$. The deviation from the certified value is zero within the uncertainties, which indicates that there is no mass related bias. By going through the

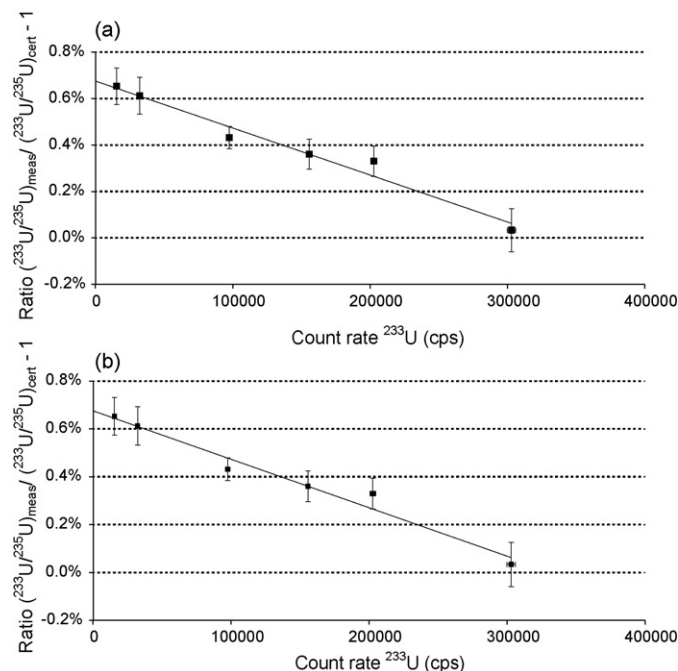


Fig. 5. (a and b) Measurements of IRMM-073/1-6 performed using the static procedure on (a) a NEPTUNE MC-ICPMS at the Paul Scherrer Institute (PSI, Villingen, Switzerland) and (b) a TRITON TIMS at IRMM. The dead time of the entire SEM system can be calculated as the slope of a regression line, for which the quantity $\{n(^{233}\text{U})/n(^{235}\text{U})\}_{\text{meas}}/n(^{233}\text{U})/n(^{235}\text{U})_{\text{CERTIFIED}} - 1\}$ was plotted versus the count rate of ^{233}U . The dead time results are $\tau = (23.4 \pm 3.4)$ ns for the SEM on the NEPTUNE at PSI and $\tau = (20.2 \pm 4.6)$ ns for the SEM on the TRITON 1 TIMS at IRMM.

Table 6
Mass cycle arrangement for the static procedure.

Step	Cup C/SEM	Cup H1	Cup H2	Cup H3
1	$^{233}\text{U}/100\text{--}400,000$ cps	$^{235}\text{U}/6.4$ mV		$^{238}\text{U}/6.4$ mV
2	$^{235}\text{U}/400,000$ cps		$^{238}\text{U}/6.4$ mV	

IRMM-073 series the ^{233}U count rate is decreased from one material to the next, which causes the dead time effect for ^{233}U to differ subsequently more from the (maximum) dead time effect observed for the ^{235}U used for the inter-calibration in step 2 of the mass cycle.

The measured data for both SEMs are well fitted by the regression lines, which indicate that there is no evidence for an inherent SEM non-linearity. The calculated results for the dead times are $\tau = (23.4 \pm 3.4)$ ns for the SEM used on the NEPTUNE at PSI and $\tau = (20.2 \pm 4.6)$ ns for the SEM used on the TRITON TIMS at IRMM. The uncertainties, with a coverage factor of $k=2$, are calculated according to the GUM [13] and using the GUM Workbench software [14] and take into account the uncertainties of all individual measurements within the series and also the uncertainty from the reference material IRMM-073. The dead times for these 2 SEMs just barely overlap, but a tight agreement of the data with the 'nominal' electronically determined dead time value of the pulse amplifier (20 ns) cannot be expected. Even if the pulse amplifiers on these two instruments are manufactured from similar electronic parts using the same scheme, the properties can still be slightly different.

In TIMS it is often more difficult to realize the required uniform intensity level for different standard solutions loaded on different filaments. Therefore the following dynamic procedure is preferentially suggested for TIMS.

4.2. Dynamic procedure

One suitable sample solution of the series, e.g., IRMM-074/3 with a $n(^{233}\text{U})/n(^{235}\text{U})$ ratio of $\cong 0.01$ is measured in peak-jumping mode at various intensity levels only using the SEM. The mass fractionation of the $n(^{233}\text{U})/n(^{235}\text{U})$ ratio is corrected internally using the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio, which is close to unity.

The dead time of the entire SEM system can be calculated from the slope of a regression line using Eq. (3) below, as shown in Fig. 6a and b, but the dead time does not equal

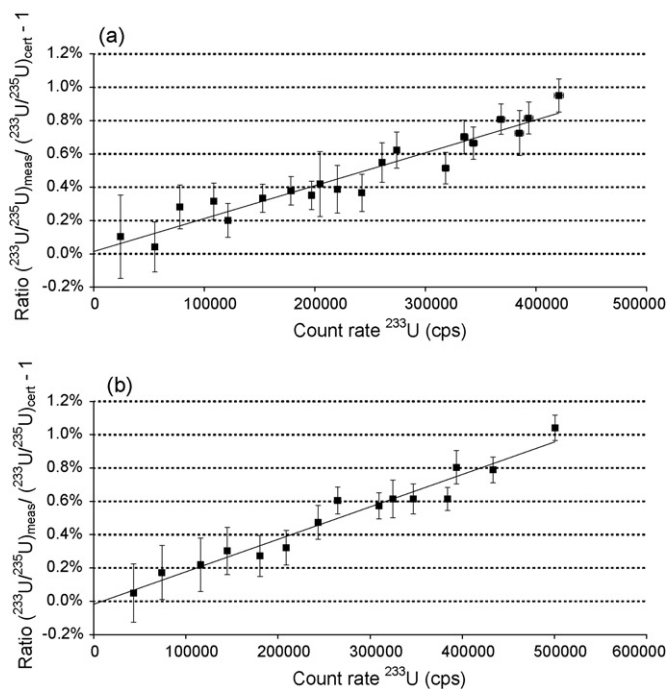


Fig. 6. (a and b) Measurements of IRMM-074/3 performed using the dynamic procedure on two different TRITON TIMS instruments at IRMM. The dead time of the entire SEM system can be calculated from the slope of a regression line according to Eq. (3) (see text), for which the quantity $\{n(^{233}\text{U})/n(^{235}\text{U})\}_{\text{meas}}/n(^{233}\text{U})/n(^{235}\text{U})_{\text{CERTIFIED}} - 1$ was plotted versus the count rate of ^{233}U . The results for the dead times are $\tau = (20.5 \pm 1.3)$ ns for the SEM used on the TRITON 1 and $\tau = (19.1 \pm 1.2)$ ns for the SEM used on the TRITON 2 at IRMM.

Table 7

Dead time determination for the SEM of TRITON 1 at IRMM.

Procedure	Dead time (ns)	U_c ($k=2$) (ns)
Dynamic procedure using IRMM-074/3, 16/11/2006	20.5	1.3
Dynamic procedure using IRMM-074/3, 12/01/2007	20.1	1.8
Static procedure using IRMM-074, 16/01/2007	19.8	1.8
Static procedure using IRMM-073, 18/01/2007	20.2	4.6

the slope, in contrast to the static procedure. In Fig. 6a and b the quantity $\{n(^{233}\text{U})/n(^{235}\text{U})\}_{\text{MEAS}}/n(^{233}\text{U})/n(^{235}\text{U})_{\text{CERTIFIED}} - 1$ is plotted versus the count rate of ^{233}U . The certified ratio $n(^{233}\text{U})/n(^{235}\text{U})_{\text{CERTIFIED}} = 0.0102288$ (25) is given in Table 2 above:

$$\tau = \frac{\{\text{slope}\}}{(1 - (^{233}\text{U}/^{235}\text{U})_{\text{CERT}})} \quad (3)$$

The principle of the dynamic procedure is to measure the dead time by detecting ^{235}U for different count rates, which constitutes a difference to the static procedure for which ^{233}U is used as the measure for the dead time effect. But in the dynamic procedure the dead time effect for ^{233}U has to be taken into account as well using Eq. (3), even if it is about 100 times smaller.

Fig. 6a and b represent measurements using IRMM-074/3 performed on two different TRITON TIMS instruments at IRMM. Also in these cases, the measured data for both SEMs fall well on regression lines. The regression lines are assumed to have an intercept of zero due to the fact that by extrapolating the data towards a zero count rate of ^{235}U (and ^{233}U) no dead time effect should remain. The calculated results for the dead times are $\tau = (20.5 \pm 1.3)$ ns for the SEM used on the TRITON 1 and $\tau = (19.1 \pm 1.2)$ ns for the SEM used on the TRITON 2 at IRMM and agree well with the 'nominal' dead time value of 20 ns for the pulse amplifier.

In order to compare results obtained using the two procedures, for the SEM on TRITON 1 the dead time was determined twice using the dynamic and twice using the static procedure. The results agree well with each other, as shown in Table 7.

The following conclusions can be drawn from the test measurements presented here:

1. The static procedure is advantageous for MC-ICPMS instruments, because all ratios are measured in a static manner in order to circumvent the instabilities of the plasma ion source. The requirement of measuring all standard samples of the IRMM-073/-074 series at one uniform ^{235}U intensity does not cause any problem, because this intensity can be easily adjusted and kept constant for ICPMS instruments. This is not always the case for TIMS instruments, where it can be more difficult to measure standard samples of the series loaded on separate filaments at the same constant ion beam intensity. For the new type of SEM used in the current example shown in Fig. 5a, no memory effects as described by Hoffmann et al. [7] have been found. In case of another type of SEM detector exhibiting such memory effects, a different procedure, e.g., as suggested by Hoffmann et al. [7], can be used.
2. For MC-ICPMS instruments the dynamic procedure is associated with significantly larger uncertainties compared to TIMS because of the plasma instabilities, as shown by Ref. [7]. The dynamic procedure is advantageous for TIMS, because, first there is no requirement to perform all measurements at a uniform intensity level, and second, peak-jumping measurements can be done using TIMS without compromising of uncertainties almost down to the level predicted from counting statistics.
3. Comparison measurements on one SEM on a TRITON TIMS system at IRMM showed good agreement between the results for both procedures.

Table 8
Dead time determinations using the dynamic and the static procedures, for SEMs on 2 TRITON TIMS at IRMM and one SEM on a NEPTUNE MC-ICPMS at PSI.

	Dynamic procedure TRITON 1 IRMM, 16/11/2006	Dynamic procedure TRITON 1 IRMM, 12/01/2007	Dynamic procedure TRITON 2 IRMM, 04/07/2008	Static procedure TRITON 1 IRMM, 16/01/2007	Static procedure TRITON 1 IRMM, 18/01/2007	Static procedure NEPTUNE PSI, 18/04/2007
Dead time (ns)	20.5	20.1	19.1	19.8	20.2	23.4
Total U_c , $k = 2$ (ns)	1.3	1.8	1.2	1.8	4.6	3.4
Rel. Uncertainty contribution to total U_c from measurements of IRMM-073/-074	51%	75%	49%	72%	56%	60%
Rel. uncertainty contribution to total U_c from Ref. materials	49%	25%	51%	28%	44%	40%

In each case the IRMM-073/-074 materials were used. The relative uncertainty contribution to the total U_c arising from reference materials includes both the uncertainty from the certified $n(^{233}\text{U})/n(^{235}\text{U})$ ratios and the uncertainties of the certified $n(^{238}\text{U})/n(^{235}\text{U})$ ratios used for mass fractionation correction.

4. The new type of SEM, developed by Thermo Fisher Scientific in collaboration with MassCom did not show any signs of any detector-inherent non-linearity, the absence of any memory effects such as reported by Hoffmann et al. [7] was confirmed as well. For 2 TRITON TIMS instruments at IRMM and one NEPTUNE MC-ICPMS at PSI the dead times measured using reference materials IRMM-073/-074 were in agreement with the 'nominal' dead time of 20 ns of all the pulse amplifiers, see Table 8. This was also confirmed by Condon et al. [10]. Nevertheless, it is considered necessary to do a linearity check for each new SEM installed into a mass spectrometer. Even for the case when the operating parameters such as the operating voltage are significantly changed, an additional check is recommended [6].

4.3. Uncertainty considerations and reference materials for dead time determination

If IRMs are used for assessing the linearity of SEMs or even for determining correction parameters, the choice of the reference materials and the uncertainties associated with the certified ratios plays a significant role. Several reference materials have been used for this purpose, the main requirement being to have (a) one or more isotope ratios which cover a large dynamic range of count rates, e.g., 2 or more orders of magnitude, and (b) to have one ratio, preferentially close to unity, which can be used for internal mass fractionation correction without being affected by non-linearity effects of the SEM detector. As described above, the IRMM-073/-074 series and the NBL U500 are suitable U reference materials for this purpose. For the static procedure the ratio used for mass fractionation correction does not have to be close to unity if it is measured by Faraday detectors. For instance, natural and slightly enriched U samples can be used in various dilutions [7] if the major $n(^{235}\text{U})/n(^{238}\text{U})$ ratio is measured using Faraday cups and the minor $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ ratios are used to assess the linearity of the SEM by measuring ^{234}U and ^{236}U using the SEM and ^{238}U using a Faraday cup. The NBL CRM 112A is a natural material frequently used for this purpose [7], although the isotopic composition is currently only based on consensus values [6], the certification is ongoing at NBL. Further materials used are NBL CRM U010 [8] based on re-measurements published in Ref. [12], the re-certified IRMM-183-187 series [16] and the certified samples of the REIMEP 18 inter-laboratory comparison [17], which have also been applied [8] successfully for SEM linearity tests.

As shown in Table 8, the uncertainty of the dead time contains a significant contribution – ranging from about 25 to 50% – from the uncertainty associated with the reference material used for the measurement. If IRMM-073/-074 are applied, the relative uncertainties of the $n(^{233}\text{U})/n(^{235}\text{U})$ ratios are 0.03% for IRMM-073 and 0.025% for IRMM-074, and the corresponding uncertainties of the $n(^{238}\text{U})/n(^{235}\text{U})$ ratios used for mass fractionation correction

are 0.020 and 0.015%, respectively; both contribute to the uncertainty of the dead time measurement. For NBL U500 the relevant $n(^{234}\text{U})/n(^{238}\text{U})$ certified ratio has been originally certified with an uncertainty of 0.18%, but new values with smaller uncertainties have been presented for re-measurements using Faraday multi-collector instruments e.g., in Refs. [5,6]. However, these results are normalized to the certified $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of NBL U500, which has a relative uncertainty of 0.1% and has been shown to have a (insignificant) relative difference of $(0.04 \pm 0.11)\%$ relative to IRMM-072 (Table 3). This has to be taken into account for measuring and comparing $n(^{234}\text{U})/n(^{238}\text{U})$ isotope ratio data (e.g. Ref. [15]), which depend on dead times values obtained using different reference materials such as NBL U500 and IRMM-072/-073/-074.

Strontium isotopic standards from NIST are also being used, for which the $n(^{88}\text{Sr})/n(^{86}\text{Sr})$ and $n(^{84}\text{Sr})/n(^{86}\text{Sr})$ ratios are used to assess the SEM linearity effects and the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ ratio of about 0.71034 (26) is used for internal mass fractionation correction. The advantages are given by the facts that no radioactive material has to be used, and that long time stable Sr ion beams are often easier to generate on TIMS instruments compared to U ion beams. On the other hand, the certified $n(^{84}\text{Sr})/n(^{86}\text{Sr})$ ratio of NIST SRM 987 has an uncertainty of about 0.25%, which would cause a significant increase on the uncertainty of the dead time measurement. For instance, if SRM 987 would have been used as reference material for the dead time measurements described above (Table 8), the result for "Dynamic TRITON 1 IRMM, 16/11/2006" within the first column, would change into a dead time of $\tau = (20.5 \pm 9.0)$ ns, with a relative contribution of 99% for the uncertainty from the reference material. Measurement of a count rate of 500,000 cps would be associated with a minimum uncertainty of 0.45%, mainly originating from the dead time correction.

As reported by Condon et al [10], NIST SRM-982 can also be used for assessing SEM linearity effects by Pb isotope ratio measurements. The $n(^{204}\text{Pb})/n(^{208}\text{Pb})$ ratio can be used to measure SEM related effects using the $n(^{206}\text{Pb})/n(^{208}\text{Pb})$, which is close to unity, for mass fractionation corrections. However, the uncertainty of the $n(^{204}\text{Pb})/n(^{208}\text{Pb})$ ratio is at the level of 0.1%, which dominates the contributions for the dead time uncertainty. The result for "Dynamic TRITON 1 IRMM, 16/11/2006" within the first column of Table 8 would change into a dead time of $\tau = (20.5 \pm 4.0)$ ns: measuring a count rate of 500,000 cps would be associated with a minimum uncertainty of 0.22%.

The certified isotope ratio and its uncertainty, for either $n(^{233}\text{U})/n(^{235}\text{U})$ in the case of IRMM-073/-074 or $n(^{234}\text{U})/n(^{238}\text{U})$ in case of NBL U500, for $n(^{84}\text{Sr})/n(^{86}\text{Sr})$ in case of NIST SRM 987 and $n(^{204}\text{Pb})/n(^{208}\text{Pb})$ in case of NIST-982, provide the traceability link to the SI system of units. It has to be pointed out that consistency of data is not sufficient for accuracy, e.g., it is not sufficient to have a set of results for R_{meas} fitting nicely on a regression line versus the count rate, because in order to obtain accurate results

the regression line has to be forced to exactly match the value for $R_{\text{certified}}$ (or ≈ 0 in case the relative deviation $R_{\text{meas}}/R_{\text{meas}} - 1$ is plotted, see Fig. 6a and b) for the extrapolation to the count rate of zero.

5. Summary and conclusions

The new IRMM-074 series of gravimetrically prepared uranium IRMs has been prepared and certified having a $n(^{235}\text{U})/n(^{238}\text{U})$ isotope ratio close to unity and the $n(^{233}\text{U})/n(^{238}\text{U})$ isotope ratios varying from 1.0 to 10^{-6} . The expectations for the uncertainties were exceeded compared to the predecessor series IRMM-072. This new series has been demonstrated to be very useful for the calibration of detectors used in isotope mass spectrometry, in particular for SEMs. Two procedures, namely the static and the dynamic procedures, have been suggested to assess the linearity of SEMs for MC-ICPMS and TIMS instruments, respectively.

The so-called restricted logarithmic rate effect (RLR), characterized by a logarithmic increase of the SEM efficiency response with the count rate, starting at a certain limiting count rate, has been observed for numerous SEM detectors at various laboratories. This appears to be an inherent effect of the SEM detector; it is opposite to the well-known dead time effect originating mainly from the pulse amplifier. In most cases it was possible to determine the RLR parameters by measurements of IRMs such as the IRMM-073/-074 series or NBL U500, which then allowed reliable corrections for data of unknown samples to be performed.

However, despite the success of the RLR correction procedure, recent technical developments have led to a new type of SEM detector that does not show any inherent non-linearity effect; this is certainly the superior solution. In this case the dead time effect of the pulse amplifier is the only remaining component of non-linearity for the entire system. The characteristics of this new SEM were observed by several laboratories up to now, but it is strongly recommended to verify them for each new SEM installed into a mass spectrometer. It has to be emphasized that this newly developed SEM detector might not necessarily be the only one currently available without an inherent non-linearity effect. Already ongoing or future developments might well lead to new types of SEM detectors with satisfactory or even further improved characteristics.

Several choices of reference materials have been compared regarding their isotopic composition and the associated uncertainties, which have an influence in the uncertainties associated with the linearity correction parameters such as the dead time. For any dead time determination as well as the measurement of unknown samples for which the dead time correction is used, the traceability link to the SI system of units is given by the used certified reference materials and their uncertainties. The uncertainties for currently available Sr and Pb isotope reference materials for dead time determination were found to be quite large compared to those obtained for the IRMM-073/-074 series. This has a significant impact on the uncertainties for isotope measurements using SEM detectors.

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