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Short communication

Re-certification of a series of uranium isotope reference materials: IRMM-183, IRMM-184, IRMM-185, IRMM-186 and IRMM-187

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Abstract

The isotopic composition of the widely used series IRMM 183-187 (IRMM-183, IRMM-184, IRMM-185, IRMM-186 and IRMM-187) of uranium isotope reference materials with ^{235}U abundances ranging from depleted to low enriched uranium (ca. 0.3%, 0.7%, 2.0%, 3.0% and 4.5%) was first certified in 1987 and updated in 1993 and 1999. Progress in the development of mass spectrometric instrumentation over the past 20 years has led to the precision and reliability of isotope ratio measurements being gradually improved. After a new thermal ionization mass spectrometer (TIMS) was installed at IRMM in January 2004, the isotopic composition of the IRMM 183–187 series was re-measured and re-certified with significantly reduced uncertainties for the ^{234}U/^{238}U and ^{236}U/^{238}U isotope ratios. The reliability of the new data was confirmed by verification measurements of synthetic isotope mixtures including the IRMM-072 series to demonstrate the linearity of both Faraday and ion counting detectors, as well as by using new synthetic calibration mixtures with ^{236}U/^{238}U ratios in the order of 10^{-6}, 10^{-7} and 10^{-8} to validate measurements of ^{236}U in ion counting mode.

Keywords: Uranium; Isotope reference materials; Thermal ionization mass spectrometry; Nuclear safeguards

1. Introduction

In nuclear safeguards, there is a need for certified isotope reference materials of the two major nuclear elements of interest, 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 uranium from the nuclear fuel cycle.

The naturally occurring isotopes ^{235}U and ^{238}U are the major isotopes whereas ^{234}U and ^{236}U are called minor isotopes because they are less abundant in most samples. The measurement of the ^{235}U/^{238}U isotope ratio, or the relative ^{235}U abundance, is the primary ratio of interest for nuclear safeguards measurements but the measurements of the minor isotope ratios as well, in particular the ^{236}U/^{238}U ratio which covers a range from about 10^{-11} for natural uranium up to ca. 10^{-2} for enriched material, are recognized as important indicators in nuclear safeguards and non-proliferation.

In order to achieve reliable uranium isotope measurements certified reference materials are needed for mass-spectrometer calibration, method validation and to fulfill quality control requirements.

In 1987 a new series of uranium isotope reference materials called IRMM 183–187 was produced and certified, with ^{235}U relative abundances of 0.3%, 0.7%, 2.0%, 3.0% and 4.5%. This series complements the widely used uranium CRM series (U010, . . ., U500, etc.) produced earlier by NIST and continued by NBL. For the IRMM 183–187 series the measurements of the ^{235}U/^{238}U ratios were performed on a VARIAN MAT 511 UF_6 gas mass spectrometer calibrated using synthetic uranium isotope mixtures. The minor isotope ratios ^{234}U/^{238}U and ^{236}U/^{238}U were analyzed by thermal ionization mass spectrometry using a Finnigan MAT260, uti-

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lizing a secondary electron multiplier in analogue mode for ^{234}U and ^{236}U.

In January 2004, a "Triton" thermal ionization mass spectrometer from Thermo Electron was installed at IRMM. The IRMM 183–187 series of reference materials has now been re-measured and re-certified for the minor isotope ratios ^{234}U/^{238}U and ^{236}U/^{238}U using this equipment. This paper describes the measurement methods applied and their validation by test measurements of synthetic uranium isotope mixtures and we publish the new re-certified isotope ratios and isotope abundances of the IRMM 183–187 series of reference materials for the first time here.

The IRMM 183–187 series are delivered in flame-sealed glass ampoules containing about 0.004 mol uranium in about 5 ml of a chemically stable 5 M HNO_3 solution.

2. Experimental

To measure the minor isotope ratios ^{234}U/^{238}U and ^{236}U/^{238}U in IRMM 183–187 the double filament technique was applied as for most elements with high ionization potential. For each sample two 1 μl drops of a 1 molar nitric solution containing 5 μg uranium were dried down on a zone-refined rhenium filament, which had been degassed for 30 min at 1800 °C to remove impurities. All prepared sample filaments together with the corresponding ionization filaments were mounted on a 21 position sample turret.

The HI ("high intensity") method to measure the minor isotope ratios ^{234}U/^{238}U and ^{236}U/^{238}U on the Triton TIMS hgs been described in detail in [1,2] and will only be recapitulated briefly here. Because of the extended dynamic range and improved signal-to-noise ratio of the Faraday multi-collector of the Triton TIMS all ^{234}U/^{238}U ratios of the IRMM 183–187 materials could be measured using a Faraday cup collector. The measurement of the intensity at mass 234 using a secondary electron multiplier (SEM) would introduce additional uncertainty contributions, arising from the linearity correction of the SEM [3] and the inter-calibration between the SEM and the Faraday multi-collector.

The ion beam intensity of ^{236}U was only sufficient for Faraday cup detection in the case of IRMM 187; for all other materials, IRMM 183–186, the ^{236}U was measured using the SEM in ion-counting mode. The inter-calibration between the SEM and the Faraday multi-collector was done using the ^{234}U beam switched between a Faraday cup and the SEM. Because the ^{234}U intensity on the Faraday cup is quite low (ca. 1–2 mV) the correction of the ^{234}U intensity for the tailing contributions from the much higher ion beams of ^{235}U and ^{238}U is important for an accurate SEM/Faraday inter-calibration.

Within the SEM ion counting detector there are tailing contributions for both ^{234}U and ^{236}U as well, originated from the much higher ion beams of ^{235}U and ^{238}U, but all tailing effects observed in the SEM are generally reduced by a factor of about 100 using an energy filter in front of the SEM detector (called "RPQ", described in detail in [4]). For the ^{234}U detection during the SEM/Faraday inter-calibration (count rate ca. 100.000 counts per second) the tailing effect contribution is negligible, but for measuring ^{236}U/^{238}U ratios in the order of 10^{-8} to 10^{-6} using the SEM ion counter there is a significant tailing contribution in the order of about 10^{-11} to 10^{-10}, which has to be corrected for.

The ^{234}U intensity on the Faraday cup and the ^{236}U on the SEM are corrected regularly for the tailing effects during the measurement. The entire measurement consists of 8–10 blocks of 5 mass cycles each. For every mass cycle the tailing effects are measured at masses 233.7 and 234.4 to provide an average tailing contribution at ^{234}U (mass = ca. 234.05 u), and at masses 235.7 and 236.4 to provide an average tailing contribution at ^{236}U (mass = ca. 236.05 u). Also the SEM/Faraday inter-calibration is performed for every mass cycle throughout the entire measurement time, which provides more reliable results than in a procedure in which the inter-calibration is only done once at the beginning prior to the measurement. The mass cycle is arranged as shown in Table 1. Step 2 is introduced to measure ^{234}U in the SEM ion counter in order to calibrate it against the Faraday multi-collector.

The fractionation correction for the ^{234}U/^{238}U and ^{236}U/^{238}U ratios is also performed for each mass cycle throughout the entire measurement time, calculated internally using the ^{235}U/^{238}U value measured by UF_6 gas mass spectrometry. Combined uncertainties of the measurement results for IRMM 183–187 were calculated according to the "Guide to the Expression of Uncertainty in Measurements" [5]. They include all sources of uncertainty originating from the corrections for fractionation, linearity of the SEM and inter-calibration of the SEM versus the Faraday collector.

In order to control the accuracy of measured isotope ratios over a wide dynamic range suitable isotope reference materials have to be used. For example the IRMM-072 series

Table 1
Mass cycle arrangement for the HI method for the measurement of the ^{234}U/^{238}U and ^{236}U/^{238}U ratios

Step	Cup L2	Cup L1	Cup C SEM	Cup H1	Cup H2	Integration time (s)	Idle time (s)
1	234U	235U	236U	237	238U	32	2
2			234U	235U		4	2
3	233.7	234.7	235.7		237.7	16	14
4	234.4	235.4	236.4		238.4	16	2

It includes corrections for tailing effects and the inter-calibration between the SEM ion counter and the Faraday multi-collector. The long idle time of 14 s in step 3 is included in order to allow signal decay within the amplifiers.

Table 2
Re-certification of the IRMM 183–187 series of reference materials

	^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U
IRMM 183	$1.975\,5(22) \times 10^{-5}$	0.003 215 7(16)	$1.483\,58(54) \times 10^{-4}$
IRMM 184	$5.313\,8(32) \times 10^{-5}$	0.007 262 3(22)	$1.244\,6(17) \times 10^{-7}$
IRMM 185	$1.794\,74(80) \times 10^{-4}$	0.020 055 2(60)	$2.888\,9(23) \times 10^{-6}$
IRMM 186	$2.936\,5(13) \times 10^{-4}$	0.030 771 1(92)	$3.321\,9(23) \times 10^{-5}$
IRMM 187	$3.870\,0(16) \times 10^{-4}$	0.047 325(14)	$7.196\,5(39) \times 10^{-5}$

The new certificates, including the isotope abundances and mass fractions can be obtained from http://www.irmm.jrc.be. The uncertainties, expressed in paranthesis for each ratio value, are combined expanded uncertainties calculated using a coverage factor of $k = 2$ according to the "Guide to the Expression of Uncertainty in Measurements" [5].

of reference materials [6] (and its replacement IRMM-074), provides certified isotope ratios ranging from 1 down to 10^{-6} for the ^{233}U/^{238}U ratio and a ^{235}U/^{238}U ratio of 1. Therefore, IRMM-072 and IRMM-074 were used to verify the linearity for the Faraday multi-collector of the Triton TIMS. This is needed as a proof for the reliability of the ^{234}U/^{238}U measurements using the entire dynamic range of the Faraday multi-collector. The IRMM-072 series was also used for the SEM used for the detection of ^{236}U to establish the parameters for a linearity correction as described in [3].

Furthermore a set of three synthetic calibration mixtures with calculated ^{236}U/^{238}U ratios of 10^{-6}, 10^{-7}, and 10^{-8} was prepared to serve for an additional validation specifically for measurements of ^{236}U in ion counting mode. These calibration mixtures were composed of one natural uranium starting material (^{236}U below detection limit) and one non-natural starting material for which the ^{236}U isotope intensity could be measured using a Faraday collector alone. The preparation and certification of these mixtures will be reported elsewhere (submitted to JAAS).

3. Conclusions

The isotopic composition of the well-known IRMM 183–187 series of reference materials with ^{235}U abundances ranging from depleted to low enriched uranium (ca. 0.3%, 0.7%, 2.0%, 3.0% and 4.5%) was first certified in 1987. Because of progress in the development of mass spectrometric instrumentation the precision and accuracy of isotope ratio measurements has been improved significantly during the past 20 years and this allowed the minor isotope ratios of the series to be re-certified.

The new values of the minor uranium isotope ratios ^{234}U/^{238}U and ^{236}U/^{238}U of the IRMM 183–187 series are in each case normalized to the major ratio ^{235}U/^{238}U, measured by UF_6 gas mass spectrometry at the time of the original certification in 1987. The UF_6 gas mass spectrometer for its part was calibrated using synthetic UF_6 mixtures, which provides the traceability to the SI system. The relative expanded uncertainties (coverage factor $k = 2$, [5]) of the certified ^{235}U/^{238}U ratios range from 0.03% for IRMM 184–187 to 0.05% for IRMM 183. For the minor ratios the relative uncertainties range from 0.04% for the ^{234}U/^{238}U ratios in e.g. IRMM 185–187 up to 0.14% for the ^{236}U/^{238}U ratio in IRMM 184. IRMM 184 is important because it represents a close-to-natural sample with a ^{234}U/^{238}U ratio of $5.3138(32)\times10^{-5}$, a ^{235}U/^{238}U ratio of 0.0072623(22) and a ^{236}U/^{238}U ratio of $1.2446(17)\times10^{-7}$. In contrast to pure natural uranium IRMM-184 contains a fair amount of ^{236}U, but the re-certified ratio of IRMM 184 is useful to calibrate mass spectrometric equipment, such as AMS, ICP-MS and RIMS applied to measure ^{236}U in close to natural samples, and generally for isotope ratio measurements over a wide dynamic range. The re-certified isotope ratios for the IRMM 183–187 series of reference materials are given in Table 2.

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