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International Journal of Mass Spectrometry 269 (2008) 145–148

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Short communication

The isotopic composition of natural uranium samples—Measurements using the new $n(^{233}U)/n(^{236}U)$ double spike IRMM-3636

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Received 3 September 2007; received in revised form 19 September 2007; accepted 21 September 2007
Available online 29 September 2007

Abstract

The new double spike isotope reference material IRMM-3636 was prepared gravimetrically using highly enriched ^{233}U and ^{236}U isotopic material. The $n(^{233}U)/n(^{236}U)$ ratio was adjusted to about 1:1 and certified with an extended relative uncertainty of 0.016% (coverage factor $k = 2$). By mixing the $n(^{233}U)/n(^{236}U)$ double spike with a sample and applying internal mass fractionation correction, the $n(^{235}U)/n(^{238}U)$ ratio of a given sample can be determined with the highest possible precision and accuracy. Due to the low relative abundance of ^{234}U for the IRMM-3636 double spike (<0.00037%) measurements for $n(^{234}U)/n(^{236}U)$ of samples close to natural isotopic composition ($n(^{234}U)/n(^{236}U) \cong 5.4 \times 10^{-5}$) are also possible with a rather small correction and without significant increase in the uncertainty.

The IRMM-3636 double spike was applied for measurements of natural uranium ore samples. The results for $n(^{235}U)/n(^{238}U)$ ratios were compared to earlier data obtained using UF_6 gas sources mass spectrometry and to the most recent IUPAC recommended value, published in 2003. The results show that the historically used “consensus value” of 1/137.88 (earlier IUPAC value) cannot be considered representative for natural uranium samples.

Keywords: Isotope reference materials; Isotope mass spectrometry; Natural uranium; Double spike

1. Introduction

In nuclear safeguards as well as in several scientific disciplines there is a well-recognized need for certified isotopic reference materials of uranium. 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 uranium from the nuclear fuel cycle. The reference materials programme at IRMM was started in the 1980s with the preparation of the IRMM-072 series, which has been shown to be a set having the highest metrological quality for certified isotopic ratios [1,2]. IRMM-072 was prepared from purified, enriched uranium isotopic material of ^{233}U, ^{235}U and ^{238}U. The IRMM-072 set was designed in particular for the determination of mass-spectrometer linearity. After the supplies of the original IRMM-072 material became exhausted the replacement series IRMM-074 has been certified in 2005.

The new so-called double spike isotope reference material IRMM-3636 is a synthetic reference material produced by gravimetrically mixing a highly enriched (99.96%) spike of ^{233}U with a highly enriched (99.97%) spike of ^{236}U. The aim was to produce an isotope mixture with a certified $n(^{233}U)/n(^{236}U)$ ratio close to 1:1 and smallest possible uncertainty.

Due to the gravimetrical preparation technique a value for the $n(^{233}U)/n(^{236}U)$ ratio of the double spike IRMM-3636 is obtained, which is traceable to the SI system of units. If applied in combination with internal mass fractionation correction (normalization) the double spike provides the most precise and accurate way of measuring $n(^{235}U)/n(^{238}U)$ isotope ratios by mass spectrometry. The double spike also allows the determination of smallest differences of the $n(^{235}U)/n(^{238}U)$ isotopic ratios between samples of different origin [3].

Within this paper the preparation, certification and verification of the double spike IRMM-3636 is briefly described.

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doi:10.1016/j.ijms.2007.09.012

Furthermore, isotopic measurements of some natural UOC (uranium ore concentrate) samples from various geographical sources are presented, part of them performed by UF_6 gas source mass spectrometry (GSMS) in 1999 [4] and part of them performed recently by thermal ionization mass spectrometry (TIMS) using the new $n(^{233}U)/n(^{236}U)$ double spike IRMM-3636.

2. Preparation and verification of the double spike IRMM-3636

In the past double spike reference materials similar to IRMM-3636 have been prepared at various laboratories. However, the unique characteristics of IRMM-3636 are the high isotopic enrichment of the starting materials and the specific preparation technique. The double spike mixture at IRMM was made gravimetrically with the basic principle of dissolving weighable amounts of highly enriched oxides into solutions and mixing the solutions in the desired proportions gravimetrically. Prior to mixing, the ^{233}U and ^{236}U starting materials were purified using the same reagents and procedures, which involved anion exchange in nitric acid medium, cation exchange in HNO_3/THF and precipitation as peroxide. The purified ^{233}U and ^{236}U starting materials were calcined under almost identical conditions of temperature and humidity in order to form U_3O_8 and to ensure that both enriched materials have the same stoichiometry. The purified and calcined ^{233}U and ^{236}U oxides were dissolved into HNO_3 solution gravimetrically and the solutions were then mixed gravimetrically to obtain the double spike. The isotopic composition was calculated based on the weights of the ^{233}U and ^{236}U starting materials and their isotopic compositions, which were measured by TIMS. Due to their high isotopic enrichments, the uncertainties of the TIMS measurements did not contribute significantly to the calculation of the $n(^{233}U)/n(^{236}U)$ isotope ratio of the double spike.

A careful mass spectrometric verification measurement of the $n(^{233}U)/n(^{236}U)$ double spike was performed using a Triton TIMS at IRMM. For this purpose the double spike "sample" was mixed with an approximate amount ratio of 1:1 with the synthetic isotope reference material IRMM-3050. IRMM-3050 is the original synthetic mixture of highly enriched ^{235}U and ^{238}U spikes, part of which was mixed with a ^{233}U spike to obtain the IRMM-074 series. For the verification measurement the known $n(^{235}U)/n(^{238}U)$ ratio of 1.000259(81) in IRMM-3050 was used for internal mass fractionation correction to measure $n(^{233}U)/n(^{236}U)$ of the "sample" IRMM-3636. The very low uncertainty of the $n(^{235}U)/n(^{238}U)$ ratio for IRMM-074 arises because the purified oxides were mixed and dissolved together to form a master solution; whereas for the double spike, IRMM-3636, solutions of ^{233}U and ^{236}U were mixed, reflected in a higher certified uncertainty for this mixture. For the verification measurement of IRMM-3636 a multi-dynamic procedure was applied in order to minimize any influence and uncertainty contributions arising from the Faraday amplifier gains and cup efficiencies. This was achieved by measuring the $n(^{235}U)/n(^{238}U)$ ratio of IRMM-3050 using the same pair of Faraday cups as the $n(^{233}U)/n(^{236}U)$ ratio of IRMM-3636.

The result for the mass spectrometric verification measurement of IRMM-3636 is given by a ratio of $n(^{233}U)/n(^{236}U) = 1.019090(86)$. The relative expanded uncertainty of 0.0086% (coverage factor $k = 2$) is only slightly higher than the relative uncertainty of 0.0081% for the IRMM-3050 synthetic reference material. This mass spectrometric result is in excellent agreement with the calculated ratio from the gravimetric mixing, $n(^{233}U)/n(^{236}U) = 1.01906(16)$.

Isotope reference materials like the double spike IRMM-3636 are prepared to be used as standards in isotope mass spectrometry. In order to avoid circular reasoning the certified $n(^{233}U)/n(^{236}U)$ ratio of this reference material should be as independent as possible from mass spectrometric measurements. Therefore the gravimetrically determined ratio and its uncertainty are used for the certification of the double spike IRMM-3636. As a result from the mass spectrometric verification measurement, the very small and insignificant relative difference of 0.0029% between the measured and certified ratios provides a strong confidence to the certified $n(^{233}U)/n(^{236}U)$ ratio of IRMM-3636. This excellent agreement also confirms the assumption of achieving similar impurity levels and stoichiometry for all enriched starting materials of ^{233}U, ^{235}U, ^{236}U and ^{238}U prior to the preparation of the mixtures.

In contrast, if a $n(^{233}U)/n(^{236}U)$ double spike would be prepared by mixing ^{233}U and ^{236}U enriched materials without careful control of the chemical purification and calcination processes, it would have to be calibrated against other readily available uranium standards by mass spectrometry. In the past, e.g., reference materials such as NBL U500 or natural uranium materials, e.g., such as SRM950a/b/c, were used for this purpose. For the natural $n(^{235}U)/n(^{238}U)$ ratio sometimes the "consensus" value of 1/137.88 [5,6] has been used [3], which is not traceable to the SI system and has no uncertainty associated to it. This type of double spike is rather suitable for differential than for absolute $n(^{235}U)/n(^{238}U)$ ratio measurements.

3. Measurements of UOC samples from various sources

In Fig. 1 various mass spectrometric measurements of the $n(^{235}U)/n(^{238}U)$ ratio for UOC (uranium ore concentrate) samples are presented. The measurements of samples 1–4 are taken from an earlier publication about isotopic fingerprinting of UOC samples [4]. They originate from Namibia, Canada, France and the Czech Republic, respectively. They were analyzed by a UF_6 gas source mass spectrometer (GSMS), using the double standard method. The UF_6 standards were calibrated based on synthetic mixtures of highly enriched ^{235}U and ^{238}U starting materials, and are therefore traceable to the SI-system. The quoted relative uncertainties of the GSMS measurements are at the level of 0.05%. These uncertainties are considered to be conservative.

Fig. 1 also contains TIMS measurements of three UOC samples from Australia, presented as samples #5–7. For each of these three samples TIMS measurements were carried out using the IRMM-3636 double spike in combination with internal normalization. The samples were mixed on the TIMS filaments with the IRMM-3636 Double Spike, using sample/spike mixing ratios

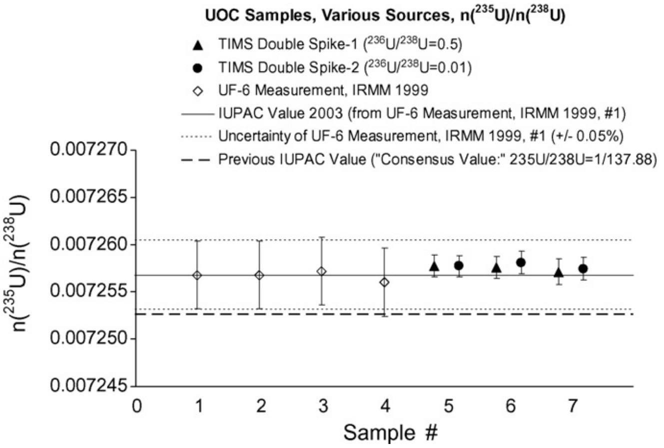

Fig. 1. Results for $n(^{235}U)/n(^{238}U)$ for seven UOC (uranium ore concentrate) samples, originating from Namibia (#1), Canada (#2), France (#3), the Czech Republic (#4) and Australia (#5–7). The results are compared to the most recent IUPAC recommended [7] value, which is originating from sample #1 [4], and to the previous IUPAC value [5] ("consensus" value of 1/137.88 [6]).

of about 1:1 and 50:1 for the uranium amount, corresponding to isotope ratios $n(^{236}U)/n(^{238}U) = 0.5$ and $n(^{236}U)/n(^{238}U) = 0.01$, respectively. The certified $n(^{233}U)/n(^{236}U)$ ratio was used for internal mass fractionation correction to determine the $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ ratios of the Australian UOC samples. The sample/spike mixing ratio of about 50:1 turned out to be advantageous, because the corrections for the ^{234}U and ^{235}U contributions from the IRMM-3636 double spike and the peak tailing contribution from ^{236}U are much less significant.

The agreement among the $n(^{235}U)/n(^{238}U)$ ratios for all seven UOC samples presented here is quite obvious, no matter if they were measured by UF_6-GSMS or TIMS. However, the smallest uncertainties for $n(^{235}U)/n(^{238}U)$ ratio measurements are obtained using the IRMM-3636 double spike with internal normalization. All results presented here are also in good agreement with the IUPAC recommended data for the "representative isotopic composition", for uranium, published in 2003 [7] and originating from sample #1 [4]. All presented ratios, most significantly those measured with the IRMM-3636 double spike, are about 0.053% higher than the previous IUPAC recommended value [5]. This previous IUPAC value is also well-known by the value of 0.72% for the molar ^{235}U abundance. It furthermore corresponds to the "consensus value" of 1/137.88 for the $n(^{235}U)/n(^{238}U)$ ratio of natural uranium [6].

In particular the measurements obtained with the new double spike strongly support the 2003 IUPAC recommended value. However, it has been reported on several occasions (e.g., in Refs. [3,8]), that natural uranium samples from different sources may differ by up to 0.13% in their $n(^{235}U)/n(^{238}U)$ ratios. Therefore it is suggested that the "consensus value" of 1/137.88 has to be considered with quite some care. From the results of interlaboratory comparisons, e.g., REIMEP 18, it appears that the "consensus value" is quite often used for mass fractionation correction or Faraday/ion counter inter-calibration performed using natural like uranium samples [9]. Therefore a careful verification measurement of any presumably natural uranium material used for calibration purposes is strongly recommended. The double spike IRMM-3636 is the ideal tool to do this with high accuracy and with expanded relative uncertainties as low as 0.016% (coverage factor $k = 2$).

The new IRMM-3636 double spike also allows measurements of $n(^{234}U)/n(^{238}U)$ ratios for natural type samples ($n(^{234}U)/n(^{238}U) \cong 5 \times 10^{-5}$) with good precision and accuracy. This is due to the quite low $n(^{234}U)/n(^{236}U)$ ratio of about 0.00036606 in the double spike, with a relative expanded uncertainty of 0.13% (coverage factor $k = 2$). For the TIMS measurements of the UOC samples #5–7 using a sample/spike mixing ratios of 50:1 (corresponding to $n(^{236}U)/n(^{238}U) = 0.01$), the relative ^{234}U contribution from the IRMM-3636 double spike to the total ^{234}U beam intensity was below 7%. This is resulting in an additional uncertainty contribution of below 0.01% for the corrected $n(^{234}U)/n(^{238}U)$ ratio, which is insignificant in most cases. As shown in Fig. 2, for the UOC samples #5–7 from Australia TIMS measurements for natural type $n(^{234}U)/n(^{238}U)$ ratios using the double spike agree well with "direct" TIMS measurements. The direct TIMS measurements were performed by internal normalization of the $n(^{234}U)/n(^{238}U)$ ratios using the corrected $n(^{235}U)/n(^{238}U)$ ratios, which were in turn based on external normalization using a certified $n(^{235}U)/n(^{238}U)$ standard. For all $n(^{234}U)/n(^{238}U)$ measurements reported here, the ^{234}U isotope was detected using a Faraday cup in combination with a $10^{12}\,\Omega$ amplifier resistor in order to improve the signal to noise ratio. The entire Faraday multi-collector system was checked for detector linearity using the IRMM-074 series of synthetic reference materials.

The relationship between the $n(^{234}U)/n(^{238}U)$ ratios and the geological structure of the sample origin is complicated and depends on genesis, age and also the water permeability of the ore body. Details about the UOC samples from Australia and their elemental and isotopic analysis will be discussed in another paper [10]. As pointed out also in [4], the results suggest that this isotope ratio may well serve as a signature for attribution of uranium ore concentrate for safeguards and non-proliferation purposes.

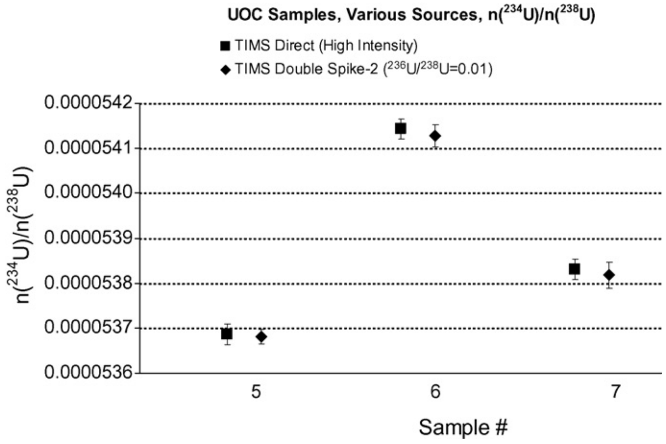

Fig. 2. Results for $n(^{234}U)/n(^{238}U)$ for three UOC (uranium ore samples) samples, originating from Australia.

4. Conclusions

The new gravimetrically prepared IRMM-3636 double spike isotope reference material is characterized by a certified $n(^{233}\text{U})/n(^{236}\text{U})$ ratio close of to 1:1 and an expanded relative uncertainty of 0.016% (coverage factor $k = 2$). Therefore IRMM-3636 is an ideal isotope reference material for $n(^{235}\text{U})/n(^{238}\text{U})$ ratio measurements performed using internal mass fractionation correction, which can be done with improved precision and accuracy. Measurements of uranium ore samples using the IRMM-3636 double spike strongly support the most recent IUPAC recommended value for natural uranium, published in 2003, over the previous one, which was given by the $n(^{235}\text{U})/n(^{238}\text{U})$ "consensus value" of 1/137.88.

Additionally, measurements of $n(^{234}\text{U})/n(^{238}\text{U})$ ratios for natural uranium can be done with small corrections and negligible additional uncertainty contributions from the application of IRMM-3636.

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