EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

Update on REIMEP-15: Isotopic Ratios of Uranium in UF_6

S. Richter, A. Alonso, W. De Bolle, H. Kühn, A. Verbruggen, R. Wellum

Report EUR 21562 EN

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Dr. Stephan Richter
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: stephan.richter@cec.eu.int

Tel.: +32 (0)14 571 701
Fax: +32 (0)14 571 863

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

EUR Report 21562 EN
Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

Update on REIMEP-15: Isotopic Ratios of Uranium in UF_6

S. Richter, A. Alonso, W. De Bolle, H. Kühn, A. Verbruggen, R. Wellum

Abstract

The REIMEP (Regular European Interlaboratory Measurement Evaluation Programme) campaign 15 for isotopic ratios of uranium in UF_6 samples was completed in 2001. The participants received 4 samples of low-enriched or slightly depleted uranium in the form of UF_6 in standard monel capsules. The samples were prepared at IRMM by mixing uranium reference materials certified by gas mass-spectrometry in the form of UF_6. The minor isotopes, ^{234}U and ^{236}U were certified at IRMM by Thermal Isotope Mass-spectrometry (TIMS) using a MAT262-RPQ mass spectrometer in ion counting mode.

Certified values were sent to the participating laboratories immediately after receiving their measured results. The measured results and their comparison with the certified values allowed an overall view of the analytical capability in the nuclear field to measure uranium isotopic ratios in UF_6 samples. However, for the so-called minor ratio $n(^{234}U)/n(^{238}U)$ the comparison of IRMM's certified values for at least one of the samples with the participant's results showed a significant relative deviation of about 2%, which is by far larger than the typical uncertainties expected for this kind of measurements. This significant deviation was considered disappointing for IRMM as the leading European nuclear safeguards metrology institute as it pointed to a possible weakness in the certification process. This problem has now been overcome firstly by measurements using the new TRITON TIMS at IRMM and secondly by a thorough investigation on the reasons for the deviation observed in the past.

Introduction

The accurate measurement of the isotopic composition of uranium hexafluoride is essential to plant operators for closing their material balance, for meeting the specifications of their customers and for economical reasons. It is furthermore essential to Safeguards Authorities for their verification measurements. REIMEP is an external quality control program, organised by IRMM for almost 20 years, which offers a tool to evaluate the individual laboratory performance relative to certified reference materials.

The results of all 3 REIMEP UF_6 campaigns (1986, 1995 and this one, REIMEP 15, from 2001) have been described in detail in /1/, /2/, /3/ and /5/. In this report, first the sample preparation and the results of the REIMEP 15 campaign will be recapitulated briefly. Second, the new measurements performed using the new TRITON TIMS at IRMM will be presented, followed by a discussion about the possible reasons for the deviation observed in the first place.

Samples

Four samples were prepared by a procedure used in mixing certified UF_6 materials which allows samples with predefined isotopic abundances of ^{234}U, ^{235}U and ^{236}U to be prepared (see /3/). The final abundances covered a range from depleted to low enriched uranium (Tab. 1) and with varying ^{234}U (from 0.012 to 0.033 %) and ^{236}U (from 0.000 03 to 0.01 %) isotopic abundances which provided a satisfactory wide range of ratios for the minor isotopic ratios. Care was taken in the selection of the starting materials to ensure that the minor isotopic and the ^{235}U abundances were not correlated in any way.

The isotopic ratios $n(^{235}U)/n(^{238}U)$ were measured in each mixture by gas-source electron impact mass-spectrometry with an standard uncertainty of 0.025%.

The minor isotopic abundances were measured by thermionic mass-spectrometry (TIMS) after hydrolysis of the UF_6 by HNO_3 and using the certified $n(^{235}U)/n(^{238}U)$ from the gas mass-spectrometry as internal standard for mass-fractionation corrections. The intensities at the masses of the minor actinides ^{234}U and ^{236}U were measured on a MAT262-RPQ TIMS by counting the ions collected at an electron multiplier, a retarding potential device, 'RPQ', situated in front of the ion counter removed ions degraded in energy, thus removing interferences from tailing of the most intense peak at mass 238. The ion counter was calibrated by measuring the 235 mass peak both by Faraday collector and electron multiplier.

This method has been proved excellent for the certification of minor isotopic ratios of uranium and is the standard method employed at IRMM. The uncertainties on the measured isotopic ratios were calculated strictly following the GUM /4/, whereby the uncertainties for the minor isotope ratios include the propagated uncertainties from the gas mass-spectrometer measurements. The samples were labelled 'REIMEP-15A', 'REIMEP-15B', 'REIMEP-15C', and 'REIMEP-15D'.

First Results of the REIMEP 15 Campaign

The following laboratories had supplied results for this measurement round at the time of preparation of this report:

- Comision Nacional de Energia Atomica, Buenos Aires, Argentina
- Centro Tecnológico da Marinha, São Paulo, Brasil
- EURODIF, Pierrelatte, France
- IAEA, Seibersdorf, Austria
- URENCO, Almelo, Netherlands
- URENCO, Capenhurst, UK
- URENCO, Gronau, Germany
- NBL, U.S. DOE, Argonne, IL, USA.

The sequence of the laboratories as mentioned above does not correspond to the code numbers in the graphs below.

For the results of main isotopic ratio $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ the conclusion was that all participating laboratories successfully measured this ratio, even while a variety of methods (gas measurement, hydrolysis and TIMS, Multicollector ICPMS, Quadrupole ICPMS) was employed. Therefore no graphs are shown for this ratio.

For the so-called minor ratios $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ which range around 1-3x10^{-4} the comparison of results shows that the laboratories are well capable of performing accurate measurements. But looking at the results for the REIMEP 15 D in particular, the sample with the highest values for both ratios, significant deviations of ca. 2% between all participant's results and the certified range by IRMM (dark grey area) were observed. This is shown for the $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ ratio in figure 1.

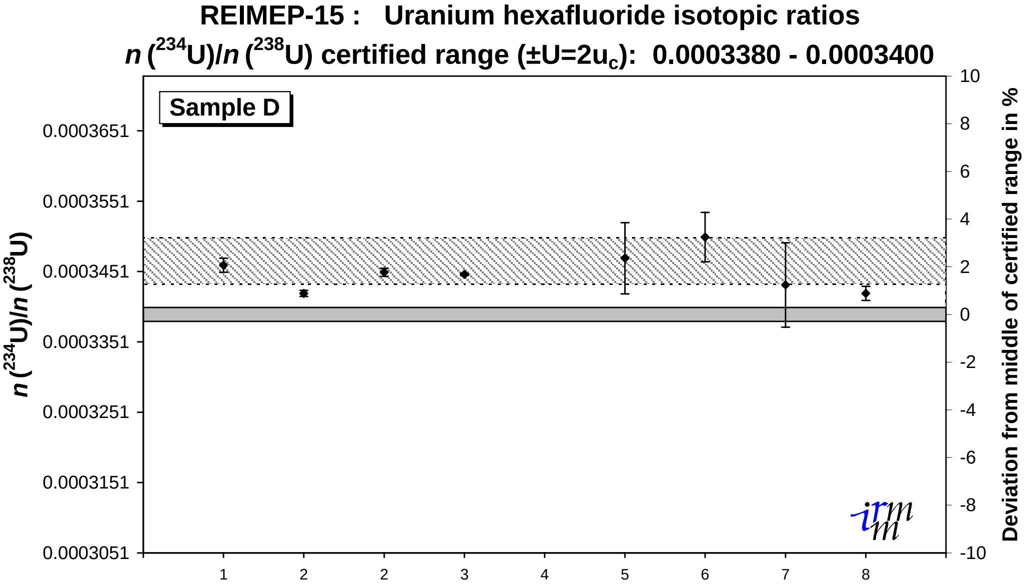

Fig. 1: Results for $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ of REIMEP 15 D from all participants (1-8)

The light grey area represents the results of mixture calculations based on the isotopic composition of the starting materials and is expressed as a range of expanded uncertainty, with coverage factor k=2.

Recent Re-Measurements at IRMM

After the new TRITON TIMS from Thermo Electron was installed at IRMM in 2004 the REIMEP 15 A-D samples were re-measured. Due to the extended dynamic range of the new Faraday-multi-collector all $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ ratios (except $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ for sample C) could be measured using Faraday detectors only. On the TRITON even the "minor" isotopes ^{234}U and ^{236}U could be detected using Faraday detectors and not using an ion counter as before using the MAT262-RPQ. This method allows circumventing the inter-calibration between Faraday cups and the ion counter as well as the linearity and the dead time corrections on the ion counter. This also leads to lower uncertainties.

The method used to measure uranium minor ratios on the TRITON TIMS takes advantage of the extended dynamic range of the Faraday detector system (for more details see /6/ and /7). It can be used to measure

- All minor ratios $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ between about $2\mathrm{x}10^{-5}$ and 1. using Faraday-collectors only.
- All minor ratios $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ below about $2\mathrm{x}10^{-5}$ using the SEM ion counter to detect ^{236}U.

During the course of the measurement $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ ratios are acquired as well, but they are used only for an internal mass fractionation correction, which is based on the certified result from the $\mathrm{UF_6}$-gas mass spectrometry measurement.
Minor ratio values $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ in a range between about $2\mathrm{x}10^{-5}$ and 1 can be measured using Faraday-collectors with the smallest uncertainty. This applies to all $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ ratios of REIMEP 15 A-D, except for $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ for REIMEP 15 C.
The ^{234}U and ^{236}U intensities are corrected for tailing effects originated from the major isotope beams ^{235}U and ^{238}U. For each mass cycle within each block the tailing effects are measured at masses 233.7 and 234.4 to provide an average tailing contribution at ^{234}U (mass=ca.234.05amu), and at masses 235.7 and 236.4, respectively, to provide an average tailing contribution at ^{236}U (mass=ca.236.05amu). The mass cycle is arranged as follows:

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

The long idle time of 14 sec. between steps 1 and 2 is required to accommodate the signal decay within the Faraday amplifier circuitry after the integration on the uranium masses in step 1.

For minor ratio values $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ lower than $1\mathrm{x}10^{-5}$ as in case of REIMEP 15 C, measurements using the SEM ion counter provide smaller uncertainties. In this case the size of one ion beam for the inter-calibration between Faraday and ion counter has to be adjusted in such a way that it has the size of about 5 mV on the Faraday cup (±20%), which corresponds to ca. 300.000 cps (counts per second) on the ion counter. Because of the dynamic range of the Triton Faraday collectors (50V), the inter-calibration can be done well using the ^{234}U beam in this case. This requires a constant ^{238}U ion beam of ca 18-20V. This way the inter calibration can be performed for every mass cycle throughout the entire measurement time, which provides more reliable

results compared to a procedure in which the ion counter is only inter-calibrated once at the beginning prior to the measurement.
Also in this case the ^{234}U and ^{236}U intensities are corrected for tailing effects originated by the major isotope beams ^{235}U and ^{238}U as described before.
For all isotope beams detected using the SEM ion counter a dead time correction was performed using the electronically determined dead time value. Furthermore, the linearity of the SEM ion counter was investigated using the series of certified isotope reference material IRMM-072. A non-linearity was found and corrected for, similar to which has been found on many SEM ion counters and which is described in detail in /8/, /9/, /10/ and /11/.
In the case of ion counting measurements for the $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ below $1\mathrm{x}10^{-5}$ the mass cycle is arranged as follows:

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

Step 2 is introduced to measure ^{234}U in the SEM ion counter in order to calibrate the ion counter against the Faraday multi-collector.

In Figure 2 the results of all participants (1-8) are shown together with new results obtained recently at IRMM. Obviously the TRITON result now agrees very well with the mainstream of all the participating laboratories.

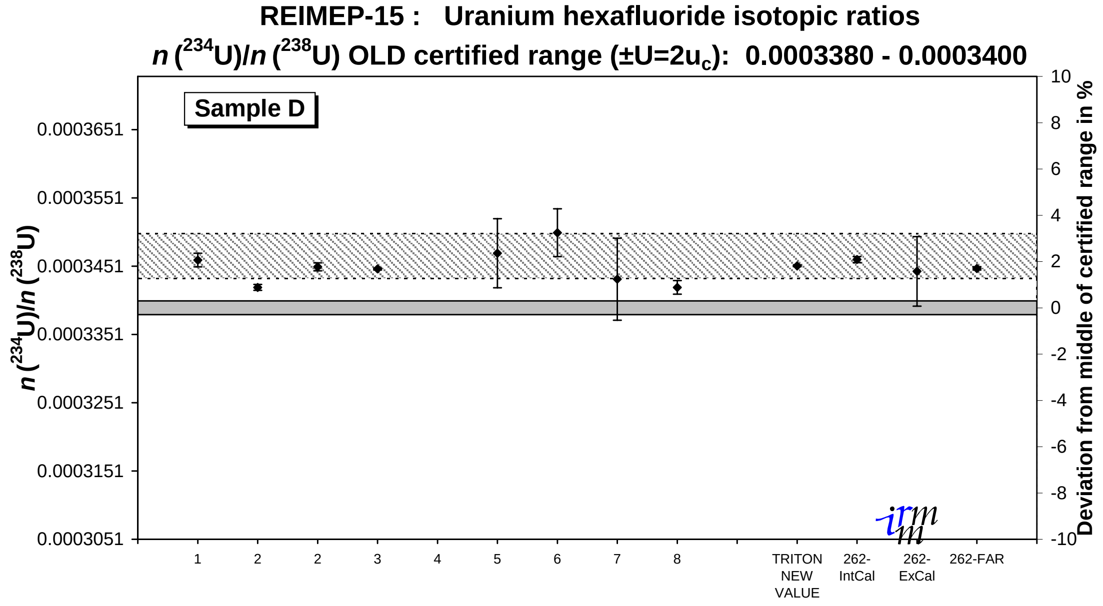

Fig. 3: Results for $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ of REIMEP 15 D from all participants (1-8), together with recent re-measurements at IRMM. The indicated "TRITON NEW VALUE" is used for the re-certification.

In addition to the new measurements on the TRITON TIMS some more tests (a, b and c) on the MAT262-RPQ were performed in order to investigate the cause of the earlier 2% deviation. Prior to those tests a linearity test was done with the MAT-RPQ ion counter according to the procedures described in /8/ and /9/ using the certified isotope reference material IRMM-072. The correction parameters were entered into the MAT262 software and the correction applied to all following test measurements.

a) The $n(^{234}U)/n(^{238}U)$ was measured by detecting the ^{234}U on the ion counter as done before. But in contrast now the intensity of the ^{235}U isotope was kept constant at a level of 5 mV on the Faraday cup (±20%), which corresponds to ca. 300.000 cps (counts per second) on the ion counter. This allows an inter-calibration of the ion counter against the Faraday collector throughout the entire measurement. On the other hand, the ^{238}U intensity is only about 700mV using this method, which is far below the maximum possible intensity of 10V. The result is displayed as “262-IntCal” in Figure 2 and agrees well with the TRITON result and the results of all other campaign participants.

b) A measurement using the MAT262-RPQ was performed using a much higher ^{238}U intensity between 5-7V. This has the advantage of better counting statistics for the ^{234}U measurement, but the disadvantage that an “internal” inter-calibration of the ion counter as done in a) is not possible here, because the ^{235}U intensity would be much too high for the ion counter. The inter-calibration had to be done at a lower sample temperature than the actual measurement temperature, using a 5mV beam of ^{235}U. It cannot be excluded that the change of sample conditions, e.g. temperature and ion beam focussing, can cause a change in the inter-calibration factor. This effect can differ from one sample filament to the next as well, causing a worsening of the reproducibility for repeated measurements. This effect can be observed in the result displayed as “262-ExCal” in Figure 2. But as in a), the result agrees well with the TRITON result and the results of all other campaign participants. This is the technique which was employed for the original certification using the MAT262-RPQ in the past, but at that time no linearity testing and correction was made for the ion counter on the MAT262-RPQ.

c) As a further test a measurement using a Faraday detector for ^{234}U was performed using the MAT262-RPQ, but with a lower ion beam intensity compared to that employed in the TRITON measurements. The result agrees well with the TRITON result and the results of all other campaign participants.

As a result all re-measurements, the $n(^{234}U)/n(^{238}U)$ ratio for REIMEP 15 D does now agree well with those of the other campaign participants. The TRITON value has the lowest uncertainty because of the highest ion beams used on this instrument. Therefore all REIMEP 15 certificates have been updated using re-measurements on the TRITON.

The re-measurements a) and b) on the MAT262-RPQ agree well with the TRITON result and the other participants’ results, but in the previous certification measurements on the MAT262-RPQ performed in a way similar to b) did not. The most likely reason for this is the lack of linearity testing and correction at that time. The type of linearity correction as described in /8/ and /9/ was not yet known at the time of the certification measurements in 2000.

According to the observation in /8/ and /9/, the sensitivity of the SEM ion counter starts to increase beyond a count rate of ca. 50.000 cps (counts per second) with a slope of ca. 0.3-1.0% per decade of the count rate. The ^{234}U count rate was always below the limit of 50.000 cps and did not require a correction, thus it was not affected by the non-linearity problem. But the ^{235}U ion beam used for the inter-calibration between Faraday and ion counter (done at 300.000cps) is affected strongly by the non-linearity and therefore the sensitivity of the ion counter (meaning the ratio [^{235}U-SEM/^{235}U-Far]) was estimated higher than it actually was. Consequently the ratio $n(^{234}U)/n(^{238}U)$ came out too low, which just explains the lower ratio measured in the past. The observed deviation of ca. 2% in Figure 1 seems slightly higher than expected from a non-corrected result on the MAT262-RPQ, but the reason for that might be a possibly poor or degrading performance of the SEM used for those measurements.

Conclusions

The problem with the observed deviation between the certified result for REIMEP 15 D and the results from all participants has been solved by re-measurements on the new TRITON TIMS at IRMM. New certificates for all REMEP 15 A-D samples have been issued based on these new data and attached to this report.
The cause of the deviation was investigated using the MAT262-RPQ which was employed for the certification measurements in the past. The most likely reason for the deviation was found to be a lack of linearity correction for the ion counting system of the MAT262-RPQ.
The results point to the need for close checking during mass spectrometric measurements. A systematic effect like the one found here can only be isolated and corrected for using independent isotopic reference materials such as IRMM-072.

References

/1/ W. De Bolle , R. Damen, P. De Biève, W. Nagel, H. Meyer, W. Lycke, W. Wolters, The state of the practice in low enriched UF_6 isotopic measurements in the European Community: Result of REIMEP UF_6. Proc.13th Annual ESARDA Symposium, Avignon, France, 14-16 May ’91, p181-185

/2/ K. Mayer, W. De Bolle, A. Alonso, M. Blanco and P. De Bièvre, REIMEP Uranium hexaflouride, II Results, Evalutation and Discussion, Proc.17th Annual ESARDA Symposium, Aachen, Germany, 9-11 May ’95, p459-467

/3/ W. De Bolle, A Alonso, A. Verbruggen, R. Wellum Proc.21th Annual ESARDA Symposium, Sevilla, Spain, 4-6 May ’99, p585-587

/4/ International Organisation for Standardisation, “Guide to the Expression of Uncertainty in Measurements”, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993.

/5/ A. Alonso, W. De Bolle, A. Verbruggen, R. Wellum, REIMEP-15 Uranium isotopic ratios and abundances, Report to participants, Internal report GE/R/IM/15/01, April 2001.

/6/ S. Richter, S. A. Goldberg (2003), Improved Techniques for High Accuracy Isotope Ratio Measurements of Nuclear Materials using Thermal Ionization Mass Spectrometry, International Journal of Mass Spectrometry, 229 (2003) 181-197.

/7/ S. Richter, A. Alonso, H. Kühn, R. Wellum, P.D.P. Taylor (2004), New Procedures for Uranium Isotope Ratio Measurements using the new TRITON Thermal Ionisation Mass Spectrometer, Internal report GE/R/IM/19/04, July 2004

/8/ S. Richter, S. A. Goldberg, P. B. Mason, A. J. Traina and J. B. Schwieters (2001), Linearity Tests for Secondary Electron Multipliers Used in Isotope Ratio Mass Spectrometry, International Journal of Mass Spectrometry, 206/1-2, 105-127.

/9/ S. Richter, S. A. Goldberg, P. B. Mason, A. J. Traina and J. B. Schwieters (2001), Linearity Tests for Secondary Electron Multipliers Used in Isotope Ratio Mass Spectrometry, Proceedings of the 2001 Annual Meeting of the American Society for Mass Spectrometry, Chicago May27-31, 2001.

/10/ D.L. Hoffmann, D.A. Richards, T.R. Elliott, P.L. Smart, C.J.Hawkesworth, (2005), Characterization of Secondary Electron Multipliers Nonlinearity using MC-ICPMS, International Journal of Mass Spectrometry, in review.

/11/ TRITON Operating Manual, section EVALUATION/1.12.

European Commission

EUR 21562 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements – Update on REIMEP-15: Isotopic Ratios of Uranium in UF_6
Authors: S. Richter, A. Alonso, W. De Bolle, H. Kühn, A. Verbruggen, R. Wellum
Luxembourg: Office for Official Publications of the European Communities
2005 – 11 pp. – 21.0 x 29.7 cm
Scientific and Technical Research series

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Publications Office
Publications.eu.int