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REIMEP 18:

Inter-Laboratory Comparison for the Measurement of Uranium Isotopic Ratios in Nitric Acid Solution

Report to Participants

S. Richter, A. Alonso, J. Truyens, H. Kühn,
A. Verbruggen, R. Wellum

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Abstract

The REIMEP 18 (Regular European Inter-laboratory Measurement Evaluation Programme) campaign was started in October 2005. For this campaign 4 samples of depleted to low-enriched uranium were chosen. State of the art certification measurements were carried out using a Varian MAT511 UF₆-gas source mass spectrometer (GSMS) for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio and using a Triton thermal-ionization mass-spectrometer (TIMS) for the minor isotope ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$. Verification measurements on ampouled samples were performed successfully and showed good agreement with the certified ratios.

REIMEP 18 has been the largest nuclear measurement campaign organized by IRMM so far. Samples were shipped in March 2006 to 85 registered participants. Most of the participating laboratories submitted their results before May 31st 2006. Due to problems with the sample containers and extended shipping times the submission deadline had to be postponed until September 30th 2006 for some of the participating laboratories. In the end IRMM received results from 71 laboratories.

The results of the REIMEP 18 campaign confirm in general the excellent capability of laboratories in measuring isotopic abundances of uranium although some problems arose for the measurements of the minor isotope ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$. This report describes the outcome of the REIMEP 18 campaign, including the graphical evaluation and discussion of the results, the evaluation of the questionnaire and the discussion of conclusions and actions to be taken.

1. Introduction

Laboratories carrying out nuclear measurements need an active quality management system to ensure their measured values are acceptable. Nuclear analytical laboratories especially are required to demonstrate their measurement capability on a regular and timely basis. One way of demonstrating measurement capability is to participate in interlaboratory comparisons. For this reason, IRMM has organized quality control campaigns for measurements of uranium and plutonium for safeguards and fissile material control for more than 20 years.

The REIMEP programme (Regular European Inter-laboratory Measurement Evaluation Programme) serves as a tool for laboratories to demonstrate their abilities to measure uranium and plutonium isotopic ratios in a variety of sample forms, chosen where possible to be typical of fissile material samples commonly found in the nuclear industry and controlled by nuclear safeguards authorities. Previous REIMEP campaigns have included samples such as uranium oxide, uranium in nitric acid, uranium in the form of UF₆ [1, 2], plutonium oxide, and others.

In October 2005 the REIMEP 18 campaign for the measurement of isotopic ratios of uranium in nitric acid solution was started. This campaign was organized in order to respond to the needs for external quality control expressed by customers from the nuclear safeguards and the scientific area. The REIMEP 18 campaign follows earlier campaigns for the measurement of uranium isotopic ratios, which turned out to be very valuable in showing the measurement capabilities of laboratories active in this measurement field. This field not only comprises the nuclear industry and laboratories working for nuclear safeguards. For REIMEP 18 a significant number of laboratories from the environmental, geochemistry and cosmo-chemistry areas were also included. The reason for this expansion was first to obtain a more representative general picture of measurement capabilities for uranium isotopic abundances and also to possibly expand the collaboration with scientists from these areas.

The field of uranium isotopic measurements includes a variety of different measurement techniques. For measuring isotopic ratios various types of inductively-coupled-plasma mass-spectrometry (ICP-MS) are widely used. Thermal-ionization mass-spectrometry (TIMS) is a well

known technique and other methods such as accelerator mass-spectrometry (AMS) and alpha spectrometry are being used as well for certain isotope ratios.

For the REIMEP 18 campaign the uranium samples were provided in nitric acid solution, which is a matrix that is easy to handle and does not require extensive sample preparation steps, such as separation from other elements or other purification steps. In REIMEP 18 the main concern was the measurements of uranium isotopic ratios by alpha spectrometry or mass spectrometry, which was quite a challenge in any case because of the large range of isotopic compositions.

For uranium or plutonium measurements on environmental samples, which usually require considerable chemical preparation prior to mass spectrometry, IRMM also carries out the Nuclear Signatures Inter-laboratory Measurement Evaluation Programme, NUSIMEP. Several NUSIMEP rounds with different sample matrices have been organized within the last few years [3, 4].

The REIMEP (and NUSIMEP) campaigns are open for all laboratories active in the nuclear and scientific field and have in common the following:

- The samples are prepared and certified at IRMM and are sent to participating laboratories as 'blind' samples;
- Participating laboratories are requested to measure the parameters specified using their standard methods and send results with uncertainties to IRMM. In return the laboratory receives a certification report including the certified values;
- A summary of the campaign results ("Participants' Report") is published giving a 'snapshot' of the laboratories' measurement capability for these samples.

All participating laboratories are asked to complete a questionnaire when submitting results. The aim of the questionnaire is to show the influence of the laboratories' experience and the techniques used for measurements on the results.

2. Sample Preparation and Certification Measurements

The sample preparation and certification is described in detail in the REIMEP 18 certification report [5] and is only recapitulated briefly here. Mass-spectrometric certification measurements for uranium isotope ratio measurements for the REIMEP 18 campaign were performed at IRMM with advanced technology, leading to state of the art precision and accuracy in isotopic measurements.

For the REIMEP 18 campaign, four samples of depleted to low-enriched uranium were selected from the IRMM stock. The original uranium samples were in UF₆ form. They were certified for the so-called "major" ratio $n(^{235}\text{U})/n(^{238}\text{U})$ using a Varian MAT511 UF₆-gas source mass spectrometer (GSMS), calibrated using certified materials traceable to synthetic isotope mixtures. The samples in UF₆ form were hydrolyzed and calcined in order to obtain the uranium in oxide form (U₃O₈). The oxides were dissolved in nitric acid to obtain the batch solutions for REIMEP 18 A-D. In order to verify the certified major ratios $n(^{235}\text{U})/n(^{238}\text{U})$, TIMS measurements were performed using the "Modified Total Evaporation" (MTE) technique as described in [6].

The batch solutions for REIMEP 18 A-D were dispensed and sealed into 100 ampoules each in order to have a sufficient supply for all interested participants. Each of the ampouled samples contained 2.5 mg uranium in 0.5 mL 0.5 M nitric acid solution. The sample amounts were chosen in order to achieve a total alpha activity of less than 1000 Bq for each set of 4 samples REIMEP 18 A-D, which allowed the sample sets to be shipped as non-nuclear material. This was a significant advantage for a large number of participating laboratories, because extensive administrative work related to nuclear transport requirements could be avoided.

The so-called "minor" uranium isotope ratios, $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ were then measured and certified using a Triton thermal-ionization mass-spectrometer (TIMS). The HI-method (HI = "high intensity") is described in detail in references [6-8]. The certificates for the samples REIMEP 18 A-D are presented in [5]. Additional verification measurements were performed at IRMM on one REIMEP 18 A-D sample set using TIMS only and showed good agreement with the certified values.

3. Participation

Invitations to participate were sent to a large number of laboratories, using participants lists from earlier REIMEP and NUSIMEP campaigns, instrument related list-servers (e.g. TIMS and Plasma-chem list-servers from Syracuse University), customer lists from instrument suppliers, personal contacts, etc. The response was very positive: registrations were received from 85 laboratories in 26 countries (Table 1). Within the U.S., the New Brunswick Laboratory (NBL, U.S. DOE) acted as co-organizer by contacting a number of laboratories that regularly participate in NBL's measurement evaluation programme.

Table 1: Countries of origin for registered and participating laboratories

Country	No. of registered participants	No. of submitted results
Australia	4	3
Austria	3	3
Belgium	3	3
Bosnia-Herzegovina	1	1
Canada	4	4
Czech Republic	1	1
France	5	5
Germania	8	7
Hungary	1	1
Israel	2	1
Italy	1	1
Japan	5	4
South Korea	1	1
Latvia	1	1
Lithuania	1	1
Netherlands	2	1
Poland	1	1
Portugal	1	1
Russia	2	0
Serbia-Montenegro	2	1
Spain	2	2
Sweden	2	1

Switzerland	2	1
Turkey	2	1
UK	13	11
US	15	14

These laboratories were active in the fields of research and development, measurement of radioactivity in the environment, monitoring of nuclear facilities, medical applications, measurements for fissile material control or safeguards as shown in table 2 (more than one answer possible).

The entire participating community falls mainly into 2 sections: in the first those doing research and development in scientific disciplines such as geochemistry (ca. 20 participants) and in the other those involved in nuclear isotope ratio measurements in the environment, in nuclear facilities or for fissile material control and safeguards purposes.

Table 2: Area of expertise of participating laboratories

Areas of Expertise	No. of participating laboratories (more than one answer possible)
Research and development	47
Measurement of radioactivity in the environment	31
Monitoring of nuclear facilities	21
Medical applications	3
Measurements for fissile material control or safeguards	27
Other	10

4. Results and Discussion

All participating laboratories were asked to measure the uranium isotopic composition for samples REIMEP 18 A-D, and present the results for $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ isotope ratios (mandatory), the ^{234}U , ^{235}U , ^{236}U and ^{238}U abundances and mass fractions (optional). Because the optional isotope abundances and mass fractions are not measured directly but only derived from the isotope ratios, only the submitted results for the isotope ratios will be evaluated and discussed here. The results for the $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ ratios are presented here in decreasing order of the ratio. The reason for this is that it allows us the possibility to evaluate the dependency of the isotope ratio measurements on the value of the ratio and to discuss possible trends observed.

In each graph presented here, the various measurement techniques are shown. The techniques are explained in Table 3. The measurements labelled SF-ICP-MS include also those from laboratories who did not specify exactly which ICP-MS instrument they used.

For each measurement technique the values submitted have been sorted according to value before plotting. This gives a quick oversight on the typical spread from each measurement technique. The numbers on the abscissa are therefore arbitrary and do not correspond to the same laboratory from one graph to the next.

Table 3: Abbreviations of measurement techniques for figures 1 - 15

Abbreviation	Technique
AMS	Accelerator mass Spectrometry
HR-ICP-MS	High Resolution Inductively-Coupled-Plasma Mass Spectrometry
ICP-IDMS	Isotope Dilution Inductively-Coupled-Plasma Mass Spectrometry
ICP-QMS	Quadrupole Inductively-Coupled-Plasma Mass Spectrometry
MC-ICP-MS	Multi-collector Inductively-Coupled-Plasma Mass Spectrometry
SF-ICP-MS	Sector Field Inductively-Coupled-Plasma Mass Spectrometry
TIMS	Thermal Ionisation Mass Spectrometry
TIMS TE	Thermal Ionisation Mass Spectrometry using Total Evaporation

4.1. Results and Discussion for the $n(^{235}\text{U})/n(^{238}\text{U})$ Ratio

The results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio are presented in Figures 1-4 in the order REIMEP 18 B-D-A-C.

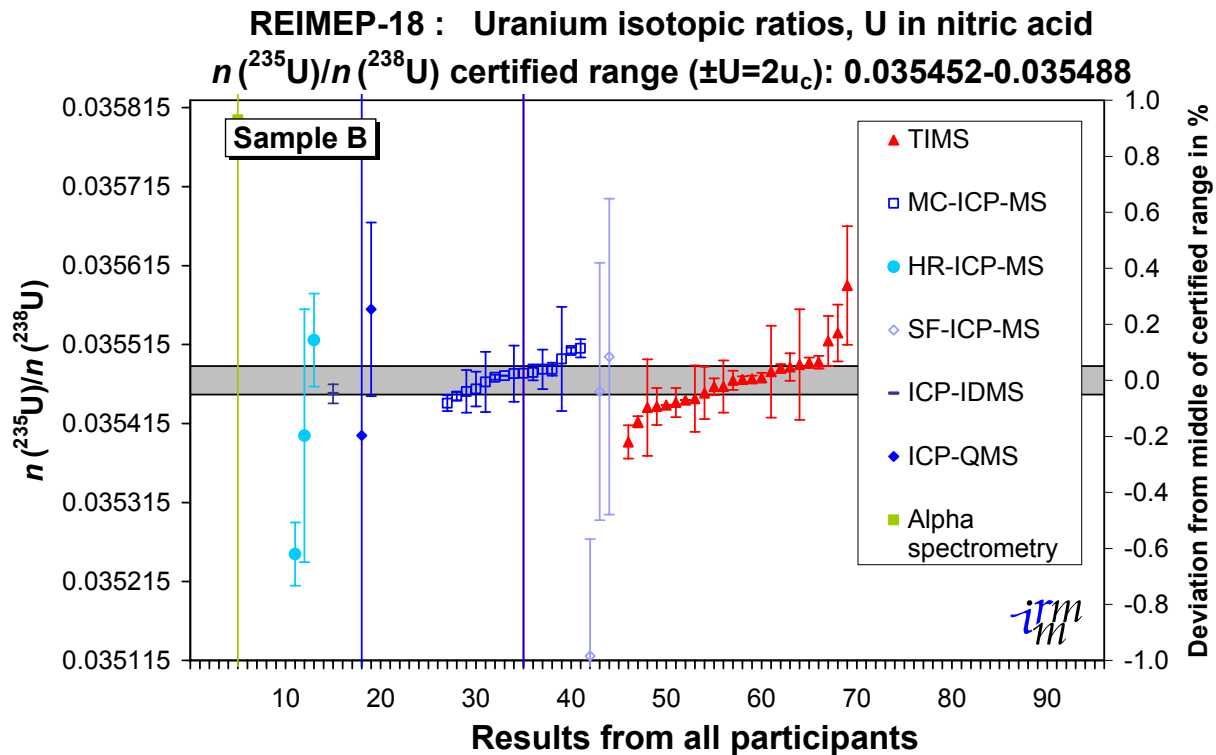


Figure 1: Results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 B

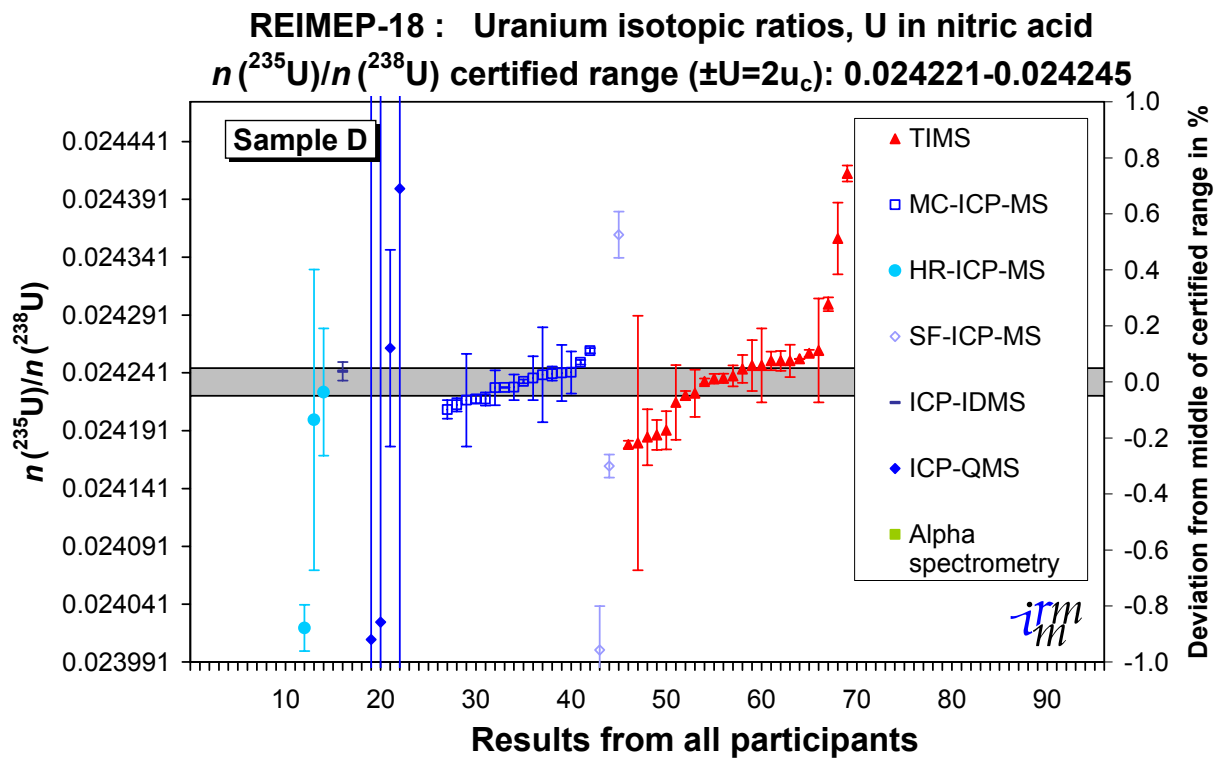


Figure 2: Results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 D

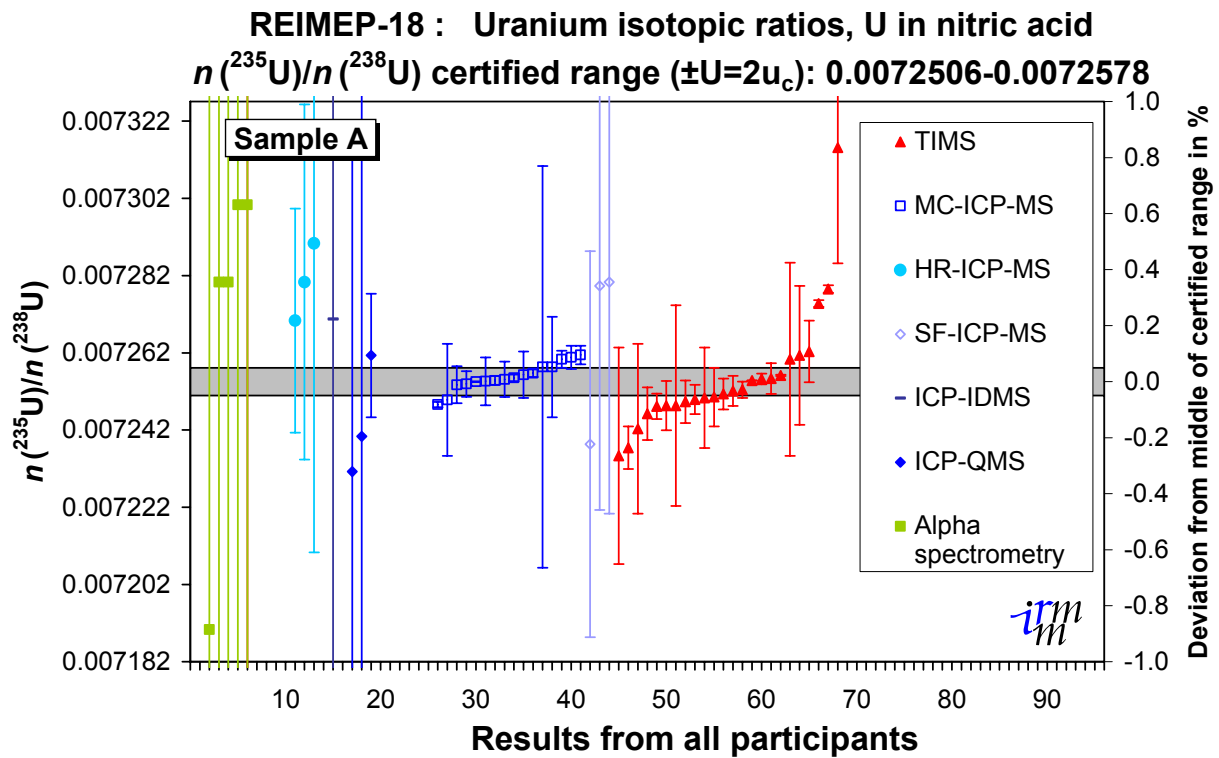


Figure 3: Results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 A

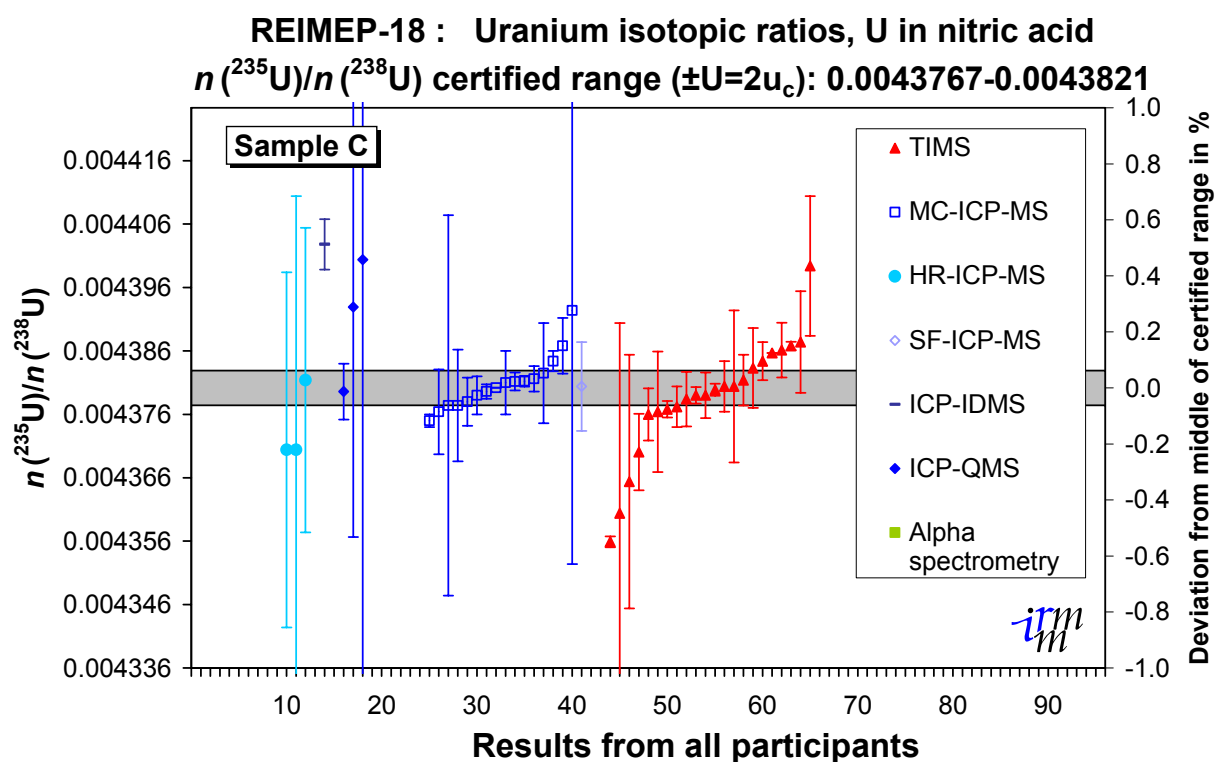


Figure 4: Results for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 C

The certified $n(^{235}\text{U})/n(^{238}\text{U})$ ratios of samples REIMEP 18 A-D lie between ca. 0.004 (depleted uranium) and 0.035 (low enriched uranium) and cover a range typical for nuclear safeguards samples. Sample REIMEP 18-A is quite close to natural uranium. From the $n(^{235}\text{U})/n(^{238}\text{U})$ results from all 71 participants the following observations can be made:

1. The spread of the data increases with decreasing $n(^{235}\text{U})/n(^{238}\text{U})$ ratio; this may simply be due to smaller ion beam intensities for the less abundant ^{235}U isotope.
2. For all techniques the spread of the data is significantly (2-3 times) higher than the certified range, which is $\pm ku_c$ with coverage factor $k = 2$, covering a $\pm 0.05\%$ relative range around the certified ratio.
3. The data spread depends on the applied techniques: MC-ICP-MS and TIMS show the smallest spread. For alpha spectrometry the results are between $\pm 1\%$ of the certified value only for sample REIMEP 18-A which has an enrichment close to natural. For all other samples the deviations are more than 1% and therefore not shown on the graphs.
4. The uncertainties reported for many of the MC-ICP-MS and TIMS results seem to be quite small and appear to be underestimated. One possible reason might be the fact that according to the answers in the questionnaire several participants used natural uranium samples as a standard for the mass fractionation correction by using the consensus value of $n(^{238}\text{U})/n(^{235}\text{U})=137.88$ as "reference value". Although this number is well known and established in the literature, it is not a certified value and moreover, it does not have any (certified) uncertainty associated with it. As a consequence, the uncertainty contribution of this standard sample used for mass fractionation correction, which is in many cases the dominant contribution, is missing within the uncertainty calculation for the corrected ratio of the sample. This neglect can lead to a dramatic underestimation of the uncertainties; in several cases this neglect might have even caused an apparent deviation of a measured ratio from the certified value.

4.2. Results and Discussion for the $n(^{234}\text{U})/n(^{238}\text{U})$ Ratio

The results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio are presented in Figs. 5 - 8 in the order REIMEP 18 B-D-C-A.

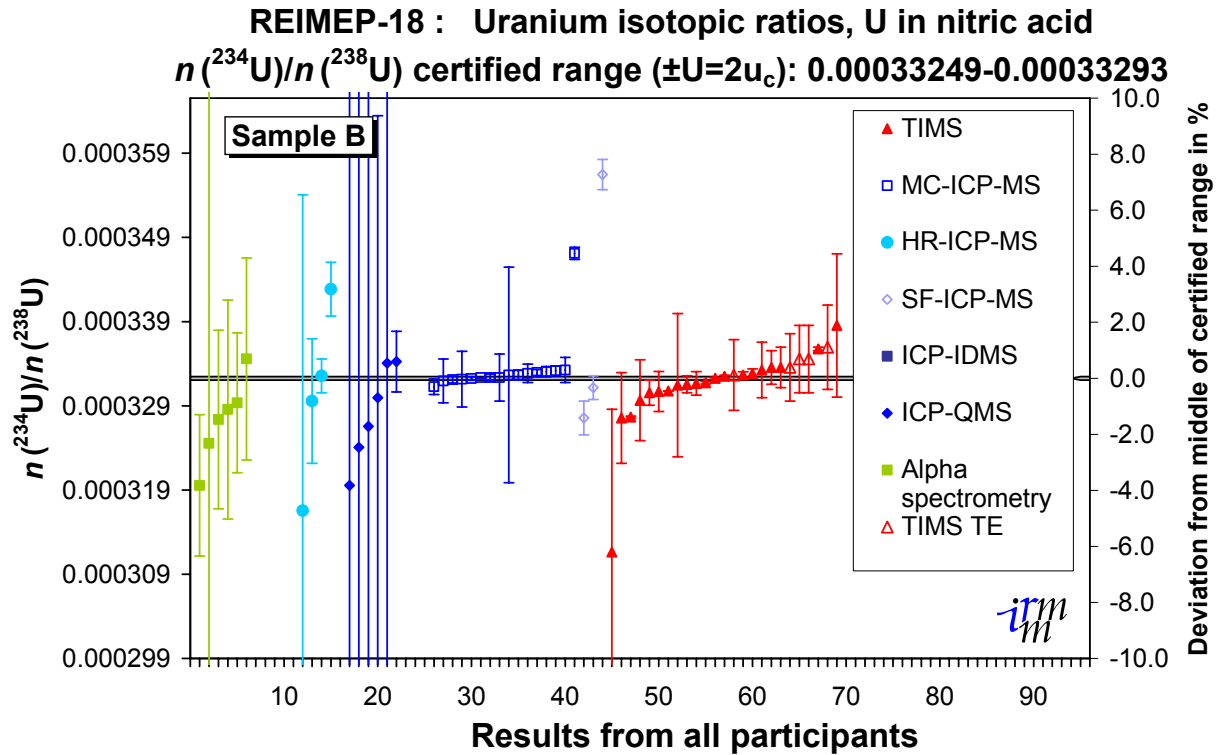


Figure 5: Results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 B

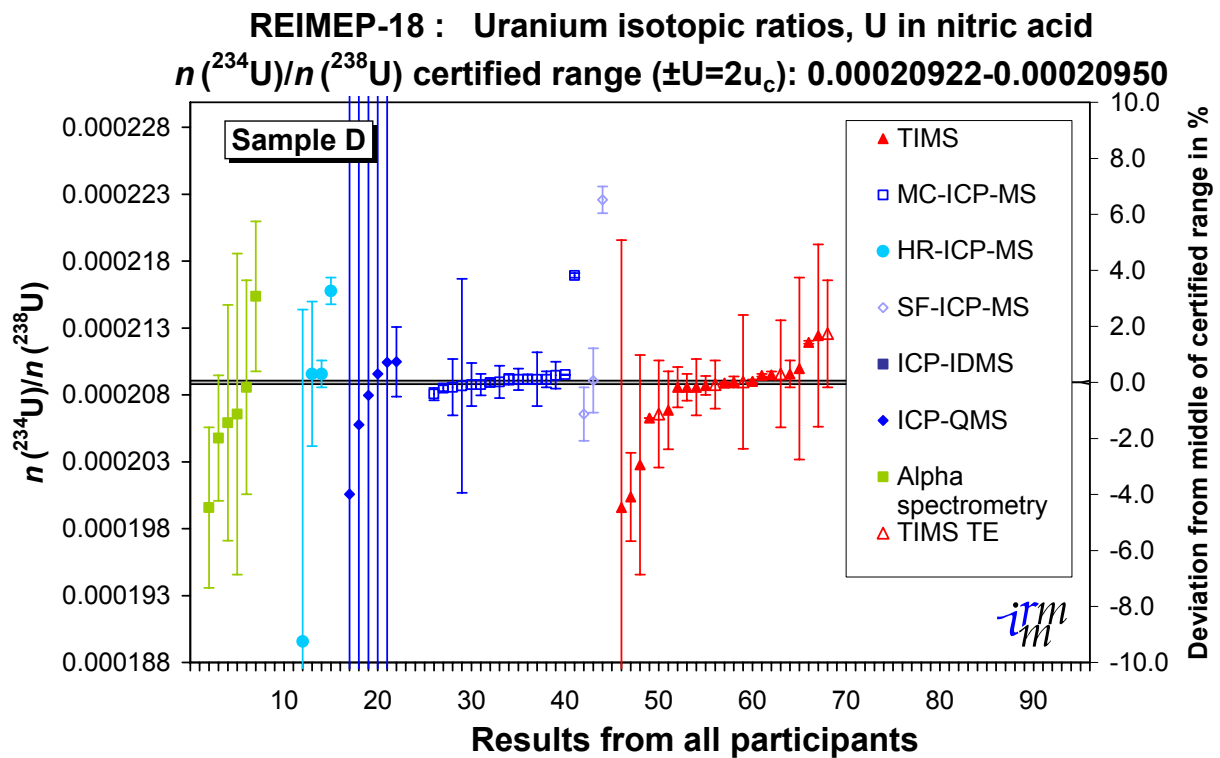


Figure 6: Results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 D

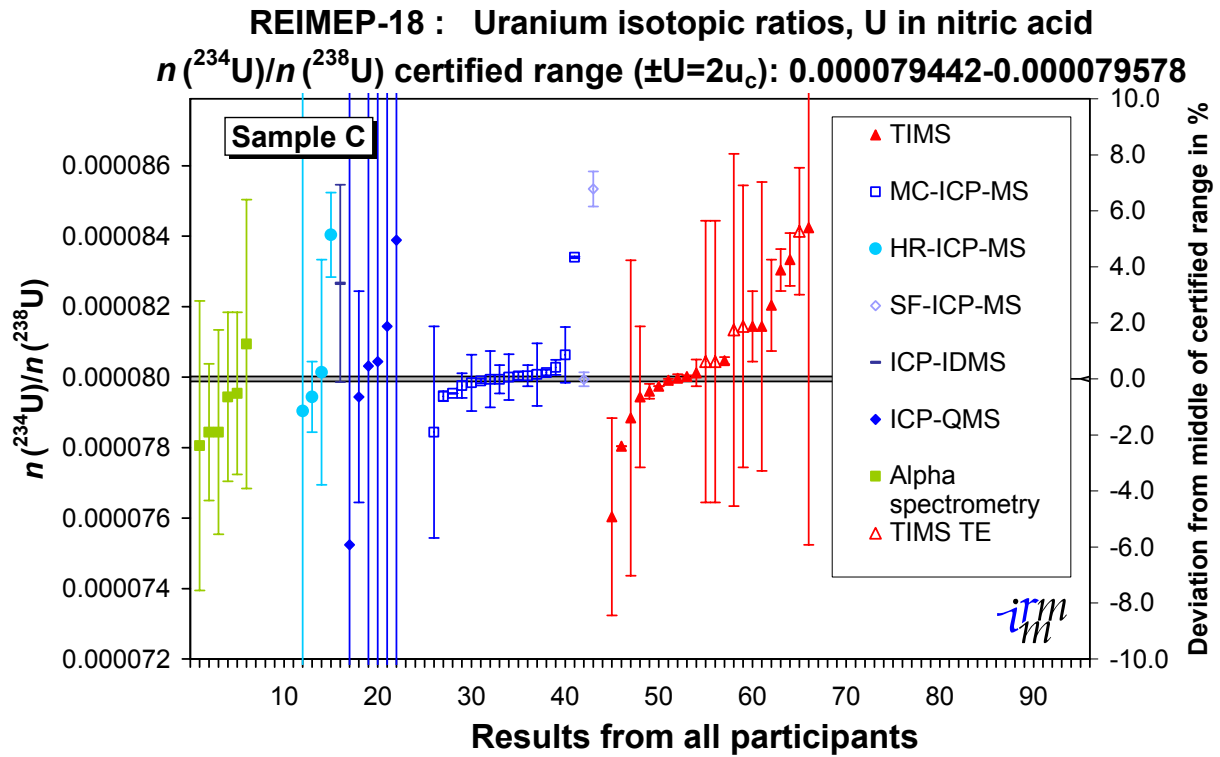


Figure 7: Results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 C

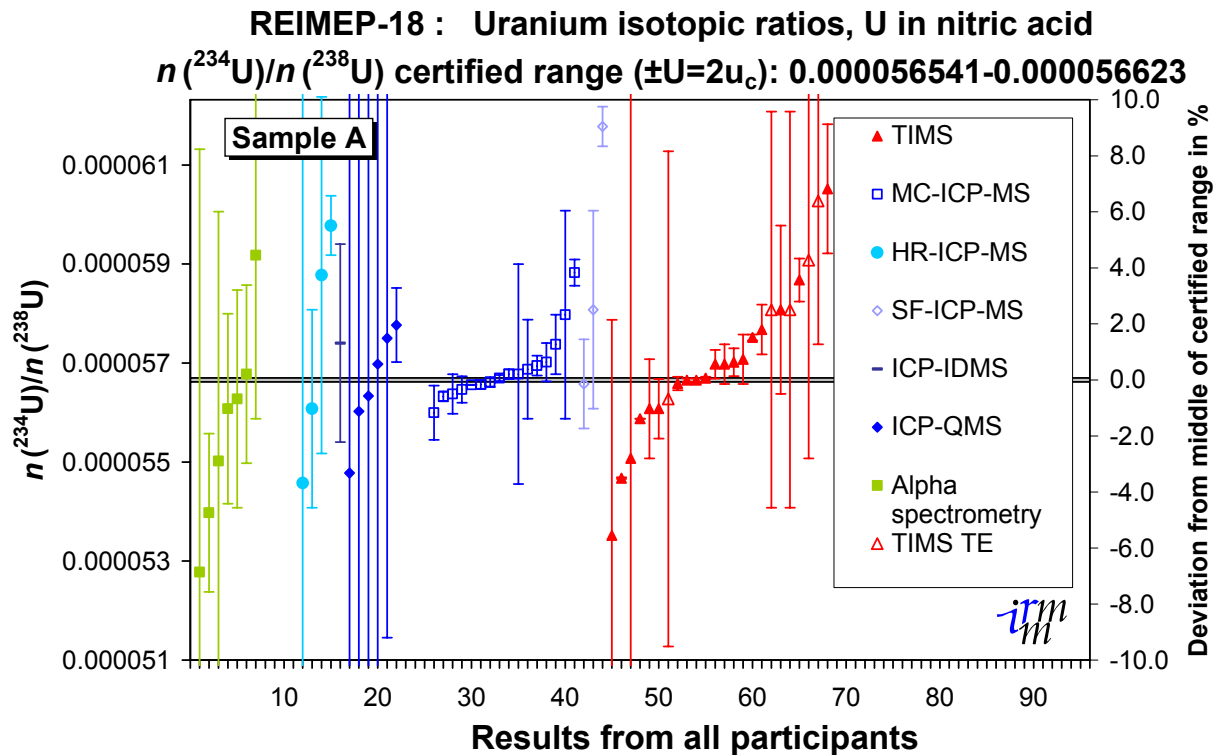


Figure 8: Results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 A

The certified $n(^{234}\text{U})/n(^{238}\text{U})$ ratios of samples REIMEP 18 A-D lie between ca. 0.000055 (close to natural uranium) and 0.00035 (slightly enriched uranium) and cover a range typical for nuclear safeguards samples. From the $n(^{234}\text{U})/n(^{238}\text{U})$ results from all 71 participants the following observations can be made:

1. The spread of the data increases with decreasing $n(^{234}\text{U})/n(^{238}\text{U})$ ratio. This is almost certainly due to the much smaller ion-beam intensities for the less abundant ^{234}U isotope.
2. For all techniques the spread of the data is significantly (2-3 times) higher than the certified range, which is $\pm k u_c$ with coverage factor $k = 2$, covering a ca. $\pm 0.06\%$ - 0.08% relative range around the certified ratio.
3. The data spread depends on the applied technique. Measurements done using MC-ICP-MS show the smallest spread followed by TIMS, then other ICP-techniques and alpha spectrometry.
4. For $n(^{234}\text{U})/n(^{238}\text{U})$ ratios smaller than about 0.0001, which applies to the samples REIMEP 18-A and REIMEP 18-D, the TIMS-TE results (TE = total evaporation) seem to be on average higher than the expected value. This is probably due to a neglect of the peak tailing correction to be done for the tailing of the "major" ion beams of ^{235}U and ^{238}U . This deviation is not as significant as found below for results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratios.
5. Some of the reported uncertainties for results from MC-ICP-MS and TIMS seem to be quite small and may be underestimated. This is visible in Figure 9, where the results for REIMEP 18-A are shown with a vertical scale of $\pm 2\%$. Possible reasons might be:
 - a. Use of a natural consensus standard for the mass fractionation correction using the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio. In this case the uncertainty of the corrected $n(^{235}\text{U})/n(^{238}\text{U})$ ratio would be underestimated, leading to incomplete uncertainty budgeting for $n(^{234}\text{U})/n(^{238}\text{U})$.
 - b. Underestimation or neglect of uncertainty contributions arising from detector inter-calibration (e.g. secondary electron multiplier versus Faraday cups) or linearity correction of detectors, especially secondary electron multipliers.

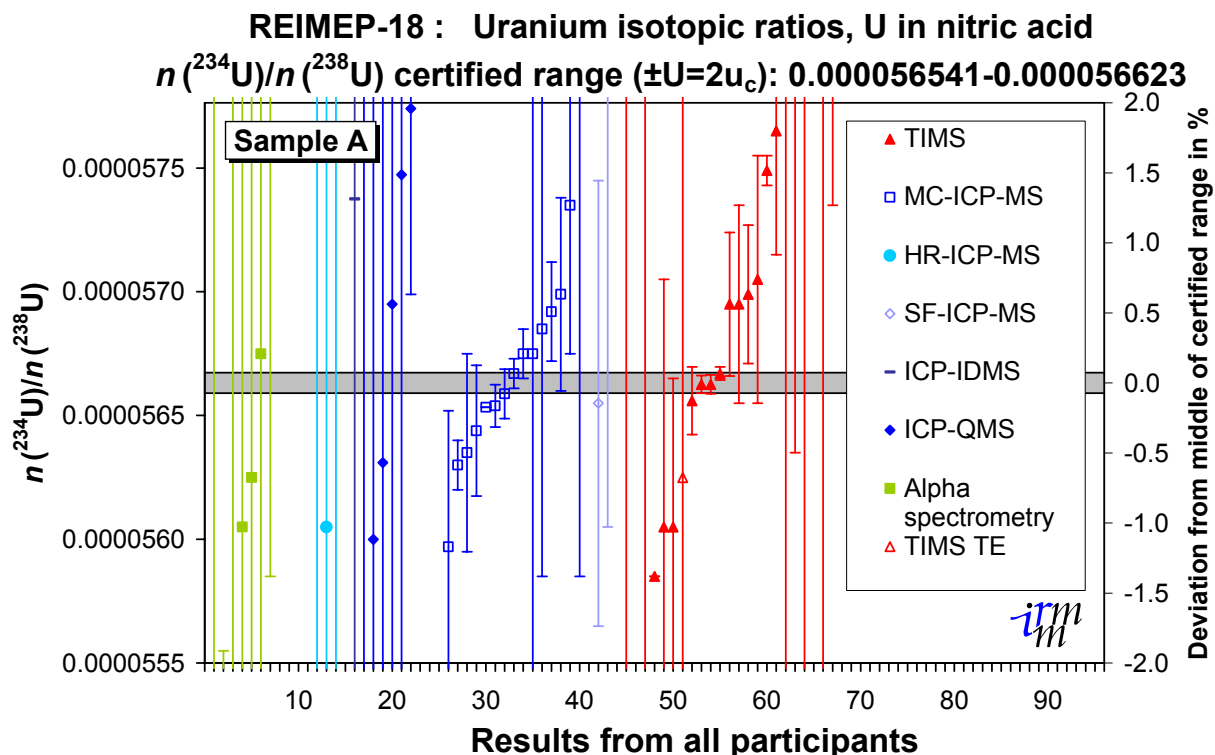


Figure 9: Results for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 A, with a vertical scale of $\pm 2\%$.

4.3. Results and Discussion for the $n(^{236}\text{U})/n(^{238}\text{U})$ Ratio

The results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio are presented in Figs. 10 -13 in the order REIMEP 18 C-B-D-A.

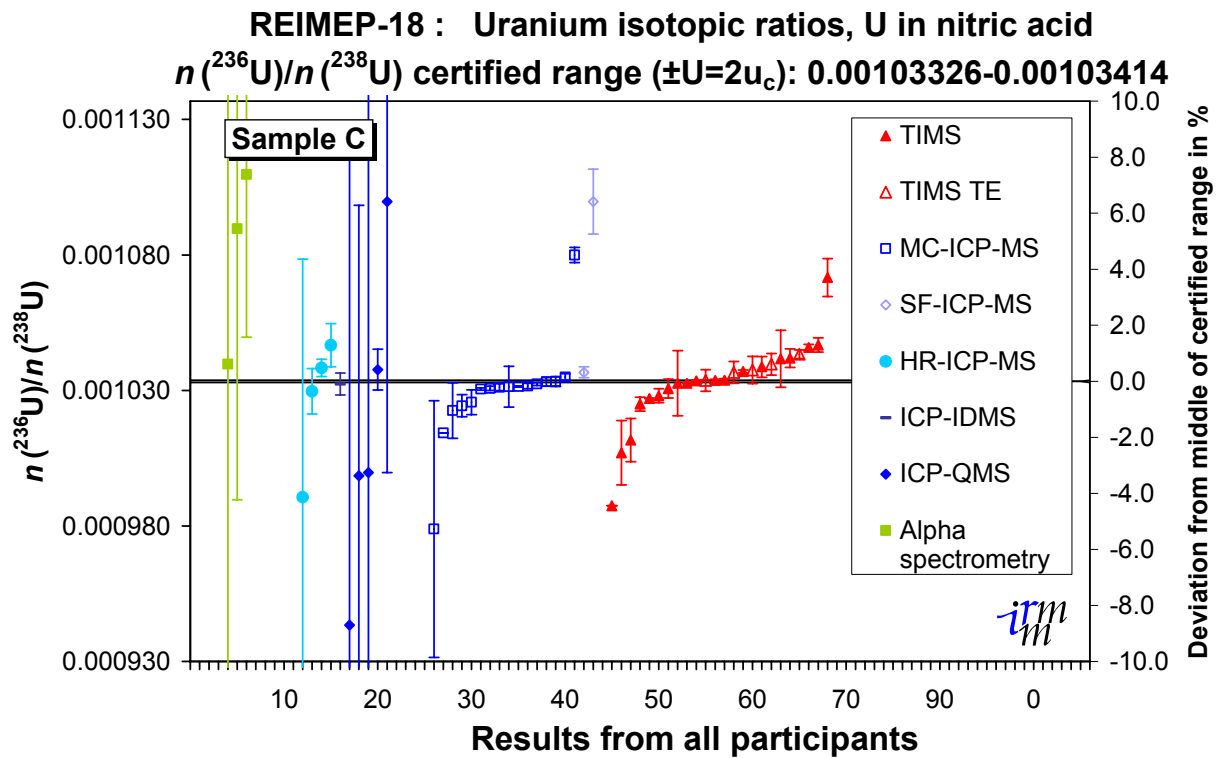


Figure 10: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 C

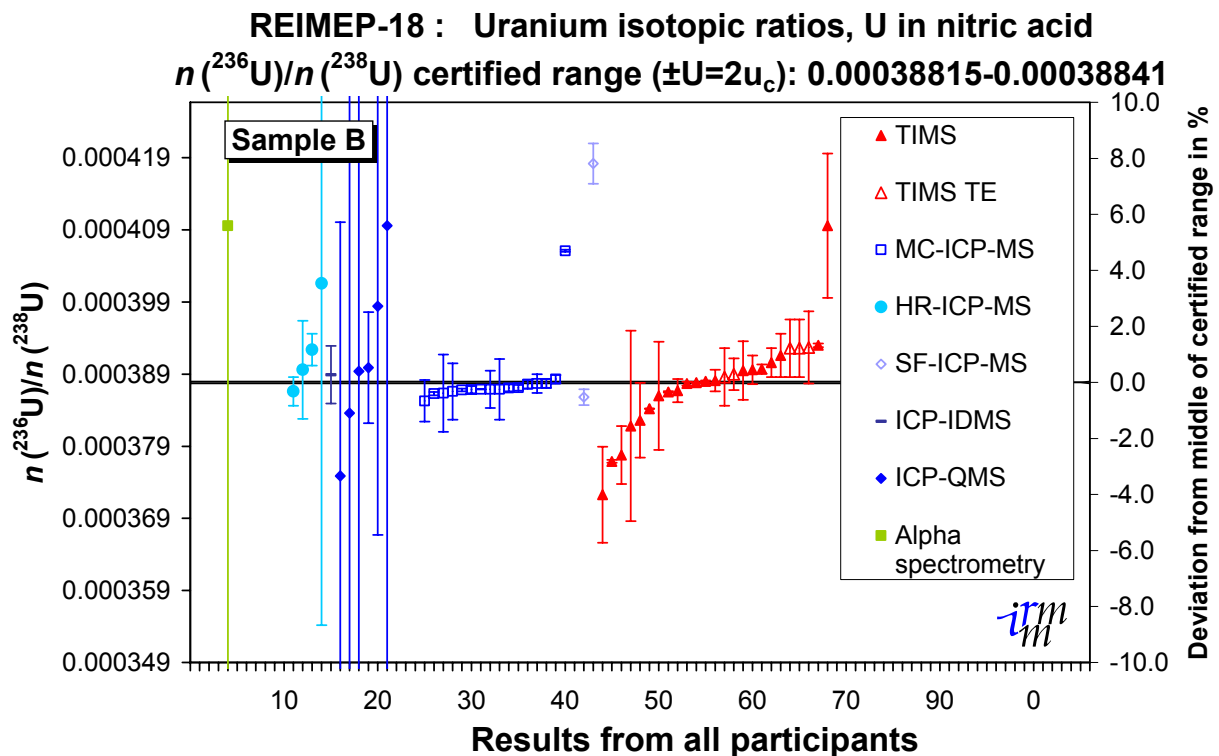


Figure 11: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 B

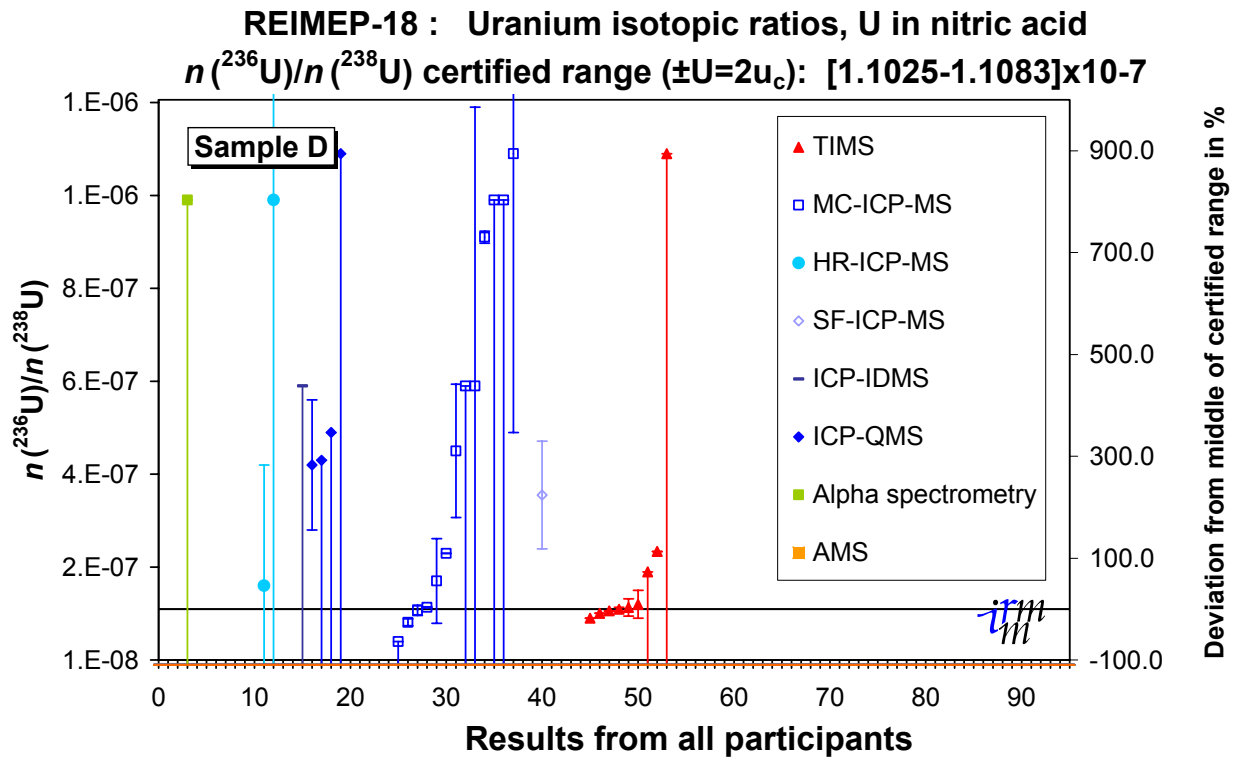


Figure 12: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 D

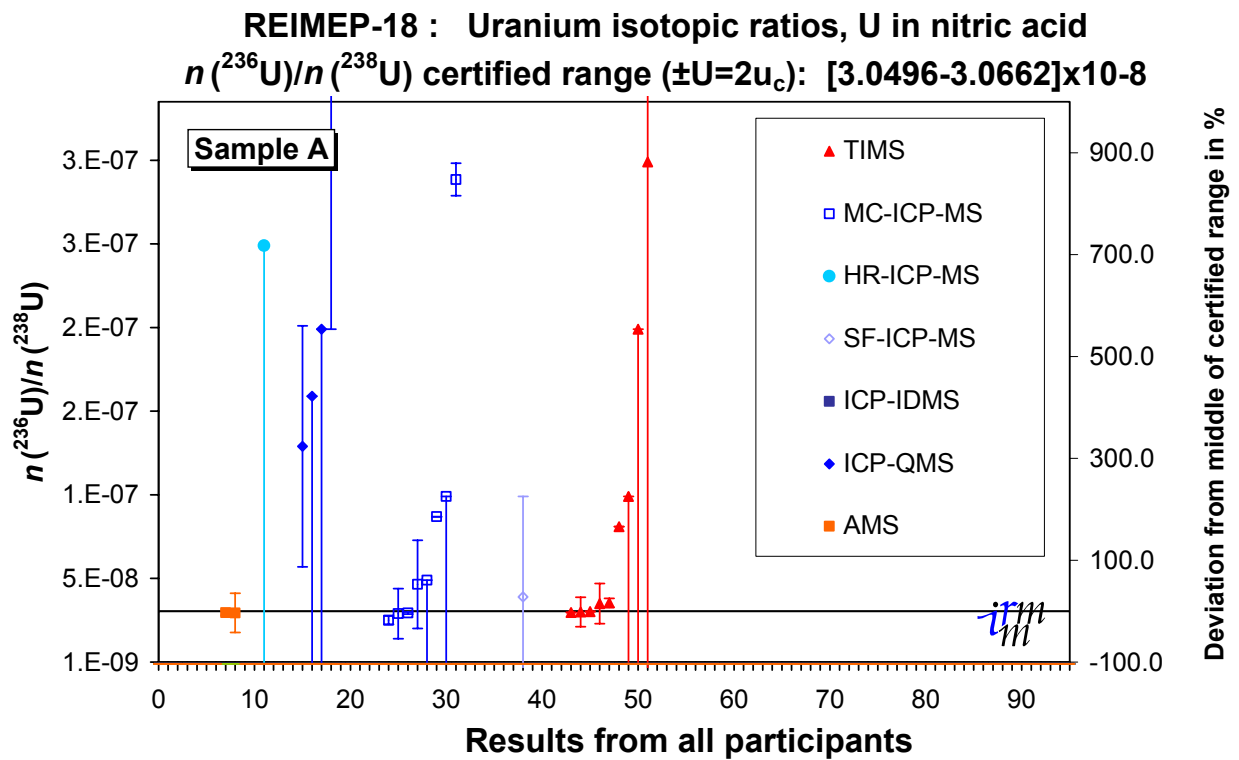


Figure 13: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 A

The certified $n(^{236}\text{U})/n(^{238}\text{U})$ ratios of samples REIMEP 18 A-D lie between ca. 10^{-8} (closest to natural uranium) and 0.001 (similar to recycled uranium). From the $n(^{236}\text{U})/n(^{238}\text{U})$ results of all 71 participants the following observations can be made:

1. The data spread depends on the techniques applied and on the order of magnitude of the ratio. For samples REIMEP 18 B and C with ratios $n(^{236}\text{U})/n(^{238}\text{U}) > 0.0001$, measurements performed using MC-ICP-MS show the smallest spread, followed by TIMS, other ICP-techniques and α -spectrometry. For samples REIMEP 18 D and A, with ratios of the order of 10^{-7} and 3×10^{-8} , AMS (only 2 results) and TIMS show the smallest spread, followed by the ICP-MS techniques.
2. For samples REIMEP 18 B and C with ratios of 0.0003 and 0.001 respectively, most of the TIMS-TE results (TE = total evaporation) are significantly higher than the expected value. These deviations are very probably due to neglecting the peak tailing correction for the ion beam at mass 238. For the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio this effect is much more pronounced than for $n(^{234}\text{U})/n(^{238}\text{U})$ and more care has to be taken for accurate measurements of the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio when measured in total evaporation mode.
3. The results for samples REIMEP 18 D and A, with $n(^{236}\text{U})/n(^{238}\text{U})$ ratios of 10^{-7} and 3×10^{-8} are shown using a range from -100% to +1000% in Figure 12 and Figure 13, and in more detail using a range from -50% to +50% in Figure 14 and Figure 15. Clearly isotopic measurements within this extreme dynamic range of 7-8 orders of magnitude still constitute a great challenge for the instrument and operator. The reported uncertainties seem to be quite often underestimated. Possibly not all uncertainty components, such as tailing effects, background, detector inter-calibration, etc, are considered sufficiently. The ICP techniques are at a disadvantage because of the larger tailing contributions compared with TIMS and even with AMS, even when an energy filter is used.
4. For AMS only 2 results were obtained for REIMEP 18 A with a $n(^{236}\text{U})/n(^{238}\text{U})$ ratio of the order of 3×10^{-8} ; no usable results were obtained for REIMEP 18 D. The 2 results shown in Figures 13 and 15 were obtained using different measurement procedures and sample loadings, at the $100\mu\text{g}$ -level and the sub- μ -level, respectively, which explains the large difference of the error bars. Certainly AMS is the mass spectrometric technique with the lowest background at ^{236}U , but it requires calibration using a standard with a known $n(^{236}\text{U})/n(^{238}\text{U})$ ratio.
5. In order to provide some proof for the reliability of the certified $n(^{236}\text{U})/n(^{238}\text{U})$ ratios around 10^{-7} and 3×10^{-8} for samples REIMEP 18 D and A, a series of 3 synthetic isotope mixtures with $n(^{236}\text{U})/n(^{238}\text{U}) = 10^{-6}, 10^{-7}, 10^{-8}$ was prepared, as described in detail in [9]. The $n(^{236}\text{U})/n(^{238}\text{U})$ ratios of these standard samples were measured using the IRMM-TIMS procedure and showed excellent agreement with the calculated ratios, as shown in Fig. 16.

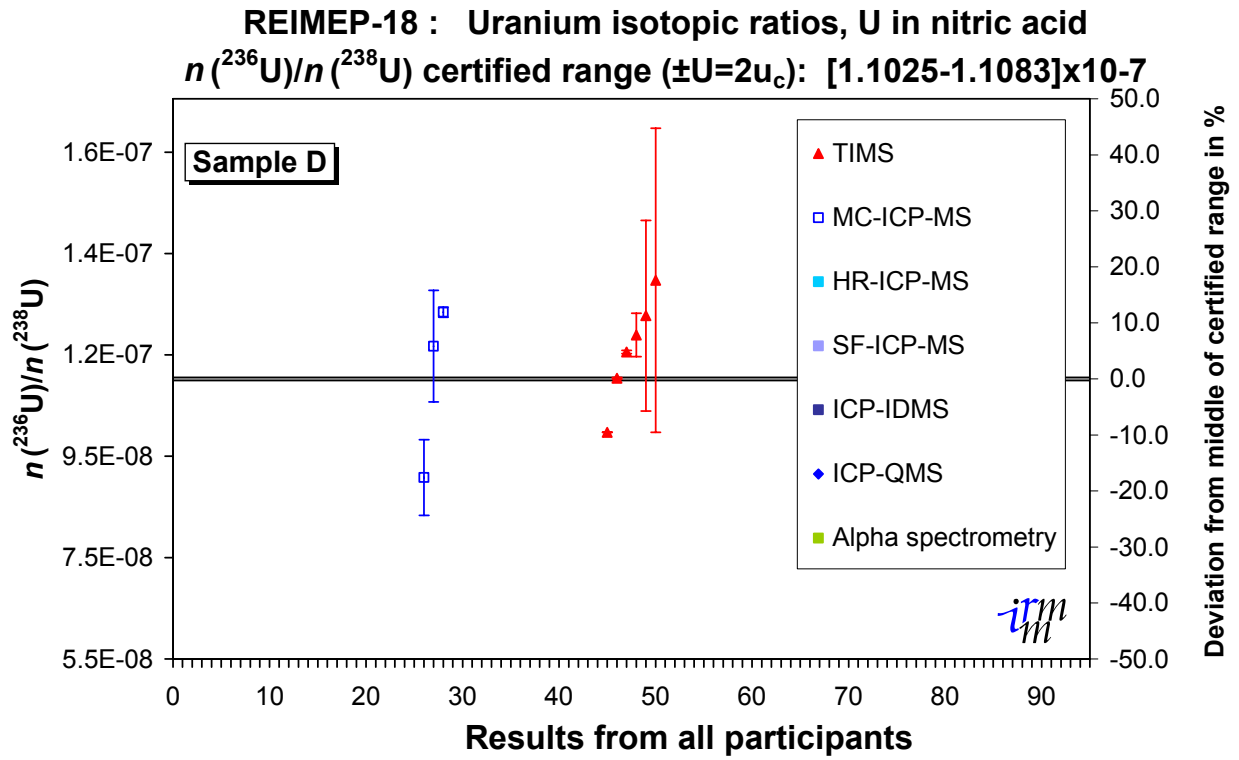


Figure 14: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 D, 50% window

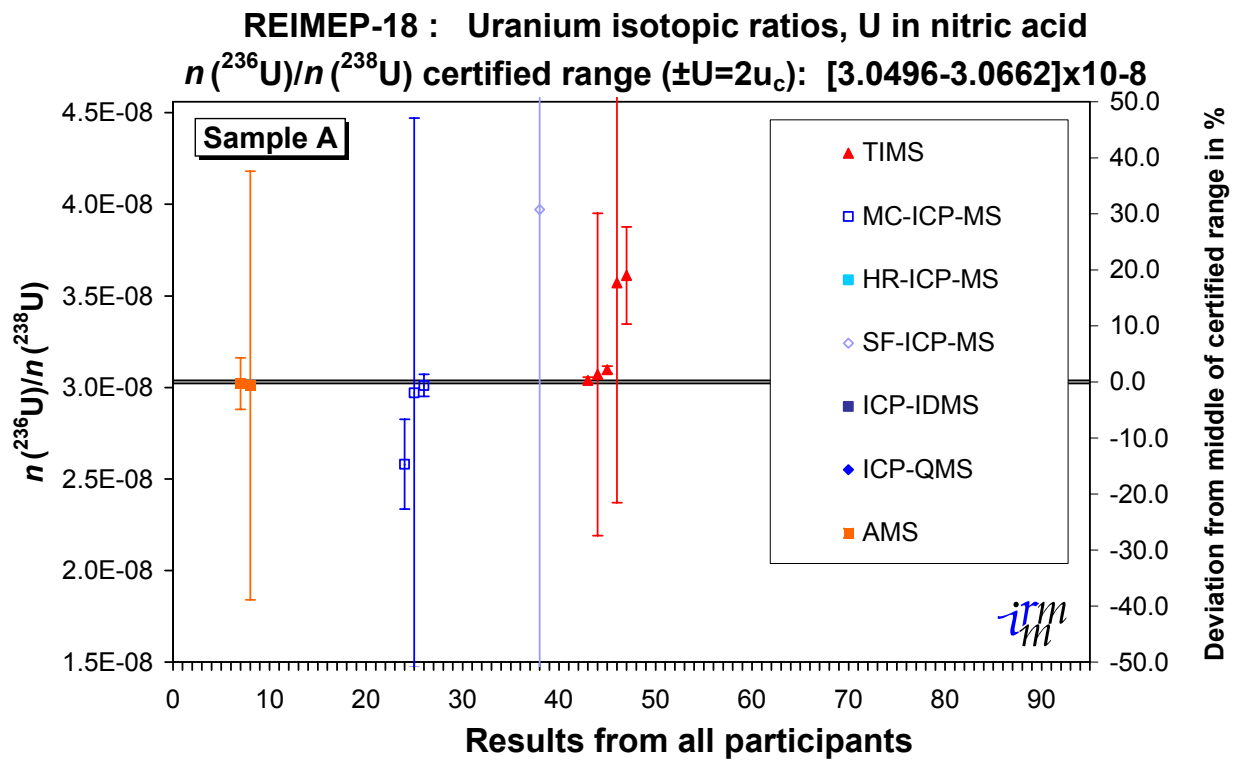


Figure 15: Results for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio for REIMEP 18 A, 50% window

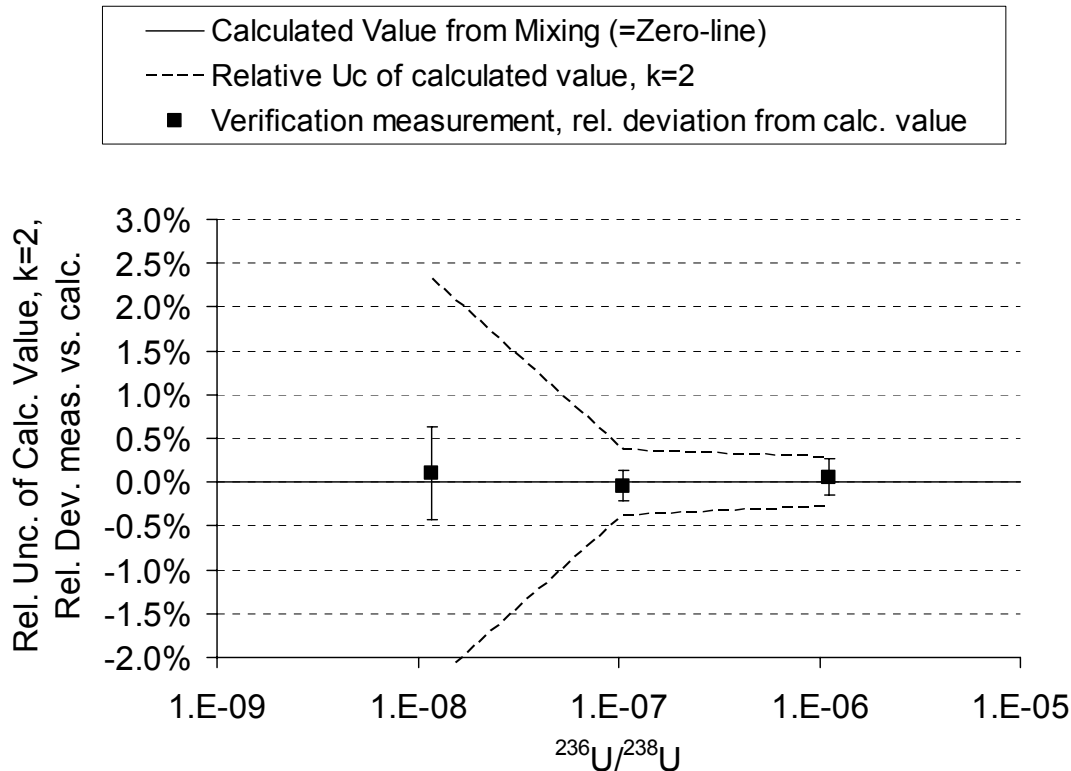


Figure 16: Comparison between the $n(^{236}\text{U})/n(^{238}\text{U})$ ratios measured using the Triton TIMS and the calculated values for each of the 3 mixtures with $n(^{236}\text{U})/n(^{238}\text{U}) = 10^{-6}, 10^{-7}, 10^{-8}$ [9].

5. Evaluation of the Questionnaire

The submission of the measured data was accompanied by a mandatory questionnaire to be completed by each participating laboratory.

The mission of the laboratory was asked for in question no. 1. This has already been discussed above (chapter 3).

Question no. 2 was about each laboratory's status regarding certification, accreditation and/or authorization. As a result 15 (21%) out of 71 participating laboratories declared themselves to be certified, 13 (18%) accredited and 31 (44%) authorized.

The use of a quality management (QM) system was the subject of question no. 3. Forty (56%) out of 71 participating laboratories have a QM system in place. 18 (25%) laboratories apply the ISO 9000 series / IS O25, 21 (30%) laboratories apply the ISO 17025, 3 (4%) laboratories from the U.S. apply special QM systems as required by the U.S. government authorities.

Question no. 4 concerned participation in inter-laboratory comparisons. Fifty seven laboratories (80%) participate regularly in these comparisons. This answer confirms the value of inter-laboratory comparisons campaigns organized by NBL, CETAMA and IRMM. The inter-laboratory comparisons organized by IRMM, such as the REIMEP and NUSIMEP series, seem to be appreciated most: 29 (41%) laboratories mentioned they participate regularly, compared with 3 (4%) and 9 (12%) laboratories mentioning the NBL-SME programme and 9 (12%) laboratories mentioning EQRAIN (CETAMA). But there are a number of other specialized inter-laboratory comparisons going on as well.

Question no. 5 was about the number of measurements of the same type as REIMEP 18 performed routinely each year. twenty two (30%) of the laboratories perform <25 measurements, 9 (13%) laboratories perform 25-50 measurements, 10 (14%) laboratories perform 50-100 measurements, and 30 (43%) laboratories perform >100 measurements of this type per year.

The results for question 6 are given in Tab. 4, showing the type of samples measured routinely by participating laboratories.

Table 4: Type of samples routinely measured by participating laboratories

Type of samples	No. of participating laboratories (more than one answer possible)
Soil	28
Sediments	33
Urine	9
Safeguards samples	25
Forensic samples	8
Samples from enrichment facilities	26
Samples from reactor facilities	17
Reference materials	46
Other (e.g. rocks, water, waste, biological and biomedical media, MOX and UO ₂ powders, etc)	22

Question 7 was about the self-assessment of the participating laboratories. As a result 53 (76%) laboratories rate themselves as experienced, 12 (17%) laboratories rate themselves as less experienced, and 5 (7%) laboratories rate themselves as not experienced.

The use of certified reference materials was the subject of question 8. Sixty three (90%) of the laboratories routinely use certified reference materials (see also questions 12 and 17).

Question 9 concerned the chemical separation prior to the mass spectrometric analysis. Only 10 (14%) of all participants performed a chemical separation, probably because this is part of their routine procedure. Five of these used a U-TEVA resin, 2 participants used TRU resin, and 2 participants specified the anion exchange resins DOWEX 1x8, 100-200 mesh and 200-400 mesh. But over 80% of all participants found a chemical separation not to be necessary, because the original sample solutions were prepared at IRMM by dissolving uranium oxide in ultra-pure nitric acid.

Questions 10 and 11 specifically asked the laboratories using α -spectrometry, which preparation technique and equipment they used. Ten out of 70 participating laboratories used α -spectrometry, 6 of them applied electro-deposition and 4 of them applied a rare earth co-precipitation. The following equipment was used: EG&G Ortec Octete Alpha Spectrometer (5), OASIS-Oxford alpha spectrometry integrated system (Tennelec), Silena AlphaQuattro, 7140 VR CANBERRA, Canberra 7401 alpha spectrometer; Ortec 916 MCA, alpha analyst.

Questions 12-16 were specific for laboratories using mass spectrometry. The majority (52) of the participating laboratories used this technique. Detailed information about their mass fractionation correction, instrumentation, detectors, calibration procedures, etc, is given in the following sections.

- Question 12: Use of reference materials for mass-fractionation correction:

44 (85%) of the 52 laboratories using mass spectrometry applied a correction for mass fractionation. Only one laboratory applied an internal correction using a $^{233}\text{U}/^{236}\text{U}$ double spike, the majority performed an external correction using a standard or reference material. In some cases even 2 bracketing standards were used.

The selection of standards or reference materials shows a significant preference for U.S. made materials (90% of mentioned materials) compared to reference materials produced at IRMM (10% of mentioned materials), the European Commission's nuclear reference materials laboratory. Possible reasons might include historically greater availability, better knowledge and lower prices. On the other hand the European-made nuclear isotopic reference materials are recognised to have smaller uncertainties, especially for uranium isotopic abundances. For instance the re-certified series IRMM183-187 is characterized by uncertainties of 0.03%-0.05% (k_{uc} , $k = 2$) for the $n(^{235}\text{U})/n(^{238}\text{U})$ ratios, 0.05%-0.06% for the $n(^{234}\text{U})/n(^{238}\text{U})$ ratios and $<0.3\%$ for $n(^{236}\text{U})/n(^{238}\text{U})$ ratios at the order of 10^{-7} . For details see reference [8].

A significant number of 12 laboratories (27% of 44) declared that they use natural uranium materials such as NBL-112A, SRM4321, NBL-U950, NBL-U960 as a standard for mass fractionation correction by using the value of $n(^{238}\text{U})/n(^{235}\text{U})=137.88$ as standard value. As noted in section 4.1., this number is well known and established in the literature, but it is not a certified ratio and more importantly, there is no uncertainty associated with it. Using this type of standard can lead to a significant underestimation of the uncertainties and is therefore not recommended.

- Question 13: Details of the mass spectrometer equipment used by participating laboratories is presented in Table 5:

Table 5: Mass spectrometers used by participating laboratories

Instrument type, brand	No. of laboratories
TIMS	25
TIMS, Thermo Electron TRITON	7
TIMS, Thermo Electron MAT261, MAT262	13
TIMS, GV Sector 54	4
TIMS, others	1
ICP-MS	28
ICP-MS, Thermo Electron Neptune	10
ICP-MS, Thermo Electron Element ½	5
ICP-MS, NU Plasma instruments	5
ICP-MS, GV	4
ICP-MS, Elan	3
Other (e.g. AMS)	4

- Question 14: Detectors for measuring uranium isotope ratios

Because uranium isotope abundances cover a quite large dynamic range, many of the participating laboratories used a combination of different detectors for the uranium isotopes ^{234}U , ^{235}U , ^{236}U and ^{238}U . Most common are Faraday cups and various types of secondary electron multipliers (SEMs). The percentages of mass-spectrometric laboratories using various detector combinations are given in Table 6.

Secondary electron multipliers (SEMs) are the preferred detectors for the "minor" isotopes ^{234}U and ^{236}U and Faraday cups are predominantly used for the "major" isotopes ^{235}U and ^{238}U .

Table 6: Use of detectors for various uranium isotopes by participating laboratories

Detector Combination (SEM = secondary electron multiplier)	Percentage of laboratories
Combination Faraday cups with SEMs	43%
Special combination: ^{234}U , ^{236}U using SEM, ^{235}U , ^{238}U using Faraday cups	14%
Unspecified combination	29%
Only SEMs for all uranium isotopes	27%
Only Faraday cups for all uranium isotopes	30%
Use of Faraday cups and SEMs for individual uranium isotopes:	
^{234}U : SEM / Faraday cup	57% / 43%
^{235}U : SEM / Faraday cup	36% / 64%
^{236}U : SEM / Faraday cup	57% / 43%
^{238}U : SEM / Faraday cup	36% / 64%

- Question 15: The inter-calibration between different detectors

The inter-calibration between different detectors such as Faraday cups and various types of secondary electron multipliers (SEMs) is an important part of the measurement procedure. Because the data submission system only allowed the participants to describe the procedure using a limited number of characters, not much detail could be retrieved from the answers. The answers are summarized in Table 7.

Most of the laboratories (55%) use standards to achieve the inter-calibration, either using one standard or even 2 standards bracketing the unknown sample ratio. But a lot of laboratories (45%) prefer to use an ion beam of the (same) sample to cross-calibrate an SEM against Faraday cups. Part of them even does an internal calibration between SEM and Faraday cup regularly throughout the sample measurement. The cross-calibration approach might have the advantage of taking into account any run-to-run variations (run of either a sample or a standard) of the calibration factor ("external" procedure), or even within-run variations ("internal" procedure). Additionally, the inter-calibration between an SEM against Faraday cups is most needed for the measurement of the "minor" uranium ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$, for which only few reliable certified standards with low uncertainties exist, e.g. the recertified series IRMM183-187. [8], in which IRMM-184 has isotopic abundances close to those of natural uranium. Also for measurements of the

$n(^{234}\text{U})/n(^{238}\text{U})$ ratio so-called "consensus" standards are in use, e.g. NBL-112A, which are not certified for this ratio.

Table 7: Inter-calibration of detectors

Inter-calibration of detectors (SEM = secondary electron multiplier)	Percentage of laboratories
<i>"Internal"</i> calibration by switching one isotope (e.g. ^{234}U or ^{235}U) between SEM and Faraday cup <i>regularly throughout the sample measurement</i>	18%
<i>"External"</i> calibration by switching one isotope (e.g. ^{234}U or ^{235}U) between SEM and Faraday cup <i>once prior to every sample measurement</i>	27%
Using standards	55%
sample-standard-bracketing	18%
single standard calibration	36%

- Question 16: Linearity testing and corrections

Each detector, Faraday cup or secondary electron multiplier (SEM), has to be checked for linearity. Usually Faraday cups do not show any deviation from linearity, which can be easily confirmed by measurements of suitable isotopic reference materials such as IRMM-072, IRMM-073 or IRMM-074 [10, 11]. In contrast, SEM detection systems usually exhibit non-linearity effects. Each SEM system operated in pulse counting mode consists of the SEM detector itself and a pulse amplifier and counter. The pulse amplifier always has a certain dead time, which is the time duration after each pulse for which the amplifier cannot accept any further count. In the first approximation the dead time correction is linear with the count rate and has been described in the literature many times. But recently, non-linearity effects have also been observed and investigated which originate from the SEM detector itself and require an additional correction [12, 13]. According to the information from the questionnaire only a few laboratories make a distinction between the dead time effect and additional effects of the SEM detector, in many cases these effects are either not present or not fully investigated. But the results from REIMEP 18, especially for the "minor" uranium ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ suggest that non-linearity effects or the lack of proper corrections still cause significant inaccuracies in the measurements of these ratios.

Question 17 was about the use of reference materials for method validation. About 70% of all participating laboratories used reference materials for method validation. For some participating laboratories the reference materials used for method validation also served to calculate mass fractionation factors.

According to question 18, 64% of all participants are familiar with the Guide for the Expression of Uncertainty in Measurements (GUM) published by ISO (1993) [14] and EURACHEM (1995) [15]. 78% of these participants reported their uncertainties according to these guides, about 50% of all participants. Out of these 50%, about 40% apply a coverage factor other than 1 (questions 19, 20).

For the evaluation of the uncertainties in most cases Microsoft Excel or the instrument operating software was used; in few cases the "GUM Workbench" software [16]. 90% of all participants report uncertainties on their measurements to their usual customers (questions 21, 22).

84% gave a positive answer when asked about their interest in participating in future REIMEP campaigns (question 23). A variety of suggestions was made for future samples, including several types of nuclear safeguards samples - related to nuclear fuel analysis for instance - but also various suggestions were made for environmental or geological samples. Additionally campaigns for different sample matrices, such as water, acid, sediment, soil, organic matter, UO₂ pellets or powder, rock material, etc, were suggested. There is interest in REIMEP campaigns for both uranium and plutonium as organized previously, but also in Ra, Np and Th and mixtures of them, and also a number of non-nuclear elements which are usually covered by the IMEP and not by the REIMEP programme at IRMM.

The remaining questions were about the organization of the current REIMEP 18 campaign. Fifteen percent of the laboratories learned about REIMEP 18 from the IRMM website, 52% were contacted and invited directly by e-mail, 20% were informed by other participants, 22% by other means. Asked for comments, suggestions or complaints about the current REIMEP 18 campaign, several participants complained about the clumsiness of the data submission system and some that not enough space was provided for answering some of the questions within the questionnaire. A few laboratories also observed degradation of the samples during transport and therefore for future campaigns more reliable sample containers will be used. But the overall rating of the campaign was positive.

6. Conclusions

The REIMEP 18 inter-laboratory comparison campaign for uranium isotope measurements in nitric acid was completed successfully. The overall response has been exceptionally high; up to now the participation in a campaign for nuclear isotopic measurements organized at IRMM has never reached the level of 85 registered and 71 actually participating laboratories. Therefore the results of this campaign may be considered as a quite representative picture of the present uranium isotopic measurement capabilities for a broad range of disciplines and on a worldwide scale.

The REIMEP 18 campaign was focused on the 'pure' measurement of uranium isotopic abundances rather than on the full analytical sample analysis procedure including e.g. chemical sample preparation. The outcome of this campaign is therefore specific to the instrumentation needed to measure uranium isotopic ratios, to the various measurement procedures, the calibration applied and correction strategies.

From the results presented in chapter 4 and the questionnaire results in chapter 5, the following main conclusions can be drawn:

1. For measurements of uranium isotopic ratios a variety of different measurement techniques is in use. Most prominent is mass spectrometry, and among different types of mass spectrometry TIMS and various types of ICP-MS, especially MC-ICP-MS, are the most frequently used.
2. Different techniques have different limitations, e.g. α -spectrometry can only be used for certain ranges of ratios, ICP-MS has limited capabilities for measurements of ratios covering a large dynamic range, e.g. for $n(^{236}\text{U})/n(^{238}\text{U})$ ratios of the order of 10^{-7} and below. For this type of measurement TIMS and AMS show a better performance.
3. For TIMS measurements, the performance for routine measurements of the minor isotope ratios, e.g. using the total evaporation technique, does not fulfil expectations and has to be improved. It seems that the capabilities provided by modern TIMS instruments are not always fully applied in order to reach the best possible performance of TIMS. Plans for improvement have been proposed by IRMM, e.g. by an expanded implementation of the "modified total evaporation" technique according to [6, 7].

4. Corrections for effects such as mass fractionation or detector non-linearity are usually performed using known isotopic standards. Many laboratories use certified isotope reference materials provided by e.g. NIST/NBL or IRMM, but quite a large number also uses "consensus" type standards of natural uranium. The advantage of the better availability is often compromised by the lack of a complete uncertainty propagation, leading to underestimated uncertainties and possibly biased results. There is an obvious need for more discussion and inter-laboratory knowledge exchange about guidelines for calculating uncertainties for isotope ratio measurements.
5. Most of the figures in chapter 4 show quite a large number of results that are significantly different from the certified values, some of them even outside the plotted range. This requires further investigation by the participants on an individual basis. One possible reason in particular for the "minor" uranium isotope ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ might be an incomplete knowledge and correction of possible detector non-linearity effects, especially for electron multipliers, as well as a neglect of peak tailing effects.

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REIMEP-18: Interlaboratory Comparison of the Measurement of Uranium Isotopic Ratios in Nitric
Acid Solution - Report to Participants

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Abstract

The REIMEP 18 (Regular European Inter-laboratory Measurement Evaluation Programme) campaign was started in October 2005. For this campaign 4 samples of depleted to low-enriched uranium were chosen. State of the art certification measurements were carried out using a Varian MAT511 UF₆-gas source mass spectrometer (GSMS) for the ²³⁵U/²³⁸U ratio and using a Triton thermal ionization mass spectrometer (TIMS) for the minor isotope ratios ²³⁴U/²³⁸U and ²³⁶U/²³⁸U. Verification measurements of ampouled samples were performed successfully and showed good agreement with the certified ratios.

REIMEP 18 has become the largest nuclear measurement campaign organized by IRMM so far. Samples were shipped in March 2006 to ca. 80 registered participants. Most of the participating laboratories submitted their results until May 31st, 2006. Due to problems with the sample containers and extended shipping times the submission deadline had to be postponed until September 30st, 2006 for some of the participating laboratories. Finally IRMM received results from 66 laboratories.

The results of the REIMEP 18 campaign confirm in general the excellent capability of laboratories in measuring isotopic abundances of uranium, some problems arose for the measurements of the minor isotope ratios ²³⁴U/²³⁸U and ²³⁶U/²³⁸U. This report describes the outcome of the REIMEP 18 campaign, including the graphical evaluation and discussion of the results, the evaluation of the questionnaire and the discussion of conclusions, actions to be taken.



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