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**NUSIMEP-3**  
**Uranium isotopic abundances in saline solutions**  
**Report to participants**

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## 1 Summary

The Nuclear Signatures Inter-laboratory Measurement Evaluation Programme (NUSIMEP) has been established to support the growing need to measure the isotopic abundances of elements characteristic of the nuclear fuel cycle present in trace amounts in the environment. Such measurements are required for safeguards applications as well as for the implementation of the Non-Proliferation Treaty (NPT). Through this and similar programmes, the degree of equivalence of measurements from individual laboratories on the international scene can be ascertained. It complements the two other, long running programmes at the Institute for Reference Materials and Measurements (IRMM), the Regular European Interlaboratory Evaluation Programme (REIMEP) in the nuclear field and the International Measurement Evaluation Programme (IMEP) in the field of non-nuclear chemical amount measurements.

The present campaign, NUSIMEP-3, follows NUSIMEP-2 [1, 2] in requiring measurements of uranium isotopic ratios but this time in saline matrices. This is step towards having samples similar to environmental samples which commonly have to be analysed by field laboratories. The samples were prepared and certified at IRMM: uranium isotopic ratios by mixing certified isotopic material as  $UF_6$  and measuring minor isotopes by TIMS. The saline matrix solutions were prepared by dissolving salts to reach prescribed concentrations matching expected saline waters and the uranium concentration in these salt mixtures was measured by IDMS using the highly enriched  $^{233}U$  spike IRMM-073 and applying a quadrupole ICP-MS (ELAN 6000).

The measured isotopic ratios are shown in a series of graphs for comparison.

## 2 Introduction

The third round of the Nuclear Signatures Measurement Evaluation Programme (NUSIMEP-3) followed NUSIMEP-2 in requiring the measurement of uranium isotopic ratios in saline media. NUSIMEP-2 was designed to be simple as far as the sample handling was concerned and 100 ng samples of near-natural uranium, in which the samples were simply dried as nitrates, were sent to the participants. Minimal chemical processing was required for the NUSIMEP-2 samples.

One of the pieces of information laboratories supplied us in the associated questionnaire was whether they used 'clean' handling facilities. No distinction could be made from the collected results in the NUSIMEP-2 campaign between measurement results from laboratories using 'clean' facilities and those not, but given the type of samples this was not unexpected.

It is of great interest, however, to know whether clean chemical facilities are important for the measurement of isotopic ratios of uranium given its ubiquitous nature and the difficulty in keeping blanks (solutions and materials) free of natural uranium. For this reason, samples were provided in which the matrix would make it difficult to measure the uranium isotope ratio directly, thus requiring laboratories to carry out separations prior to measuring. Three saline solutions approximating natural waters were available at IRMM from previous work. These were nominally free from uranium, but the blank content had to be verified. It was decided to supply 20 mL of each of these solutions (as the total volume was limited) and have a uranium concentration of 5 ng/mL so as to have a total uranium amount of about 100 ng. A fourth solution was made starting with a commercially available salt mixture used for seawater aquariums. This salt mixture contained a low but measurable concentration of uranium which had to be removed before use. It was decided to supply this solution to participants in a more dilute form but larger volume. The reasoning was so that even if laboratories found they could measure uranium isotopics directly in the first three solutions (a possibility for modern high-resolution ICP-MS mass-spectrometers), the stronger saline solution and higher dilution factor of the last solution would make a direct measurement very difficult.

We asked laboratories to measure the ratios of the isotopes  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{236}\text{U}$  to the main isotope  $^{238}\text{U}$  and supply these values, not amount or mass abundances, as the transformation of ratios to abundances is relatively trivial and would also not be possible for laboratories that could not measure all three isotopes ratios.

The isotopic abundances of the uranium were chosen to test the laboratories' measurement capabilities. In particular, the abundances of  $^{236}\text{U}$  differed considerably between the samples and this abundance was kept at a very low value for the sample with the highest  $^{235}\text{U}$  enrichment (see Tab. 1 below).

Participating laboratories received, as for NUSIMEP-2, certified test samples (with undisclosed isotopic composition) and they were requested to analyse them using the laboratory's routine procedures. The samples were approximately 100 ng uranium total in either 20mL or 50mL volumes; the uranium was low enriched in  $^{235}\text{U}$ . No information was given about the solution matrices, except that they were saline solutions of different compositions and salt concentrations. The laboratories were requested to supply values for the measured ratios together with an uncertainty, preferably calculated following the ISO or Eurochem guides, giving a range in which it is claimed the true value of the ratio was to be found.

One lesson learnt from NUSIMEP-2 was that radiometric methods were normally not capable of measuring isotopic ratios of uranium, at least in the amounts provided. The easiest ratio to measure by alpha spectrometry is  $n(^{234}\text{U})/n(^{238}\text{U})$  and it was expected also that some laboratories would attempt to measure at least this ratio radiometrically in NUSIMEP-3. It was also expected that some laboratories would send results only for the isotope ratio  $n(^{235}\text{U})/n(^{238}\text{U})$  as this is the largest ratio and can possibly be measured without elaborate equipment and (possibly) with no chemical processing.

As for NUSIMEP-2 a questionnaire was enclosed with the reporting form asking details about measurement methods and other information. Details of these responses and possible conclusions are included in this report.

### 3 Samples

The uranium for the NUSIMEP-3 samples was prepared by mixing in the gas phase certified uranium material in the form of  $\text{UF}_6$  [3]. The minor isotopic ratios were measured by hydrolysing a sample of the  $\text{UF}_6$ , converting to the nitrate, purifying and measuring the ratios on a thermal ionisation mass-spectrometer as described for the NUSIMEP-2 campaign. In this method, the  $n(^{235}\text{U})/n(^{238}\text{U})$  is predicted from the mixing process and confirmed and certified by measuring the  $\text{UF}_6$  directly in an electron-excitation gas mass-spectrometer. This  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio is then used in the TIMS measurement of the minor isotopic ratios,  $n(^{234}\text{U})/n(^{238}\text{U})$ ,  $n(^{234}\text{U})/n(^{238}\text{U})$  to correct for mass-fractionation. This method produces values for isotopic ratios with very low uncertainties.

The certified values of the isotopic ratios of the four uranium samples are given in Tab. 1 and the nominal contents of the matrix solutions in Tab. 2.

The matrix solutions were mixtures of salts chosen to mimic surface waters of various types, including sea-water. Three of the solutions had been previously made up at IRMM and the uranium content checked and certified. However it was decided to remeasure the natural uranium content of these solutions as the blank uranium slightly effects the uranium isotopics in the solutions after adding the previously certified uranium to a level of 2 or 5 ng/mL.



**Tab. 1: Certified values of the uranium isotopic ratios for the NUSIMEP samples. Expanded uncertainties (k=2) are given in brackets and apply to the last two digits of the value.**

Isotope ratio	Sample A	Sample B
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000 358 4 (16)	0.000 550 8 (33)
$n(^{235}\text{U})/n(^{238}\text{U})$	0.017 442 6 (85)	0.051 241 (24)
$n(^{236}\text{U})/n(^{238}\text{U})$	0.005 819 7 (63)	0.001 535 (10)

Isotope ratio	Sample C	Sample D
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000 178 8 (21)	0.000 338 9 (48)
$n(^{235}\text{U})/n(^{238}\text{U})$	0.009 006 9 (45)	0.033 863 (17)
$n(^{236}\text{U})/n(^{238}\text{U})$	0.004 101 (13)	0.000 000 132 4 (37)

**Tab. 2: matrix constituents of the 4 solutions (g/L)**

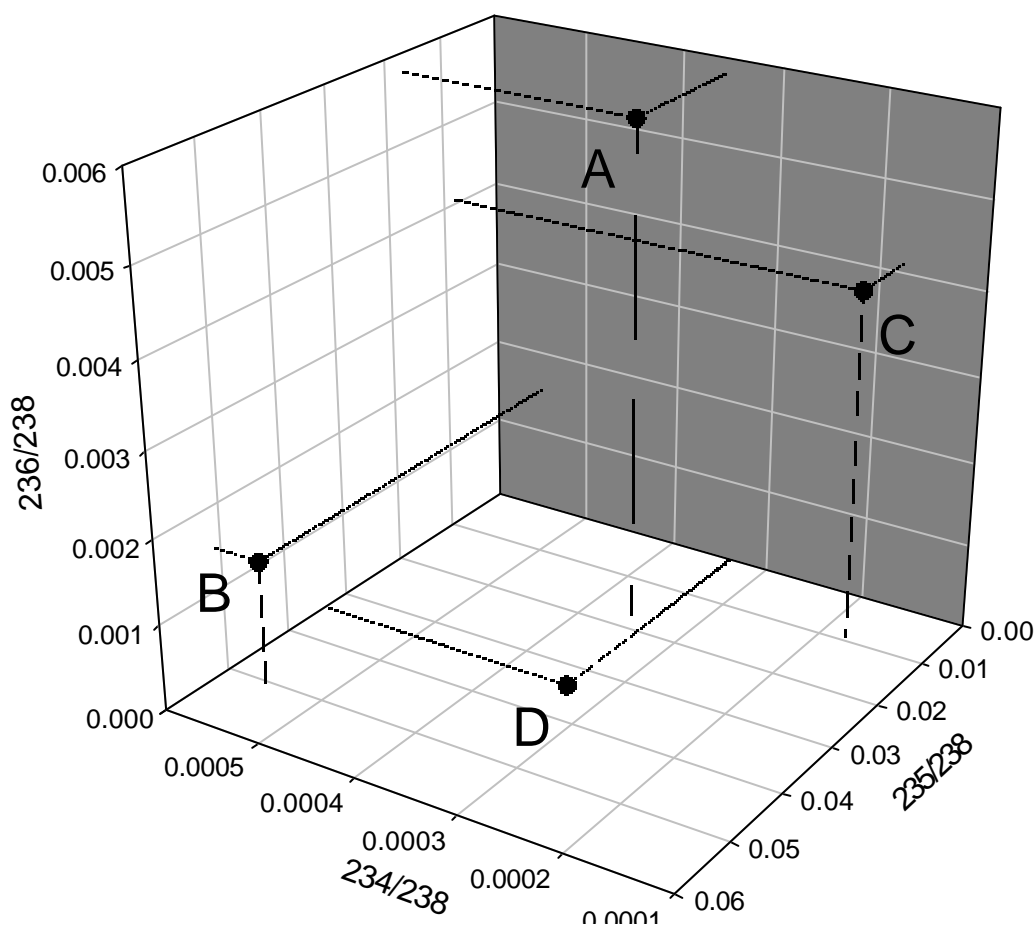
	Sample A	Sample C	Sample D
NaCl	7	6	30
KCl	2	2	0.8
MgCl <sub>2</sub>	3	2	0.5
CaCl <sub>2</sub>	9	4	1.9
FeCl <sub>3</sub>	0.4	2	-
MnCl <sub>2</sub>	-	2	-
CrCl <sub>2</sub>	-	2	-

**Sample B:**

Ion	Concentration in g/L
Cl	19.2
Na	10.8
SO <sub>4</sub>	2.7
Mg	1.3
K	0.4
Ca	0.4

The solution for sample B was of commercial origin and had indicative contents of the most abundant salts but no indication of the uranium content. The salt was analysed by IDMS using the highly enriched  $^{233}\text{U}$  spike IRMM-058. A level of natural uranium was found which, after adding the certified uranium prepared originally as  $\text{UF}_6$ , would affect the certified value of uranium in this sample and so a solution of the salt was passed through a EICHROM U-TEVA column to selectively remove the uranium. The uranium content measured after this process was low enough to allow its use as matrix material for this campaign.

In none of the samples was  $^{233}\text{U}$  present in measurable amounts. For future uranium rounds of NUSIMEP we will consider addition of small amounts of this isotope. As in the NUSIMEP-2 campaign, the uranium isotopic abundances were chosen so that there was no correlations between them (Fig. 1). This was simply so that measurement of an isotopic ratio for one sample could not be extrapolated to other samples. One sample had a very low abundance of  $^{236}\text{U}$ . This isotope was found to be difficult to measure in the NUSIMEP-2 campaign for the sample with low abundance  $^{236}\text{U}$  and we were interested to see if better performances would be reached in the present one.



**Fig. 1: Isotopic ratios of uranium in the 4 NUSIMEP-3 samples**

### **3.1 Bottling and Transport**

Cleaned polythene bottles with polythene screw caps were chosen to transport the solutions. The bottles were cleaned in the IRMM Ultra-clean Chemical Laboratory (UCCL) using the laboratory standard technique and the cleaning process was checked by keeping a 1 M HNO<sub>3</sub> solution in sample bottles and analysing the natural uranium leached over a period of ca. 2 weeks. The uranium content of the blanks was measured either by measuring directly or by spiking with ca. 0.1 ng IRMM-058 spike (highly enriched <sup>233</sup>U and measuring the  $n(^{238}\text{U})/n(^{233}\text{U})$  ratio on a Quadrupole Inductively Coupled Plasma Mass-Spectrometer (Q-ICP-MS).

20 mL of the solutions A, B and C were provided. These had a nominal concentration of 5 ng·g<sup>-1</sup> U. Solution B was prepared from a commercial sea-water salt mixture, purified from uranium and in this solution the concentration was 2 ng·g<sup>-1</sup> U. The calculated activity of the uranium content was in all cases well below levels whereby radioactive transport regulations would apply.

The bottles were heat sealed twice into polythene bags for containment and 4 bottles, one from each of samples A, B, C and D were packed together in a transport box. The solutions were sent out in October 2001 with a request for measurement by the end of November 2001.

During the transport, about a third of the laboratories reported visible leakage of solutions into the first polythene bag. This was worse for samples which had undergone long transport by plane. As the polythene bags were clean (although they had not undergone the extensive cleaning process used for the bottles) it was not expected that the results would be compromised by leakages, when only a few mL of the solutions were found in the polythene bag. Laboratories were therefore advised to continue with their measurements except where the amount of leakage was severe.

A number of samples were therefore sent again for those laboratories which had suffered unacceptable losses: some 8 extra shipments were made.

Inevitably this delayed measurements and sending results and because of this (and the onset of the Christmas holidays) the deadline for results was postponed until the end of January 2002 and indeed some results were accepted through into March 2002 because of local problems in certain laboratories.

## 4 Participation

Fewer laboratories participated in NUSIMEP-3 than in NUSIMEP-2: 30 registered and 21 sent results for one or more isotopic ratio. This was probably a reflection of the fact that measurement in the matrices supplied for this campaign was somewhat more difficult than for the 'simpler' samples in NUSIMEP-2 and possibly also some laboratories learning from NUSIMEP-2 the difficulties in measuring isotopic ratios in small amounts of uranium.

**Tab. 3: Distribution of results over different countries**

country	Number
Australia	1
Austria	1
Brazil	3
Bulgaria	1
France	1
Germany	2
Japan	3
Lithuania	1
Czech Republic	1
Slovakia	1
Slovenia	1
Sweden	1
Switzerland	2
United Kingdom	2

## 5 Evaluation of the questionnaire

Together with the samples, the participants received a questionnaire (see Annex). The questions and the answers of the participants are summarised below.

Participants were asked to indicate their level of experience for this type of analysis. Of those answering this question, 7 judged themselves to be experienced and 11 to be less or non-experienced.

The number of samples of a similar type as the NUSIMEP samples that the laboratories process per year is shown in Tab. 4. The laboratories were also asked which types of samples they regularly analyse. Water, urine, sediments, milk were the normal types of samples analysed. At least 2 of the laboratories also analyse irradiated nuclear materials

and for them as well as at least 2 other laboratories, measurements of uranium isotopic ratios in saline samples was a new area of activity.

**Tab. 4: Samples analysed per year**

Samples of this type per year	Number of laboratories
< 25	12
25 – 50	5
> 50	1
No response	3

**Tab. 5: Types of instrumentation used by the NUSIMEP-3 participants**

Instrument type	Number
Multi-collector ICP-MS (MC-ICP-MS)	4
Magnetic sector field (high resolution) ICP-MS (HR-ICP-MS)	5
Quadrupole ICP-MS (Q-ICP-MS)	3
Thermal Ionisation Mass-spectrometry (TIMS)	2
Accelerator mass-spectrometry (AMS)	1
Radiometry (alpha- or gamma-spectrometry)	6

The instrument types used by laboratories are given in Tab. 5. It is noticeable that more laboratories are applying multiple collector ICP-MS techniques compared with the NUSIMEP-2 campaign. Being able to measure isotopic ratios in static mode is clearly a big advantage for these instruments, although the minor isotopic ratios will be more difficult to measure and from these laboratories the observation was made that the minor isotopic ratios were measured using single collectors and SEM/Daly detectors.

More sector field single collector, i.e. high-resolution ICP mass-spectrometers, were applied. These instruments are able to measure the isotopic ratios in very small amounts of uranium and in many ways appear to be displacing quadrupole ICP-MS (3 laboratories) as the preferred technique for measuring environmental samples.

Two laboratories used TIMS to good effect and one laboratory used an accelerator mass-spectrometer, but in this case only  $n(^{236}\text{U})/n(^{238}\text{U})$  was reported. As with NUSIMEP-2, the laboratories employing radiometric methods (alpha- or gamma-spectrometry) were not very successful in analysing the samples, whether chemical separations were employed or not and the most results were for given the  $n(^{234}\text{U})/n(^{238}\text{U})$  ratio where the activities of the uranium isotopes are more suitable for ratio measurements by alpha-spectrometry.

Ten of the laboratories were applying QA in the form of ISO 9000, EN 45000, ISO 17025 or national QA systems and 4 laboratories were 'certified' and 5 'authorised' although it was not always clear from the replies if the certification or authorisation were meant specifically for the type of samples measured in this campaign.

The chemistry applied varied between simple dilution for HR-ICP-MS in 2 cases and complicated chemistry using extraction chromatography and ion-exchange in others. Co-precipitation with  $\text{Fe}(\text{OH})_2$  or  $\text{Al}(\text{OH})_3$  was also applied as the first step in 3 cases.

Among the laboratories using mass-spectrometry, 8 applied corrections for mass-bias and 4 did not. Quite a proportion of the laboratories had clean facilities (8 in total), applied for the whole of the chemical handling or only critical parts of the process.

A high proportion of the laboratories (15) stated they apply GUM methods to calculate their uncertainties on the submitted results.

## 6 Conclusions and comments

The comparative results are shown in the following figures. It was noticeable generally that considerably higher uncertainties were given for this campaign compared with NUSIMEP-2 and for the graphs showing all three ratios together, Figs 2 -5, the results were plotted on a scale of  $\pm 50\%$  relative to the certified values.

For each laboratory the three ratios are given grouped in the order  $n(^{234}\text{U})/n(^{238}\text{U})$ ,  $n(^{235}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$ . The appropriate scales are shown on the left of each graph for  $n(^{234}\text{U})/n(^{238}\text{U})$  and on the right for  $n(^{235}\text{U})/n(^{238}\text{U})$  and then  $n(^{236}\text{U})/n(^{238}\text{U})$ . For sample D where the  $^{236}\text{U}$  concentration was very low ( $1.324(37)\cdot 10^{-7}$ ,  $k=2$ ) a separate graph for the measured data is shown with a logarithmic scale (Fig. 28).

The laboratory order in the first figures is random, depending simply on the order of each laboratory in the databank and not on measurement technique. The same order is used for all the figures in this set.

It is noticeable that some laboratories have grouped results, i.e. all three isotopic ratios tend in the same direction, positive or negative relative to the certified values. This points strongly to instrument effects, not chemical blanks.

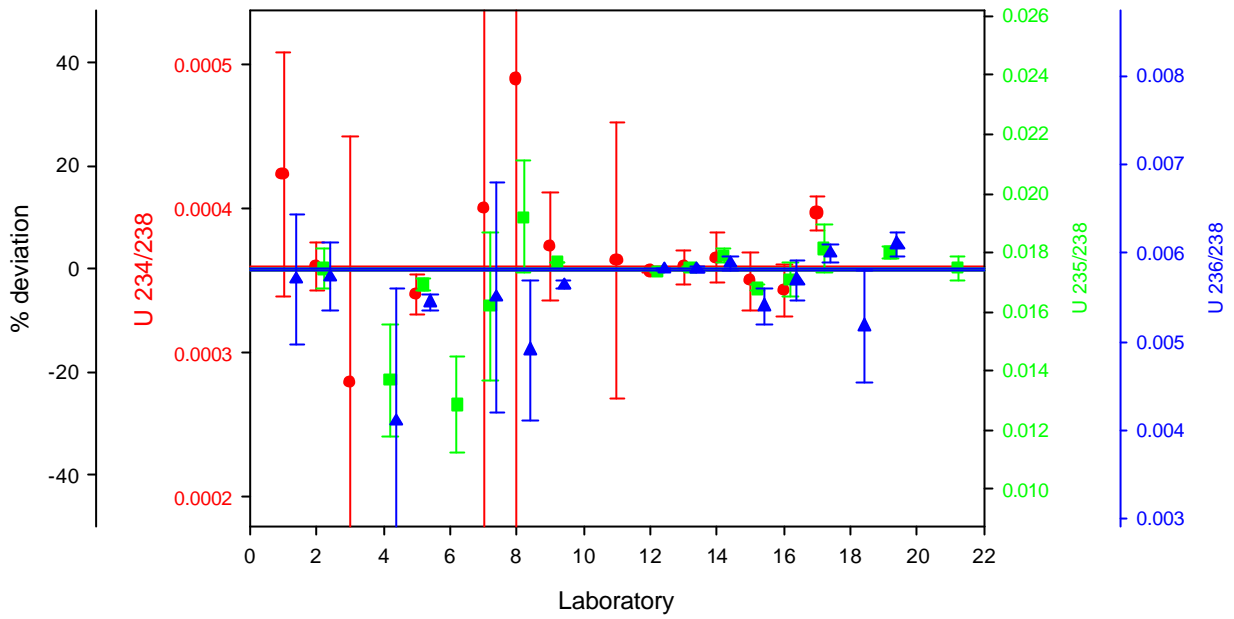
The following set of figures show the results ordered by technique (Figs. 6 to 28). The order of laboratories is the same throughout this set but different to that of the combined data figures. Where a results is not shown it is either because no value was given by the laboratory or the result was outside the plot area. A scale of 50% relative to the certified values is also employed in this set of figures with some plots repeated with a relative scale of 10% or 5% depending on the ratio. This is in order to give an expanded view of the measured values close to the certified values.

A set of graphs (Figs. 29 – 34) show the measurement results for samples A and B with the laboratories grouped into those which stated that they used 'clean' facilities and those which did not. The first set of results, shown as filled points, includes laboratories with all gradations of clean facilities, from individual laminar-flow boxes to completely integrated clean laboratories specific for the measurement of these types of samples.

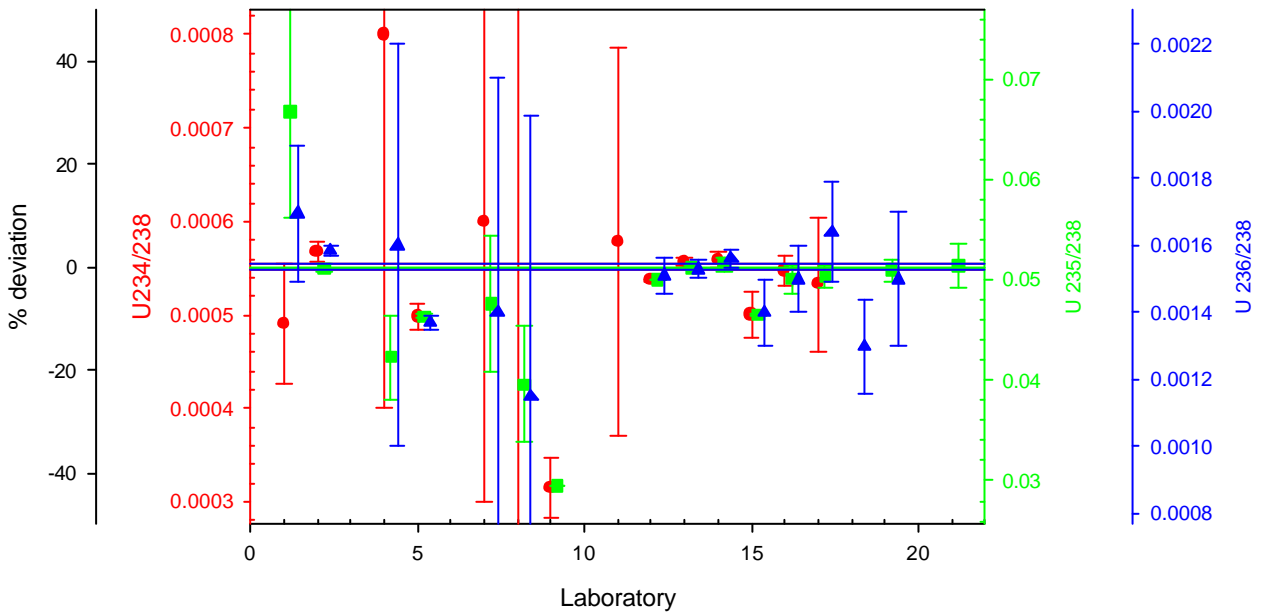
The hoped-for effect of working in clean environments is not apparent from these graphs. Although the results closest to the certified values for all three isotopic ratios are achieved from the group of laboratories using clean facilities, nevertheless it seems that, on the one hand, the availability of such facilities does not guarantee correct results and, on the other hand, some laboratories without such facilities also achieved results close to the certified values.

As a final remark to the results, it appears that there were many difficulties experienced by laboratories in carrying out good measurements. The greater spread of the values compared with those of the NUSIMEP-2 campaign implies that the sample matrix certainly played a role here. Moreover, the careful planning of isotopic ratios and the different strengths of the saline solutions do not show in the final results. From this fact we make the conclusion that future campaigns with uranium in environmental samples can be done with a simpler experimental design, reducing the matrix variability and the range of isotopic abundances. At least one sample with a very low  $^{236}\text{U}$  abundance should be included however, to track the progress of laboratories in measuring the difficult  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio.

From IRMM side, lessons have been learned with the transport of liquids. For future rounds a more secure containment will be used. We were nevertheless encouraged by comments from participants who found the campaign valuable and we hope the results will allow individual laboratories to locate weaknesses in their procedures and reasons why the expected values were not achieved.

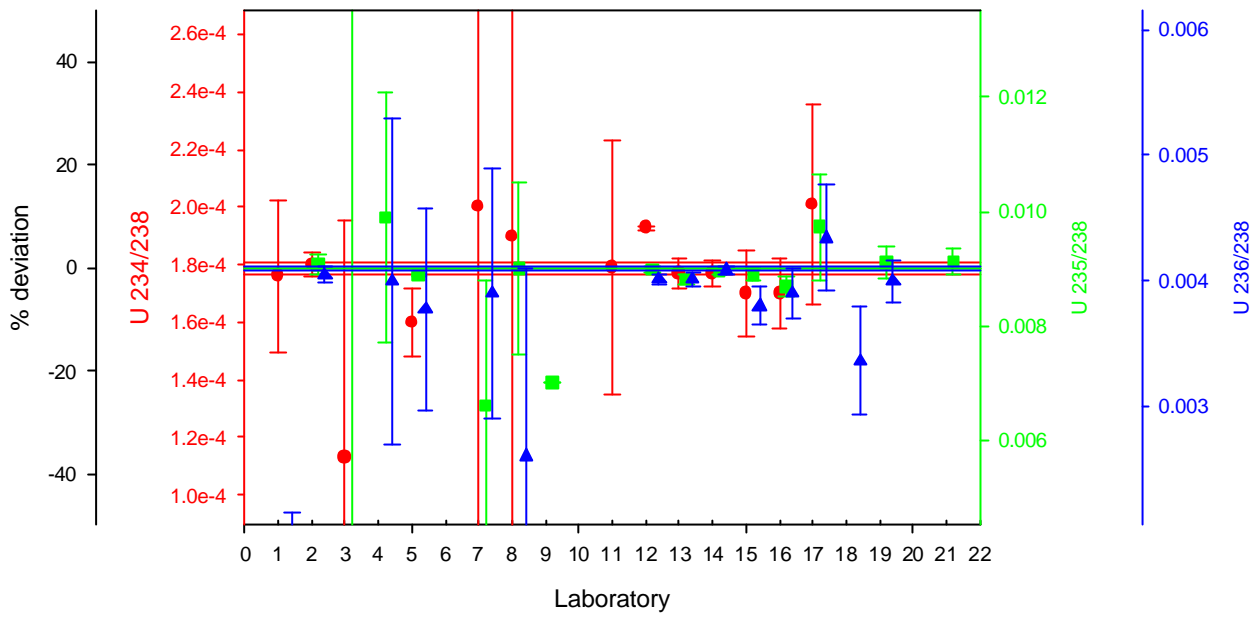


**Fig. 2: Measured isotopic ratios in sample A, relative scale:  $\pm 50\%$ .**  
 $(n(^{234}\text{U})/n(^{238}\text{U}) > 50\% = 3, n(^{235}\text{U})/n(^{238}\text{U}) > 50\% = 2)$

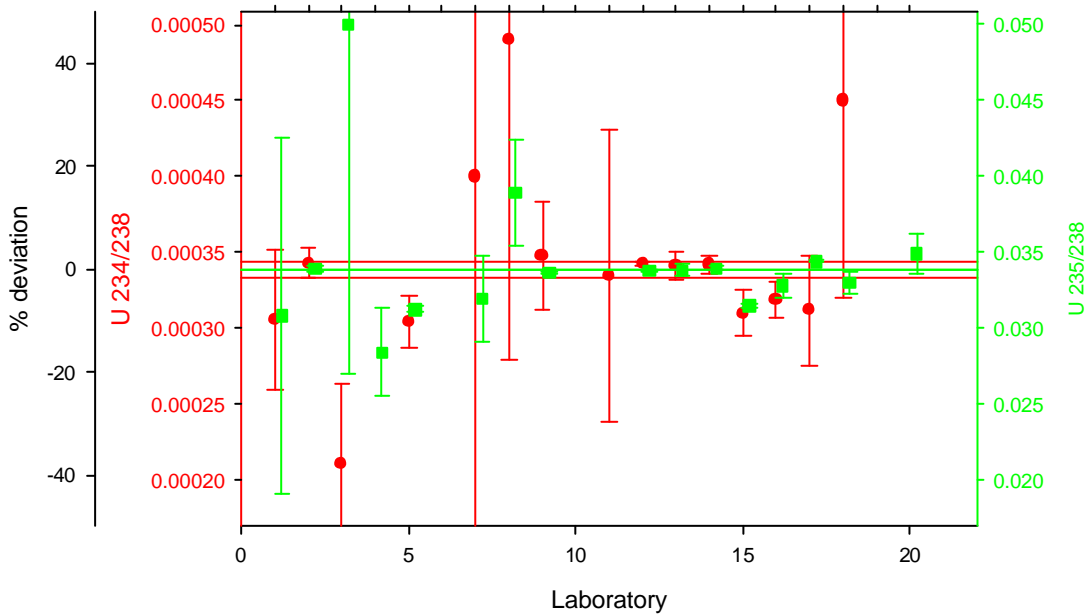


**Fig. 3: Measured isotopic ratios in sample B, relative scale:  $\pm 50\%$ .**  
 $(n(^{234}\text{U})/n(^{238}\text{U}) < 50\% = 1, > 50\% = 3, n(^{235}\text{U})/n(^{238}\text{U}) < 50\% = 2, n(^{236}\text{U})/n(^{238}\text{U}) < 50\% = 1)$

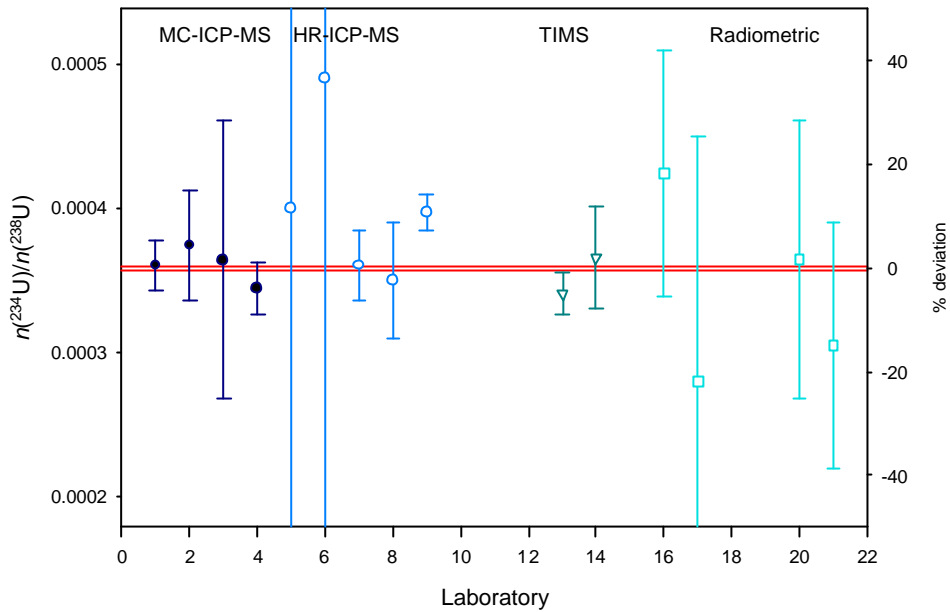




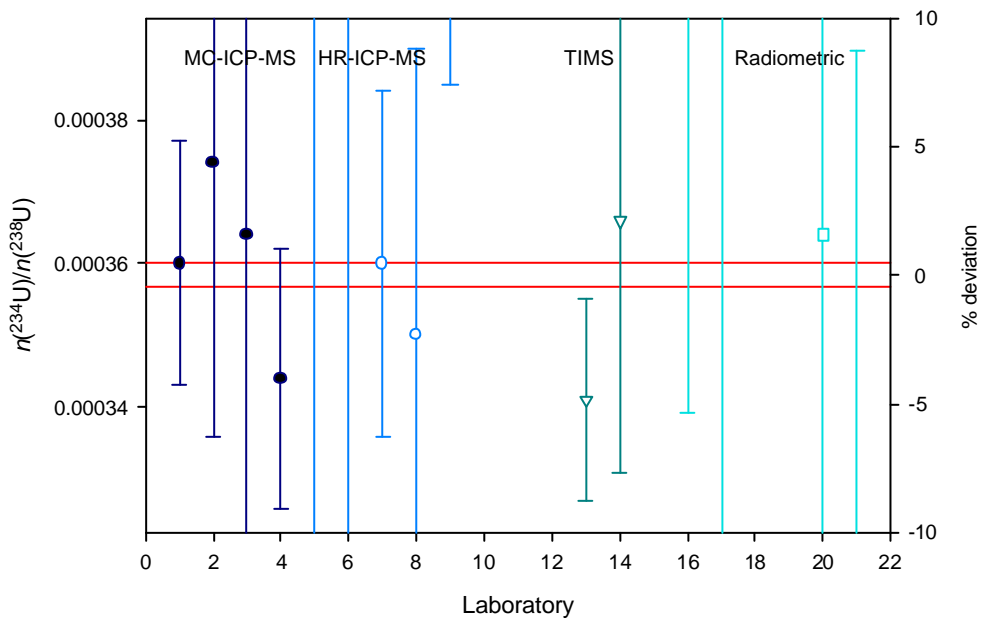
**Fig. 4: Measured isotopic ratios in sample C, relative scale:  $\pm 50\%$ .  
 $(n(^{234}\text{U})/n(^{238}\text{U})) < 50\% = 1, > 50\% = 3, n(^{235}\text{U})/n(^{238}\text{U}) > 50\% = 3, n(^{236}\text{U})/n(^{238}\text{U}) > 50\% = 2)$**



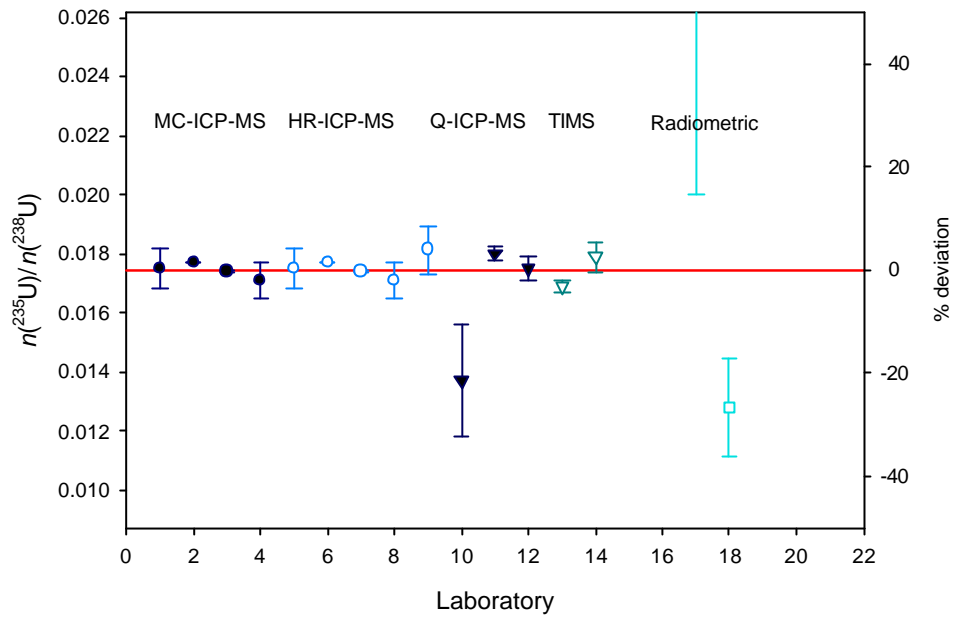
**Fig. 5: Measured isotopic ratios for  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{235}\text{U})/n(^{238}\text{U})$  in sample D, relative scale:  $\pm 50\%$ .  
 $(n(^{234}\text{U})/n(^{238}\text{U})) > 50\% = 2, n(^{235}\text{U})/n(^{238}\text{U}) < 50\% = 1)$**



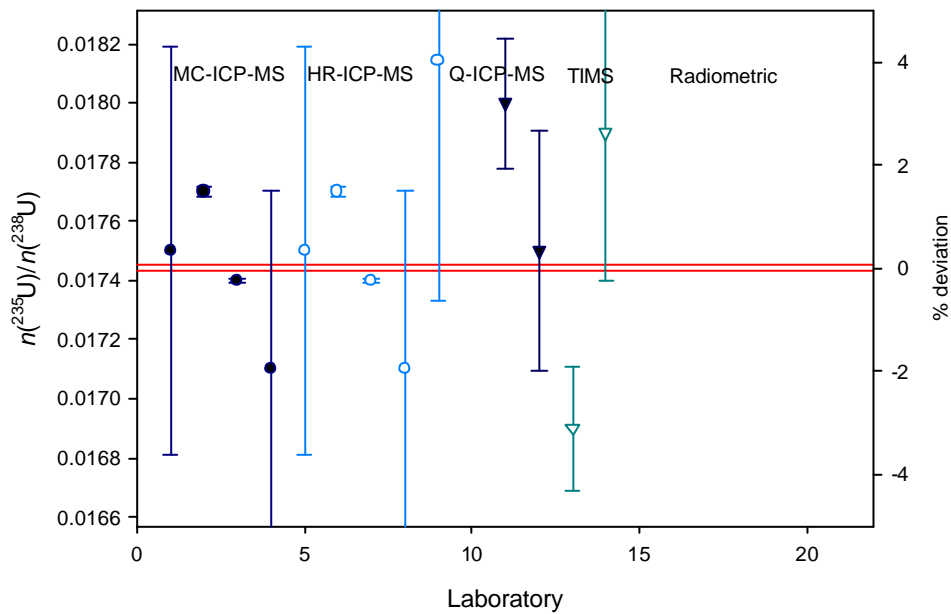
**Fig. 6: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 50\%$ . Grouped by measurement techniques. (Same number of results outside scale as shown in Fig. 2)**



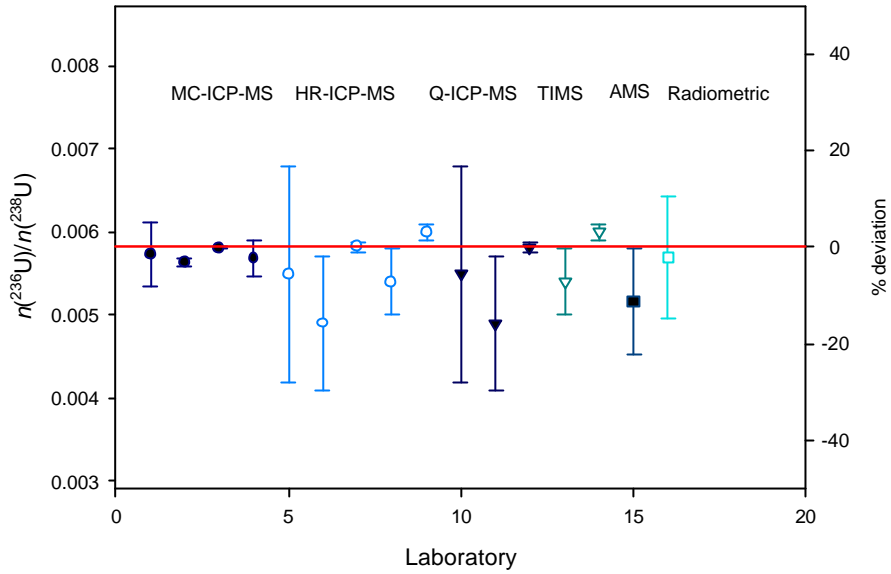
**Fig. 7: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 10\%$ . Grouped by measurement techniques.**



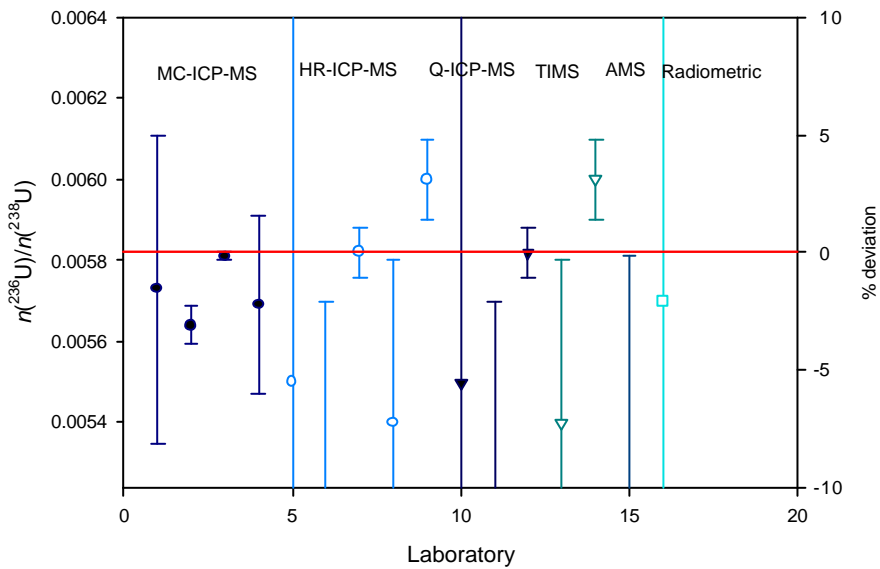
**Fig. 8: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



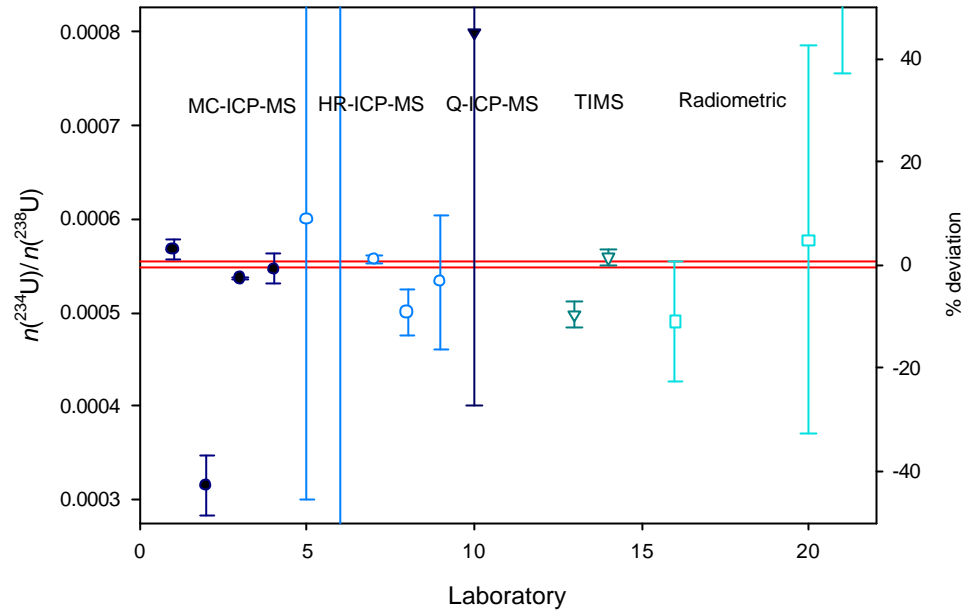
**Fig. 9: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 5\%$ . Grouped by measurement techniques.**



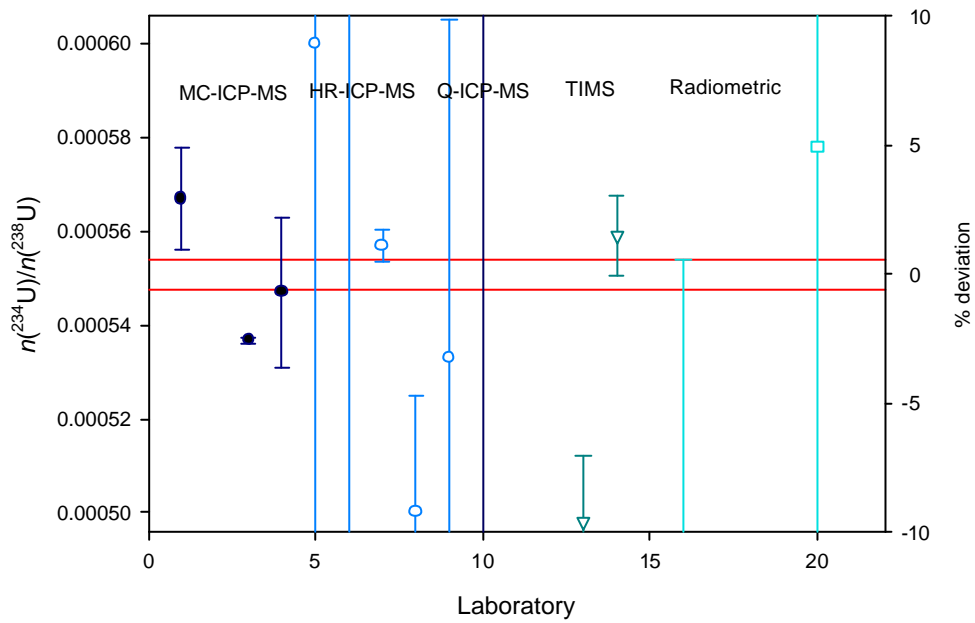
**Fig. 10: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



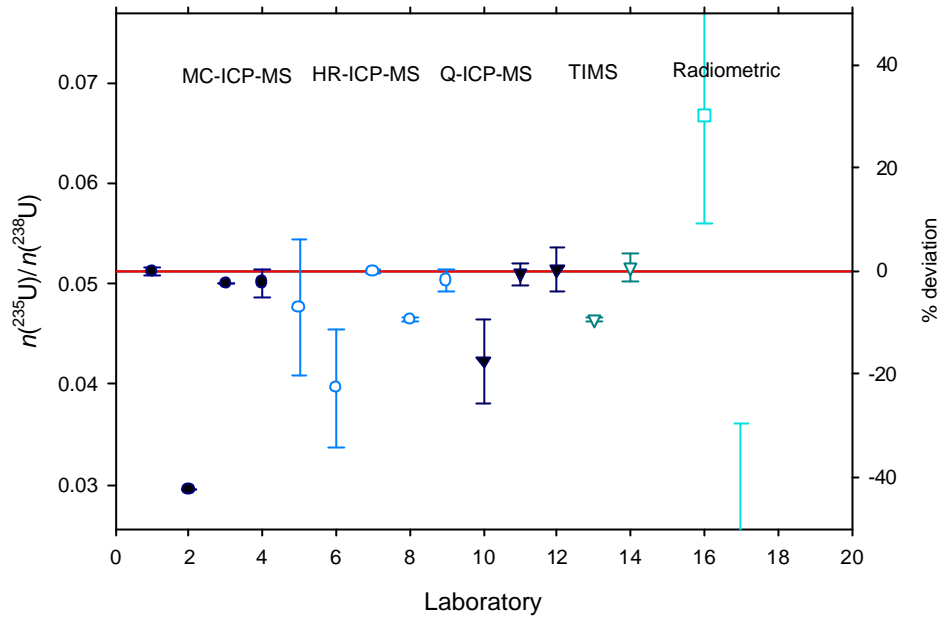
**Fig. 11: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A, relative scale  $\pm 10\%$ . Grouped by measurement techniques.**



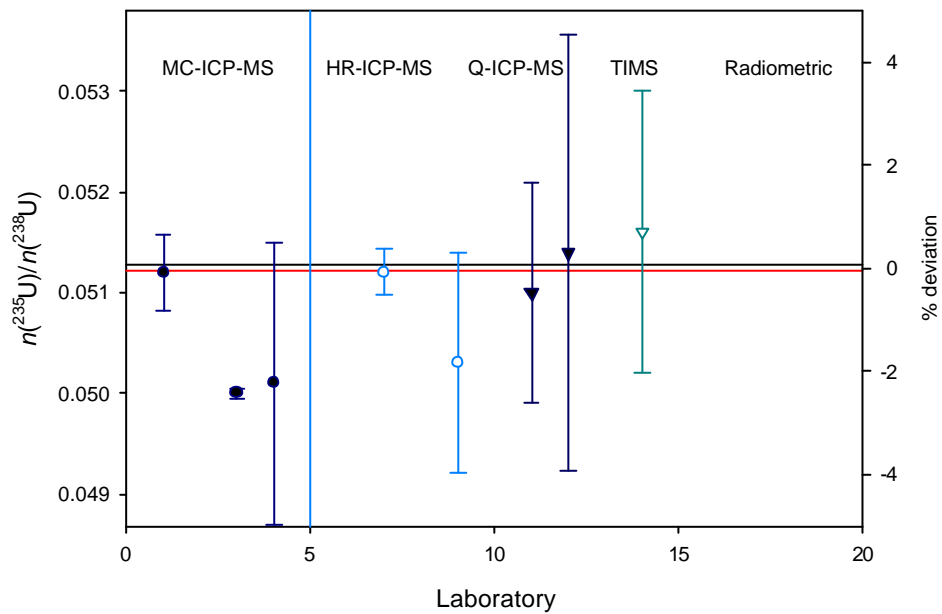
**Fig. 12: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



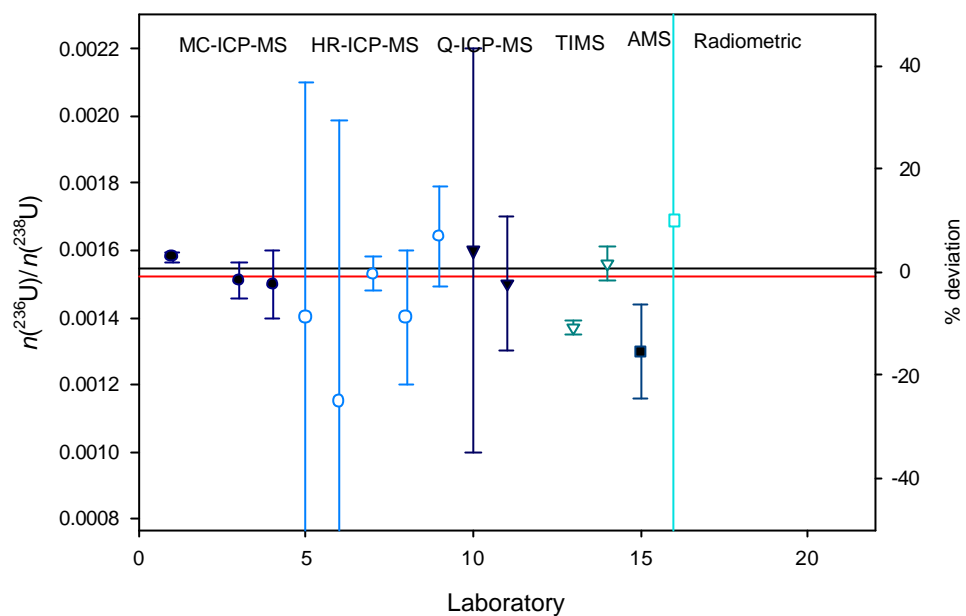
**Fig. 13: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 10\%$ . Grouped by measurement techniques.**



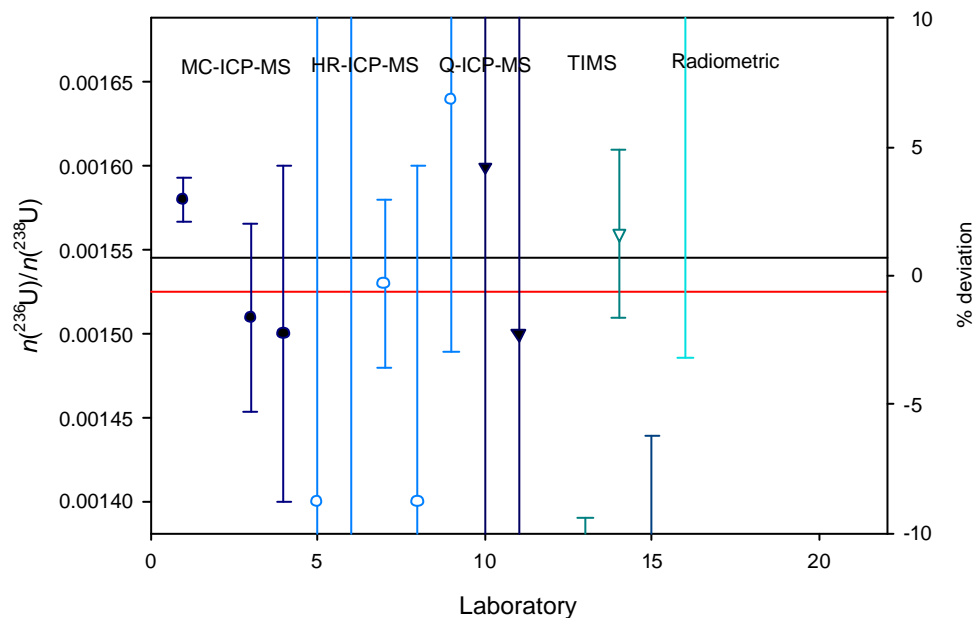
**Fig. 14: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



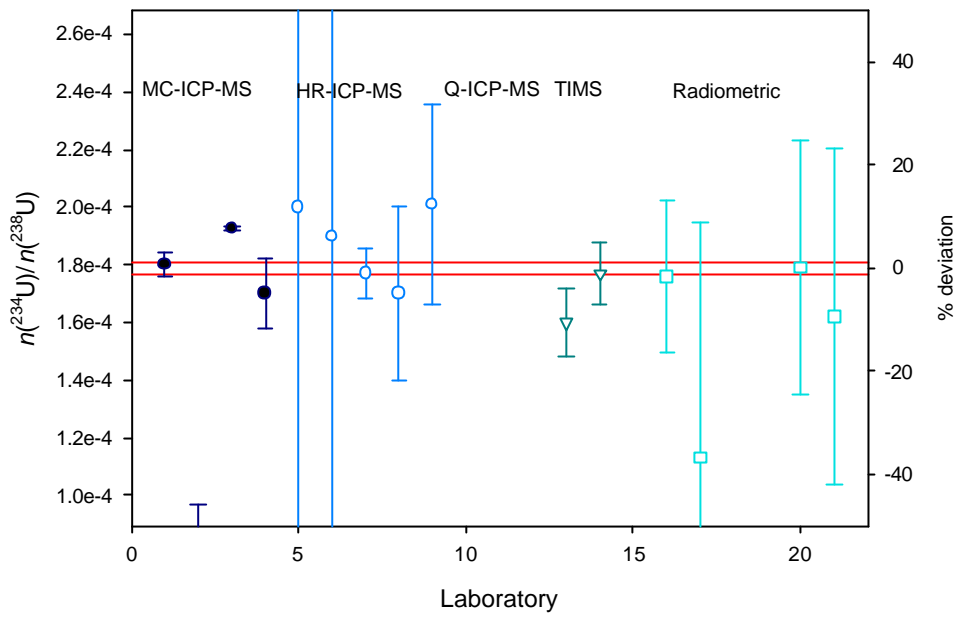
**Fig. 15: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 5\%$ . Grouped by measurement techniques.**



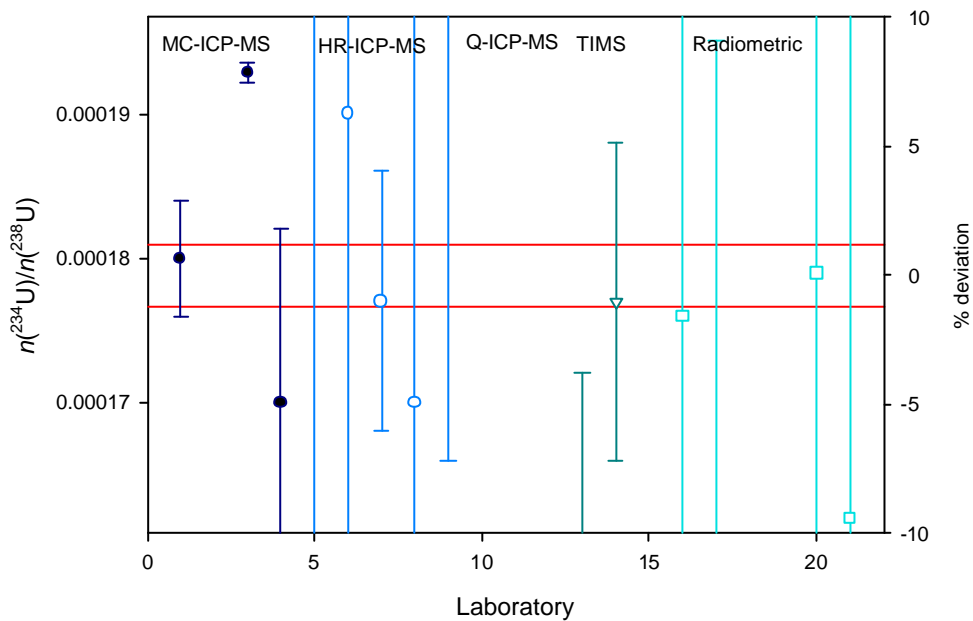
**Fig. 16: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



**Fig. 17: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B, relative scale  $\pm 10\%$ . Grouped by measurement techniques.**

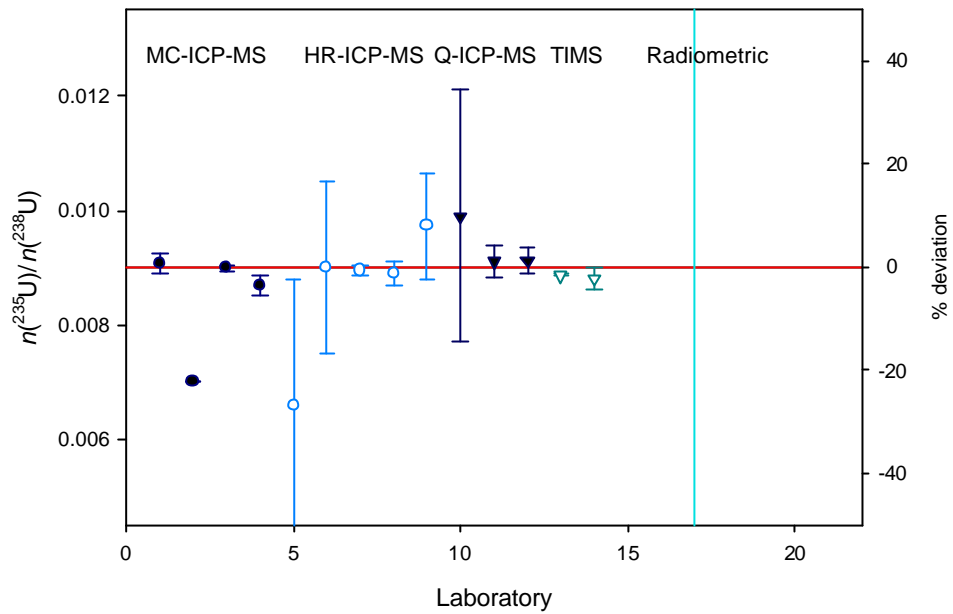


**Fig. 18: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**

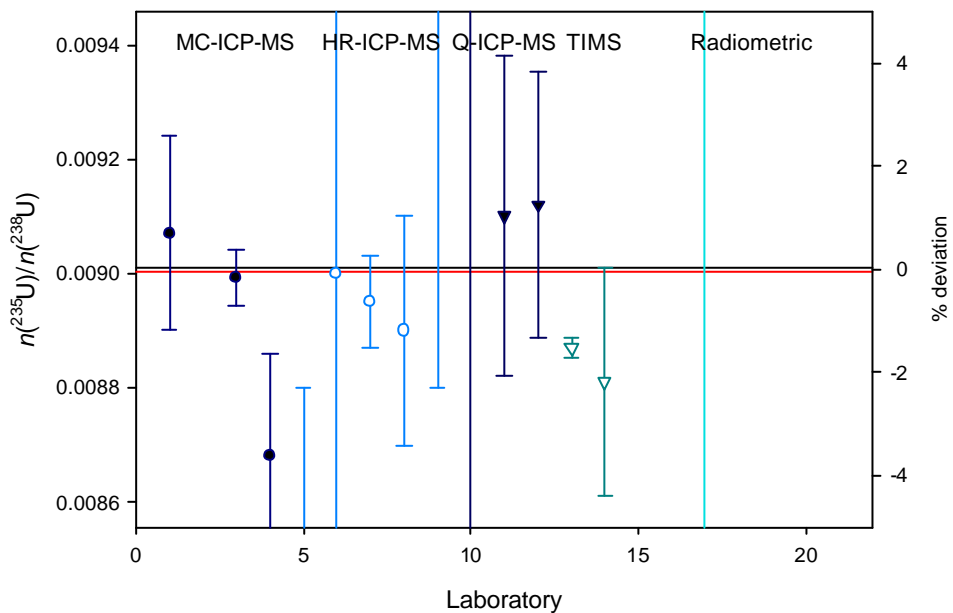


**Fig. 19: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 10\%$ . Grouped by measurement techniques.**

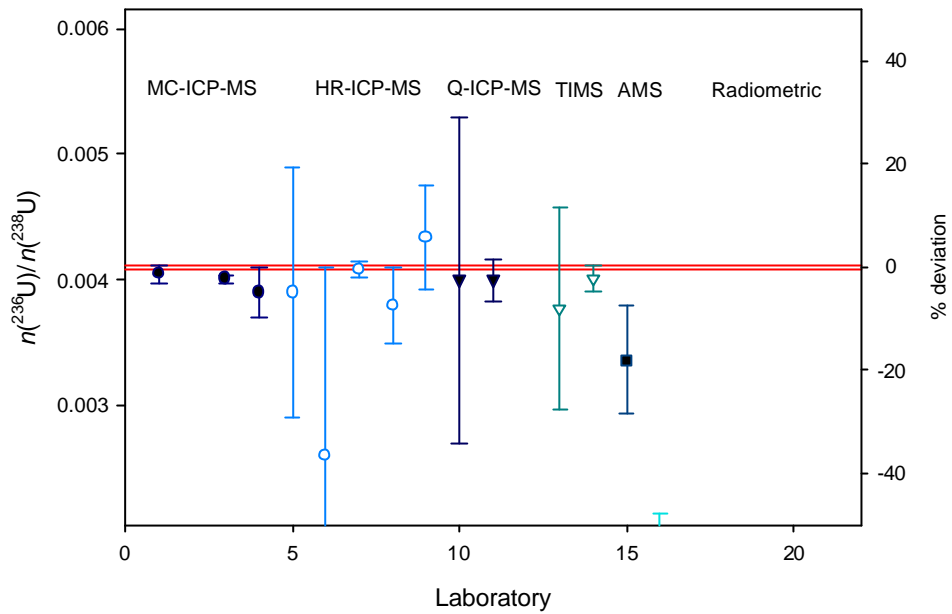




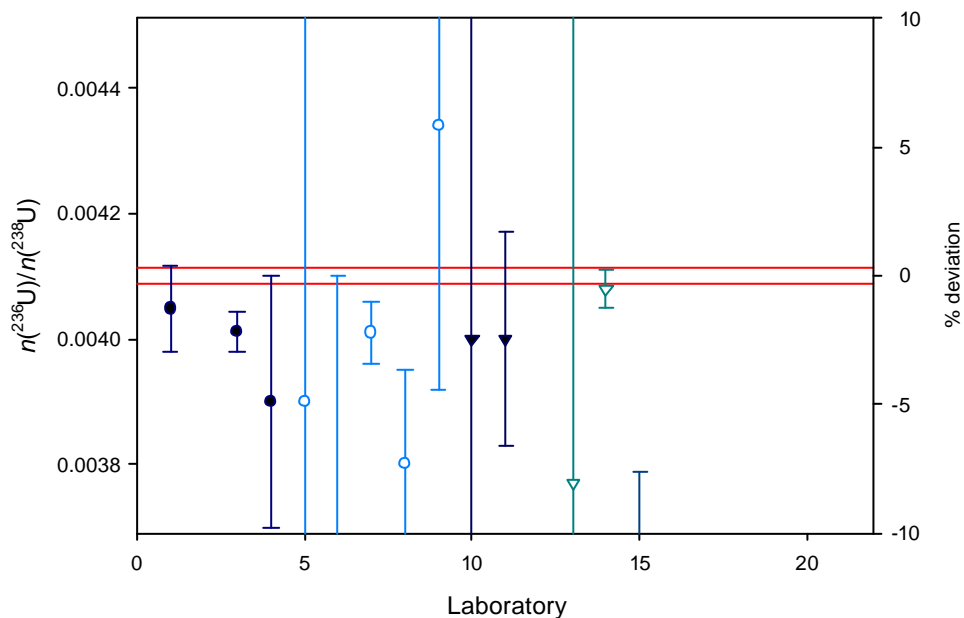
**Fig. 20: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 50\%$ . Grouped by measurement techniques.**



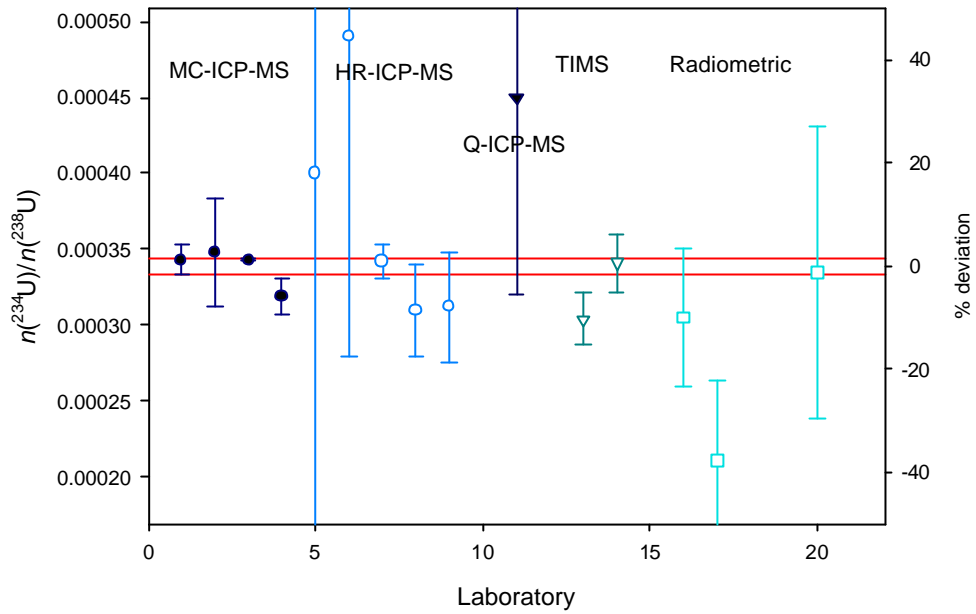
**Fig. 21: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 5\%$ . Grouped by measurement techniques.**



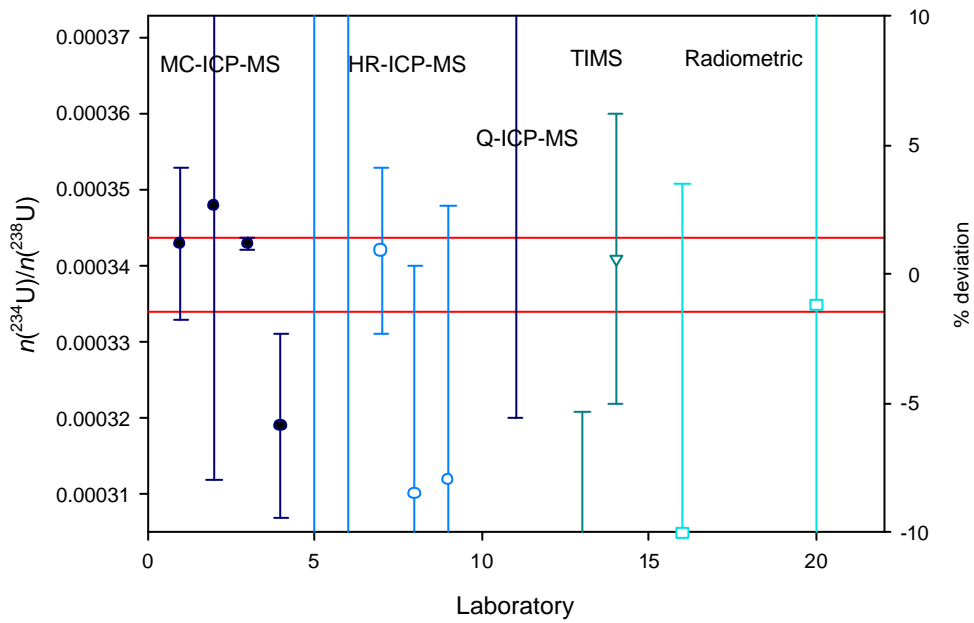
**Fig. 22: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 50\%$ . Grouped by measurement techniques**



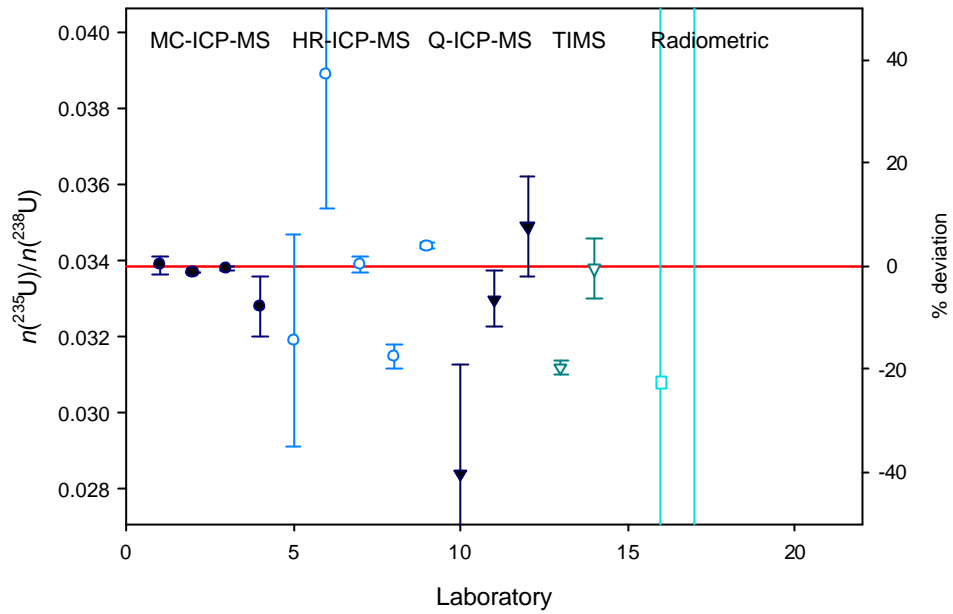
**Fig. 23: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C, relative scale  $\pm 10\%$ . Grouped by measurement techniques**



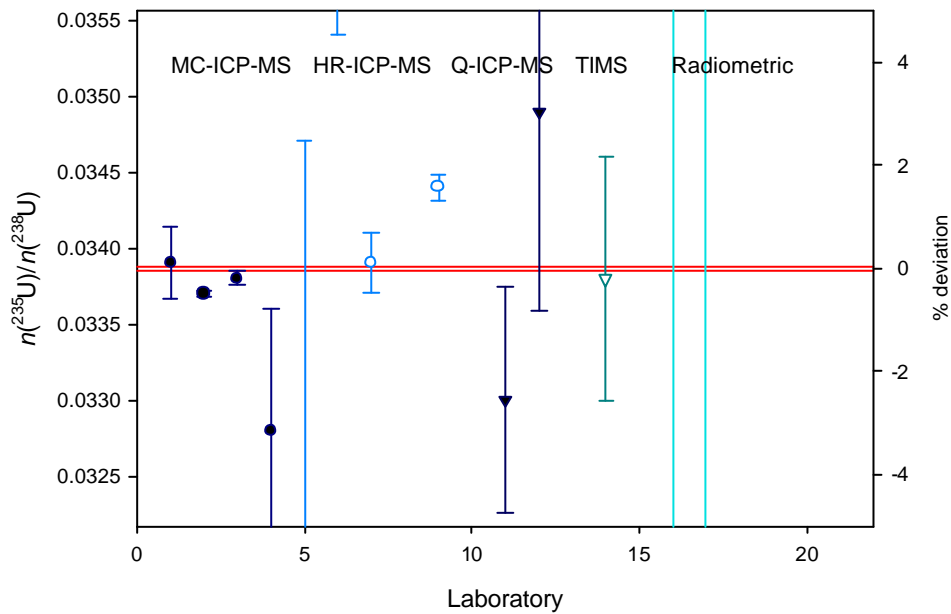
**Fig. 24: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D, relative scale  $\pm 50\%$ . Grouped by measurement techniques**



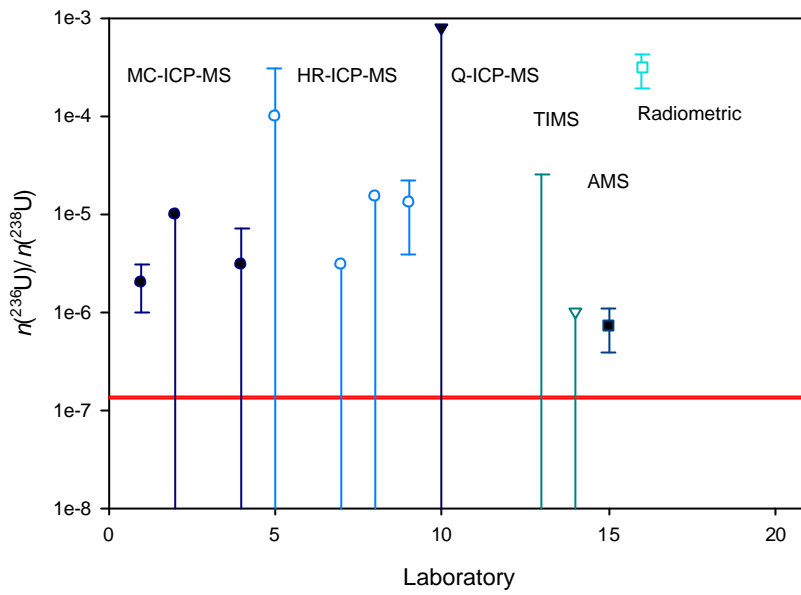
**Fig. 25: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D, relative scale  $\pm 10\%$ . Grouped by measurement technique**



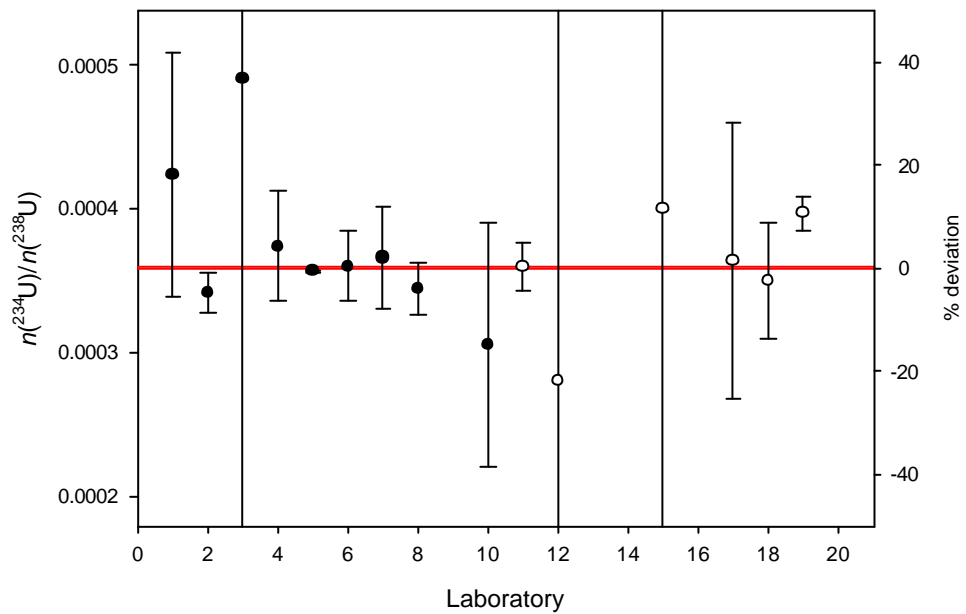
**Fig. 26: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D, relative scale  $\pm 50\%$ . Grouped by measurement technique**



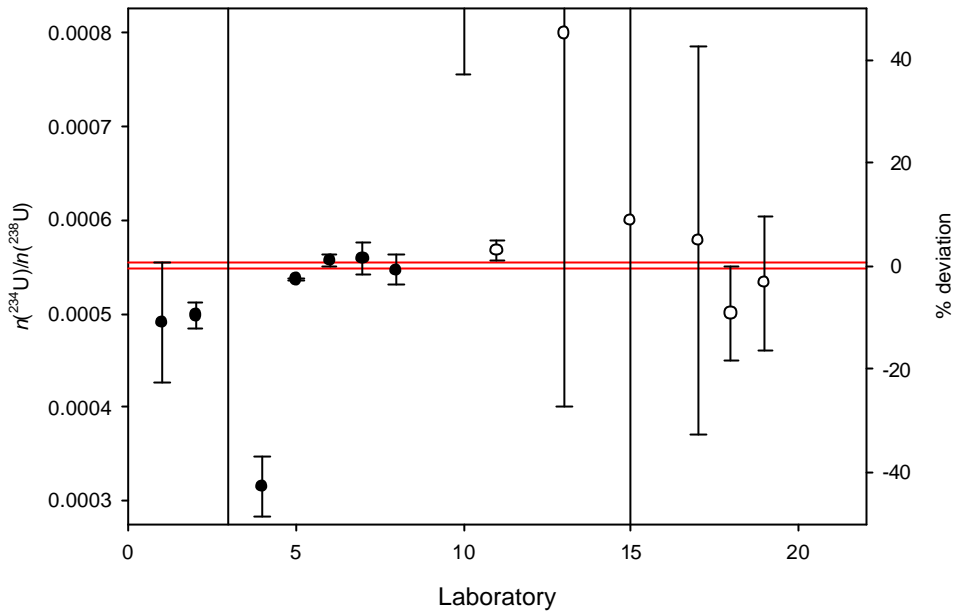
**Fig. 27: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D, relative scale  $\pm 5\%$ . Grouped by measurement technique**



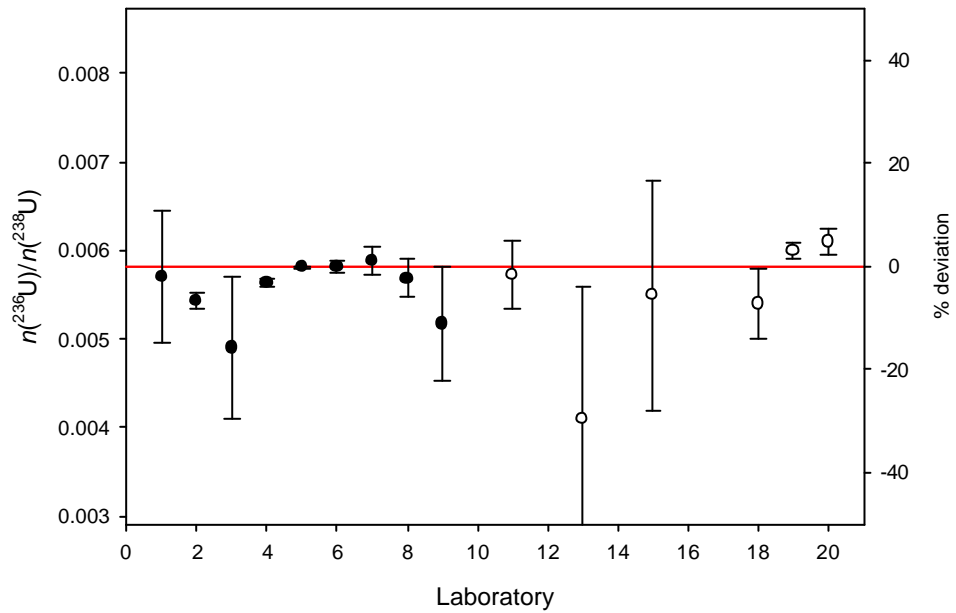
**Fig. 28: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D, Log plot; grouped by measurement technique.**



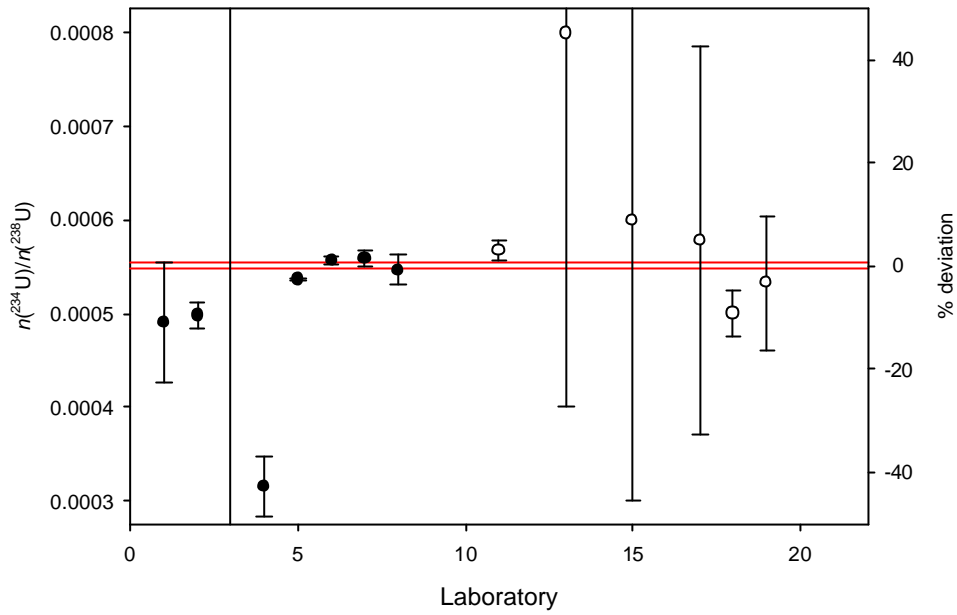
**Fig. 29: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A; solid points: laboratories declaring clean conditions**



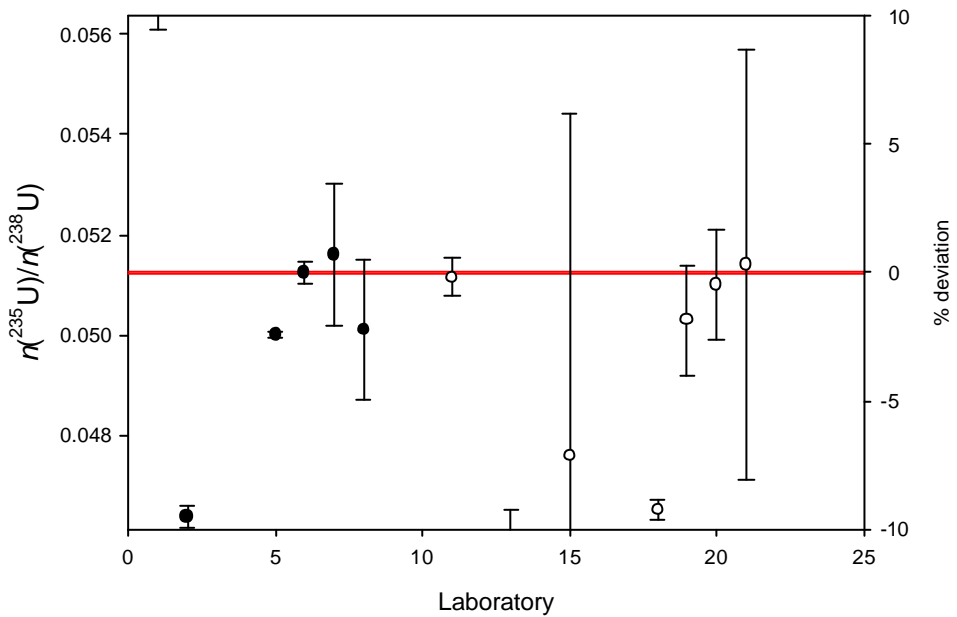
**Fig. 30: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A; solid points: laboratories declaring clean conditions**



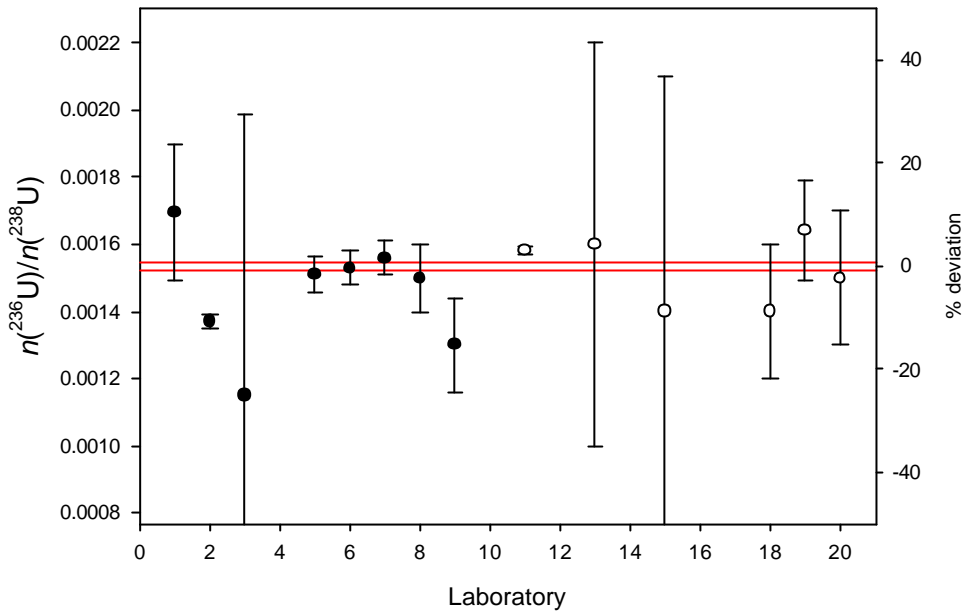
**Fig. 31: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample A; solid points: laboratories declaring clean conditions**



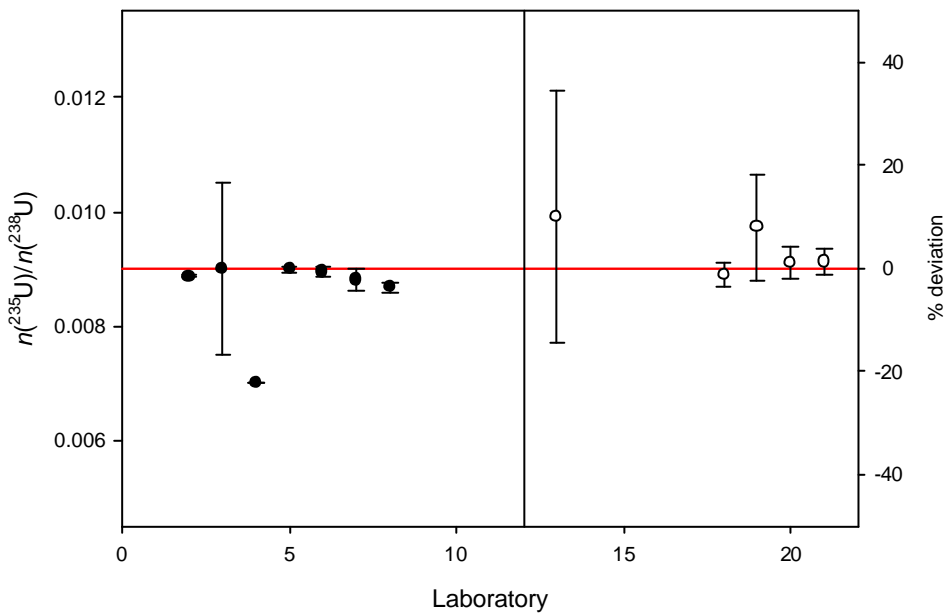
**Fig. 32: Measured  $n(^{234}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B; solid points: laboratories declaring clean conditions**



**Fig. 33: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B; solid points: laboratories declaring clean conditions**

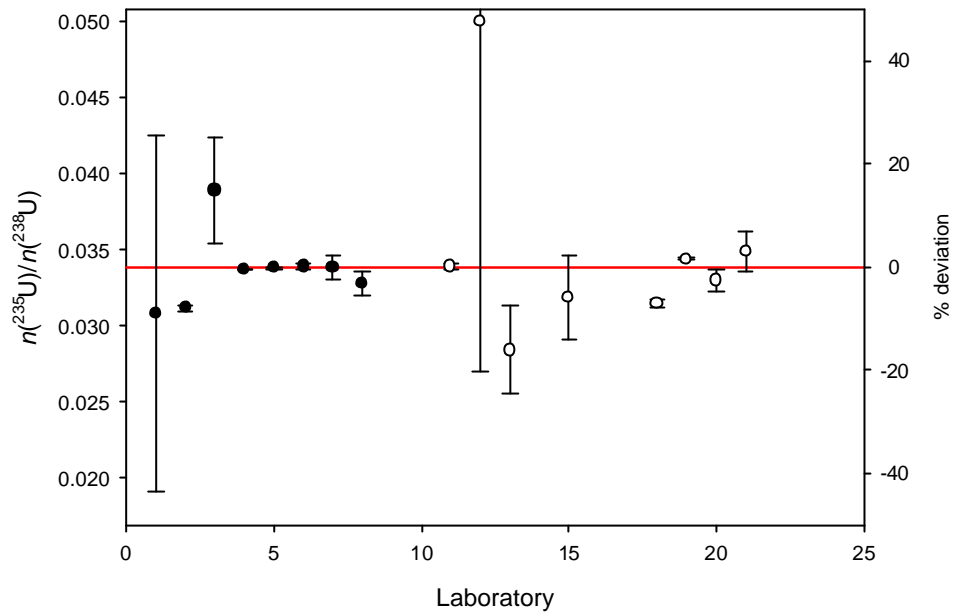


**Fig. 34: Measured  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample B; solid points: laboratories declaring clean conditions**



**Fig. 35: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample C; solid points: laboratories declaring clean conditions**





**Fig. 36: Measured  $n(^{235}\text{U})/n(^{238}\text{U})$  isotopic ratios in sample D; solid points: laboratories declaring clean conditions**

#### References

- [1] NUSIMEP-2: Uranium Isotopic Abundances. Report to participants. EUR 19744/EN, 2001
- [2] Nuclear signatures interlaboratory measurement evaluation programme: NUSIMEP-2. A Held, A. Alonso, W. De Bolle, A. Verbruggen, R. Wellum, European Plasma Winter Conference, Lillehammer, Norway, 4-8 February, 2001.
- [3] The blending of  $\text{UF}_6$  for the preparation of isotopic reference materials with specified  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{236}\text{U}$  abundances, W. De Bolle, A. Alonso, A. Verbruggen, R. Wellum, Symposium on Safeguards and Nuclear Material Management. ESARDA: Sevilla, 4-6 May 1999

## Annex: Report form and questionnaire



NUSIMEP-3:  
uranium in saline solutions



### REPORT FORM

Lab Identification : «title» «firstname» «surname»  
«companyinstitute»  
«department»  
«address»  
«zip» «town»  
«state»  
«country»

Report the isotope ratios for as many isotopes as possible. Please also report the uncertainty related to you ratio. Measurement uncertainty can, e.g. be evaluated according to guides issued by ISO1 and EURACHEM2. Clearly indicate in the questionnaire (question 12) how the measurement uncertainty was evaluated.

**The uncertainty indicated on this report form, should be a range claiming  
- for all practical purposes - to contain the true value**

#### NUSIMEP-3 sample A

Isotope ratio	value	uncertainty
$^{234}\text{U}/^{238}\text{U}$		
$^{235}\text{U}/^{238}\text{U}$		
$^{236}\text{U}/^{238}\text{U}$		

#### NUSIMEP-3 sample B

value	uncertainty

#### NUSIMEP-3 sample C

Isotope ratio	value	uncertainty
$^{234}\text{U}/^{238}\text{U}$		
$^{235}\text{U}/^{238}\text{U}$		
$^{236}\text{U}/^{238}\text{U}$		

#### NUSIMEP-3 sample D

value	uncertainty

---

Date :

Signature :



## NUSIMEP-3: uranium in saline solutions

### PARTICIPANT QUESTIONNAIRE

The purpose of this questionnaire is to enable the organiser of NUSIMEP-3 to correlate measurement performance with other factors such as analytical techniques, self-assessment of experience, accreditation and present this to the participants in a graphical form.

**ALL ANSWERS WILL BE TREATED CONFIDENTIALLY,**

**i.e. non-disclosure of the identity of the laboratories is guaranteed.**

If the space provided is not sufficient, please feel free to add additional page(s).

1. Does your laboratory consider itself, in matters of this type of measurement, as experienced or less experienced?

Experienced  
experienced

less

2. How many measurements of this type does your laboratory routinely carry out per year?

< 25

25-50

> 50

In what type of matrices do you routinely measure the isotopic composition of small amounts of uranium?

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3. Was the NUSIMEP-sample analysed by the same analyst who usually performs such analyses ?

YES

NO

If "NO" please rate the experience of the IMEP-analyst: more/same/less  
Why was the same analyst not used?

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4. Was the NUSIMEP-3 sample treated according to the same analytical procedure as routinely used for this sample type ?

YES  NO

If "NO" why not?

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5. Does your laboratory routinely use certified reference materials (CRMs)?

YES  NO

If "YES", please state which CRM and supplier and state also how the CRM is used in your laboratory (validation of procedures/ calibration of instruments/ etc)

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6. Does your laboratory participate regularly in a proficiency testing scheme to assess performance for this type of analysis?

YES  NO

If "YES", please state which proficiency testing scheme and organiser

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7. Is your laboratory using a quality management system ?

YES  NO

If "YES", please state which system :

EN 45000series / ISO 25  ISO 9000series

other (e.g. CEN, GLP, EPA, TQM, national standards), specify:

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8. Is your laboratory certified, accredited or authorised for this type of analysis ?

YES certified  YES accredited  
 YES authorised  NO

9. Please describe briefly your sample preparation:

Did you carry out a separation prior to the measurement:

YES  NO

If "YES", please describe the separation:

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What kind of reagents were used in the sample preparation (type and quality of reagents, etc):

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Where was the sample preparation carried out:

in a conventional laboratory

in a clean environment

Please specify:

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---

Other details:

---

---

10. Please describe briefly your measurement procedure:

Instrument used:

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Special measurement conditions, if applicable:

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Other details:

---

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If you used a mass spectrometric technique, did you apply a correction for mass fractionation / mass bias?

YES  NO

If "YES", how was the mass fractionation / mass bias factor determined?

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11. Are you familiar with the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1993) and/or EURACHEM (1995)?

YES  NO

12. Were the reported uncertainties calculated according to the in above mentioned guides?

YES  NO

If "YES", what did you report as an uncertainty?

combined uncertainty

expanded uncertainty with a coverage factor of  $k=$  \_\_\_\_\_

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If "NO", how was the measurement uncertainty evaluated?

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13. Do you report uncertainties on chemical measurements to your usual customers ?

YES  NO

14. Who filled in the questionnaire ?

the analyst  the laboratory supervisor

15. Who filled in the report form ?

the analyst  the laboratory supervisor

16. Would you be interested in participating in future NUSIMEP rounds?

YES  NO

If "YES", what type of samples would you be interested in (radionuclides to be measured, matrices, etc)?

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- 1 International Organisation for Standardisation, "Guide to the Expression of Uncertainty in Measurement", ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993.
  - 2 EURACHEM, "Quantifying Uncertainty in Analytical Measurement", ISBN 0-948926-08-2, ©Crown copyright, 1995, LGC Information Services, Queens Road, Teddington, Middlesex, TW11 0LY, England.