



**NUSIMEP 4:**

**Uranium isotopic abundances  
in simulated urine**

**Report to participants**

A. Stolarz, A. Alonso, W. De Bolle, A. Moens,  
E. Ponzevera, C. Quétel, S. Richter, A. Verbruggen, R. Wellum



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## 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 of 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 Inter-laboratory Evaluation Programme (REIMEP) in the nuclear field and the International Measurement Evaluation Programme (IMEP) for measurements of amounts of chemical substances.

The first three NUSIMEP campaigns were devoted to measurements of uranium in various media ranging from simple dried nitrate salts to a complex saline solution matrix. In NUSIMEP 4 the matrix was made somewhat more complex: a simulated urine solution was prepared from the saline solution used in NUSIMEP 3 with the addition of urea. The samples for NUSIMEP 4 are proposed as test samples not only for laboratories measuring uranium in urine but also for laboratories measuring uranium isotopes in complex, biological matrices. The samples were prepared and certified at IRMM: uranium isotopic ratios by mixing certified isotopic material as  $\text{UF}_6$  and measuring minor isotopes by TIMS. The matrix solution was prepared by dissolving salts to reach prescribed concentrations and pure urea was added. The uranium traces in the matrix solution components were removed by absorbing them on Eichrom U-TEVA columns. The very low residual uranium concentration in the matrix solution was measured by ICP-MS at IRMM.

Two solutions with uranium of different isotopic abundances at a concentration of  $5 \text{ ng}\cdot\text{g}^{-1}$  were supplied to the participating laboratories in the same matrix solution.

The uranium isotopic ratios were mainly measured by the participating laboratories by inductively-coupled-plasma mass-spectrometry (ICP-MS). For certain uranium isotopes, mainly  $^{234}\text{U}$ , measurements of radioactivity by alpha spectrometry (RAS) were also employed by some laboratories although previous NUSIMEP campaigns have shown that these methods cannot compete with mass-spectrometry in sensitivity and in the final levels of uncertainty. Thermal-ionisation mass-spectrometry (TIMS) and accelerator mass spectrometry (AMS for measurements of  $^{236}\text{U}$ ) were applied as well.

The measurement results are shown as a set of graphs in which each laboratory is specified only as a number. Details of the laboratories' experience, qualifications and of their measurement methods were requested in a questionnaire and these are summarised also in this report.





## 1. Introduction

The NUSIMEP campaigns were started as a tool for laboratories to confirm their abilities to measure isotopic abundances of small amounts of nuclear materials in environmental samples. This programme is built on the experience gained in similar external quality control campaigns over many years: the Regular European Inter-laboratory Measurement Evaluation Programme, REIMEP and the International Measurement Evaluation Programme, IMEP. These programmes are open for all laboratories active in the appropriate 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 required parameters using their standard methods and send results with uncertainties to IRMM. In return the laboratory receives the certified values.

This campaign follows earlier campaigns for the measurement of uranium isotopic ratios in various media. The previous campaigns were valuable in showing generally the measurement capabilities of laboratories active in this measurement field. It is a field characterized by very different methods. For measuring the isotopic ratios inductively-coupled-plasma mass-spectrometry (ICP-MS) is of increasing importance, although thermal-ionisation mass-spectrometry (TIMS) is still employed. For certain uranium isotopes, mainly  $^{234}\text{U}$ , measurements of radioactivity by alpha spectrometry (RAS) are also employed by some laboratories although earlier NUSIMEP campaigns showed that such methods cannot compete with mass-spectrometry in sensitivity and in the final levels of uncertainty.

Each NUSIMEP campaign up to now has had a matrix more complicated than the previous round. This is partly to approach more closely the problems encountered in natural samples and to show how they affect the measurement results. In NUSIMEP 1 (the only campaign with limited participation) the uranium was in a simple (aquatic) matrix, in NUSIMEP 2 dry uranium nitrate samples were sent to participants and in NUSIMEP 3 a saline solution was used as matrix. In NUSIMEP 2 and 3, four samples were provided, each with different isotopic abundances for the isotopes specified ( $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ ). The measured values were more scattered for NUSIMEP 3 than for NUSIMEP 2, which was the result of a more complex matrix (3 % saline solution).

In NUSIMEP 4 the intention was to look at the measurement capability of laboratories measuring a very relevant type of sample: urine. However some compromises had to be made. For the certification we prefer to use very well certified bulk samples of uranium and add this to a matrix that is shown to be free of (natural) uranium. This method has been described for the previous campaigns. It is a method we have long used at IRMM although it can involve considerable work to eliminate sources of uranium before preparing the final samples. Slight cor-

rections had to be made to the final certified isotopic ratios after taking into account minor contributions from the matrix (the main additional contribution, even after extensive cleaning), the reagents and lab-ware (much lower contributions).

It was decided to use simulated urine as a matrix: a mixture of inorganic salts and urea dissolved in a weak acid medium. This is only an approximation to urine in complexity but the inorganic part can be well cleaned from uranium and pure, nearly uranium-free, urea can be used, thus reducing natural uranium in the matrix to a very low level. This is a big advantage in sample preparation and certification. However the handling and chemical problems it affords to the laboratories are similar to that of 'real' urine and it is therefore also a challenge to measure the uranium in such a matrix.

The second compromise was the choice of a 5 ppb concentration of uranium in the samples. This level of uranium had been used in the previous NUSIMEP campaigns. It has proven to be a level that causes measurement problems for many laboratories, especially for the minor isotopes.

In the present campaign two 20 ml samples, each containing 5 ng U·g<sup>-1</sup> solution (5 ppb) were provided for measurement. As in previous campaigns the isotopic abundances of specified isotopes (<sup>234</sup>U, <sup>235</sup>U, <sup>236</sup>U, <sup>238</sup>U) were different in each sample. One sample (A) had an enrichment (<sup>235</sup>U abundance) close to natural and the second (B) an enrichment close to 1.8%.

20 ml of solution meant that the laboratory had 100 ng of uranium to separate out and measure for each sample and the choice was left to the participants whether they maximised the amount of uranium or measure it in aliquots of the solutions.

The level of uranium in the NUSIMEP 4 solutions therefore is up to a factor of 100 more concentrated than normally expected in natural urine samples. This could be expected to cause problems of cross-contamination for laboratories that routinely measure uranium in urine; on the other hand laboratories treating these samples as typical contaminated environmental materials might not have this problem.

The main reason for the relatively high concentration of uranium compared to natural levels expected in urine was to ensure the uranium stability in this matrix. This was a stronger argument than striving to reach the levels of 'real' samples.

The present campaign also differed from previous campaigns in that it was coupled with a BIPM CCQM (Bureau International des Poids et Mesures, Comité Consultatif pour Quantité de Matière) inter-comparison round. This CCQM campaign, Pilot Study P-48, is the first isotope measurement campaign ever organized by CCQM and was based on the same matrix and the samples were taken from the same group of bulk uranium samples as NUSIMEP 4. In one sense the two campaigns were competing but the purposes were different. NUSIMEP 4 is a tool to aid laboratories currently measuring, or preparing to measure samples of similar complexity and who wish to have an external comparison to prove their abilities to perform good measurements on such samples. The CCQM P-48 campaign had the purpose of demonstrat-

ing the measurement capabilities of metrology laboratories world-wide and was addressed to invited laboratories. Further details of this campaign can be found in [1].

It is planned to combine the results of NUSIMEP 4 and P-48 and publish the overall comparison in the future when both campaigns have been completed.

## 2. Samples

The details of the preparation of the samples can be found in the preparation report [2] sent to the participants after receipt of their results.

To summarise: two samples of different uranium isotopic abundances were made up with an approximate uranium concentration of  $5 \text{ ng}\cdot\text{g}^{-1}$ . The matrix solution was a saline solution ( $17 \text{ g}\cdot\text{l}^{-1}$  of mixed salts) with the addition of  $17 \text{ g}\cdot\text{l}^{-1}$  of urea. The salt solution in 3 M nitric acid was purified from uranium before use by passing the solution through pre-packed Eichrom U-Teva columns (2 ml of 100-150  $\mu\text{m}$  resin). Blank values of uranium in the cleaned saline solution and organic material, mixed to form the matrix solution, were measured by ICP-MS. The isotopic abundances of the two uranium samples were certified from the bulk material which in turn was prepared by mixing isotopic certified uranium fluoride samples in the gas phase and then hydrolysing and treating to form a uranyl nitrate solution [3].

The reference values of the NUSIMEP 4 samples given in the report [2] were corrected for the small contributions of the natural uranium remaining in the matrix components.

The solutions were delivered to the participating laboratories in cleaned polypropylene screw-cap bottles. Precautions were taken to avoid problems of leakages known from previous NUSIMEP campaigns although a few laboratories reported leakages in this campaign, noticeably for samples exposed to long air flights. As the sample bottles were additionally double-bagged in clean, uranium-free polyethylene it was recommended to continue analysis with the remaining solution where the remaining amount was sufficient. New samples were only dispatched in one case when in addition to the leakage a break in the internal bag sealing was reported.

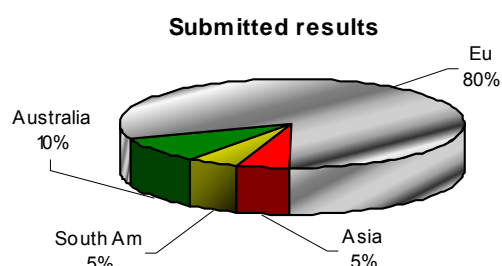
### 3. Participation

Out of twenty seven laboratories from 14 countries which registered to participate in the comparison, 21 submitted results together with the questionnaire except one, which submitted results without returning the questionnaire. A list of the laboratories that submitted results is given in annex (2).

Unfortunately 3 of the registered laboratories reported important problems with their mass spectrometers, which could not be resolved before the final deadline for reporting results. One laboratory faced heavy contamination of the NUSIMEP 4 samples because of an urgent request to measure highly active waste material at the same time. The laboratory reported the problem too late to repeat the measurements with a new set of NUSIMEP 4 samples.

Table 1: Country of participant origin

country	no of registered participants	no of submitted results
Argentina	1	1
Australia	2	2
Austria	2	2
Brazil	3	0
France	1	1
Germany	3	2
Italy	3	2
Lithuania	1	1
Netherlands	1	0
Poland	2	2
Slovenia	1	1
Spain	2	2
Thailand	1	1
UK	4	4
total	27	21



Most of the participating laboratories had already participated either in previous NUSIMEP campaigns (7) or in other inter-laboratory campaigns organised internationally or nationally by IAEA, US/DOE or national organisations.

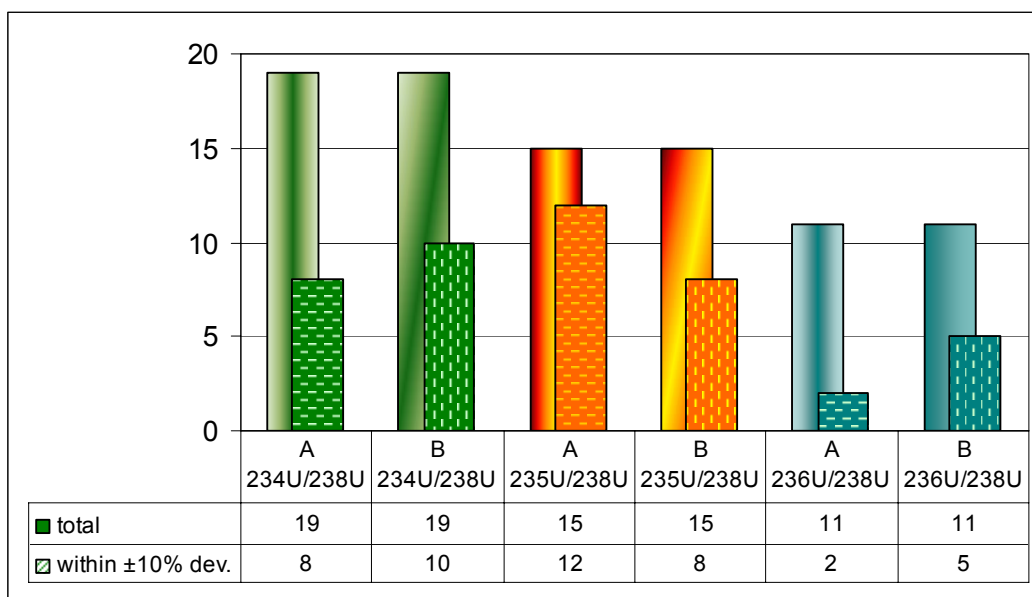
Only 5 laboratories (out of the 15 that sent us information about the matrices with which they work routinely) stated they measure uranium in urine. Most of the laboratories are working with biological or environmental materials such as bone, teeth, grass, soil, sediment, biota, water and swipes or air filters.

## 4. Results and discussion

Even though the number of participating laboratories was moderate, some conclusions can be made about the measurement results.

The aim of the campaign was to measure the molar ratios  $n(^{234}\text{U})/n(^{238}\text{U})$ ,  $n(^{235}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  in both samples but partial results were submitted and accepted. It appears that the measurement of uranium isotopic ratios in a simulated biological matrix with these levels of uranium concentration is a bigger challenge that was expected. Only 9 participating laboratories out of 21 submitted results for all 6 ratios. Five ratios were submitted by 2 laboratories, 4 by 3 and two ratios were submitted by 7 participants. The numbers of submitted results per ratio and sample are presented in table 2. The  $\pm 10\%$  deviation from the reference value was considered by us as a criterion of a 'good result' and the number of results which are in this range is given in second row of the table 2.

Table 2: Number of submitted results per sample and ratio



The participating laboratories used Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Radiometry – Alpha Spectrometry (RAS), Thermal Ionisation Mass Spectrometry (TIMS) and Accelerator Mass Spectrometry (AMS) for measurements.

More detailed information is given in table 3:

Table 3: Techniques applied for NUSIMEP 4 samples measurements

Technique	number
ICP-MS	10
Quadrupole	2
High Resolution	2
Multi-collector	2
Single collector	1
Insufficient information	3
RAS	9
TIMS	1
AMS	1

The second TIMS result presented on the graphs (position 22) is from verifying measurements performed at IRMM and is not taken into account at any of the statistics and discussions presented here.

The deviation of the submitted results from the reference values show a high degree of scattering for some ratios although the majority of the laboratories achieved acceptable agreement with the certified values. The measured values are plotted for each isotopic ratio and sample in Figs. 1 – 6. A scale of  $\pm 50\%$  was chosen for most of the graphs except for the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratios where scale of  $\pm 25\%$  was deemed more appropriate and for the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio in sample A for which a logarithmic scale was found to be necessary.

All values are plotted with expanded uncertainty ( $k=2$ ) as declared by the laboratory. The significance of this is that the laboratory expects the true value to lie within the uncertainty range. Taking into account the  $\pm 10\%$  deviation criterion of a ‘good result’ it is clear that results obtained by ICP-MS measurements are more often within the 10% criterion range than results obtained by RAS. In the case of ICP-MS about 70% of the results submitted for sample A and 68% for sample B are in this range while for RAS it is approximately 12% for both samples. Curiously, the results submitted using RAS for sample B have almost uniformly a negative bias relative to the reference value. The results for sample A show a tendency in the opposite direction.

#### 4.1. Results of measurements of individual ratios

##### 4.1.1. $n(^{234}\text{U})/n(^{238}\text{U})$

Most of all submitted results were reported for  $n(^{234}\text{U})/n(^{238}\text{U})$  ratio. They were obtained by ICP-MS, RAS and TIMS techniques. The values in both samples are well within the capability of measurement by ICP-MS as well as by RAS. The uncertainties of the results for  $n(^{234}\text{U})/n(^{238}\text{U})$  are greater for the RAS technique compared to mass-spectrometry as can be seen in Figs. 1 and 2, nevertheless both techniques give good measurement estimates. The negative bias for sample B, mentioned above, is very clear for RAS measurements but can be

seen in some ICP-MS measurement results as well. One of the reasons could be a peak tailing effect from  $^{235}\text{U}$  for RAS and a similar mass-tailing effect for the ICP-MS measurements.

#### 4.1.2. $n(^{235}\text{U}) / n(^{238}\text{U})$

Results for the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio were mainly obtained by ICP-MS (20 out of 30 submitted results for both samples). For sample A 80 % of the ICP-MS results (8 out of 10 submitted) are in the range of  $\pm 2$  % deviation from the reference value. For sample B the picture is somewhat worse and only 40 % of the results (4 out of 10) are in the range of  $\pm 2$  % deviation (and only 7 in the  $\pm 10\%$  range). The cause of such differences is not clear especially as the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio in sample A was lower than that of sample B.

The RAS technique is a very limited tool for measurements of the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio. Four laboratories submitted results obtained by RAS measurements and they are very inconsistent. The result for sample A submitted by laboratory 11 is almost within the  $\pm 10$  % criterion but the result for sample B submitted by this laboratory was considerably poorer. An equivalent but inverse picture is seen for the results submitted by laboratory 14: the result for sample B deviates by about 20 % while that for sample A deviates by more than 100 % from the reference value. The values submitted by two other labs deviate by 127 % and 593 % (for sample A) and by 78 % and 100 % respectively (for sample B) from the reference values. It appears the measurement values have a large random error component.

#### 4.1.3. $n(^{236}\text{U}) / n(^{238}\text{U})$

Measurement of the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio appears to be very difficult at this level of uranium concentration and  $^{236}\text{U}$  abundance. Out of 11 results submitted for sample A only two are within the  $\pm 10$  % criterion range; the results are presented on a logarithmic scale in Fig. 5. For sample B, where the  $^{236}\text{U}$  abundance is two orders of magnitude higher, five out of 11 submitted results are within the  $\pm 10$  % criterion range (Fig. 6).

Table 4: Number of results submitted per technique (the number of results in the range of  $\pm 10$  % deviation from the reference value is given in brackets).

Ratio	ICP-MS	RAS	TIMS	AMS
A $n(^{234}\text{U})/n(^{238}\text{U})$	9 (6)	9 (1)	1 (1)	0
A $n(^{235}\text{U})/n(^{238}\text{U})$	10 (10)	4 (1)	1 (1)	0
A $n(^{236}\text{U})/n(^{238}\text{U})$	5 (1)	4 (0)	1 (1)	1 (0)
B $n(^{234}\text{U})/n(^{238}\text{U})$	9 (6)	9 (3)	1 (1)	0
B $n(^{235}\text{U})/n(^{238}\text{U})$	10 (7)	4 (0)	1 (1)	0
B $n(^{236}\text{U})/n(^{238}\text{U})$	6 (4)	3 (0)	1 (1)	1 (0)

## **4.2. Correlations of measured ratios**

The results of some laboratories show consistent biases that are mirrored in more than one ratio. This tendency is more visible when results of all ratios for each sample are plotted together. For sample A results of the  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{235}\text{U})/n(^{238}\text{U})$  ratios only are presented in Fig. 7 and for sample B results of all 3 ratios are presented in Fig. 8. The values of the submitted results are plotted with the uncertainty declared by the laboratory. Large differences in the declared uncertainties are evident. It is not easy to say whether the biases found are due to instrument calibration errors or cross-contamination problems without knowing more details about procedures and measurement techniques.

Some general conclusions on error type can be drawn from the Youden plots (Fig. 9) where each point corresponds to the measured value of a ratio in sample A versus the measured value in sample B. Points close to the reference line but displaced from the reference value, represented on the graphs by an empty square, indicate systematic errors (related for example to calibration) and the further the point lies from the reference value the bigger those errors are. The 10% deviation contour is shown on the graphs.

## **4.3. Separation prior to measuring**

Values from laboratories that separated the uranium prior to measurement are indicated by shadowed symbols in Figs 1 to 6. Measurements by RAS need in any case a prior separation and deposition on a planchet for measurement. For laboratories that used ICP-MS, better results are generally found for  $n(^{234}\text{U})/n(^{238}\text{U})$  when a chemical separation was carried out, particularly for sample A. This is not observed for the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio nor for the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio which showed highly scattered values, evidently due to problems in the measurement (blanks, isobaric interferences or mass-fractionation).

Laboratories reported using Dowex, U-TEVA or TRU resins. Out of 10 laboratories applying ICP-MS only 3 separated U prior to measurement and all 3 used U-TEVA resin. Laboratories applying RAS for measurements used U-TEVA, TRU resins as well as conventional ion-exchange resins.

## **4.4. Experience**

There is a noticeable correlation between the quality of the results and the number of the samples analysed by the laboratory per year. Nearly all results submitted by laboratories that measure more than 50 samples of a similar type per year (declared by 4 laboratories) are within the 10% criterion range.

Such a correlation was not noticed for results submitted by laboratories experienced in work with urine as a matrix. However, of the 5 laboratories that stated they regularly measure ura-



niium in urine, 2 using ICP-MS and 3 RAS, only 2 submitted all 6 ratios and the results of only one laboratory are within  $\pm 10\%$  deviation range for all ratios.

Table 5: Number of results per sample and ratio submitted by laboratories experienced in measurements of uranium in urine (numbers in brackets corresponds to results in the range of  $\pm 10\%$  deviation from reference value)

Ratio \ Sample	$^{234}\text{U} / ^{238}\text{U}$	$^{235}\text{U} / ^{238}\text{U}$	$^{236}\text{U} / ^{238}\text{U}$
A	4 (2)	3 (2)	2 (1)
B	4 (1)	3 (2)	2 (1)

In most cases measurements were performed by the same analyst who does such measurements routinely and applying the same procedure (15 laboratories). In 2 laboratories both analyst and procedure were different to that applied routinely and in 3 laboratories the analyst performing the measurements was the same but applied a procedure different to the normal one. From the results of those five laboratories it appears that this had no significant influence on the quality of the measurements.

## 5. Evaluation of the questionnaire

The questions related to aspects which might influence the measurements and their impacts on the submitted results (routine matrix and experience in measuring uranium in it, techniques used for measurement, application or not of the chemical separation, etc) have been discussed above.

### *Lab category:*

Among the participating laboratories 12 are authorised, 4 accredited and one authorised, accredited and certified. Three do not belong to any of these categories.

### *Application of CRM's and QMS:*

A proportion of the laboratories (6 out of 20 replying this question) do not use Certified Reference Materials in their routine work. Only 11 laboratories are working within a Quality Management System. Most of these laboratories are following ISO 9000 (5) or EN 45000 series/ISO 25 (2), ISO 17025 (1) and GLP (1). There are also laboratories that work according to more than one QMS: ISO 9000 + 17025 (1) and ISO 9000 + EN 45000 series/ISO 25 + GLP (1). Among those not applying QMS, 8 are either authorised or certified.

### *Uncertainty:*

All results were reported with measurement uncertainties. Twelve laboratories reported expanded uncertainties as requested and 8 based their calculations on a statistical evaluation. In many cases the uncertainties appear to be considerably under- or over- estimated. Seven out of 9 laboratories using ICP-MS applied a correction for mass fractionation. Two of the laboratories declared that they do not report the uncertainty value to the customer. Fifteen out of 20 laboratories are familiar with “Guide to the Expression of Uncertainty in Measurement” [3] and/or with “Quantifying Uncertainty in Analytical Measurement” [4] but only 12 reported NUSIMEP 4 results with uncertainty calculated according to those guides.

## **6. Conclusions and comments**

Evaluating the submitted results it appears that the difficulties of measuring uranium isotopic ratios in a simulated biological matrix were greater than expected. Although the concentration of uranium (5 ppb level) was up to 100 times higher than normally expected in natural urine samples the results are scattered over a wide range. The measurements of  $n(^{236}\text{U})/n(^{238}\text{U})$  at this level of concentration and  $^{236}\text{U}$  abundance seem especially difficult.

As can be seen from Figs. 7 and 8 and also in Fig 9, the measured values of certain laboratories are systematically biased judging by the deviation of the results (for both samples and all ratios) in the same direction relative to the reference value.

The submitted results also confirm the limited capabilities of radiometric techniques except for the measurements of  $n(^{234}\text{U})/n(^{238}\text{U})$ .

From problems with sample delivery it is clear that even after taking precautions to seal the screw-cap containers, used in this and previous NUSIMEP campaigns, they are not ideally suited for transportation of liquid samples, especially when long air flights have to be taken into consideration. We plan to use plastic heat-sealable ampoules for future campaigns.

More conclusions on the results of this exercise will be drawn when these measured values are compared with the results of the CCQM P-48 intercomparison exercise that will be completed shortly.

### **6.1. Future campaigns**

We would like to thank participants for their suggestions for future campaigns. The suggested matrices include water, soil/sediments/biota, filters, swipes, and waste categories.

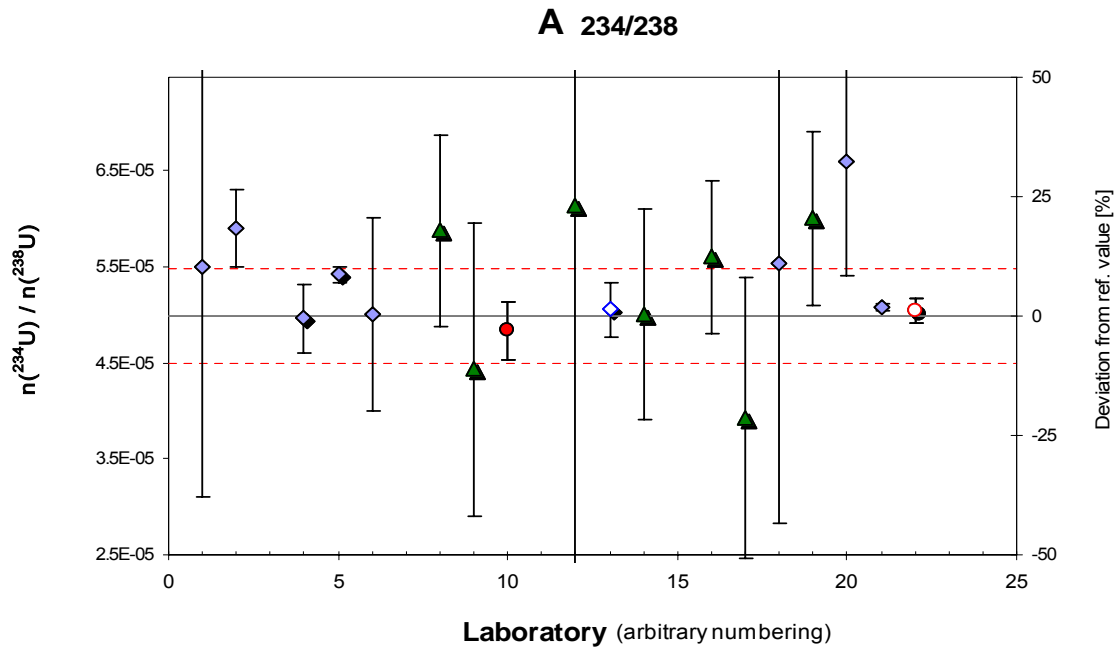
Also analytes such as  $\alpha$ ,  $\beta$  and  $\gamma$  emitters were suggested for analysis in these matrices.

All those suggestions will be strongly taken into account while planning future NUSIMEP comparison campaigns.

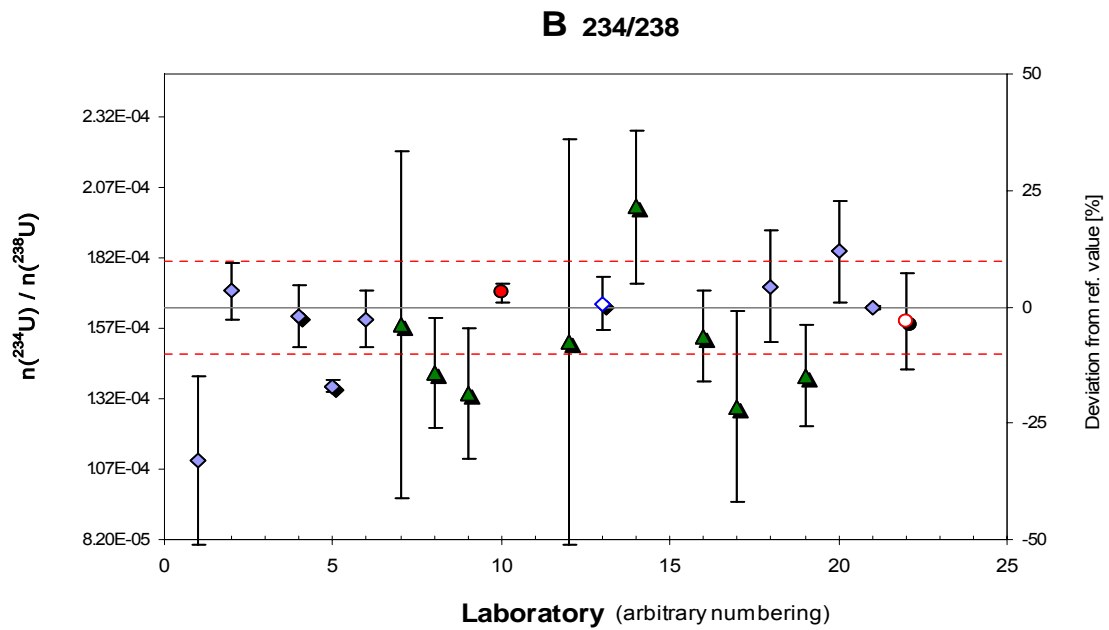
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**Figure 1:** Submitted results of  $n(^{234}\text{U})/n(^{238}\text{U})$  ratio in sample A  
(two results lie outside the plotted range)

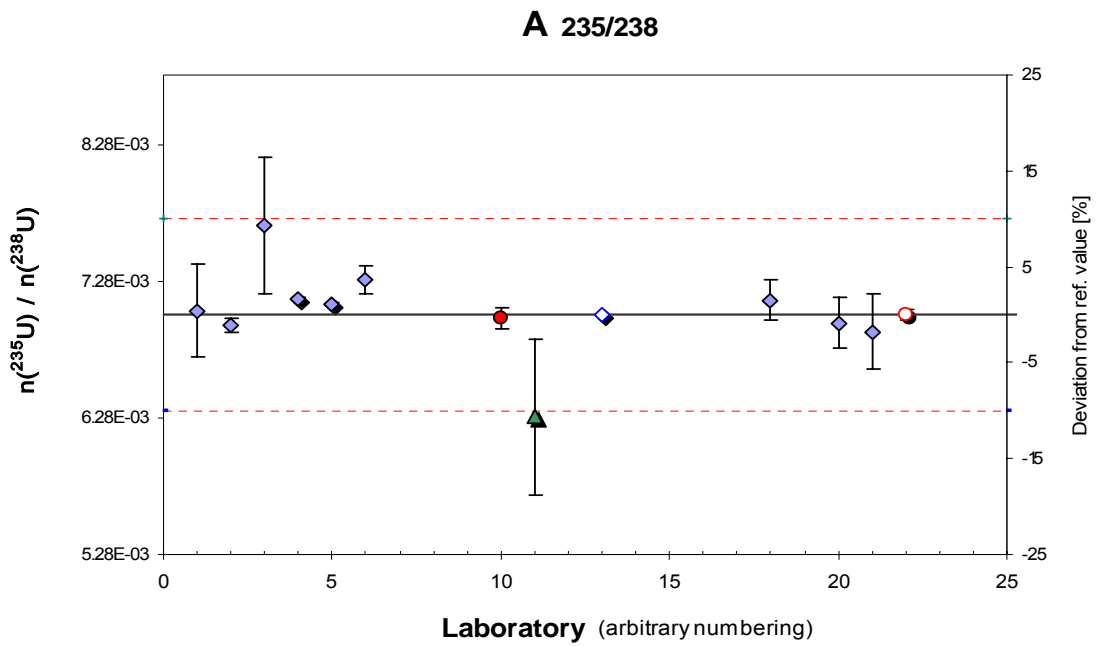


**Figure 2:** Submitted results of  $n(^{234}\text{U})/n(^{238}\text{U})$  ratio in sample B  
(one result lies outside the plotted range)

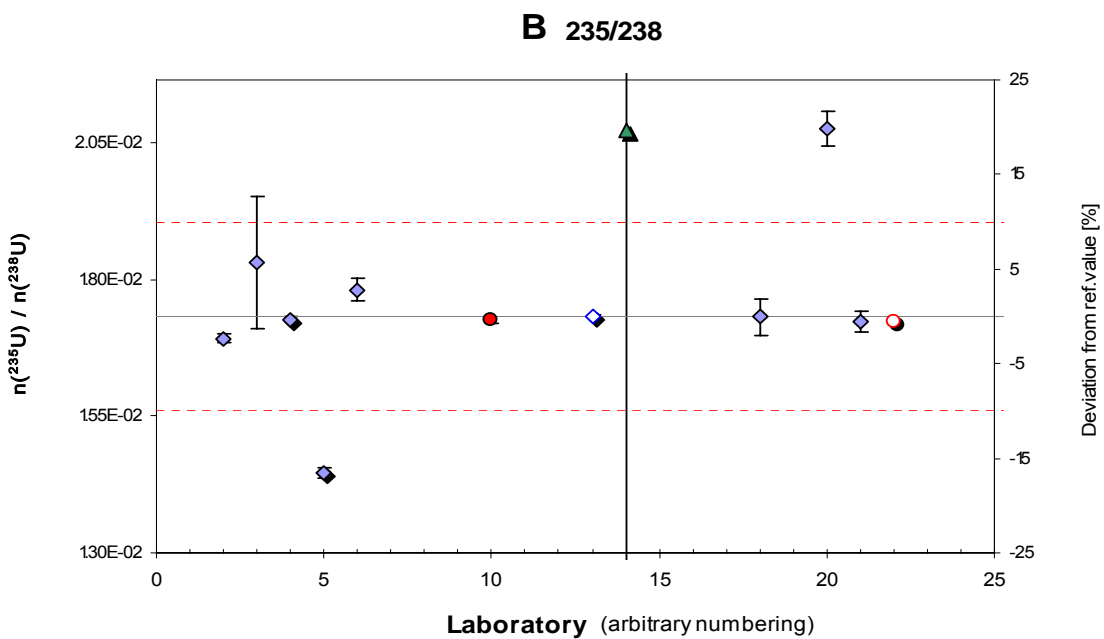
◆ ICPMS; ▲ RARS; ● TIMS;

The shadowed symbols indicate separation prior to measurements;

An open symbol indicates that chemical preparations were carried out in a clean laboratory



**Figure 3:** Submitted results of  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio in sample A  
(three results lie outside the plotted range)

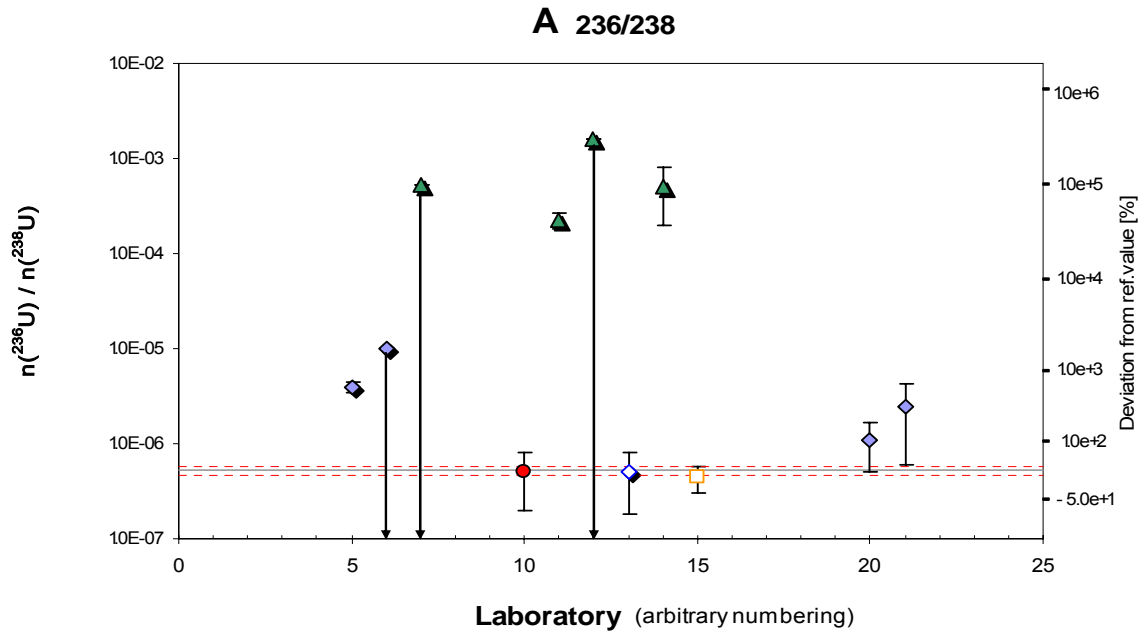


**Figure 4:** Submitted results of  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio in sample B  
(four results lie outside the plotted range)

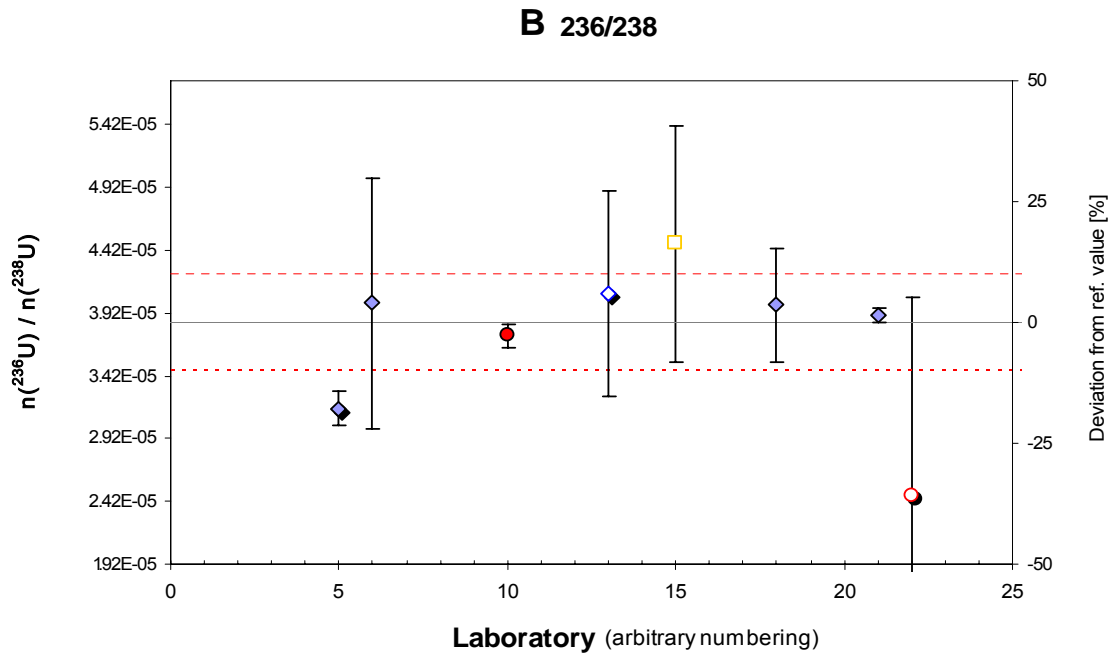
◆ ICPMS; ▲ RARS; ● TIMS;

The shadowed symbols indicate separation prior to measurements;

An open symbol indicates that chemical preparations were carried out in a clean laboratory



**Figure 5:** Submitted results of  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio in sample A



**Figure 6:** Submitted results of  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio in sample B  
(four results lie outside the plotted range)

◆ ICPMS; ▲ RARS; ● TIMS; ■ AMS;

The shadowed symbols indicate separation prior to measurements;

An open symbol indicates that chemical preparations were carried out in a clean laboratory

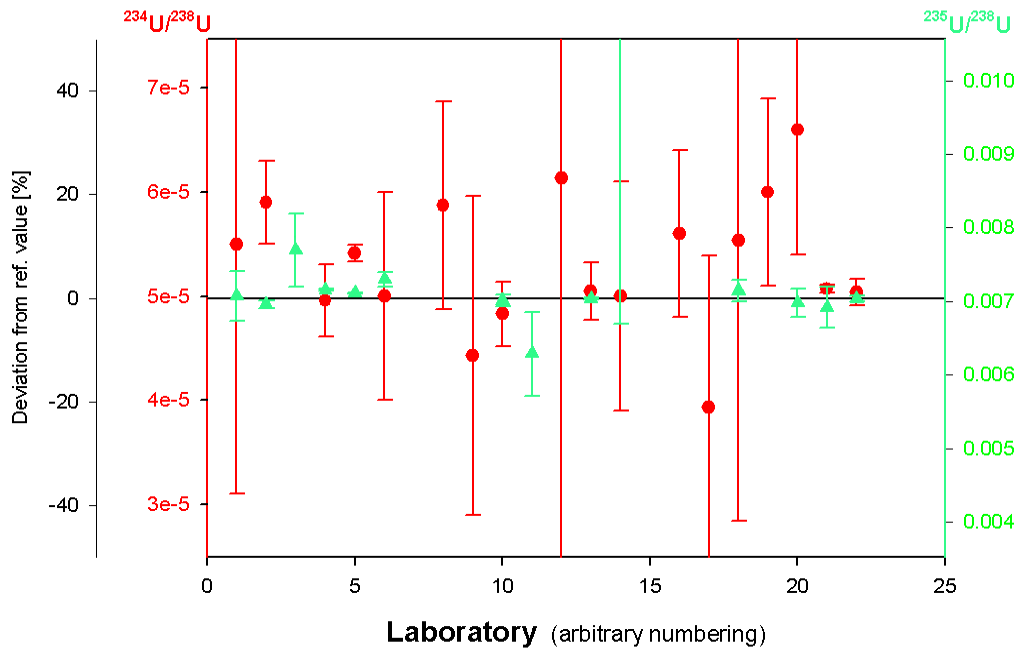


Figure 7: Combined ratios of  $^{234}\text{U}/^{238}\text{U}$  and  $^{235}\text{U}/^{238}\text{U}$  for sample A

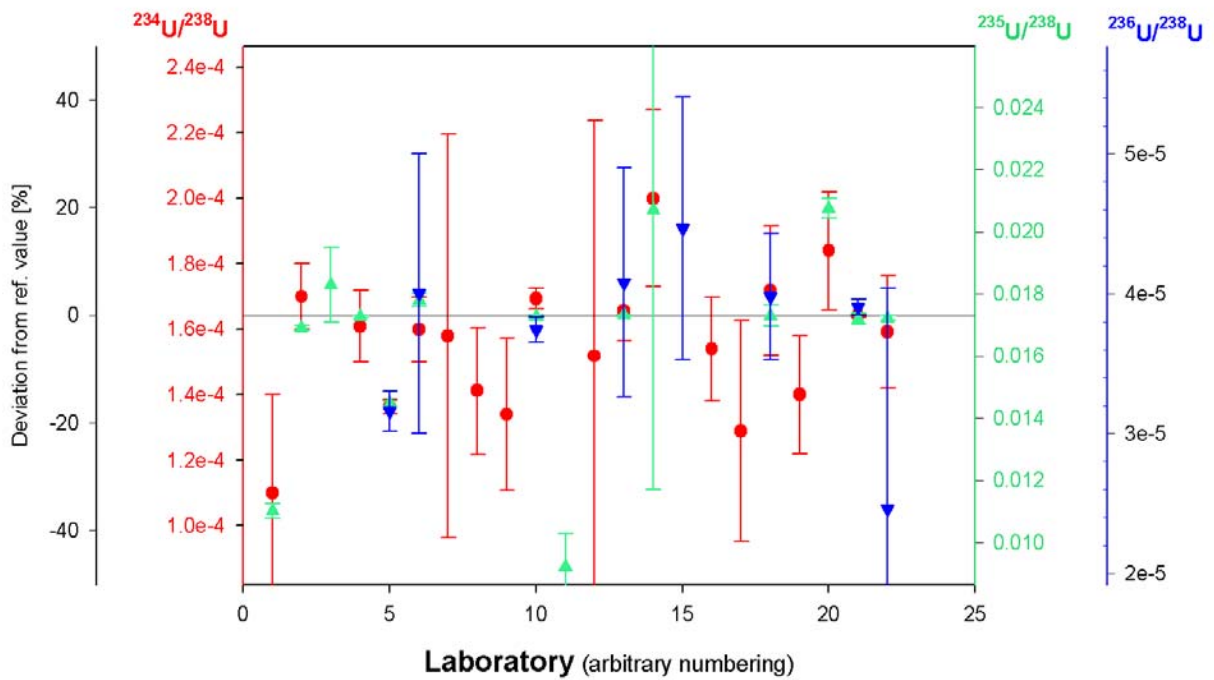


Figure 8: Combined ratios of  $^{234}\text{U}/^{238}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  for sample B



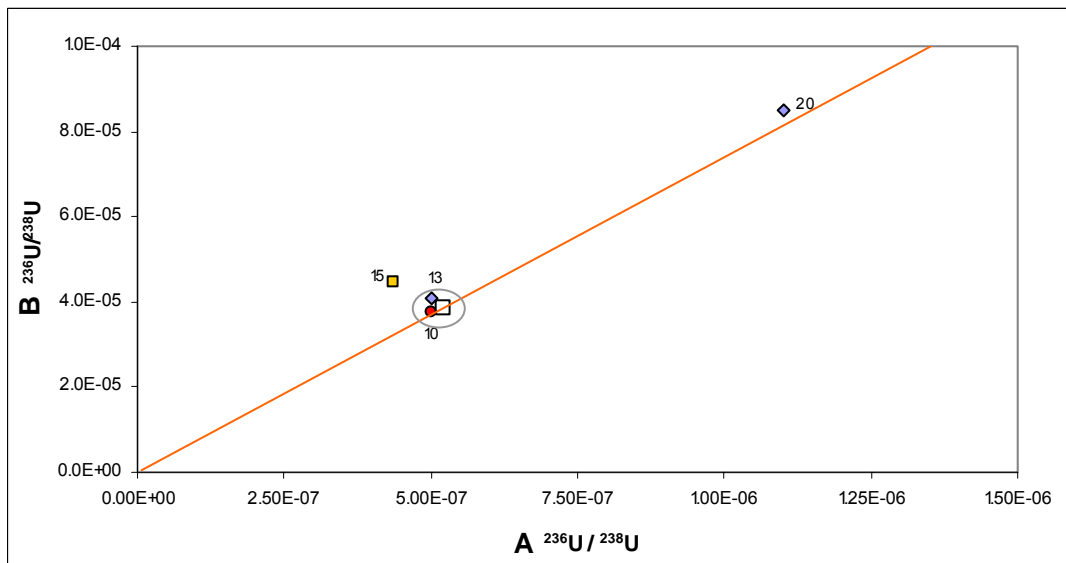
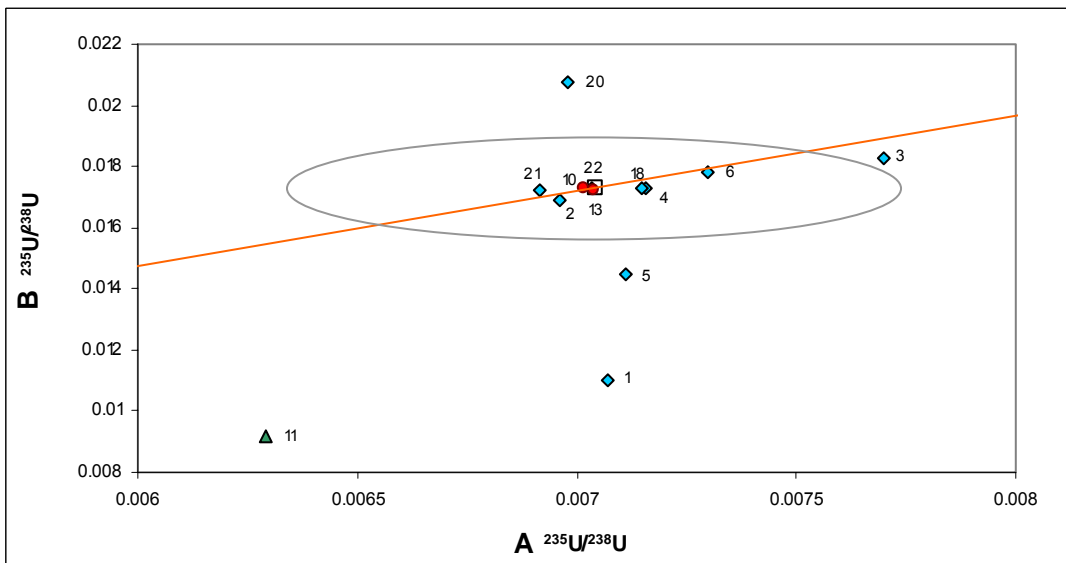
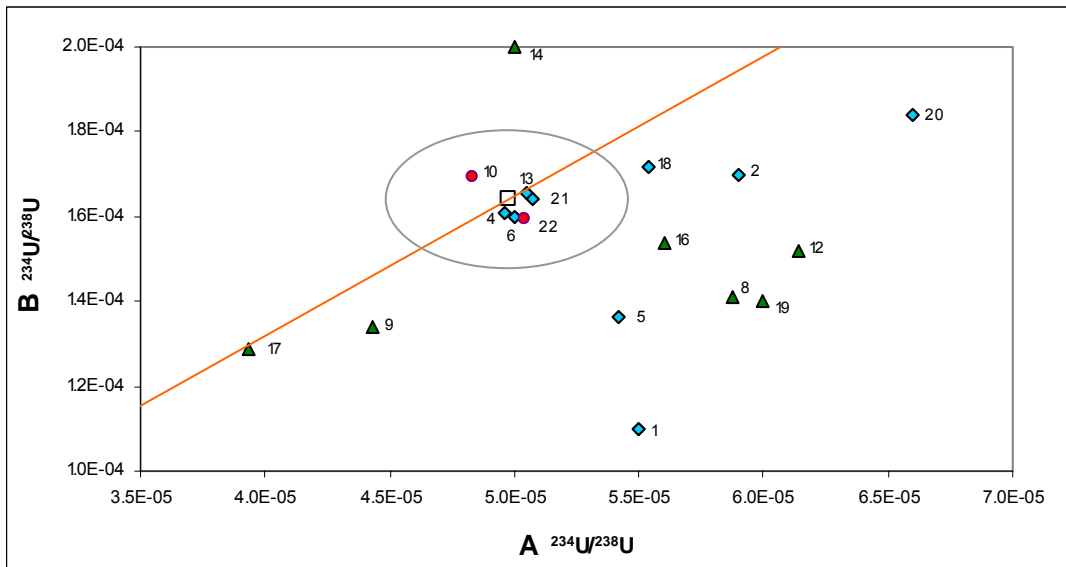


Figure 9: Youden plots for  $n(^{234}\text{U})/n(^{238}\text{U})$ ,  $n(^{235}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios.

## Annex 1: List of laboratories which submitted results

COUNTRY	CITY	ORGANISATION NAME
Argentina	Cordoba	DIOXITEK S.A.
Australia	Lucas Heights, NSW	ANSTO
Austria	Vienna	IAEA
Austria	Seibersdorf	ARC Seibersdorf Research GmbH
France	Orsay	IRSN
Germany	Karlsruhe	European Commission
Italy	Rome	C.R. E.N.E.A.-(CASACCIA)
Italy	Milano	ARPA LOMBARDIA
Lithuania	Vilnius	Institute of Physics
Poland	Krakow	Institute of Nuclear Physics
Poland	Sopot	Institute of Oceanology
Slovenia	Ljubljana	Jozef Stefan Institute
Spain	Bilbao	University of Basque Country
Spain	Madrid	CIEMAT
Thailand	Bangkok	Office of Atoms for Peace
United Kingdom	Moor Row	Geoffrey Schofield Laboratory
United Kingdom	Glasgow	National Radiological Protection Board
United Kingdom	Nottingham	British Geological Survey
United Kingdom	Reading	AWE PLC

The number of laboratories in the table is smaller than the number of participants. In the case of two institutions two different groups, routinely using different techniques, participated in the campaign.

## Annex 2: Results reporting form and questionnaire

IMPORTANT : Disclaimer, Confidentiality Notice and rules on Privacy Protection



European Commission  
Joint Research Centre  
Institute for Reference Materials and Measurements

IRMM Interlaboratory Comparison

> Login > Results

Functions

Result input for NUSIMEP 4

Results

Dr. Roger Wellum

European Commission BELGIUM

Page 1 of 2

Sample Code XXXXXXXXXX

Isotopic ratio n(234U)/n(238U) Optional  
 Measurement #1

Select measurement unit from the allowable units:

ratio  
 Result value   ± Uncertainty value

Coverage factor  k

Technique used

OTHER. Please specify,

Isotopic ratio n(235U)/n(238U) Optional  
 Measurement #1

Select measurement unit from the allowable units:

ratio  
 Result value   ± Uncertainty value

Coverage factor  k

Technique used

OTHER. Please specify,

Isotopic ratio n(236U)/n(238U) Optional  
 Measurement #1

Select measurement unit from the allowable units:

ratio  
 Result value   ± Uncertainty value  Cov-

erage factor  k

Technique used

OTHER. Please specify,

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1. Is your laboratory participating for the first time in a interlaboratory comparison?

Yes  No

If NO, please give the name of the comparison(s) in which you have already participated.

2. Does your laboratory consider itself in matters of this type of measurement as, experienced or less/not experienced?

experienced  less experienced  not experienced

3. How many measurements of this type does your laboratory routinely perform per year?

<25  25-50  >50

4. In what type of matrices do you routinely measure the isotopic composition of small amounts of uranium? (If no comments please iput Not Applicable)

5. Was the NUSIMEP-4 sample analysed by the same analyst who usually performs such analyses?

Yes  No

more same less

If NO, please rate the experience of the NUSIMEP analyst:

6. Were the NUSIMEP-4 samples treated according to the same analytical procedure as routinely used for the same type of samples?

Yes  No

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

Yes  No

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

8. Does your laboratory participate regularly in proficiency testing schemes to assess performance for this type of analysis?

Yes  No

If YES, please state which proficiency testing scheme and the organiser.

9. Is your laboratory working according to a quality management system?

Yes  No

If YES, please state which system: (You can make more than one choice)

EN 45000 series / ISO 25

Yes

ISO 9000 series

Other (e.g. CEN, GLP, EPA, TQM, national standards)

If Other, please supply additional information

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

Yes No

Certified

Accredited

Authorised

**11. Did you carry out a separation prior to the measurement?**

Yes  No

If YES, please answer the following:

in a conventional laboratory  in a clean environment

Where was the sample preparation carried out?

Please specify the type of laboratory

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

Please describe the separation

**12. Please describe briefly your measurement procedure**

Technique and instrument used

Special measurement conditions

Other details (If no comments please input Not Applicable)

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

Yes  No  Not applicable

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

**14. 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

**15. Were the reported uncertainties calculated according to the mentioned guides in Question 14?**

Yes  No

combined uncertainty  expanded uncertainty with a coverage factor of  $k=2$

If YES, what did you report as an uncertainty?

If NO, how was the measurement uncertainty evaluated

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

Yes  No

**17. Would you be interested in participating in future NUSIMEP comparisons?**

Yes  No

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

**18. Questionnaire completed by:**

Name and position



European Commission

**EUR 21839 – DG Joint Research Centre, Institute for Reference Materials and Measurements**

NUSIMEP 4: Uranium isotopic abundances in simulated urine

*A. Stolarz, A. Alonso, W. De Bolle, A. Moens, E. Ponzevera, C. Quérel, S. Richter, A. Verbruggen, R. Wellum*

Luxembourg: Office for Official Publications of the European Communities

2005 – 28 pp. – 21 x 29.7 cm

Scientific and Technical Research series

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**Abstract**

The NUSIMEP 4 external quality control campaign followed previous campaigns for the measurement of uranium isotopes in different matrices. Two uranium mixtures were prepared and certified at IRMM by mixing  $UF_6$  in the gas phase. The matrix was prepared from a mixture of salts to produce a 2 % saline solution which was chemically purified from uranium and mixed with urea to form a simulated urine solution. Uranium was added to yield 2 solutions with  $5 \text{ ng}\cdot\text{g}^{-1}$  (5 ppb) of uranium; the uranium had different isotopic abundances in each solution.

The collected results of the isotope ratios are presented to give a picture of the recent capabilities of measurements of uranium isotopes on 5 ppb level of uranium concentration by laboratories active in the field.

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.

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