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Isotope Measurements Unit

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NUSIMEP-2
Uranium isotopic abundances
Report to participants
EUR 19744/EN (2001)

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1 Summary

The Nuclear Signatures Interlaboratory 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.

This report contains all participants' results (in graphical form) obtained in the present round of this programme, NUSIMEP-2: uranium isotopic ratios. The participants were asked to measure isotopic compositions of uranium of natural or close to natural isotopic composition on a sample of restricted size (approximately 100 ng uranium as dry uranyl nitrate). The participating laboratories received certified test samples (with undisclosed isotopic composition), which they were asked to analyse using the laboratory's routine procedures. The measurement results of participants were evaluated against certified reference values, traceable to the SI.

In total 45 laboratories participated in the NUSIMEP-2 round. Thirty sets of results were finally submitted, originating from 17 countries all over the world.

This report presents in a graphical form the results of all participants together with the reference values. Sorting of the results was done according to different criteria, which were derived from the participants' questionnaire, such as analytical techniques or degree of experience.

2 Introduction

The second round of the Nuclear Signatures Measurement Evaluation Programme (NUSIMEP-2) focused on the measurement of small isotopic variations of uranium of natural or close to natural isotopic composition on a sample of restricted size. Participating laboratories received certified test samples (with undisclosed isotopic composition), which were to be analysed using the laboratory's routine procedures. The samples were approximately 100 ng uranium as dry uranyl nitrate in small 2 mL plastic vials. The samples had to be redissolved in a suitable matrix by the participants. Four samples were prepared for measurement in NUSIMEP-2, with enrichments ranging from depleted to low-enriched uranium. The enrichment ($n(^{235}\text{U}) / n(^{238}\text{U})$ ratio) was of primary concern for these measurements, but the abundances of the minor isotopes were also certified and could be measured by the participants.

3 Samples

Four samples were prepared for NUSIMEP-2, samples I to IV. Each sample was prepared by mixing UF_6 certified reference materials [1]. After thorough mixing and measurement of the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio a portion of the UF_6 was hydrolysed, treated with nitric acid to convert to uranyl nitrate and remove traces of fluorine and the resulting solution diluted as necessary. Aliquots containing 100 ng uranium were dried in clean plastic vials. Only sub-boiling distilled acid and water were used for the dilutions and blanks were carefully monitored.

Certification of the isotopic composition of those samples was achieved by measurement of the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio by gas source MS on the original UF_6 mixtures; the minor isotopes were measured by TIMS on the hydrolysed material [2].

The reference values for the four NUSIMEP-2 samples are given in Table 1.

NUSIMEP-2 sample I

Isotope ratio	value	uncertainty
$n(^{233}\text{U})/n(^{238}\text{U})$	< 0.000 000 01	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000 309 1	0.000 001 3
$n(^{235}\text{U})/n(^{238}\text{U})$	0.024 592	0.000 017
$n(^{236}\text{U})/n(^{238}\text{U})$	0.001 516 0	0.000 006 4

NUSIMEP-2 sample II

Value	uncertainty
< 0.000 000 01	
0.000 068 07	0.000 000 24
0.007 268 90	0.000 000 52
0.000 321 2	0.000 001 0

NUSIMEP-2 sample III

Isotope ratio	value	uncertainty
$n(^{233}\text{U})/n(^{238}\text{U})$	< 0.000 000 01	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.000 043 08	0.000 000 15
$n(^{235}\text{U})/n(^{238}\text{U})$	0.006 246 5	0.000 003 0
$n(^{236}\text{U})/n(^{238}\text{U})$	0.000 000 073	0.000 000 013

NUSIMEP-2 sample IV

Value	uncertainty
< 0.000 000 01	
0.000 194 97	0.000 000 64
0.019 832	0.000 010
0.000 382 82	0.000 000 92

Table 1: Reference values for the NUSIMEP-2 samples. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ using a coverage factor of $k=2$, where u_c is the combined standard uncertainty calculated according to the ISO and EURACHEM guides [3,4].

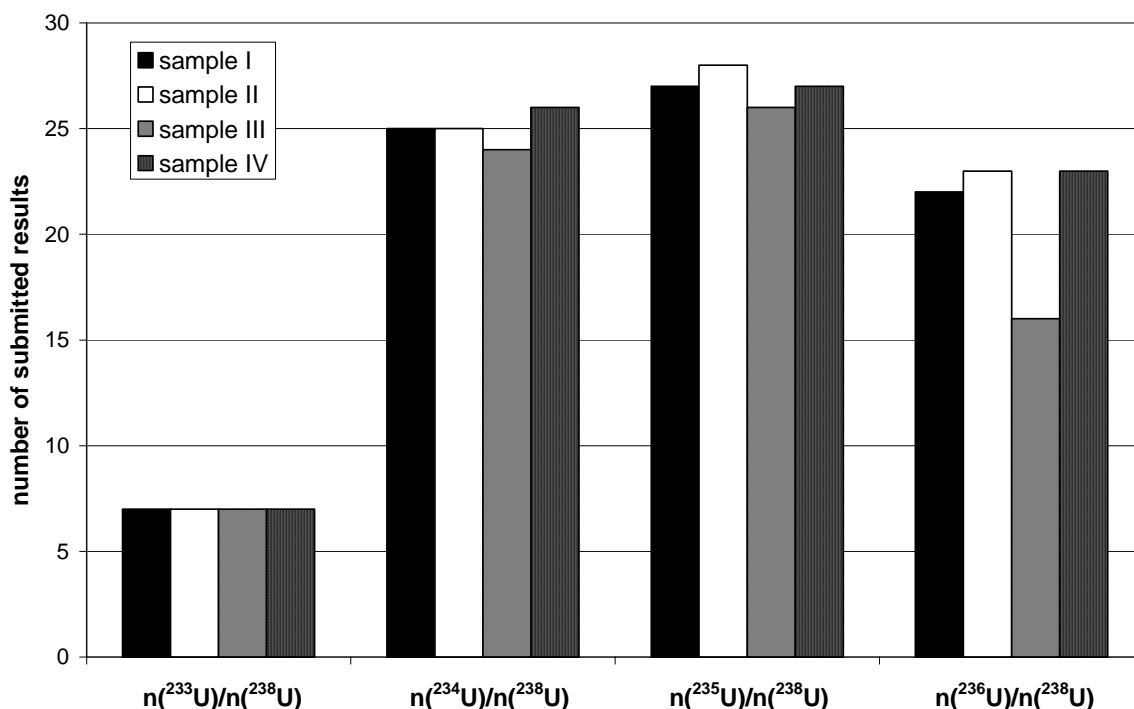


Figure 1: Number of submitted results per ratio

4 Participation

In total, 45 laboratories registered for NUSIMEP-2; Thirty laboratories from 17 countries provided results before the specified date (31 October 2000). The distribution of the participants over the different countries is shown in Table 2. Not all participants provided results for all ratios under investigation. The distribution of the measured values is shown in Figure 1.

country	Number
Argentina	3
Australia	1
Austria	2
Brazil	3
Bulgaria	1
Finland	1
Germany	2
Japan	4
Latvia	1
Lithuania	1
Norway	1
Poland	1
Rep. of Korea	2
Slovenia	1
Spain	1
Sweden	3
United Kingdom	2

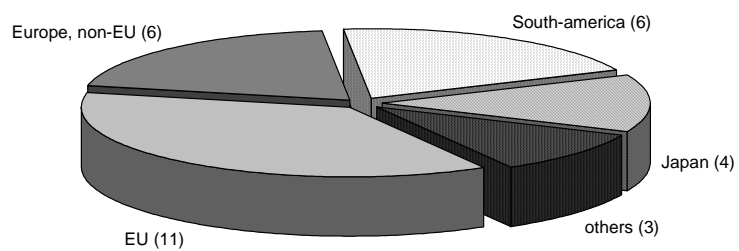


Table 2: Distribution of participants that provided results over different countries

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. 9 judged themselves to be experienced, 20 to be less or non-experienced, 1 did not answer. This is also reflected by the number of samples of a similar type as the NUSIMEP samples that the laboratories process per year (Table 3).

Samples of this type per year	Number of laboratories
< 25	17
25 – 50	6
> 50	5

Table 3: Samples analysed per year

Instrument type	Number
α -spectrometry	5
α -, γ - and β -spectrometry	1
γ -spectrometry	1
Accelerator mass-spectrometry (AMS)	1
Multi-collector ICP-MS (ICP-MC-MS)	2
Quadrupole ICP-MS (ICP-QMS)	9
Magnetic sector field ICP-MS (ICP-SFMS)	4
Thermal ionisation MS (TIMS)	7

Table 4: Types of instrumentation used by the NUSIMEP-2 participants. ('ICP-MS' is 'inductively-coupled plasma mass-spectrometry')

Participants were asked about the type of instrumentation used for the measurements (Table 4). Those participants using mass spectrometric techniques (23 in total) were also asked about the use of mass bias/fractionation correction. 13 laboratories applied mass bias/fractionation correction, 9 did not.

48 % of the participating laboratories made use of a clean environment for the sample preparation.

93 % of the laboratories routinely use certified reference materials (CRM). Only 14 % of the laboratories regularly participate in proficiency testing. 45 % of the laboratories have a quality management system in place. Only 27 % of the laboratories are certified, accredited or authorised for this kind of analysis.

68 % of the laboratories are familiar with the Guides for Quantifying Measurement Uncertainty (GUM) [3] and / or the EURACHEM guide [4]. 55 % also reported uncertainties according to those guides. 79 % of the laboratories usually report uncertainties to their customers.

6 Conclusions and comments

This NUSIMEP campaign was the first to be offered world-wide and for this reason we are gratified at the response, not only to returning results but also at replying to the questionnaire.

It was also rewarding to see how many laboratories were capable of good measurements and also were well capable of estimating their measurement uncertainties. Most of the graphs given in this report are easily understood. Not all possible combinations of results and parameters from the questionnaire could be included without breaking the bounds of the report and so the main results are given as graphs together with some selected results grouped according to the answers given in the questionnaire.

It is clear that radiometric methods of analysis were, with few exceptions, not adequate to measure isotopic abundances in such small samples. However the range of mass-spectrometry techniques was impressive, with the newer forms of ICP mass-spectrometers, particularly those with high resolution capabilities (sector-field instruments: ICP-SFMS) and multi-collectors (ICP-MC-MS) , providing results competing with the traditional TIMS instruments.

Clearly, some laboratories underestimate their measurement uncertainties and a few overestimate them. This is a general problem in chemical measurements and will certainly improve in time as the ideas in the 'Guide to the Expression of Uncertainties in Measurements' spread through the measurement community.

Many laboratories would judge their measurements as 'correct' if the uncertainty of a given result overlaps the certified value, as illustrated by the grey band in each graph.

The material chosen for this campaign was purposefully selected so as not to be a great challenge for the sensitive measurement methods available today. The chemical matrix was kept as simple as possible – the laboratories only had to dissolve the material and dilute if necessary – and the amount provided was highly adequate for a laboratory which regularly measures environmental samples. Following this experience, in future campaigns we will supply smaller samples, possibly in a matrix which does not allow the sample to be measured without chemical treatment. In the latter case we expect the effect of clean laboratory facilities to be more obvious. We also plan to include other elements to be analysed: Pu and other radionuclides.

We would like to take this opportunity to expressly thank the participating laboratories. We hope the experience was positive for them and look forward to including them in future campaigns.

7 Overview of graphs presented

Figure number	NUSIMEP-2 sample number	Ratio	Description
Figure 2	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 3	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to the type of instrumentation used
Figure 4	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from participants using mass spectrometric techniques labelled according to use of mass bias/fractionation correction
Figure 5	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to self-declared level of experience
Figure 6	sample I	$n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 7	sample I	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 8	sample I	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to the type of instrumentation used
Figure 9	sample I	$n(^{233}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 10	sample II	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 11	sample II	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to the type of instrumentation used
Figure 12	sample II	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to number of measurements of this type performed per year
Figure 13	sample II	$n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 14	sample II	$n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to the type of instrumentation used
Figure 15	sample II	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 16	sample II	$n(^{233}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 17	sample III	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 18	sample III	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to lab environment for samples preparation
Figure 19	sample III	$n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 20	sample III	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants

Figure 21	sample III	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to type of uncertainty statement
Figure 22	sample III	$n(^{233}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 23	sample IV	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 24	sample IV	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to type of uncertainty statement
Figure 25	sample IV	$n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 26	sample IV	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 27	sample IV	$n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants labelled according to the type of instrumentation used
Figure 28	sample IV	$n(^{233}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 29	sample I vs. II	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 30	sample II vs. III	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 31	sample III vs. IV	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 32	sample I vs. IV	$n(^{235}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 33	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$ vs. $n(^{234}\text{U})/n(^{238}\text{U})$	Results from all participants
Figure 34	sample I	$n(^{235}\text{U})/n(^{238}\text{U})$ vs. $n(^{236}\text{U})/n(^{238}\text{U})$	Results from all participants

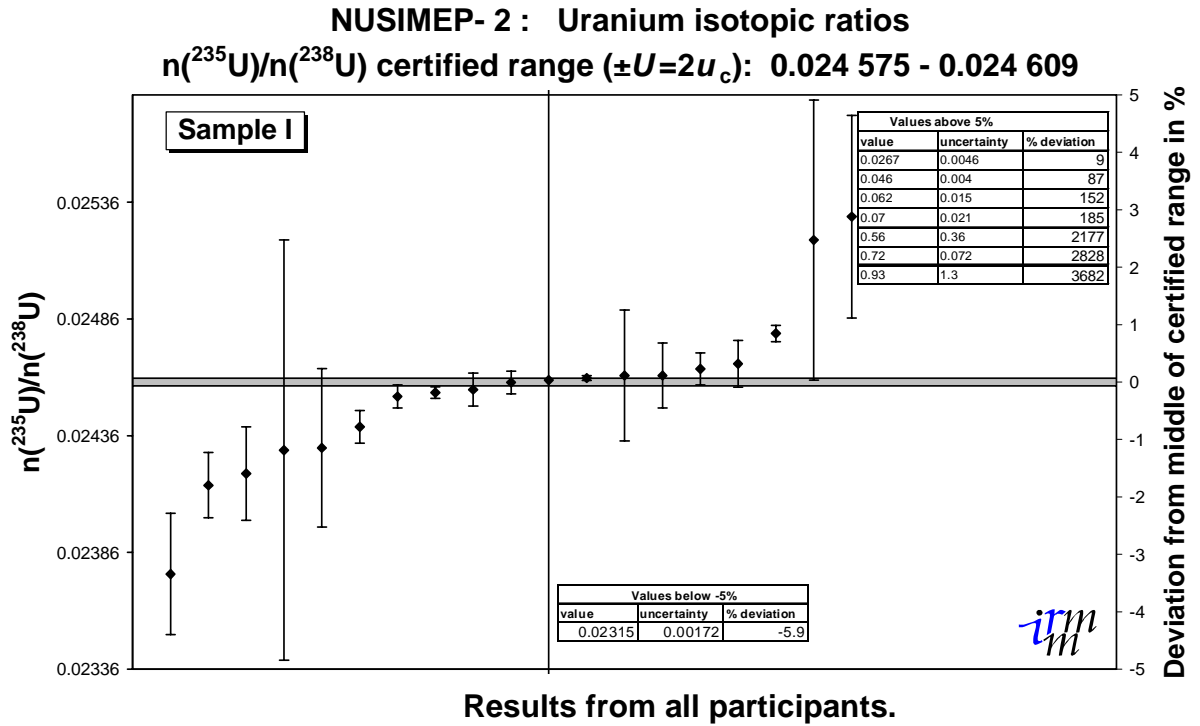


Figure 2

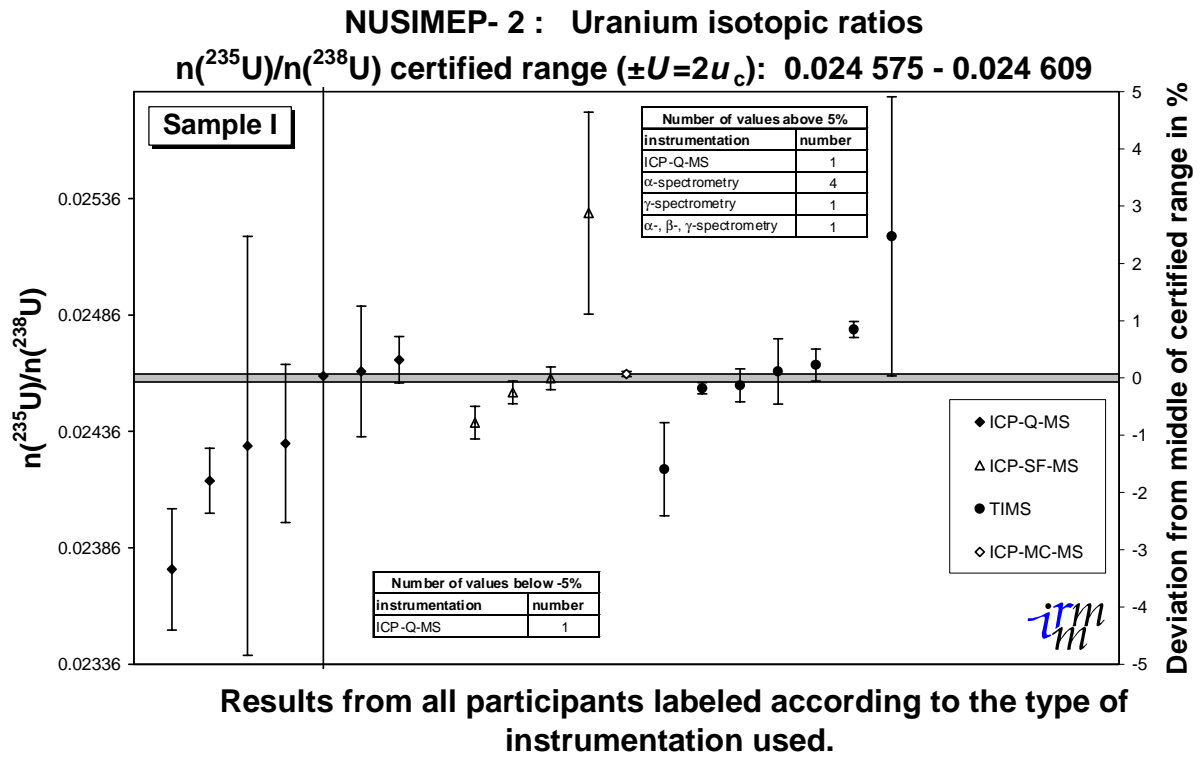
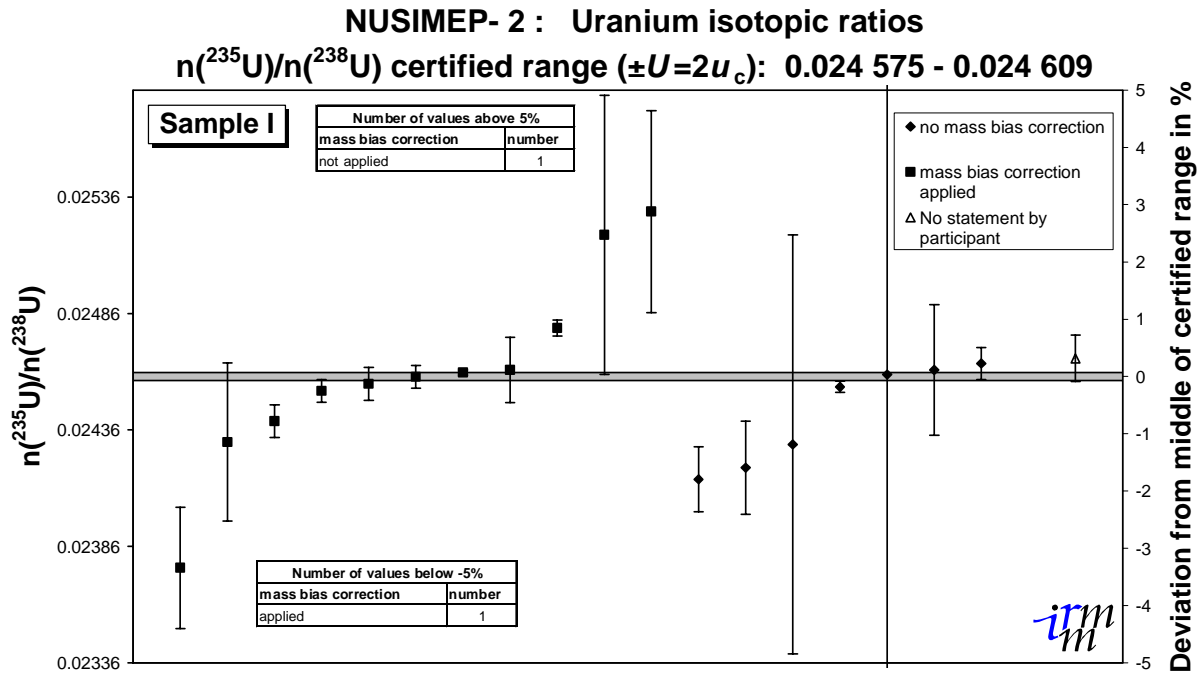
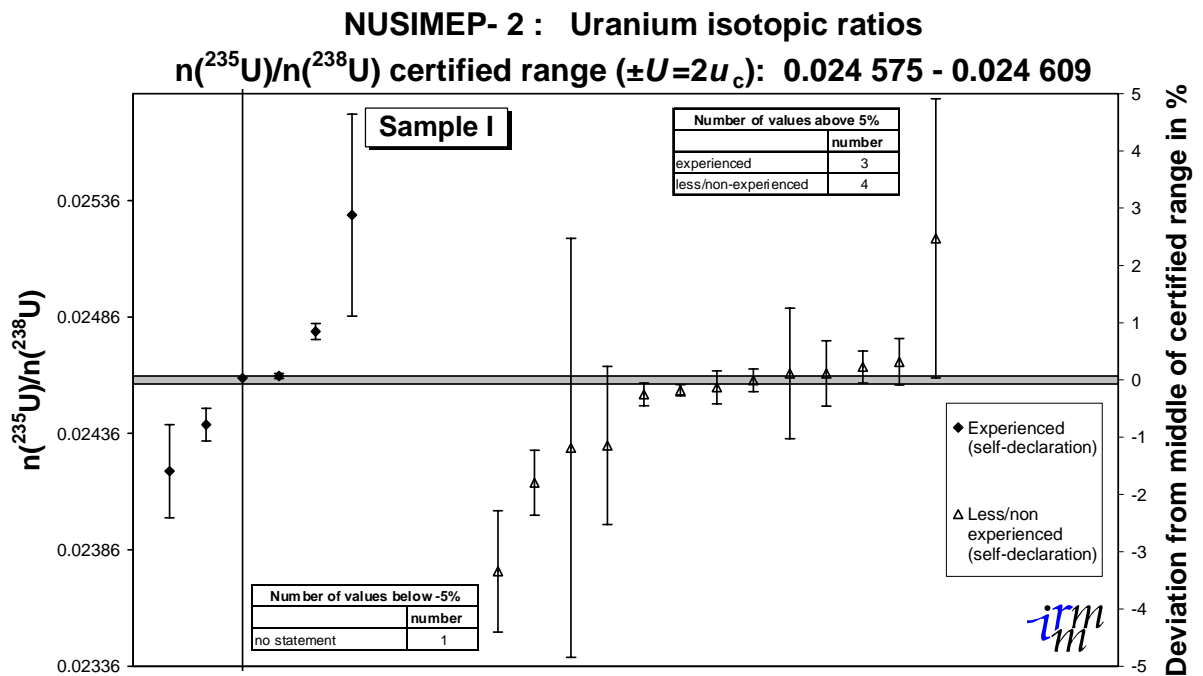


Figure 3



Results from participants using mass spectrometric techniques labeled according to use of mass bias/fractionation correction.

Figure 4



Results from all participants labeled according to self declared level of experience.

Figure 5

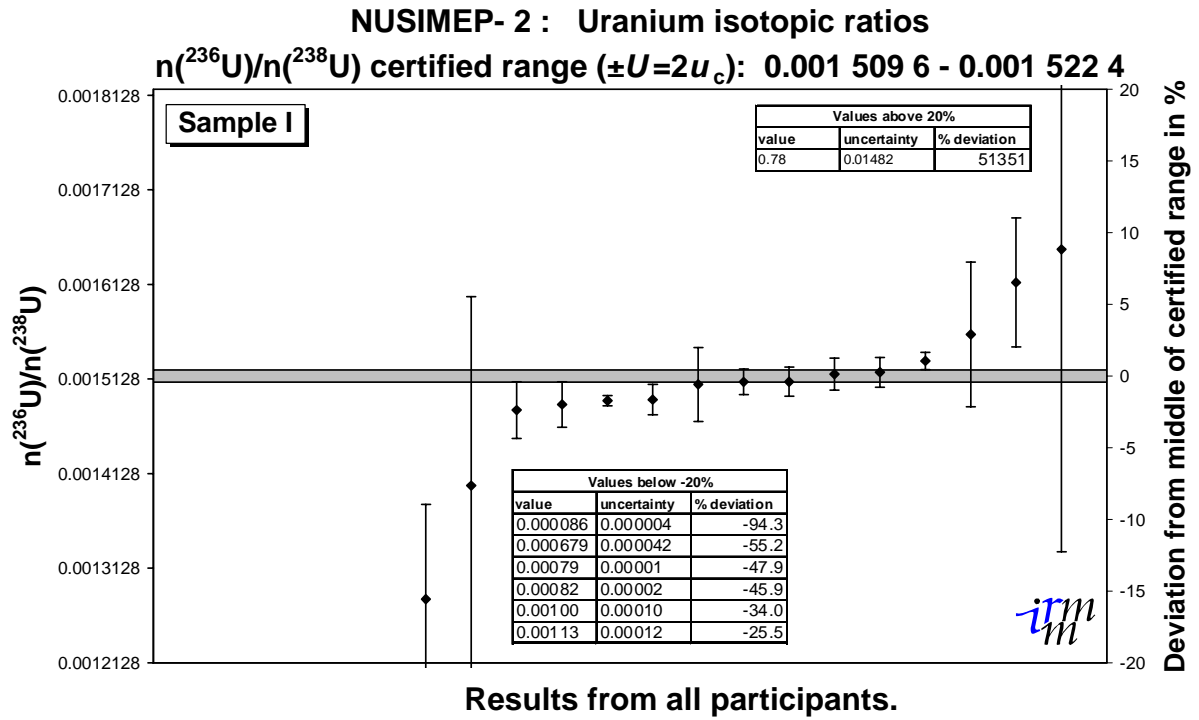


Figure 6

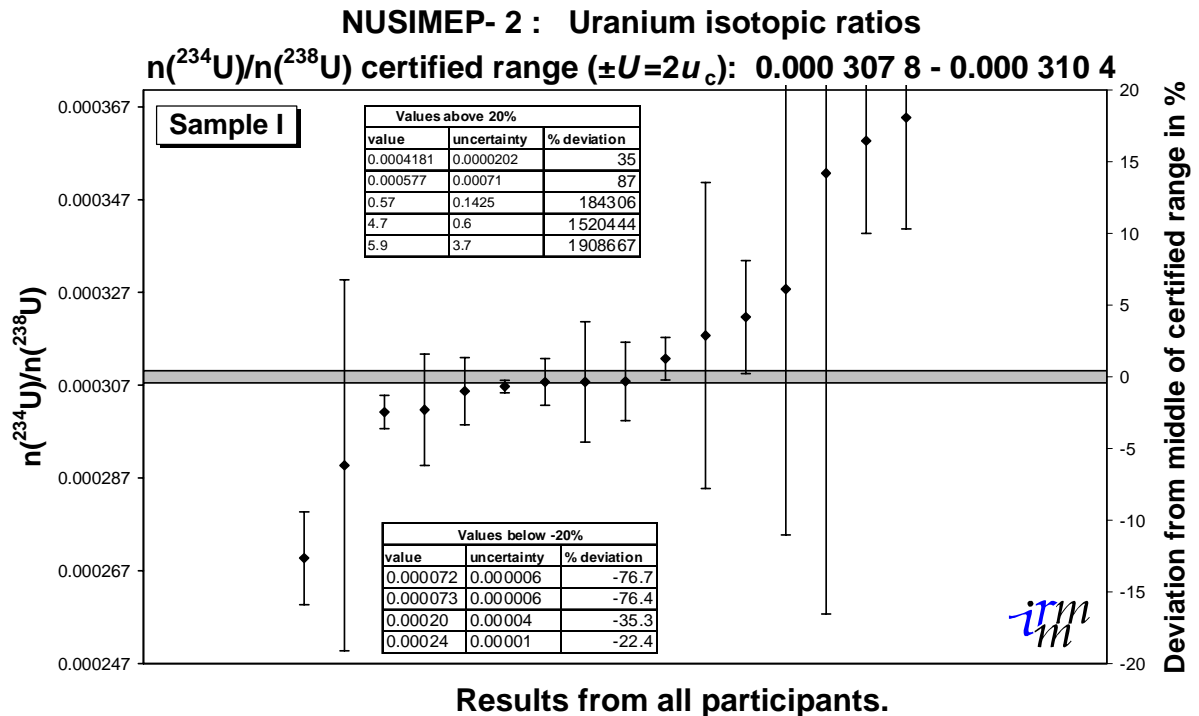
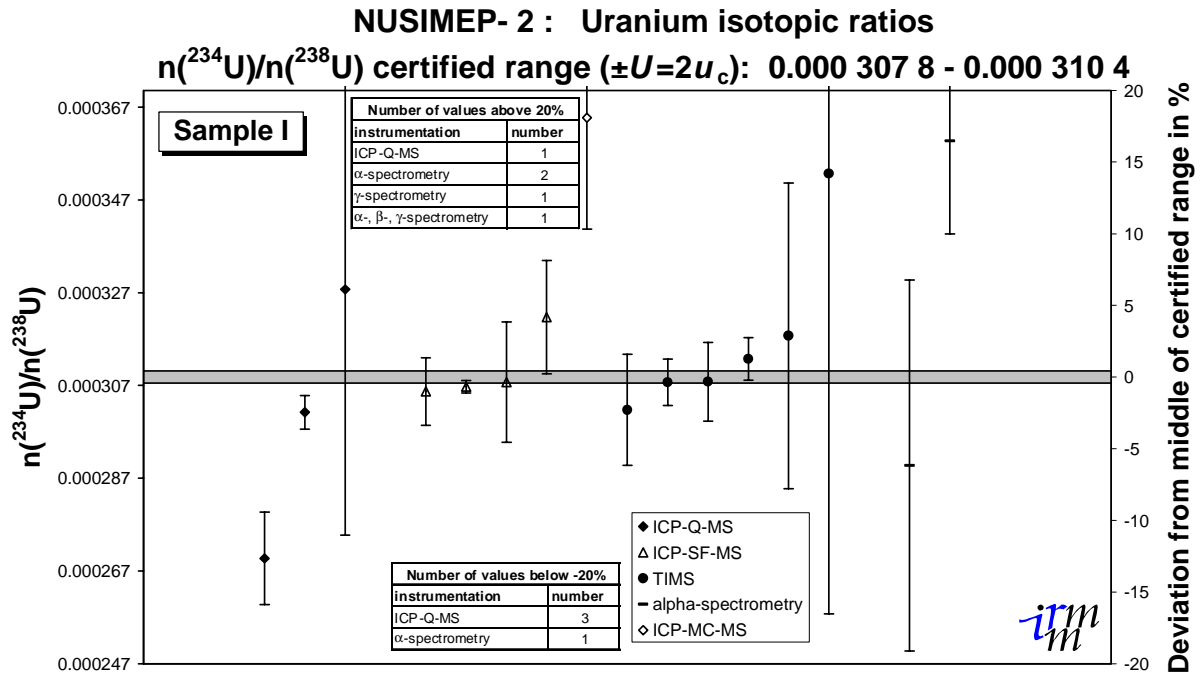
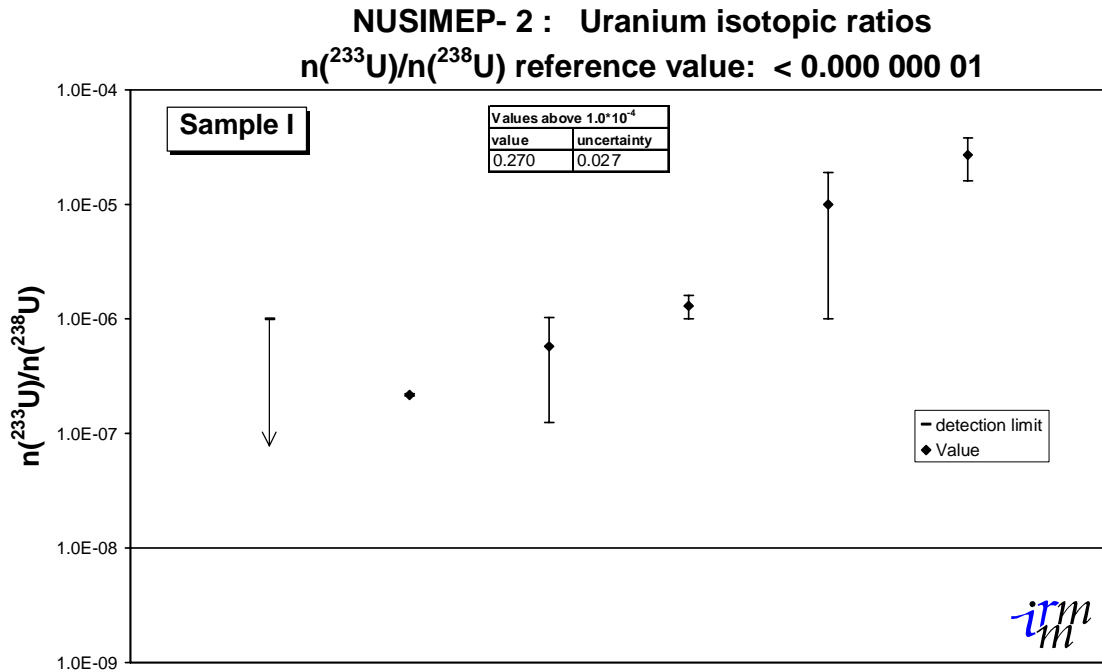


Figure 7



Results from all participants labeled according to the type of instrumentation used.

Figure 8



Results from all participants.

Figure 9

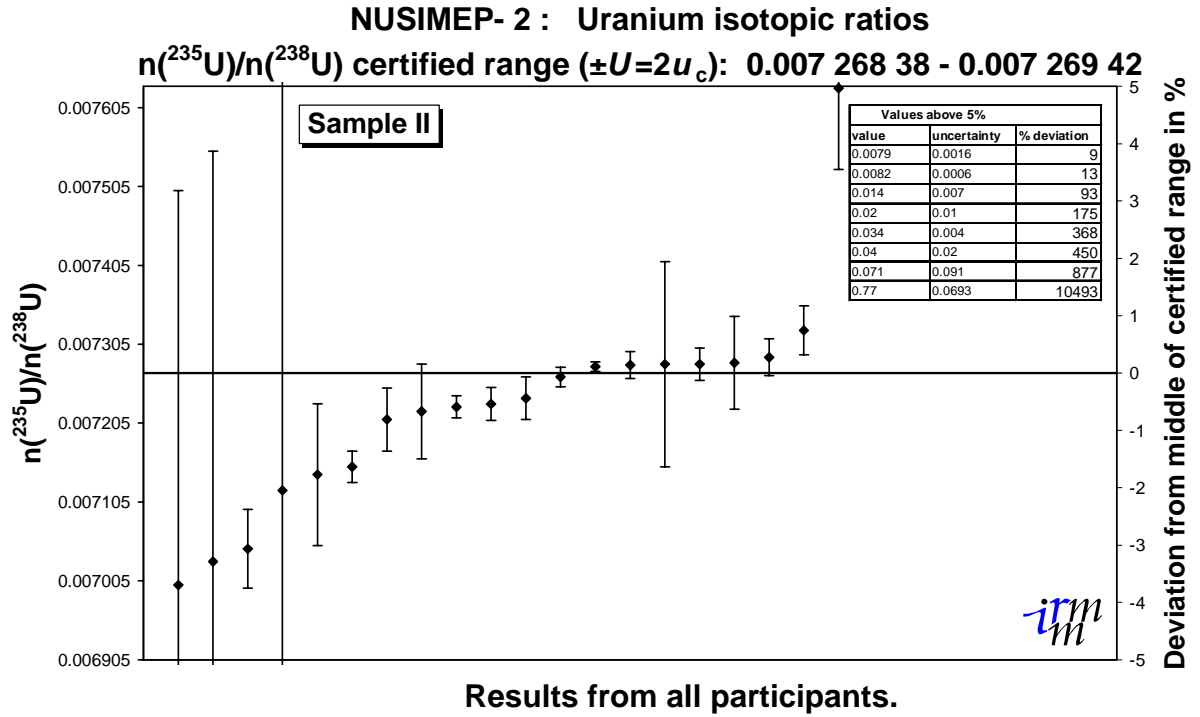


Figure 10

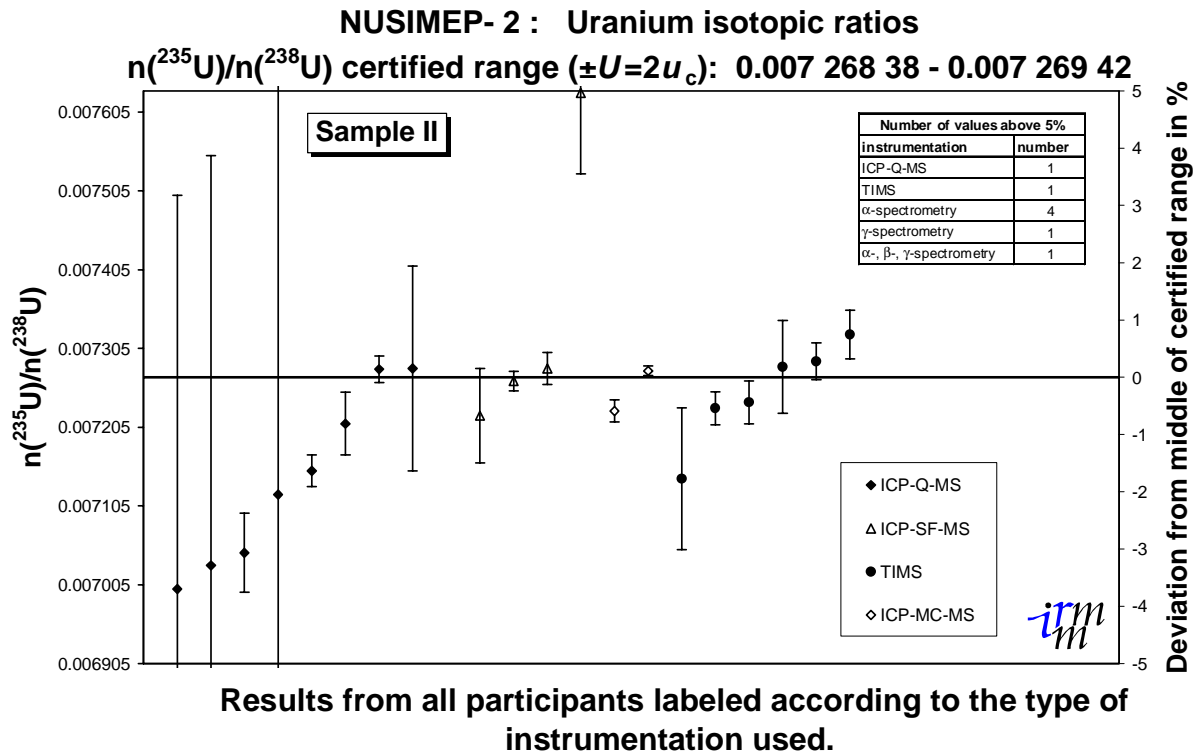


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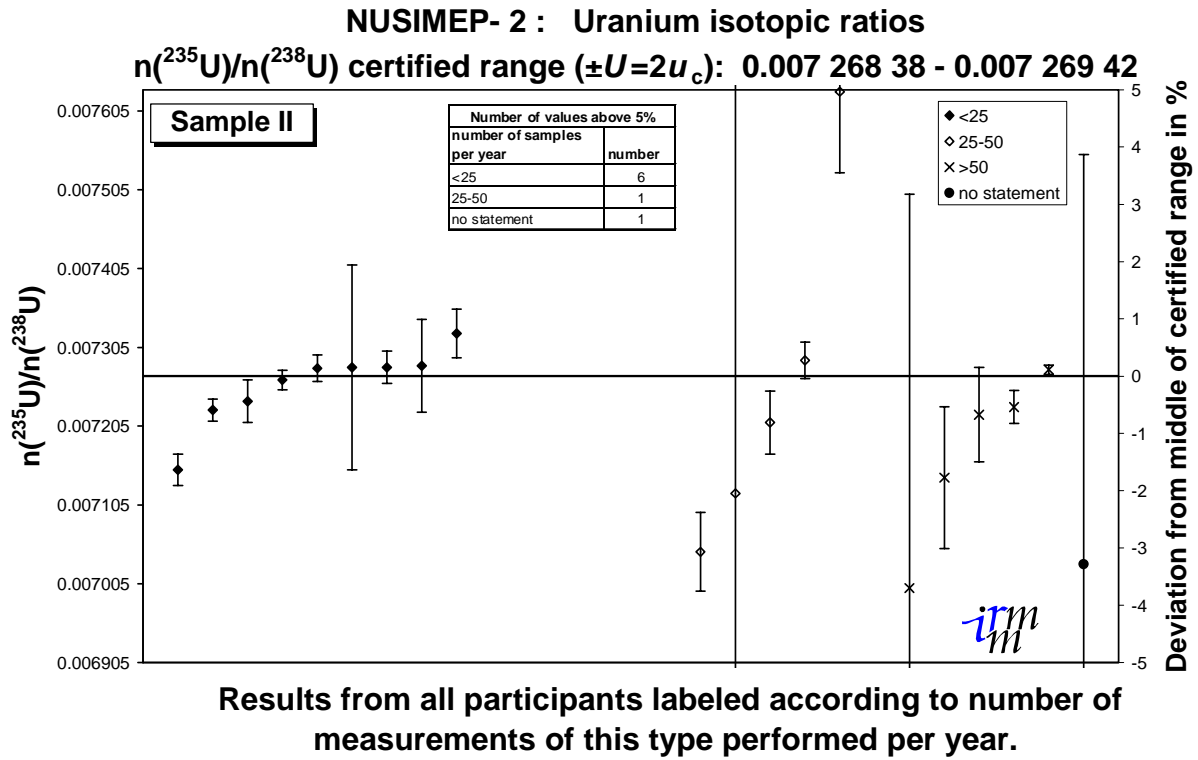


Figure 12

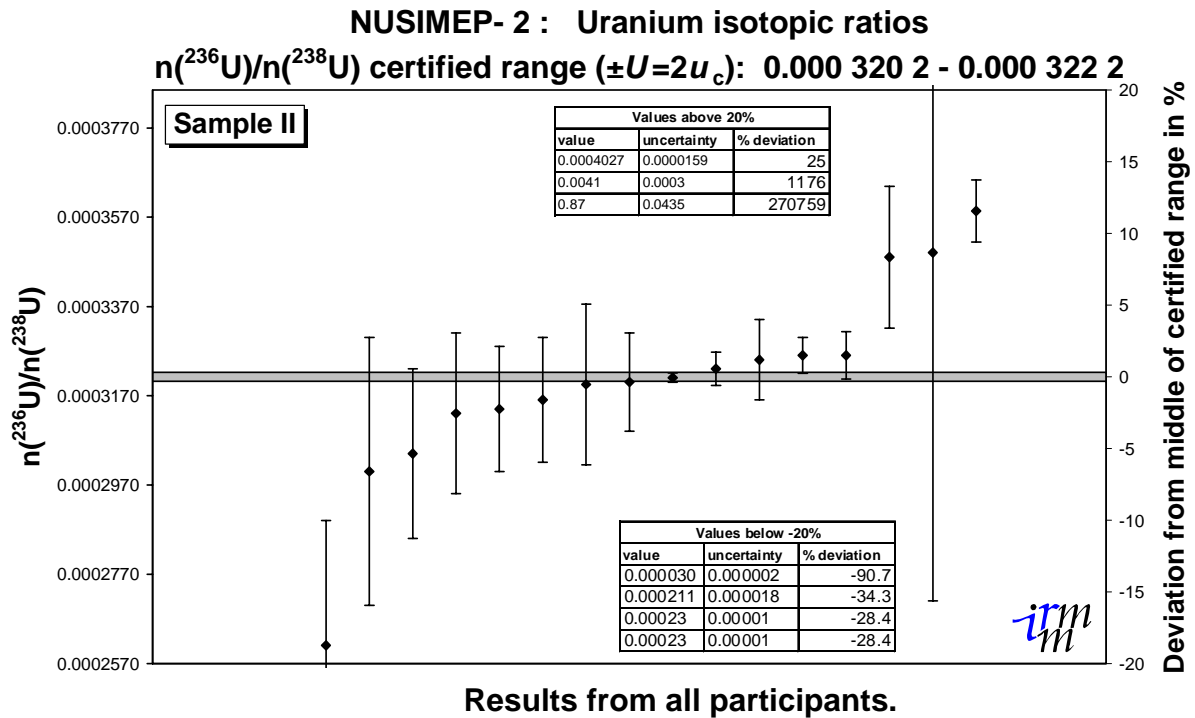


Figure 13

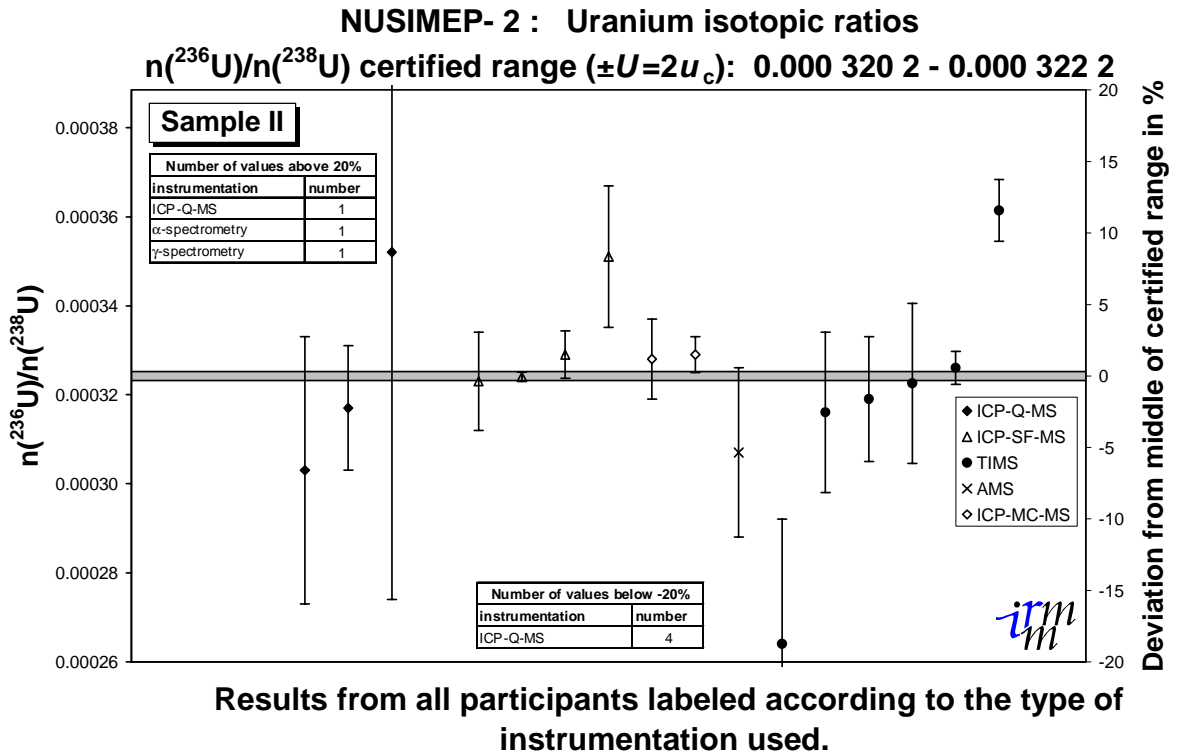


Figure 14

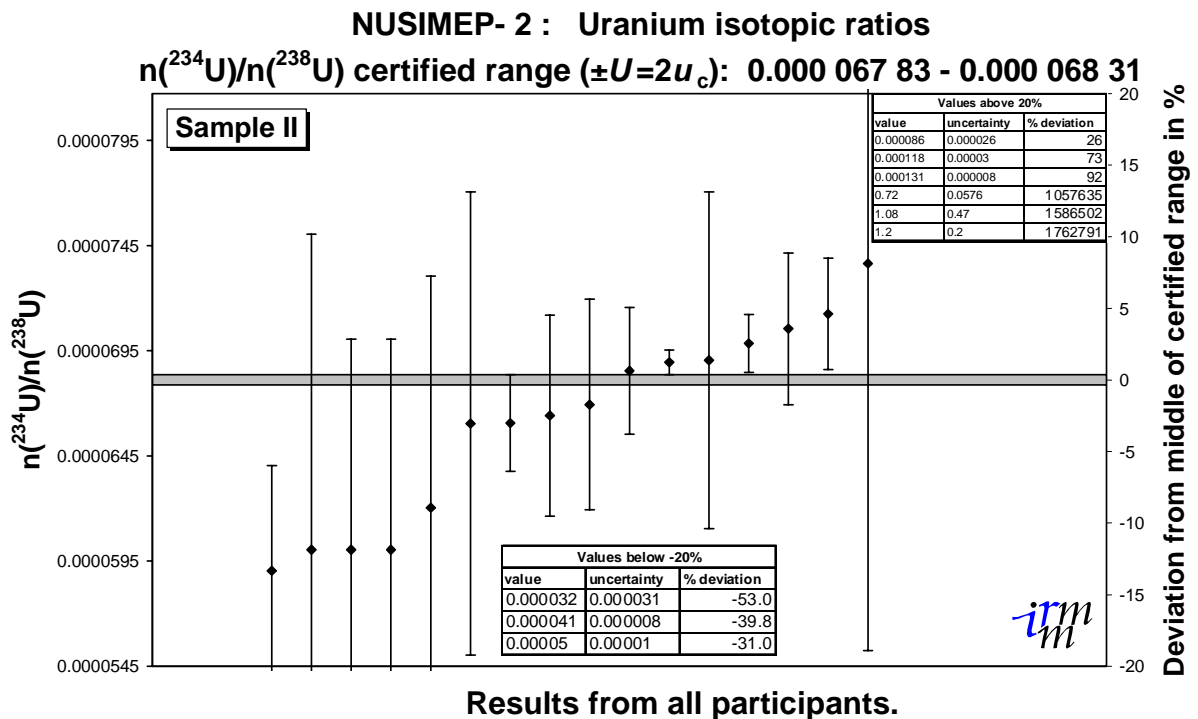


Figure 15

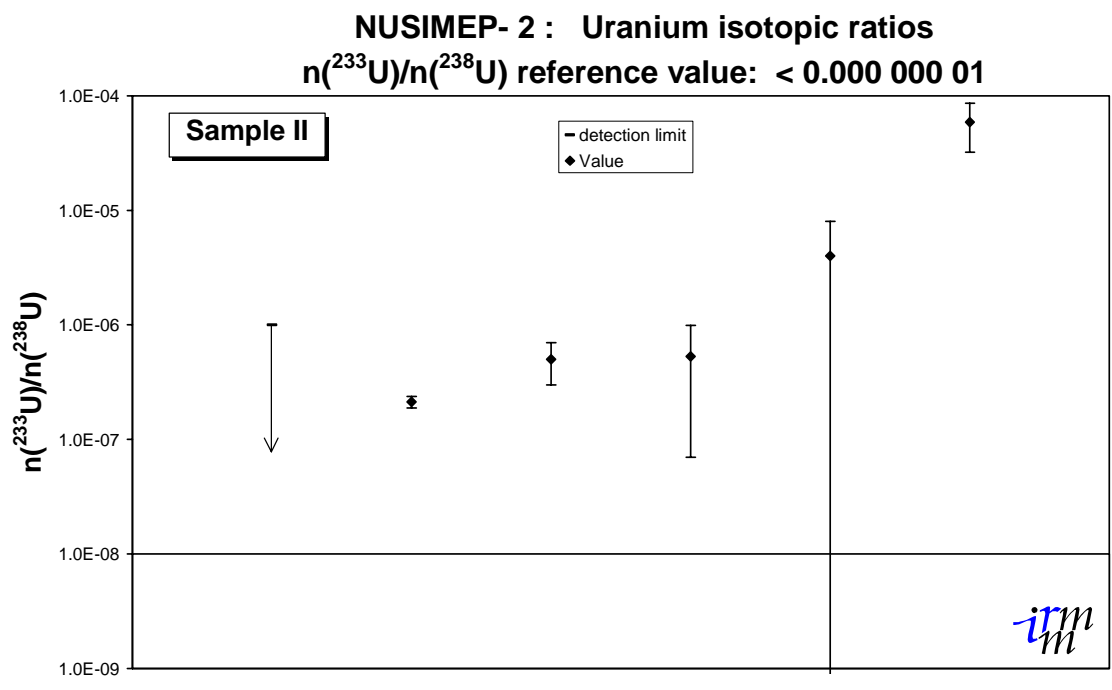


Figure 16

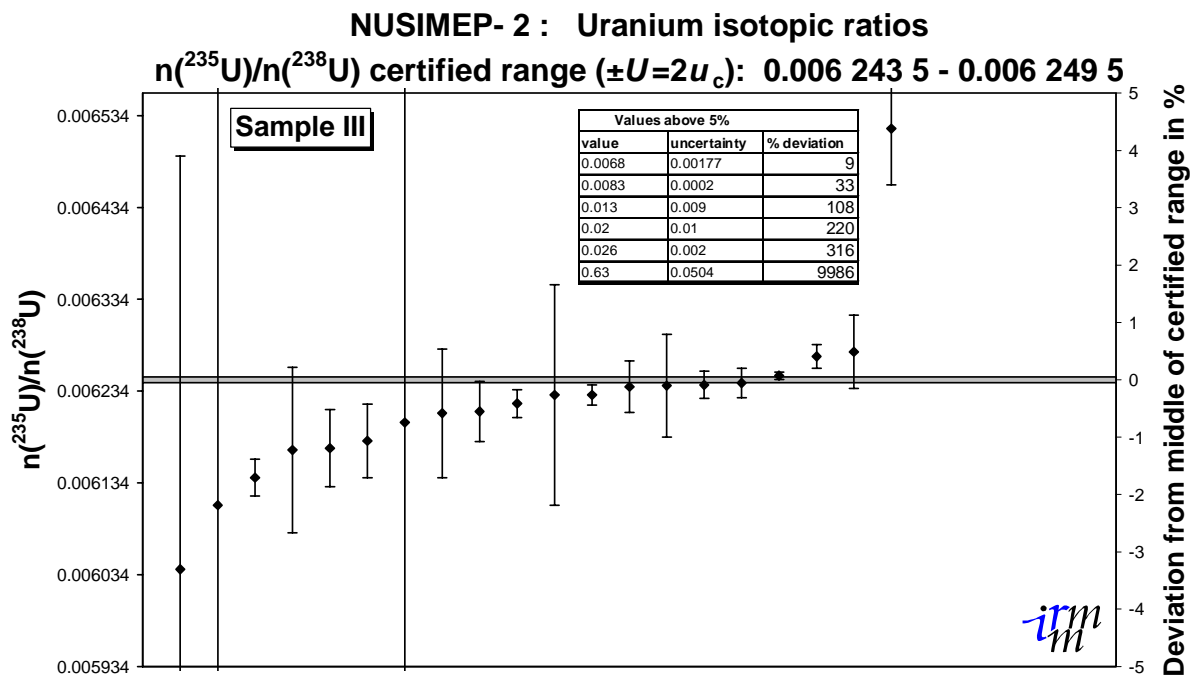


Figure 17

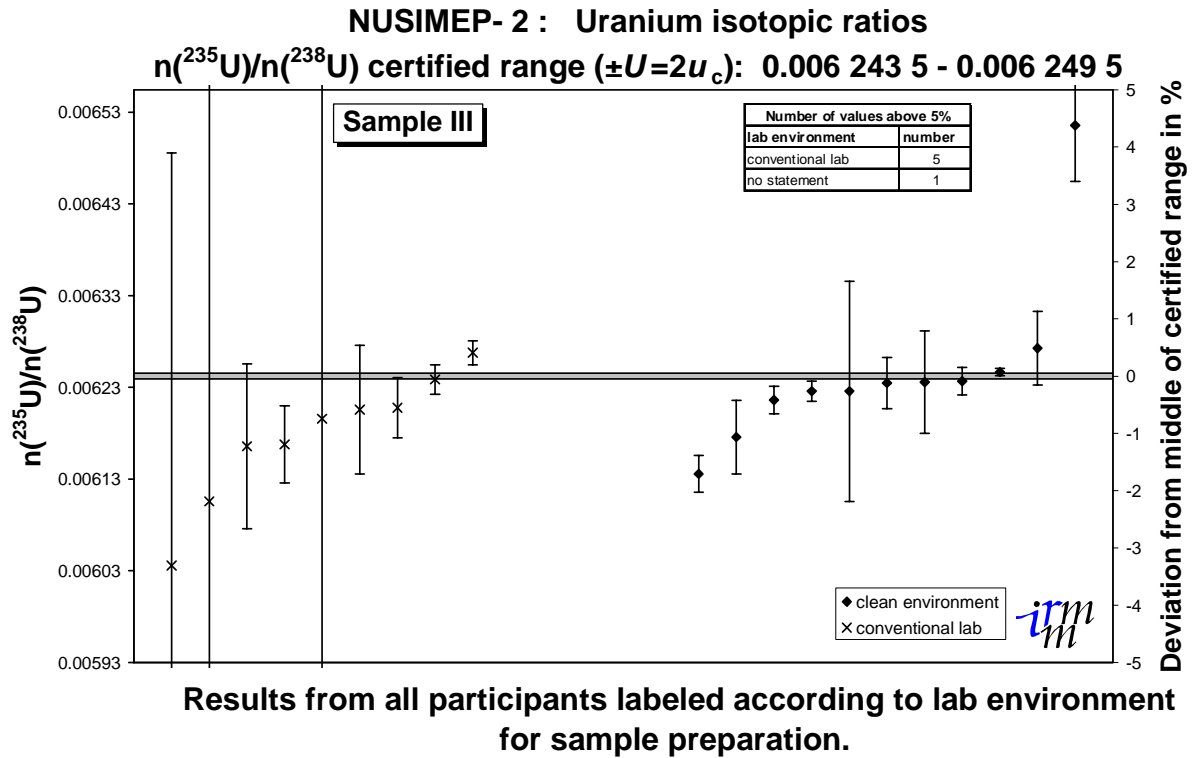


Figure 18

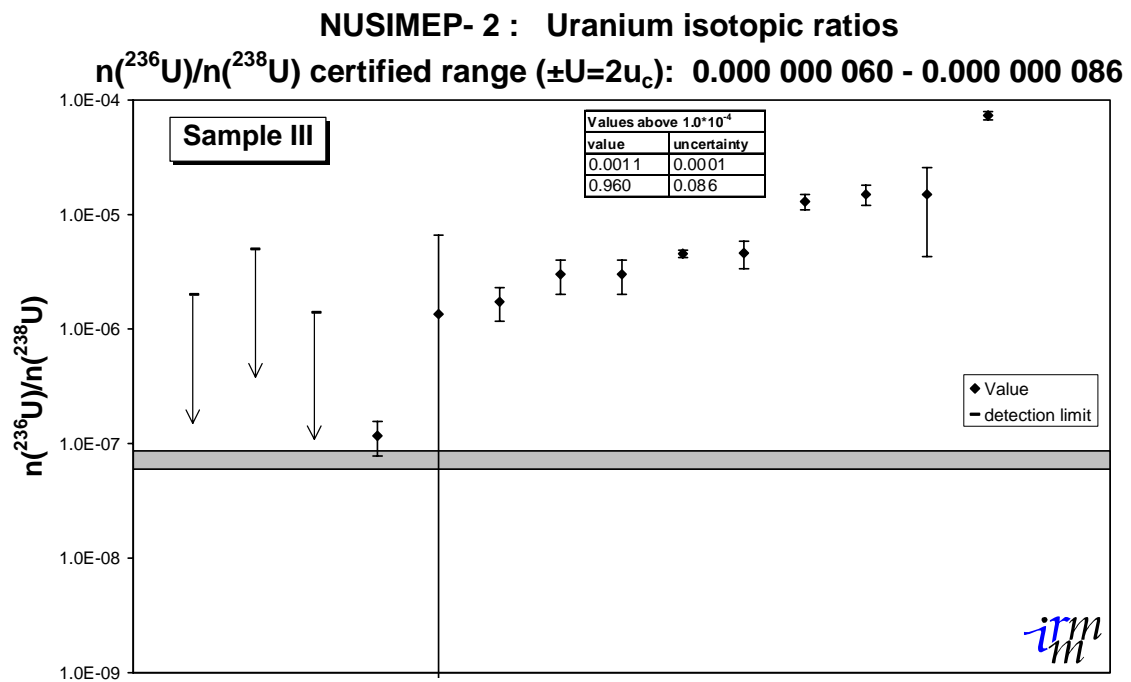


Figure 19

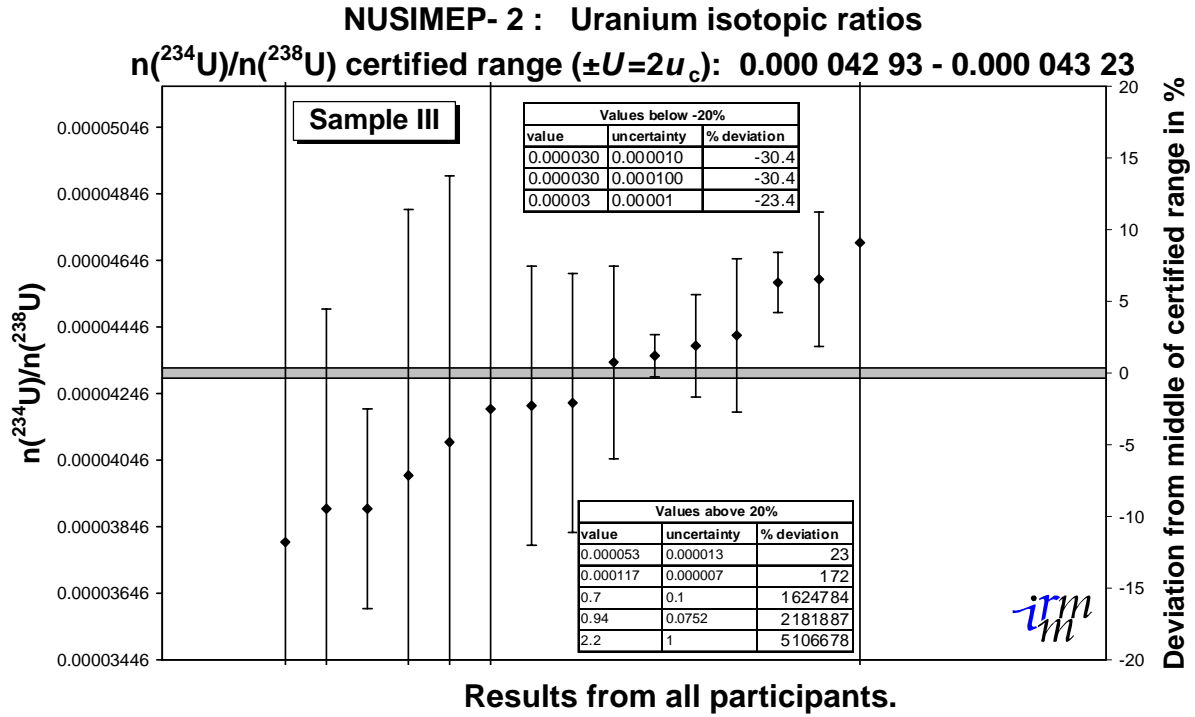


Figure 20

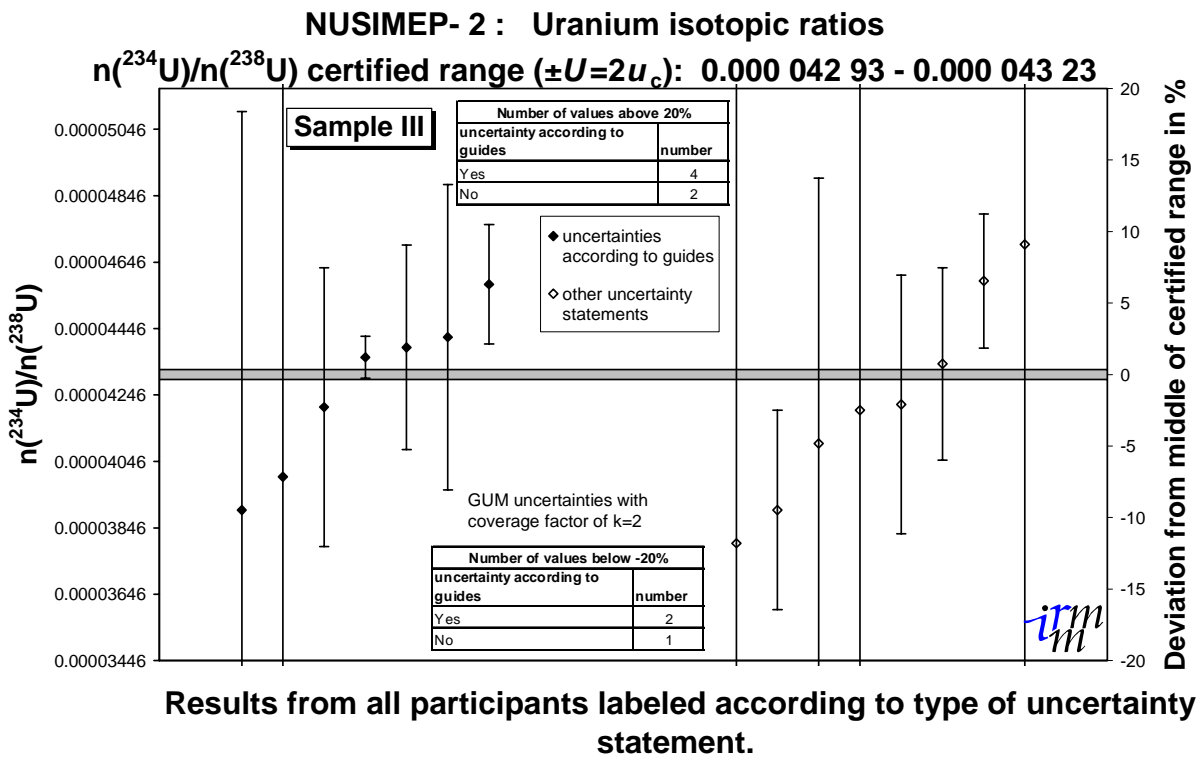
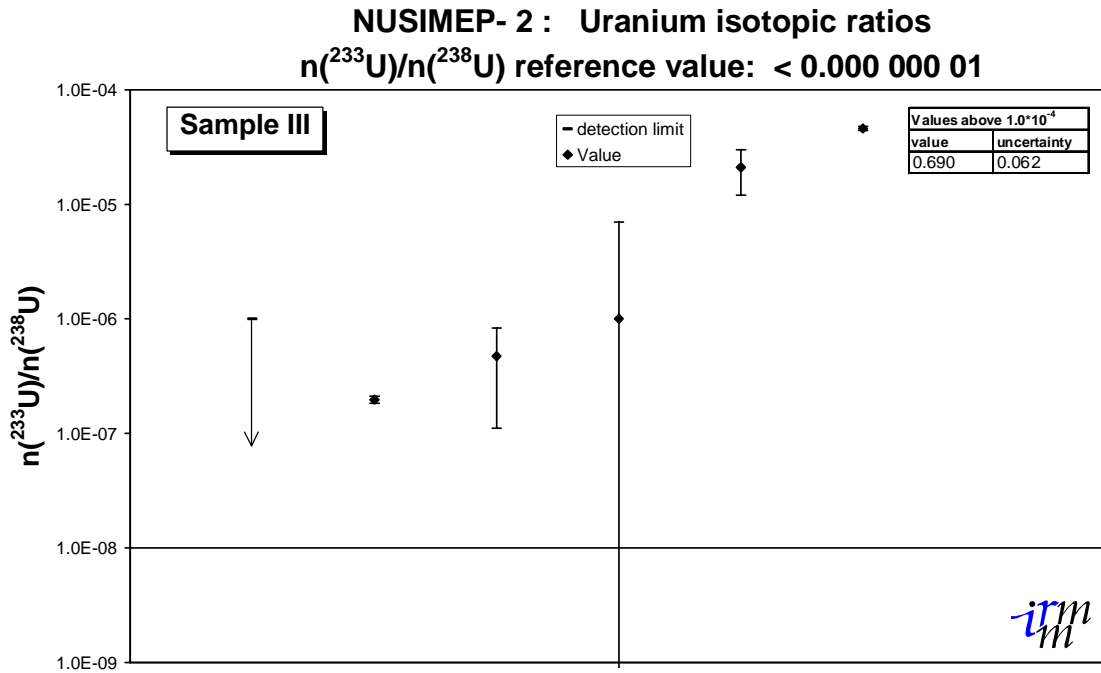
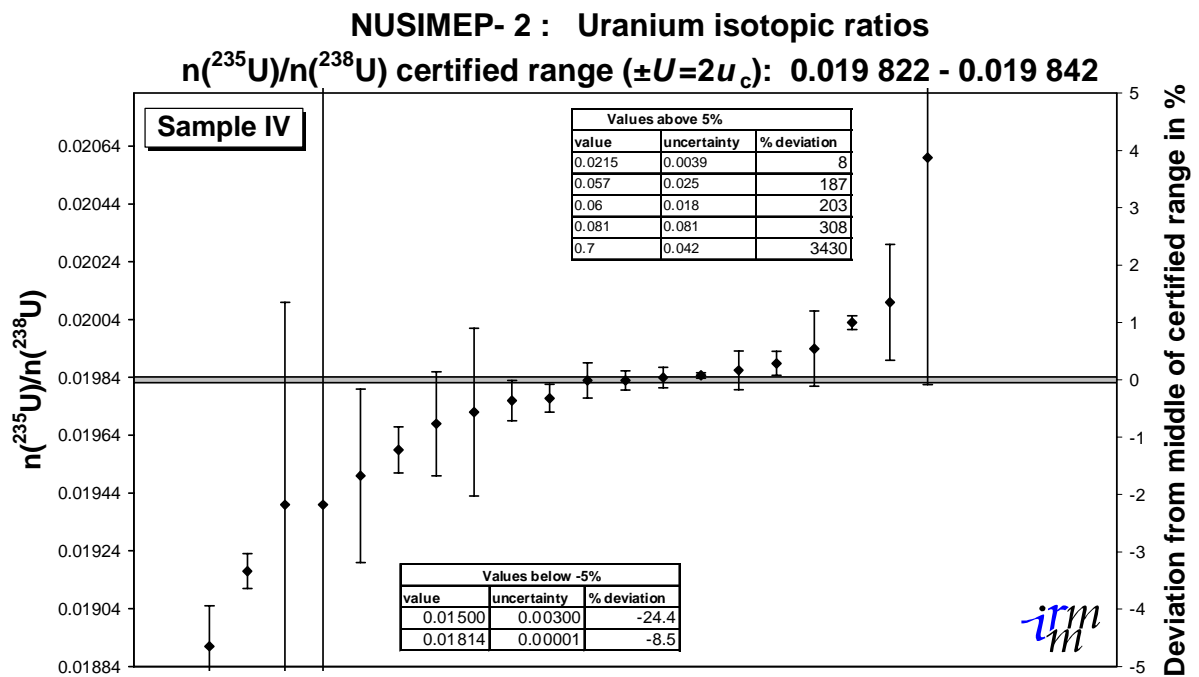


Figure 21



Results from all participants.

Figure 22



Results from all participants.

Figure 23

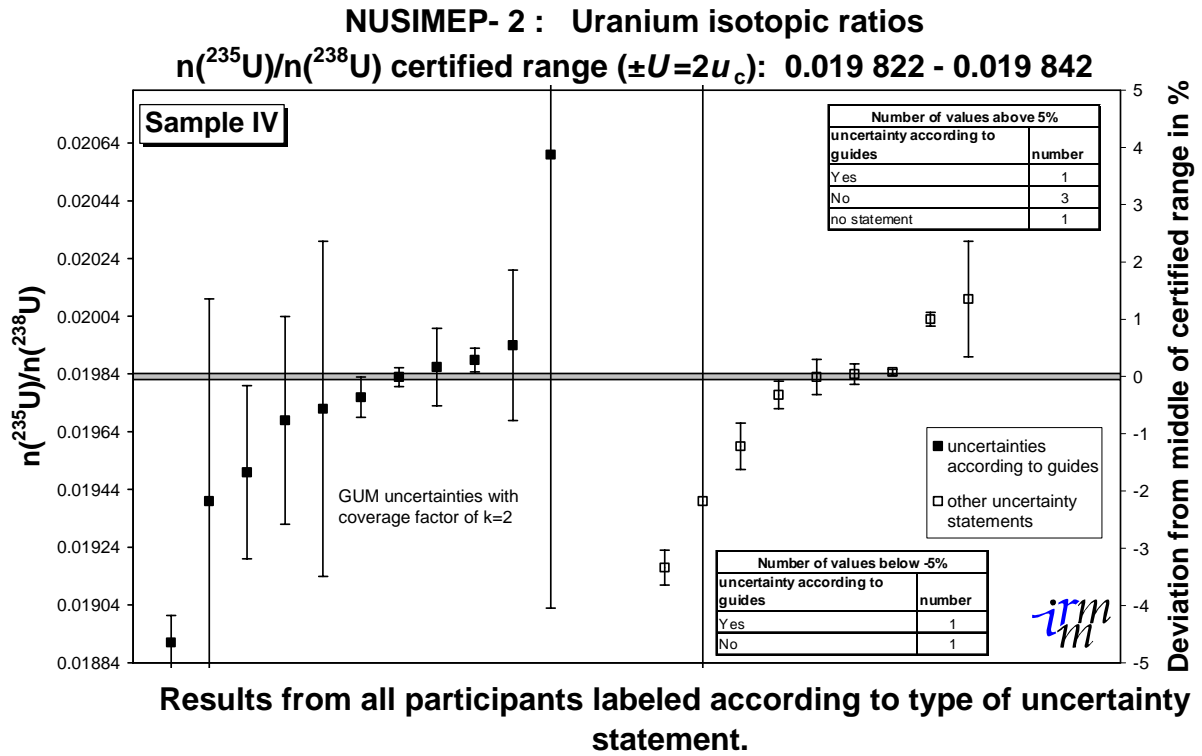


Figure 24

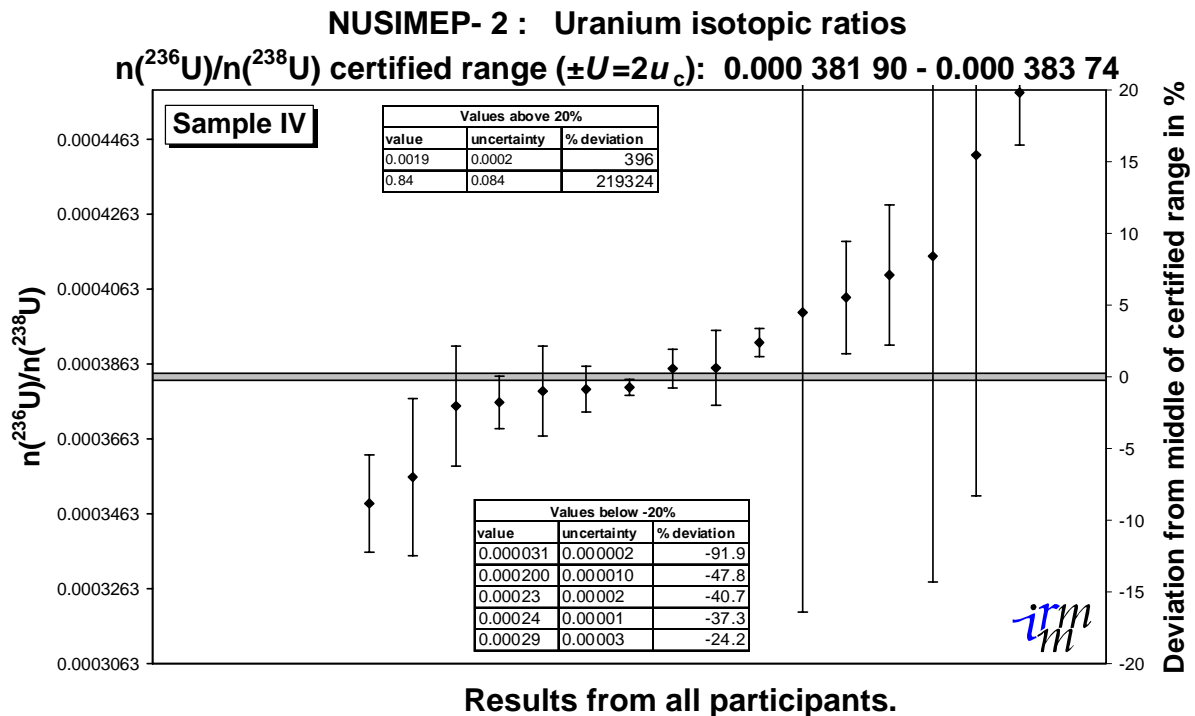


Figure 25

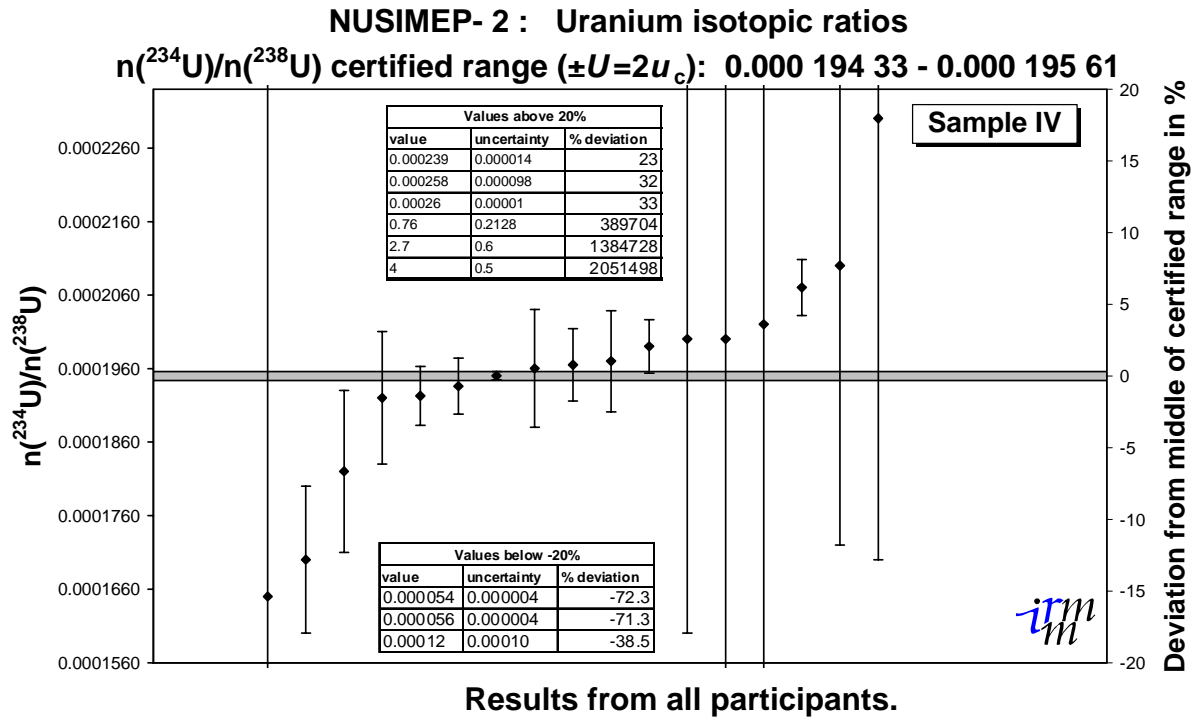


Figure 26

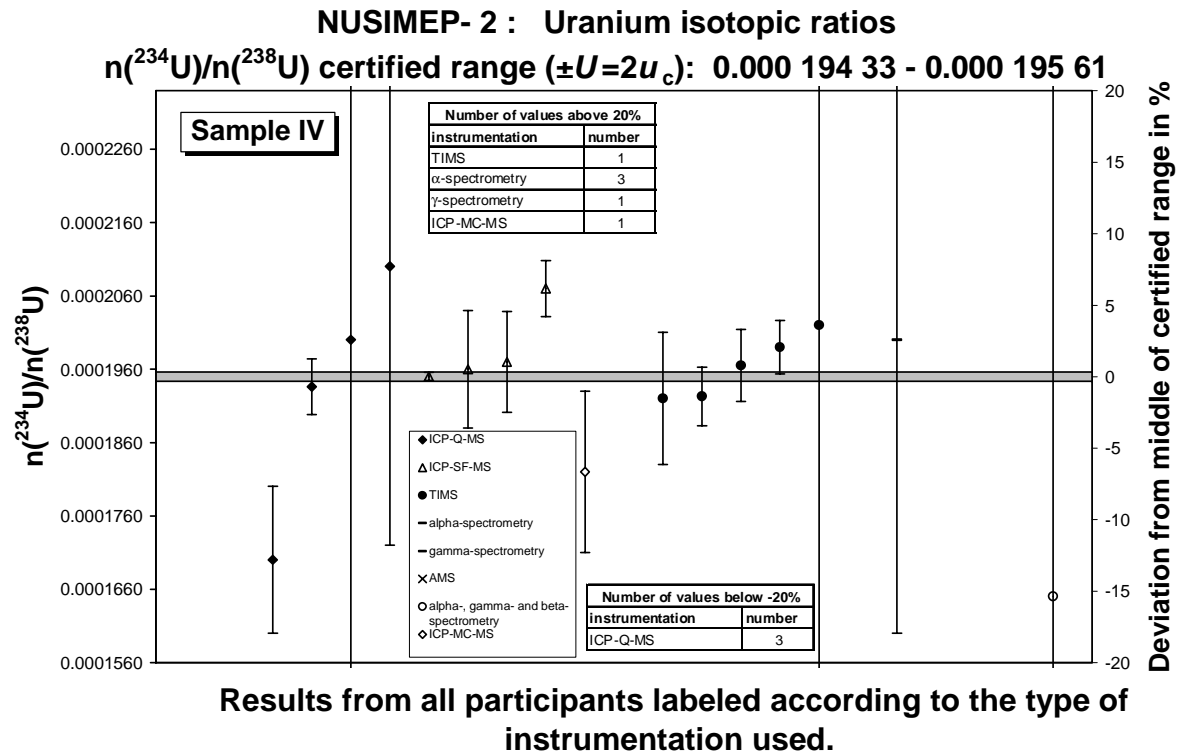
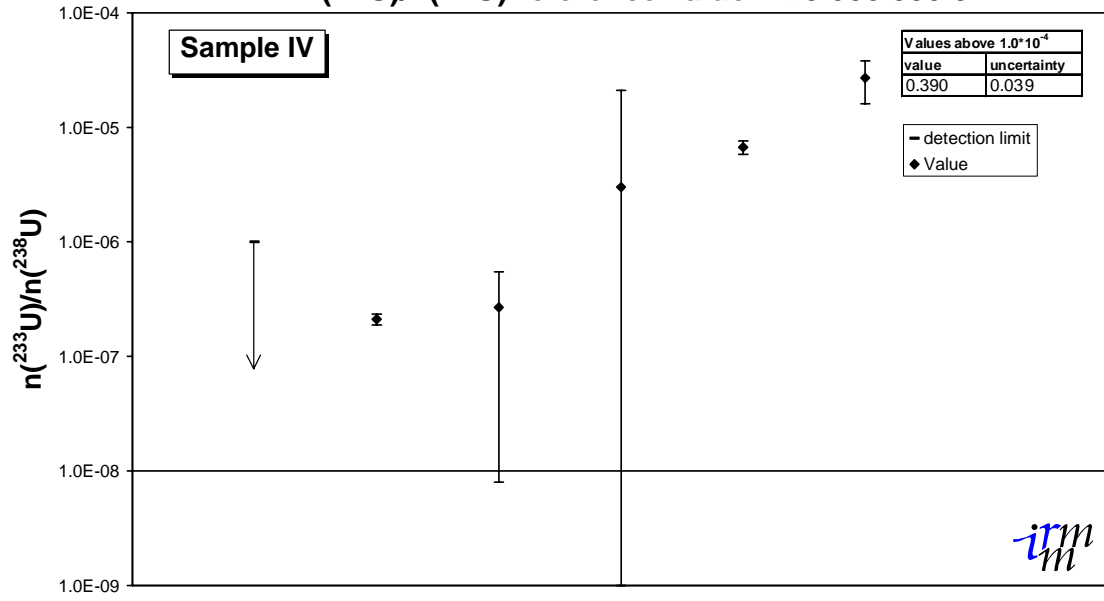


Figure 27

NUSIMEP- 2 : Uranium isotopic ratios

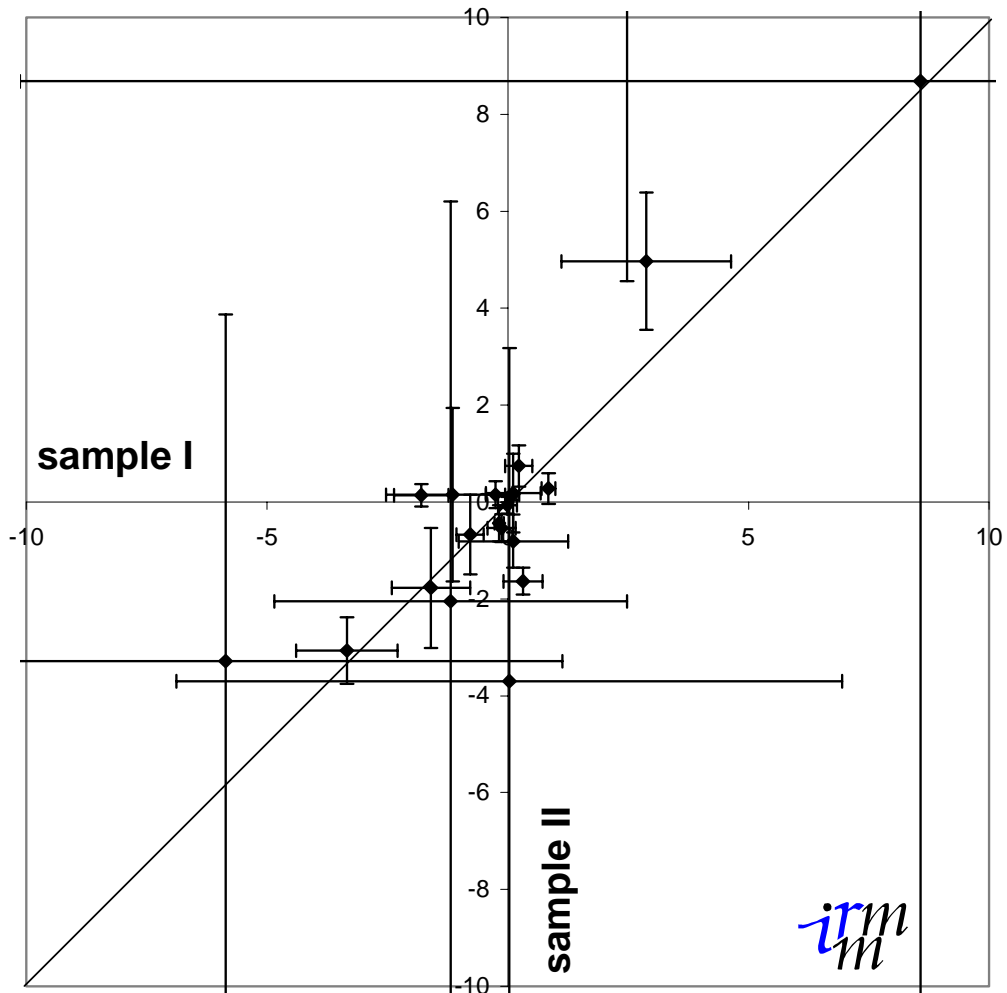
$n(^{233}\text{U})/n(^{238}\text{U})$ reference value: < 0.000 000 01



Results from all participants.

Figure 28

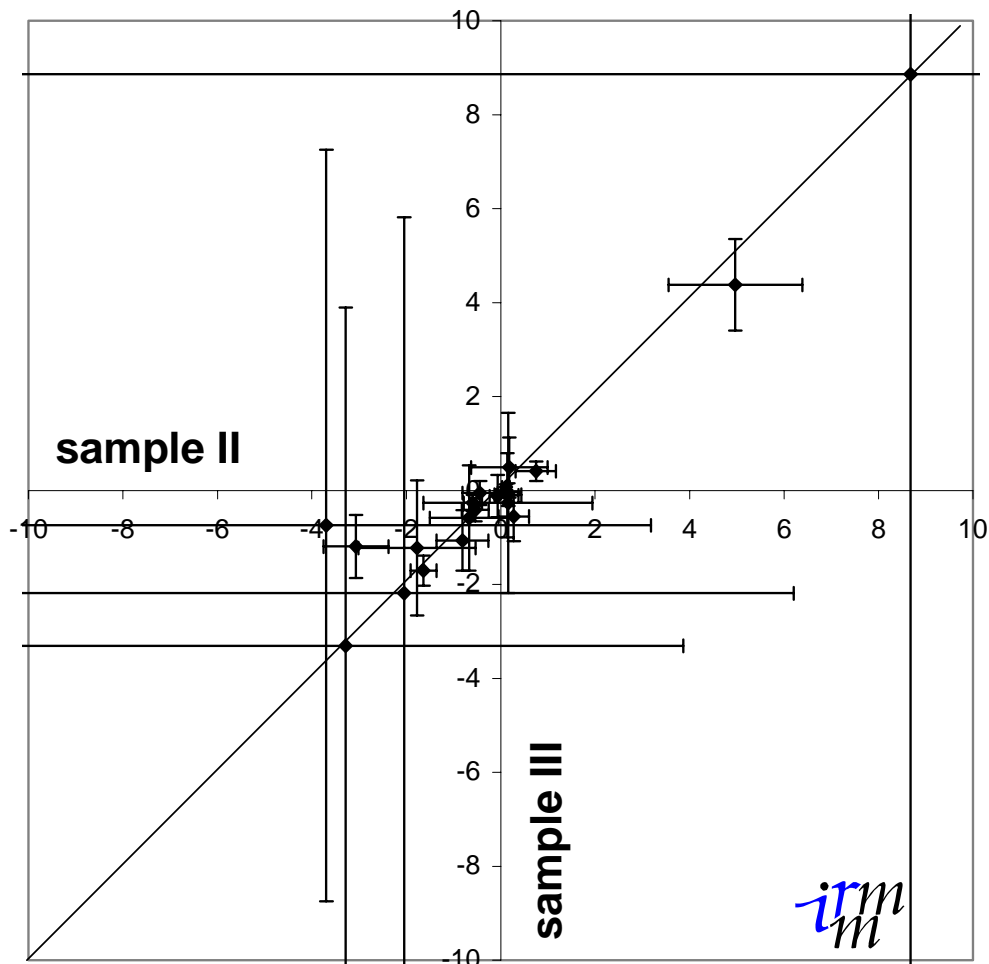
**NUSIMEP- 2 : Uranium isotopic ratios
deviation from certified value for
 $n(^{235}\text{U})/n(^{238}\text{U})$ in % for samples I and II**



Results from all participants.

Figure 29

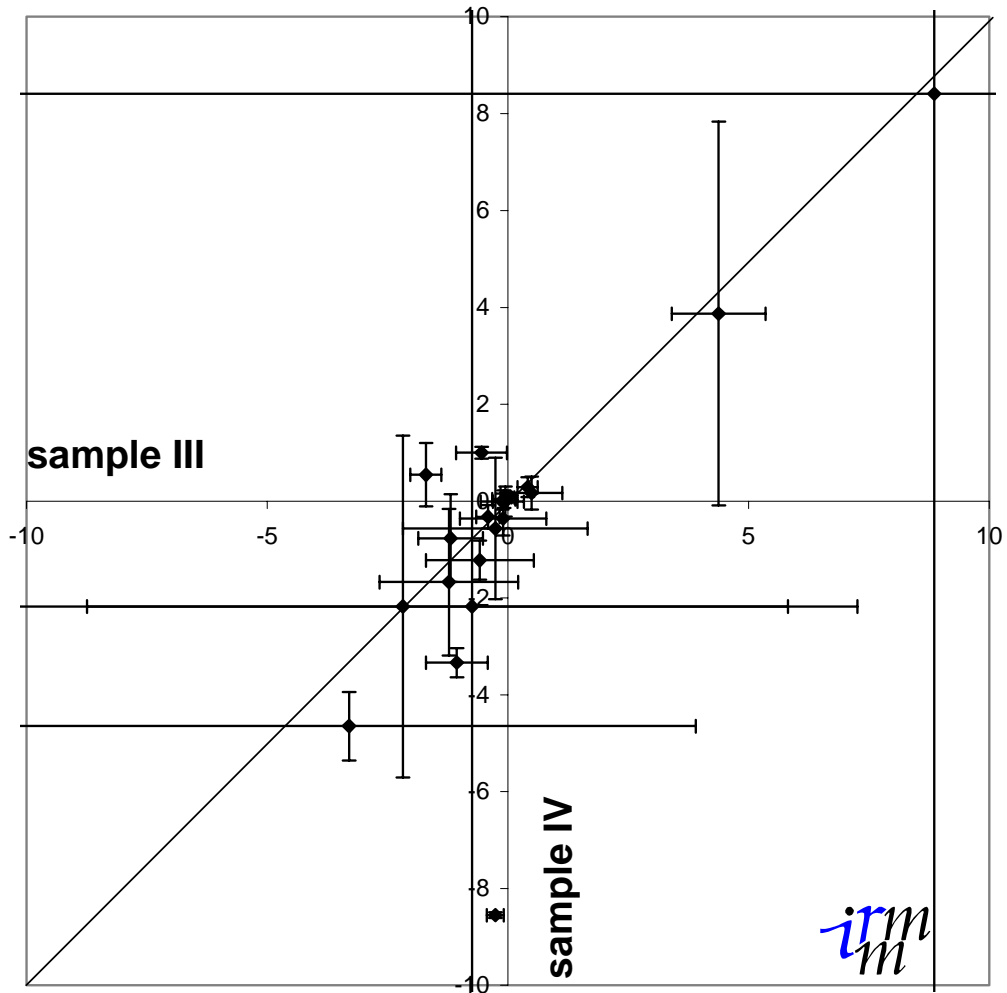
**NUSIMEP- 2 : Uranium isotopic ratios
deviation from certified value for
 $n(^{235}\text{U})/n(^{238}\text{U})$ in % for samples II and III**



Results from all participants.

Figure 30

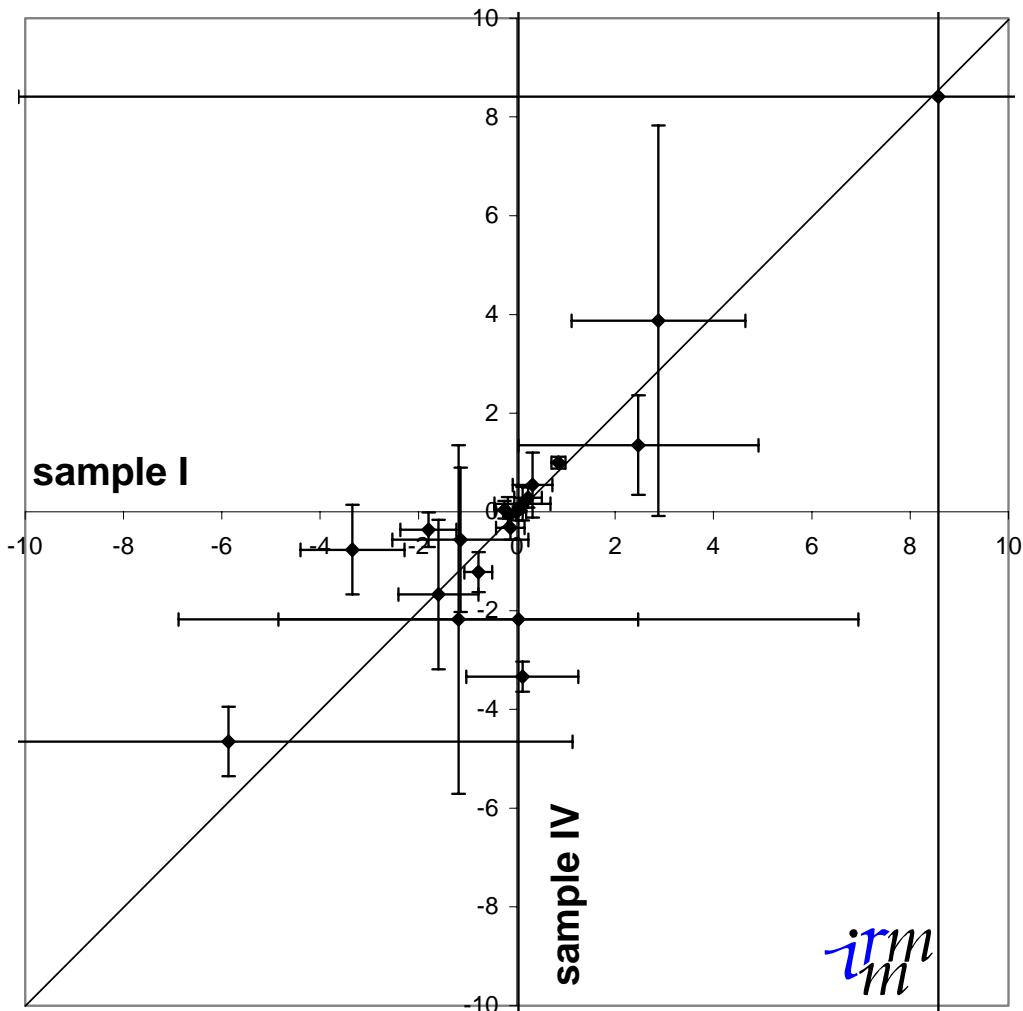
NUSIMEP- 2 : Uranium isotopic ratios deviation from certified value for $n(^{235}\text{U})/n(^{238}\text{U})$ in % for samples III and IV



Results from all participants.

Figure 31

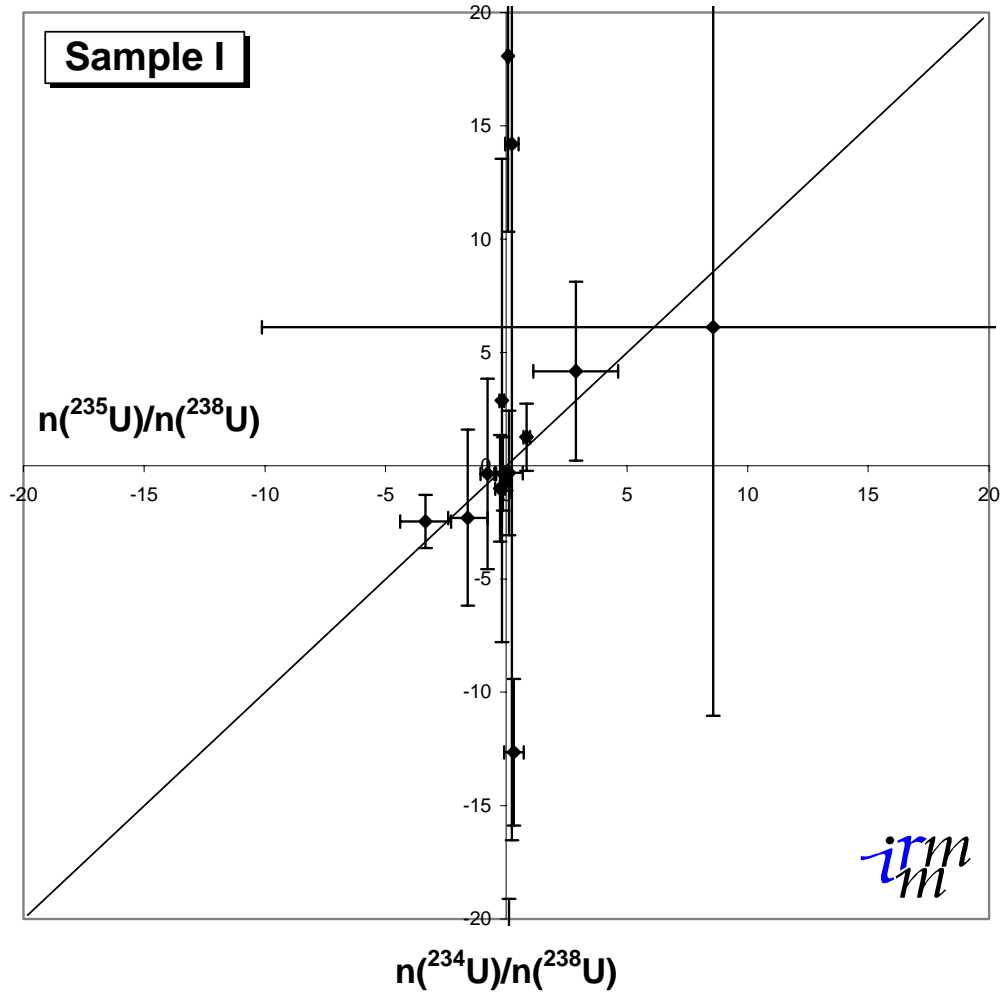
**NUSIMEP- 2 : Uranium isotopic ratios
deviation from certified value for
 $n(^{235}\text{U})/n(^{238}\text{U})$ in % for samples I and IV**



Results from all participants.

Figure 32

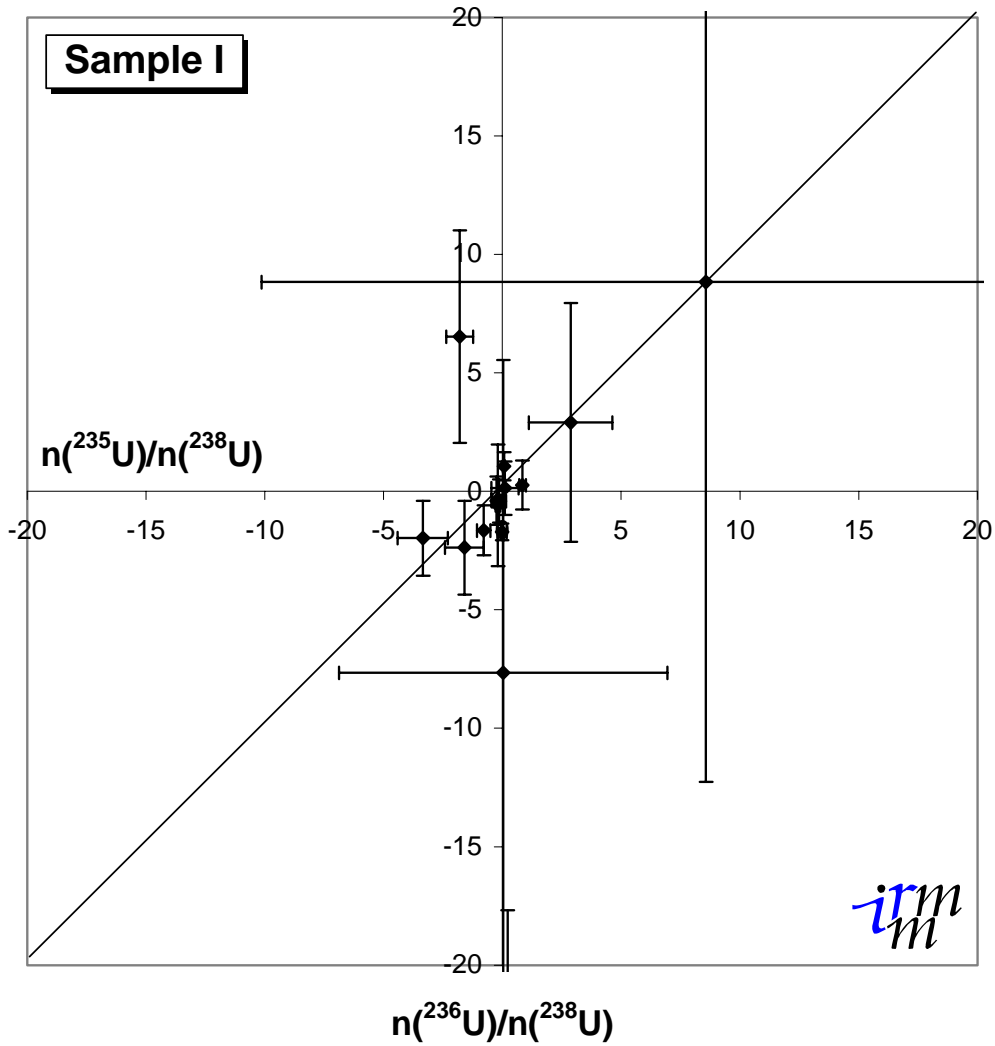
NUSIMEP- 2 : Uranium isotopic ratios deviation from certified value in %



Results from all participants.

Figure 33

**NUSIMEP- 2 : Uranium isotopic ratios
deviation from certified value in %**



Results from all participants.

Figure 34

8 Acknowledgements

The authors would like to thank the “IMEP-team”, in particular Mrs L. van Nevel and Mrs P. Smeyers for their technical support in the execution and evaluation of this round.

9 References

- [1] "Blending UF₆ for the Preparation of Isotopic Reference Materials to ²³⁵U AND ²³⁶U Target Abundances", W.De Bolle, R. Ovaskainen, M.Blanco, A.Alonso, K.Mayer, P.De Bièvre, ESARDA Safeguards Symposium, Montpellier,France, 13-15 May 1997
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- [4] EURACHEM, "Quantifying Uncertainty in Analytical Measurement", ISBN 0-948926-08-2, ©Crown copyright, 1995, LGC Information Services, Queens Road, Teddington, Middlesex, TW11 0LY, England.

Annex: Report form and questionnaire



NUSIMEP-2: uranium



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 ISO and EURACHEM. 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-2 sample I

Isotope ratio	value	uncertainty
$^{233}\text{U}/^{238}\text{U}$		
$^{234}\text{U}/^{238}\text{U}$		
$^{235}\text{U}/^{238}\text{U}$		
$^{236}\text{U}/^{238}\text{U}$		

NUSIMEP-2 sample II

value	uncertainty

NUSIMEP-2 sample III

Isotope ratio	value	uncertainty
$^{233}\text{U}/^{238}\text{U}$		
$^{234}\text{U}/^{238}\text{U}$		
$^{235}\text{U}/^{238}\text{U}$		
$^{236}\text{U}/^{238}\text{U}$		

NUSIMEP-2 sample IV

value	uncertainty

Date :

Signature :

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.

PARTICIPANT QUESTIONNAIRE

The purpose of this questionnaire is to enable the organiser of NUSIMEP-2 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

less

experienced

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?

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?

4. Was the NUSIMEP-2 sample treated according to the same analytical procedure as routinely used for this sample type ?

YES

NO

If "NO" why not?

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)

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

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:

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:

Final concentration of dilution:

What kind of matrix was used for the dilution (acid concentration, quality of reagents, etc):

Where was the sample preparation carried out:

in a conventional laboratory
in a clean environment

Please specify:

Other details:

10. Please describe briefly your measurement procedure:

Instrument used:

Special measurement conditions, if applicable:

Other details:

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?

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 $k=$ _____

—

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

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)?
