EUROPEAN COMMISSION
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Joint Research Centre

Institute for Reference Materials and Measurements

REIMEP 16

Plutonium isotopic ratios and abundances
Report to participants

A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe
S. Richter, R. Wellum

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

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

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1 Summary

A new REIMEP external QC campaign has been organised. The measurement of plutonium isotopic ratios is carried out regularly by laboratories concerned with nuclear material accountancy and safeguards. The present campaign has been designed for these laboratories so that they can confirm their measurement capabilities for measuring Pu isotopic abundances.
Following the principles applied to earlier REIMEP rounds, the samples were sent 'blind' to the laboratories, who are requested to report measurement values and the associated uncertainties.
A series of four samples was prepared by mixing and homogenising certified plutonium materials so as to arrive at typical isotopic abundances of the Pu isotopes.
The certification of the isotopic ratios of the samples was planned, as in earlier campaigns, on mass metrology. During verification measurements on the Pu isotopic ratios carried out at IRMM, discrepancies were found between the measured ratios and those calculated from the certified values of the starting materials and the mass-metrology of the solution mixing. It was decided not to establish certified values for the samples but to disclose the measurement values from IRMM.
The campaign is to be considered as an evaluation program which shows the situation for plutonium measurement capability at present in laboratories concerned with nuclear safeguards and nuclear materials accountancy and control.

2 Introduction

The Regular European Inter-laboratory Measurement Evaluation Programme: 'REIMEP' is part of the framework programme of the Isotope Measurements Unit (IM) at IRMM and has been pursued for some 20 years. Samples are prepared suitable for quality control for laboratories measuring uranium and plutonium for fissile material control and accountancy. Previous REIMEP campaigns were for the measurement of uranium isotopic amount content (REIMEP 13 and REIMEP 14) and for uranium isotopic abundances, especially enrichment, in UF_6 samples (REIMEP 15). REIMEP 16 is directed towards the measurement of Pu isotopic ratios by mass-spectrometry, which is a basic measurement performed routinely in many nuclear laboratories handling plutonium samples.
A method of preparing samples was chosen that in principle would allow us a good control over the certified values. In this method, certified isotopically enriched materials were mixed under strict metrological conditions so that the final isotopic ratios would be certified from the certificates of the starting materials and the masses of the solutions mixed together.
It was decided to prepare four different solutions with a range of isotopic abundances typical of 'real' samples, in particular for the $n(^{240}Pu)/n(^{239}Pu)$ ratio but also for the minor isotopes, ^{238}Pu, ^{241}Pu and ^{242}Pu. The starting materials were chosen to be IRMM-081 and IRMM-083. IRMM-081 is a ^{239}Pu spike, certified for isotopic content; IRMM-083 is a ^{240}Pu spike also certified for isotopic content. It is a material prepared and ampouled at the Khlopin Radiochemical Institute, St. Petersburg but which was certified for ^{240}Pu content at IRMM in the year 2000 by

isotope dilution against four different spikes,IRMM-081 (^{239}Pu), IRMM-049b (^{242}Pu), IRMM-049c (^{242}Pu) and CRM 926 (^{244}Pu).

3 Samples

3.1 Preparation

Four samples were prepared by mixing certified starting materials of ^{239}Pu (IRMM-081) and a diluted solution of ^{240}Pu (IRMM-083), by weighing solutions in appropriate amounts under strict metrological control to form four individual mixtures, each having 40 g of solution containing about 2 mg plutonium.
From these, samples of 2 g containing 100 µg Pu were transferred into penicillin vials. The final concentration of plutonium in each mixture was approximately 50 µg of Pu per gram solution. The solutions were dispensed into cleaned penicillin vials, evaporated to dryness and coated with a thin layer of cellulose acetate butyrate (CAB). The coating was to ensure the material remained on the bottom of the vials and not dislodged during transport to the participating laboratories.
The vials were then sealed with a Teflon-coated stopper and an aluminium seal for transport. One sample of each was delivered to the laboratories. For each mixture, the sample vials were engraved using the following system: R-A-(1-20), R-B-(1-20), R-C-(1-20), R-D-(1-20).
The four mixtures were designed to have a range of the isotopic ratio $n(^{240}Pu)/n(^{239}Pu)$ to cover values typically found in plutonium produced in the nuclear cycle.

4 IRMM measurements

The isotopic amount ratios $n(^{238}Pu)/n(^{239}Pu)$, $n(^{240}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{239}Pu)$, $n(^{242}Pu)/n(^{239}Pu)$ were measured in each mixture by thermionic mass-spectrometry (TIMS) after chemical preparation and separation by ion-exchange as described below. The uncertainties on the certified isotopic ratios were calculated strictly following GUM /1/. The isotopic ratios were measured in two individual sets of mixtures, a CAB coated and a non-coated one, by thermionic mass-spectrometry (TIMS).

4.1 Chemical preparation of sample for measurement

Before each isotopic measurement the organic layer was removed from the sample according to the following procedure: Conc. HNO_3 (0.5 ml) was added to each of the coated samples and evaporated to near dryness at a temperature of 70°-90°C. To destroy possible remaining CAB, 1 ml of conc. HNO_3 was added and evaporated to dryness again.
This procedure was not carried out on the non-coated samples.
Both the non-coated and coated samples were then dissolved in 200 µl of 2M HNO_3. To achieve isotopic equilibrium and convert the Pu to the correct valency for separation, 50µL 1.25M ferrous chloride and 100µL 1M hydroxyl ammonium chloride were added to reduce the plutonium to Pu(III) followed by 100µL 1M sodium nitrite to oxidise Pu(III) to Pu(IV). Finally 430 µL concentrated nitric acid were added to obtain Pu(IV) in 8M nitric acid media.
The separation was accomplished by passing the solution through an anion-exchange column (Bio-Rad AG1-X4, 100-200 mesh). The column was washed

with 8M nitric acid to remove americium in particular and plutonium was eluted with 0.35M nitric acid. The plutonium fraction was evaporated and dissolved in 1M nitric acid to give a concentration of approximately 1mg Pu·mL^{-1}.

4.2 Sample loading

The samples were loaded onto the mass-spectrometer filaments in a glove-box for subsequent mass-spectrometric measurements. One microlitre of the plutonium solution (4 nmol of Pu) was deposited on a rhenium filament. The sample droplet was dried according to a standard procedure (a programmable heating device ensured a reproducible heating pattern with standardised temperatures steps and heating times). When a set of filaments had been prepared, the sample turret was then loaded into the mass spectrometer.

4.3 Mass-spectrometry measurements

Measurements of the isotope amount ratios concerned were performed as soon as possible after separation of the americium and calibration of the spectrometer.
Isotope ratio measurements were performed by thermal-ionisation mass-spectrometry (TIMS) using a Finnigan MAT261 equipped with a 13 location sample turret, a double Faraday collector and a secondary-electron multiplier (SEM). Measurements were done on a single collector by magnetic scanning for $n(^{240}Pu)/n(^{239}Pu)$ and $n(^{241}Pu)/n(^{239}Pu)$ and using the SEM for $n(^{238}Pu)/n(^{239}Pu)$ and $n(^{242}Pu)/n(^{239}Pu)$. Synthetic plutonium mixtures, IRMM-290, were used as a standard to calibrate the mass spectrometer for mass-fractionation.
Two series of measurements, 6 turrets in total, were carried out. The first series consisted of one turret for each mixture, loaded with 8 samples and 5 standards. In the second series two turrets were loaded with 2 samples of each mixture and 5 standards.

4.4 Mass-spectrometry results

Normally for a REIMEP campaign at least two independent methods are applied to certify materials. For REIMEP 16 the intention was to certify the isotope ratios based on the certified values of the two spikes, IRMM-081 and IRMM-083 together with the weights of solution, and verify these values by mass spectrometry of the mixtures as described above.
However in this case, the results were not concordant, even after re-measuring the isotopic ratios of the two spikes. In the end it was concluded that one of these spikes (IRMM-081) has apparently degraded during storage and an investigation is on-going to understand this phenomenon. The decision was therefore made not to certify the REIMEP 16 materials but to provide the IRMM measured values to participants.
The IRMM values are given below in Table 1.

Table 1: IRMM Measured isotopic ratios of REIMEP samples (expanded certainty given in brackets, k=2)

Sample	n(^{238}Pu)/n(^{239}Pu)	n(^{240}Pu)/n(^{239}Pu)	n(^{241}Pu)/n(^{239}Pu)	n(^{242}Pu)/n(^{239}Pu)
REIMEP 16 A	0.000 074 9(72)	0.657 45(91)	0.002 323(36)	0.000 416 4(69)
REIMEP 16 B	0.000 065 8(24)	0.427 08(19)	0.001 632(57)	0.000 284(10)
REIMEP 16 C	0.000 067 0(37)	0.246 195(91)	0.001 053(34)	0.000 176 7(58)
REIMEP 16 D	0.000 067 4(19)	0.110 967(68)	0.000 711(17)	0.000 110 0(27)

5 Participation

Invitations to participate were sent to a number of laboratories active in the field. Expressions of interest were received from 15 laboratories.
AWE(A) Aldermaston, UK
Institute for Transuranium Elements, JRC, Germany
Euratom On-site Laboratory, Sellafield, UK
Euratom Laboratoire sur site, La Hague, France
KAERI, Korea
BNFL, Sellafield, UK
SCK.CEN, Belgium
US DOE New Brunswick Laboratory, USA
Paul Scherrer Institute, Switzerland
Lawrence Livermore National Laboratory, USA
Brookhaven National Laboratory, USA
IAEA, Austria
CEA de Valduc, France
CEA Valrho, France
Cogema, La Hague, France

Samples were sent to 7 participants: 2 will still receive their samples in the beginning of this year. Two laboratories informed us later they could not participate and four laboratories still have not fulfilled all conditions for the transport of the materials. Therefore, at present, results were received from 6 laboratories only. Nonetheless the report has been compiled when we believe the main part of the expected results have been sent to us. Possibly three other laboratories will still send results in the course of this year; we will then update this report as necessary.

6 Compilation of comparative results

The isotopic amount ratios for the ^{238}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu relative to ^{239}Pu are shown for each sample, REIMEP-16A, -16B, -16C, -16D in the following graphs. The results provided by the participants are plotted with expanded uncertainty (k=2).
The points are plotted in order of the laboratory number assigned to each laboratory, which should be able to locate the position of its results on the plots

without difficulty. The IRMM measurement results are also shown on each plot with Lab ID 1.
The right axis in each plot shows the percent difference of the points from the average value of all received results. Results received with values exceeding two standard deviations from the mean were not included in the calculation of the mean and the corresponding error lines on the graphs. The scale varies according to the isotopic ratio and therefore the scatter of the measured values.
The lines showing ± 1 standard deviation from the mean are also given in the graphs.

7 Evaluation of questionnaire

A questionnaire (Annex 1) accompanied the result forms and participating laboratories were asked to fill it in. Only six laboratories have provided data and some conclusions are distilled here, although the sample number is too small to make generalisations.
Most laboratories measured more than 50 samples per year. All the samples were measured by the normal analyst, i.e. the results can be assumed to be typical of routine measurement results.
All laboratories used one or more certified reference material to calibrate and control their mass-spectrometers. These included NBL CRM-136, -137, -138, -128 NBS-SRM-948 and IRMM-290.
Most laboratories took part in proficiency schemes of some type and two were 'Certified' and two were 'Accredited'.
The measurement techniques were TIMS or ICP-MS; two labs used alpha spectrometry to determine $n(^{238}Pu)/n(^{239}Pu)$.
Sample treatments were rather specific, according to the measurement method employed, although most of the laboratories included an ion-exchange separation stage to remove ^{241}Am impurities.
Mass-bias corrections were generally applied, except where a total evaporation TIMS measurement technique was used.
The uncertainty evaluation varied. Three laboratories quoted uncertainties following GUM recommendations /1/, either as standard or expanded uncertainties. The other laboratories relied on a statistical evaluation by propagation of reproducibilities of multiple runs, uncertainties on control samples and reference materials, as the definition of their measurement uncertainties. No uncertainty budget was requested in the campaign.
It was of interest to see that in most cases it was a person in supervisory function who filled in the questionnaire and the report form. This probably reflects the importance given to these measurements, but may also be the common laboratory practice for all such measurements.
A wide number of future materials for REIMEP rounds were proposed. A repeat of this campaign was generally asked for, but as well as this, uranium isotopic abundances in nitrate solutions and other matrices, Pu and U content in powder and nitrate matrices, MOX, spent fuel, burnup U, Pu, Nd, trace elements in nuclear fuel were also requested. We hope to meet some of these demands in the future.

8 Conclusion

The instability in one of the Pu solutions used to mix the samples (IRMM-081) has meant that this REIMEP campaign is limited compared to previous campaigns. In essence we were unable to certify the solutions based on weights of certified materials mixed together. The values measured at IRMM have therefore been inserted on the graphs in the first position and in each case the mean and standard deviation from all laboratories, after removing outliers was plotted. Nevertheless conclusions can already be drawn from the comparative data:

1. The scatter of the results for $n(^{240}Pu)/n(^{239}Pu)$ indicates that a relative standard uncertainty of 0.1% can be expected for this measurement, which complies with the International Target Values of 0.1% /2/. Only in the case of sample B was the standard deviation greater than this value.
2. The values reported for $n(^{238}Pu)/n(^{239}Pu)$ show large differences between laboratories, possibly due to uranium isobaric interferences in mass spectrometry. Values obtained by alpha spectrometry are indicated by a '○', mass spectrometry by '●'.
3. There appears to be a small influence from ^{241}Am in the results reported for $n(^{241}Pu)/n(^{239}Pu)$. This can be seen by comparing the scatter from this ratio with that from $n(^{242}Pu)/n(^{239}Pu)$.
4. Some laboratories produced individual measurement values that differed considerably from those of other laboratories (and the mean value).

The general transport problems for these Pu samples led to large delays in reporting so that even at the time of writing this report certain laboratories still have not yet received their samples. As a change to the normal routine for REIMEP, late results will be added when received and the results file updated.

This campaign clearly pointed out deficiencies in the overall capability of laboratories to measure Pu isotopes. A repeat will be organized in the near future.

References

/1/ International Organisation for Standardisation, "Guide to the Expression of Uncertainty in Measurements", ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993

/2/ IAEA, International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials

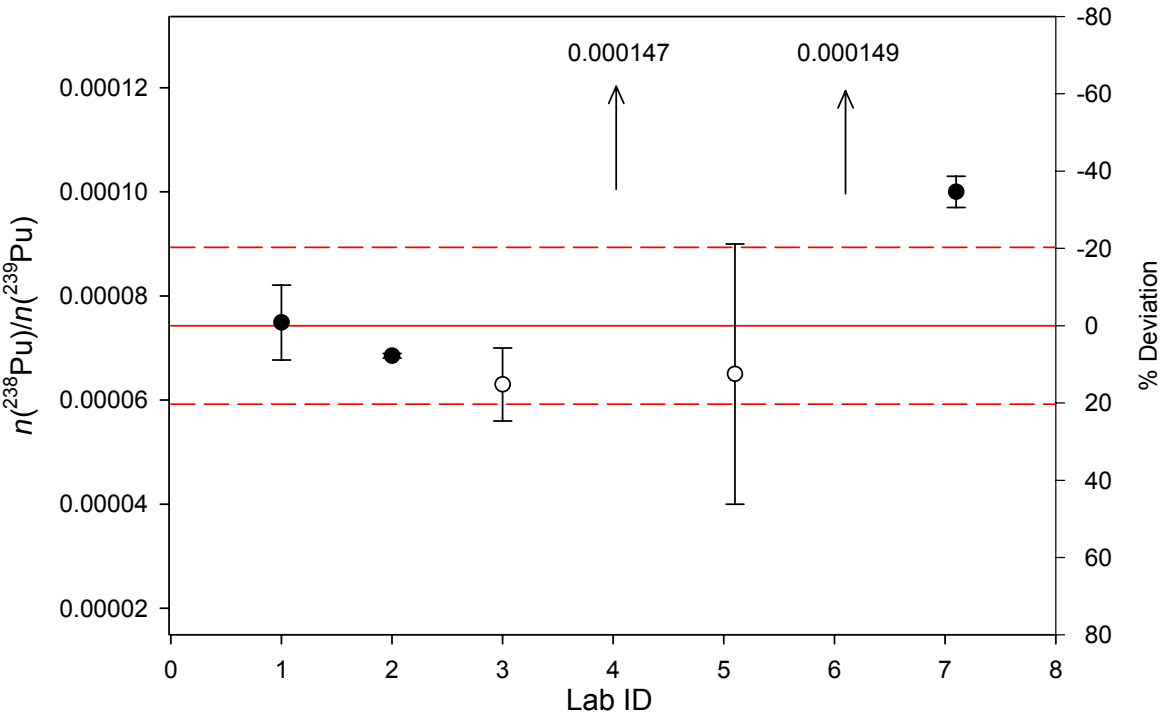

Figure 1: Sample A - $n(^{238}Pu)/n(^{239}Pu)$

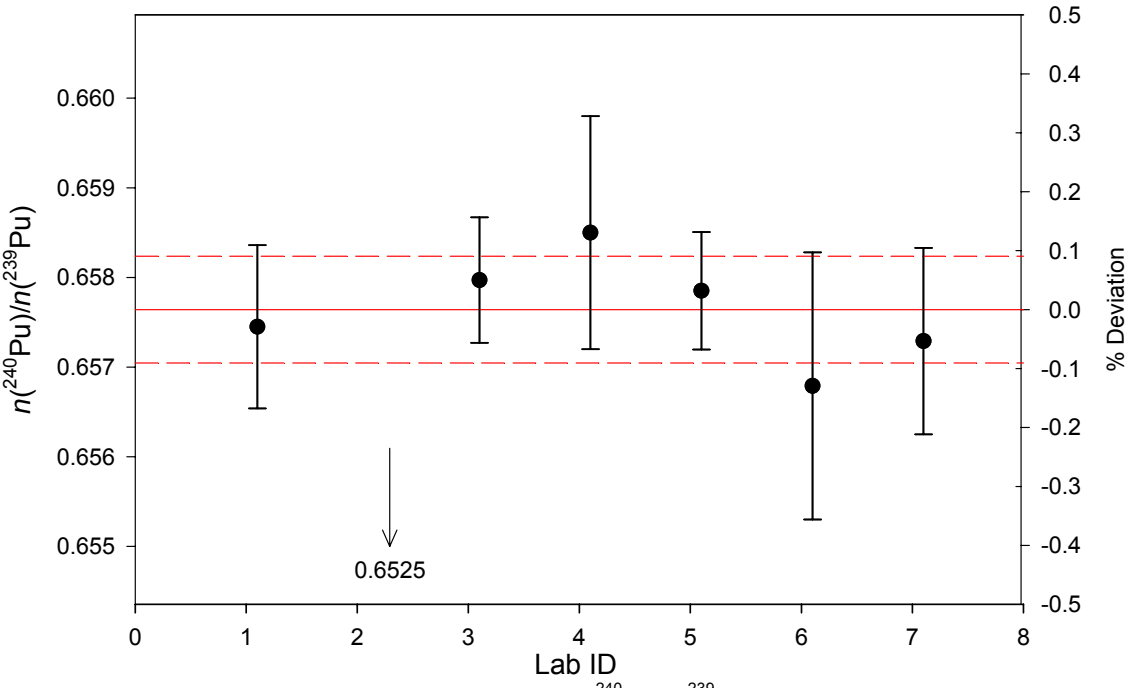

Figure 2: Sample A - $n(^{240}Pu)/n(^{239}Pu)$

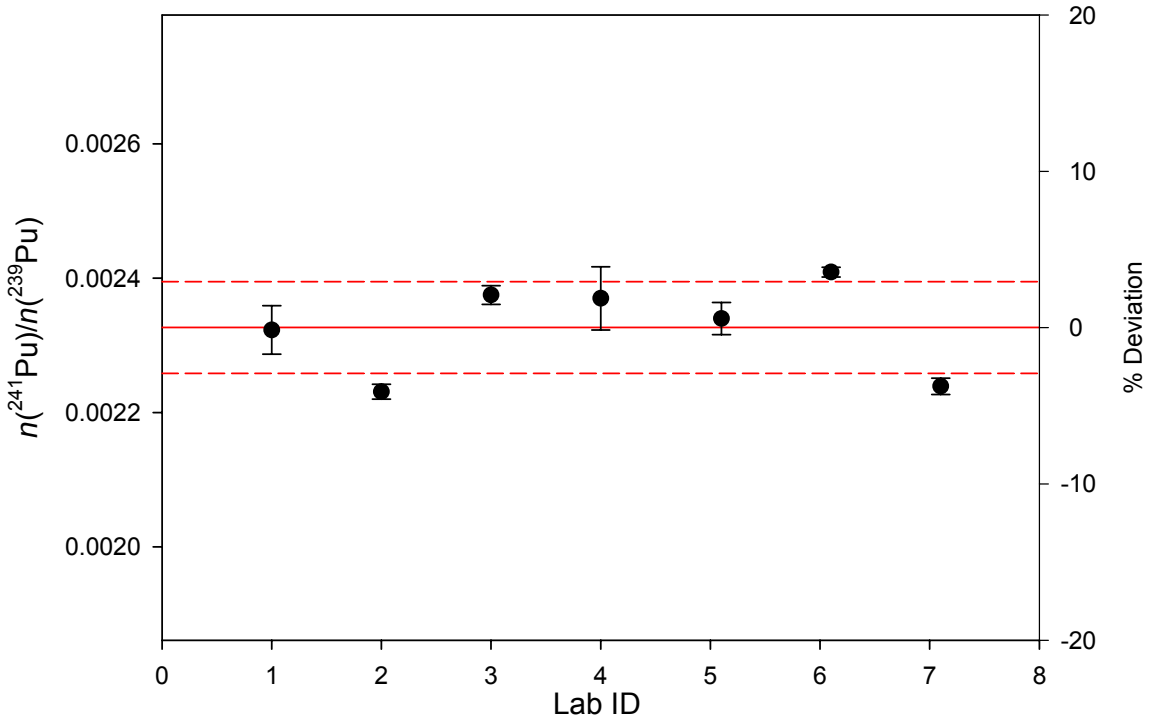

Figure 3: Sample A - $n(^{241}Pu)/n(^{239}Pu)$

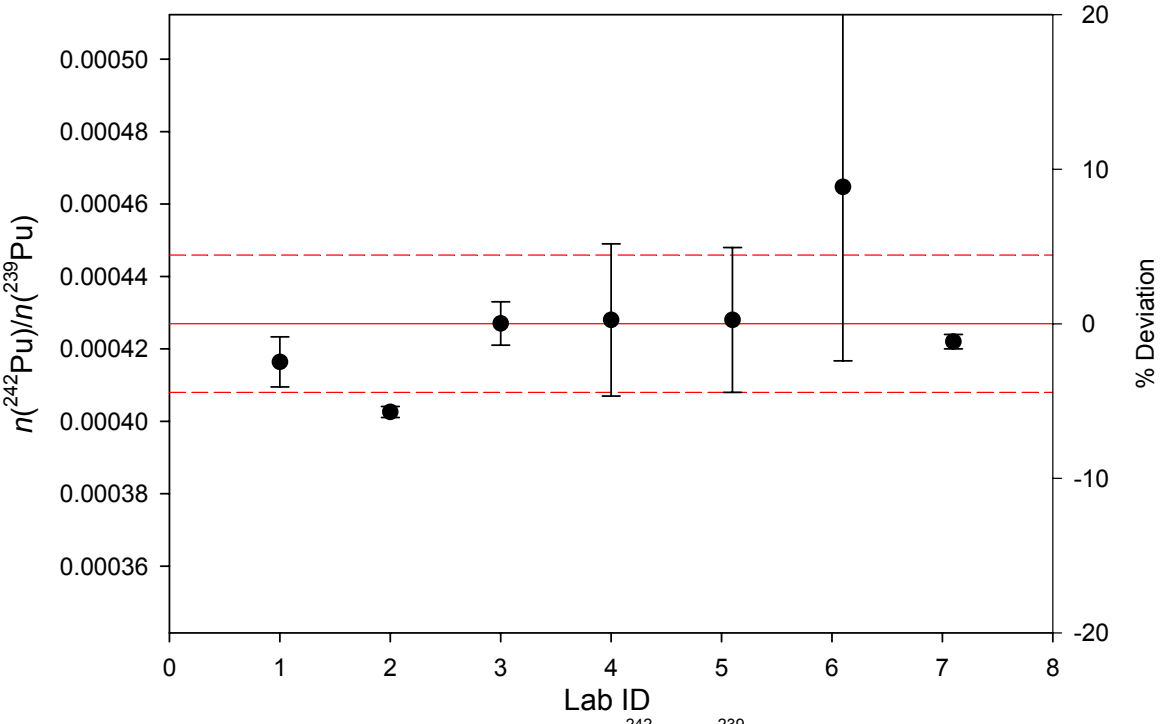

Figure 4: Sample A - $n(^{242}Pu)/n(^{239}Pu)$

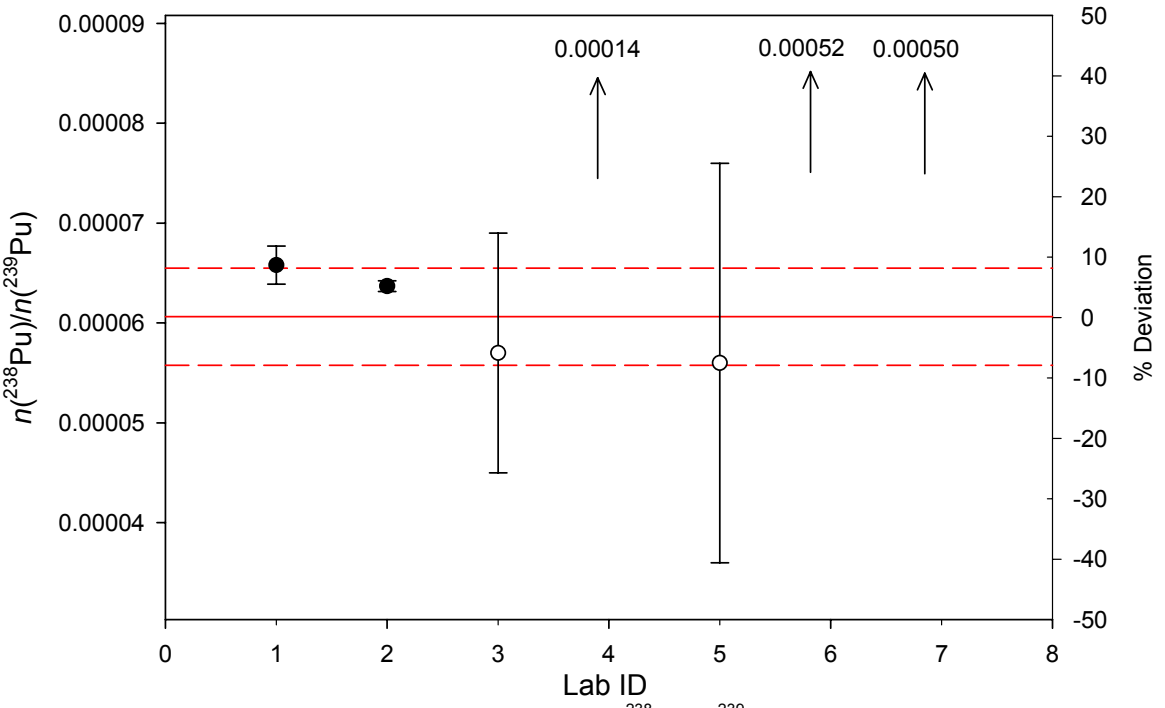

Figure 5: Sample B - $n(^{238}Pu)/n(^{239}Pu)$

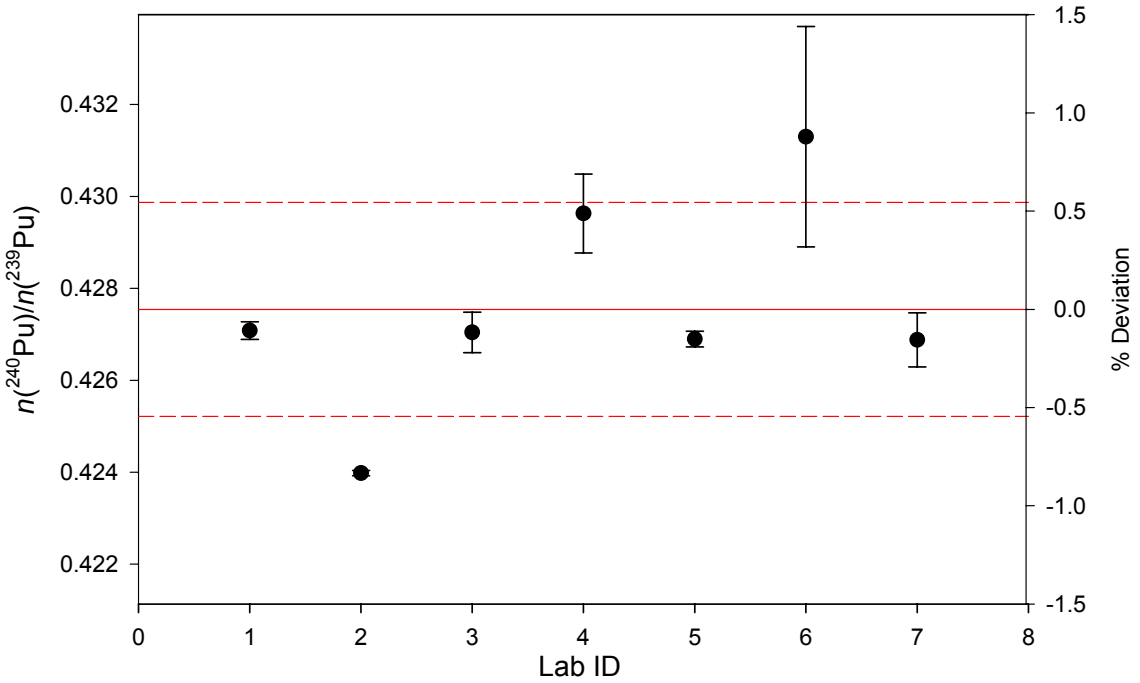

Figure 6: Sample B - $n(^{240}Pu)/n(^{239}Pu)$

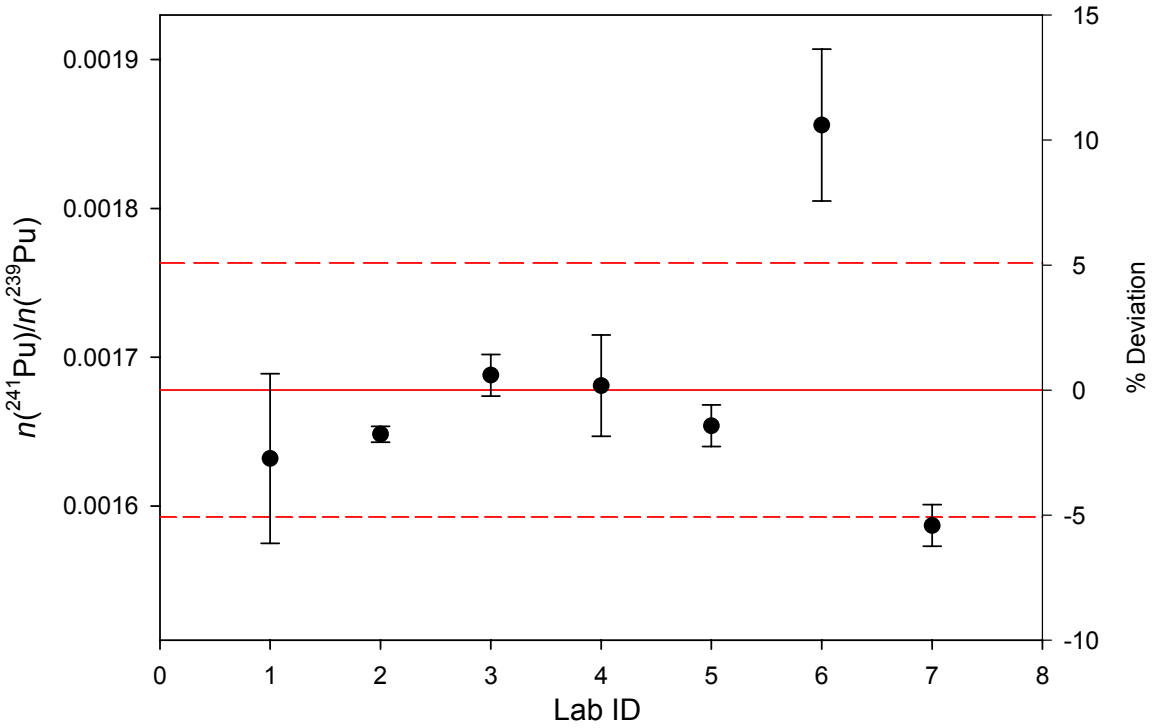

Figure 7: Sample B - $n(^{241}Pu)/n(^{239}Pu)$

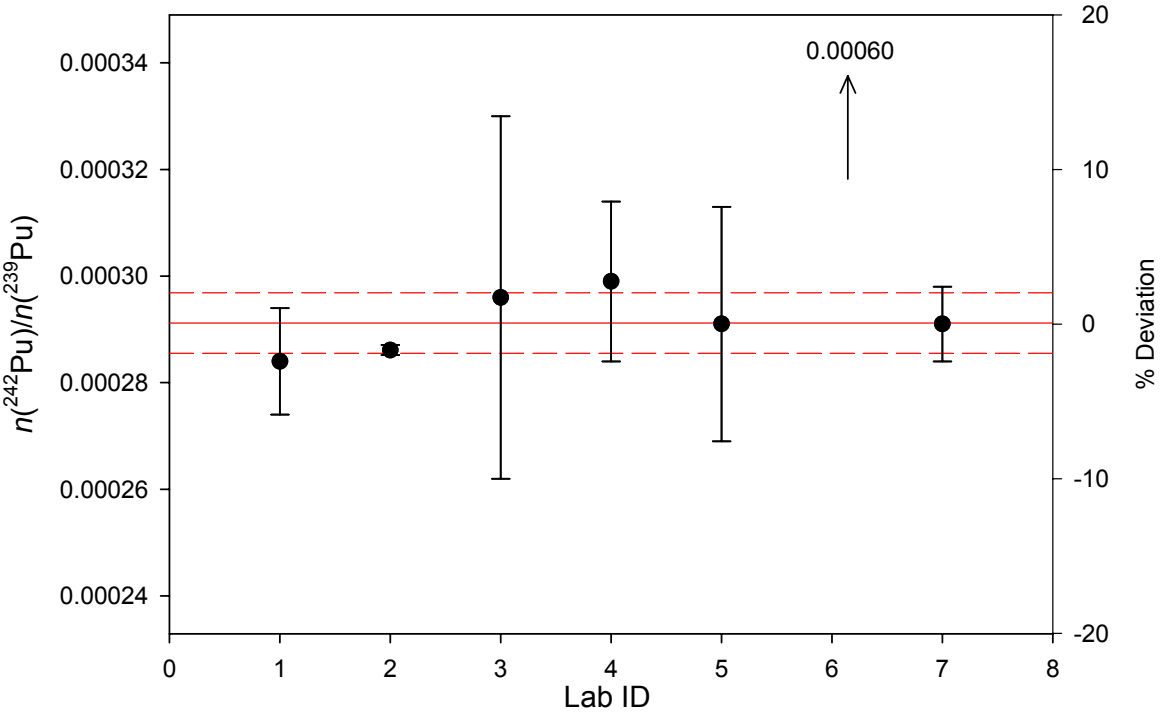

Figure 8: Sample B - $n(^{242}Pu)/n(^{239}Pu)$

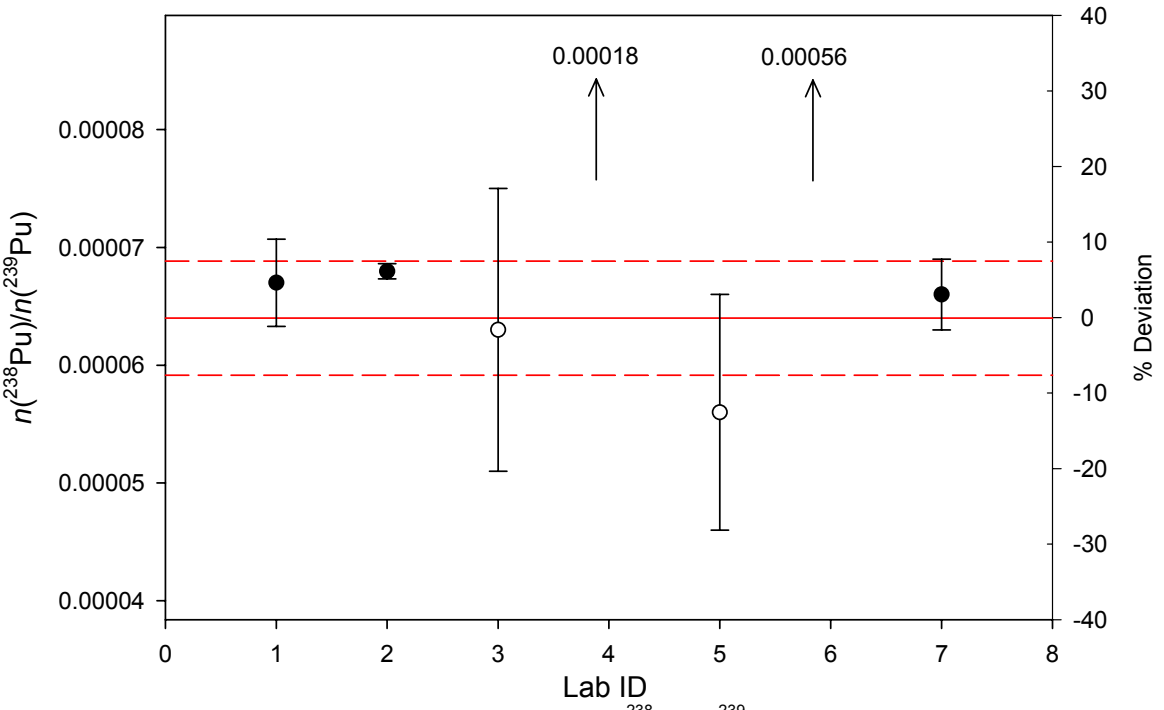

Figure 9: Sample C - $n(^{238}Pu)/n(^{239}Pu)$

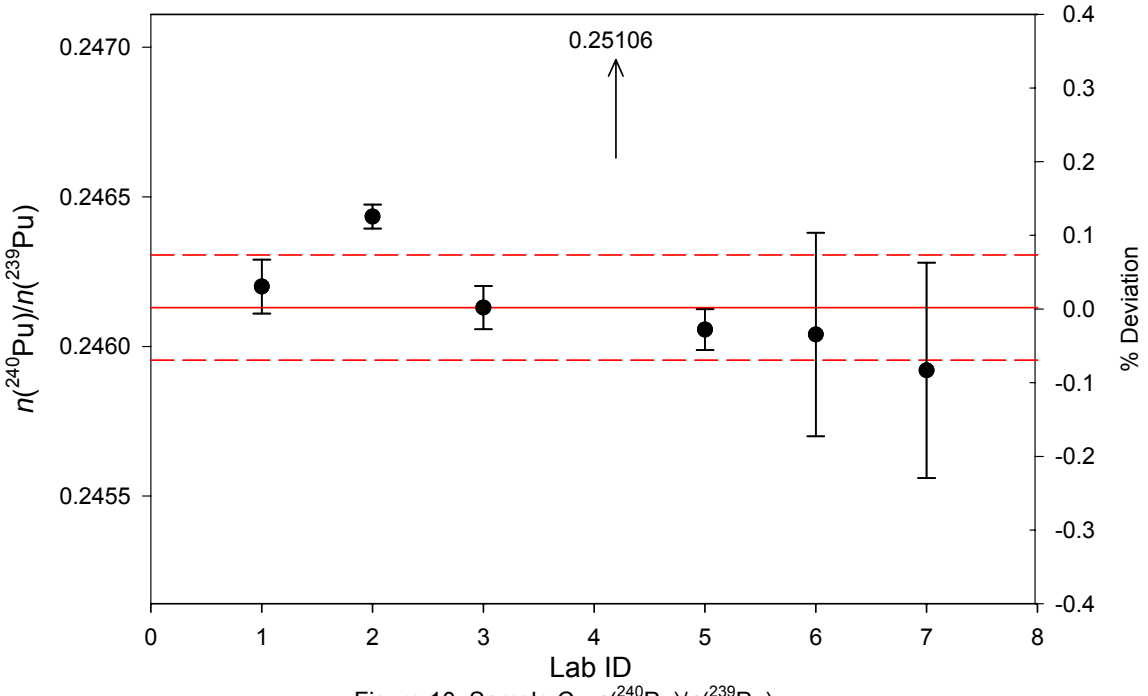

Figure 10: Sample C - $n(^{240}Pu)/n(^{239}Pu)$

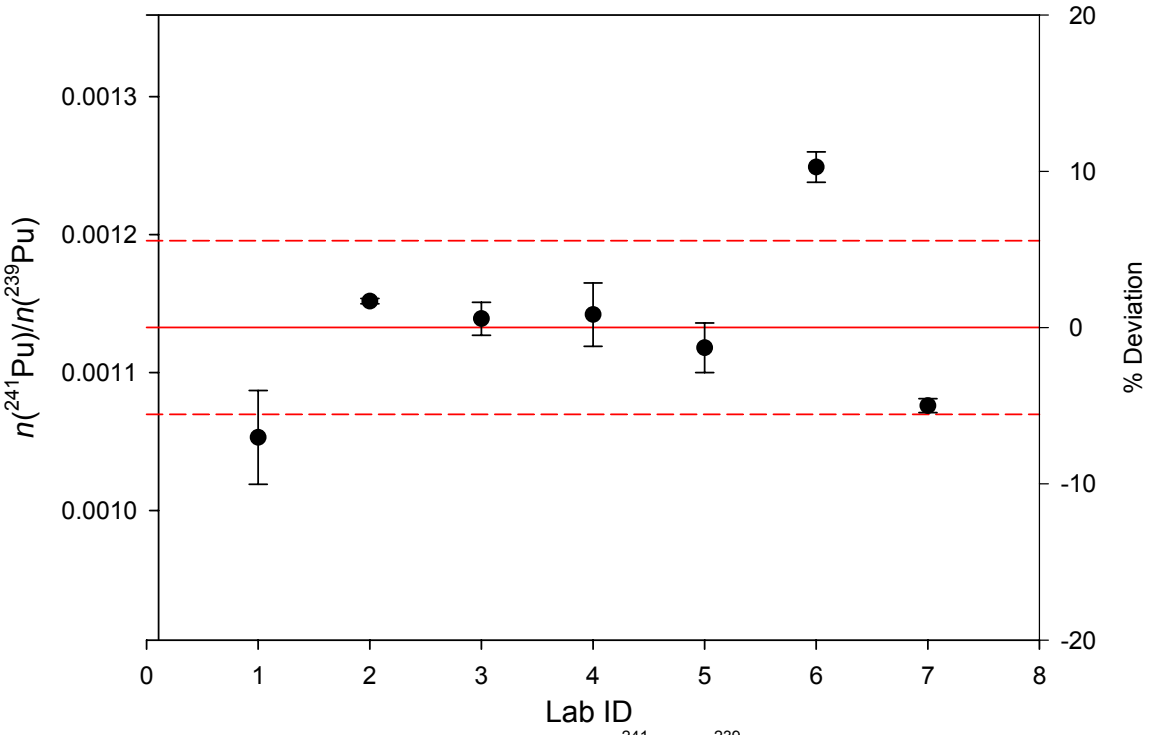

Figure 11: Sample C - $n(^{241}Pu)/n(^{239}Pu)$

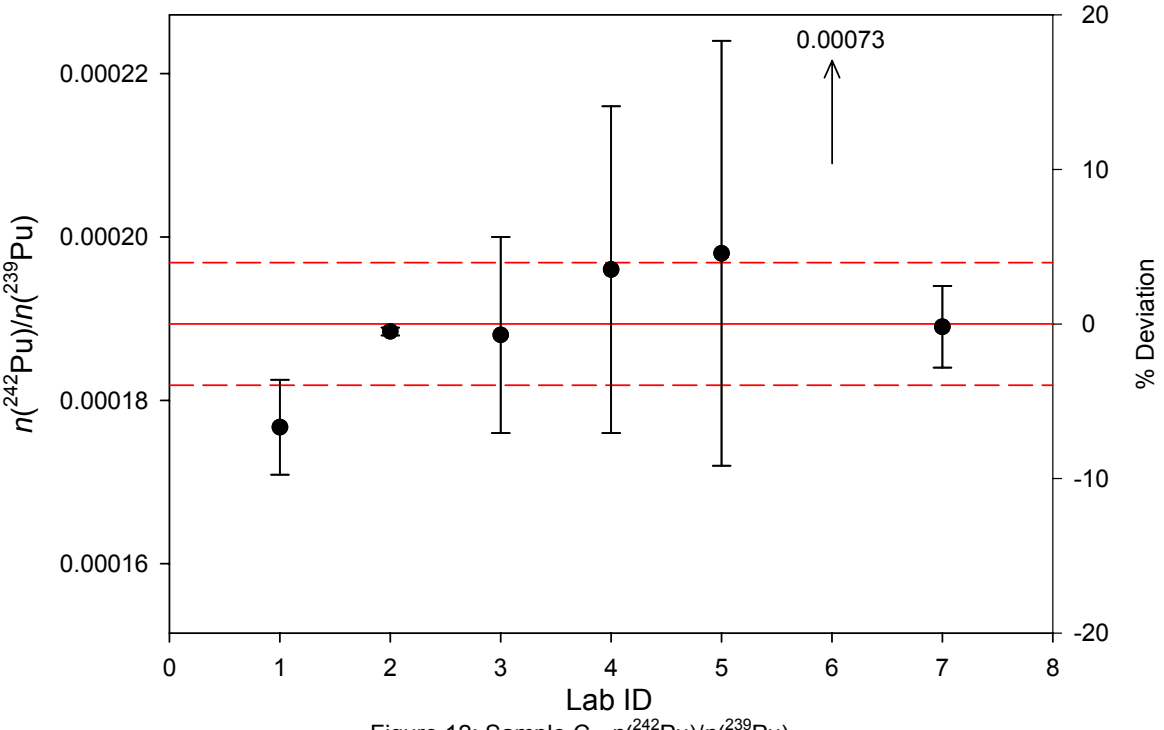

Figure 12: Sample C - $n(^{242}Pu)/n(^{239}Pu)$

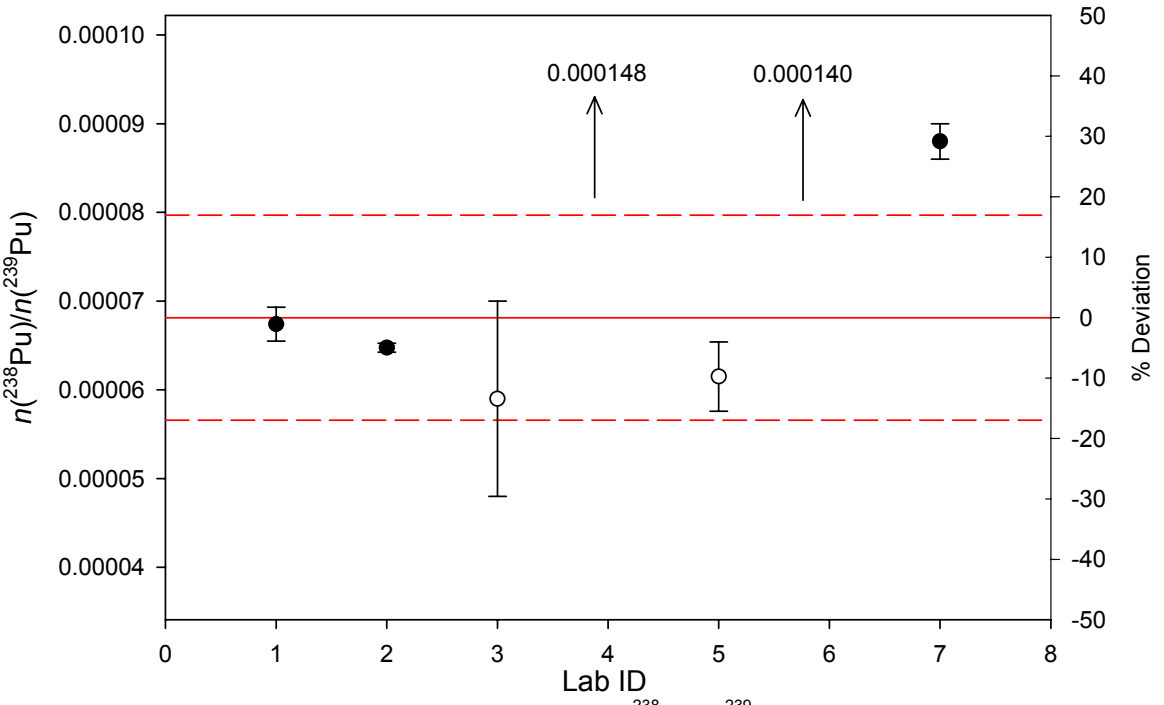

Figure 13: Sample D - $n(^{238}Pu)/n(^{239}Pu)$

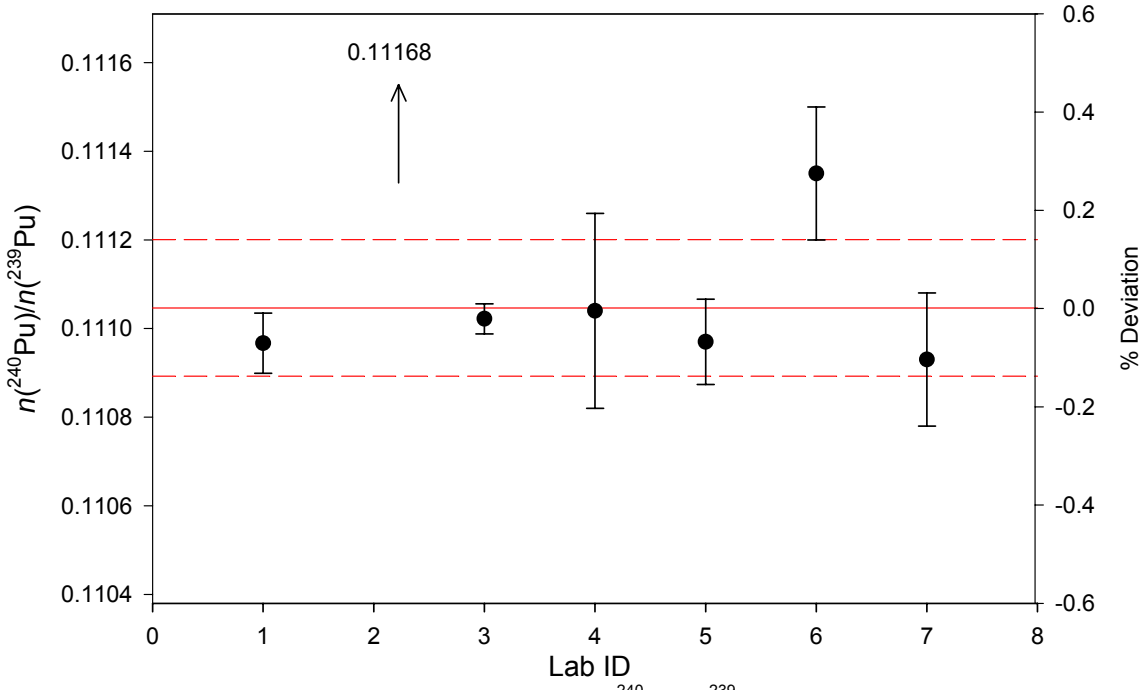

Figure 14: Sample D - $n(^{240}Pu)/n(^{239}Pu)$

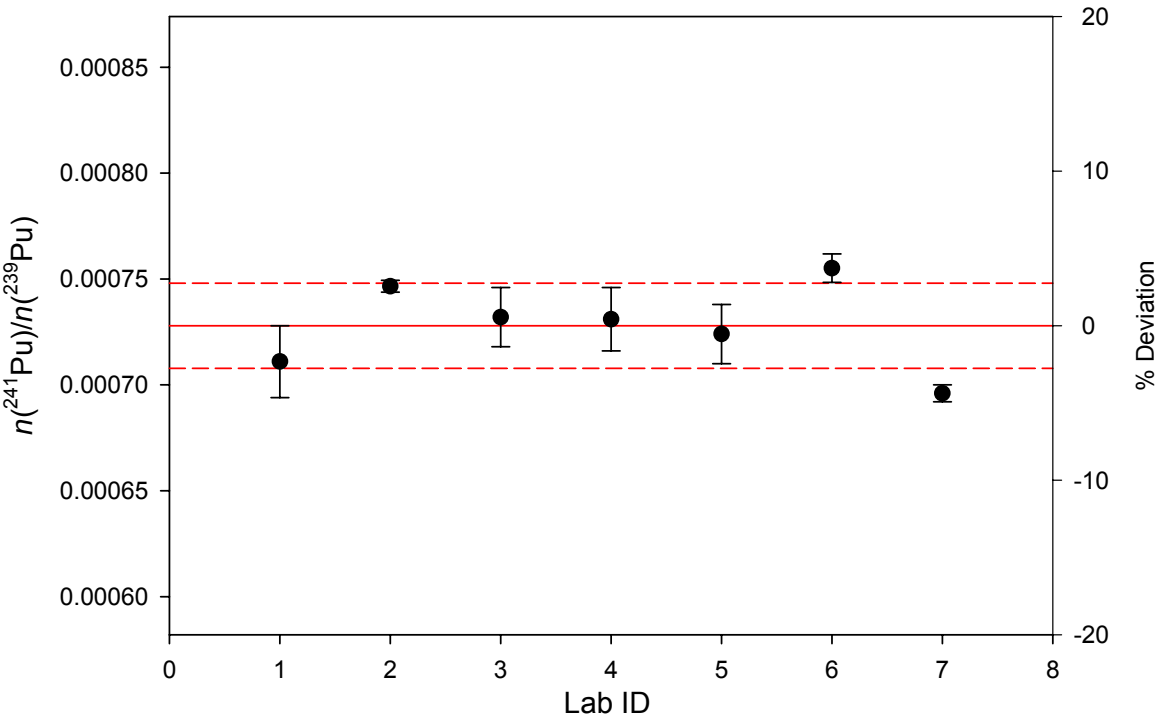

Figure 15: Sample D - $n(^{241}Pu)/n(^{239}Pu)$

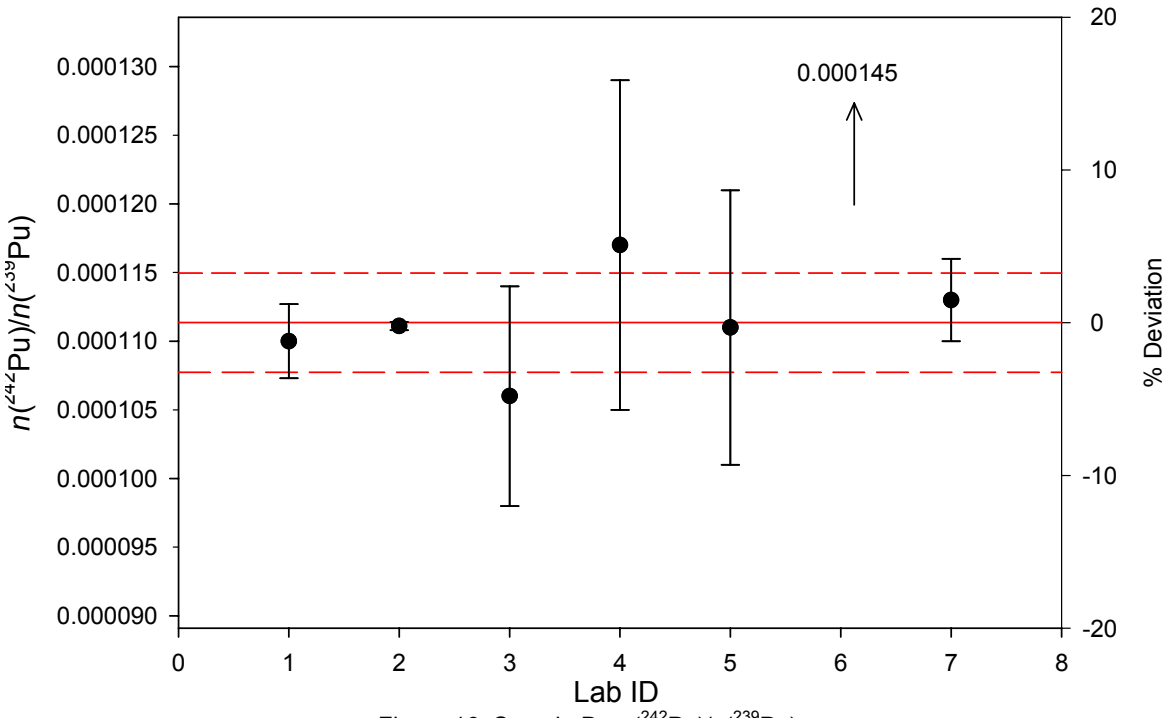

Figure 16: Sample D - $n(^{242}Pu)/n(^{239}Pu)$

Annex 1: Questionnaire

REIMEP-16: dried Pu nitrate

PARTICIPANT QUESTIONNAIRE

The purpose of this questionnaire is to enable the organiser of REIMEP-16 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. How many measurements of this type does your laboratory routinely carry out per year?

   ☐ < 25 ☐ 25-50 ☐ > 50

2. Was the REIMEP sample analysed by the same analyst who usually performs such analyses ?

   ☐ YES ☐ NO

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

.
.

3. Was the REIMEP-16 sample treated according to the same analytical procedure as routinely used for this sample type ?

   ☐ YES ☐ NO

   If "NO" why not?

.
.

4. Does your laboratory routinely use certified reference materials for the measruement of Pu isotopic ratios(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)

.
.

5. 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

.
.

6. Is your laboratory using a quality management system ?

☐ YES ☐ NO

If "YES", please state which system :
☐ EN 45000series / ISO 25 ☐ ISO 9000series ☐ ISO 17025
other (e.g. CEN, GLP, EPA, TQM, national standards), specify:

.
.

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

☐ YES certified ☐ YES accredited ☐ YES authorised ☐ NO

8. Please describe briefly your sample treatment:

.
.
.

9. Please describe briefly your measurement procedure:

Instrument used:

.
.

Special measurement conditions, if applicable:

.
.

Other details:

.
.

10. 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. If you measured ^{241}Am, please describe the technique used: .

12. 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

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

☐ YES ☐ NO

14. If "YES", what did you report as an uncertainties?

☐ standard uncertainties
☐ expanded uncertainties with a coverage factor of k=_____

15. If "NO", how were the measurement uncertainties evaluated?

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

☐ YES ☐ NO

17. Who filled in the questionnaire ?

☐ the analyst ☐ the laboratory supervisor

18. Who filled in the report form ?

☐ the analyst ☐ the laboratory supervisor

19. Would you be interested in participating in future REIMEP rounds?

☐ YES ☐ NO

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

European Commission

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