DOI: 10.7795/810.20251106

D6: Inter-laboratory comparison report, describing sample preparation requirements, sample introduction methods, and uncertainty budgets

Acknowledgement:

The project 21GRD09 MetroPOEM has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

Funder name: European Partnership on Metrology

Funder ID: 10.13039/100019599

Grant number: 21GRD09 MetroPOEM

Originally published at:
10.1016/j.apradiso.2025.112204

21GRD09 MetroPOEM

D6: Inter-laboratory comparison report, describing sample preparation requirements, sample introduction methods, and uncertainty budgets.

Organisation name of the lead participant for the deliverable: CEA

List of Authors: Lucille Chambon (CEA), Marina Amaral Saraiva, (CEA), Soumya Gupta (CEA), Hélène Isnard (CEA), Simon Jerome (NMBU), Aaron Lehnert (LUH), Andrius Puzas (FTMC), Susanna Salminen-Paatero (UH), Marcus Christl (ETHZ), José Corcho (SpiezLab), Janine Eberhardt (PTB), Lukas Flierl (PTB), Karin Hain (UNIVIE), Jelena Krneta Nikolic (VINS), Sonia North (Agilent), Habacuc Perez-Tribouiller (ETHZ), Sophie Pichler (AGES), Stefan Röllin (SpiezLab), Marko Štrok (JSI), Sinikka Virtanen (STUK), Stella Winkler (HZDR)

Due date of the deliverable: 30/09/2025

Actual submission date of the deliverable: 24.09.2025

Glossary

AMS: Accelerator Mass Spectrometry

ICP-MS: Inductively coupled plasma mass spectrometry

ICP-QMS: Single quadrupole inductively coupled plasma mass spectrometry

ICP-MS/MS: Inductively coupled plasma tandem mass spectrometry

MC-ICP-MS: Multi-collector inductively coupled plasma mass spectrometry

ICP-SF-MS: Sector field Inductively coupled plasma mass spectrometry

ILC: Interlaboratory comparison

RM: Reference materials

RN: radionuclide

Table of contents

1 Summary

The interlaboratory comparison (ILC) described in this document was performed in the framework of Work package 3 of the MetroPOEM project. Two traceable candidate reference materials (RM) were prepared by spiking a matrix with ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Am and ^{237}Np, and were measured by participants using mass spectrometry and radiometric techniques. For the liquid RM used in the liquid ILC, the matrix was natural seawater, while for the solid RM used in the solid ILC, the matrix was a synthetic sand obtained by a *sol-gel* process.

The measurands selected were the mass fraction of ^{238}U, ^{239}Pu, ^{241}Am and ^{237}Np, and the $^{234/238}$U, $^{235/238}$U, $^{236/238}$U and $^{239/240}$Pu isotope ratios. The liquid comparison involved 11 participants, who produced a total of 83 results. The solid comparison involved 11 participants who produced a total of 79 results.

This report presents the characteristics of the liquid and solid RM used, and the assigned values for each measurand, the results of the participants and their analysis following statistical criteria and eventually the comparison of the experimental procedures of the participants.

This report will be updated after publication, to include additional results from participants who did not have time to submit, and the analyses and comments will be updated accordingly.

2 Introduction

Measuring pollutants, particularly radioactive ones, is necessary for protecting human health and the environment. Scientists, authorities, and agencies need valid measurement data for assessing pollution levels in the environment and humans, enforce safety standards, and respond effectively to any contamination events.

Even low concentrations of radioactive pollutants in the environment, food and drinking water can pose long-term health risks. Therefore, especially in low-level measurements, it is crucial to maintain and improve the analytical accuracy and quality control for obtaining reliable data. To reach this goal, low-level and traceable radionuclide standards and reference materials (RM) are needed. Novel reference materials containing multiple radionuclides (RN) in low and traceable activity levels can provide more consistent quality assurance data, resulting in more valid measurement data for real samples. Introduction of the low-level and traceable radionuclide standards and reference materials further supports scientific research, regulatory compliance, and international collaboration in monitoring radioactivity in environment. These benefits from the reference materials can be gained via interlaboratory comparisons and in-house method tests.

The aim of this interlaboratory comparison (ILC) was to compare the performances of different mass spectrometer and radiometric detection techniques. Two reference materials, liquid and solid, were prepared from well-characterized raw materials and radioactivity standard solutions with low activity concentrations. The mass spectrometric techniques used in this intercomparison were ICP-QMS (quadrupole inductive coupled plasma-mass spectrometry), ICP-MS/MS (inductively coupled plasma tandem mass spectrometry), ICP-SFMS (sector field inductively coupled plasma mass spectrometry), MC-ICP-MS (multicollector inductively coupled plasma-mass spectrometry) and AMS (accelerator mass spectrometry). Gamma and alpha spectrometry were used as radiometric detection techniques for the reference materials.

Thirteen participants received liquid reference materials samples, and the same number received solid reference material sample, to participate in the ILC. Out of the thirteen, eleven results were received for both ILC. Laboratories participating in the liquid ILC measured as many as 14 measurands, for a total of 83 results. For the solid ILC, participants measured as many as 14 measurands, for a total of 79 results.

For both ILCs, each participant was identified using the same confidential code, corresponding to the code of the solid reference material bottle received. This code allows them to compare their results to those of the other participants. All results are presented with their standard uncertainties, using a coverage factor of $k = 1$, which corresponds to a confidence level of around 68 %.

The list of the laboratories that received liquid or solid sample is given in Appendix 1. The partners of Work package 3 are committed to continue updating this deliverable with more results, and to expand upon the analysis and comments.

The results provided by the participants were compared to assigned values, obtained by the measurement of the solutions used to spike the matrix, by a single laboratory (CEA/LANIE), following the recommendations of ISO 17043 [5].

3 Liquid RM ILC

3.1 Production and characterisation of the liquid RM

The following sections describe the main characteristics of the produced liquid RM. The details of the production of this material, and the scheme for the evaluation of the homogeneity and stability are presented in the Deliverable 5 of the project. The main outcomes are summarised here.

3.1.1 Scheme for the production of the liquid RM

The liquid RM was obtained by spiking 40 L of seawater sampled in the North Sea by Helmholtz-Zentrum Hereon in mid-May 2023. More details are given in the stable isotope CRM certification report. The spiking solutions were selected and characterised with mass spectrometry, gamma-ray spectrometry and alpha spectrometry. They were first mixed to obtain a multi-RN spiking mixture, which was also characterised using mass spectrometry (Figure 1). All the dilutions were performed with calibrated and accurate balances, which allowed to derive the assigned values of the mass fractions of each radionuclide gravimetrically, and by direct measurement.

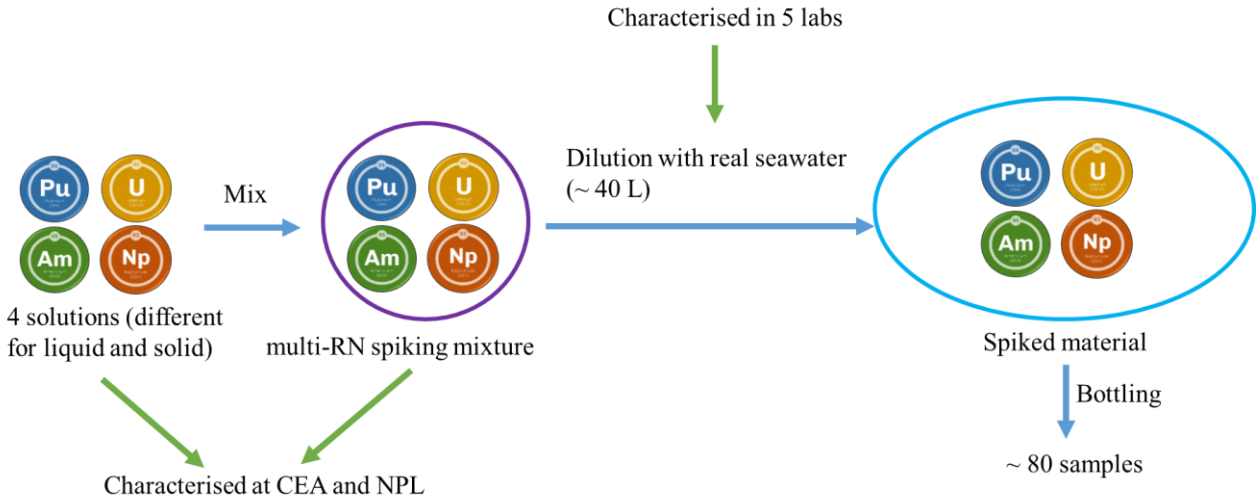

Figure 1: Illustration of the 2-step spiking procedure selected to prepare the candidate liquid RM.

3.1.2 Homogeneity assessment – liquid RM

The homogeneity of the liquid RM was assessed by measuring ^{241}Am by gamma spectrometry, and ^{238}U and ^{239}Pu by mass spectrometry. More details concerning the homogeneity study are published in [1], and follow the guidelines of ISO 33405 [3].

Specific samples were prepared for each measurement, from the same bottles n° 8, n° 14, n° 34 and n° 71. The numbers corresponded to the filling order, and the bottles were chosen to span the whole batch, to possibly identify a bias due to the filling order.

Since mass spectrometry measurements require to take sub-samples from units of the reference material, the homogeneity within bottles was assessed, as well as the homogeneity between bottles.

For gamma spectrometry, two different sample sizes were measured: 50 mL and 15 mL, while for mass spectrometry, 5 mL samples were used (Figure 2). The gamma spectrometry samples did not undergo any chemical separation, concentration or spiking steps, while the mass spectrometry ones were of different/other isotopes, ^{235}U for U (U970, a home-made standard prepared at CEA and qualified by reverse isotope dilution) and ^{242}Pu for Pu (IRMM-049e), to apply the isotope dilution technique. Furthermore, the U and Pu fractions were separated using UTEVA (Triskem international) resin columns. MC-ICP-MS was used for the measurements.

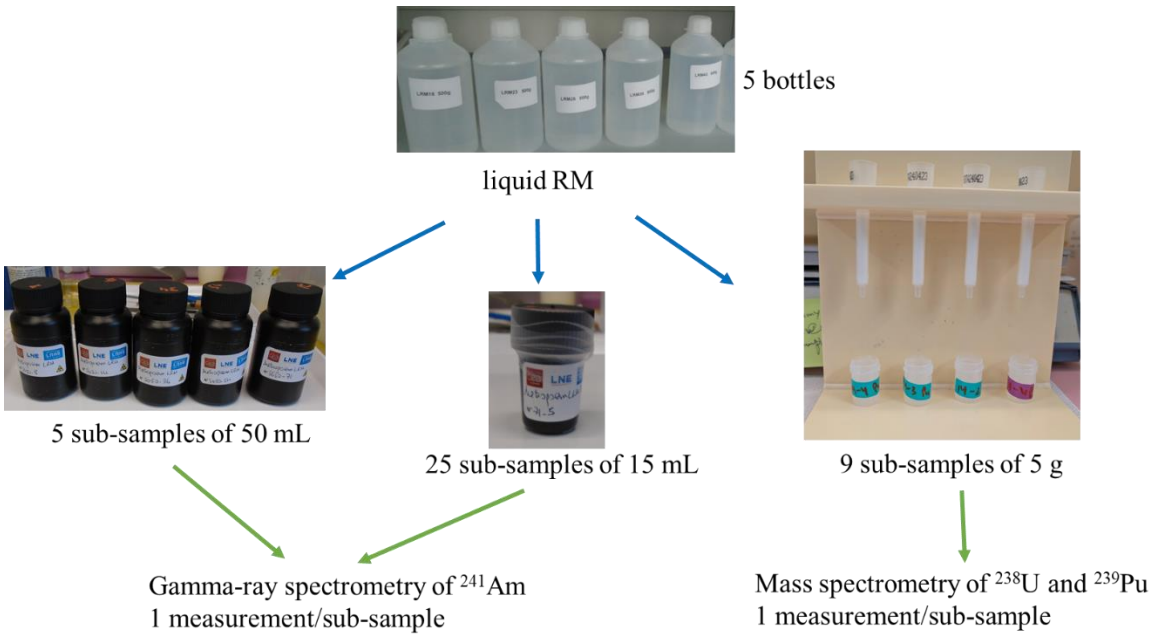

Figure 2. Schematics of the samples prepared to assess the homogeneity of the liquid RM

The results of the mass spectrometry measurements (three 5 mL sub-samples from three bottles), for ^{238}U and ^{239}Pu, and of the gamma-ray spectrometry of ^{241}Am (five 50 mL samples and five 15 mL sub-samples from five bottles) are presented in Figure 3.

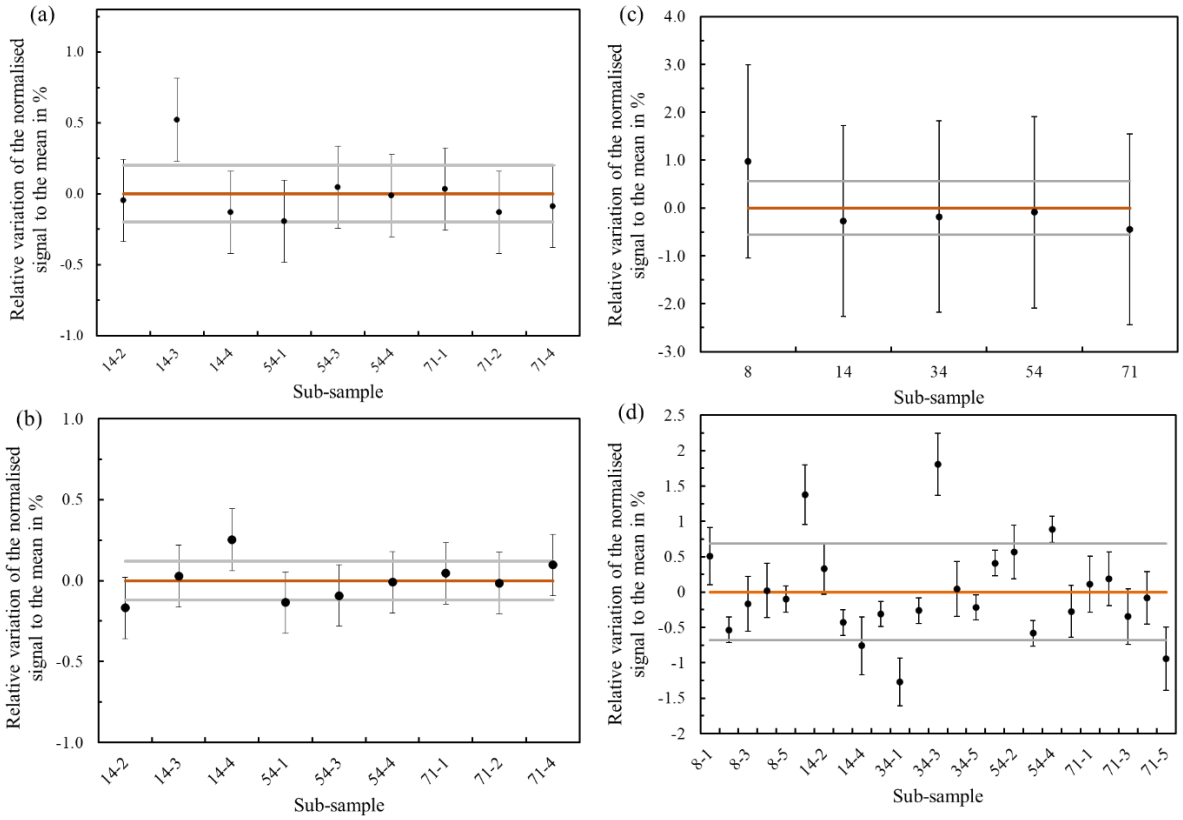

Figure 3. Relative variation of the mass spectrometry measurements of ^{238}U (a) and ^{239}Pu (b) to the average of the results, for the nine sub-samples of 5 mL of the liquid RM, and relative variation of the gamma-ray spectrometry measurements of ^{241}Am for (c) five sub-samples of 50 mL and (d) twenty-five sub-samples of 15 mL. The bars represent the uncertainty of each individual measurement, at k = 1. The orange line represents the average of the values of the sub-samples, and the grey lines represent the standard deviation among the values of the sub-samples.

For ^{238}U, sub-sample 14-3 was flagged as suspicious by a Grubbs test [4], and no outlier was detected for the other radionuclides, using the same test. No upward or downward trend was observed with the filling order of the bottles.

A one-way analysis of variance (ANOVA) was performed to compare the variance within-bottles to the variance between-bottles, for the mass spectrometry measurements of the 5 mL sub-samples and the gamma-ray spectrometry of the 15 mL sub-samples.

Table 1. Summary of the between-bottle variance and within-bottle variance for ^{238}U, ^{239}Pu and ^{241}Am, for the liquid RM

Radionuclide	Technique	Size of subsample in ml	Between-bottle variance s_{bb} in %	Within-bottle variance s_{wb} in %	Uncertainty of measurement, at k = 1 in %
^{238}U	MC-ICP-MS	5	0	0.2	0.29
^{239}Pu	MC-ICP-MS	5	0	0.1	0.19
^{241}Am	Gamma-ray	15	0	0.7	0.2 to 0.5

For all the radionuclides, the between-bottle variance was negligible, and the within-bottle variance was below 1 %.

3.1.3 Stability assessment – liquid RM

The stability monitoring was performed by gamma-ray spectrometry, on ^{241}Am, with sub-samples of 15 mL. The measurements were performed in the same manner as the homogeneity assessment, and the results were calculated at the same reference date (2025-01-01). The short-term and long-term stability measurements were performed in one run, four months after the homogeneity measurements.

The short-term stability study aims to recreate extreme conditions that may happen during transport, over a short period of time. Three bottles (n° 18, n° 43 and n° 58) were selected and placed at 4 °C, 20 °C and 40 °C, for one week. Then, three sub-samples of 15 mL were prepared from each bottle (Figure 4).

The long-term stability study was performed at 4 °C and 20 °C, on bottles n° 23 and n° 28, to test normal storage conditions. Only the first set of measurement, after four months, is presented here, but additional measurements will be performed after eight and twelve months. Three sub-samples were also taken from each long-term stability bottle (Figure 4).

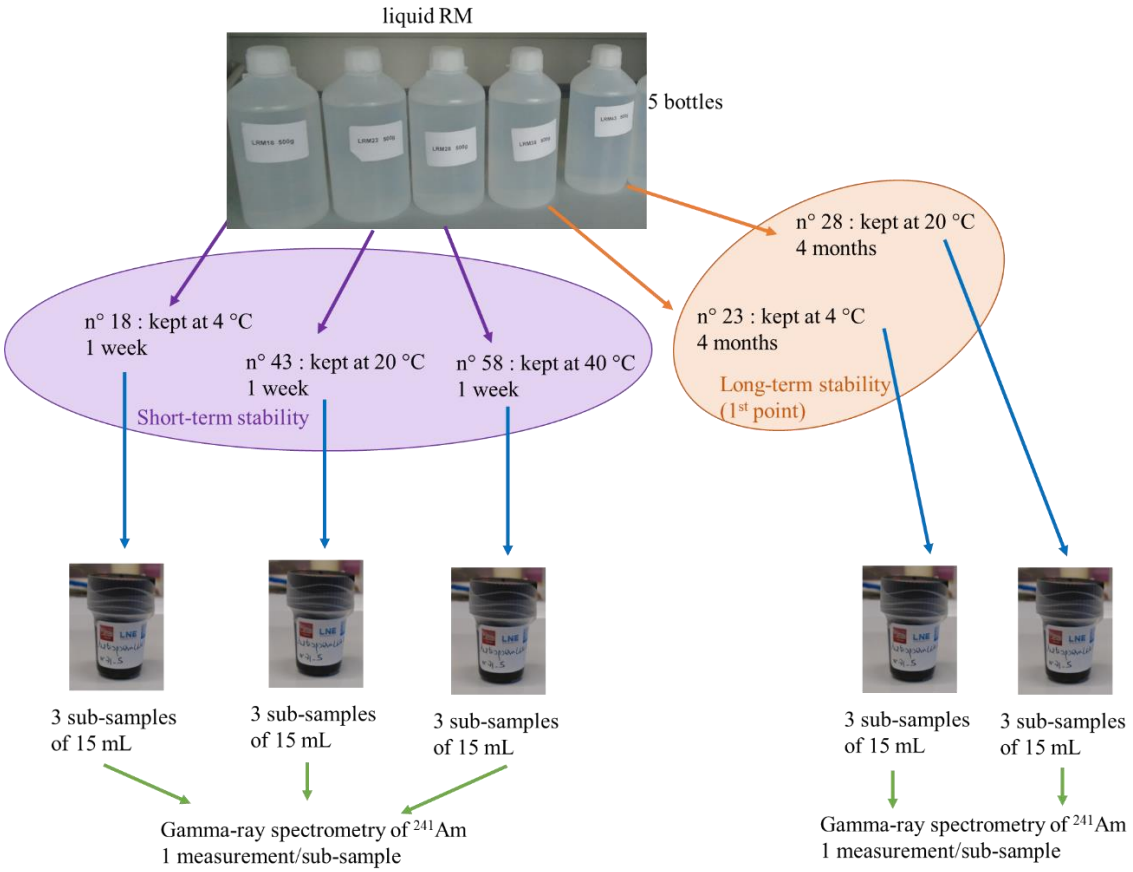

Figure 4. Scheme for the assessment of the short-term and long-term stability study for the liquid reference material.

The gamma-ray spectrometry instrument used was not calibrated for the 15 mL samples, however, the mass corrected signal (in counts/s/g) can be compared for each sample. The average of the measurements of all the sub-samples corresponding to a test condition was calculated and compared to the average of the measurements initially performed for the homogeneity assessment (Figure 5).

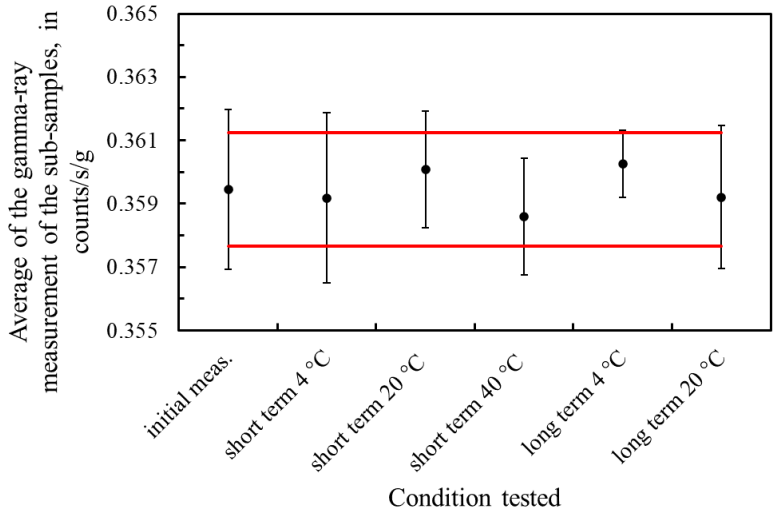

Figure 5. Comparison between the average of the measurements of the sub-samples for the initial measurement, for homogeneity (twenty-five sub-samples), for the short-term stability samples kept at 4 °C, 20 °C and 40 °C, and for the long-term stability samples kept at 4 °C and 20 °C (3 sub-samples each). The bars represent the standard deviation among the sub-samples, and the red lines represent the uncertainty of the gamma-ray spectrometry measurement.

The results of the gamma-ray spectrometry measurement of ^{241}Am for all the stability conditions tested are very similar. The overall standard deviation between the conditions is very low, at 0.2 %.

The dispersion of the sub-samples was comparable for all the stability conditions tested, from 0.3 % to 0.8 %, and was also similar to the overall dispersion obtained during the homogeneity study (0.7 %).

As a result, no significant instability was observed for the liquid reference material, and the contribution of the stability to the overall uncertainty is null.

3.1.4 Assigned values – liquid RM

The assigned values were determined by characterisation by a single laboratory, as recommended in the case of proficiency testing with a small number of participants [5]. The *Laboratoire de développement Analytique Nucléaire Isotopique et Elementaire* (LANIE), at CEA, was selected.

For each radionuclide except for ^{237}Np, “direct” measurements were performed on the liquid reference material, using MC-ICP-MS, and the isotope dilution method with a step of chemical separation.

Furthermore, the value for each radionuclide can also be derived gravimetrically from the measurement of the individual starting solutions (U, Pu, Am and Np), and from the “multi-RN” mixture, taking into account the radionuclides introduced by the raw seawater (mainly U isotopes).

The measurements of the “multi-RN” mixture were performed by multi-collector ICP-MS and isotope dilution. The measurements of the starting U solution were performed by TIMS, using isotope dilution. The Np solution was characterised by multi-collector ICP-MS, using a calibration curve. The Pu solution was measured by alpha spectrometry, without any chemical separation, and contained ^{241}Am as a decay product. The ^{241}Am content in the Am solution was characterised by ionisation chamber, and the ^{237}Np content (decay product) in the Am solution was characterised by multi-collector ICP-MS, using a calibration curve.

All results were reported at the reference date of the 1st of January 2025, and compared.

*Table 2. Comparison between the property values determined from the measurement of the starting solutions, of the multi-RN spiking mixture and from direct measurement, for the liquid reference material. The uncertainties (shown in parentheses) are presented at k = 1. *Value obtained from a mass spectrometry measurement, **value obtained from an alpha spectrometry measurement; *** value obtained from a gamma spectrometry measurement.*

Measurand	Value obtained from starting solutions + gravimetric dilutions, in µg/g	Value obtained from multi-RN spiking mixture + gravimetric dilutions, in µg/g	Value obtained by direct measurement, in µg/g	Comment
$w(^{234}U)$	2.006 (12) E-06*	2.007 (54) E-06*	2.008 (41) E-06*	3 meas. compatible $k = 1$
$w(^{235}U)$	2.648 (11) E-04*	2.642 (13) E-04*	2.642 (8) E-04*	3 meas. compatible $k = 1$
$w(^{236}U)$	Not detected*	2.42 (12) E-07*	2.41 (12) E-07*	2 meas. compatible $k = 1$
$w(^{237}Np)$	4.96 (27) E-04*	4.99 (69) E-04*	Not performed	2 meas. compatible $k = 1$
$w(^{238}U)$	3.69 (13)E-2*	3.673 (18)E-2*	3.670 (11)E-2*	3 meas. compatible $k = 1$
$w(^{239}Pu)$	6.102 (80) E-04**	6.443 (20) E-04*	6.436 (25) E-04*	Mix/ direct compatible $k = 1$; non compatible with starting sol.
$w(^{240}Pu)$	5.939 (8) E-05**	6.264 (19) E-05*	6.290 (65) E-05*	Mix/ direct compatible $k = 2$; non compatible with starting sol.
$w(^{241}Am)$	8.701 (50) E-05**	8.597 (86) E-05*	8.85 (18) E-05*	3 meas. compatible $k = 2$

For the mass fractions of ^{234}U, ^{235}U, ^{237}Np, ^{238}U and ^{241}Am, all the measurements performed agreed, within uncertainties (Table 2). The mass fraction of ^{236}U was below the detection limit in the starting solution, while it was easily detected in the multi-RN spiking mixture and the liquid reference material. It is likely that this radionuclide did not come from the U solution, but rather the Pu solution, due to the decay of ^{240}Pu. Due to time constraints, the mass fraction of ^{236}U in the Pu solution could not be measured.

The results of the mass fractions of ^{239}Pu and ^{240}Pu agreed between the multi-RN spiking mixture and the direct measurement, but the values expected from the concentrations of the starting solutions were lower. It is possible that some ^{239}Pu and ^{240}Pu were present in another solution (for example ^{241}Am and ^{237}Np). Due to time constraints investigation could not be done to confirm this hypothesis.

Since the measurement of the multi-RN spiking mixture is the most complete dataset, these values were used as assigned values.

The uncertainty of the assigned value for each mass fraction, and for the isotopic ratios of interest depends on the uncertainty of the measurement performed (on the final liquid RM, on the multi-RN spiking mixture or on the starting solutions), but also on the homogeneity and stability of the reference material. In fact, it is possible that the preparation steps (dilution, mixing) induce a repartition of the radionuclides which is not perfectly homogeneous. Furthermore, the reference material might age and the concentration of the radionuclides of interest might vary over time. It is important for reference materials producers to evaluate the differences between and within the units produced (homogeneity), and to follow several units over time (short term and long-term stability). If significant differences are observed, the reference material might still be perfectly useful to users, however the uncertainty of the assigned values must be corrected. It is common to increase the uncertainty of an assigned value using homogeneity and stability contributions [3]:

$$u_{\mathrm{RM}}^2 = u_{\mathrm{char}}^2 + u_{\mathrm{bb}}^2 + u_{\mathrm{wb}}^2 + u_{\mathrm{st}}^2 + u_{\mathrm{lt}}^2$$

Where:

u_{char} is the uncertainty of the measurement used to characterise one measurand of the reference material;

$u_{\mathrm{bb}}$is the uncertainty component coming from the difference between bottles of the reference material;

u_{wb} is the uncertainty component coming from the difference within bottles of the reference material;

u_{st} is the uncertainty component coming from the difference in the reference material, after a short period of time;

u_{lt} is the uncertainty component coming from the difference in the reference material, after a long period of time.

Following the discussions of sections 3.2.2 and 3.2.1, the stability contribution is negligible, and the uncertainty contributions for homogeneity are taken as the variances calculated with ANOVA. The homogeneity was assessed only on ^{238}U, ^{239}Pu and ^{241}Am, therefore the variances obtained for ^{238}U were applied to the other U isotopes, and the isotopic ratios, the variances obtained for ^{239}Pu were applied to ^{240}Pu and the isotope ratios, and the variances obtained for ^{241}Am were applied to ^{237}Np. The uncertainty components are summarised in Table 3.

Table 3. Assigned values and uncertainty components for the liquid RM.

Measurand	Assigned value in µg/g	u_{char} in %	u_{bb} in %	u_{wb} in %	u_{st} in %	u_{lt} in %	u_{RM} in %
$w(^{234}U)$	2.007E-06	2.7	0	0.2	0	0	2.7
$w(^{235}U)$	2.642E-04	0.5	0	0.2	0	0	0.5
$w(^{236}U)$	2.42E-07	5.0	0	0.2	0	0	5.0
$w(^{237}Np)$	4.993E-04	1.4	0	0.7	0	0	1.6
$w(^{238}U)$	3.673E-02	0.5	0	0.2	0	0	0.5
$w(^{239}Pu)$	6.443E-04	0.3	0	0.1	0	0	0.3
$w(^{240}Pu)$	6.264E-05	0.3	0	0.1	0	0	0.3
$w(^{241}Am)$	8.60E-05	1.0	0	0.7	0	0	1.2
Measurand	Assigned value in mol/mol	u_{char} in %	u_{bb} in %	u_{wb} in %	u_{st} in %	u_{lt} in %	u_{RM} in %
$R(^{234}U/^{238}U)$	5.56E-05	2.7	0	0.2	0	0	2.7
$R(^{235}U/^{238}U)$	7.286E-03	0.7	0	0.2	0	0	0.7
$R(^{236}U/^{238}U)$	6.65E-06	5.0	0	0.2	0	0	5.0
$R(^{239}Pu/^{240}Pu)$	9.681E-02	0.4	0	0.1	0	0	0.4

3.2 Comparison of participants' experimental procedures

3.2.1 Sample preparation

Different experimental procedures used by intercomparison participants in analysis of liquid RM are presented in Table 39, in Appendix 2. A summary is provided in Table 4. One laboratory (n° 25) measured the liquid RM directly after dilution, whereas other laboratories performed sample spiking with tracer isotopes, prior to radiochemical separation of analytes by co-precipitation, ion exchange or extraction chromatography.

The number of subsamples varied from 1 to 7 among the laboratories, and the sample mass from 0.05 g to 20 g. The dilution factors from 1:5 to 1:200 were used among those laboratories, who reported their dilution factors. Almost all laboratories used tracers or standard reference materials in the measurements, for controlling yield and for mass bias calculations.

Table 4. Summary of the sample preparation performed by the participants to the liquid ILC

Ref participant	Number of Subsamples and amount of sample	Tracer	Chemical treatment	Chemical separation of interferences	RN pre-concentration
20	5 / 5 g	U-233	no info	yes	yes
25	6 / 5 g	-	Yes	no	no
30	5 / 20 g	Am-243, Pu-242, U-236	Yes	no	no
33	10 g	Pu-242 & U-232	Yes	yes	no
40	3 /	No	no	no	no
45	7 / 0.1 g	Pu-242, Am-243	Yes	yes - U separation on UTEVA for isotope ratios, Am separation on DGA column	no
50	1 / 0.05 g	242-Pu (IRMM-085), 233-U (IRMM-058), and 243-Am (NIST 4332e)		yes	yes
53			yes	no	no
60	1 / 0.12 g	Pu-242, Am-243	no	yes	no
65	5 / 1 g	For Am, U and Np, mass bias was calculated based on the measurement of U solution IRRM (2008-03-0022). For Pu mass bias calculations, Pu certified solution UK Pu 5/92138 was used.	Yes	yes	no
73	2 for isotopic composition / 20 g & 5 for IDMS / 6.6 g	U-235	Yes	yes	yes

3.2.2 MS instruments and sample introduction methods

Information related to the instrument used are summarized in Table 5, with details in Table 40 (Appendix 2).

Most of the participants (eight out of ten) used inductively coupled mass spectrometry (ICP-MS) to measure the samples, and the other two used radiometric techniques (alpha spectrometry and gamma-ray spectrometry). Four participants used ICP tandem mass spectrometry ICP-MS/MS, two participants used accelerator mass spectrometry (AMS), one participant used quadrupole ICP-MS (ICP-QMS), one participant used multi-collector ICP-MS (MC-ICP-MS) and one participant used ICP sector field mass spectrometry (ICP-SFMS).

Table 5. Summary of the instrumental parameters used by the participants to the liquid ILC.

Ref participant	System	ICP-MS sample introduction system	Blank correction	Mass bias correction	iRM	Type of quantification
20	AMS	Cs sputtering ion source	yes	no info	yes, U-233	
25	ICP-QMS	no info	yes	no	no info	
30	ICP-MS/MS	no info	yes	yes, Spiking with Am-243, Pu-242, U-236	no info	
33	ICP-MS/MS	peristaltic pump, quartz cyclonic spray chamber, PFA-ST nebulizer, quartz injector, iCap Q quartz torch	yes	automatic correction	yes, 'IAEA-384 Fangataufa', 'IAEA-385 Irish Sea Sediment'; TDMA 51.6	
40	Gamma spec	not applicable	yes	no	Secondary reference material made of multi-radionuclide solution (CMI)	Calibration standard
45	ICP-SF-MS	Twinnabar-type, Apex (ESI)	yes	no	yes, natural U to check the isotope ratio measurement	
50	AMS	Cs sputtering ion source	yes	no	yes, use of isotope standards	
53	ICP-MS/MS	Standard quartz sample introduction system - Ni plated sampling cone + standard NI skimmer cone	no	no	isotope standards for U, Np, and Pu	Calibration curve (radiometric standards)
60	Alpha spec	not applicable	no	not applicable	yes, Am-243 and Pu-242 for spectrometer calibration	
65	ICP-MS/MS	no info	no	yes, for Am, U and Np, mass bias was calculated based on the measurement of U solution IRRM (2008-03-0022). For Pu mass bias calculations, Pu certified solution UK Pu 5/92138 was used.	yes, IRRM-075 (Uranium), Pu 5/92138 (Plutonium) UK	Isotope dilution
73	MC-ICP-MS	CETAC Aridus 2 Desolvating Nebulizer System and Nebulizer: Savillex PFA, self-aspirating, 50 µL/min	yes	yes, mass bias correction was done by SSB using IRMM-184 as isotopic reference	yes, IRMM-184 for mass bias correction, NBL CRM 145 as concentration standard	Isotope dilution

3.2.3 Uncertainty budgets

The detailed uncertainty budgets provided by the participants are presented in Table 43, in Appendix 4.

The main uncertainty contributions identified by the partners are: mass fraction of the reference material, the counting statistics, the efficiency of the measurement or the standard used, the tracer(s), the weighing, the standard deviation between sub-samples, the radiochemical separation and the mass bias.

3.3 Participants' results – liquid RM

In interlaboratory comparisons, it is usual to detect outliers using tests such as Grubbs or Pierce [4]. However, those tests are only appropriate for large datasets (typically above 10). In this ILC the participants submitted between 3 and 8 results for each measurand. Therefore, those tests were not performed and the outliers were determined graphically, for each measurand.

3.3.1 Results for the mass fraction of ^{234}U

The participants' results for the mass fraction of ^{234}U, sorted by increasing order, are presented in Figure 6. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

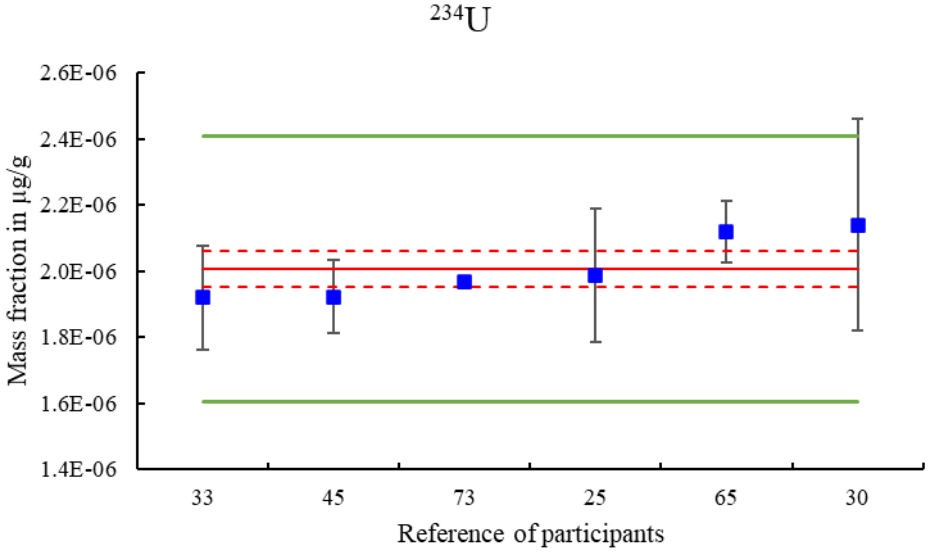

Figure 6. Results for the mass fraction of ^{234}U (increasing order) – liquid RM.

Five participants did not give any results for the mass fraction of ^{234}U. All reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 6.

Table 6. Results obtained for the mass fraction of ^{234}U and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{234}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.007E-06	5.4E-08	2.7				
25	ICP-QMS	1.99E-06	2.0E-07	10	-1.0	S	-0.1	S
30	ICP-MS/MS	2.14E-06	3.2E-07	15	6.6	S	0.4	S
33	ICP-MS/MS	1.92E-06	1.6E-07	8.2	-4.3	S	-0.5	S
45	ICP-SF-MS	1.92E-06	1.1E-07	5.8	-4.2	S	-0.7	S
65	ICP-MS/MS	2.118E-06	9.4E-08	4.4	5.5	S	1.0	S
73	MC-ICP-MS	1.9686E-06	6.1E-09	0.31	-1.9	S	-0.7	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{234}U, because the activity of this radionuclide in the samples was too low. For the determination of uranium isotopic composition in the environmental matrices such as seawater, alpha spectrometry requires very high degree of chemical purification [6]. A low isotopic abundance of ^{234}U significantly limits the analytical capability of gamma-ray spectrometry, because the observed peaks cannot be accurately deduced from the low-energy background, causing undetectable count rates for its analytical peaks at 53.2 keV (0.123 %) or 120.9 keV (0.034 %) of ^{234}U [7].

The participants that used AMS did not give a result for this measurand, because this technique is not very well suited for this type of measurement when compared to ICP-MS [8].

For all techniques, the uncertainties were below 15 %, with the lowest uncertainty for the analysis performed by MC-ICP-MS (0.31 %) as expected, since it is the same analysis technique used to determine the assigned value, because MC-ICP-MS technique has a very high sensitivity, and is the state-of-the-art technique for isotope ratio measurements at a per-mil level of uncertainty [9]. Additionally, determining elemental concentrations with a per-mil level of uncertainty using the isotope dilution (ID) method in conjunction with MC-ICP-MS is also possible [10].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicates that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for all reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties.

3.3.2 Results for the mass fraction of ^{235}U

The participants' results for the mass fraction of ^{235}U, sorted by increasing order, are presented in Figure 7. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Six of the results presented here were directly reported by participants (blue squares) and the other was calculated from reported mass activity (black dots).

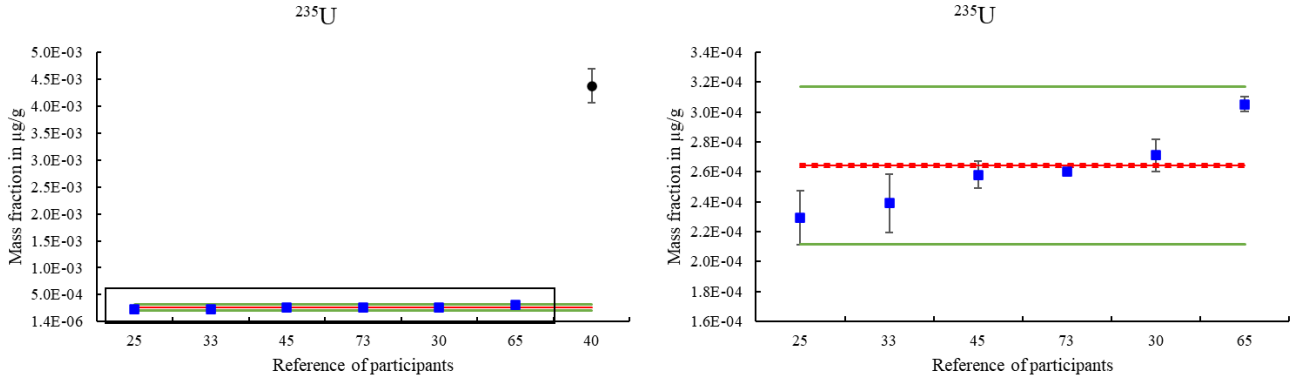

Figure 7. Results for the mass fraction of ^{235}U (increasing order) – liquid RM.

Four participants did not give any results for the mass fraction of ^{235}U. The result n° 40 was discrepant compared to the other results. Six of the results received deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 7.

Table 7. Results obtained for the mass fraction of ^{235}U and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{235}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.642E-04	1.3E-06	0.5				
25	ICP-QMS	2.29E-04	1.8E-05	7.9	-13	S	-1.9	S
30	ICP-MS/MS	2.71E-04	1.1E-05	4.1	2.6	S	0.6	S
33	ICP-MS/MS	2.39E-04	2.0E-05	8.2	-9.6	S	-1.3	S
40	gamma spec	4.38E-03	3.1E-04	7.1	1557	NS	13.2	NS
45	ICP-SF-MS	2.581E-04	9.2E-06	3.6	-2.3	S	-0.7	S
65	ICP-MS/MS	3.053E-04	4.7E-06	1.5	16	D	8.4	NS
73	MC-ICP-MS	2.60094E-04	7.8E-07	0.30 %	-1.6	S	-2.7	D

For all techniques, the uncertainties were below 14 %, with the lowest uncertainty for the analysis performed by MC-ICPMS (0.30 %) and the highest for gamma spectrometry.

The first criterion, the deviation from the assigned value, e_p, was Satisfactory for five results, which indicated that these participating laboratories achieved a good accuracy for this measurand. It was Discrepant for one result, n° 65, which was overestimated by 16 %, and it was Non-Satisfactory for result n° 40. Since this result was obtained with gamma-ray spectrometry, it is possible that there were interferences coming from other radionuclides in the ray used to quantify ^{235}U, which lead to the overestimation of the activity in the sample.

The second criterion, the zeta score ζ_p, was Satisfactory for four results, which indicated that those were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for the result n° 73, and Non-Satisfactory for results n° 40, n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 73) or k = 3 (n° 40 and n° 65).

3.3.3 Results for the mass fraction of ^{236}U

The participants' results for the mass fraction of ^{236}U, sorted by increasing order, are presented in Figure 7. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

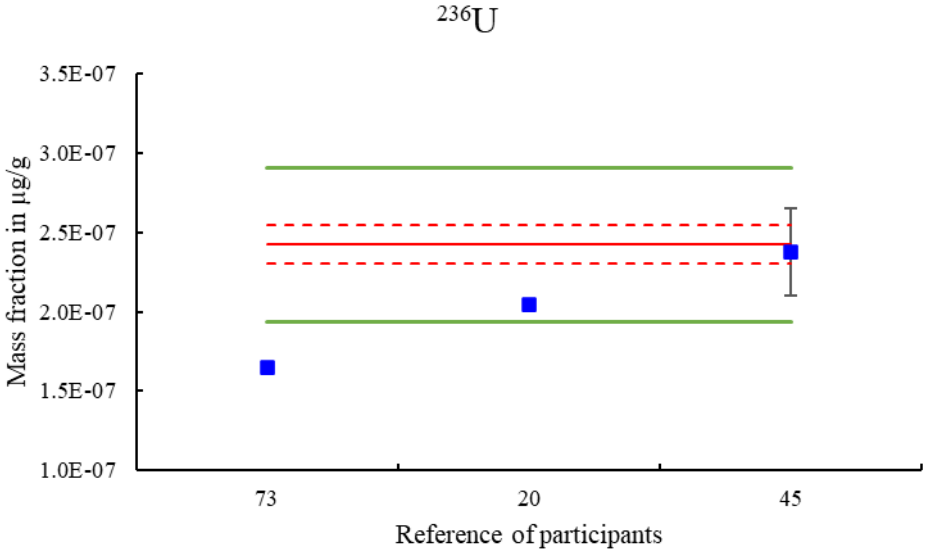

Figure 8. Results for the mass fraction of ^{236}U (increasing order) – liquid RM.

Eight participants did not give any results for the mass fraction of ^{236}U, and it could not be calculated. Two of the reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 7.

Table 8. Results obtained for the mass fraction of ^{236}U and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{236}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.42E-07	1.2E-08	5.0				
20	AMS	2.047E-07	1.8E-09	0.9	-15	D	-3.1	NS
45	ICP-SF-MS	2.38E-07	2.7E-08	11	-1.8	S	-0.1	S
73	MC-ICP-MS	1.651E-07	2.6E-09	1.6	-32	NS	-6.2	NS

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{236}U, because the activity of this radionuclide in the samples was too low.

For all techniques, the uncertainties of participants' results ranged between 1.6 % and 11 %, with the lowest uncertainty for the analysis performed by MC-ICP-MS technique (n° 73) and the highest for the ICP-SFMS (n° 45).

The first criterion, the deviation from the assigned value, e_p, was Satisfactory for only one result, n° 45. It was Discrepant for one result, n° 20, and it was Non-Satisfactory for the result n° 73.

The second criterion, the zeta score ζ_p, was Satisfactory the result n° 45, which indicated that it was compatible to the assigned values, within uncertainties. The zeta score was Non-satisfactory for results n° 20 and n° 73, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 3.

For MC-ICP-MS, the result obtained was not as expected, with "NS" scores for both criteria. The mass fraction of ^{236}U in the liquid RM was close to the limit of detection of MC-ICP-MS, therefore the discrepant result could be due to the contribution of the blank correction.

The ICP-SFMS technique had "S" scores for both criteria despite having the highest uncertainty value, perhaps due to the low sample quantity used for analysis (0.1 g).

3.3.4 Results for the mass fraction of ^{237}Np

The participants' results for the mass fraction of ^{237}Np, sorted by increasing order, are presented in Figure 9. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Six of the results presented here were directly reported by participants (blue squares) and the others were calculated from reported mass activity (black dots).

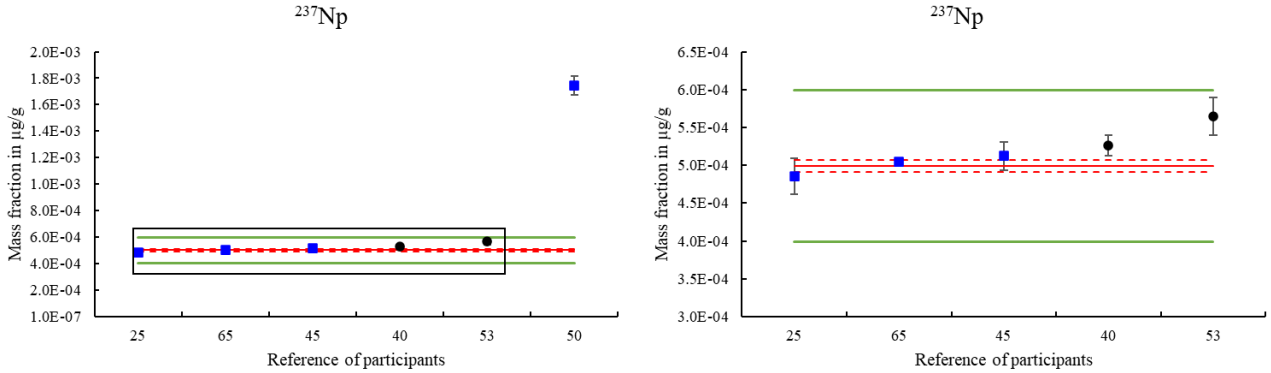

Figure 9. Results for the mass fraction of ^{237}Np (increasing order) – liquid RM.

Five participants did not give any results for the mass fraction of ^{237}Np. The result n° 50 was discrepant compared to the other results.

Five of the results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 9.

Table 9. Results obtained for the mass fraction of ^{237}Np and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{237}Np mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	4.993E-04	8.0E-06	1.6				
25	ICP-QMS	4.85E-04	2.3E-05	4.8	-2.8	S	-0.6	S
40	gamma spec	5.26E-04	1.3E-05	2.6	5.4	S	1.7	S
45	ICP-SF-MS	5.12E-04	1.9E-05	3.7	2.6	S	0.6	S
50	AMS	1.744E-03	7.3E-05	4.2	249	NS	16.9	NS
53	ICP-MS/MS	4.80E-04	2.5E-05	5.1	-3.8	S	-0.7	S
73	ICP-MS/MS	5.050E-04	1.6E-06	0.32	1.1	S	0.7	S

For five techniques, the uncertainties of participants results ranged between 0.32 % and 4.8 %, with the lowest uncertainty for the analysis performed by ICP-MS/MS technique (n° 65) and the highest for the same technique (n° 53).

No results were submitted by alpha spectrometry. In fact, for ^{237}Np, this technique is unable to separate the alpha particles emitted from those of ^{234}U due to small energy differences [12].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for four results, which indicated that these participating laboratories achieved a good accuracy for this measurand. It was above 20 % for result n° 50.

The second criterion, the zeta score ζ_p, was Satisfactory for four results, which indicated that those were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for the result n° 50, indicating that the deviation to the assigned value was not covered by the reported uncertainty, at k = 3.

The results n° 25, n° 53, and n° 65 confirm what is described in the literature about ICP-MS/MS technique, which has become one of the most powerful methods for determining ultra-trace levels of ^{237}Np in many types of samples (environmental, biological, and uranium fuel), despite the sensitivity of abundance being limited by molecular interferences, such as $^{235}UH_2^+$ [12]. Gamma spectrometry also seems to be a very appropriate technique for this radionuclide, for this concentration, with the added advantage of no radiochemical separation.

The result of the AMS technique was approximately 3 times more than ^{237}Np at the assigned value, which may show that the technique is not the most suitable for measuring this isotope, with a possible interference from another isotope.

In addition, ^{237}Np is probably one of the least studied actinides, mainly due to limitations imposed by the lack of a long-lived isotopic tracer of Np that could be added to the original sample matrix to control for losses during sample processing and that could be used as a standard isotope during MS determinations [13].

3.3.5 Results for the mass fraction of ^{238}U

The participants' results for the mass fraction of ^{238}U, sorted by increasing order, are presented in Figure 10. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

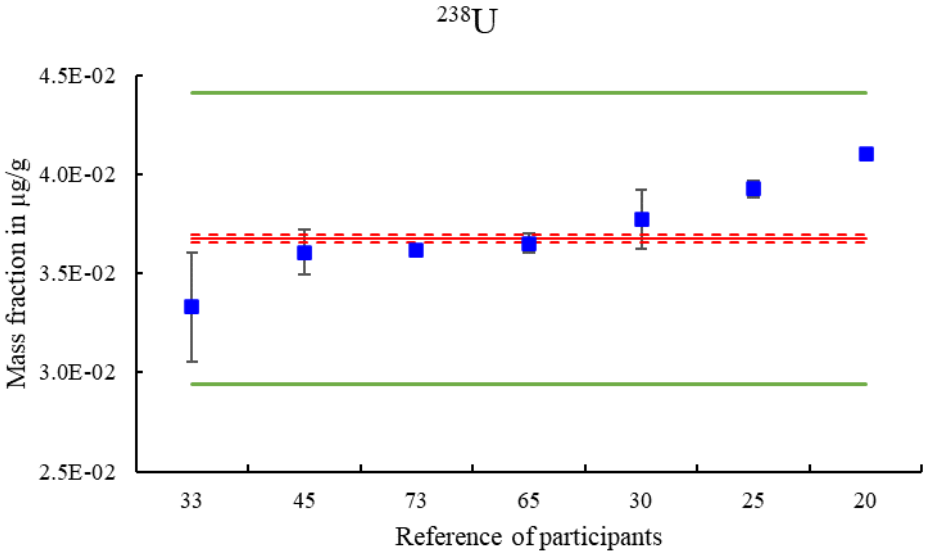

Figure 10. Results for the mass fraction of ^{238}U (increasing order) – liquid RM.

Four participants did not give any results for the mass fraction of ^{238}U, and it could not be calculated from other reported results. All of the reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 10.

Table 10. Results obtained for the mass fraction of ^{238}U and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{238}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	3.673E-02	1.8E-04	0.5				
20	AMS	4.100E-02	3.0E-04	0.7	11	S	12	NS
25	ICP-QMS	3.924E-02	4.0E-04	1.0	6.8	S	5.8	NS
30	ICP-MS/MS	3.77E-02	1.5E-03	4.0	2.6	S	0.6	S
33	ICP-MS/MS	3.33E-02	2.7E-03	8.2	-9.3	S	-1.2	S
45	ICP-SF-MS	3.61E-02	1.2E-03	3.2	-1.8	S	-0.6	S
65	ICP-MS/MS	3.651E-02	4.7E-04	1.3	-0.6	S	-0.4	S

73	MC-ICP-MS	3.614E-02	1.1E-04	0.30	-1.6	S	-2.8	D

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{238}U, because the activity of this radionuclide in the samples was too low.

The uncertainties of participants' results ranged between 0.30 % and 8.2 %, with the highest for the ICP-MS/MS technique (n° 33).

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicates that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for four results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for result n° 73 and Non-Satisfactory for results n° 20 and n° 25, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 73) or k = 3 (n° 20 and n° 25). The reported uncertainties associated with these results might have been under-estimated.

Overall, the results were good for all analyses performed by ICPMS (ICP-MS/MS, ICP-SFMS and MC-ICPMS).

There is clear evidence that the AMS methodology is a powerful technique for measuring isotopic ratios and actinide concentrations and provides measurements across a wide range of isotopic ratios, especially for ^{238}U [14], so the 'NS' score obtained for the second criterion may be linked to the sample preparation used for this work.

3.3.6 Results for the mass fraction of ^{239}Pu

The participants results for the mass fraction of ^{239}Pu, sorted by increasing order, are presented in Figure 11. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

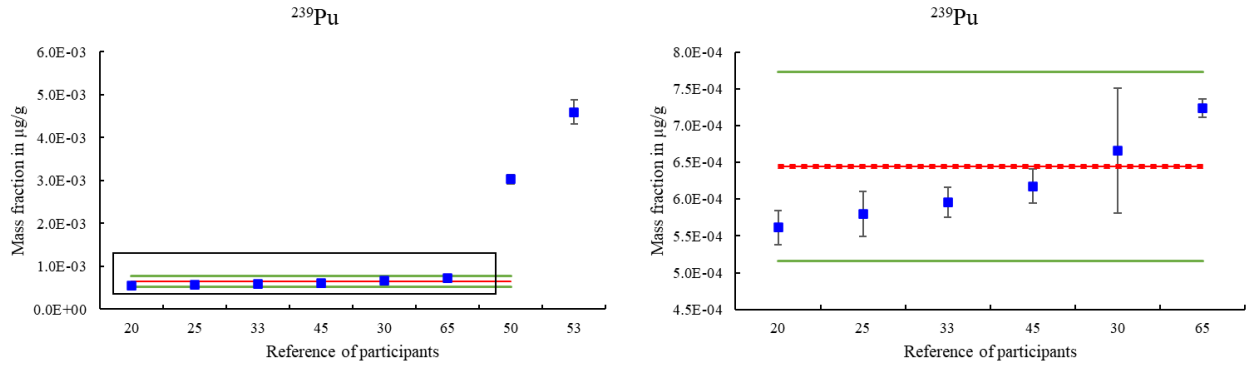

Figure 11. Results for the mass fraction of ^{239}Pu (increasing order) – liquid RM.

Three participants did not give any results for the mass fraction of ^{239}Pu. Six of the eight reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 11.

Table 11. Results obtained for the mass fraction of ^{239}Pu and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{239}Pu mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	6.443E-04	1.9E-06	0.3				
20	AMS	5.61E-04	2.3E-05	4.1	-13	S	-3.6	NS
25	ICP-QMS	5.80E-04	3.0E-05	5.2	-10	S	-2.1	D
30	ICP-MS/MS	6.66E-04	8.5E-05	13	3.4	S	0.3	S
33	ICP-MS/MS	5.96E-04	2.0E-05	3.4	-7.5	S	-2.3	D
45	ICP-SF-MS	6.18E-04	2.3E-05	3.8	-4.2	S	-1.1	S
50	AMS	3.03E-03	1.0E-04	3.3	370	NS	24	NS
53	ICP-MS/MS	4.60E-03	2.9E-04	6.3	614	NS	14	NS
65	ICP-MS/MS	7.2E-04	1.2E-05	1.7	12	S	6.4	NS

The participant n° 60, using alpha spectrometry, did not report any ^{239}Pu mass activity fraction, because this radionuclide cannot be separated from ^{240}Pu. Instead, the total mass activity of those two radionuclides was reported, and is analysed in section 3.3.9.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for six out of eight reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for two results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for results n° 25 and n° 33, and Non-Satisfactory for results n° 20, n° 50, n° 53 and n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 or k = 3. The reported uncertainties associated with results n° 20, n° 25, n° 33 and n° 65 might have been under-estimated.

Out of the four results obtained by the ICP-MS/MS technique, two were satisfactory for both criteria, which showed the potential of the technique for this isotope (^{239}Pu).

The result n° 50, provided by the AMS technique, may be linked to problems in sample preparation or interference from another isotope or errors in mass bias, due to the value being higher (times 5) when compared to the assigned value. The new generation of AMS allows the detection of heavier elements (actinides) and the estimation of isotopic ratios between them. Mass spectrometry methods (e.g., AMS, TIMS, ICP-MS) potentially have a higher sensitivity than α particle counting, with values as low as ~1 fg, but are sensitive to possible molecular interferences (^{238}UH, ^{208}Pb, etc.) that can interfere with the measurement of

^{239}Pu [16]. The amount of ^{239}Pu in the sample was also higher than that usually measured with AMS, which could lead to a less precise measurement.

3.3.7 Results for the mass fraction of ^{240}Pu

The participants' results for the mass fraction of ^{240}Pu, sorted by increasing order, are presented in Figure 12. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

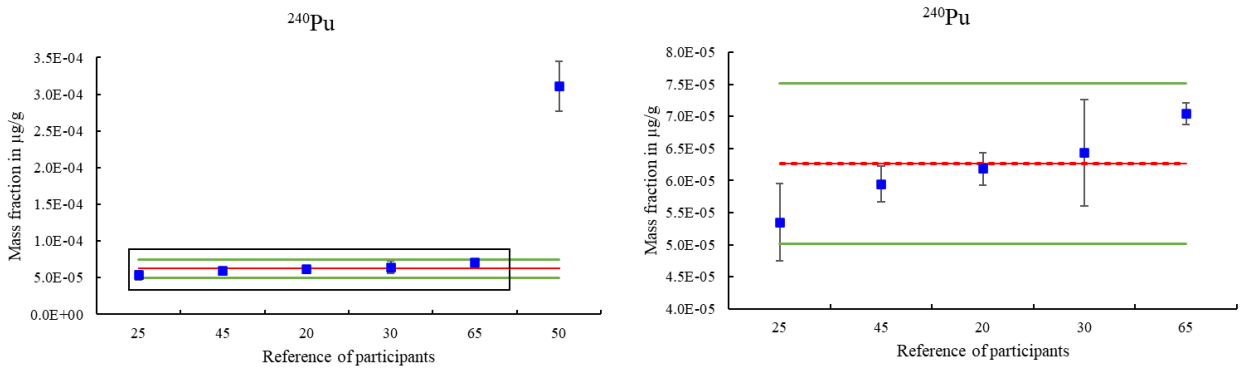

Figure 12. Results for the mass fraction of ^{240}Pu (increasing order) – liquid RM.

Five participants did not give any results for the mass fraction of ^{240}Pu. Five of the six reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 12.

Table 12. Results obtained for the mass fraction of ^{240}Pu and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{240}Pu mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	6.264E-05	1.9E-07	0.3				
20	AMS	6.18E-05	2.5E-06	4.1	-1.3	S	-0.3	S
25	ICP-QMS	5.35E-05	6.0E-06	11	-15	S	-1.5	S
30	ICP-MS/MS	6.43E-05	8.3E-06	13	2.7	S	0.2	S
45	ICP-SF-MS	5.94E-05	2.8E-06	4.7	-5.1	S	-1.2	S
50	AMS	3.11E-04	3.4E-05	11	396	NS	7.4	NS
65	ICP-MS/MS	7.04E-05	1.7E-06	2.4	12	S	4.6	NS

The participant n° 60, using alpha spectrometry, did not report any ^{240}Pu mass activity fraction, because this radionuclide cannot be separated from ^{239}Pu. Instead, the total mass activity of those two radionuclides was reported, and is analysed in section 3.3.9.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for four out of five reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for three results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for results n° 50 and n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 3. The reported uncertainties associated with results n° 65 might have been under-estimated.

The results obtained by the ICP-MS techniques used were generally satisfactory for both criteria, demonstrating the potential of the technique for this isotope (^{240}Pu).

Also, for ^{240}Pu, the result n° 50 provided by the AMS technique may be linked to problems in sample preparation or interference from another isotope or errors in mass bias, due to the value being higher (times 5) when compared to the assigned value. The result n° 20, obtained with the same technique, performed better.

3.3.8 Results for the mass fraction of ^{241}Am

The participants' results for the mass fraction of ^{241}Am, sorted by increasing order, are presented in Figure 13. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Six of the results presented here were directly reported by participants (blue squares) and the other three were calculated from reported mass activities (black dots).

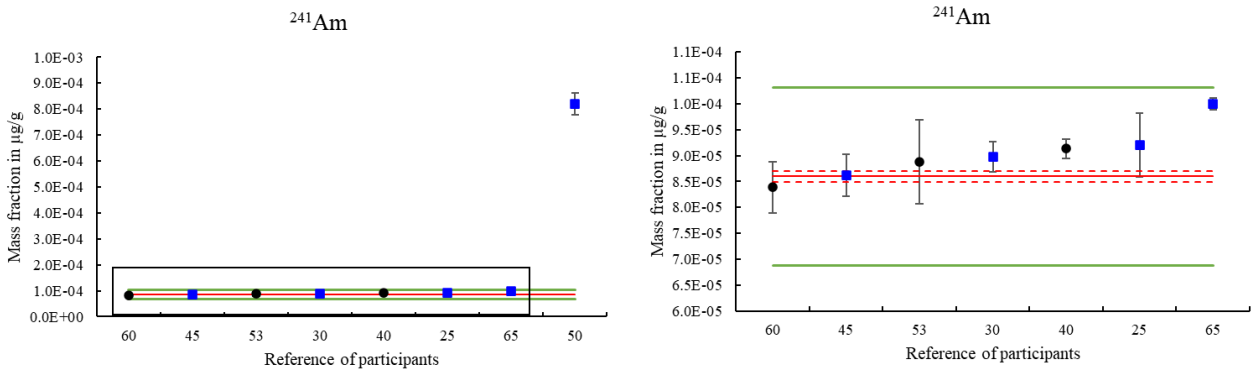

Figure 13. Results for the mass fraction of ^{241}Am (increasing order) – liquid RM.

Three participants did not give any results for the mass fraction of ^{241}Am. Seven of the eight reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 13.

Table 13. Results obtained for the mass fraction of ^{241}Am and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{241}Am mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	8.60E-05	1.0E-06	1.2				
25	ICP-QMS	9.20E-05	6.1E-06	6.7	7.0	S	1.0	S
30	ICP-MS/MS	8.97E-05	2.9E-06	3.2	4.3	S	1.2	S
40	gamma spec	9.13E-05	1.9E-06	2.1	6.2	S	2.5	D
45	ICP-SF-MS	8.61E-05	4.0E-06	4.7	0.2	S	0.0	S
50	AMS	8.19E-04	4.2E-05	5.1	853	NS	17.5	NS
53	ICP-MS/MS	8.88E-05	8.2E-06	9.2	3.3	S	0.3	S
60	alpha spec	8.39E-05	4.9E-06	5.9	-2.4	S	-0.4	S
65	ICP-MS/MS	1.000E-04	1.2E-06	1.2	16	D	9.0	NS

The first criterion, the deviation from the assigned value, e_p, was below 15 % for six out of eight reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for five results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for the result n° 40, Non-Satisfactory for results n° 50 and n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 40) or k = 3 (n° 50 and n° 65). The reported uncertainties associated with results n° 40 and n° 65 might have been under-estimated.

The results that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) were Satisfactory for both criteria, which showed that this technique is well suited to ^{241}Am measurement. This was expected since, out of all the radionuclides in this reference material, ^{241}Am is the one with the lowest half-life, meaning that has the highest activity for similar mass fractions, and therefore was more readily detected with radiometric techniques.

Out of the two results obtained by the ICP-MS/MS technique, one was Satisfactory for both criteria, and one was Discrepant for the first criterion and Non-Satisfactory for the second. The problem encountered by participant n° 65 may be related to sample preparation or application of mass bias.

The results were not satisfactory for the ^{241}Am, similarly to those of Pu, using the AMS technique. The value is 10 times higher when compared to the assigned value, may be linked to problems in sample preparation or interference from another isotope. It should be noted that a very small sub-sample (0.05 g) was used compared to other techniques, because the amount of ^{241}Am in the liquid RM was too high for this technique. The homogeneity of the material was not tested at this small scale, and the weighing uncertainty is higher for such small mass.

3.3.9 Results for the mass activity of ^{239}Pu and ^{240}Pu

One participant, n° 17, could not measure ^{239}Pu and ^{240}Pu separately, due to the measurement technique used. Instead, they reported the mass activity of both those radionuclides. To compare with other participants, the mass activity of ^{239}Pu and ^{240}Pu, corresponding to the reported mass fractions, were calculated when possible. The results for the mass activity of ^{239}Pu and ^{240}Pu sorted by increasing order, are presented in Figure 14. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

One of the results presented here were directly reported by participants (blue squares) and the others were calculated from reported mass fractions (black dots).

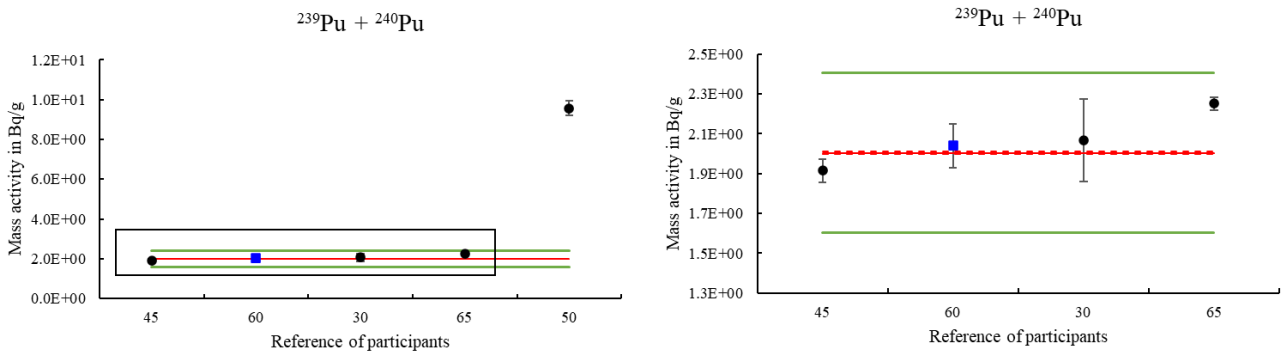

Figure 14. Results for the ^{239}Pu + ^{240}Pu mass activity (increasing order) – liquid RM.

The result of the alpha spectrometry (n° 60) was close to the assigned value and to the other mass spectrometry measurements, except for n° 50.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 14.

Table 14. Results obtained for the ^{239}Pu + ^{240}Pu mass activity and performance statistics – liquid RM.

Ref Participant	Meas. technique	^{239}Pu + ^{240}Pu mass activity in Bq/g	Uncertainty at k = 1 in Bq/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.0048	0.0060	0.3				
30	ICP-MS/MS	2.07	0.21	10	3.1	S	0.3	S
45	ICP-SF-MS	1.915	0.059	3.1	-4.5	S	-1.5	S
50	AMS	9.56	0.36	3.8	377	NS	20.7	NS
60	alpha spec	2.04	0.11	5.4	1.8	S	0.3	S
65	ICP-MS/MS	2.252	0.032	1.4	12	S	7.7	NS

As could be expected, the participants using mass spectrometry had similar results for the calculated mass activity of ^{239}Pu and ^{240}Pu as for the mass fractions of individual radionuclides

The result of the participant n° 60 was very good, as both criteria were Satisfactory. Alpha spectrometry, even if it does not discriminate between ^{239}Pu and ^{240}Pu, allowed for an accurate measurement of the sum of those two radionuclides, after separation from other elements.

3.3.10 Results for the total U content

The participants' results for the total U content, sorted by increasing order, are presented in Figure 15. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other four were calculated from individual ^{234}U, ^{235}U, ^{236}U and ^{238}U mass fractions (black dots).

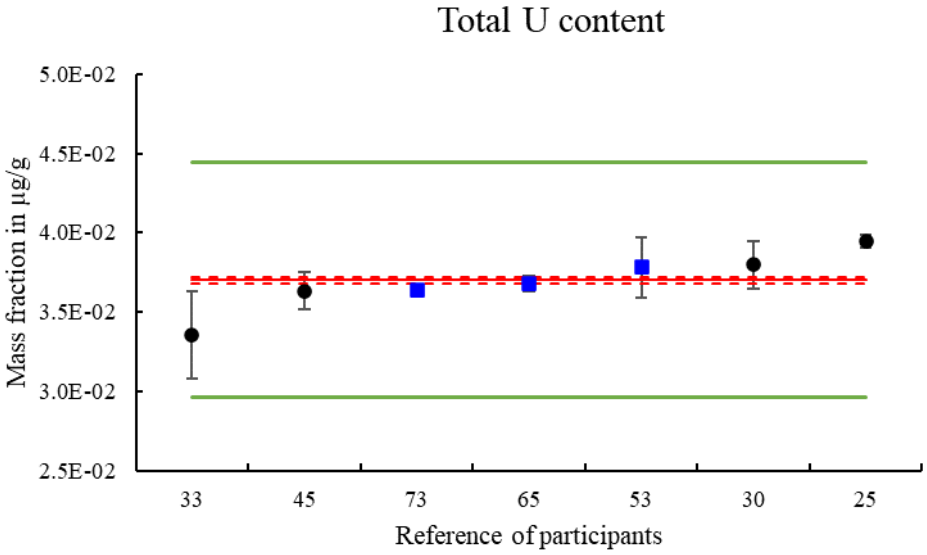

Figure 15. Results for the total U content (increasing order) – liquid RM.

Four participants did not give any results for the total U content, and it could not be calculated. All results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 15.

Table 15. Results obtained for the total U content and performance statistics – liquid RM.

Ref Participant	Meas. technique	Total U content in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	3.700E-02	1.8E-04	0.5				
25	ICP-QMS	3.947E-02	4.0E-04	1.0	6.7	S	5.7	NS
30	ICP-MS/MS	3.80E-02	1.5E-03	4.0	2.6	S	0.6	S
33	ICP-MS/MS	3.35E-02	2.7E-03	8.2	-9.3	S	-1.3	S
45	ICP-SF-MS	3.63E-02	1.2E-03	3.2	-1.8	S	-0.6	S
53	ICP-MS/MS	3.78E-02	1.9E-03	5.0	2.2	S	0.4	S
65	ICP-MS/MS	3.677E-02	4.7E-04	1.3	-0.6	S	-0.4	S
73	MC-ICP-MS	3.640E-02	1.1E-04	0.30	-1.6	S	-2.8	D

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicates that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for five out of the seven reported and calculated results, which indicates that the results of the participants were compatible to the assigned values, within uncertainties. This criterion was Discrepant for result n° 73 and Non-Satisfactory for the result n° 25 which indicated that the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 or k = 3. The uncertainties associated with these results might have been under-estimated.

3.3.11 Results for the $^{234}U/^{238}U$ isotope ratio

The participants' results for the $^{234}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 16. The bars represent the uncertainty of each measurement, at $k = 1$. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Four of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{234}U and ^{238}U mass fractions (black dots).

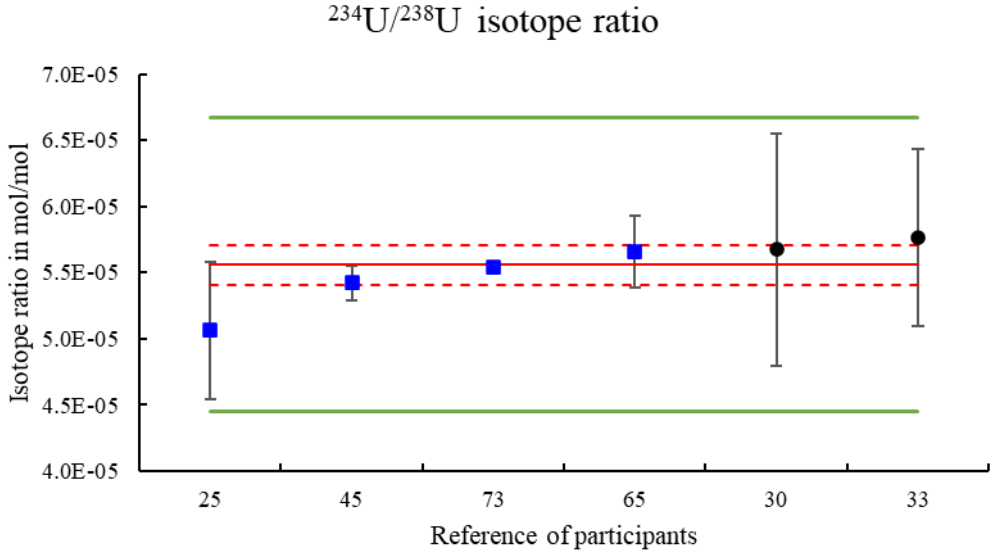

Figure 16. Results for the $^{234}U/^{238}U$ isotope ratio (increasing order) – liquid RM.

Five participants did not give any results for the $^{234}U/^{238}U$ isotope ratio, and it could not be calculated from other reported results. It seems that the calculated results and their uncertainties were higher than the reported ones, because calculation is less precise than a direct measurement.

All results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 16.

Table 16. Results obtained for the $^{234}U/^{238}U$ isotope ratio and performance statistics – liquid RM.

Ref Participant	Meas. technique	Isotope ratio $^{234}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	5.56E-05	1.5E-06	2.7				
25	ICP-QMS	5.06E-05	5.2E-06	10	-8.9	S	-0.9	S
30	ICP-MS/MS	5.68E-05	8.8E-06	15	2.1	S	0.1	S
33	ICP-MS/MS	5.77E-05	6.7E-06	12	3.7	S	0.3	S
45	ICP-SF-MS	5.42E-05	1.3E-06	2.4	-2.4	S	-0.7	S
65	ICP-MS/MS	5.66E-05	2.7E-06	4.8	1.8	S	0.3	S
73	MC-ICP-MS	5.55E-05	1.1E-07	0.20	-0.2	S	-0.1	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{234}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples were too low.

The uncertainties of participants' results ranged between 0.20 % and 15 %, with the highest for the ICP-MS/MS technique (n° 30). MC-ICP-MS once again demonstrated that it provides highly precise and accurate measurements compared to ICP-MS/MS [15]. This leads to very small uncertainties, as can be seen in the result provided by n° 73.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicates that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for all reported and calculated results, which indicates that the results of the participants were compatible to the assigned values, within uncertainties.

The presence of isobaric interferences caused by molecular ions can pose major obstacles for the accurate measurement of $^{234}U/^{238}U$ isotopic ratio by mass spectrometry techniques. The ICP-MS are widely used and are becoming an effective tool for individual particle analysis for nuclear safeguards, [17] while variability in both the molecular and tail contributions limit the sensitivity of ICP-MS to the $^{236}U/^{238}U$ ratio of 10^{-7} level [18]. Accelerator mass spectrometry (AMS) has advantages over conventional mass spectrometry, such as TIMS and inductively-coupled plasma mass spectrometry (ICP-MS), in better suppression of molecular interferences leading to improved sensitivity and lower detection limits [18].

3.3.12 Results for the $^{235}U/^{238}U$ isotope ratio

The participants' results for the $^{235}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 17. The bars represent the uncertainty of each measurement, at k = 1. Bars might be too small to show on the

figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{235}U and ^{238}U mass fractions (black dots).

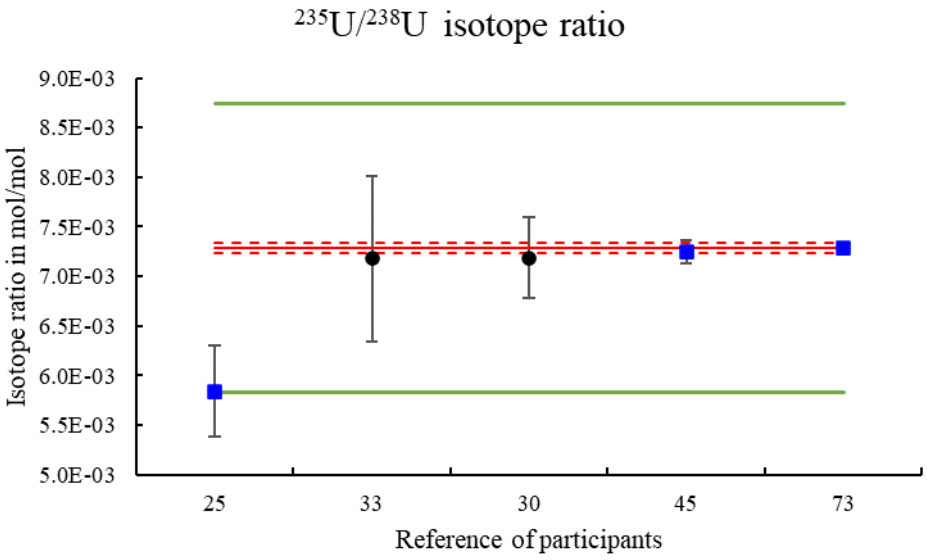

Figure 17. Results for the $^{235}U/^{238}U$ isotope ratio (increasing order) – liquid RM.

Six participants did not give any results for the $^{235}U/^{238}U$ isotope ratio, and it could not be calculated. It seems that the calculated results and their uncertainties were higher than the reported ones, probably because the calculation is less precise than direct measurements.

Four results, reported and calculated, deviated by less than 20 % from the assigned value, and the deviation of the last one was close to 20 %.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 17.

Table 17. Results obtained for the $^{235}U/^{238}U$ isotope ratio and performance statistics – liquid RM.

Ref Participant	Meas. technique	Isotope ratio $^{235}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	7.286E-03	5.1E-05	0.7				
25	ICP-QMS	5.84E-03	4.6E-04	7.9	-20	D	-3.1	NS
30	ICP-MS/MS	7.19E-03	4.1E-04	5.7	-1.3	S	-0.2	S
33	ICP-MS/MS	7.18E-03	8.3E-04	12	-1.5	S	-0.1	S
45	ICP-SF-MS	7.25E-03	1.2E-04	1.6	-0.5	S	-0.3	S
73	MC-ICP-MS	7.2894E-03	6.1E-06	0.08	0.1	S	0.1	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{235}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples were too low.

The uncertainties of the participants' results ranged between 0.08 % and 12 %, with the highest for the ICP-MS/MS technique (n° 33).

The first criterion, the deviation from the assigned value, e_p, was Satisfactory for four reported and calculated results, which indicated that these participating laboratories achieved a good accuracy for this measurand. The last result, n° 25, was Discrepant. It seemed that ICP-QMS was less precise than other mass spectrometry techniques for the measurement of isotopic ratios.

The second criterion, the zeta score ζ_p, was Satisfactory for four reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties. The zeta score of the last result, n° 25, was Non-Satisfactory (NS), the result was underestimated, and the difference was not covered by the reported uncertainties, at k = 3. The uncertainty associated with this result might have been under-estimated.

3.3.13 Results for the $^{236}U/^{238}U$ isotope ratio

The participants' results for the $^{236}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 18. The bars represent the uncertainty of each measurement, at k = 1. Bars might be too small to show on the figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

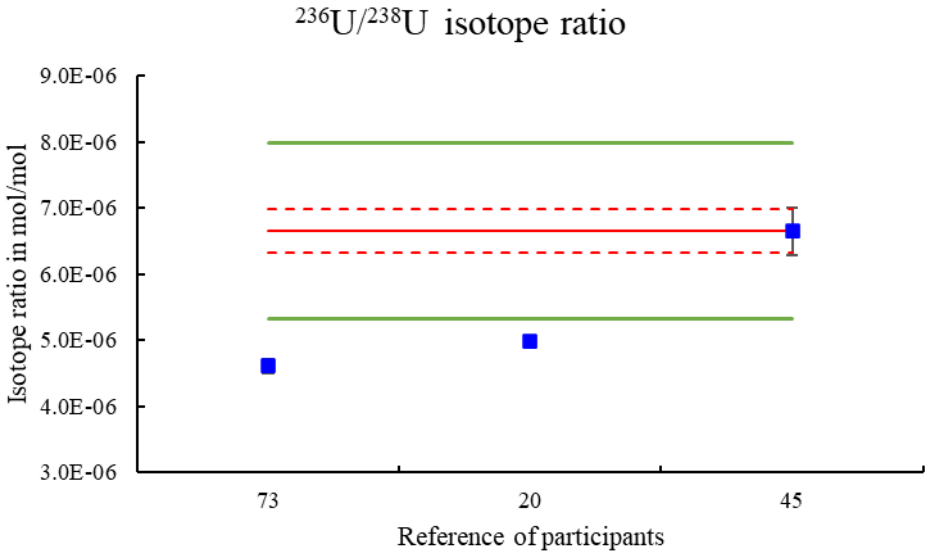

Figure 18. Results for the $^{236}U/^{238}U$ isotope ratio (increasing order) – liquid RM.

Eight participants did not give any results for the $^{236}U/^{238}U$ isotope ratio, and it could not be calculated from individual mass fraction results. Only one reported result deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 18.

Table 18. Results obtained for the $^{236}U/^{238}U$ isotope ratio and performance statistics – liquid RM.

Ref Participant	Meas. technique	Isotope ratio $^{236}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	6.65E-06	3.3E-07	5.0				
20	AMS	4.982E-06	5.7E-08	1.1	-25	NS	-4.9	NS
45	ICP-SF-MS	6.65E-06	3.6E-07	5.5	0.0	S	0.0	S
73	MC-ICP-MS	4.61E-06	2.3E-07	4.9	-31	NS	-5.1	NS

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{236}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples were too low.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for participant n° 45. The other two results, n° 20 and n° 73, deviated from the assigned value by 25 % and 30 %, respectively.

The second criterion, the zeta score ζ_p, was Satisfactory for result n° 44, which indicated that this result was compatible to the assigned values, within uncertainties. The zeta score of the last two results were Non-Satisfactory (NS), the difference between these results and the assigned value was not covered by the reported uncertainties, at k = 3.

Usually, accelerator mass spectrometry (AMS) has advantages over conventional mass spectrometry, such as TIMS and inductively-coupled plasma mass spectrometry (ICP-MS), in better suppression of molecular interferences leading to improved sensitivity and lower detection limits [18]. Therefore, the Non-Satisfactory scores obtained for this measurand by participant n° 20 cannot be explained by the technique used. It could be due to the amount of the radionuclides in the reference material being too high, rendering the sample preparation even more arduous. In fact, the ICP-MS method requiring an easier sample pre-treatment and chemical separation than the AMS method, researchers have turned to the analysis of the $^{236}U/^{238}U$ isotope ratio by the ICP-MS method [19].

3.3.14 Results for the $^{240}Pu/^{239}Pu$ isotope ratio

The participants' results for the $^{240}Pu/^{239}Pu$ isotope ratio, sorted by increasing order, are presented in Figure 19. The bars represent the uncertainty of each measurement, at k = 1. Bars might be too small to show on the figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{240}Pu and ^{239}Pu mass fractions (black dots).

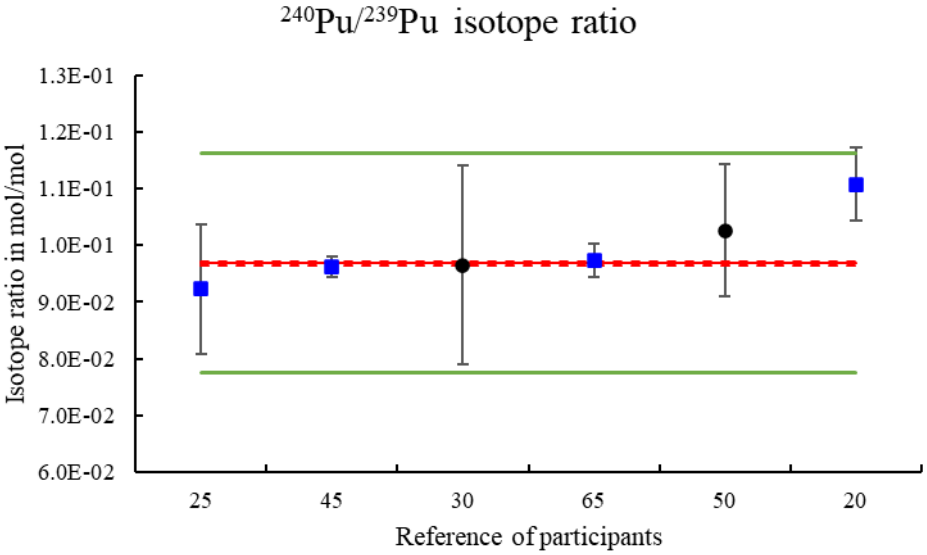

Figure 19. Results for the $^{240}Pu/^{239}Pu$ isotope ratio (increasing order) – liquid RM.

Five participants did not give any results for the $^{240}Pu/^{239}Pu$ isotope ratio, and it could not be calculated from individual mass fraction results. All results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 19.

Table 19. Results obtained for the $^{240}Pu/^{239}Pu$ isotope ratio and performance statistics – liquid RM.

Ref Participant	Meas. technique	Isotope ratio $^{240}Pu/^{239}Pu$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	9.681E-02	3.9E-04	0.4				
20	AMS	1.11E-01	6E-03	5.8	14	S	2.2	D
25	ICP-QMS	9.2E-02	1.1E-02	12	-4.7	S	-0.4	S
30	ICP-MS/MS	9.7E-02	1.8E-02	18	-0.3	S	0.0	S
45	ICP-SF-MS	9.62E-02	1.8E-03	1.9	-0.6	S	-0.3	S
50	AMS	1.03E-01	1.2E-02	11	6.0	S	0.5	S
65	ICP-MS/MS	9.73E-02	2.9E-03	3.0	0.5	S	0.2	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{240}Pu/^{239}Pu$ isotope ratio, because the activity of these radionuclides in the samples were too low for gamma spectrometry, and alpha spectrometry does not discriminate between the two isotopes.

The uncertainties of participants results ranged between 3.0 % and 18 %, with the highest for the ICP-MS/MS technique, which was calculated from reported mass fractions (n° 30).

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicated that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for five reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties. It was Discrepant for result n° 20, obtained by AMS, indicating that the uncertainties might have been underestimated, probably because of the high ^{239}Pu content in the liquid RM.

Although the AMS technique (n° 50) did not achieve Satisfactory results for ^{239}Pu and ^{240}Pu, it did achieve good results for the isotope ratio of $^{240}Pu/^{239}Pu$. This might indicate that the problem encountered with the concentration of the isotopes was due to the quantification, rather than the measurement itself.

3.4 Discussion – general comments of liquid ILC

The results obtained allowed to give general considerations on the advantages and disadvantages of several techniques, depending on the concentration of the radionuclides present in the liquid RM. It is concluded that radiometric techniques (alpha spectrometry and gamma-ray spectrometry) could not measure some radionuclides due to their low concentration (µg/g or µmol/mol), such as: ^{234}U mass fraction (2.0×10^{-6} µg/g), ^{236}U mass fraction (2.6×10^{-4} µg/g) and ^{238}U (3.7×10^{-2} µg/g). In some other cases, radiometric techniques could

not provide activity data for a single isotope because it is not possible to separate the peaks due to the influence of another isotope, as for the case with ^{240}Pu and ^{239}Pu.

The technique that had the most difficulty to measure the different RN in this liquid RM was the AMS, used by two participants, for a total of eleven results submitted, in which eight were “NS” for at least one of the criteria or both. The concentration of the radionuclides in the liquid RM was not appropriate for AMS, which performs best to detect very low levels of contamination.

ICP-SF-MS provided 14 results out of 14, of which all were “S” for both criteria. The range of mass fractions and isotope ratios of this reference material seem to be very appropriate for this technique.

MC-ICP-MS had lower uncertainties compared to other analysis techniques.

In general, the results were less satisfactory for the mass fraction determination compared to the results for total U and the different isotopic ratios, which outlines that mass fraction determination is a critical process, which can be biased by several processes, such as loss of material during radiochemical processes, the use of spikes and tracers, and of reference materials.

All participants’ results for the isotopic ratios of ^{234}U/^{238}U and ^{240}Pu/^{239}Pu were satisfactory for all analytical techniques (radiometric techniques not included).

4 Solid RM ILC

4.1 Production and characterisation of the solid RM

The following sections describe the main characteristics of the produced solid RM. The details of the production of this material, and the scheme for the evaluation of the homogeneity and stability are presented in the Deliverable 5 of the project.

4.1.1 Scheme for the production of the solid RM

The solid RM was synthesised by adapting a method by [2]. It was obtained by spiking a reaction medium containing silica precursors, which subsequently solidified. The spiking solutions were selected and characterised with mass spectrometry, gamma-ray spectrometry and alpha spectrometry. They were first mixed to obtain a multi-RN spiking mixture, which was also characterised using mass spectrometry (Figure 20). All the dilutions were performed with calibrated and accurate balances, which allowed to derive the assigned values of the mass fractions of each radionuclide gravimetrically, and by direct measurement.

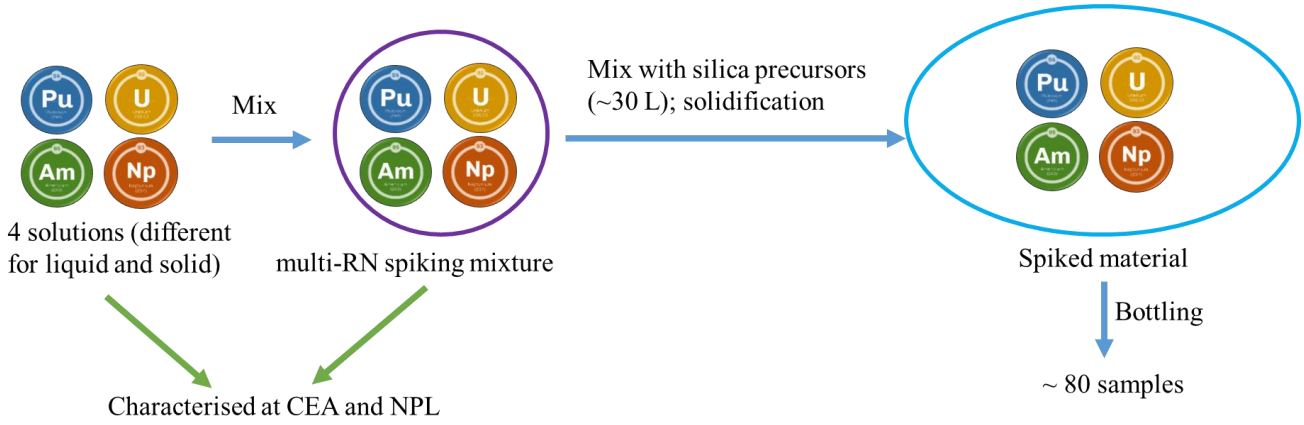

Figure 20: Illustration of the 2-step spiking procedure selected to prepare the candidate solid RM.

4.1.2 Homogeneity assessment – solid RM

The homogeneity of the solid RM was assessed by measuring ^{241}Am by gamma spectrometry, and ^{238}U and ^{239}Pu by mass spectrometry. More details concerning the homogeneity study are published in [1], and follow the guidelines of ISO 33405 [3].

Specific samples were prepared for each measurement, from the bottles n° 8, n° 14, n°24, n° 34, n°44, n°54, n°64 and n° 71. The numbers corresponded to the filling order, and the bottles were chosen to span the whole batch, to possibly identify a bias due to the filling order.

Since mass spectrometry measurements require to take sub-samples from units of the reference material, the homogeneity within bottles was assessed, as well as the homogeneity between bottles.

For gamma spectrometry, two different sample sizes were measured: 7 g and 0.7 g, while for mass spectrometry, 0.5 g samples were used (Figure 21). The gamma spectrometry samples did not undergo any treatment, while the mass spectrometry ones were dissolved, and ^{209}Bi was added as an internal standard to correct for matrix effects. Quadrupole mass spectrometry was used for the measurement.

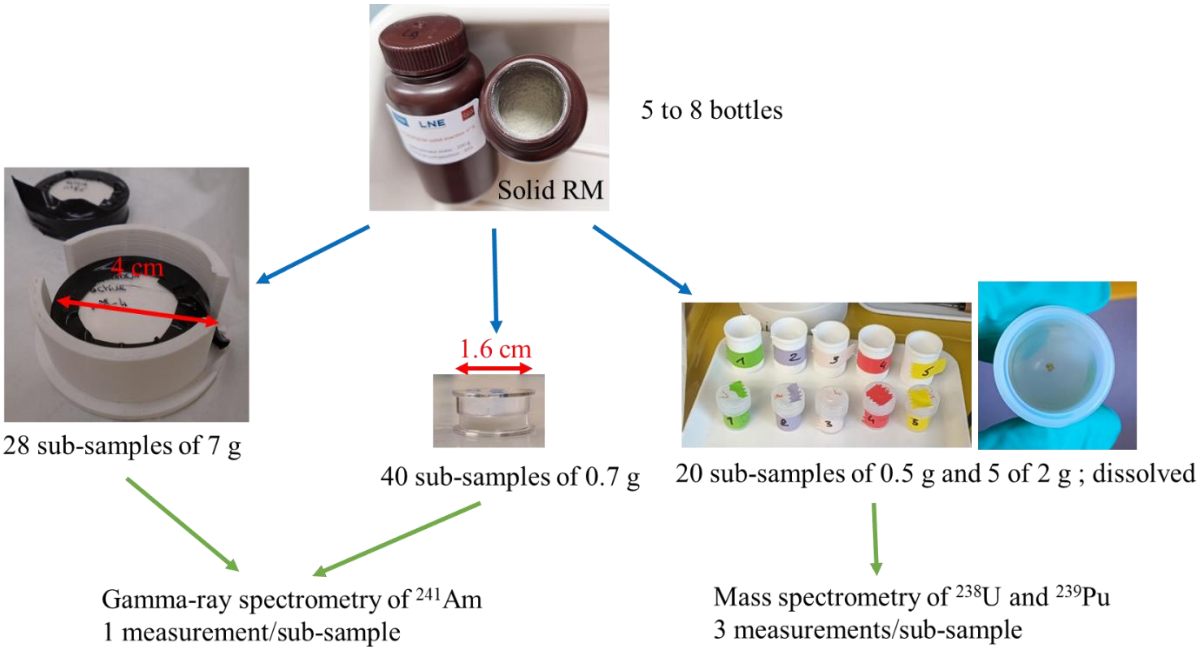

Figure 21. Sampling scheme for the evaluation of the homogeneity of the solid reference material.

The results of the mass spectrometry measurements (four 0.5 g sub-samples and one 2 g sub-sample from five bottles), for ^{238}U and ^{239}Pu, and of the gamma-ray spectrometry of ^{241}Am (three to five 7 g sub-samples from five bottles and five 0.5 g sub-samples from eight bottles) are presented in Figure 22.

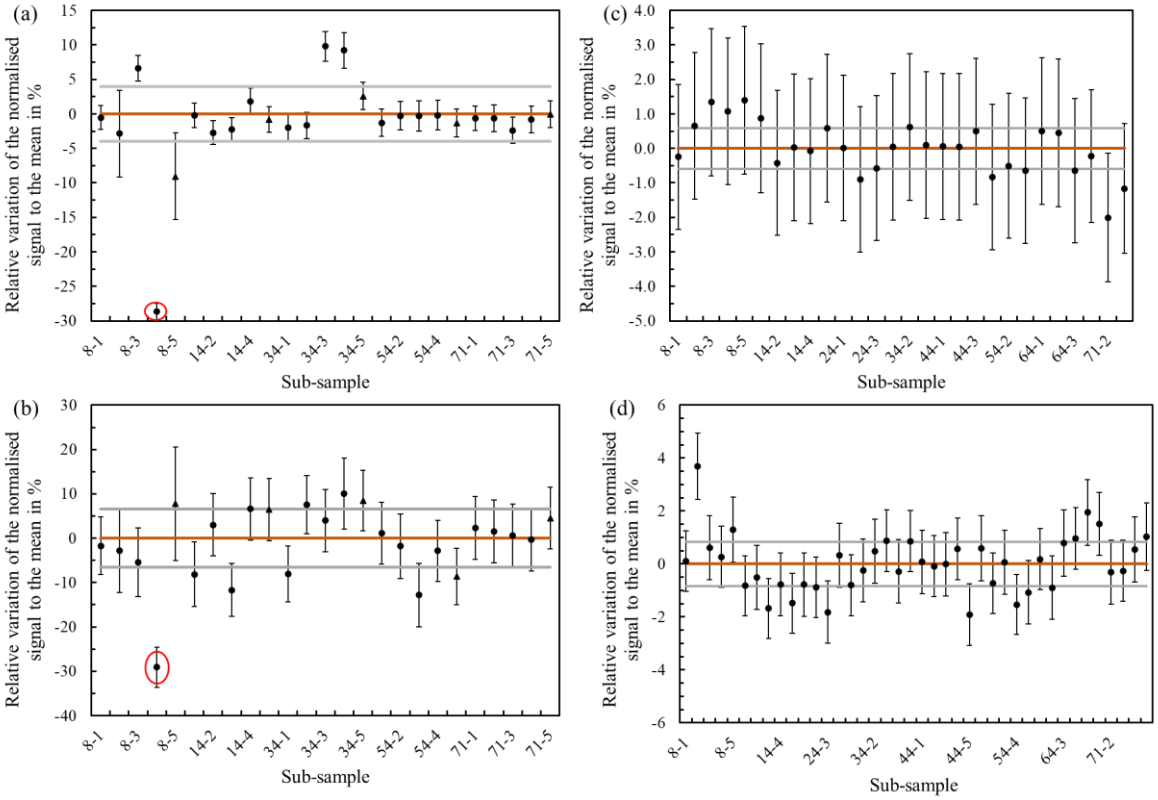

Figure 22. Relative variation of the mass spectrometry measurements of ^{238}U (a) and ^{239}Pu (b) to the average of the results, for the twenty sub-samples of 0.5 g (dots) and five sub-samples of 2 g (triangles) of the solid RM, and relative variation of the gamma-ray spectrometry measurements of ^{241}Am for (c) three to five sub-samples of 7 g and (d) forty sub-samples of 0.7 g. The bars represent the uncertainty of each individual measurement, at k = 1. The orange line represents the average of the values of the sub-samples, and the grey lines represent the standard deviation among the values of the sub-samples.

For ^{238}U and ^{239}Pu, sub-sample 8-4 was flagged as aberrant by a Grubbs test [4] and was removed from the analysis. No outlier was detected for ^{241}Am, using the same test. No upward or downward trend was observed with the filling order of the bottles.

A one-way analysis of variance (ANOVA) was performed to compare the variance within-bottles to the variance between-bottles.

Table 20. Summary of the between-bottle variance and within-bottle variance for ^{238}U, ^{239}Pu and ^{241}Am, for the solid RM. The asterisk (*) indicated that the ANOVA test flagged the parameter as significant.

Radionuclide	Technique	Size of subsample m in g	Between-bottle variance s_{bb} in %	Within-bottle variance s_{wb} in %	Uncertainty of measurement, at k = 1 in %
^{238}U	ICP-QMS	0.5	0.4	3.8*	1.7 to 7
^{239}Pu	ICP-QMS	0.5	0.9	6.3*	6 to 12
^{241}Am	Gamma-ray	0.7	0.7*	0.9	1.2

For ^{238}U and ^{239}Pu, the within-bottles variation was statistically significant, and was the highest contribution to the overall variance, while for ^{241}Am, a significant variation between bottles was detected, which could not be

explained by the variation within the bottles. This could indicate a different distribution of ^{241}Am compared to ^{238}U and ^{239}Pu in the solid reference material, however, it is more likely that any inhomogeneity among bottles was masked by the higher within-bottle variance due to the dissolution of the sample, and the higher variation of the measurement, for the mass spectrometry measurement.

4.1.3 Stability assessment – solid RM

The stability monitoring was performed by gamma-ray spectrometry, on ^{241}Am, with sub-samples of 0.7 g. The measurements were performed in the same manner as the homogeneity assessment, and the results were calculated at the same reference date (2025-01-01). The short-term and long-term stability measurements were performed in one run, four months after the homogeneity measurements. The dry mass of all the sub-samples was measured and used for corrections (from 1.5 % to 2.6 %).

The short-term stability study aims to recreate extreme conditions that may happen during transport, over a short period of time. Three bottles (n° 18, n° 38 and n° 58) were selected and placed at 4 °C, 20 °C and 40 °C, for one week. Then, three sub-samples of 0.7 g were prepared from each bottle (Figure 23).

The long-term stability study was performed at 20 °C, on bottle n° 23, to test normal storage conditions. Lower storage temperatures were not considered to reduce the possibility of moisture condensing on the material over time. Only the first set of measurement, after four months, is presented here, but additional measurements will be performed after eight and twelve months. Three sub-samples were also taken from the long-term stability bottle (Figure 23).

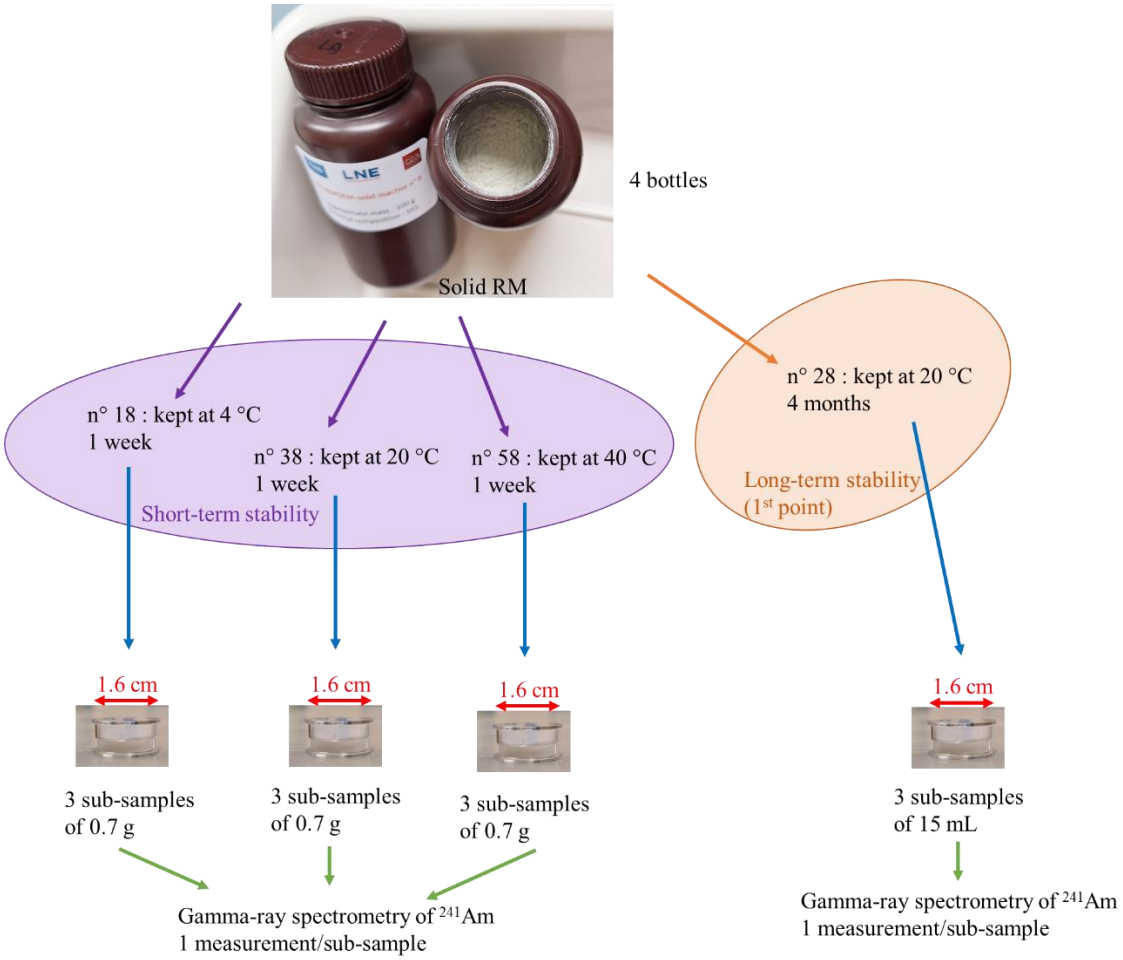

Figure 23. Scheme for the assessment of the short-term and long-term stability study for the solid reference material.

The gamma-ray spectrometry instrument used was not calibrated for the 0.7 g samples, however, the mass corrected signal (in counts/s/g) can be compared for each sample. The average of the measurements of all the sub-samples corresponding to a test condition was calculated and compared to the average of the measurements initially performed for the homogeneity assessment (Figure 24).

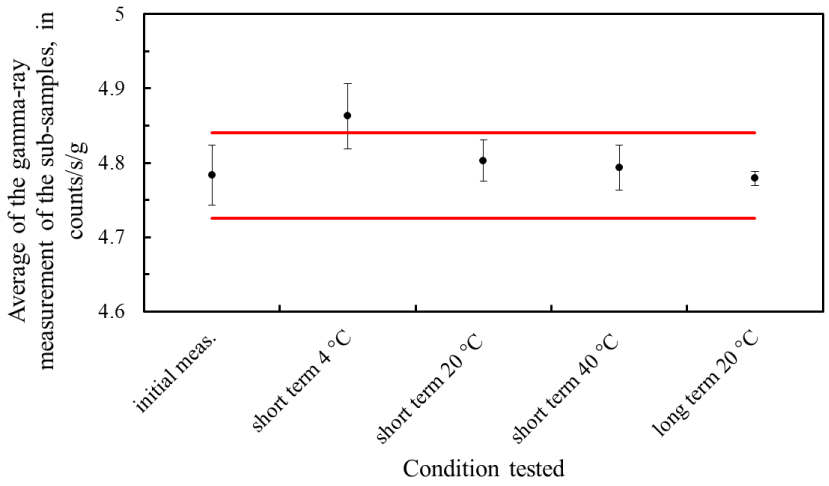

Figure 24. Comparison between the average of the measurements of the sub-samples for the initial measurement, for homogeneity (forty sub-samples), for the short-term stability samples kept at 4 °C, 20 °C and 40 °C, and for the long-term stability samples kept at 20 °C (3 sub-samples each). The bars represent the standard deviation among the sub-samples, and the red lines represent the uncertainty of the gamma-ray spectrometry measurement.

The results of the gamma-ray spectrometry measurement of ^{241}Am for the stability conditions tested are very similar, except for the sample kept at 4 °C for one week, which is 1.7 % higher than the initial measurement. The overall standard deviation between the conditions is low, at 0.7 %, and it decreases to 0.2 % when the short-term stability sample at 4 °C is removed. The lower storage condition may induce an increased moisture adsorption on the material, which may degrade the material.

The dispersion of the sub-samples was comparable for all the stability conditions tested, from 0.2 % to 0.9 %, and was also similar to the overall dispersion obtained during the homogeneity study (0.8 %).

A low instability was observed at 4 °C after one week. Since it is possible that this temperature was reached during transport, an uncertainty contribution due to the stability was added. Since only one measurement point was taken, a squared distribution of probability was considered, and $u_{st} = \frac{value_{init} - value_{1\,week\,4\,°C}}{\sqrt{12}} = 0.5\ \%$

The first assessment of the long-term stability did not reveal any significant variation, therefore $u_{st} = 0$

4.1.4 Assigned values – solid RM

The assigned values were determined by characterisation by a single laboratory, as recommended in the case of proficiency testing with a small number of participants [5]. The *Laboratoire de développement Analytique Nucléaire Isotopique et Elementaire* (LANIE), at CEA, was selected.

For the solid reference material, the direct measurement could not be performed by mass spectrometry, due to time constraints. Measurements of ^{241}Am were performed on the solid reference material by gamma spectrometry, without any dissolution or chemical separation.

Furthermore, the value for each radionuclide was derived gravimetrically from the measurement of the individual starting solutions (U, Pu, Am and Np), and from the “multi-RN” mixture.

The measurements of the “multi-RN” mixture were performed by multi-collector ICP-MS and isotope dilution. The measurements of the starting U solution were performed by TIMS, using inverse isotope dilution. The Np solution was characterised by multi-collector ICP-MS, using a calibration curve. The Pu solution was measured by alpha spectrometry, without any chemical separation, and contained ^{241}Am as a decay product. The ^{241}Am

content in the Am solution was characterised by ionisation chamber, and the ^{237}Np content (decay product) in the Am solution was characterised by multi-collector ICP-MS, using a calibration curve.

All results were reported at the reference date of the 1st of January 2025, and compared.

*Table 21. Comparison between the property values determined from the measurement of the starting solutions, of the multi-RN spiking mixture and from direct measurement, for the solid reference material. The uncertainties are presented at k = 1. *Value obtained from a mass spectrometry measurement, **value obtained from an alpha spectrometry measurement; *** value obtained from a gamma spectrometry measurement.*

Measurand	Value obtained from starting solutions + gravimetric dilutions, in µg/g	Value obtained from multi-RN spiking mixture + gravimetric dilutions, in µg/g	Value obtained by direct measurement, in µg/g	Comment
$w(^{234}U)$	1.7933 (53) E-06*	1.818 (44) E-06*	/	2 meas. compatible k = 1
$w(^{235}U)$	3.346 (10) E-04*	3.3596 (80) E-04*	/	2 meas. compatible k = 2
$w(^{236}U)$	2.3065 (69) E-06*	2.38 (12) E-06*	/	2 meas. compatible k = 1
$w(^{237}Np)$	5.56 (17) E-04*	5.727 (80) E-04*	/	2 meas. compatible k = 1
$w(^{238}U)$	3.3421 (94) E-02*	3.3370 (77) E-02*	/	2 meas. compatible k = 1
$w(^{239}Pu)$	1.097 (13) E-03**	1.1463 (31) E-03*	/	2 meas. non-compatible
$w(^{240}Pu)$	2.469 (29) E-05**	2.5868 (77) E-05*	/	2 meas. non-compatible
$w(^{241}Am)$	4.122 (23) E-04**	4.187 (42) E-04*	4.281 (90) E-04***	3 meas. compatible k = 2

For the ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{238}U and ^{241}Am, all the performed measurements agreed, within uncertainties (Table 21).

The results of ^{239}Pu and ^{240}Pu calculated from the starting solutions were lower than the ones measured on the multi-RN spiking mixture. It is likely that, similarly to the liquid reference material, some ^{239}Pu and ^{240}Pu was present in another solution (^{241}Am and/or ^{237}Np). Due to time constraints no investigation could be done to confirm this hypothesis.

Since the measurement of the multi-RN spiking mixture was the most complete dataset, these values were used as assigned values.

The uncertainty of the assigned value for each radionuclide, and for the isotopic ratios of interest depends on the uncertainty of the measurement performed (on the final liquid RM, on the multi-RN spiking mixture or on the starting solutions), but also on the homogeneity and stability of the reference material. In fact, it is possible

that the preparation steps (dilution, mixing) induce a repartition of the radionuclides which is not perfectly homogeneous. Furthermore, the reference material might age and the concentration of the radionuclides of interest might vary over time. It is important for reference materials producers to evaluate the differences between and within the units produced (homogeneity), and to follow several units over time (short term and long-term stability). If significant differences are observed, the reference material might still be perfectly useful to users, however the uncertainty of the assigned values must be corrected. It is common to increase the uncertainty of an assigned value using homogeneity and stability contributions [3]:

$$u_{\mathrm{RM}}^2 = u_{\mathrm{char}}^2 + u_{\mathrm{bb}}^2 + u_{\mathrm{wb}}^2 + u_{\mathrm{st}}^2 + u_{\mathrm{lt}}^2$$

Where:

u_{char} is the uncertainty of the measurement used to characterise one measurand of the reference material

u_{bb} is the uncertainty component coming from the difference between bottles of the reference material

u_{wb} is the uncertainty component coming from the difference within bottles of the reference material

u_{st} is the uncertainty component coming from the difference in the reference material, after a short period of time

u_{lt} is the uncertainty component coming from the difference in the reference material, after a long period of time

The homogeneity was assessed only on ^{238}U, ^{239}Pu and ^{241}Am, therefore the variances obtained for ^{238}U were applied to the other U isotopes, and the isotopic ratios, the variances obtained for ^{239}Pu were applied to ^{240}Pu and the isotope ratio, and the variances obtained for ^{241}Am were applied to ^{237}Np. The stability was only assessed on ^{241}Am; therefore, the uncertainty contribution calculated for this radionuclide was applied to all measurands. The uncertainty components are summarised in Table 22.

Table 22. Assigned values and uncertainty components, for the solid RM.

Measurand	Assigned value in µg/g	u_{char} in %	u_{bb} in %	u_{wb} in %	u_{st} in %	u_{lt} in %	u_{RM} in %
$w(^{234}U)$	1.818E-06	2.4	0.4	3.8	0.5	0	4.6
$w(^{235}U)$	3.360E-04	0.2	0.4	3.8	0.5	0	3.9
$w(^{236}U)$	2.38E-06	5.0	0.4	3.8	0.5	0	6.3
$w(^{237}Np)$	5.73E-04	1.4	0.7	0.9	0.5	0	1.9
$w(^{238}U)$	3.337E-02	0.2	0.4	3.8	0.5	0	3.9
$w(^{239}Pu)$	1.1463E-03	0.3	0.9	6.3	0.5	0	6.4
$w(^{240}Pu)$	2.587E-05	0.3	0.9	6.3	0.5	0	6.4
$w(^{241}Am)$	4.187E-04	1.0	0.7	0.9	0.5	0	1.6
Measurand	Assigned value in mol/mol	u_{char} in %	u_{bb} in %	u_{wb} in %	u_{st} in %	u_{lt} in %	u_{RM} in %
$R(^{234}U/^{238}U)$	5,54E-05	2.4	0.4	3.8	0.5	0	4.6
$R(^{235}U/^{238}U)$	1,0197E-02	0.3	0.4	3.8	0.5	0	3.9
$R(^{236}U/^{238}U)$	7,20E-05	5.0	0.4	3.8	0.5	0	6.3
$R(^{239}Pu/^{240}Pu)$	7,20E-05	0.4	0.9	6.3	0.5	0	6.3

4.2 Comparison of participants' experimental procedures

4.2.1 Sample preparation

Procedures used in sample preparation with the solid RM are presented in Table 23, and in details in Table 41, in Appendix 3.

Part of the laboratories reported sample drying before starting the radioanalytical separation procedure.

For most techniques used, the solid reference material had to undergo an additional preparation step, compared to the liquid one: a dissolution step. This might lead to material loss. The samples were decomposed by ashing and wet-ashing, by borate fusion, nitric acid leaching, or by microwave-assisted digestion.

Most laboratories used extraction chromatography or ion exchange as purification methods for the radionuclides of interest. Depth of the obtained details about the sample preparation methods varied widely.

As with the liquid RM, also with the solid RM most laboratories used tracers or standard reference materials in the measurements, for controlling yield and for mass bias calculations.

The number of subsamples varied from 1 to 7 among the laboratories. The used subsample mass varied from 0.01 g to 20 g. . Obtained information about the sample introduction was incomplete in some cases.

Table 23. Summary of the sample preparation performed by the participants to the solid ILC.

Ref participant	Number of subsamples and amount of sample	Dry mass correction	Tracer	Chemical treatment	Chemical separation of interferences	RN pre-concentration
10	6/1 g or 2.5 g		None	None	None	None
25	0.5 g	0.942	Pu-242, U-236, Am-243	yes	no	no
30	5 / 0.5 g	Yes	Am-243, Pu-242, U-236	yes	no	no
33	5/ 1 g	Yes	Pu-242 & U-232	yes	yes	no
40	5 / 20 g		None	no	no	no
45	4 / 5 g		Pu-242, Am-243	yes	yes	no
50	5 / 0.06 g		242-Pu (IRMM-085), 233-U (IRMM-058), and 243-Am (NIST 4332e)	yes	yes	yes
53	0.5 g	Fixed at 2 %		yes	no	no
60	5 / 0.01 g for Pu, 0.02 g for Am	Yes	Am-243, Pu-242, U-232	yes	yes	no info
65	5 / 1 g	Yes	U, Pu	yes	yes	no
73	5 / 2 g for IDMS and 7 / 2 g for isotopic composition	Yes	235U: IRMM-054.	yes	yes	yes

4.2.2 MS instruments and sample introduction methods

Information related to the instruments used are summarized in Table 24, and details are given in Table 42 (Appendix 3).

Most of the participants (eight over ten) used inductively coupled mass spectrometry (ICP-MS) to measure the samples, and the other two used radiometric techniques (alpha spectrometry and gamma-ray spectrometry). Four participants used ICP tandem mass spectrometry ICP-MS/MS, two participants used accelerator mass spectrometry (AMS), one participant used quadrupole ICP-MS (ICP-QMS), one participant used multi-collector ICP-MS (MC-ICP-MS) and one participant used ICP sector field mass spectrometry (ICP-SFMS).

Table 24. Summary of the instrumental parameters used by the participants to the solid ILC.

Ref participant	System	ICP-MS sample introduction system	Blank correction	Mass bias correction	iRM	Type of quantification
10	Gamma spec	Not applicable	none	none	none	Calibration standard
25	ICP-QMS	no info	yes	no	no info	
30	ICP-MS/MS	ICP-MS torch	yes	yes, Spiking with Am-243, Pu-242, U-236	no	
33	ICP-MS/MS	peristaltic pump, quartz cyclonic spray chamber, PFA-ST nebulizer, quartz injector, iCap Q quartz torch	yes	automatic correction	yes, 'IAEA-384 Fangataufa', 'IAEA-385 Irish Sea Sediment'; TDMA 51.6	
40	Gamma spec	not applicable	yes	no	yes, Secondary reference material made of multy-radionuclide solution CMI	Calibration standard
45	ICP-SF-MS	Twinnabar-type, Apex (ESI)	yes	no	yes, natural U to check the isotope ratio measurement	
50	AMS	Cs sputtering ion source	yes	no	yes, use of isotope standards	
53	ICP-MS/MS	Standard quartz sample introduction system - PFA inert kit and Ni-plated Pt-tipped sampling and skimmer cones	yes	no	isotope standards	Calibration curve (radiometric standards)
60	Alpha spec	not applicable	no	not applicable	yes, Am-243 and Pu-242 for spectrometer calibration	
65	ICP-MS/MS	no info	no	yes, for Am, U and Np, mass bias was calculated based on the measurement of U solution IRRM (2008-03-0022). For Pu mass bias calculations, Pu certified solution UK Pu 5/92138 was used.	yes, IRRM-075 (Uranium), Pu 5/92138 (Plutonium) UK	Isotope dilution
73	MC-ICP-MS	CETAC Aridus 2 Desolvating Nebulizer System and Nebulizer: Savillex PFA, self-aspirating, 50 µL/min	yes	yes, mass bias correction was done by SSB using IRMM-184 as isotopic reference	IRMM-184	Isotope dilution

4.2.3 Uncertainty budgets

The detailed uncertainty budgets provided by the participants are presented in Table 44, in Appendix 5.

The main uncertainty contributions identified by the partners are: mass fraction of the reference material, the counting statistics, the efficiency of the measurement or the standard used, the tracer(s), the weighing, the standard deviation between sub-samples, the radiochemical separation and the mass bias.

4.3 Participants' results – solid RM

In interlaboratory comparisons, it is usual to detect outliers using tests such as Grubbs or Pierce [4]. However, those tests are only appropriate for large datasets (typically above 10). However, the participants submitted between 3 and 8 results for each measurand. Therefore, those tests were not performed and the outliers were determined graphically, for each measurand.

4.3.1 Results for the mass fraction of ^{234}U

The participants' results for the mass fraction of ^{234}U, sorted by increasing order, are presented in Figure 25. The bars represent the uncertainty of each measurement, at $k = 1$. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

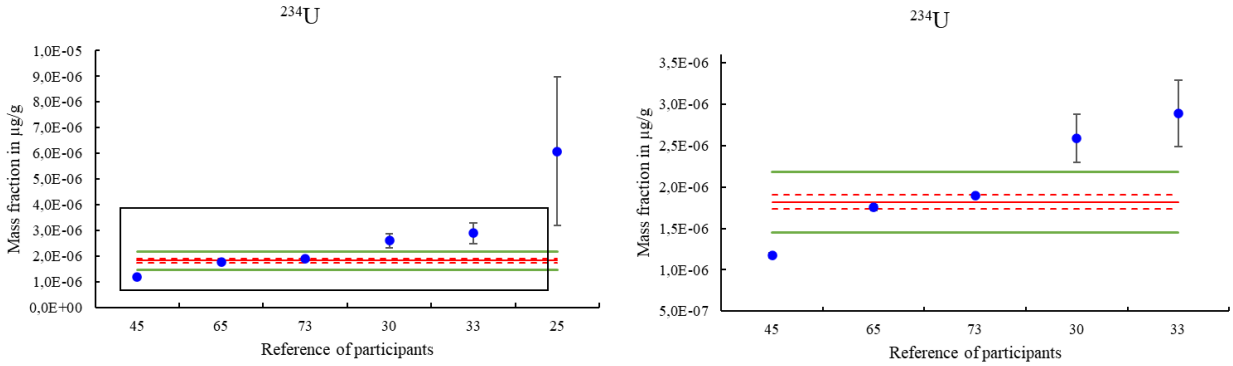

Figure 25. Results for the mass fraction of ^{234}U mass fraction (increasing order) – solid RM.

Five participants did not give any results for the mass fraction of ^{234}U. Two out of the six reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 25.

Table 25. Results obtained for the mass fraction of ^{234}U and performance statistics – solid RM.

Ref Participant	Meas. technique	^{234}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	1.818E-06	8.4E-08	4.6				
25	ICP-QMS	6.1E-06	2.9E-06	48	234	NS	1.5	S
30	ICP-MS/MS	2.59E-06	2.9E-07	11	42	NS	2.6	D
33	ICP-MS/MS	2.89E-06	4.0E-07	14	59	NS	2.6	D
45	ICP-SF-MS	1.173E-06	2.7E-08	2.3	-35	NS	-7.4	NS
65	ICP-MS/MS	1.754E-06	3.5E-08	2.0	-3.5	S	-0.7	S
73	MC-ICP-MS	1.893E-06	1.6E-08	0.85	4.1	S	0.9	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{234}U, because the activity of this radionuclide in the samples was too low.

For all ICP-MS/MS, ICP-SFMS and MC-ICP-MS techniques, the uncertainties were below 14 %, with the lowest uncertainty for the analysis performed by MC-ICP-MS (0.85 %) as expected, since it is the same analysis technique used to determine the assigned value and also because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for two results, n° 65 and n° 73, which indicates that the participating laboratories achieved a good accuracy for this measurand. This criterion was Non-Satisfactory for the other four results, with deviations to the assigned value ranging from 35 % to 235 %.

The second criterion, the zeta score ζ_p, was Satisfactory for three results, n° 25, n° 65 and n° 73, which indicated that these results were compatible to the assigned values, within uncertainties. The second criterion was Discrepant for results n° 30 and n° 33, and Non-Satisfactory for result n° 45, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 30 and n° 33) or k = 3 (n° 45).

Two of the three results obtained by the ICP-MS/MS technique were “NS” for the first criterion and “D” for the second one, which may indicate an error in the preparation/pre-concentration of the samples or interference at the time of analysis, since the value found is approximately 1.3 times higher than the assigned value.

The result n° 45 (ICP-SFMS technique) had excellent results for the liquid RM for ^{234}U but not for the solid RM, which may indicate that the problem is not related to the measurement technique but rather to the method of U extraction from the matrix, as it is more complex and the result obtained was lower (1.5x) than the assigned value. In fact, the participant reported using acid leaching, which was probably not 100 % efficient.

4.3.2 Results for the mass fraction of ^{235}U

The participants' results for the mass fraction of ^{235}U, sorted by increasing order, are presented in Figure 26. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Six of the results presented here were directly reported by participants (blue squares) and the other was calculated from reported mass activity (black dots).

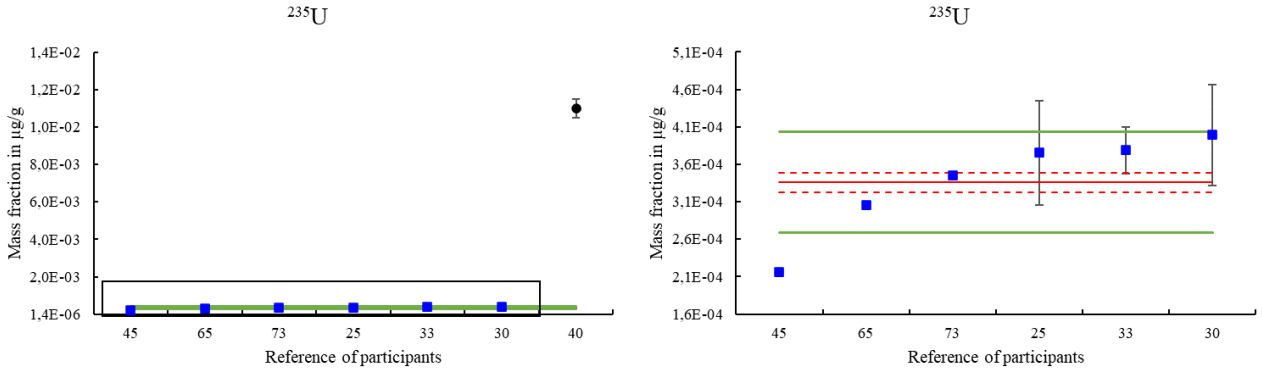

Figure 26. Results for the mass fraction of ^{235}U (increasing order) – solid RM.

Four participants did not give any results for the mass fraction of ^{235}U. The result n° 40 was discrepant compared to the other results. Five of the results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 26.

Table 26. Results obtained for the mass fraction of ^{235}U and performance statistics – solid RM.

Ref Participant	Meas. technique	^{235}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	3.36E-04	1.3E-05	3.9				
25	ICP-QMS	3.75E-04	7.0E-05	19	12	S	0.6	S
30	ICP-MS/MS	3.99E-04	6.7E-05	17	19	D	0.9	S
33	ICP-MS/MS	3.79E-04	3.1E-05	14	13	S	1.3	S
40	Gamma spec	1.101E-02	5.0E-03	9.1	3177	NS	21	NS
45	ICP-SF-MS	2.16E-04	4.5E-06	2.1	-36	NS	-8.7	NS
65	ICP-MS/MS	3.053E-04	4.7E-06	1.5	-9.1	S	-2.2	D
73	MC-ICP-MS	3.4542E-04	5.8E-07	0.17	2.8	S	0.7	S

For all techniques, the uncertainties were below 19 %, with the lowest uncertainty for the analysis performed by MC-ICP-MS (0.17 %), which is expected because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for four results, which indicated that these participating laboratories achieved a good accuracy for this measurand. It was below 20 % for one result, n° 30, which was overestimated by 19 %, and it was above 20 % for results n° 40 and n° 45. Since the result n° 40 was obtained with gamma-ray spectrometry, it is possible that there were interferences coming from other radionuclides in the ray used to quantify ^{235}U, which lead to the overestimation of the activity in the sample. For participant n° 45, the lower result is probably linked to the method of U extraction in the matrix (acid leaching), rather than to the technique (ICP-SFMS), which performed correctly for the liquid RM.

The second criterion, the zeta score ζ_p, was Satisfactory for four results, which indicated that those were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for the result n° 65 and Non-Satisfactory for results n° 40 and n° 45, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 65) or k = 3 (n° 40 and n° 45).

4.3.3 Results for the mass fraction of ^{236}U

The participants' results for the mass fraction of ^{236}U, sorted by increasing order, are presented in Figure 27. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

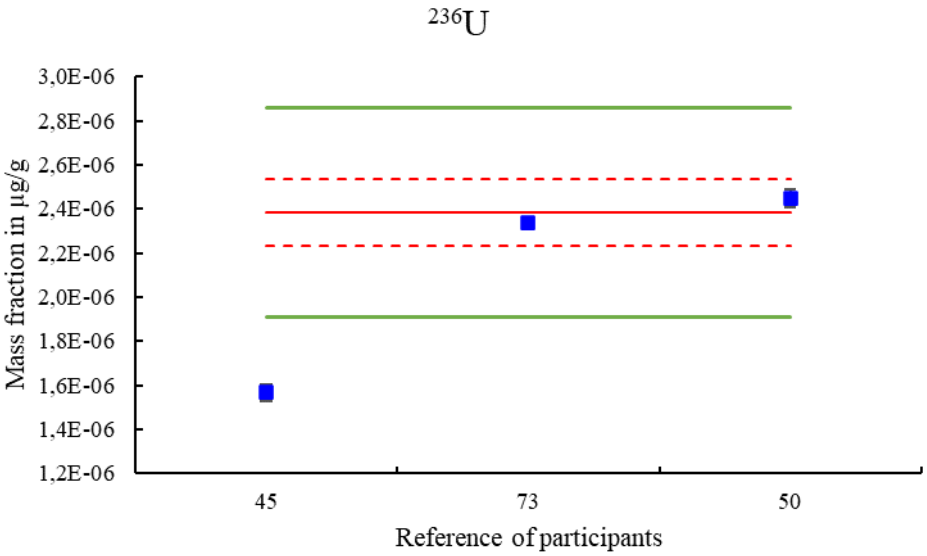

Figure 27. Results for the mass fraction of ^{236}U (increasing order) – solid RM.

Eight participants did not give any results for the mass fraction of ^{236}U. Two of the reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 27.

Table 27. Results obtained for the mass fraction of ^{236}U and performance statistics – solid RM.

Ref Participant	Meas. technique	^{236}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.38E-06	1.5E-07	6.3				
45	ICP-SF-MS	1.566E-06	3.8E-08	2.4	-34	NS	-5.3	NS
50	AMS	2.448E-06	4.0E-08	1.6	2.7	S	0.4	S
73	MC-ICP-MS	2.335E-06	2.6E-08	1.1	-2.1	S	-0.3	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{236}U, because the activity of this radionuclide in the samples was too low.

For all three techniques, the uncertainties were between 1.1 % and 2.4%, with the lowest uncertainty for the analysis performed by MC-ICP-MS, as expected, since it is the same analysis technique used to determine the assigned value and also because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for two results, n° 50 and n° 73. It was above 20 % for one result, n° 45. The result n° 45 (ICP-SFMS technique) performed correctly for the measurement of ^{236}U in the liquid RM, which may indicate that the problem is rather to the method of U extraction in the matrix (acid leaching), as the result obtained was lower (1.5 times lower) than the assigned value.

The second criterion, the zeta score ζ_p, was Satisfactory the results n° 50 and n° 73, which indicated that those were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for result n° 45, indicating that the deviation to the assigned value was not covered by the reported uncertainties, at k = 3.

4.3.4 Results for the mass fraction of ^{237}Np

The participants' results for the mass fraction of ^{237}Np, sorted by increasing order, are presented in Figure 28. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Six of the results presented here were directly reported by participants (blue squares) and the other was calculated from reported mass activity (black dots).

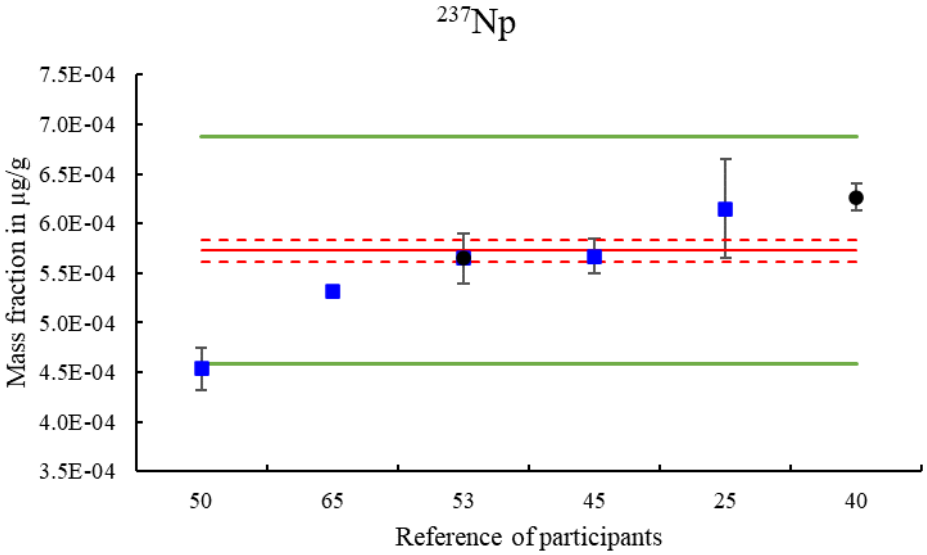

Figure 28. Results for the mass fraction of ^{237}Np (increasing order) – solid RM.

Five participants did not give any results for the mass fraction of ^{237}Np. Five of the results deviated by less than 20 % from the assigned value, and the last one was close to 20 %.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 28.

Table 28. Results obtained for the mass fraction of ^{237}Np and performance statistics – solid RM.

Ref Participant	Meas. technique	^{237}Np mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	5.73E-04	1.1E-05	1.9				
25	ICP-QMS	6.15E-04	5.0E-05	8.1	7.4	S	0.8	S
40	Gamma spec	6.26E-04	1.3E-05	2.1	9.4	S	3.1	NS
45	ICP-SF-MS	5.67E-04	1.7E-05	3.1	-1.0	S	-0.3	S
50	AMS	4.54E-04	2.1E-05	4.6	-21	NS	-5.0	NS
53	ICP-MS/MS	5.65E-04	2.5E-05	4.4	-1.4	S	-0.3	S
65	ICP-MS/MS	5.314E-04	1.6E-06	0.30	-7.2	S	-3.8	NS

For all the different techniques, the uncertainties were between 0.30 % and 8.1%.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for five results, which indicated that these participating laboratories achieved a good accuracy for this measurand. It was above 20 % for result n° 50.

The second criterion, the zeta score ζ_p, was Satisfactory for three results, which indicated that those were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for results n° 40, n° 50 and n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 3.

For the AMS technique the scores were Non-satisfactory for both criteria. The problem could be linked to the method of ^{237}Np extraction in the matrix, as the result obtained was lower than the assigned value.

It can be noted that for the measurement of ^{237}Np, the participant n° 45 performed better than for the U isotopes results. In fact, these measurements were performed on dissolved samples, while the U ones were obtained after acid leaching, which probably did not extract all the U from the samples.

4.3.5 Results for the mass fraction of ^{238}U

The participants' results for the mass fraction of ^{238}U, sorted by increasing order, are presented in Figure 29. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

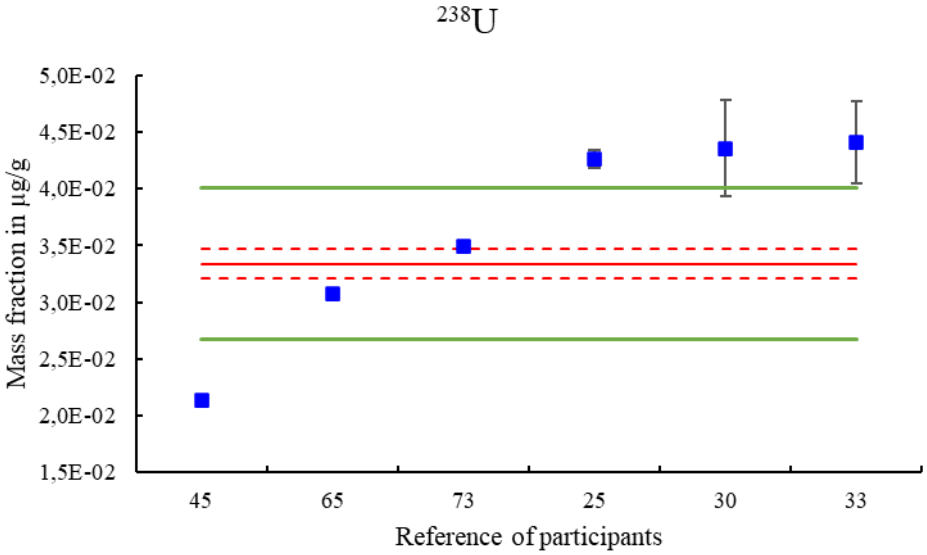

Figure 29. Results for the mass fraction of ^{238}U (increasing order) -solid RM.

Five participants did not give any results for the mass fraction of ^{238}U. Two of the reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 29.

Table 29. Results obtained for the mass fraction of ^{238}U and performance statistics – solid RM.

Ref Participant	Meas. technique	^{238}U mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	3.34E-02	1.3E-03	3.9				
25	ICP-QMS	4.262E-02	7.7E-04	1.8	28	NS	6.1	NS
30	ICP-MS/MS	4.36E-02	4.2E-03	10	31	NS	2.3	D
33	ICP-MS/MS	4.41E-02	3.6E-03	8.2	32	NS	2.8	D
45	ICP-SF-MS	2.139E-02	4.1E-04	1.9	-36	NS	-8.8	NS
65	ICP-MS/MS	3.076E-02	4.0E-04	1.3	-7.8	S	-1.9	S
73	MC-ICP-MS	3.4887E-02	5.8E-05	0.17	4.5	S	1.2	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the mass fraction of ^{238}U, because the activity of this radionuclide in the samples was too low.

For all six techniques, the uncertainties were between 0.17 % and 10 %, with the lowest uncertainty for the analysis performed by MC-ICP-MS, as expected, since it is the same analysis technique used to determine the assigned value and also because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for two results, n° 65 and n° 73 which indicated that the participating laboratories achieved a good accuracy for this measurand. This criterion was Non-Satisfactory for the other four results, with deviations to the assigned value ranging from 28 % to 36 %, in absolute value.

The second criterion, the zeta score ζ_p, was Satisfactory for two results, n° 65 and n° 73, which indicated that these results were compatible to the assigned values, within uncertainties. The second criterion was Discrepant for results n° 30 and n° 33, and Non-Satisfactory for results n° 25 and n° 45, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2 (n° 30 and n° 33) or k = 3 (n° 25 and n° 45).

Only ICP-MS/MS and MC-ICP-MS analytical techniques passed for both criterions. Two of the three ICP-MS/MS results were higher than the assigned value, which may indicate that there was a matrix effect during the analysis. On the other hand, for the ICP-SFMS technique, the result found was lower, which may indicate a deficiency in the extraction of this isotope from the solid RM, due to the acid leaching.

4.3.6 Results for the mass fraction of ^{239}Pu

The participants' results for the mass fraction of ^{239}Pu, sorted by increasing order, are presented in Figure 30. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value,

and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

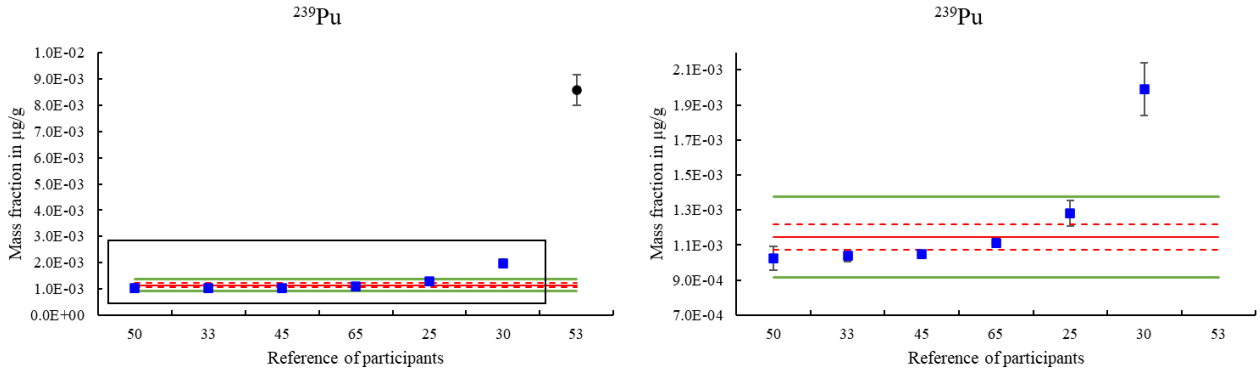

Figure 30. Results for the mass fraction of ^{239}Pu (increasing order) – solid RM.

Four participants did not give any results for the mass fraction of ^{239}Pu. Five of the seven reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 30.

Table 30. Results obtained for the mass fraction of ^{239}Pu and performance statistics – solid RM.

Ref Participant	Meas. technique	^{239}Pu mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	1.146E-03	7.3E-05	6.4				
25	ICP-QMS	1.28E-03	7E-05	5.8	12	S	1.3	S
30	ICP-MS/MS	1.99E-03	1.5E-04	7.5	74	NS	5.1	NS
33	ICP-MS/MS	1.040E-03	3.5E-05	3.4	-9.3	S	-1.3	S
45	ICP-SF-MS	1.047E-03	1.5E-05	1.4	-8.7	S	-1.3	S
50	AMS	1.026E-03	6.8E-05	6.6	-10	S	-1.2	S
53	ICP-MS/MS	8.58E-03	5.8E-04	6.8	649	NS	12.7	NS
65	ICP-MS/MS	1.112E-03	2.2E-05	2.0	-3.0	S	-0.5	S

The participant n° 60, using alpha spectrometry, did not report any ^{239}Pu mass activity fraction, because this radionuclide cannot be separated from ^{240}Pu. Instead, the total mass activity of those two radionuclides was reported and is analysed in section 4.3.9.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for five out of seven reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand. The other two results (n° 30 an n° 53) deviated by more than 20 % from the assigned value.

The second criterion, the zeta score ζ_p, was Satisfactory for five results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for the results n° 30 and n° 53, indicating the deviation to the assigned value was not covered by the reported uncertainties, at k = 3.

Participants n° 30 and n° 53 were two of the four that used ICP-MS/MS, but had a higher result than the assigned value, which may indicate an error due to the matrix effect, or to the sample preparation.

4.3.7 Results for the mass fraction of ^{240}Pu

The participants' results for the mass fraction of ^{240}Pu, sorted by increasing order, are presented in Figure 31. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value,

and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

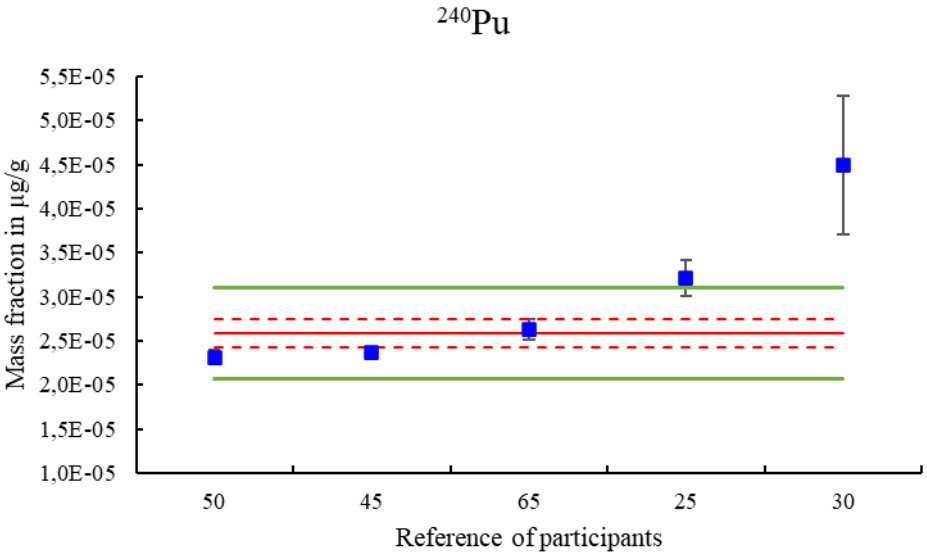

Figure 31. Results for the mass fraction of ^{240}Pu (increasing order) – solid RM.

Six participants did not give any results for the mass fraction of ^{240}Pu. Three of the five reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 31.

Table 31. Results obtained for the mass fraction of ^{240}Pu and performance statistics – solid RM.

Ref Participant	Meas. technique	^{240}Pu mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.59E-05	1.7E-06	6.4				
25	ICP-QMS	3.22E-05	2.0E-06	6.3	24	NS	2.4	D
30	ICP-MS/MS	4.49E-05	7.9E-06	18	74	NS	2.4	D
45	ICP-SF-MS	2.363E-05	3.4E-07	1.4	-8.7	S	-1.3	S
50	AMS	2.312E-05	8.1E-07	3.5	-11	S	-1.5	S
65	ICP-MS/MS	2.63E-05	1.2E-06	4.6	1.7	S	0.2	S

The participant n° 17, using alpha spectrometry, did not report any ^{240}Pu mass activity fraction, because this radionuclide cannot be separated from ^{239}Pu. Instead, the total mass activity of those two radionuclides was reported and is analysed in section 4.3.9.

For five techniques, the uncertainties were between 1.4 % and 18 %, the lowest being ICP-SFMS and the highest ICP-MS/MS.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for three out of five reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for three results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Discrepant for results n° 25 and n° 30, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 2.

ICP-QMS (n° 25) and ICP-MS/MS (n° 30), both obtained values higher than the assigned value, which may indicate a matrix effect during the analysis.

4.3.8 Results for the mass fraction of ^{241}Am

The participants' results for the mass fraction of ^{241}Am, sorted by increasing order, are presented in Figure 32. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Five of the results presented here were directly reported by participants (blue squares) and the other three were calculated from reported mass activity (black dots).

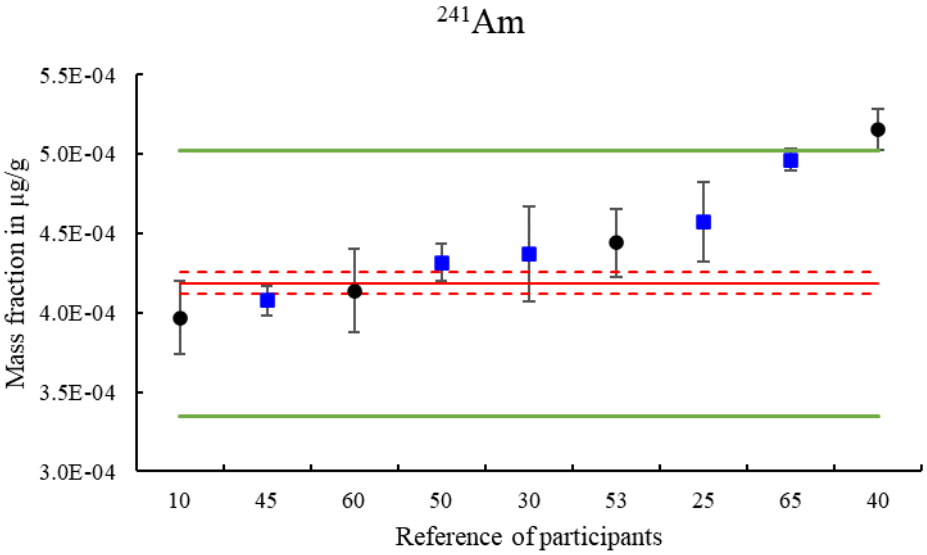

Figure 32. Results for the mass fraction of ^{241}Am (increasing order) – solid RM.

Two participants did not give any results for the mass fraction of ^{241}Am. Eight of the nine reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 32.

Table 32. Results obtained for the mass fraction of ^{241}Am and performance statistics – solid RM.

Ref Participant	Meas. technique	^{241}Am mass fraction in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	4.187E-04	6.7E-06	1.6				
10	Gamma spec	3.97E-04	2.3E-05	5.9	-5.2	S	-0.9	S
25	ICP-QMS	4.57E-04	2.5E-05	5.5	9.2	S	1.5	S
30	ICP-MS/MS	4.37E-04	3.0E-05	6.9	4.4	S	0.6	S
40	Gamma spec	5.16E-04	1.3E-05	5.0	23	NS	6.6	NS
45	ICP-SF-MS	4.076E-04	9.3E-06	2.3	-2.6	S	-1.0	S
50	AMS	4.32E-04	1.2E-05	2.8	3.1	S	1.0	S
53	ICP-MS/MS	4.44E-04	2.2E-05	4.9	6.1	S	1.1	S
60	Alpha spec	4.14E-04	2.6E-05	12.6	-1,1	S	-0.2	S
65	ICP-MS/MS	4.963E-04	6.8E-06	1.4	19	D	8.2	NS

The first criterion, the deviation from the assigned value, e_p, was below 15 % for seven out of nine reported results, which indicated that most participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for seven results, which indicated that they were compatible to the assigned values, within uncertainties. The zeta score was Non-Satisfactory for results n° 40 and n° 65, indicating that for these results, the deviation to the assigned value was not covered by the reported uncertainties, at k = 3.

The results n° 40 and n° 65 were obtained by the technique of ICP-MS/MS (1 in 2) and gamma spectrometry, with results higher than the assigned value, which may indicate an error due to the matrix effect or interference from another isotope.

4.3.9 Results for the mass activity of ^{239}Pu and ^{240}Pu

One participant, n° 17, could not measure ^{239}Pu and ^{240}Pu separately, due to the measurement technique used. Instead, they reported the mass activity of both those radionuclides. To compare with other participants, the mass activity of ^{239}Pu and ^{240}Pu, corresponding to the reported mass fractions, were calculated when

possible. The results for the mass activity of ^{239}Pu and ^{240}Pu, sorted by increasing order, are presented in Figure 33. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

One of the results presented here were directly reported by participants (blue squares) and the others were calculated from reported mass fractions (black dots).

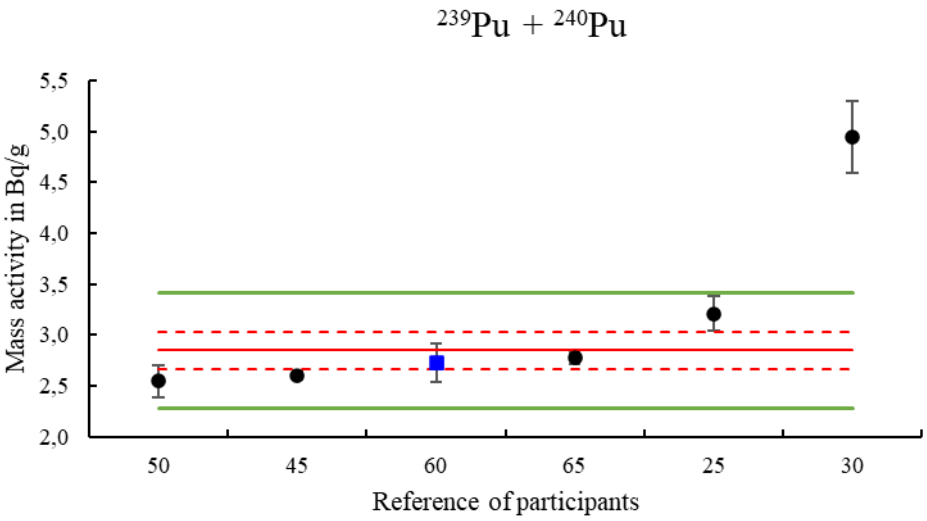

Figure 33. Results for the ^{239}Pu + ^{240}Pu mass activity (increasing order) – solid RM.

The result of the alpha spectrometry (n° 17) was close to the assigned value and to the other mass spectrometry measurements, except for n° 53.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 33.

Table 33. Results obtained for the $^{239}Pu + ^{240}Pu$ mass activity and performance statistics - solid RM.

Ref Participant	Meas. technique	$^{239}Pu + ^{240}Pu$ mass activity in Bq/g	Uncertainty at k = 1 in Bq/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.85	0.18	6.4				
25	ICP-QMS	3.21	0.17	5.4	13	S	1.4	S
30	ICP-MS/MS	4.94	0.35	7.1	74	NS	5.3	NS
45	ICP-SF-MS	2.599	0.034	1.3	-8.7	S	-1.3	S
50	AMS	2.55	0.16	6.1	-11	S	-1.3	S
60	Alpha spec	2.73	0.19	7.0	-4.1	S	-0.3	S
65	ICP-MS/MS	2.771	0.051	1.9	-2.7	S	-0.4	S

As could be expected, the participants using mass spectrometry had similar results for the calculated mass activity of ^{239}Pu and ^{240}Pu as for the mass fractions of individual radionuclides

Both criteria were Satisfactory for the participant n° 60. Alpha spectrometry, even if it does not discriminate between ^{239}Pu and ^{240}Pu, allowed for an accurate measurement of the sum of those two radionuclides, after separation from other elements.

4.3.10 Results for the total U content

The participants' results for the total U content, sorted by increasing order, are presented in Figure 15. The bars represent the uncertainty of each measurement, at $k = 1$. The red line represents the assigned value, and the red dotted lines represent the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other four were calculated from individual ^{234}U, ^{235}U, ^{236}U and ^{238}U mass fractions (black dots).

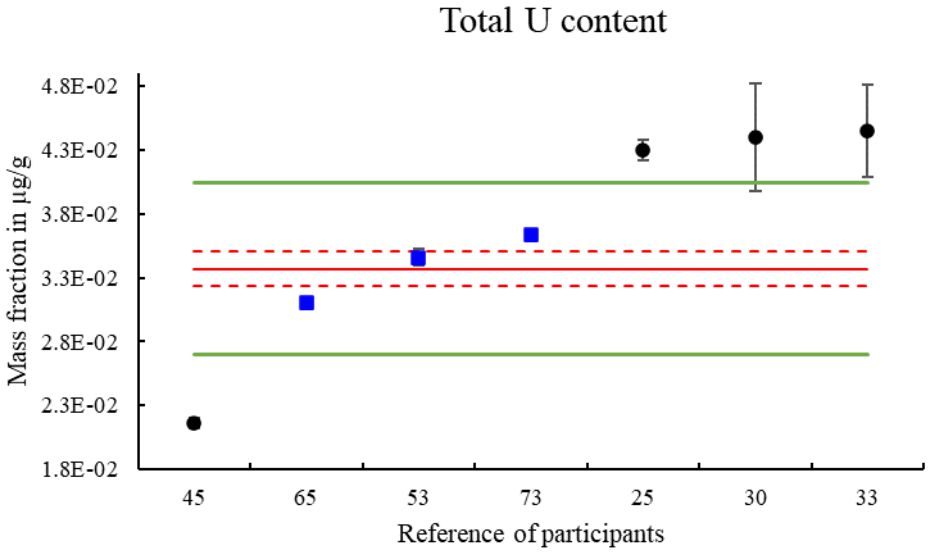

Figure 34. Results for the total U content (increasing order) – liquid RM.

Four participants did not give any results for the total U content, and it could not be calculated. Three reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 15.

Table 34. Results obtained for the total U content and performance statistics – liquid RM.

Ref Participant	Meas. technique	Total U content in µg/g	Uncertainty at k = 1 in µg/g	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	3.37E-02	1.3E-04	0.5				
25	ICP-QMS	4.301E-02	7.7E-04	1.8	28	NS	6.1	NS
30	ICP-MS/MS	4.4E-02	4.2E-03	9.5	31	NS	2.3	D
33	ICP-MS/MS	4.45E-02	3.6E-03	8.2	32	NS	2.8	D
45	ICP-SF-MS	2.161E-02	4.1E-04	1.9	-36	NS	-8.8	NS
53	ICP-MS/MS	3.461E-02	6.2E-04	1.8	2.7	S	0.6	S
65	ICP-MS/MS	3.106E-02	4.0E-04	1.3	-7.9	S	-1.9	S
73	MC-ICP-MS	3.640E-02	1.1E-04	0.30	8.0	S	2.0	D

The results were similar to those of ^{238}U, except for participant n° 53 who could only measure the total U content.

The first criterion, the deviation from the assigned value, e_p, was Satisfactory for three reported results, which indicates that the participating laboratories achieved a good accuracy for this measurand. It was Non-Satisfactory for the results n° 25, n° 30, n° 33 and n° 45.

The second criterion, the zeta score ζ_p, was Satisfactory for two out of the six reported and calculated results, which indicates that the results of the participants were compatible to the assigned values, within uncertainties. This criterion was Discrepant for result n° 30, n° 33 and n° 73, and Non-Satisfactory for results n° 25 and n° 45, which indicated that the deviation to the assigned value was not covered by the reported uncertainties, at k = 2, or k = 3.

4.3.11 Results for the $^{234}U/^{238}U$ isotope ratio

The participants' results for the $^{234}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 35. The bars represent the uncertainty of each measurement, at k = 1. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{234}U and ^{238}U mass fractions (black dots).

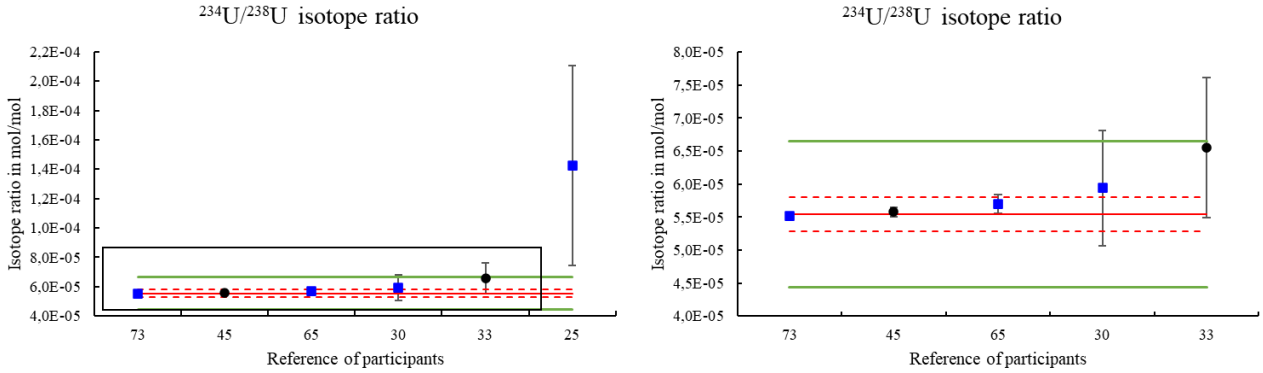

Figure 35. Results for the $^{234}U/^{238}U$ isotope ratio (increasing order) – solid RM.

Five participants did not give any results for the $^{234}U/^{238}U$ isotope ratio, and it could not be calculated from reported results. Five results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 35.

Table 35. Results obtained for the $^{234}U/^{238}U$ isotope ratio and performance statistics – solid RM.

Ref Participant	Meas. technique	Isotope ratio $^{234}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	5.54E-05	2.5E-06	4.6				
25	ICP-QMS	1.43E-04	6.8E-05	48	157	NS	1.3	S
30	ICP-MS/MS	5.94E-05	8.8E-06	15	7.2	S	0.4	S
33	ICP-MS/MS	6.6E-05	1.1E-05	16	18	D	0.9	S
45	ICP-SF-MS	5.577E-05	6.8E-07	1.2	0.6	S	0.1	S
65	ICP-MS/MS	5.70E-05	1.4E-06	2.5	2.8	S	0.5	S
73	MC-ICP-MS	5.518E-05	4.7E-07	0.85	-0.4	S	-0.1	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{234}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples was too low.

For all techniques, the uncertainties were between 0.85 % and 16 %, with a higher uncertainty for the result no.25 (ICP-QMS) at 45 %. The lowest uncertainty for the analysis performed by MC-ICP-MS (0.85 %) as expected, since it is the same analysis technique used to determine the assigned value and also because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for four reported and calculated results, which indicated that most of the participating laboratories achieved a good accuracy for this measurand. It was Discrepant for result n° 33 (calculated) and Non-Satisfactory for result n° 25. Calculating the isotopic ratio from mass fractions measured by ICP-MS/MS (result n° 33) is less precise than a direct isotopic ratio measurement. Furthermore, ICP-QMS, used by participant n° 25, is also a technique which is not targeted at isotopic ratio measurements. This is reflected in the uncertainties reported by the two participants and can explain the scores obtained by those participants to the first criterion.

The second criterion, the zeta score ζ_p, was Satisfactory for all reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties. The uncertainties reported by participants n° 25 and n° 33 covered the deviation to the assigned value.

The participant n° 45, whose results for the mass fractions of the individual U isotopes were Non-Satisfactory, obtained very good scores for the $^{234}U/^{238}U$ isotope ratios, comforting the hypothesis of an imperfect acid leaching of the U isotopes.

4.3.12 Results for the $^{235}U/^{238}U$ isotope ratio

The participants' results for the $^{235}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 36. The bars represent the uncertainty of each measurement, at k = 1. Bars might be too small to show on the figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{235}U and ^{238}U mass fractions (black dots).

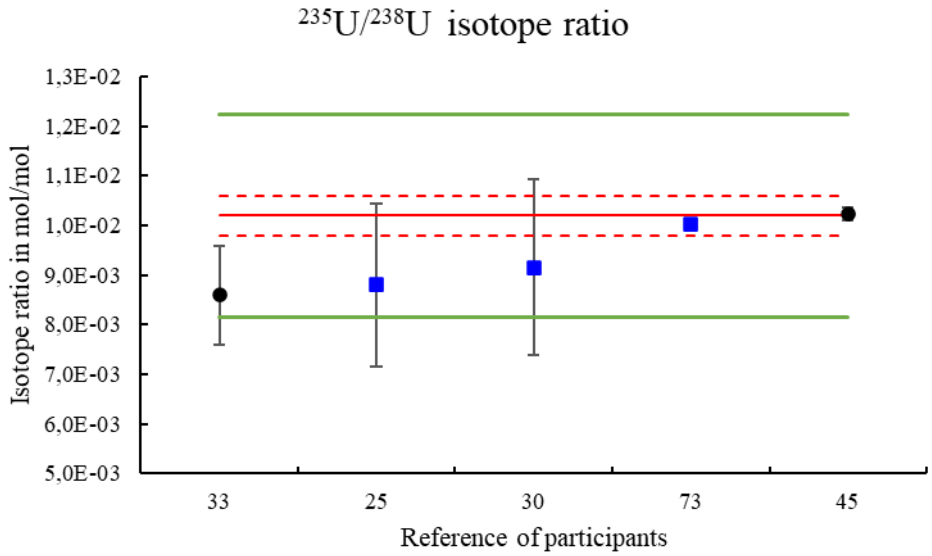

Figure 36. Results for the $^{235}U/^{238}U$ isotope ratio (increasing order) – solid RM.

Six participants did not give any results for the $^{235}U/^{238}U$ isotope ratio, and it could not be calculated from reported results. All the results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 36.

Table 36. Results obtained for the $^{235}U/^{238}U$ isotope ratio and performance statistic – solid RMs.

Ref Participant	Meas. technique	Isotope ratio $^{235}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	1.020E-02	4.0E-04	3.9				
25	ICP-QMS	8.8E-03	1.6E-03	19	-14	S	-0.8	S
30	ICP-MS/MS	9.2E-03	1.8E-03	19	-10	S	-0.6	S
33	ICP-MS/MS	8.6E-03	1.0E-03	12	-16	D	-1.5	S
45	ICP-SF-MS	1.023E-02	1.4E-04	1.3	0.3	S	0.1	S
73	MC-ICP-MS	1.0028E-02	1.7E-05	0.17	-1.7	S	-0.4	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{235}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples was too low.

For all techniques, the uncertainties were below 19 %, with lowest uncertainty for the analysis performed by MC-ICP-MS (0.17 %) as expected, since it is the same analysis technique used to determine the assigned value and also because MC-ICP-MS technique has a very high sensitivity [9].

The first criterion, the deviation from the assigned value, e_p, was below 15 % for four reported and calculated results, which indicated that these participating laboratories achieved a good accuracy for this measurand. The last result, n° 33, was Discrepant. This result was calculated from mass fractions measured by ICP-MS/MS, which is less precise than a direct isotopic ratio measurement. This is also reflected in the associated uncertainties.

The second criterion, the zeta score ζ_p, was Satisfactory for all reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties.

The participant n° 45, whose results for the mass fractions of the individual U isotopes were Non-Satisfactory, obtained very good scores for the $^{235}U/^{238}U$ isotope ratios, comforting the hypothesis of an imperfect acid leaching of the U isotopes.

4.3.13 Results for the $^{236}U/^{238}U$ isotope ratio

The participants' results for the $^{236}U/^{238}U$ isotope ratio, sorted by increasing order, are presented in Figure 37. The bars represent the uncertainty of each measurement, at k = 1. Bars might be too small to show on the figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

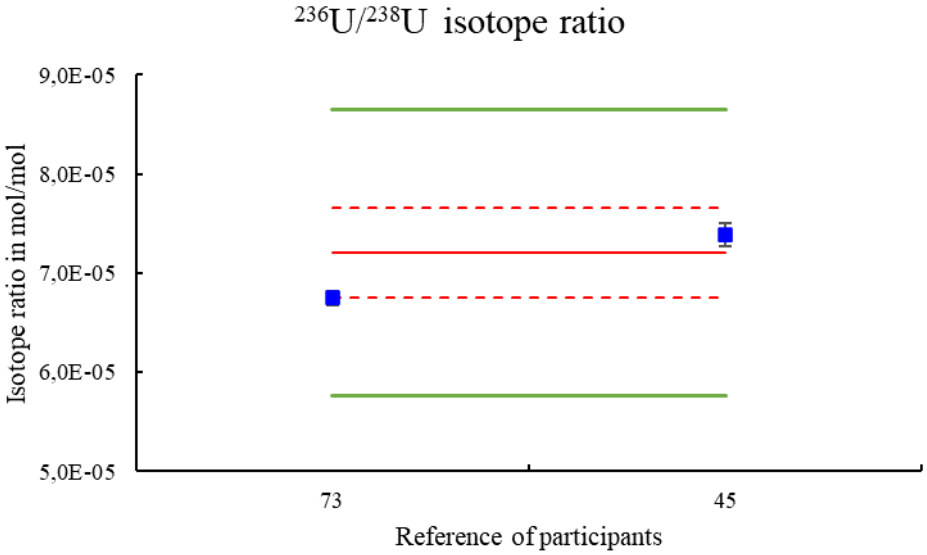

Figure 37. Results for the $^{236}U/^{238}U$ isotope ratio (increasing order) – solid RM.

Nine participants did not give any results for the $^{236}U/^{238}U$ isotope ratio, and it could not be calculated from individual mass fraction results. The two reported results deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 37.

Table 37. Results obtained for the $^{236}U/^{238}U$ isotope ratio and performance statistics – solid RM.

Ref Participant	Meas. technique	Isotope ratio $^{236}U/^{238}U$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	7.20E-05	4.5E-06	6.3				
45	ICP-SF-MS	7.38E-05	1.1E-06	1.5	2.5	S	0.4	S
73	MC-ICP-MS	6.749E-05	7.3E-07	1.1	-6.3	S	-1.0	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{236}U/^{238}U$ isotope ratio, because the activity of these radionuclides in the samples was too low.

The first criterion, the deviation from the assigned value, e_p and second criterion, the zeta score ζ_p, were Satisfactory for both reported results. This indicated that the results were close to the assigned value, and were compatible to the assigned values, within uncertainties.

The participant n° 45, whose results for the mass fractions of the individual U isotopes were Non-Satisfactory, obtained very good scores for the $^{236}U/^{238}U$ isotope ratios, comforting the hypothesis of an imperfect acid leaching of the U isotopes.

4.3.14 Results for the $^{240}Pu/^{239}Pu$ isotope ratio

The participants' results for the $^{240}Pu/^{239}Pu$ isotope ratio, sorted by increasing order, are presented in Figure 38. The bars represent the uncertainty of each measurement, at $k = 1$. Bars might be too small to show on the figure. The red line represents the assigned value, and the red dotted lines represents the standard uncertainty of the assigned value. The green lines represent the values between -20 % and +20 % of the assigned value.

Three of the results presented here were directly reported by participants (blue squares) and the other two were calculated from individual ^{240}Pu and ^{239}Pu mass fractions (black dots).

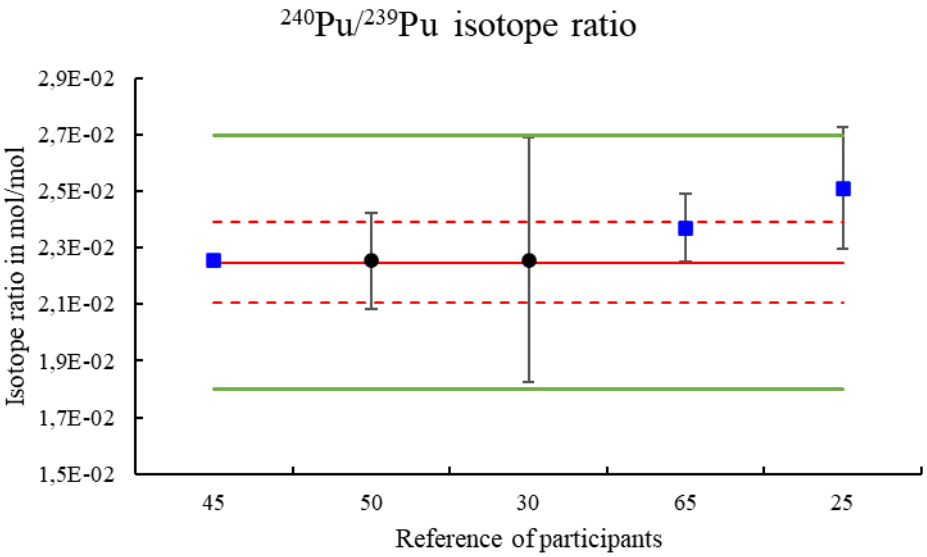

Figure 38. Results for the $^{240}Pu/^{239}Pu$ isotope ratio (increasing order) – solid RM.

Six participants did not give any results for the $^{240}Pu/^{239}Pu$ isotope ratio, and it could not be calculated from individual mass fraction results.

All results, reported and calculated, deviated by less than 20 % from the assigned value.

The performance of the participants was analysed using two criteria, described in [5], and explained in Appendix 6. Those criteria, as well as the reported and calculated results, are presented in Table 38.

Table 38. Results obtained for the $^{240}Pu/^{239}Pu$ isotope ratio and performance statistics – solid RM.

Ref Participant	Meas. technique	Isotope ratio $^{240}Pu/^{239}Pu$ in mol/mol	Uncertainty at k = 1 in mol/mol	Relative uncertainty at k = 1 in %	e_p in %		ζ_p	
Assigned value	MC-ICP-MS	2.25E-02	1.4E-03	6.4				
25	ICP-QMS	2.51E-02	2.1E-03	8.6	12	S	1.0	S
30	ICP-MS/MS	2.26E-02	4.3E-03	19	0.4	S	0.0	S
45	ICP-SFMS	2.253E-02	1.8E-04	0.8	0.3	S	0.0	S
50	AMS	2.25E-02	1.7E-03	7.5	0.3	S	0.0	S
65	ICP-MS/MS	2.37E-02	1.20E-03	5.1	5.5	S	0.7	S

The participants that used radiometric techniques (alpha spectrometry and gamma-ray spectrometry) did not measure the $^{240}Pu/^{239}Pu$ isotope ratio, because the activity of these radionuclides in the samples were too low for gamma spectrometry, and alpha spectrometry does not discriminate between the two isotopes.

The first criterion, the deviation from the assigned value, e_p, was below 15 % for all reported and calculated results, which indicated that the participating laboratories achieved a good accuracy for this measurand.

The second criterion, the zeta score ζ_p, was Satisfactory for all reported and calculated results, which indicated that the results of the participants were compatible to the assigned values, within uncertainties.

4.4 Discussion – general comments on the solid RM ILC

Overall, the obtained results from analysis of the solid RM represented good accuracy, even though it has to be noted that the size of the dataset is limited.

Sample dissolution step of the RM was found to affect significantly on some of the reported mass fraction values. In case the reported values were lower than the assigned values, an incomplete dissolution of the RM and therefore also an incomplete release of RNs was possibly the reason. Analysis of a solid RM is therefore much more challenging than a liquid RM. The effect of sample dissolution on the determined mass fractions was particularly shown in the concentrations of U isotopes by ICP-SF-MS.

The sensitivity of radiometric methods was not adequate for determination of all investigated radionuclides, e.g., U isotopes and isotope ratios of U and Pu. Furthermore, separate activity concentrations of ^{239}Pu and ^{240}Pu cannot be determined by alpha spectrometry due to their similar alpha decay energies.

The results for total U and ^{238}U were those with the highest number of “NS” results, 4 out of 7 and 4 out of 6 respectively, both for the first criterion (e_p).

Both ICP-QMS and ICP-SF-MS worked well in determination of ^{237}Np. However, matrix-related issues might have occurred with ^{237}Np determination by AMS, likely due to sample treatment.

MC-ICP-MS was the most sensitive and accurate one compared to other detection methods, in determination of U isotopes and $^{234/238}U$ and $^{235/238}U$ isotope ratios.

Matrix effect might have interfered ^{239}Pu determination by ICP-MS/MS and ^{240}Pu determination by ICP-QMS and ICP-MS/MS, and ^{241}Am by gamma spectrometry and ICP-MS/MS. Other possible reasons for observed discrepancies between reported and assigned values are interferences from other isotopes and sample treatment.

References

[1] Chambon ARI 2025

[2] Harms, A., Gilligan, C., 2012. Development of synthetic environmental radioactivity reference materials. Appl. Radiat. Isot., Proceedings of the 18th International Conference on Radionuclide Metrology and its Applications 70, 1940–1943. https://doi.org/10.1016/j.apradiso.2012.02.055

[3] ISO 33405, 2024. Reference materials - Guidance for characterization and assessment of homogeneity and stability.

[4] ISO 5725-2, 2022. Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

[5] ISO 13528 Statistical methods for use in proficiency testing by interlaboratory comparison

[6] Gavini M.B., Rocco F.G., Kim S.M., 1981. A new radiochemical procedure for uranium assay in environmental samples. J. Radioanal. Nucl. Chem., 67, 43-444. https://doi.org/10.1007/bf02516356

[7] H. Yücel, A. N. Solmaz, E. Köse, D. Bor, 2010. Methods for spectral interference corrections for direct measurements of ^{234}U and ^{230}Th in materials by gamma-ray spectrometry, Radiat Prot Dosimetry, 138 (3), 264–277. https://doi.org/10.1093/rpd/ncp239

[8] Dong Ke-Jun, Wang Chen, He Ming, Lin De-Yu, Zhao Xing-Hong, LI Li-Li, Zhao Yong-Gang, Dou Liang, Xie Lin-Bo, Wu Shao-Yong, Yin Xin-Yi, Wang Xiang-Gao, Shen Hong-Tao, You Qu-Bo, Jiang Shan, 2014. Methodological Study on AMS Measurement of U Isotope Ratios in Nanogram U Samples, Chin. Phys. Lett., 31(1), 010701. https://10.1088/0256-307X/31/1/010701

[9] Prohaska T., Irrgeher J., Zitek A., Jakubowski, N., 2014. Sector field mass spectrometry for elemental and isotopic analysis. New developments in mass spectrometry, The Royal Society of Chemistry, ISBN: 978-1-84973-392-2. https://doi.org/10.1039/9781849735407

[10] Heumann K. G., 1992. Isotope dilution mass spectrometry, Int. J. Mass Spectrom., 118-119, 575–592. http://10.1016/0168-1176(92)85076-C

[11] Jian Zheng, Sarata Kumar Sahoo, Tatsuo Aono, 2022. Recent progress on mass spectrometric analysis of artificial radionuclides in environmental samples collected in Japan. Nuclear Analysis, 1(3),100025, 2773-1839. https://doi.org/10.1016/j.nucana.2022.100025

[12] Guan Y, Sun S, Wang H, et al., 2019. Accelerator Mass Spectrometry Analysis of ^{237}Np in Environmental Samples. Radiocarbon., 61(5), 1423-1430. https://10.1017/RDC.2019.67

[13] Mercedes L-L., Elena C., 2019. Accelerator Mass Spectrometry of ^{237}Np, ^{239}Pu and ^{240}Pu for environmental studies at the Centro Nacional de Aceleradores, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 455, 39-51, ISSN 0168-583X, https://doi.org/10.1016/j.nimb.2019.06.018

[14] De Cesare M., Tims S.G., Fifield, L.K., 2015. Uranium comparison by means of AMS and ICP-MS and Pu and 137Cs results around an Italian Nuclear Power Plant, EPJ Web of Conferences, 91, https://doi.org/10.1051/epjconf/20159100004

[15] Albarède F., Telouk P., Blichert-Toft J., Boyet M., Agranier A., Nelson B., 2004. Precise and accurate isotopic measurements using multiple-collector ICPMS. Geochimica et Cosmochimica Acta ,68(12), 2725-2744, ISSN 0016-7037, https://doi.org/10.1016/j.gca.2003.11.024

[16] Wyse EJ., Lee SH., Rosa JL., Povinec P., Mora SJ., 2001. Accelerator mass spectrometry (AMS) in plutonium analysis, J Anal Atom Spectr 16:1107

[17] Esaka F., Magara M., Lee CG., Sakurai S., Usuda S., Shinohara N., 2009. Comparison of ICP-MS and SIMS techniques for determining uranium isotope ratios in individual particles. Talanta, 78(1), 290-4. https://10.1016/j.talanta.2008.11.011

[18] Fifield, L.K., 2008. Accelerator mass spectrometry of the actinides. Quaternary Geochronology, 3(3), 276-290.

[19] Masaharu T., Naoki S., Emmanuel P., Germain B., 2013. Determination of ultra-low 236U/238U isotope ratios by tandem quadrupole ICP-MS/MS. J. Anal. At. Spectrom., 2013,28, 1372-1376

Appendix 1: Participants to the liquid and solid ILCs

Participant	Contact name(s)	Reception date	
		Liquid RM	Solid RM
AGES - Austrian Agency for Health and Food Safety	Sophie PICHLER (sophie.pichler@ages.at)	10/03/2025	12/12/2024
Agilent Technologies LDA UK Ltd	Sonia NORTH (sonia.north@agilent.com)	15/04/2025	23/12/2024
ETH Zürich	Habacuc PEREZ-TRIBOUILLIER (hperez@phys.ethz.ch)	13/02/2025	20/11/2024
Center for Physical Sciences and Technology - Nuclear Research dept. (FTMC)	Andrius PUZAS (andrius.puzas@ftmc.lt) ; Arunas GUDELIS (arunas.gudelis@ftmc.lt)	does not participate	27/11/2024
University of Vienna and Helmholtz-Zentrum Dresden-Rossendorf	Karin HAIN (karin.hain@univie.ac.at) ; Stella WINKLER (s.winkler@hzdr.de)	02/12/2024	27/11/2024
Jožef Stefan Institute	Marko STROK (Marko.Strok@ijs.si)	11/12/2024	21/11/2024
Gottfried Wilhelm Leibniz Universitaet Hannover - Institut fuer Radiooekologie und Strahlenschutz	Aaron LEHNERT (lehnert@irs.uni-hannover.de)	29/11/2024	21/11/2024
Norwegian University of Life Sciences (NMBU), Faculty of Environmental Sciences and Natural Resource Management (MINA) - Isotope laboratory	Simon JEROME (simon.mark.jerome@nmbu.no)	11/02/2025	21/11/2024
Physikalisch-Technische Bundesanstalt - 6.12 Umweltradioaktivität / Environmental Radioactivity	Janine EBERHARDT (janine.eberhardt@ptb.de);Lukas FLIERL (lukas.flierl@ptb.de)	10/12/2024	20/11/2024
Labor Spiez - Nuclear Chemistry Division	Stefan ROLLIN (stefan.roellin@babs.admin.ch); José CORCHO (jose.corcho@babs.admin.ch)	08/04/2025	22/11/2024
STUK Radiation and Nuclear Safety Authority - MIT Measurement and Analysis	Sinikka VIRTANEN (Sinikka.Virtanen@stuk.fi)	10/12/2024	20/11/2024
Institute of Nuclear Sciences Vinca – VINS - Department of Radiation and Environmental Protection	Jelena NIKOLIC (jnikolic@vin.bg.ac.rs)	21/02/2025	23/01/2025

Appendix 2: Experimental procedures – liquid RM

Table 39. Detailed sample preparation procedures used among participating laboratories for the liquid RM.

Ref participant	Sample preparation
Assigned values	UTEVA Chemistry for U, Pu and Am Cleaning and conditioning steps with different amounts of HNO3 (0.02mM to 6M), MQ water, HF (5mM) and final conditioning with 6M HNO3 + 0.3% H2O2 Sample addition step with 6M HNO3 + 0.3% H2O2 Purification and extraction steps: 6M HNO3 + 0.3% H2O2 (for Am); 2M HNO3 + 2.10-3 M ascorbic acid + 5.10-3 sulfamic acid (for Pu); 2M HNO3 + 2.10-3 M ascorbic acid + 5.10-3 sulfamic acid (Queue Pu) and 0.02M HNO3 (for U)
20	An aliquot of 5 g of the sample was weighed and spiked with 1 pg of a U-233 tracer, then left to equilibrate overnight. Next, 15 mL of MQ water and approximately 50 mg of Fe^{3+} were added, and the sample was mixed thoroughly. Around 1.5 mL of aqueous NH_3 was then added, followed by further mixing, and the resulting precipitate was allowed to settle. The sample was then centrifuged, and the supernatant was discarded. The precipitate was placed on a hotplate at 70 °C and dried to incipient dryness. It was subsequently redissolved in 5 M HNO_3, and 200 mg of Mohr's salt were added and allowed to react for approximately 30 minutes. Immediately afterward, the sample was passed through a tandem array of TEVA–UTEVA–DGA resins at a flow rate of approximately 1 mL/min. The cartridges were rinsed with 5 M HNO_3 and then separated for individual elutions. TEVA columns were rinsed with 5 mL of concentrated HCl, and plutonium was eluted with 15 mL of 0.01 M HNO_3, followed by 5 mL of MQ water. Uranium isotopes were eluted from the UTEVA resins with 0.05 M HNO_3 and MQ water. The DGA cartridges were rinsed with 3 M HCl, and americium isotopes were then eluted with 0.05 M HNO_3 and MQ water. Each of the resulting actinide-containing fractions was precipitated, oxidized, mixed with Nb powder, and finally pressed into an AMS cathode. Measurements were conducted using a Multi-Isotope Low-Energy AMS. Samples were introduced via an ion sputtering source as negative ions, accelerated to a terminal voltage of 300 kV, and passed through a helium stripping chamber, which converted them to positive ions and removed molecular interferences. The ions were further accelerated through a series of mass-dependent and electrostatic filters. Uranium ions were detected in the 3^+ charge state with U-238 being detected on a Faraday cup, while isotopes 233 and 236 using a dual-anode gas ionization chamber. The resulting ratios were normalized using the in-house Zutri standard, blank-corrected (background and spike), and concentrations were calculated based on the spiked amount of U-233.
25	Sample diluted and measured
30	Radiochemical separation with TEVA, TRU and/or UTEVA.
33	The sample was acidified with concentrated $HNO_{3\ s.p.}$, water was bubbled through with compressed air for one hour, the tracers Pu-242 and U-232 were added, the oxidation state was adjusted with $Na_2S_2O_8$, precipitation with Fe(OH)3, adjustment of the oxidation state of Pu and Np with $TiCl_3$, radiochemical separation with TEVA® TRU cartridge, Pu: elution with 0.1 M HCl – 0.01 M $TiCl_3$ – 0.05 M HF; U via TRU: 0.1 M $(NH_4)_2(C_2O_4)$, micro-precipitation to determine the chemical yield of U-232 using alpha spectroscopy.
40	None
45	U separation on UTEVA for isotope ratios, Am separation on DGA column
50	UTEVA and DGA (for purifying 241Am). The fractions were (co-)precipitated as iron hydroxide, dried, and calcinated at 600 °C for 2 hours. The iron oxide powder was then mixed with same mass of Nb and pressed into an AMS sample holder for use in a Cs sputter ion source. In the measurement the relevant mass settings were slow-cycled several times to account for changes in ion-source output. Inhouse standards were used to account for instrument mass bias. For Pu the 'ColPus' standard covers masses 239,240,242,244. Np was measured together with Pu, and a 242Pu/237Pu inhouse reference was used for normalisation. An in-house preparation of ViennaKkU natural Uranium and IRMM-058 was used for normalisation of U results. For 241Am/243Am mass bias assumptions are based on ColPus. Uncertainties include the uncertainty of the standard/mass bias measurement and the sample raw ratio measurement (counting statistics or scatter). A blank level was subtracted from the sample results based on the results of the spike-only (blank) sample.
53	
60	DOWEX +TRU ion exchange resins
65	Samples were digested, using Milestone digestion system UltraClave, in the mix of nitric and hydrofluoric acids.
73	Five sample aliquots of approximately 6.5 g from MetroPOEM spiked Sea Water were weighed directly into 300 mL PFA beakers. 1.75 g of IRMM-054 ^{235}U spike solution with 150 ng/g were added to each of the five samples and weighed. In addition, five references, each with 1.5 g of NBLCRM 145 reference solution of 150 ng/g and 1.75 g of IRMM-054 235U spike solution with 150 ng/g, were weighed into 300 mL PFA beakers. The solutions were evaporated to dryness using a hotplate (at 120 °C). The residue was redissolved in 5 mL 65 % HNO_3 (subboiled, Merck), evaporated to dryness again and then dissolved in 5 mL 3 mol/L HNO3 (subboiled, Merck). The resulting clear solutions were loaded onto preconditioned Triskem UTEVA resin columns (UT-C50-A, Lot # FUTA220808, 2 mL pre-packed). The separation was carried out according to the modified Eichrom "Analytical Procedure Method No. ACS07", for details see table below. Each U fraction was collected in a 17 mL PFA vessel and evaporated to dryness. The residue was re-dissolved in 1 mL 65 % HNO_3 (subboiled, Merck p.a.) and 1 mL 31 % H_2O_2 (ultrapur, Merck) and evaporated to dryness. In the last step the resulting residue was redissolved in 12 mL 2.5 % HNO_3 (subboiled, Merck p.a.) to yield measurement solutions with a uranium content of approximately $w(U) \approx 30$ ng/g. These sample solutions were transferred into thoroughly pre-cleaned 4 mL PFA autosampler vials. All masses were corrected for air buoyancy. The reference spike mixtures underwent the same procedure as the samples what rendered an additional blank determination superfluous. All preparations have been done gravimetrically. The density of the liquid reference material was determined at (1.02884 g/cm^3 ± 0.00035 g/cm^3).

Table 40. Details of instrument setups used among participating laboratories for the liquid RM.

Ref partcipant	System	Interferences	Details
20	AMS	no info	no info
25	ICP-QMS	no interferences accounted for or encountered	no info
30	ICP-MS/MS	no interferences accounted for or encountered	no info
33	ICP-MS/MS	no interferences accounted for or encountered	Internal standard correction (Lu-175: 1µg/L), Uran-isotopic measurements: SQ-He-Modus, collision gas: helium with flow rate: 7.8 ml/min, Nebulizer Flow: 1.11 ml/min, on-mass modus; yield correction via U-232 tracer via alpha spectroscopy measurement (lack of U-236 tracer), blank correction, rinsing with 0.1% HF-solution & 1% HNO3 to avoid cross-contamination, U- calibration range U-234: 0.00024 - 0.493 ng/L ; U-235: 0.0293 ng/L - 58.587 ng/L, U-238: 0.0407 - 8.157 µg/L; Isotopic standard solution U nat, 415120; Pu- Measurement: TQ with Helium and Oxygen; mass-shift m/z = 271 PuO2+, reaction gas: oxygen with flow rate: 0.2 ml/min; collision gas: helium with flow rate: 7,2 ml/min; Pu-242 tracer for yield determination, rinsing between samples with 0.1% HF and 1% HNO3 to avoid cross-contamination, additional correction for U-238 interferences, pu calibration range: Pu-239 0.1395 - 6.973 ng/L ; Pu-242 1.366 - 68,287 ng/L; Pu isotopic Standard: AN-Pu-242-1-2022
40	gamma	no interferences accounted for or encountered	no info
45	ICP-SF-MS	yes - U and Th tailing were corrected, traces of Pu isotopes in the Pu-242 tracer and Am-241 in the Am-242 tracer were corrected	no info
50	AMS	no interferences accounted for or encountered	no info
53	ICP-MS/MS		No Gas MS/MS mode used for the measurement of Np 237 and U 238. NH3 MS/MS cell gas mode used for the measurement of Pu 239 and Am 241. Bi 209 used as internal standard for all measurements.
60	alpha	radiochemical separation	no info
65	MC-ICP-MS	no interferences accounted for or encountered	Uranium was measured on a Neptune Plus (Thermo Fisher Scientific) by MC-ICP-MS, which was coupled to a desolvator, Cetac Aridus II. Nickel Skimmer X Cones and Nickel Jet Cones were used. Uranium was measured in low resolution mode and five faraday cups were used for the determination of the uranium isotopes.
73	MC-ICP-MS		For Am, Np and U measurement, Agilent 8900 ICP-MS instrument, equipped with Optional Advanced Valve System (AVS MS), concentric nebulizer and Ni-tipped cones, was used. Perkin Elmer, equipped with cyclonic spray chamber, concentric nebulizer and Pt-tipped cones was used for the measurement of Pu isotopes.

Appendix 3: Experimental procedures – solid RM

Table 41. Details on the sample preparation of the participants to the solid RM inter-laboratory comparison.

Ref participant	Sample preparation
Assigned values	UTEVA Chemistry for U, Pu and Am Cleaning and conditioning steps with different amounts of HNO3 (0.02mM to 6M), MQ water, HF (5mM) and final conditioning with 6M HNO3 + 0.3% H2O2 Sample addition step with 6M HNO3 + 0.3% H2O2 Purification and extraction steps: 6M HNO3 + 0.3% H2O2 (for Am); 2M HNO3 + 2.10-3 M ascorbic acid + 5.10-3 sulfamic acid (for Pu); 2M HNO3 + 2.10-3 M ascorbic acid + 5.10-3 sulfamic acid (Queue Pu) and 0.02M HNO3 (for U)
10	The dried sample aliquots have been prepared for measurement by gamma-ray spectrometry in two runs: 1) 3 samples of about 2.5 g each were measured 5-10 March 2025; 2) 3 samples of 1.0 g each were measured 22 April – 8 May 2025.
25	Sample dried, ashed and tracers added to 5 ml conc. HF and 2 ml conc. HNO3. Solvent evaporated, rinsed with 2% HNO3 three times, filtered and diluted.
30	Samples dried in 105°C overnight. Radiochemical separation with TEVA, TRU and/or UTEVA.
33	Sample dried, ashed, and tracers added to 2 ml HNO3 and 8 ml HF in a microwave-assisted digestion vessel (160 °C), neutralization of HF with B(OH)3 filtration, adjustment of the oxidation state with Na2S2O8, precipitation with Fe(OH)3, adjustment of the oxidation state of Pu and Np with TiCl3, radiochemical separation with TEVA® TRU cartridge, Pu: elution with 0.1 M HCl – 0.01 M TiCl3 – 0.05 M HF; U via TRU: 0.1 M (NH4)2(C2O4), micro-precipitation to determine the chemical yield of U-232 using alpha spectroscopy; no significant differences between crystal and powder measurements
40	
45	Dissolution in 2% HNO3/0.2% HF. Pu/Np separation on a TEVA column, Am separation on DGA column. The plutonium/ neptunium concentrations depend on the dissolution technique. With nitric acid leaching only about 50% of the plutonium/neptunium are dissolved compared to a borate fusion. The Pu and Np results correspond to the borate fusion. A 100% dissolution of Pu was assumed. The background for uranium is too high with a borate fusion. Therefore, for the uranium determination, the sample was leached with nitric acid. The amount of uranium in the leaching might depend on the leaching method. The uncertainty of the leaching could not be estimated.
50	UTEVA and DGA (for purifying 241Am). The fractions were (co-)precipitated as iron hydroxide, dried, and calcinated at 600°C for 2 hours. The iron oxide powder was then mixed with same mass of Nb and pressed into an AMS sample holder for use in a Cs sputter ion source. In the measurement the relevant mass settings were slow-cycled several times to account for changes in ion-source output. Inhouse standards were used to account for instrument mass bias. For Pu the 'ColPus' standard covers masses 239,240,242,244. Np was measured together with Pu, and a 242Pu/237Pu inhouse reference was used for normalisation. An in-house preparation of ViennaKkU natural Uranium and IRMM-058 was used for normalisation of U results. For 241Am/243Am mass bias assumptions are based on ColPus. Uncertainties include the uncertainty of the standard/mass bias measurement and the sample raw ratio measurement (counting statistics or scatter). A blank level was subtracted from the sample results based on the results of the spike-only (blank) sample.
53	
65	
73	Five sample aliquots of approximately 2 g from CEA MetroPOEM-solid n° 73 (active solid CRM candidate) were weighed directly into 100 mL TFM tubes. 1 g of IRMM-054 ^{235}U spike solution with 75 ng/g were added to each of the five samples and weighed. In addition, five references, each with 2.7 g of NBL CRM 145 reference solution of 25 ng/g and 1 g of IRMM-054 ^{235}U spike solution with 75 ng/g, were weighed into 100 mL TFM tubes. For each TFM tube, 14 mL 48 % HF (ultrapur, Merck), 3 mL 65 % HNO3 (subboiled, Merck p.a.), and 1 mL 31 % H_2O_2 (ultrapur, Merck) were used to digest the samples and references, in an MLS (Milestone) Ethos.lab microwave system within 2.5 h duration at 210 °C (30 min linear ramp from room temperature to 210 °C, 1 h constant at 210 °C, 1 h cooling to room temperature). After cooling down, the solutions were evaporated to complete dryness within 7 h in an MLS (Milestone) ETHOS.lab evaporation system at 70 °C and approximately p < 450 mbar (combiVAC). The residues were re-dissolved in 8 mL 3 mol/L HNO_3 (subboiled, Merck p.a.). The resulting clear solutions were loaded onto preconditioned Triskem UTEVA resin columns (UT-C50-A, Lot # FUTA220808, 2 mL pre-packed). The separation was carried out according to the modified Eichrom “Analytical Procedure Method No. ACS07” [3], for details see table below. Each U fraction was collected in a 17 mL PFA vessel and evaporated to dryness. The residue was re-dissolved in 1 mL 65 % HNO3 (subboiled, Merck p.a.) and 1 mL 31 % H2O2 (ultrapur, Merck) and evaporated to dryness. In the last step the resulting residue was redissolved in 12 mL 2.5 % HNO_3 (subboiled, Merck p.a.) to yield measurement solutions with a uranium content of approximately w(U) ≈ 30 ng/g. These sample solutions were transferred into thoroughly pre-cleaned 4 mL PFA autosampler vials. All masses were corrected for air buoyancy. The reference spike mixtures underwent the same procedure as the samples what rendered an additional blank determination superfluous.

Table 42. Sample introduction methods used among participating laboratories for the solid RM.

Ref participant	System	Interferences	Details
10	Gamma spec	no interferences accounted for or encoutered	no info
25	ICP-QMS	no interferences accounted for or encoutered	no info
30	ICP-MS/MS	no interferences accounted for or encoutered	Radiochemical separation prior measurement: Sample dried, ashed and tracer Pu-242 & U-232 added in 2 ml HNO3 and 8 ml HF in microwave assisted digestion vial, neutralizing of the HF with B(OH)3 filtration, adjusting oxidation state with Na2S2O8 , precipitation with FeOH3, adjusting oxidation state of Pu and Np using TiCl3, radiochemical separtion using TEVA® TRU-Cartridge, Pu: eluation with 0.1M HCl - 0.01M TiCl3 - 0.05M HF; U via TRU: 0.1 M (NH4)2(C2O4), microprecipitation for chemical yield determination of U-232 via alpha spectroscopy; No significant differences between crystals and powder measurements.
33	ICP-MS/MS	no interferences accounted for or encoutered	no info
40	gamma	U and Th tailing were corrected, traces of Pu istopes in the Pu-242 tracer and Am-241 in the Am-242 tracer were corrected	no info
45	ICP-SFMS Apex (ESI) for isotope ratios of uranium	no interferences accounted for or encoutered	no info
50	AMS	none	"NoGas SQ mode used to measure all elements.
53	ICP-MS/MS	radiochemical separation	no info
60	alpha	no info	"Samples were digested, using Milestone digestion system UltraClave, in the mix of nitric and hydrofluoric acids.
65	ICP-MS/MS	For Am, Np and U measurement, Agilent 8900 ICP-MS instrument, equipped with Optional Advanced Valve System (AVS MS), concentric nebulizer and Ni-tipped cones, was used. Perkin Elmer, equipped with cyclonic spray chamber, concentric nebulizer and Pt-tipped cones was used for the measurement of Pu isotopes.	
73	MC-ICP-MS	no interferences accounted for or encoutered	Uranium was measured on a Neptune Plus (Thermo Fisher Scientific) by MC-ICP-MS, which was coupled to a desolvator, Cetac Aridus II. Nickel Skimmer X Cones and Nickel Jet Cones were used. Uranium was measured in low resolution mode and five faraday cups were used for the determination of the uranium isotopes.

Appendix 4: Uncertainty budgets – liquid RM

Table 43. Summary of the details on the uncertainty calculations given by the participants, for the liquid RM

Reference of participant	Notes on uncertainties
20	Uncertainty budget includes measurement uncertainty, blank correction uncertainty and standard correction. Additionally sample weighing error and spike weighing error are also included in the uncertainty budget.
25	Uncertainty is calculated as the square root of the sum of the squares of the relative standard uncertainties associated with the counting statistics, efficiency determination and sample weighing. All other potential sources of uncertainty are negligible due to their insignificant contribution to the overall uncertainty budget.
30	Uncertainty is maximum of either combined standard uncertainty of single measurement or standard deviation of all measurements taken into account to calculate average value.
33	Summation of uncertainties of the radiochemical preparation (pipettes, scales, activities of the tracers, volume of the elution solution, efficiency of the alpha counter (Uranium), ..) and the uncertainty of the intensities of the measured samples (RSD) with $(\sqrt{(u)^2+(u)^2})*1.65$
40	Relative measurement uncertainty is calculated as a square root of the sum of squares of contributions (in %), coverage factor 2. Contributions: 1) Statistical uncertainty of counting; 2) uncertainty of measurement time (negligible); 3) uncertainty of mass (around 1%): 4) uncertainty of gamma yield; 5) uncertainty of efficiency (separate budget, around 3%; 6) uncertainty of calibration transfer coefficients (MEFFTRAN, around 3%)
45	Uncertainty Pu-242 tracer: 2%, Uncertainty sample weight: 2%, uncertainty counting statistics about 2% Uncertainty Am-243 tracer: 3%. Uncertainty sample weight: 2%, uncertainty counting statistics about 2% Uncertainty U-238 standard: 1%, Uncertainty sample weight: 0.5%, uncertainty external calibration 2%, uncertainty matrix suppression 2%, uncertainty mass discrimination: 1.5%
50	
53	
60	Uncertainty related to radiochemical separation and radioactivity measurement with alpha spectroscopy. Uncertainty related to counting efficiency, number of net and background counts, k=2.
65	Quadrature sum of relative uncertainties associated with: Sample weighing Count rate from ICP-MS Instrument calibration (Np-237) Radionuclide half-lives as appropriate Isotope dilution tracer concentration as appropriate (except Np-237) Mass bias correction
73	Mass fraction of the CRM, isotope ratio of spike; counting efficiency of the sample; counting efficiency of the spike; molar masses

Appendix 5: Uncertainty budgets – solid RM

Table 44. Summary of the details on the uncertainty calculations given by the participants, for the solid RM.

Reference of participant	Notes on uncertainties
10	The uncertainty budget includes the following main contributions: counting statistics, weighing, emission probability, efficiency curve determination. The uncertainty is calculated as a square root from the sum of all components added quadratically.
25	Uncertainty is calculated as the square root of the sum of the squares of the relative standard uncertainties associated with the counting statistics, efficiency determination, tracer dilution and sample weighing. All other potential sources of uncertainty are negligible due to their insignificant contribution to the overall uncertainty budget.
30	Uncertainty is maximum of either combined standard uncertainty of single measurement or standard deviation of all measurements taken into account to calculate average value.
33	Summation of uncertainties of the radiochemical preparation (pipettes, scales, activities of the tracers, volume of the elution solution, efficiency of the alpha counter (Uranium), ..) and the uncertainty of the intensities of the measured samples (RSD) with $(\sqrt{(u)^2+(u)^2})*1.65$
40	Relative measurement uncertainty is calculated as a square root of the sum of squares of contributions (in %), coverage factor 2. Contributions: 1) Statistical uncertainty of counting; 2) uncertainty of measurement time (negligible); 3) uncertainty of mass (around 1%): 4) uncertainty of gamma yield; 5) uncertainty of efficiency (separate budget, around 3%; 6) uncertainty of calibration transfer coefficients (EFFTRAN, around 3%)
45	The Pu, Np and Am-241 results correspond to the borate fusion. A 100% dissolution of Pu, Np and Am was assumed. Uncertainty Pu-242 tracer: 2%, Uncertainty sample weight: 1%, uncertainty counting statistics about 0.7% Uncertainty Am-243 tracer: 3%. Uncertainty sample weight: 2%, uncertainty counting statistics about 1% The uranium results correspond to a nitric acid leaching. The uncertainty of the leaching could not be considered. Uncertainty U-238 standard: 1%, Uncertainty sample weight: 1%, uncertainty external calibration 3%, uncertainty matrix suppression 5%, uncertainty mass discrimination: 1.5%"
50	
53	
60	Uncertainty related to radiochemical separation and radioactivity measurement with alpha spectroscopy. Uncertainty related to counting efficiency, number of net and background counts, k=2.
65	Quadrature sum of relative uncertainties associated with: Sample weighing Count rate from ICP-MS Instrument calibration (Np-237) Radionuclide half-lives as appropriate Isotope dilution tracer concentration as appropriate (except Np-237) Mass bias correction
73	dry mass correction; isotope ratio of spike; counting efficiency of the sample; counting efficiency of the spike; molar masses; mass fraction of CRM; isotope ratio of CRM; weighing of sample, spike and CRM

Appendix 6: Statistics for the evaluation of performance

The results of each participating lab were compared to the assigned values by calculating performance statistics as follows:

- First criterion: normalised deviation to the assigned value

$$e_p = \frac{A_p - A_{\mathrm{RM}}}{A_{\mathrm{RM}}} \times 100\ \%$$

Where:

A_p is the result reported by participant *p*

A_{RM} is the assigned value

- Second criterion: zeta score

$$\zeta_p = \frac{A_p - A_{\mathrm{RM}}}{\sqrt{u_p^2 + u_{\mathrm{RM}}^2}}$$

Where:

u_p is the standard uncertainty at *k* = 1, reported by participant *p*

u_{RM} is the standard uncertainty at *k* = 1, associated to the assigned value

Scores are attributed to the performance statistics of each lab, following:

1st criterion, e_p	2nd criterion, ζ_p	Score
$\lvert e_p \rvert \leq 15\ \%$	$\lvert \zeta_p \rvert \leq 2$	S: Satisfactory
$15\ \% < \lvert e_p \rvert \leq 20\ \%$	$2 < \lvert \zeta_p \rvert \leq 3$	D: Discrepant
$\lvert e_p \rvert > 20\ \%$	$\lvert \zeta_p \rvert > 3$	NS: Non-Satisfactory

Please delete before you submit your report

Document Control Page

Document Title:	European Partnership on Metrology Contracts Reporting Template 7: Deliverable Cover Sheet	
Document Code:	P-CON-TMP-207	Version 1.0
Document Control:	Approved: Programme Manager	2023-08-24