D1: Inter-laboratory comparison report for low-level radionuclide detection by mass spectrometry

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D1: Inter-laboratory comparison report for low-level radionuclide detection by mass spectrometry

Organisation name of the lead participant for the deliverable: NPL

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Deliverable Cover Sheet

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The project 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.

Glossary

AMS – accelerator mass spectrometry

IDMS – isotope dilution mass spectrometry

ICP-MS/MS – tandem inductively coupled plasma tandem mass spectrometry

ICP-QMS – inductively coupled plasma mass spectrometry

ICP-SFMS – sector field inductively coupled plasma mass spectrometry

ICP-TOF-MS – inductively coupled plasma time of flight mass spectrometry

LSC – Liquid Scintillation Counting

MC-ICP-MS – multi-collector inductively coupled plasma mass spectrometry

Multi-cathode source of negative ions by caesium sputtering

SEM – secondary electron multiplier

SIMS – secondary ionisation mass spectrometry

SNMS – sputtered neutral mass spectrometry

TIMS – thermal ionisation mass spectrometry

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1 Summary

This report describes the preparation of a range of single and mixed radionuclide standards for an interlaboratory comparison exercise, focusing on comparing the capabilities of different mass spectrometers for low-level radioactivity measurement. Participating labs around Europe were asked to determine activity levels for a range of actinides (^{234}U, ^{236}U, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{Nat}U and $^{239/240}$Pu) and ^{90}Sr. Standards were prepared from starting materials at NPL through a series of dilutions using a dedicated source preparation facility and characterised for their activity per unit mass and impurities using a combination of decay counting and mass spectrometric techniques. Standards were distributed to participating laboratories along with a form for submitting the results and details of the measurements made. There were delays in sending of the materials to the participating laboratories, however, results were submitted for all radionuclides using multiple techniques. This provides valuable information on the capabilities of mass spectrometry for low-level radionuclide measurement and can inform the development of future standards and comparison exercises.

2 Introduction

Accurate and traceable radioactivity measurement is of critical importance in ensuring the safety of the public and the natural environment. In the case of low-level radioactivity measurement, various mass spectrometric techniques are increasingly being used as a rapid and sensitive alternative to decay counting techniques.

As mass spectrometry is increasingly applied to low-level radioactivity measurement, this must be supported with standards and reference materials to validate techniques and provide confidence in measurement.

The aim of this comparison exercise was to compare the performance of mass spectrometric techniques for measurement of multiple single and mixed radionuclide standards. Standards were prepared at low levels at chemistries deemed suitable for direct measurement by mass spectrometry with no sample preparation, such that the comparison could focus on the performance of the mass spectrometric techniques. A further aim was that the standards would support measurement of the two reference materials prepared as part of Work Package 3.

Results are presented for each radionuclide standard, covering the technique used, the agreement with the NPL reference value and any feedback from the participating laboratory on the nature of the standards received of the measurements made. The value of the comparison exercise is evaluated, along with recommendations for future exercises.

3 Production of standards

3.1 Selection of activity levels to prepare representative samples

The radionuclides of interest were defined during the preparation of the project proposal. There was some consideration of ^{226}Ra but this was not taken forwards. To ensure the samples developed were relevant, a form was prepared and circulated to participating laboratories requesting the following information for each radionuclide:

- Activity range of interest.
- Detection limits achievable.
- Isotope ratio range of interest.
- Additional radionuclides and stable interferences that could be added to the standards.
- Major interferences affecting measurement.
- Minimum sample volume required.
- Sample chemistry.
- Any additional information relevant to standards.

The responses received are summarised below. A significant range of activity levels and detection limits were reported (Table 1), which is expected given the range of instrument designs and applications across the partners in the project.

Table 1. Range of responses received from participating laboratories on activity range and detection limit for radionuclides of interest.

Radionuclide	**Activity range of interest in Bq g^{-1}**	**Limit of detection achievable in Bq g^{-1}**
^{90}Sr	$1 \times 10^{-3} – 2.6 \times 10^{5}$	$3.1 \times 10^{-4} – 5.1 \times 10^{2}$
^{234}U	1×10^{-6} – 10	1×10^{-8} – 12
^{235}U	$8 \times 10^{-7} – 1.6 \times 10^{-2}$	$1 \times 10^{-8} – 8 \times 10^{-3}$
^{236}U	1×10^{-6} – 10	$4.8 \times 10^{-9} – 1 \times 10^{-8}$
^{238}U	6.2×10^{-10} – 10	$1.2 \times 10^{-9} – 1.2 \times 10^{-4}$
^{237}Np	1×10^{-6} – 10	$1.3 \times 10^{-8} – 2.5 \times 10^{-2}$
^{239}Pu	1×10^{-4} – 11	1×10^{-8} – 11
^{240}Pu	1×10^{-4} – 42	1×10^{-8} – 48
^{241}Am	1×10^{-3} – 63	1×10^{-4} – 63

There were fewer responses regarding the uranium isotopic ratio values of interest, with a significantly wider range for U isotopes compared to Pu (Table 2).

Table 2 Responses received from participating laboratories on isotopic ratio values of interest.

Isotopic ratio	$R(^{236}\mathrm{U}/^{238}\mathrm{U})$	$R(^{239}\mathrm{Pu}/^{240}\mathrm{Pu})$
Number of responses	8	7
Range of isotopic ratio values in mol/mol	$0.1 – 1 \times 10^{-12}$	0 – 10

The fewest number of responses was regarding the spiking of standards with interferences. Responses were only received for ^{90}Sr, where there was interest in the addition of ^{90}Zr (an isobaric interference for mass spectrometry measurement) and ^{88}Sr (a tailing and potential polyatomic interference through $^{88}\mathrm{Sr}^{1}\mathrm{H}_2$ formation) (Table 3).

Table 3. Responses received from participating laboratories on interferences that should be considered for radionuclides included in the interlaboratory comparison.

Interference	**^{88}Sr**	**^{90}Zr**
Number of responses	1	4
Max. concentration level in ng g^{-1}	20	0.001 – 10 000

The other major outcomes from the questionnaire were:

- The desired sample volume of the standards ranged from 0.1 mL to 200 mL.
- The samples should be prepared in nitric acid (HNO_3), with desired concentrations ranging from 0.1 mol/L to 2 mol/L.
- Bottles should be cleaned in sub-boiled HNO_3 prior to use.
- Impurity levels in the starting materials should be measured and chemically separated if necessary.

The general aim was to prepare standards at the lower range of the activity concentrations requested. There were several motivations for this. Firstly, low level measurements are where mass spectrometric techniques offer a distinct advantage over decay counting techniques with regards to sensitivity and rapid measurement capabilities. Secondly, regulatory compliance increasingly requires laboratories to characterise radionuclides at lower activity levels, and establishing the capabilities of mass spectrometric techniques for such measurements is valuable. Finally, measurement at higher activity levels is not representative of the majority of mass spectrometric applications in this field and would be less likely to demonstrate the relative strengths and limitations of this technique.

3.2 **Preparation of standards**

3.2.1 Starting materials

All starting materials were prepared from standardised solutions available in the NPL Nuclear Metrology Group that are traceable to national standards of radioactivity. Most standards were in flame sealed glass ampoules, whilst the ^{240}Pu starting source was in an Azlon bottle and standardised using alpha liquid scintillation counting prior to being prepared for the project. The starting activities of the sources used are given in Table 4.

Table 4. Starting activity of radionuclides used at the reference date of 01/02/2024.

Radionuclide	Starting Activity in Bq g^{-1}
^{234}U	102.2
^{236}U	10.1
^{Nat}U	100.5
^{239}Pu	50.1
^{240}Pu	5.2
^{241}Am	3965.2
^{237}Np	1012.6
^{90}Sr	78.6

Of the radionuclides of interest, ^{90}Sr was the most problematic with regards to interferences. All ^{90}Sr standards available contained high concentrations (10 ppm to 100 ppm) of stable Sr, which was added as a carrier to stabilise the ^{90}Sr in solution. Some also contained similar concentrations of stable yttrium carrier. NPL discussed this with CEA, who also had ^{90}Sr standards containing stable carriers. It was decided to proceed with starting material containing these carriers, on the grounds that these represent interferences that mass spectrometry must be able to deal with for low-level ^{90}Sr analysis.

No interferences were added to any of the starting materials as part of this project.

3.2.2 Sample preparation and measurement

All samples were prepared using 0.1 mol/L sub-boiled HNO_3 (Fisher Scientific). The background count rate of several acid grades was performed using the NPL Nuclear Metrology Group inductively coupled plasma tandem mass spectrometer (ICP-MS/MS). Whilst this instrument is not the most sensitive design, the lowest background count rates were recorded for sub-boiled HNO_3.

All standards were prepared in the NPL Nuclear Metrology Group source preparation facility, using certificated five and six figure balances. A series of dilutions were made from the starting materials. The number of dilutions made was dependent on the starting activity and is summarised for each radionuclide in Appendix 1.

All weights were recorded on dedicated radioactive source preparation sheets. During the preparation of each dilution bottle, the dilution factor was determined gravimetrically (GDF). To validate this, each gravimetric dilution factor was validated by ICP-MS/MS where four high level and four low level check samples were prepared to determine mass spec dilution factor (MSDF).

All dilution checks were performed using ICP-MS/MS using two setups:

(1) A perfluoroalkoxy alkane (PFA) sample introduction system comprising of a PFA micro flow nebuliser and double pass spray chamber. This set-up is based on the standard sample introduction used most often by the NMG for routine analysis of radionuclides.
(2) An APEX Q sample introduction system that has an order of magnitude higher sensitivity than the standard sample introduction system.

The sensitivity of the Apex Q had previously been proven through work at NPL to achieve sensitivities approximately 10 times higher than the standard setup. The sensitivities achieved using the PFA sample introduction system are comparable to the standard glass-based sample introduction system. Dilution checks were performed for all radionuclides using the PFA and Apex Q sample introduction systems. The results of the dilution checks were processed using an internally developed NPL dilution check spreadsheet.

In addition to dilution checks, homogeneity check sources were prepared at the same level as the bottles dispatched to the MetroPOEM participants. Each source was measured using both set-ups outlined above.

The following internally produced NPL software was used in the determination of the activity, homogeneity and stability for each radionuclide:

- EWTXL v3.1: this was used to determine the mass of active in each of the mass spectrometry vials.
- MSDC: this is a newly developed spreadsheet that was used to determine the gravimetric dilution factor (GDF), mass spec dilution factor (MSDF) and their associated uncertainties.
    - For each dilution stage, both factors were compared and assigned a pass or fail result. For the lowest dilution level, a 'fail' result was expected due to the limit of detection of the NMG ICP-MS instrument being reached. With this expectation, it was decided that customer bottles should still be prepared at this low level for other mass spec users to measure and report an activity concentration which was the aim of the project.
- DBAC v1.3: this was used to determine the activity concentration per unit mass of the dilution bottles prepared during source preparation using the GDFs calculated using MSDC.

3.2.3 Impurity assessment

All starting materials had previously been measured at NPL using decay counting techniques (alpha spectrometry, liquid scintillation counting and gamma spectrometry). Given the focus on mass spectrometric measurement, these were re-measured for long-lived radioactive and stable impurities by ICP-MS/MS (Table 5).

For ^{90}Sr, no contaminants were reported during the previous characterisation of this material. Further ICP-MS/MS measurement as part of this comparison confirmed the presence of stable ^{88}Sr and ^{89}Y that were deliberately added as carriers when the material was first characterised to aid in long-term stability.

The main contaminant detected in the starting ^{234}U starting source was ^{232}U (1.37 Bq g^{-1} ± 0.45 Bq g^{-1}) at a reference time of 2019-06-01 12:00 UTC. Further ICP-MS/MS measurement showed a minor contribution from ^{235}U, ^{236}U and ^{238}U.

For ^{236}U, the main contaminant reported in the starting material was ^{235}U (0.00050 Bq g^{-1} ± 0.00030 Bq g^{-1}) at a reference time of 2014-01-01 12:00 UTC. ICP-MS/MS measurement confirmed the presence of ^{236}U along with minor contamination from ^{234}U and ^{238}U.

The main contaminant reported in the starting ^{237}Np material was less than 0.01 % ^{229}Th, ^{239}Pu and ^{240}Pu. Further ICP-MS/MS measurement showed no significant counts from either ^{239}Pu or ^{240}Pu (equivalent to less than 0.00005 % of the counts at ^{237}Np).

There were no contaminants reported for ^{241}Am from the initial characterisation. Measurement by ICP-MS/MS showed no significant counts from ^{243}Am (equivalent to less than 0.01 % of the counts for ^{241}Am). For ^{Nat}U, a minor ^{236}U contamination was reported that was confirmed by ICP-MS/MS.

The ^{239}Pu and ^{240}Pu single standards were also used in the creation of the mixed Pu standard. For ^{239}Pu, the main contaminant in the starting material was ^{241}Pu and ^{240}Pu, with impurities calculated as the equivalent of 0.26 % and 0.44 % of the ^{239}Pu activity, respectively, at a reference time of 2021-01-01 12:00 UTC. Further ICP-MS/MS measurement showed no significant counts from either ^{240}Pu or ^{241}Pu (equivalent to less than 0.11 % of the counts at ^{239}Pu). In the case of ^{240}Pu, the starting solution had not previously been characterised. An initial activity check was performed using alpha LSC and an impurity check using gamma spectrometry. The main impurity detected was ^{241}Am at an equivalent of 0.1 % of the activity of ^{240}Pu at a reference time of 2024-06-02 12:00 UTC by gamma spectrometry. ICP-MS/MS measurement also detected ^{239}Pu in the ^{240}Pu (equivalent to 1 % of the counts at ^{240}Pu.)

There are more sensitive mass spectrometric techniques being used in the comparison exercise and the reporting form provided the option to record any impurities detected. The results for any impurities detected by NPL in other standards is given in

Table 5. Again, some mass spectrometric techniques could potentially detect lower impurity levels, and this could be reported as part of the participants results.

Table 5. Preliminary impurity levels detected in starting materials.

Standard	Impurity level ratio detected (by ICP-MS/MS unless stated otherwise)
^{234}U	^{235}U (8 × 10^{-4}) ^{236}U (4 × 10^{-4}) ^{238}U (8 × 10^{-5})
^{236}U	^{234}U (8 × 10^{-4}) ^{235}U (3 × 10^{-4}) ^{238}U (1 × 10^{-3})
^{Nat}U	^{236}U / ^{234}U (3 × 10^{-2}) ^{236}U / ^{235}U (2 × 10^{-4}) ^{236}U / ^{238}U (2 × 10^{-6})
^{237}Np	^{234}U (4 × 10^{-5}) ^{235}U (1 × 10^{-3}) ^{238}U (1 × 10^{-3})
^{239}Pu	^{240}Pu (<1× 10^{-3}) ^{241}Pu (3 × 10^{-3}) (LSC)
^{240}Pu	^{239}Pu (1 × 10^{-2}) ^{241}Am (1× 10^{-2}) (gamma spectrometry)

3.2.4 Assigned values

At the start of the project, the aim was for several laboratories to determine the starting activity values of the standards used for the comparison. It was realised at an early stage of the project that several of these laboratories also planned to participate in the comparison exercise, and taking part in the characterisation could result in a conflict. It was agreed that NPL had the facilities and capabilities to assign the values for the starting materials without aid. These values are given in Table 6 and

Table 7.

Table 6. Assigned values for radionuclide standards used in the comparison exercise.

Radionuclide	**Assigned value in Bq g^{-1}**	**Uncertainty (k = 2) in Bq g^{-1}**
^{90}Sr	7.66×10^{-3}	7.00×10^{-5}
^{234}U	7.31×10^{-6}	6.10×10^{-8}
^{236}U	1.57×10^{-5}	1.50×10^{-7}
^{237}Np	1.94×10^{-4}	1.60×10^{-6}
^{239}Pu	4.12×10^{-3}	1.70×10^{-5}
^{240}Pu	5.40×10^{-3}	2.80×10^{-5}
^{241}Am	4.76×10^{-3}	5.20×10^{-5}

Table 7. Values for radionuclides used in isotopic ratio standards for the comparison exercise.

Radionuclide	**Activity in Bq g^{-1}**	**Uncertainty (k = 2) in Bq g^{-1}**
^{Nat}U		
^{234}U	2.58×10^{-4}	8.90×10^{-6}
^{235}U	1.23×10^{-5}	4.20×10^{-7}
^{238}U	2.58×10^{-4}	6.90×10^{-6}
^{240}Pu / ^{239}Pu		
^{239}Pu	1.03×10^{-2}	3.40×10^{-4}
^{240}Pu	2.39×10^{-3}	1.40×10^{-5}

3.2.5 Dispatch of materials

The radioactive dispatch team organised the delivery of the final samples to the participating laboratories. The delivery of the samples was subcontracted to the following organisations:

The Courier Company (UK) Limited
11 James Way Marshall Court
Milton Keynes, MK1 1SU, UK

Circle Express
Unit 1
Polar Park
Bath Rd
West Drayton, UB7 0EX, UK

Export licences were applied for to allow dispatch of the materials from the UK around Europe. Depending on the dispatch date, an additional requirement was raised for NPL regarding the safety of dispatching materials containing HNO_3.
Not all laboratories had the capabilities or interest in measuring all the radionuclide standards prepared. Additionally, some laboratories stated that the starting activities were lower than they could measure and requested for higher activity standards to be prepared. Given the dilution approach described, it was possible to provide these additional samples. In total, 98 samples were dispatched to the participating laboratories.

The low radioactivity levels meant the samples could be considered as below of permitted limit for transport purposes. However, it was still a requirement for NPL to assign these standards as active material. This presented a logistical challenge to some of the participating laboratories depending on their licence arrangements and the materials they were able to receive.

4 Results and Discussion

4.1 Handling of data

4.1.1 Reporting Spreadsheet

A reporting spreadsheet was prepared for participating laboratories. A series of tabs were prepared:

1. General information about the participating laboratory.
2. Instrumentation: type and model of instrument used, additional components e.g. specific sample introduction systems.
3. A tab for each radionuclide- information including samples received, sample treatment, measurement protocol, activity or isotopic ratio measured, limit of detection, sensitivity, uncertainty budget.
4. Information on additional files if relevant.

Given the significant delays in sending the samples to the laboratories, a simplified version of the reporting format was agreed amongst the participating laboratories, who were encouraged to submit as much information as they were able to.

4.1.2 Data processing

The results reported by each participating laboratory were compared with the reference value derived by NPL earlier in the project. The comparison was performed by calculating the degrees of equivalence d_i (DoE), defined as the difference between the reported value x_i and the reference value x_{ref} shown in Equation 1:

$$d_i = x_i - x_{\text{ref}} \qquad \text{(Equation 1)}$$

The associated uncertainty of each d_i is shown in Equation 2:

$$u(d_i) = \sqrt{u^2(x_i) + u^2(x_{\text{ref}})} \qquad \text{(Equation 2)}$$

If zero is within the interval $[d_i-2u(d_i), d_i+2u(d_i)]$, the reported value of participant i is statistically consistent with the reference value. In other words, there is no significant difference between these two values at a 95 % confidence level.

All reported values were plotted in increasing order, since this allows to identify a bimodal distribution. Furthermore, the reference value plus/minus its expanded uncertainty (*k* = 2) were plotted as horizontal orange lines. The error bars represent the associated uncertainties with *k* = 2.

Additionally, the DoEs were plotted in the same order as the results, right side. The horizontal red line represents a DoE of zero, if the error bars encompass zero the reported value and the reference value are indistinguishable. Here again all error bars represent the expanded uncertainty with *k* = 2.

4.2 **Results for radionuclide standards**

For each of the radionuclides, the results are plotted against the NPL reference values, along with the degree of equivalence, the measurement technique used, and any comments from the participating laboratories.

4.2.1 Instrumentation used

A range of ICP-MS designs, AMS and decay counting techniques were used to measure radionuclide standards. Any additional details provided from the participants are shown in Table *8*.

Table 8. Instrument details provided

Instrument (model)	**Sample introduction**	**Detector details**
ICP-MS/MS (Agilent)	Standard glass spray chamber Apex Q	Dual mode SEM (secondary electron multiplier)
MC-ICP-MS (Nu Plasma II)	Savillex PFA self-aspirating nebuliser	Five Faraday cups with 10^{-11} Ω resistors
ICP-TOF-MS (ICP-TOF2R)	MicroMist nebuliser, quartz cyclonic spray chamber, self-aspirating	10^{-11} Ω resistors
MC-ICP-MS (Neptune Plus)	Savillex PFA, self-aspirating	Low resolution mode, 4 Faraday Cups with 10^{-11} Ω and one with 10^{-13} Ω resistors
AMS	Multi-cathode source of negative ions by caesium sputtering (MC-SNICS)	-

4.2.2 Sample preparation

Given that the samples received only contained single radionuclides or mixed radionuclides of the same element, several laboratories measured the samples directly without sample preparation. Any additional information on sample preparation for specific radionuclides are detailed in the relevant radionuclide section. One laboratory deliberately noted that sample preparation before measurement was kept to a minimum, whilst for AMS one laboratory described pre-concentration and treatment to prepare the standard for measurement. Chromatographic separation was used in some cases prior to decay counting measurements.

4.2.3 Uncertainty Budget

All participating laboratories provided an activity concentration and uncertainty. The level of detail in the uncertainty budget varied, with the following contributing factors the most frequently highlighted: mass fraction of the reference material, isotope ratio of the reference material, sample weighing, measured ratio, calibration offset, calibration slope, dilution factor, and half-life.

4.2.4 Strontium-90

The results submitted for ^{90}Sr are shown in Figure 2, Figure 2 and

Table 9. Four results were measured for ^{90}Sr. Two laboratories used decay counting techniques, with one using AMS and one using ICP-MS/MS.

One laboratory did not submit a result as they had limited experience in measuring ^{90}Sr using ICP-MS, with several laboratories reporting that the activity concentration of the sample received was too low to measure. This is expected as, of all the radionuclides in this comparison, ^{90}Sr was the most challenging to measure given the relatively short half-life. The reference value of 7.66×10^{-3} Bq g^{-1} is equivalent to 1.50×10^{-15} g g^{-1}, which is extremely challenging.

The result using AMS calculated a higher activity of 9.43×10^{-3} Bq g^{-1}. Whilst the measurement uncertainty recorded by ICP-MS/MS was higher than decay counting and (AMS), it is impressive that this instrumentation is capable of ^{90}Sr measurement at such low levels.

The two results submitted by decay counting techniques showed the closest agreement with the NPL reference values, with values of 7.40×10^{-3} Bq g^{-1} $\pm$ 1.1×10^{-3} Bq g^{-1} and 8.00×10^{-3} Bq g^{-1} $\pm$ 0.90×10^{-3} Bq g^{-1}, respectively. One laboratory measuring ^{90}Sr by liquid scintillation counting (LSC) described the sample preparation performed: 30 mg of inactive Sr-carrier was added to the sample, which was then dried under a heat lamp. The residue was dissolved to 3M HNO_3 and ^{90}Sr was separated using Sr resin (Eichrom Industries). Strontium was precipitated as carbonate with ammonium carbamate and transferred to a liquid scintillation vial with 1 M hydrochloric acid and an aliquot was taken for yield determination with ICP-MS. Strontium-90 was measured with low background liquid scintillation counter (1220 Quantulus) after 7 days ingrowth of daughter nuclide ^{90}Y and efficiency was determined from the calibration curve.

Whilst mass spectrometry is increasingly being used for determination of relatively short-lived radionuclides such as ^{90}Sr, decay counting techniques are still a favoured approach by some laboratories, as despite the relatively long measurement times, very low detection limits are achievable.

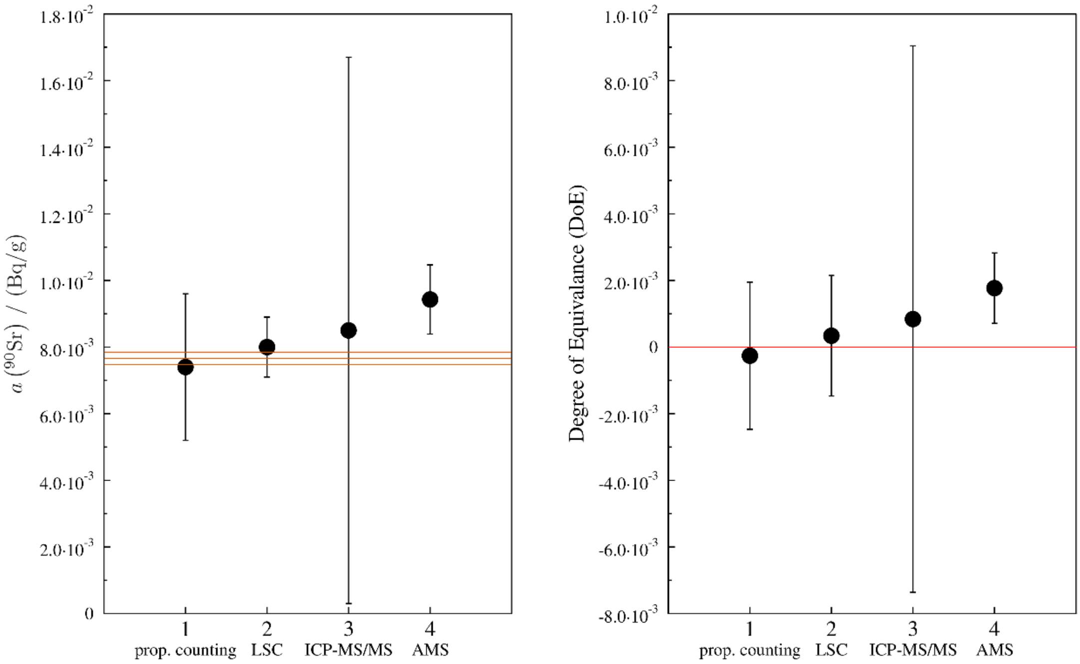


Figure 1. Results for measurement of ^{90}Sr standard and Figure 2. Degree of equivalence for measurement of ^{90}Sr standard

Table 9. Table of results and performance for ^{90}Sr standard

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (*k* = 2)	E_n	DoE
1 Proportional counting	7.40 × 10^{-3}	2.20 × 10^{-3}	0.118	-2.60 × 10^{-4}
2 LSC	8.00 × 10^{-3}	9.00 × 10^{-4}	0.373	3.40 × 10^{-4}
3 ICP-MS/MS	8.50 × 10^{-3}	8.20 × 10^{-3}	0.102	8.40 × 10^{-4}
4 AMS	9.43 × 10^{-3}	1.04 × 10^{-3}	1.686	1.77 × 10^{-3}

4.2.5 Uranium-234

The results for ^{234}U are shown in Figure 3, Figure 4, Figure 6, Figure 7 and

Table 10. The reference value was 7.31 × 10^{-6} Bq g^{-1}, equivalent to 3.17 × 10^{-14} g g^{-1}. Five results were reported for ^{234}U using three mass spectrometric techniques (ICP-MS/MS, ICP-SFMS and MC-ICP-MS). Of these, MC-ICP-MS was the most common technique (three measurements), with a single result each from ICP-MS/MS and ICP-SFMS. One laboratory requested measurement of a higher activity standard, which was prepared

from an earlier dilution stage and showed good agreement with the reference value within uncertainty (Figure 4). One laboratory reported that the activity concentration was below the limit of detection for their ICP-MS/MS instrument.

The results reported were generally higher than the reference value, with the result submitted using ICP-SFMS showing the closest agreement. The use of reference standards was reported by one laboratory using MC-ICP-MS IRMM-184 for mass bias correction and IRMM-054 for single IDMS spike.

One laboratory performed measurement by MC-ICP-MS but used alpha spectrometry to measure ^{232}U as a tracer for ^{234}U. The sample was evaporated and the precipitate dissolved in concentrated HCl. The sample was then run through an ion exchange method (using Dowex 1x8, 50/100 mesh). Uranium was co-precipitated with CeF_3 for the alpha measurement and the sample counted with AlfaAnalyst spectrometer (Canberra).

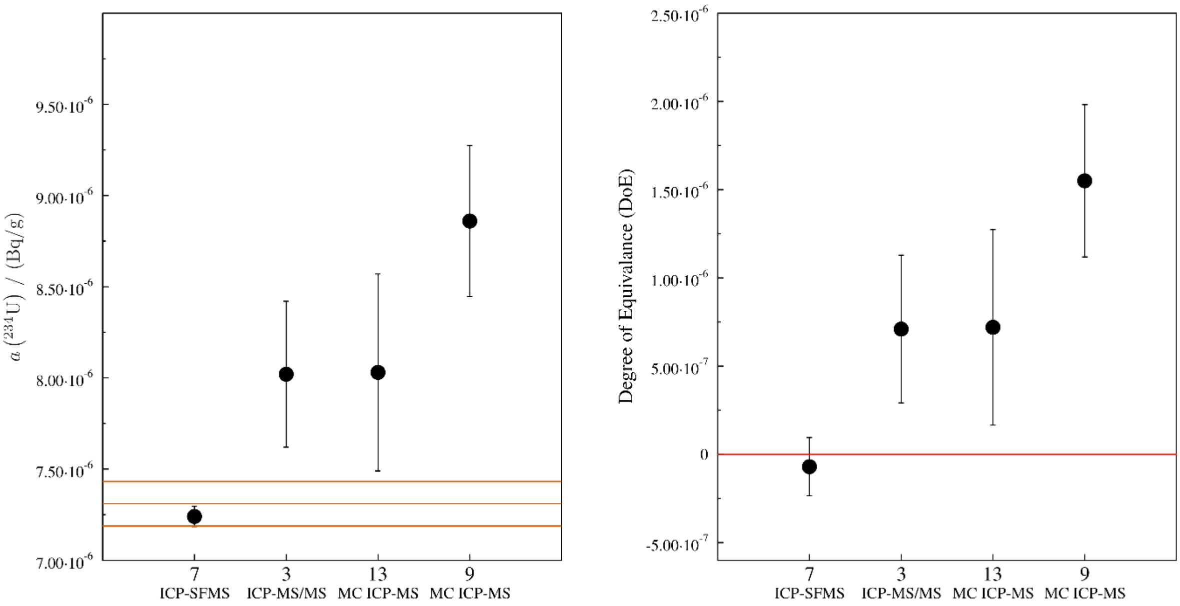
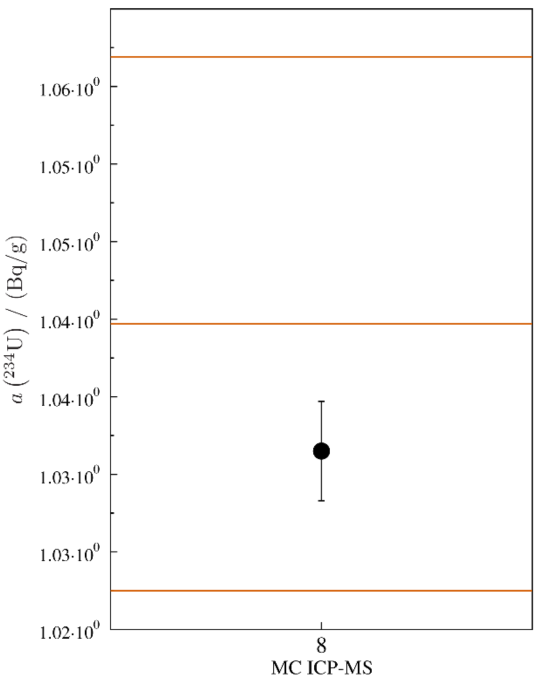


Figure 3. Results of measurement of ^{234}U standard and Figure 4. Degree of equivalence for ^{234}U standard



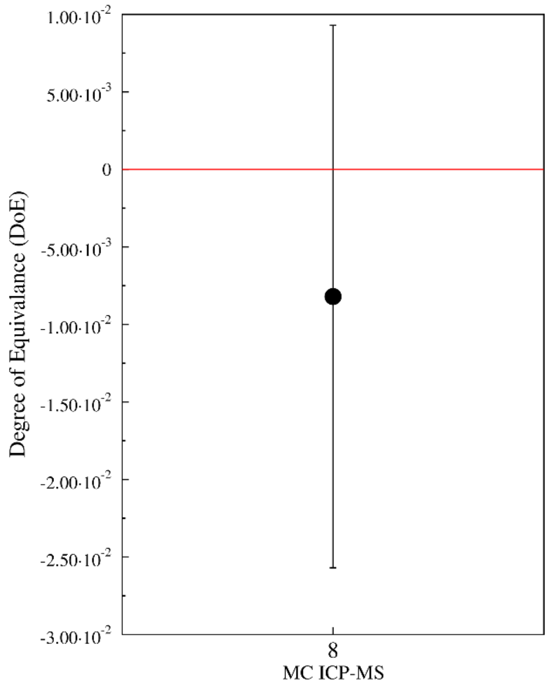


Figure 5. Results of measurement of higher activity ^{234}U standard

Figure 6. Results of measurement of higher activity ^{234}U standard *and* Figure 7. Degree of equivalence for measurement of higher activity ^{234}U standard

Figure 8. Degree of equivalence for measurement of higher activity ^{234}U standard

Table 10. Table of results and performance for ^{234}U standard. *Calculated for higher activity standard

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (*k* = 2)	E_n	DoE
7 ICP-SFMS	7.24×10^{-6}	$5.57E \times 10^{-8}$	0.546	-7.33×10^{-8}
3 ICP-MS/MS	8.02×10^{-6}	4.00×10^{-7}	1.688	7.06×10^{-7}
13 MC-ICP-MS	8.03×10^{-6}	5.40×10^{-7}	1.293	7.16×10^{-7}
9 Other	8.86×10^{-6}	4.14×10^{-7}	3.578	1.55×10^{-6}
8 MC-ICP-MS	1.04×10^{0}	3.20×10^{-3}	0.469*	-8.20×10^{-3} *

4.2.6 Uranium-236

The results for ^{236}U are shown in Figure 9, Figure 10, **Fehler! Verweisquelle konnte nicht gefunden werden.**, Figure 13 and **Fehler! Verweisquelle konnte nicht gefunden werden.**. The reference value was 1.57 × 10^{-5} Bq g^{-1}, equivalent to 6.56 × 10^{-12} g g^{-1}. Six results were reported for measurement of ^{236}U. MC-ICP-MS and AMS were the most used technique with two results each, with a single measurement using ICP-MS/MS, ICP-SFMS and AMS. One lab requested a higher concentration of the starting material, and the result showed very strong agreement with the reference value (Figure 10). One laboratory requested measurement of a higher activity standard, which was prepared from an earlier dilution stage. One laboratory using ICP-MS/MS reported that the ^{236}U activity concentration was close to the instrument limit of detection.

The results followed a similar pattern to ^{234}U, with the measurement by ICP-SFMS showing the closest agreement to the reference value. One laboratory using MC-ICP-MS reported the use of IRMM-184 for mass bias correction, IRMM-3636a as a reference for double IDMS and IRMM-054 as a spike material for the double IDMS.

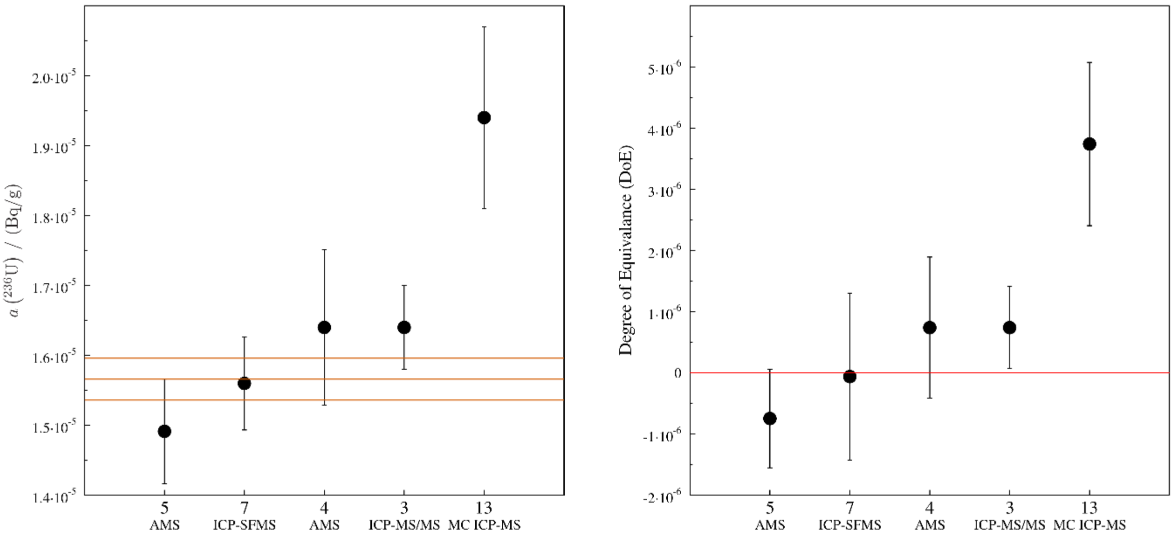


Figure 9. Results for measurement of ^{236}U standard and Figure 10. Degree of equivalence for ^{236}U standard

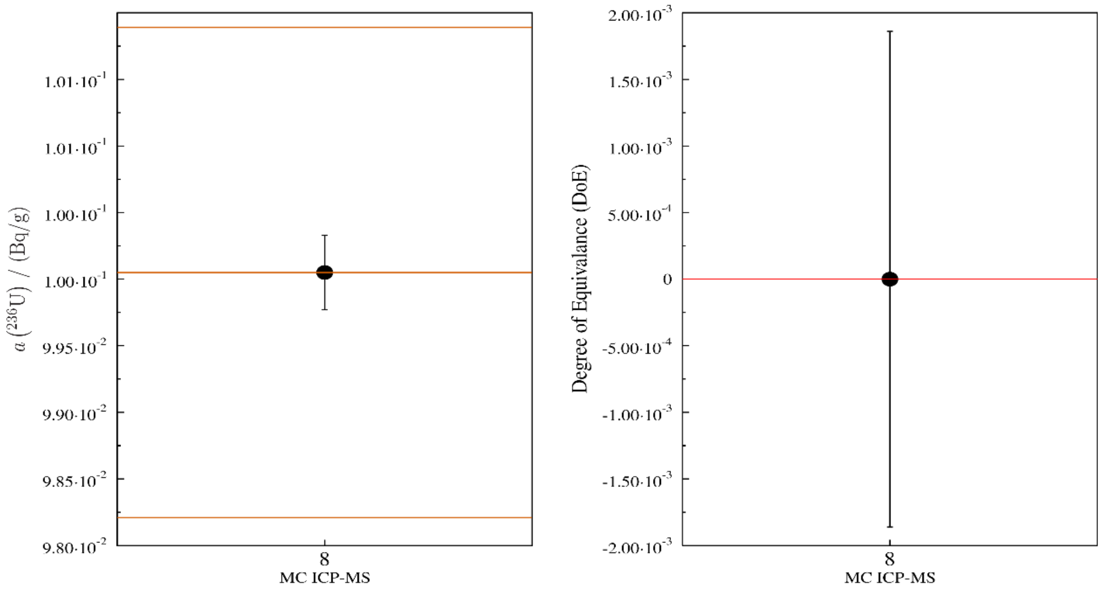


Figure 11. Figure 12. Results for measurement of higher activity ^{236}U standard and Figure 13. Degree of equivalence for higher activity ^{236}U standard.

Table 11. Table of results and performance for ^{236}U standard. *Assessed against higher activity starting standard

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (k = 2)	E_n	DoE
5 AMS	1.49×10^{-5}	7.46×10^{-7}	0.927	-7.45×10^{-7}
7 ICP-SFMS	1.56×10^{-5}	6.65×10^{-7}	0.127	-9.28×10^{-8}
4 AMS	1.64×10^{-5}	1.11×10^{-6}	0.599	6.91×10^{-7}
3 ICP-MS/MS	1.64×10^{-5}	6.00×10^{-7}	1.103	7.40×10^{-7}
13 MC-ICP-MS	1.94×10^{-5}	1.30×10^{-6}	2.803	3.74×10^{-6}
8 MC-ICP-MS	1.00E-01	2.80×10^{-4}	0.00*	0.00*

4.2.7 Neptunium-237

The results for ^{237}Np are shown in Figure 14, Figure 15 and Table 12. Five results were reported for ^{237}Np using four different mass spectrometric techniques (ICP-MS/MS, ICP-SFMS, MC-ICP-MS and AMS). No results were reported using decay counting techniques. Given the long half-life, measurement using mass spectrometric techniques is expected. Peak tailing from ^{238}U is a potential interference, however, this was not detected in the starting material.

The reference value of 1.94×10^{-4} Bq g^{-1} is equivalent to 7.45×10^{-12} g g^{-1}. The results by ICP-SFMS and ICP-MS/MS showed the closest agreement with the reference values, whilst AMS and MC-ICP-MS had similar results that were slightly higher than the reference value.

The laboratory using AMS reported using a mixture of IRMM-085 ^{242}Pu and ^{237}Np spike, with the absence of a suitable ^{236}Np tracer for ^{237}Np highlighted.

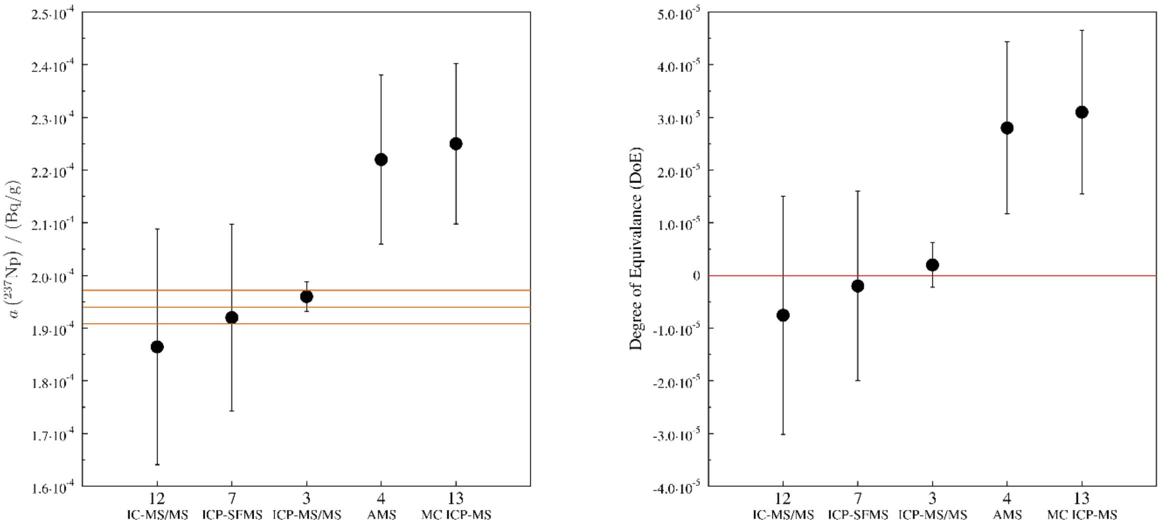


Figure 14. Results for measurement of ^{237}Np standard and Figure 15. Degree of equivalence for ^{237}Np standard

Table 12. Table of results and performance for ^{237}Np standard

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (*k* = 2)	E_n	DoE
12 ICP-MS/MS	1.86 × 10^{-4}	2.24 × 10^{-5}	0.334	-7.55 × 10^{-6}
7 ICP-SFMS	1.92 × 10^{-4}	1.77 × 10^{-5}	0.116	-2.08 × 10^{-6}
3 ICP-MS/MS	1.96 × 10^{-4}	2.80 × 10^{-6}	0.517	2.20 × 10^{-6}
4 AMS	2.22 × 10^{-4}	1.60 × 10^{-5}	1.706	2.79 × 10^{-5}
13 MC-ICP-MS	2.25 × 10^{-4}	1.52 × 10^{-5}	1.996	3.10 × 10^{-5}

4.2.8 Plutonium-239

The results for ^{239}Pu are shown in Figure 16, and Figure *17* and

Table 13. Plutonium-239 was the most reported radionuclide, with ten results. Most results used mass spectrometry, including ICP-MS/MS (two), ICP-SFMS (one), AMS (three) and MC-ICP-MS (two). There were three results submitted using decay counting techniques, two by alpha spectrometry and one by Liquid Scintillation Counting.

The reference value of 4.12 × 10^{-3} Bq g^{-1} is equivalent to 1.79 × 10^{-12} g g^{-1}, which is challenging but achievable by mass spectrometry. The activity concentrations reported using decay counting techniques were lower than the reference value, and the results reported by mass spectrometric techniques tended to be slightly higher.

One laboratory that performed alpha spectrometry measurement provided additional information on the sample preparation: A ^{242}Pu tracer was added to the samples. $NaNO_2$ was added and samples were heated and let to stand for three hours. Plutonium was then separated from other radionuclides by ion exchange using Dowex 1x8, 50/100 mesh. Plutonium was co-precipitating with CeF_3 for the alpha measurement (AlfaAnalyst spectrometer (Canberra)). It was noted that the alpha spectrometry resolution is not sufficient to resolve ^{239}Pu and ^{240}Pu and it was assumed that the ^{239}Pu standard did not contain any traces of ^{240}Pu and vice versa.

The reported mass spectrometry results agreed or were slightly higher than the reference values, with a relatively narrow distribution across the results. With regards to interferences, tailing from ^{238}U, polyatomic ^{238}U^{1}H can overlap with ^{239}Pu, but given that this was a single element standard, this interference was not expected to influence the result.

The result recorded by ICP-SFMS showed the closest agreement with the reference value (4.07 × 10^{-3} Bq g^{-1}). There was a single result using ICP-QMS and MC-ICP-MS, both of which were slightly higher than the reference value, with activity concentrations of 4.46 × 10^{-3} Bq g^{-1} and 4.66 × 10^{-3} Bq g^{-1}, respectively. The most popular technique was AMS, with three results submitted. Results for AMS ranged from 4.27 × 10^{-3} Bq g^{-1} to 4.57 × 10^{-3} Bq g^{-1}.

For one AMS laboratory, additional details on the sample preparation were provided: 15 mL of 2 M HNO_3 were added to each pre-prepared aliquot, followed by the addition of a ^{242}Pu spike. The solution was left to equilibrate overnight. Next, approximately 25 mg of Fe^{3+} were added, the sample was shaken, and aqueous NH_3 was added until precipitation was evident. The pH was adjusted to 8–9, and the precipitate was allowed to settle for 3 hours. Afterward, the samples were centrifuged and the supernatant removed. The remaining precipitate was rinsed with 5 mL of ethanol, centrifuged again, and the ethanol was discarded. The precipitate was then transferred into a quartz crucible, dried, and oxidized in a muffle oven at 650 °C. This step was performed to convert to an oxidized form, enhancing ionization efficiency.

With regards to AMS measurement, the same laboratory reported Pu detection in the 3^{+} charge state using a dual-anode gas ionisation chamber. The resulting ^{239}Pu/^{242}Pu ratios were normalized using the standards, blank-corrected, and concentrations were calculated based on the spiked amount of ^{242}Pu.

Mass spectrometry is increasingly favoured as the preferred technique for measurement of ^{239}Pu. Alpha spectrometry cannot distinguish between the similar decay energies of ^{239}Pu and ^{240}Pu, however, this is possible by mass spectrometry, enabling measurement of both the activity concentrations and isotopic ratio value. This is significant given the variation in this ratio depending on the source of contamination e.g. reactor operation, weapons test fallout, or following a nuclear accident.

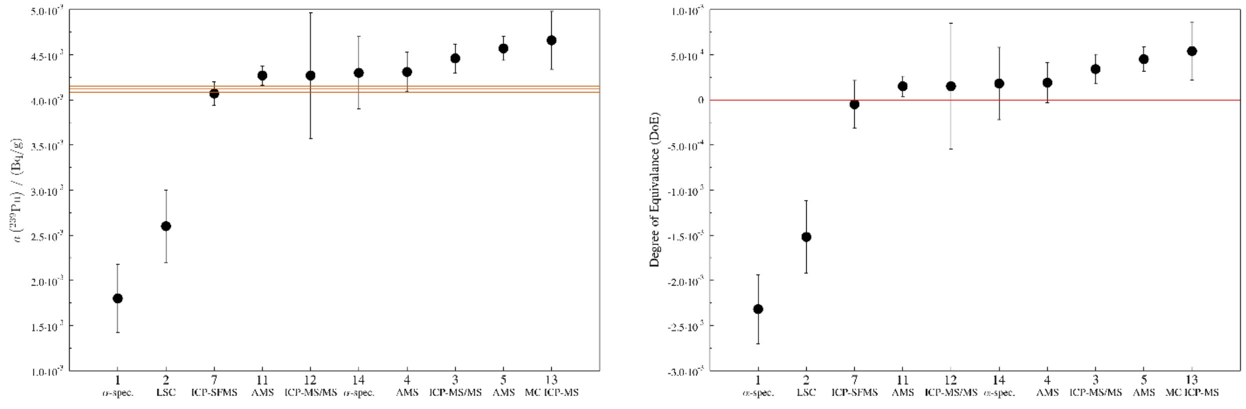


Figure 16. Results for measurement of ^{239}Pu standard and Figure 17. Degree of equivalence for measurement of ^{239}Pu standard

Table 13. Table of results and performance for ^{239}Pu standard

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (k = 2)	E_n	DoE
1 Alpha spectrometry	1.80×10^{-3}	3.80×10^{-4}	6.078	-2.32×10^{-3}
2 LSC	2.60×10^{-3}	4.00×10^{-4}	3.784	-1.52×10^{-3}
7 ICP-SFMS	4.07×10^{-3}	1.31×10^{-4}	0.326	-4.41×10^{-5}
11 AMS	4.27×10^{-3}	1.07×10^{-4}	1.366	1.53×10^{-4}
12 ICP-MS/MS	4.28×10^{-3}	6.95×10^{-4}	0.238	1.66×10^{-4}
4 AMS	4.31×10^{-3}	2.20×10^{-4}	0.857	1.91×10^{-4}
14 Alpha spectrometry	4.30×10^{-3}	4.00×10^{-4}	0.451	1.81×10^{-4}
3 ICP-MS/MS	4.46×10^{-3}	1.60×10^{-4}	2.085	3.41×10^{-4}
5 AMS	4.57×10^{-3}	1.32×10^{-4}	3.302	4.50×10^{-4}
13 MC-ICP-MS	4.66×10^{-3}	3.20×10^{-4}	1.681	5.41×10^{-4}

4.2.9 Plutonium-240

The results for ^{240}Pu are shown in Figure 18, and Figure *19* and Table 14. The single ^{240}Pu standard received ten results. The range of techniques used was the similar as ^{239}Pu (alpha spectrometry, ICP-QMS, ICP-SFMS, AMS and MC-ICP-MS). The reference value of 5.40×10^{-3} Bq g^{-1} is slightly higher than ^{239}Pu but due to the shorter half-life has a lower mass equivalent concentration of 6.43×10^{-13} g g^{-1}.

Some of the trends observed with ^{239}Pu were also seen for ^{240}Pu. For example, the results submitted by alpha spectrometry were generally lower than the reference value, with an activity concentration of 1.12×10^{-3} Bq g^{-1}. This suggests that the sample treatment or data processing for the two radionuclides may have had a similar impact. For one result submitted by alpha spectrometry, the description of sample preparation and assumptions of sample purity have been described in the ^{240}Pu section. By comparison, the result submitted by LSC showed good agreement with the reference value, with a calculated activity concentration of 5.20×10^{-3} Bq g^{-1}.

As with ^{239}Pu, there was a narrow spread of results around the reference value for mass spectrometric techniques. The results submitted by ICP-SFMS and AMS showed the closest agreement with the reference values, whilst one using ICP-MS/MS and the only result using MC-ICP-MS were the highest values reported, which is also like that seen for ^{239}Pu. Tailing from ^{239}Pu^{1}H can present a polyatomic interference, however, the trace-level ^{239}Pu impurity present means this is not expected to be an issue.

For AMS measurement, the same laboratory that described the sample preparation and measurement setup for ^{239}Pu described a similar process for ^{240}Pu.

As explained for ^{239}Pu, mass spectrometry is considered the favourable technique for ^{240}Pu, and the measurement of the ^{239}Pu/^{240}Pu ratio is commonly seen using this technique.

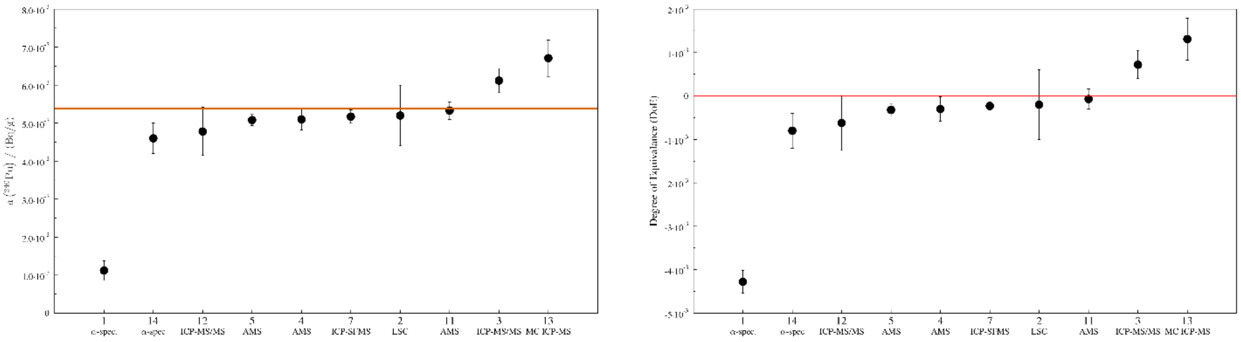


Figure 18. Results for measurement of ^{240}Pu standard and Figure 19. Degree of equivalence for measurement of ^{240}Pu standard.

Table 14. Table of results and performance for ^{240}Pu standard.

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (k = 2)	E_n	DoE
1 Alpha spectrometry	1.12×10^{-3}	2.60×10^{-4}	16.093	-4.28×10^{-3}
14 Alpha Spectrometry	4.60×10^{-3}	4.00×10^{-4}	1.980	-8.00×10^{-4}
12 ICP-MS/MS	4.78×10^{-3}	6.32×10^{-4}	0.977	-6.20×10^{-4}
5 AMS	5.08×10^{-3}	1.47×10^{-4}	2.042	-3.21×10^{-4}
4 AMS	5.10×10^{-3}	2.82×10^{-4}	1.043	-3.00×10^{-4}
7 ICP-SFMS	5.17×10^{-3}	1.74×10^{-4}	1.283	-2.35×10^{-4}
2 LSC	5.20×10^{-3}	8.00×10^{-4}	0.249	-2.00×10^{-4}
11 AMS	5.33×10^{-3}	2.32×10^{-4}	0.300	-7.17×10^{-5}
3 ICP-MS/MS	6.12×10^{-3}	3.20×10^{-4}	2.216	7.20×10^{-4}
13 MC-ICP-MS	6.71×10^{-3}	4.80×10^{-4}	2.711	1.31×10^{-3}

4.2.10 Americium-241

The results for ^{241}Am are shown in Figure 20, Figure 21 and Table 15. Nine results were submitted for measurement of ^{241}Am, including alpha spectrometry, gamma spectrometry, LSC and four different mass spectrometers (ICP-MS/MS, ICP-SFMS, MC-ICP-MS and AMS). One laboratory with ICP-MS/MS capability reported that measurement was not possible due to time constraints. One laboratory reported the use of ^{243}Am as a tracer.

The reference value of 4.76 × 10^{-3} Bq g^{-1} is equivalent to 3.75 × 10^{-14} Bq g^{-1}. After ^{90}Sr, this is the lowest mass concentration of any of the radionuclides measured in this comparison. As with ^{90}Sr, ^{241}Am is increasingly measured using mass spectrometric techniques, particularly in combination with other actinides. However, the relatively short half-life does make low-level measurement challenging.

The result reported by LSC (4.60 × 10^{-3} Bq g^{-1}) showed a good agreement with the reference value, whilst the result reported by alpha spectrometry was slightly lower (4.03 × 10^{-3} Bq g^{-1}).

Of the mass spectrometric techniques used, ICP-SFMS and MC-ICP-MS showed the closest agreement with the reference value, whilst the two AMS and ICP-MS/MS results reported similar activity concentrations, all with higher values than the reference value.

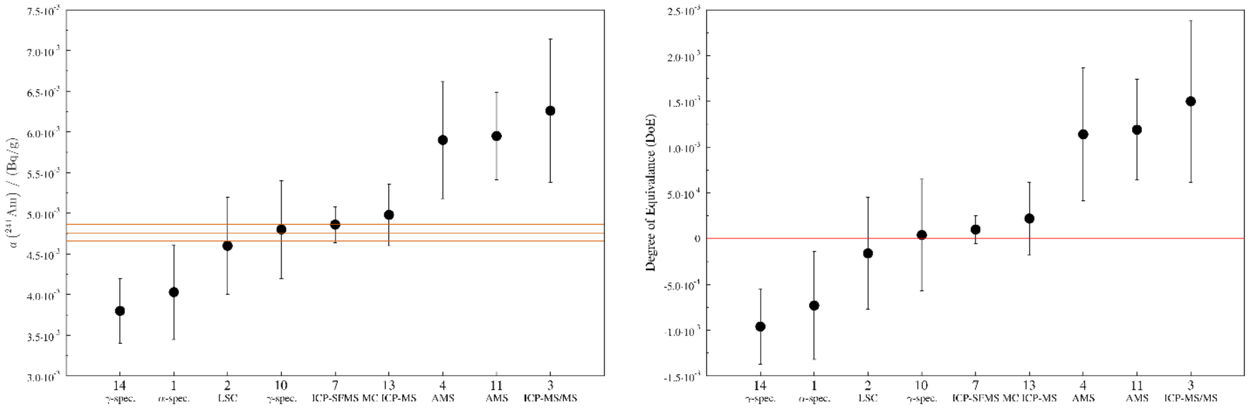


Figure 20. Results for measurement of ^{241}Am standard and Figure 21. Degree of equivalence for measurement of ^{241}Am standard.

Table 15. Table of results and performance for ^{241}Am standard.

Lab	Activity in Bq g^{-1}	Uncertainty in Bq g^{-1} (k = 2)	E_n	DoE
14 Other	3.80×10^{-3}	4.00×10^{-4}	2.332	-9.64×10^{-4}
1 Alpha spectrometry	4.03×10^{-3}	5.80×10^{-4}	1.246	-7.34×10^{-4}
2 LSC	4.60×10^{-3}	6.00×10^{-4}	0.269	-1.64×10^{-4}
10 Other	4.80×10^{-3}	6.00×10^{-4}	0.059	3.60×10^{-5}
7 ICP-SFMS	4.86×10^{-3}	2.22×10^{-4}	0.408	9.99×10^{-5}
13 MC-ICP-MS	4.98×10^{-3}	3.80×10^{-4}	0.548	2.16×10^{-4}
4 AMS	5.90×10^{-3}	7.30×10^{-4}	1.540	1.14×10^{-3}
11 AMS	5.95×10^{-3}	5.37×10^{-4}	2.165	1.19×10^{-3}
3 ICP-MS/MS	6.26×10^{-3}	8.74×10^{-4}	1.700	1.50×10^{-3}

4.2.11 Uranium isotopic ratios

Results for the uranium isotopic standard are shown in

Table 16 and Figure 22. Three laboratories reported the activity concentrations of uranium isotopes as well as the isotopic ratio.

The $^{235}U/^{238}U$ values reported ranged from 7.13 × 10^{-3} mol/mol to 7.52 × 10^{-3} mol/mol. This is the only application where results were reported using inductively coupled plasma time of flight mass spectrometry (ICP-TOF-MS). Aliquots of the sample solutions were decanted into pre-cleaned 15 mL plastic tubes and used in the measurement without further dilution. Notch filters were used to reduce the intensity of argon ion signals. The option of using a collision gas for removal of polyatomic interferences was not employed as the samples were single element standard solutions containing no matrix elements.

A laboratory using MC-ICP-MS described the use of NIST SRM 981 as a reference material. Initial analyte concentration screening showed that only the sample, ^{Nat}U, had concentration of the analyte (natural uranium) higher than instrumental limit of quantification. An additional aliquot of this sample was taken and then spiked with solution of common Pb NIST SRM 981 at a concentration level of 10 ppb for the latter to serve as internal standard for uranium isotope ratio measurements. A uranium ICP standard was used for calibration.

Another laboratory also applied MC-ICP-MS (ID 8), but instead of a lead standard, used a uranium isotope reference material, IRMM-184, to perform measurements with the standard sample bracketing approach. Therefore, the sample was measured directly as it was delivered, with no dilutions or mixing of the sample. Each sample measurement was bracketed with a standard (IRMM-184) to correct for the mass bias occurring during the measurement.

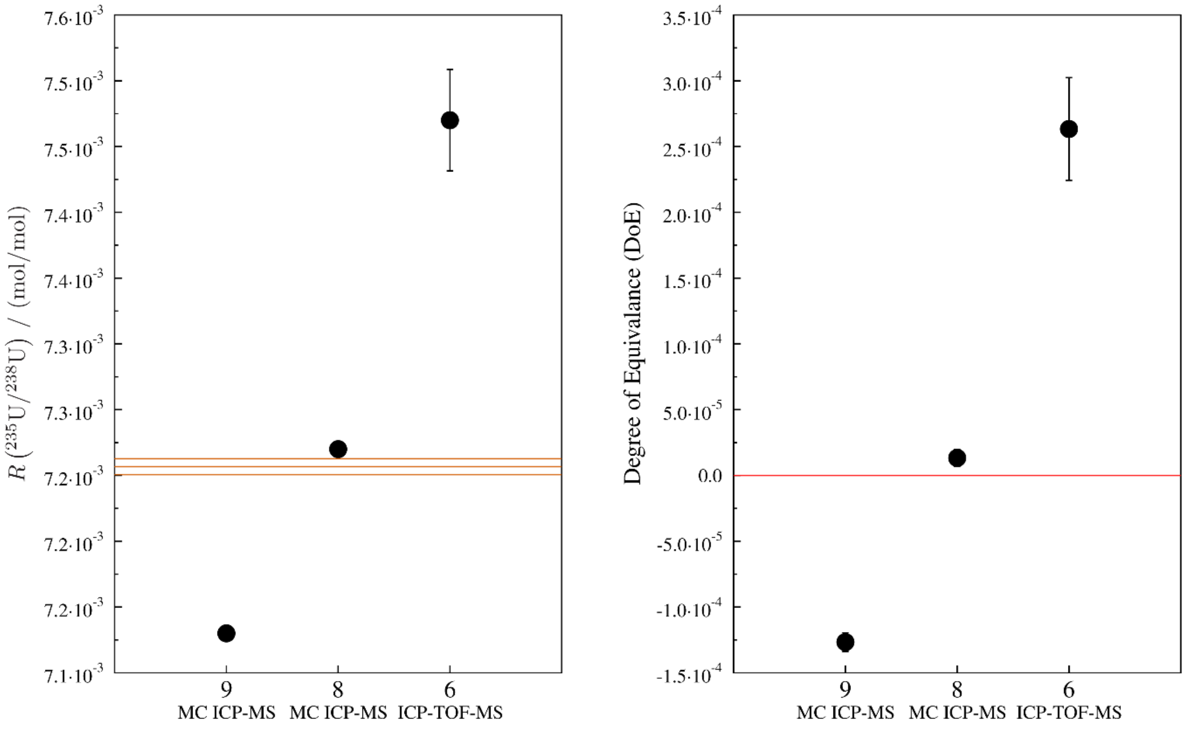


Figure 22. Results for measurement of ^{Nat}U and Figure 20. Degree of equivalence for measurement of ^{Nat}U standard.

Table 16. Table of results for uranium mixed standard

Lab	$R(^{235}\mathrm{U}/^{238}\mathrm{U})$ in mol/mol	$u(R(^{235}\mathrm{U}/^{238}\mathrm{U}))$ in mol/mol (k=2)
9 MC-ICP-MS	7.13×10^{-3}	1.86×10^{-6}
8 MC-ICP-MS	7.27×10^{-3}	2.00×10^{-6}
6 ICP-TOF-MS	7.52×10^{-3}	3.86×10^{-5}

4.2.12 Plutonium isotopic ratios

Results for the Plutonium isotopic standard are shown in

Table 17 and **Fehler! Verweisquelle konnte nicht gefunden werden.**. Two results were submitted, both using AMS, with ^{240}Pu/^{239}Pu values of 0.0567 and 0.0603. The uncertainties in the measurements were 4.8 % and 6.4 % (k = 1). Several laboratories reported not being able to submit results due to time constraints.

As described, results for alpha spectrometry were not expected as they cannot resolve the difference in decay energy between ^{239}Pu and ^{240}Pu. Given that ^{239}Pu and ^{240}Pu were two of the most frequently measured single radionuclide standards, there is interest in such isotopic ratio measurements.

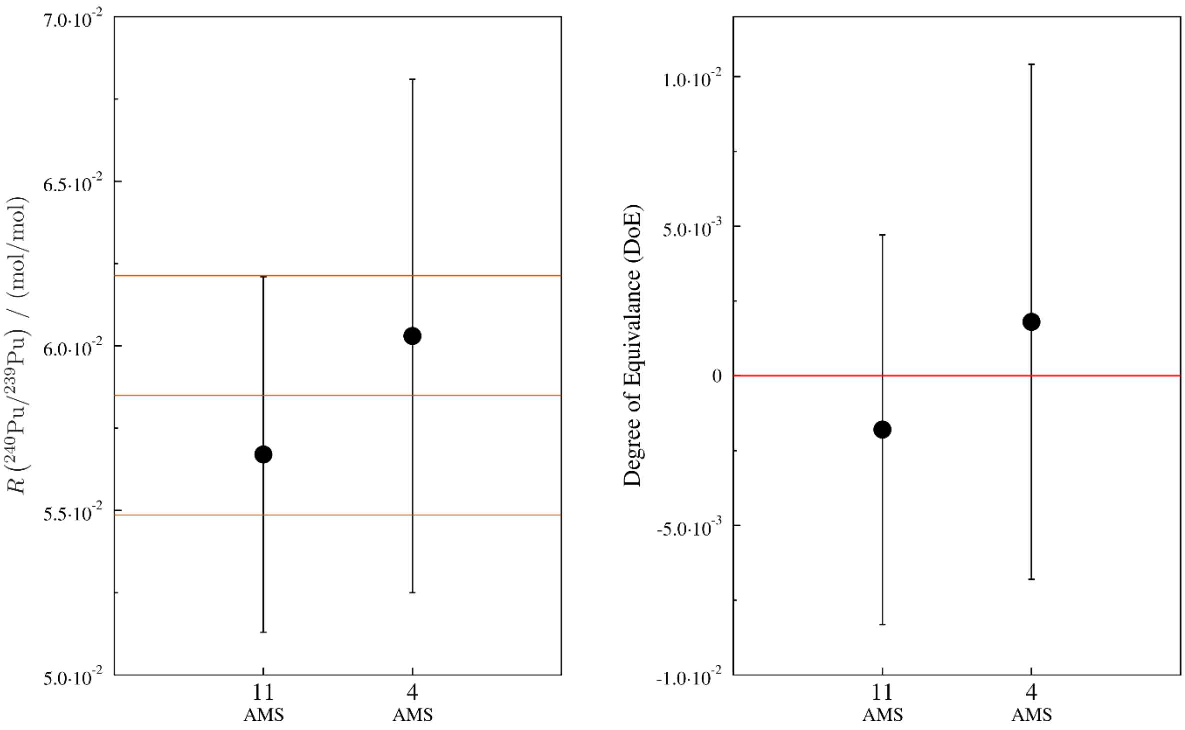


Figure 21. Results for measurement of ^{240}Pu/^{239}Pu and Figure 22. Degree of equivalence for measurement of ^{240}Pu/^{239}Pu standard

Table 17. Table of results and performance for Plutonium mix standard

Lab	R(^{240}Pu/^{239}Pu) in mol/mol	u(R(^{240}Pu/^{239}Pu)) in mol/mol (k=2)
11 AMS	0.0567	0.0055
4 AMS	0.0603	0.0077

4.3 **Discussion and Conclusions**

4.3.1 Value of the comparison and feedback from participants

This comparison exercise provides further evidence that mass spectrometry is of growing interest for low level radionuclide measurement. A range of radionuclides have been measured using different mass spectrometric techniques as well as radiometric techniques.

The delays in preparing and dispatching the materials meant that not all planned measurements were achieved. Of the mass spectrometric techniques available at the start of the project, results were not submitted for thermal ionisation mass spectrometry (TIMS), secondary ionisation mass spectrometry (SIMS) or sputtered neutral mass spectrometry (SNMS). Results were received for ICP-QMS, ICP-SFMS, MC-ICP-MS, AMS and ICP-TOF-MS. The details of the measurement approach provided by different laboratories also varied, which is understandable given the delays in receiving the materials.

Several labs reported that the activity levels of some or all of the samples were challenging to measure, and results could not be reported for all of the radionuclides received. It was a challenge to balance the values of interest of the participating laboratories with the low-level activities that meant the results of the comparison gave meaningful results. In the case of SNMS, it was also reported that the nature of how the standards were prepared was not suitable for measurement.

Results were reported for every radionuclide that was dispatched, and these demonstrate that very low level (equivalent to the pg g^{-1} to fg g^{-1} range) measurement of multiple radionuclides is achievable by mass spectrometry. Of the radionuclides measured, the lowest number of results were reported for ^{90}Sr, with the maximum number for ^{239}Pu, ^{240}Pu and ^{241}Am. There was also the lowest range of measurement techniques used for ^{90}Sr, with decay counting being the most common. This is perhaps expected, as ^{90}Sr has the shortest half-life of any of the radionuclides in this exercise and is therefore the most challenging to measure by mass spectrometry. The presence of stable Sr as a carrier also presents a significant interference. Whilst this radionuclide is increasingly being measured by mass spectrometry, it is perhaps not at the stage where it can be considered as routine. For some radionuclides, only mass spectrometric techniques were used with no results submitted using decay counting techniques. For isotopic ratio measurements, there were a limited number of results for both ^{Nat}U and ^{240}Pu/^{239}Pu from which to draw meaningful conclusions; an isotopic ratio mix could be of value in future exercises to provide the opportunity for both single radionuclide and isotopic ratio measurements.

4.3.2 Considerations for future exercises

The number of participating laboratories and range of techniques available should be considered for future exercises of this kind. There are additional laboratories who are not members of the MetroPOEM consortium who have enquired about the standards prepared and would be interested in future exercises.

There are several aspects to consider in the development of a future exercise. In this study, laboratories received a bespoke set of single or mixed radionuclide standards depending on their measurement needs and/or what they were able to receive at their laboratories in terms of activity. The annual NPL Environmental Radioactivity Proficiency Test Exercise and other comparison exercises are more likely to send an individual mix or the same materials to all participating laboratories. The preparation of a range of standards for this study likely improved the number of participating laboratories but was a more challenging approach and contributed to the delays in the preparation and sending of the material.

The range of radionuclides covered half-life values from approximately 28.8 (7) years (^{90}Sr) where mass spectrometry measurement is feasible but challenging, to approximately 4.468 (5) × 10^9 years (^{238}U), where mass spectrometry can be considered the preferred analytical technique. The nature of the standards prepared in this study can serve as useful calibration standards to support the measurement of real materials such as the reference materials developed in Work Package 3.

All of the radionuclides included in this study had been measured on multiple occasions by mass spectrometry in the past. There are difficult to measure radionuclides where mass spectrometry is increasingly being proven as a feasible technique, including ^{93}Zr, ^{129}I and ^{135}Cs. In many cases, there are no suitable standards to validate the measurement of these radionuclides. The development of such standards and inclusion as analytes in future comparison exercises will be of increasing importance.

One limitation of the standards developed was the absence of interferences, with the exception of ^{90}Sr that already contained stable Sr and Y carriers. If the aim is to produce mass spectrometry-relevant standards, then the inclusion of interferences is not needed, however, for a comparison exercise, a mix containing radionuclides and potential interferences could be of interest. The standards used in this comparison meant that online interference removal capabilities such as sector field and collision/reaction cell capabilities could not be fully tested.

The starting chemistry of these standards was more dilute nitric acid than the standards normally prepared by NPL (0.1 M HNO_3 compared to approximately 2M HNO_3). This was with the intention that samples could be run directly without sample preparation, such that the focus was on mass spectrometric capabilities. If mass spectrometric standards are to be prepared in this way in the future, long term testing of the stability must be considered. NPL is performing these measurements on the samples from this study.

5 Appendices

Appendix 1. Information on starting materials and sample preparation

For each radionuclide, key information on the sources prepared are given.

5.1 Strontium-90

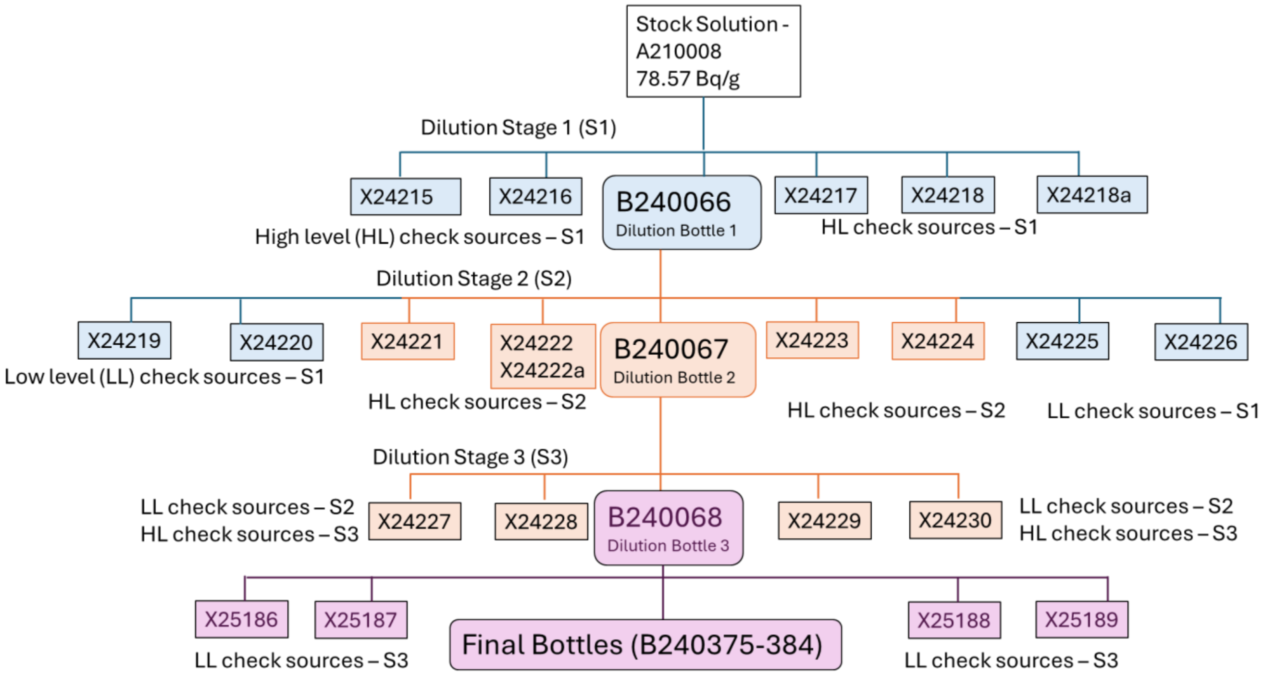


Figure 23. Sources made from the dilution of ^{90}Sr.

5.2 Uranium-234

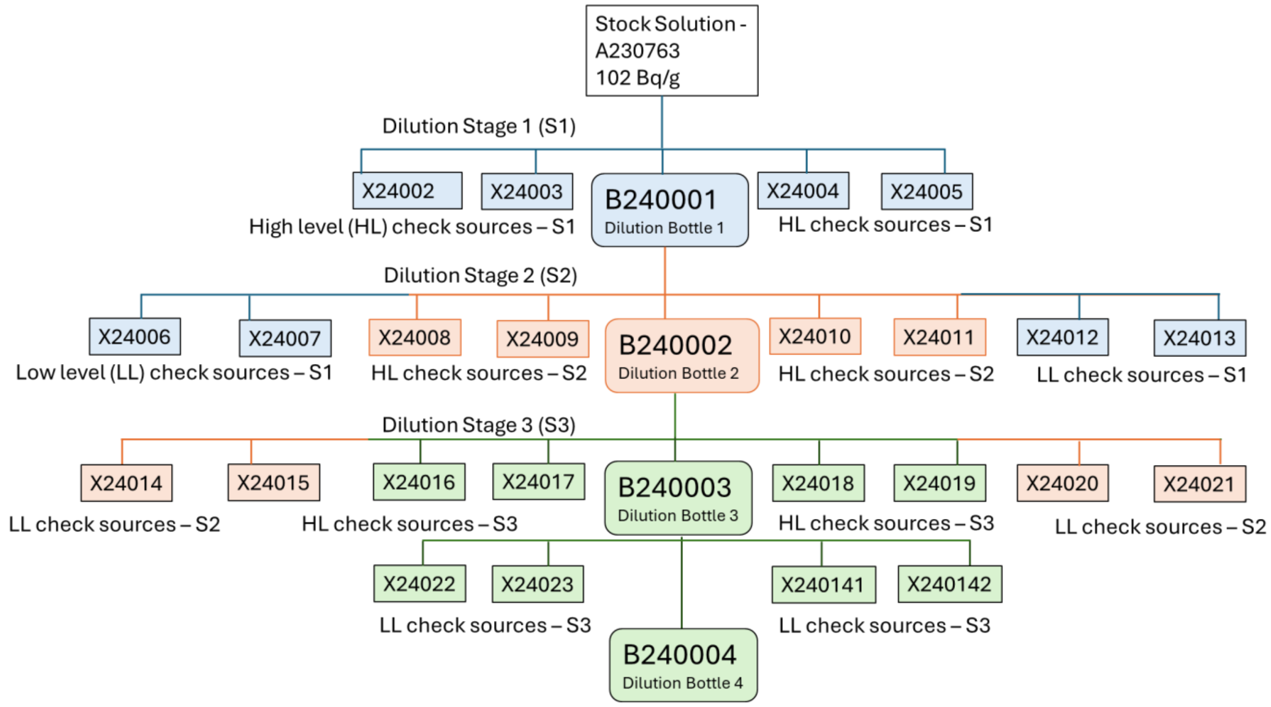


Figure 24. Sources made during the first dilution using ^{234}U starting solution.

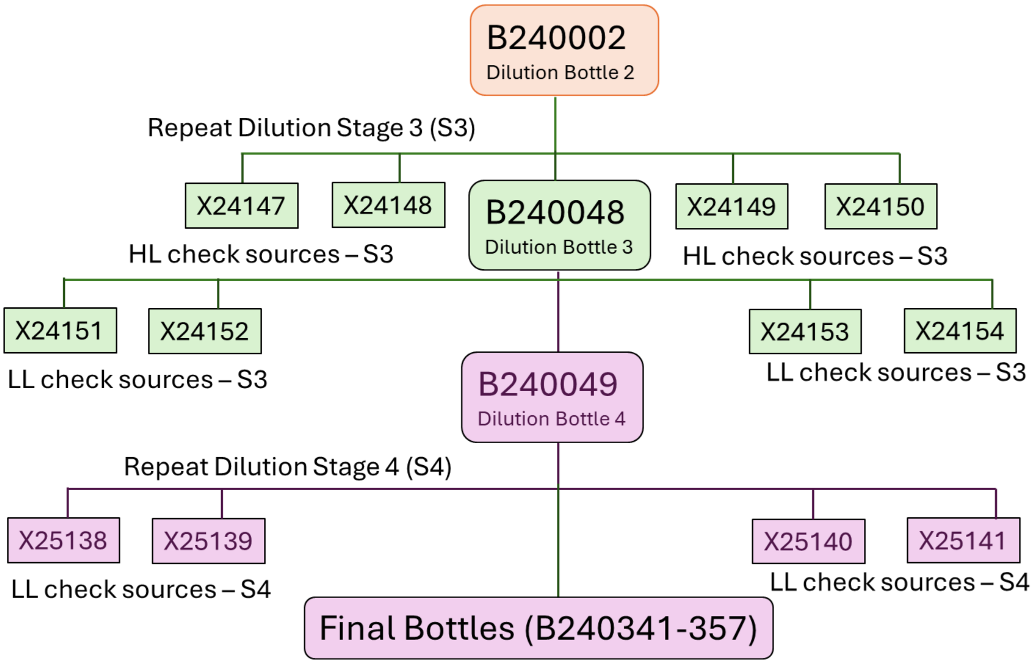


Figure 25. Sources made during the repeat dilution (Dilution Stage 3) of ^{234}U.

5.3 Uranium-236

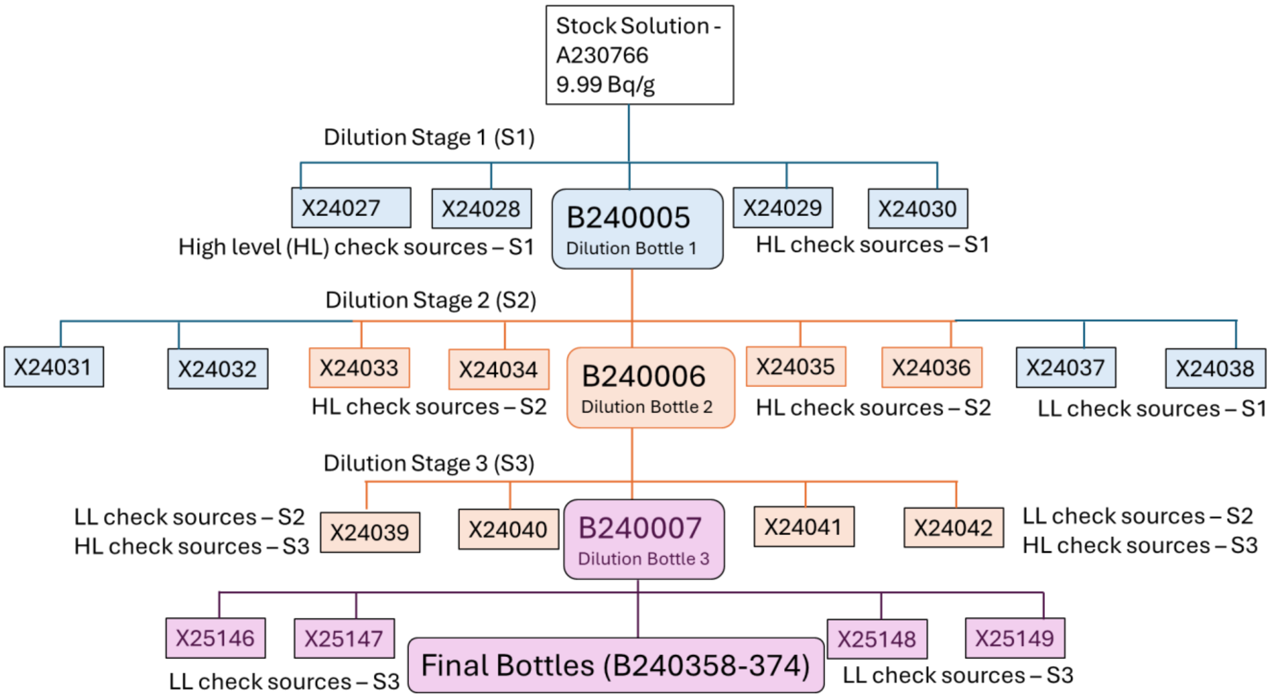


Figure 26. Sources made from the dilution of ^{236}U.

5.4 Neptunium-237

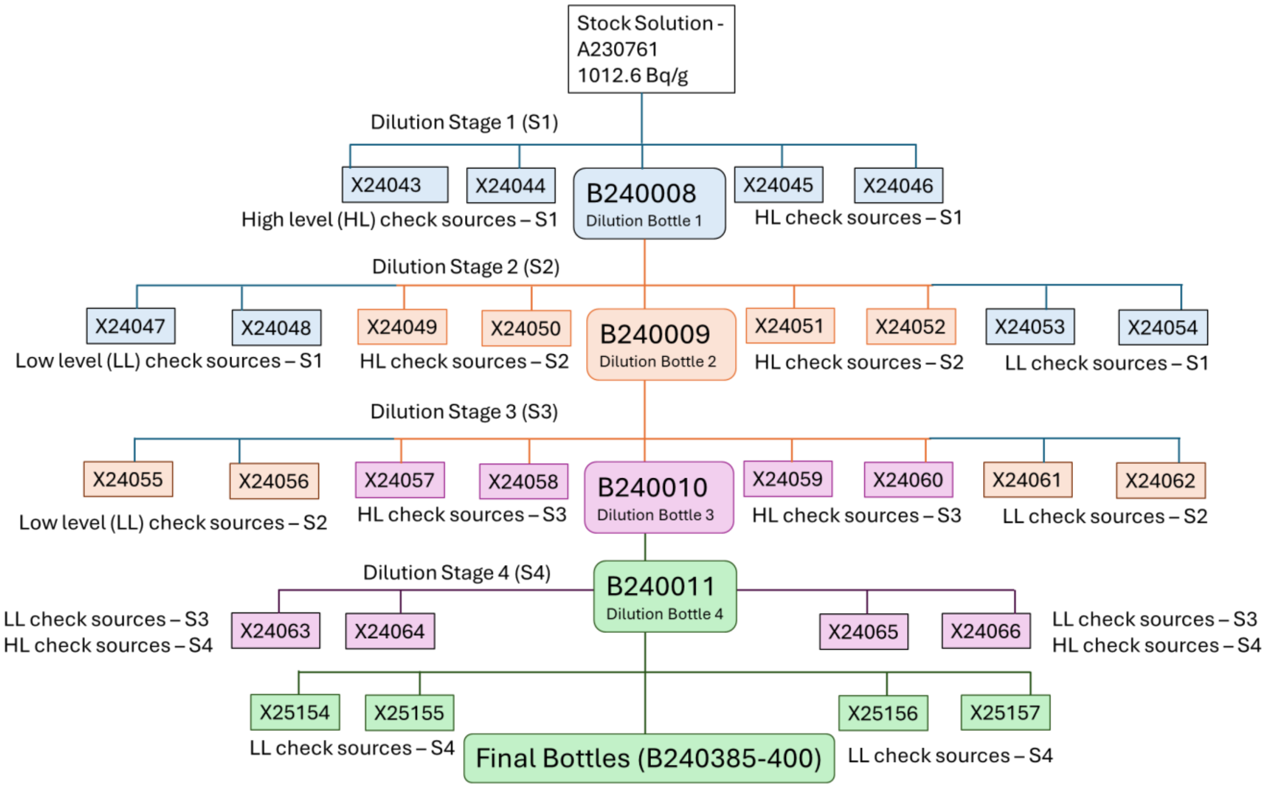


Figure 27. Sources made during the dilution of ^{237}Np.

5.5 Plutonium-239

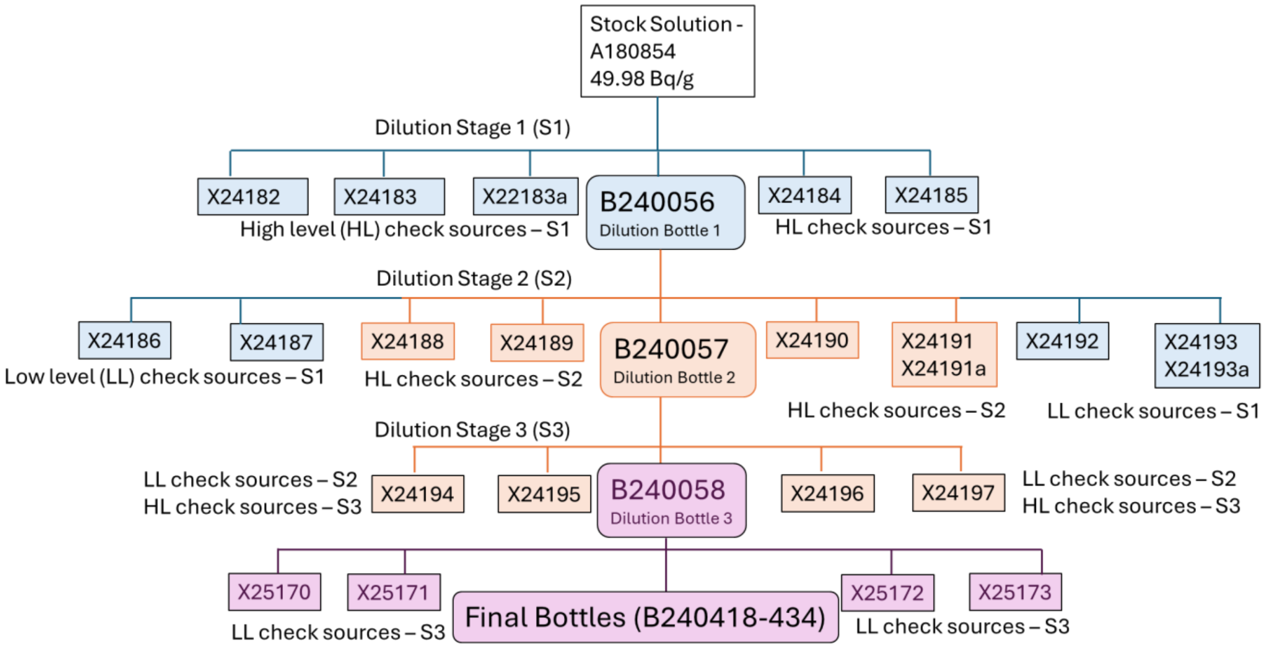


Figure 28. Sources made during the dilution of ^{239}Pu.

5.6 Plutonium-240

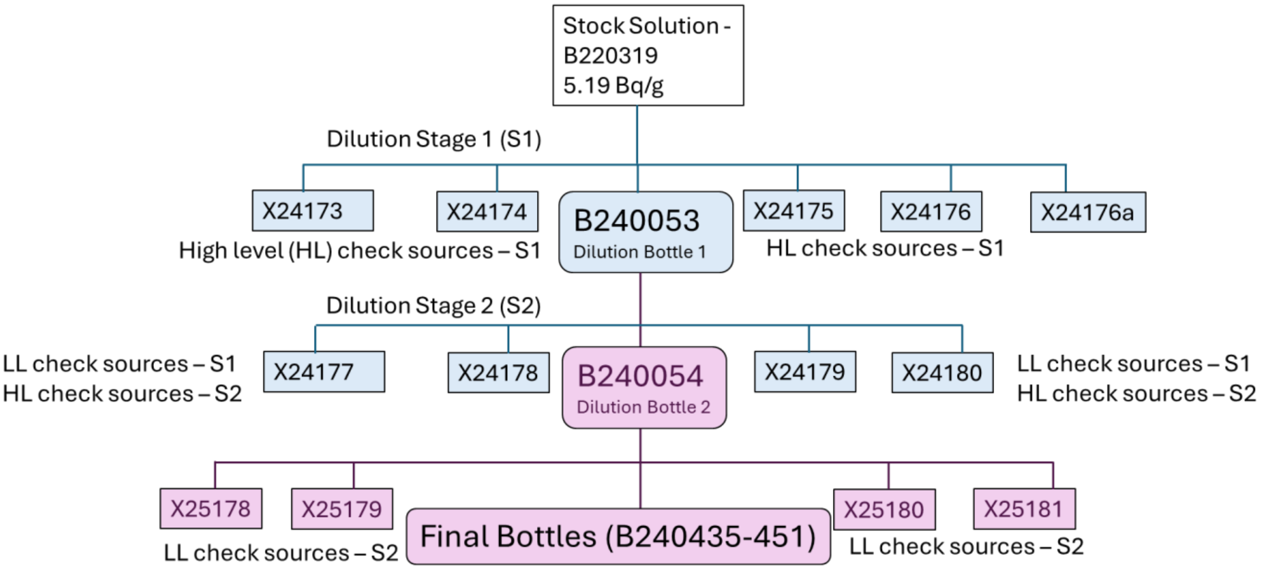


Figure 29. Sources made during the dilution of ^{240}Pu.

5.7 Americium-241

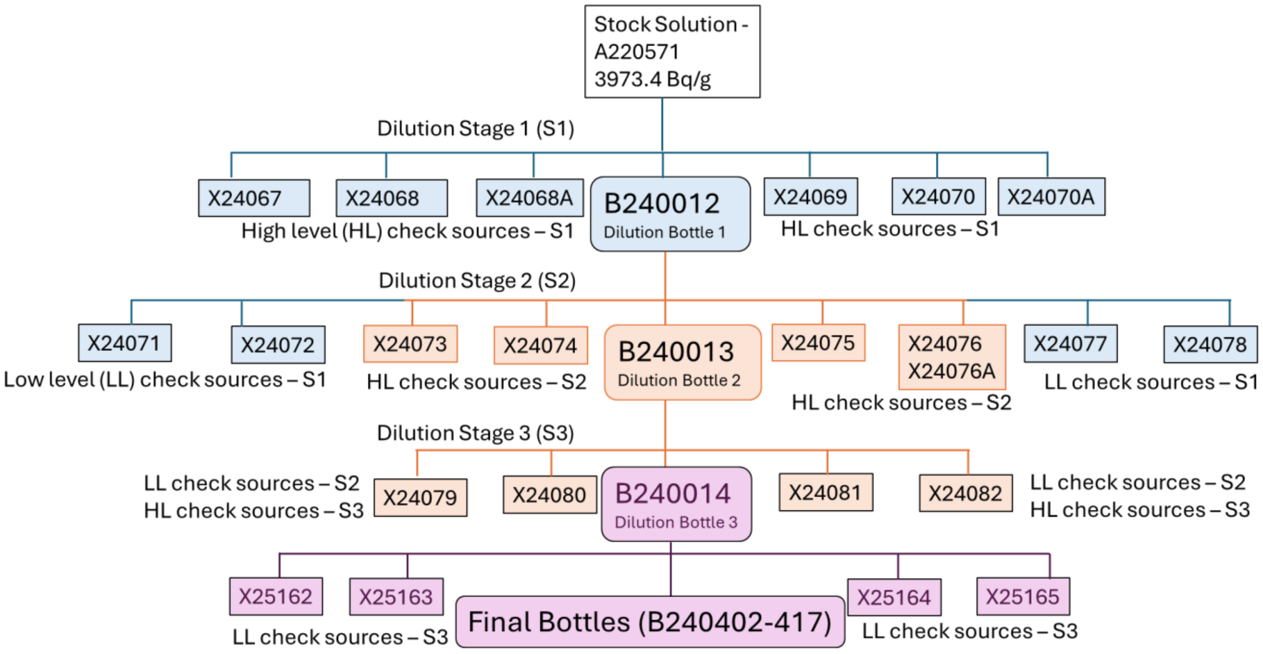


Figure 30. Sources made during the dilution of ^{241}Am.

5.8 Uranium isotopic mix

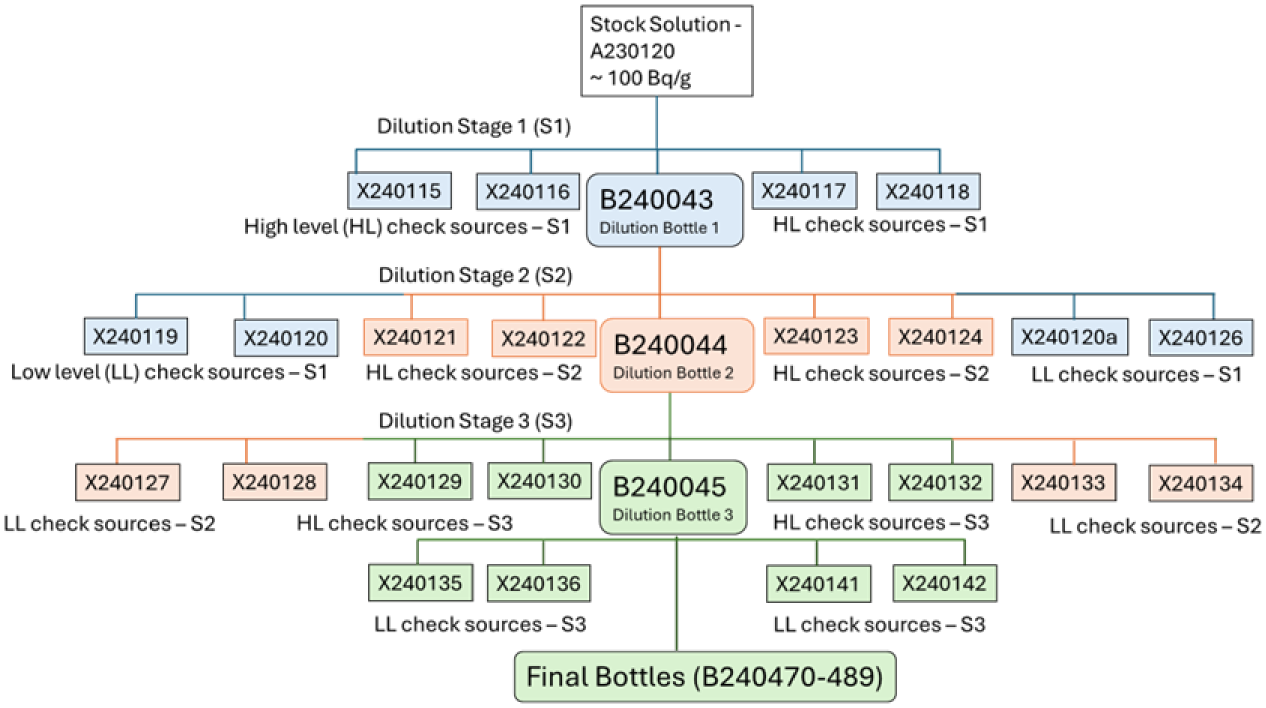


Figure 31. Sources made during the dilution of ^{Nat}U.

5.9 Plutonium isotopic mix

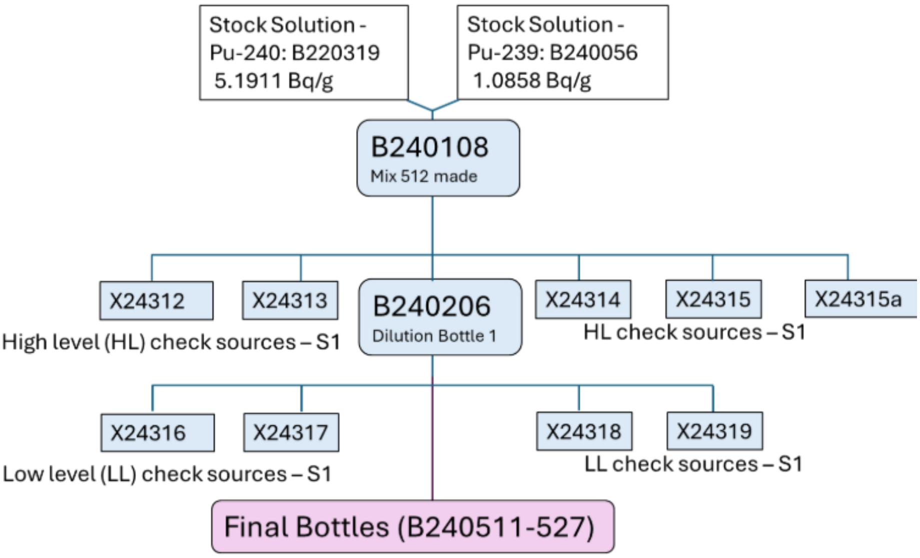


Figure 32. Sources made during the dilution of ^{237}Np.

Appendix 2. Participants in the comparison exercise

Table 18. Participants in comparison exercise for measurement of radioactivity standards.

Participant	**Measurement capability**
STUK	LSC
NMBU	ICP-MS/MS
HZDR and UNIVIE	AMS
ETHZ	AMS
LGC	ICP-TOF-MS
SPIEZ	ICP-SFMS
PTB	MC-ICP-MS
AU & UGOT	MC-ICP-MS
JSI	Alpha spectrometry, MC-ICP-MS
VINS	Other
IFIN-HH	AMS
UH	Alpha spectrometry, gamma spectrometry
DTU	ICP-MS/MS