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# RESINA – Intercomparison exercise on alpha radionuclide analysis in spent ion exchange resin

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## **Abstract**

An intercomparison exercise was carried out for difficult to measure (DTM) alpha radionuclides in spent ion exchange resin samples. The same spent resin was studied as in the previous intercomparison exercise on gamma and DTM beta radionuclides (DTM Decom III). The results were analysed according to the ISO 13528 standard. The performance assessment was carried out using z score. The report includes an overview of the radioanalytical procedures, preliminary and final results, and performance assessments.

## **Key words**

Decommissioning, Difficult-to-measure alpha radionuclides, intercomparison exercise, spent ion exchange resin

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## **Final Report from the RESINA activity**

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## Table of Contents

1. Introduction to RESINA	3
2. Survey of capabilities in the beginning of the project	3
3. Sample information	4
4. Uncertainty calculations	5
5. Limit of detection calculations	9
6. Radiochemical analysis	11
6.1. Radiochemical procedures for U-, Pu-, Cm-isotopes and Am-241	12
6.2. Radiochemical procedures for gross alpha measurements	18
7. Gamma spectrometry	20
8. Preliminary results	21
9. Methodology for statistical analysis of the reported results	33
9.1 Statistical analysis according to ISO 13528	33
9.2 Extended statistical analysis	34
10. Final results	34
10.1. DTM results with less than 4 data entries	35
10.2. DTM results with ISO 13528 statistical analysis	40
10.3. Extended statistical analysis results	44
11. Summary	45
12. Acknowledgements	46
13. References	46

## 1. Introduction to RESINA

The RESINA project consisted of an intercomparison exercise on radiochemical analysis of alpha emitters in a spent ion exchange resin. The project was a continuation to the DTM Decom III project in which beta and gamma emitters were studied in the same spent ion exchange resin [Leskinen et al. 2022a]. As with any difficult to measure (DTM) radionuclide, the radiochemical analysis of alpha emitters requires efficient purification of the radionuclide of interest from other interfering radionuclides as alpha spectral analysis may be complicated due to interfering radionuclides. For example, Pu-238 and Am-241 have similar alpha energies and several natural radionuclides have interfering alpha energies with those of Pu-238, Pu-239 and Pu-240. Additionally, isobaric interferences (e.g. U-238 in Pu-238 determination, Pu-241 in Am-241 determination, etc.) are a common problem in mass spectrometric measurements of actinides. Preparation of the measurement targets for the alpha spectrometry measurements needs to be carried out carefully to produce a virtually weightless measurement target in which the radionuclides have been deposited on an as thin as possible layer to prevent self-absorption of alpha particles. The presence of stable elements in high amounts may also cause significant self-absorption. The thickness of the source is linked with broadening of the alpha spectrum peaks with a consequent loss of resolution. Therefore, an efficient purification and sample preparation method is needed for determination of alpha emitters by both alpha spectrometry and inductively coupled plasma mass spectrometry (ICP-MS).

The DTM Decom III results had concluded that the spent ion exchange resin contained both corrosion and spent fuel related radionuclides [Leskinen et al. 2022a]. Therefore, analysis of alpha emitters originating from the fuel was expected to be feasible. The selected radionuclides were Am-241 and uranium-, plutonium-, and curium-isotopes. Plutonium-241 was selected as optional even though it is a beta emitter and can be measured using liquid scintillation counting (LSC). Additionally, gross alpha and Np-237 analyses were selected as optional analyses.

The RESINA intercomparison exercise was carried out according to ISO 13528 standard [International Standard 2015]. The results were assessed using z score and additionally Am-241 results according to Harms's approach [Harms 2009]. The RESINA project followed the established schedule of the previous intercomparison exercises [Leskinen et al. 2020a, 2020b, 2021a, 2021b, 2022a, 2022b]. The radionuclides of interest were selected by the partners in the kick-off meeting. The radiochemical analysis time began promptly after the kick-off meeting as majority of the partners already had the samples from attendance in DTM Decom III. The radiochemical analysis time was open until October when a preliminary meeting was held to discuss the analysis results and difficulties encountered. After the preliminary meeting, partners had the possibility to re-evaluate their results and carry out further experiments until November when the final meeting was held. Both the preliminary and final results are presented in this report.

## 2. Survey of capabilities in the beginning of the project

In the beginning of the project, a survey of the alpha DTM analysis capabilities of the participating laboratories was carried out. The results are shown in Table 1. The affiliation

codes and the sample numbers in the following sections do not correspond to the samples in order to enable anonymous reporting. The capabilities of the participating laboratories show that some laboratories were well advanced with several methods ready for DTM analyses whereas some laboratories were in the method development phase.

**Table 1 Capabilities of the participating laboratories on analysis of alpha DTMs in spent ion exchange resin in the beginning of the project**

<b>Affiliation code</b>	<b>Capabilities in alpha DTM analyses</b>
<b>A</b>	Pu-239,240, Pu-238, Am-241, Cm-243,244, Cm-242, U-234, U-235,236, U-238. Gross alpha by LSC.
<b>B</b>	Methods of routine analysis for Pu-238, Pu-239,240, Pu-241, Am-241, Cm-242, Cm-244 in spent resin are ready to be used.
<b>C</b>	In development of methods for analysis of Ni-59, Ni-63, uranium, neptunium, plutonium, curium and other alpha emitters and gross alpha.
<b>D</b>	Long experience of actinide measurement and currently building capacity for nuclides of significance for nuclear decommissioning challenges, specifically Ca-41, Ni-59, Ni-63, Se-79, Zr-93, Tc-99, Pd-107, Sn-126, Cs-135, &co.
<b>E</b>	Experience on several radiochemical methods and sample matrices in determination of alpha emitting radionuclides of Pu, Am, Cm, Np, U and Th.
<b>F</b>	Routine analysis for U-235, U-238, Pu-238, Pu-239, Pu-240, Am-241 and Cm-244 in radioactive samples at low and intermediate level activity (liquids, effluents, concretes and resins). Analysis of Np-237 under development. Measurement of gross alpha activity is also available
<b>G</b>	Methods for determination of Anthropogenic alpha emitters U-234, U-235, U-236, U-238, Pu-238, Pu-239, Pu-240, Np-237, Am-241, Cm-242, Cm-234,244) in resin are ready to be used. The method for nature alpha emitters including Po-210 and Ra-226 are available.
<b>H</b>	Methods for determination of alpha emitters U-234, U-235, U-238, Pu-238, Pu-239, Pu-240, Am-241, Cm-234,244 by alpha spectrometry are ready to be used.
<b>I</b>	Methods for determination of alpha emitters U-234, U-235, U-238, Th-232, Th-230, Th-228, Pu-238, Pu-239, Pu-240, Am-241, Cm-242, Cm-234,244 by alpha spectrometry are ready to be used. Gross alpha also available with LSC.

### 3. Sample information

Approximately 0.8 g of spent ion exchange resin (FINEX C/A 850 H mixed exchanger in powder form, nuclear grade) was sent to the participating laboratories during DTM-Decom III in 2021 (Figure 1). Additional shipments were made in spring for self-funded laboratories. The sample set had been measured to be homogenous in the DTM Decom III project in which each sample was measured twice by placing them 20 cm distance from top of an HPGe detector of an ISOCS counting system for 15 minutes [Leskinen et al. 2022a]. Constant measurement geometry was ensured by placing the sample carefully in the centre of an adapter and the efficiency calibrations were carried out using Geometry composer [Leskinen et al. 2022a]. Initially, the homogeneity was determined by calculating the relative standard deviation of the Co-60 and Cs-137 results, which were 0.9% and 1.1%, respectively, and therefore the samples were initially considered to be homogenous [Leskinen et al. 2022a]. The homogeneities were also assessed using Equation 1 according to the ISO13528 standard after the submission of

participants' results [International Standard 2015]. Between-sample standard deviation,  $s_s$  was calculated from sample averages, between test portion ranges, general average, standard deviation of sample averages, within sample deviation and between sample standard deviation [International Standard 2015]. The results showed that the samples were homogenous also according to the ISO standard [Leskinen et al. 2022a].

$$s_s \leq 0,3 \cdot \sigma_{pt} \quad (1)$$

Where

$s_s$ : between-sample standard deviation

$\sigma_{pt}$ : robust standard deviation of participant results

The stability of the sample had been established in the DTM Decom III project [Leskinen et al. 2022a].



**Figure 1. Example of a studied spent ion exchange resin sample (0.8 g) in a liquid scintillation vial**

## 4. Uncertainty calculations

A variety of equations for uncertainty calculations were used by the participating laboratories. The overarching theme was combination of uncertainties:

- The uncertainties were calculated as combined uncertainty, considering uncertainty sources in radiochemical separation procedure (e.g., uncertainty in tracer activity, pipetting, weighing) and in alpha measurements (statistical error of radioactive decay, uncertainty in activity of a calibration standard).
- For Pu-241, uncertainties with a coverage factor  $k=2$  were obtained with combining the uncertainties due to the digestion step, the weights, the tracer measurement by alpha spectrometry, the counting efficiency and the LSC countings.
- An overall uncertainty was estimated, which including the measurement statistics (alpha spectrometry, ICP-MS) for the samples, blank and standard, the uncertainty of standard/yield tracer (U-233, Pu-242, Am-243), stability/replicability of the ICP-MS measurement, weight of sample and standards, as well as the subtraction of blanks, the major contribution is from the measurement, the standard (1.5-2.5%) also contribute some extent of the uncertainty.

Combination of uncertainties expressed in equation or set of equations:

## Equation 2.

$$\left(\frac{\partial u}{\partial u}\right)^2 = \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 \quad (2)$$

## Equations 3 and 4.

$$u(x_i) = \frac{\sigma_i}{\sqrt{n}} \quad (3)$$

in which

$\sigma_i$ : standard deviation of each components

$$u(Ut) = \sqrt{[u(C)]^2 + [u(eff)]^2 + [u(V)]^2 + [u(y)]^2} \quad (4)$$

$u(C)$ : Uncertainty of the counting rates of nuclides

$u(eff)$ : Uncertainty of counting efficiency

Combined with uncertainty of the standard source, LSC/alpha spectrometry counting efficiency, and nuclide half-life

$u(V)$ : uncertainty in weighing of sample mass

Uncertainty of the electronic scale

$u(y)$ : Uncertainty of chemical recovery

$u(Ut)$ : Combined uncertainty

## Equations 5-7.

$$\Delta Ac = \frac{\text{counts}_{\text{sample}} \cdot A_{\text{tracer}}}{\text{counts}_{\text{tracer}} \cdot m_{\text{sample}}} \sqrt{\left(\frac{\Delta \text{counts}_{\text{sample}}}{\text{counts}_{\text{sample}}}\right)^2 + \left(\frac{\Delta \text{counts}_{\text{tracer}}}{\text{counts}_{\text{tracer}}}\right)^2 + \left(\frac{\Delta A_{\text{tracer}}}{A_{\text{tracer}}}\right)^2 + \left(\frac{\Delta m_{\text{sample}}}{m_{\text{sample}}}\right)^2} \quad (5)$$

$$\Delta \text{Yield}\% = \frac{\frac{\text{counts}_{\text{tracer}}}{t_{\text{live}}}}{A_{\text{tracer}}} \cdot 100\% \sqrt{\left(\frac{\Delta \text{counts}_{\text{tracer}}}{\text{counts}_{\text{tracer}}}\right)^2 + \left(\frac{\Delta t_{\text{live}}}{t_{\text{live}}}\right)^2 + \left(\frac{\Delta \varepsilon}{\varepsilon}\right)^2 + \left(\frac{\Delta A_{\text{tracer}}}{A_{\text{tracer}}}\right)^2} \quad (6)$$

Where

$$\Delta A_{\text{tracer}} = \frac{A_{\text{tracer}}}{m_2} \cdot m_3 \sqrt{\frac{\Delta \text{counts}_x = \sqrt{\text{counts}_x}}{\left(\frac{\Delta A_{\text{tracer}}}{A_{\text{tracer}}}\right)^2 + \left(\frac{\Delta m_1}{m_1}\right)^2 + \left(\frac{\Delta m_2}{m_2}\right)^2 + \left(\frac{\Delta m_3}{m_3}\right)^2}} \quad (7)$$

$m_1$  and  $m_2$ : the masses of the first and second dilutions of the tracer

$m_3$ : the mass on added tracer solution to the analysed sample

$\Delta m_{\text{sample}}$  and  $\Delta m_3$ : 0.0002 g, which is given in the manual of used scale

$\Delta A_{\text{tracer}}$ : total uncertainty of tracer activity at the 99 % confidence level

$m_1$  and  $m_2$ : 0.1 g, given for larger range scale used for the tracer dilutions

$t_{\text{live}}$ : live counting time

$\varepsilon$ : efficiency

### Equation 8.

- Uncertainty on number of counts,  $n$ :  $\sqrt{n + 1}$
- Uncertainty on tracer activity was derived from calibration certificates
- Uncertainty recorded mass due to balance resolution:  $\pm \frac{0,0001}{\sqrt{3}} g$
- Uncertainty recorded mass repeatability:  $\pm 0,0012 g$
- Summed uncertainty from repeatability and resolution:  $\pm 0,0021 g$
- Uncertainty from difference loss/gain:  $\pm \frac{\Delta mass}{\sqrt{12}} g$
- Total mass uncertainty:  $\sqrt{0,0021^2 + \left[\frac{\Delta mass}{\sqrt{12}}\right]^2}$
- Model equation for activity concentration: 
$$C_A = r_{net} \cdot \frac{r_t}{c_t \cdot m_t} \cdot \frac{1}{m_r} \quad (8)$$

Where:

$C_A$ :	activity concentration of nuclide of interest	units: Bq g <sup>-1</sup>
$r_{net}$ :	net count rate of nuclide of interest	units: s <sup>-1</sup>
$r_t$ :	net count rate of tracer nuclide	units: s <sup>-1</sup>
$c_t$ :	activity concentration of tracer nuclide	units: Bq g <sup>-1</sup>
$m_t$ :	mass of tracer nuclide added	units: g
$m_r$ :	mass of resin analysed	units: g

### Equations 9-12 for alpha spectrometry.

The standard counting uncertainty ( $u_{count}$ ) associated with each alpha spectrometry measurement (at equivalent count times):

$$u_{count} = \sqrt{\frac{N_{analyte} + 2 \cdot B_{analyte}}{N_{analyte}^2} + \frac{N_{tracer} + 2 \cdot B_{tracer}}{N_{tracer}^2}} \quad (9)$$

Where the background count rate is < 5 % of the analyte and tracer count rate this equation simplifies to:

$$u_{count} = \sqrt{\frac{1}{G_{analyte}} + \frac{1}{G_{tracer}}} \quad (10)$$

The propagated standard uncertainty ( $u_{prop}$ ) using the following data obtained from prior uncertainty budget analysis

$$u_{prop} = \sqrt{u_{count}^2 + u_{others}^2} \quad (11)$$

From the propagated standard uncertainty, the expanded uncertainty,  $U_{exp}$  with a coverage factor  $k = 2$  is

$$U_{exp} = 2 \cdot u_{prop} \cdot activity \text{ (Bq/L or Bq/g)} \quad (12)$$

### Equations 13-20 for Pu-241.

Channel A liquid scintillation counting uncertainty is given by:

$$\sigma_A = \sqrt{\frac{G_{cpm_A}}{t_G} + \frac{2 \cdot Bgd_{cpm_A}}{t_{Bgd}} + \frac{Std_{241cpm}}{t_{241}} \left( + \frac{Fe-55cpm\ correctio}{t_G} \right)} \quad (13)$$

- $G_{cpm_A}$ : Gross sample c/m in Channel A  
 $t_G$ : Sample count time (mins)  
 $Bgd_{cpm_A}$ : Background c/m in Channel A  
 $t_{Bgd}$ : Background count time (mins)  
 $Std_{241cpm}$ : Pu-241 standard source c/m in Channel A  
 $t_{241}$ : Pu-241 standard source count time (mins)

Channel B liquid scintillation counting uncertainty is given by:

$$\sigma_B = \sqrt{\frac{G_{cpm_B}}{t_G} + \frac{2 \cdot Bgd_{cpm_B}}{t_{Bgd}}} \quad (14)$$

- $G_{cpm_B}$ : Gross sample c/m in Channel B  
 $Bgd_{cpm_B}$ : Background c/m in Channel B

Counting uncertainties from the alpha determination

$$\sigma_\alpha = \sqrt{\frac{G_{238+239/240+242}}{t_{G\alpha}^2} + \frac{Bgd_{238+239/240+242}}{t_{Bgd\alpha}^2}} \quad (15)$$

- $G_{238+239/240+242}$ : Sum of the sample gross counts for Pu-238, 239/240 and Pu-242 from alpha spectrometry counting  
 $t_{G\alpha}$ : Sample count time for alpha spectrometry counting (seconds)  
 $Bgd_{238+239/240+242}$ : Sum of the background counts for Pu-238, 239/240 and Pu-242 from alpha spectrometry counting  
 $t_{Bgd\alpha}$ : Background count time for alpha spectrometry counting (seconds)

The Pu-241 fractional combined counting uncertainty ( $u_{241\ comb}$ ) can now be calculated as follows:

$$u_{241\ comb} = \sqrt{u_{241A}^2 + u_{241B}^2 + u_\alpha^2} \quad (16)$$

Where

$$u_{241A} = \frac{\sigma_A}{Net\ cpm_A} \quad (17)$$

$$u_{241B} = \frac{\sigma_B}{Net\ cpm_B} \quad (18)$$

$$u_\alpha = \frac{\sigma_\alpha}{Net\ cps_{238+239/240+242}} \quad (19)$$

Where

- $Net\ cpm_A$ : net sample liquid scintillation counting cpm in channel A,  
 $Net\ cpm_B$ : net sample liquid scintillation counting cpm in channel B, and  
 $Net\ cps_{238+239/240+242}$ : summation of the Pu-238, Pu-239,240 and Pu-242 net count rates (c/s) from alpha spectrometry counting.

The Pu-241 the expanded uncertainty,  $U_{exp}$  with a coverage factor  $k = 2$  is:

$$U_{exp} = 2 \cdot A_{241} \cdot \sqrt{u_{241\ comb} + 0,027^2} \quad (20)$$

Where  $A_{241}$  is above and 0,027 comes from prior uncertainty budget analysis.

## 5. Limit of detection calculations

Several equations and written explanations were submitted for the calculation of the limit of detection.

- LODs were estimated using the formula ( $LOD = \frac{4.65 \cdot S_b}{\frac{h}{m} \cdot \sqrt{n}}$ ),  $S_b$  is the standard deviation of the measurements of the procedure blanks,  $n$  is the number of blank samples and  $\eta$  is overall efficiency including chemical yield and measurement/counting efficiency;  $m$  is the mass of samples used for analysis. The blank samples were analyzed using the entire analytical procedure and the results were used for the estimation of LOD.
- Less than values are quoted when a result falls below the level that can be determined as an exact activity (minimum detectable activity or MDA). The MDA is a function of the background (or blank) counts and is based on a multiple (4.65) of the standard deviation of the counts (i.e.  $4.65 \cdot \sigma_b$ ). The MDA formulae are based on the Currie paper [Currie 1968] and are documented in an American National Standard [American National Standard 1996].

### Equation 21.

$$LLD \left[ \frac{Bq}{g} \right] = \frac{4.66 \cdot S_b}{60 \cdot \varepsilon \cdot m \cdot y} \quad (21)$$

Where,

4.66:	critical value of confidence ( $2\sigma$ )
$S_b$ :	STDEV of background [counts/min]
60:	DPM/Bq
$\varepsilon$ :	detector efficiency
$m$ :	mass of the sample
$y$ :	fractional yield

### Equation 22.

$$\frac{4,65 \cdot S_b + 2,71}{60 \cdot E \cdot W \cdot Y \cdot T} \quad (22)$$

Where

- $E$ : counting efficiency  
 $W$ : weight  
 $S_b$ : standard deviation of the blank counts  
 $Y$ : yield  
 $T$ : counting time

### Equation 23.

Calculated in accordance with ISO 11929.

Decision threshold:  $y^* = \left(\frac{k \cdot c_A}{r_{net}}\right) \cdot \sqrt{2 \cdot (n_0 + 1)}$

Detection limit:  $y = \left(\frac{k \cdot c_A}{r_{net}}\right) \cdot \left[ \frac{k + \sqrt{8 \cdot (n_0 + 1)}}{1 - k^2 \cdot \left\{ \left[\frac{u(r_t)}{r_t}\right]^2 + \left[\frac{u(c_t)}{c_t}\right]^2 + \left[\frac{u(m_t)}{m_t}\right]^2 + \left[\frac{u(m_r)}{m_r}\right]^2 \right\}} \right]$  (23)

Where:

- $n_0$ : background counts observed for nuclide of interest (in this case, 0)  
 $k$ : coverage factor (in this case, 2)

### Equation 24

Currie formula  $LOD = \frac{2.71 + 4.65 \sqrt{\frac{counts_{bg} \cdot t_{sample}}{t_{bg}}}}{eff \times \eta \times t_{sample}}$  (24)

Where:

- $counts_{bg}$ : total count for the background measurement  
 $t_{sample}$ : counting time of the sample  
 $t_{bg}$ : counting time of the background  
 $eff$ : efficiency of the Quantulus for this sample  
 $\eta$ : chemical yield

### Equations 24-26 [Currie 1968, America National Standard 1996]

The MDA is defined as a function of the background count rate

$MDA = K \cdot D \cdot \frac{3,29 \cdot \sqrt{N_0 \cdot \frac{t_s}{t_b} \left(1 + \frac{t_s}{t_b}\right)} + 3}{t_s \cdot E \cdot R \cdot V_S}$  (24)

Where:

- $t_b$ : bgd count time (s)  
 $E$ : Counting efficiency  
 $t_s$ : sample count time (s)  
 $R$ : Chemical yield  
 $V_S$ : Volume of the sample in  $cm^3$   
 $D$ : Decay Factor  
 $N_0$ : counts observed in bgd count time  $t_b$

$K$ : Volume Correction Factor ( $\text{cm}^3/\text{g}$ )

If  $t_b = t_s = t$ , then

$$MDA = K \cdot D \cdot \frac{3,29 \cdot \sqrt{2 \cdot N_0 + 3}}{t_s \cdot E \cdot R \cdot V_S} = \frac{4,65 \cdot \sqrt{N_0 + 3}}{t_s \cdot E \cdot R \cdot V_S} \quad (25)$$

Where  $N_0 > 100$ , the MDA formulation simplifies to the following:

$$MDA = K \cdot D \cdot \frac{4,65 \cdot \sqrt{N_0}}{t_s \cdot E \cdot R \cdot V_S} \quad (26)$$

## 6. Radiochemical analysis

Participants carried out the radiochemical analyses according to either internal or published procedures [Atomic and Nuclear Data online application, Calin et al. 2013, Chen et al. 1991, Eichrom technologies 2014, Hou et al. 2020, Ikäheimonen 2000, Kressin 1977, Lopez-Lora et al. 2019, Mercedes (2018), Salminen-Paatero et al. 2021, Sidhu 2002, Sidhu 2004, Sidhu et al. 2004, Talvitie 1972, UKNNL internal procedures, Wang et al. 2021]. The procedures are compiled in Table 2 to

Table 6. Section 6.1 presents the radiochemical procedures for Uranium-, Plutonium-, Curium-isotopes and Am-241 whereas section 6.2 presents the gross alpha measurement procedures.

### **6.1. Radiochemical procedures for U-, Pu-, Cm-isotopes and Am-241**

Table 2 summarises the information on added carriers and tracers. The results show that carriers/hold-back carriers were utilised only in analysis of Sample 8. Two uranium-isotopes, U-233 and U-232, were utilised as uranium tracers with activities ranging from 10 to 700 mBq. Three isotopes of plutonium, Pu-239, Pu-242 and Pu-241, were utilised as plutonium tracers with activities ranging from 10 mBq to 5 Bq. Two isotopes of americium Am-241 and Am-243, were utilised as americium tracers with activities ranging from 10 mBq to 5 Bq. Curium tracers were not utilised but curium yields were assumed to be the same as those for americium.

Table 3 summarises the sample sizes, pre-treatments and acid digestion methods with the outcomes i.e. complete or partial dissolution of the matrix. The acid digested sample sizes ranged from 10 to 250 mg. Pre-treatment was carried out only for the analysis of Sample 4. As concluded in DTM Decom III project, the resin was effectively dry as the masses did not fluctuate during storage [Leskinen et al. 2022a]. Different acid mixtures (i.e., *Aqua Regia*, HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>, HCl:HNO<sub>3</sub>, HNO<sub>3</sub>, HCl:HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>:HClO<sub>4</sub>, Fenton's reagent and HNO<sub>3</sub>) and digestion vessels (i.e., using a hot plate, using a microwave and under reflux) were utilised resulting in total dissolution of the matrix in almost all cases. Filtrations to remove a residue were carried out for Samples 2, 6 and 10.

Table 4 summarises the purification procedures. Coprecipitation prior to anion exchange or extraction chromatography separations were carried out for Samples 2, 7 and 8. Anion exchange and extraction chromatography separations were carried out using different chromatographic resins (i.e., TEVA, TRU, UTEVA, and DGA) and anion exchange resins (Bio-Rad AG1).

Table 5 summarises the preparation of measurement targets and measurement methods of Samples 2 to 10. Alpha spectrometric measurement targets were prepared using precipitation and filtration (Samples 2 and 5) and electrodeposition (Samples 3, 4, 8, 9 and 10). Plutonium-241 was analysed in Sample 7 using LSC whereas the yield was determined via alpha spectrometric measurement of Pu-239. Pu-241 samples for LSC measurements were also prepared for Samples 2-4 and 10 via dissolving of the precipitate (Sample 2), measurement of an aliquot (initial results of Sample 3), measurement of an aliquot (Sample 4) and acid stripping (Sample 10 and final results of Sample 3). ICP-MS for measurement of uranium isotopes were utilised for Samples 3 and 8. Gamma spectrometric measurement of Am-241 and U-235 were carried out for Samples 3 and 10.

**Table 2 Added carriers and tracers.**

<b>Sample</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>Carriers/hold-back carriers</b>	4 mg Fe	-	-	-	-	-	4 mg Fe, 2 mg Co, 2 mg Ni, 1 mg Eu, 2mg Cs, 1 mg Sb, 1 mg Sr	-	-
<b>U-233</b>	-	-	-	-	-	-	11 mBq	0,7 Bq	-
<b>U-232</b>	-	400-500 mBq	-	50 mBq	10 mBq	-	-	-	0,11 Bq
<b>Pu-239</b>	-	-	-	-	-	36 Bq	-	-	-
<b>Pu-242</b>	30 mBq	400-500 mBq	5 Bq	50 mBq	10 mBq	-	100 mBq	0,06 Bq	0,13 Bq
<b>Pu-241</b>	-	-	5 Bq	-	-	-	-	-	-
<b>Am-241</b>	-	-	5 Bq	-	-	-	-	-	-
<b>Am-243</b>	30 mBq	400-500 mBq	-	50 mBq	10 mBq	-	100 mBq	0,2 Bq	0,11 Bq

**Table 3 Acid digestion methods for decomposition of the spent ion exchange resin**

Sample	2	3	4	5	6	7	8	9	10
<b>Sample size (g)</b>	0.1-0.2	0.050	0.030-0.010	0.010-0.020	0.100	0.1	0.1-0.3	0.1-0.2	0.25
<b>Pre-treatment</b>	None	None	Dried at 150 °C. Ashed at 500 °C	None	None	None	None	None	None
<b>Acid digestion</b>	Aqua Regia on a hot plate + 2 ml of H <sub>2</sub> O <sub>2</sub> towards the end (4 h in total)	HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> , microwave	HCl + HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> on a hot plate	20 ml HNO <sub>3</sub> , microwave	12 ml H <sub>2</sub> SO <sub>4</sub> + 4 ml HNO <sub>3</sub> + 1 ml HClO <sub>4</sub> on a sand bath	10 ml HNO <sub>3</sub> + 5 ml HCl microwave	conc HNO <sub>3</sub> , HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> and HCl under heating and reflux	10 ml HNO <sub>3</sub> , microwave at 260°C for ~2 hours	Fenton's reagent → inefficient, filtration → HNO <sub>3</sub> .  Dilution to 250 ml.
<b>Total dissolution</b>	No	Yes	Yes	Yes	Total dissolution for 1 of triplicate.	Yes	Yes	Yes	No
<b>Filteration</b>	Glass fibre filters	No	No	No	2/3 filtered through Glass fibre filter	No	No	No	Yes

**Table 4 Purification procedures of Samples 2-10**

Sample	2	3	4	5	6	7	8	9	10
<b>Precipitation</b>	Actinide coprecipitation with iron hydroxide twice.	-	-	-	-	Lanthanum coprecipitation in ammonia	Coprecipitation of actinides with Fe(OH) <sub>3</sub>	Fe(OH) <sub>3</sub> / NH <sub>4</sub> OH	-
<b>Resin treatment</b>	TEVA to separate Am/U/Cm and Pu DGA to purify Am/Cm	UTEVA + TRU	TRU to separate Am/Cm and Pu	TRU+ UTEVA	UTEVA and TRU	Anion exchange resin (after redox cycle)	UTEVA, TEVA and DGA resins was applied for the separation of U, Pu and Am/Cm.	Tandem AG1×8 and UTEVA	Pu, Cm and Am using anion exchange (AG 1x8) and extraction chromatography (TRU). U using extraction chromatography (UTEVA)

**Table 5 Preparation of measurement targets and measurement methods of Samples 2-10**

Sample	2	3	4	5	6	7	8	9	10
<b>Source preparation</b>	Micro-co-precipitation with NdF3 and 0,1 µm filtration	Electrodeposition	On stainless steel discs by electrodeposition	Filtration through Resolve-filters and mounting on Al-disc		Mixing with LLT liquid scintillation cocktail for Pu-241 analysis	Electrodeposition on stainless disc for alpha spectrometry measurement of Pu, Am and Cm isotopes, 3% HNO <sub>3</sub> medium for ICP-MS measurement of uranium isotopes	5V and ~0,1-0,2 A onto steel from a NaHSO <sub>4</sub> /Na <sub>2</sub> SO <sub>4</sub> electrolyte	Pu, Am, Cm with electrodeposition on platinum discs.  Pu-241 acid stripped from the Pu sources following alpha-spec.
<b>Measurement</b>	Ortec alpha spectrometer. Pu-241 with Quantulus LSC (Pu filters dissolved	ULTRA™-AS detectors, Alpha Ensemble®, Ortec and MAESTRO-32-software Hidex 300 SL LSC for Pu-241 (aliquot	Alpha spectrometry for Pu-238, Pu-239/240, Am-241, Cm-242, Cm-244 LSC for Pu-241	Alpha PIPS detector	Ortec alpha counter with Maestro software	Pu-241 activity using AccuFLEX LSC-8000 from Hitachi with LLT UltimaGo	U isotopes by ICP-MS/MS (Agilent 8800, ICP-QQQ-MS) Pu, Am, Cm isotopes by alpha spectrometry	Single chamber Canberra 7400 alpha spectrometry chambers	Alpha spectrometry Ortec Ortec. Pu-241 using LSC (Perkin Elmer Tri-Carb 2910TR).

	in dilute boric acid)	prior to electrodeposition.*				ld + Pu-239 activity using alpha spectrometry (Grid Chamber, Canberra)			
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\* Final results: U fractions were dissolved from the electrodeposited steel plates and measured with HR-ICP-MS (Elements2, ThermoScientific). Yield (%) was determined by remeasuring with alpha spectrometer. Pu fractions were dissolved also from the electrodeposited steel plates and measured again with LSC (Hidex 300 SL). Yield (%) was determined by remeasuring with alpha spectrometer.

## 6.2. Radiochemical procedures for gross alpha measurements

Table 6 summarises the gross alpha determination procedures. Sample 3 was directly weighed in the LSC vial in which 100  $\mu\text{l}$  of 8 M  $\text{HNO}_3$  was added prior to mixing with LSC cocktail. The gross alpha measurements were carried out using LSC with alpha beta separation. Sample 7 was first acid digested completely with a  $\text{HNO}_3$  and  $\text{HCl}$  mixture in a microwave after which the sample was evaporated on a planchet and measured using alpha spectrometry. Sample 10 was acid digested with Fenton's reagent and after filtration with  $\text{HNO}_3$ . The solutions were combined and diluted to 250 ml out of which different aliquots (see Table 3) were taken. The Sample 10 gross alpha source was prepared via evaporation and measured using twin channel LSC with alpha beta discrimination.

**Table 6. Radiochemical procedures of gross alpha measurements**

Sample	2	3	4	5	6	7	8	9	10
<b>Sample size (g)</b>	-	0.003 g	-	-	-	0.1 g	-	-	Aliquot from acid digested 0.25g diluted to 250 ml.
<b>Acid digestion</b>	-	100 µl 8 M HNO <sub>3</sub>	-	-	-	Complete destruction of matrix using HNO <sub>3</sub> :HCl in microwave oven (Discover from CEM)	-	-	Fenton's reagent, filtration, HNO <sub>3</sub> . -> Filtration and dilution to 250 ml.
<b>Sample preparation</b>	-	Mixed with 10 ml HiSafe	-	-	-	Evaporation	-	-	Gross alpha source with evaporation and addition of Ultima Gold AB.
<b>Measurement</b>	-	Hidex LSC	-	-	-	Measurement of the planchet using alpha spectrometry (Grid Chamber, Canberra)	-	-	Gross alpha by twin channel LSC with alpha/beta discrimination (Wallac 1415). Results calculated with reference to Am-241.

## 7. Gamma spectrometry

DTM Decom III results did not include quantitative Am-241 and U-235 results even though they can be measured using gamma spectrometry [Leskinen et al. 2022a, 2022b]. The spent resin contained several gamma emitters, which either masked the Am-241 and U-235 peaks or their activity concentrations below limit of detection. However, gamma spectrometry measurements were carried out for Sample 3 (U-235 and Am-241 detection in purified fractions) and Sample 10 (Am-241 in original and acid digested samples).

After purification of americium and uranium fractions, attempts were made to measure Am-241 and U-235 in Sample 3. A total of four specimens in liquid form with an approximate volume of 20 ml each were selected for measurements. Every specimen corresponded, respectively, to: a blank (only tracer), the uranium fraction, the americium/curium fraction, and the plutonium/neptunium fraction. Measurements were carried out with a p-type, ISOCS-characterized HPGe semiconductor detector manufactured by Mirion Technologies, with 16 % relative efficiency evaluated at 1332 keV. At this energy, the resolution (FWHM) was 1.69 keV. Acquisition was done in 8192 channels using a DSA-LX multi-channel analyser and Genie 2000 software. In order to maximise detection efficiency, the samples were positioned 20 mm above the detector endcap. In order to correct for possible True Coincidence Summing (TCS) effects, corrections were applied to the mathematical efficiency model setup with the Geometry Composer software version 4.4. In spite of the close sample-detector geometry, very low dead times (of the order of 0.03 %) were obtained. These dead times are typical of a background spectrum in the laboratory. The background spectrum was acquired in a setup where all four samples to undergo measurement were present in the laboratory. Background subtraction was performed on all sample spectra. However, no photo-peaks corresponding to either Am-241 or U-235 were observed in the purified fractions, and thus it was decided not to proceed with the measurement of the blank sample. Counting times ranged from approximately 22 h to 72 h. All samples contained varying amounts of Co-60, whereas the americium/curium fraction also indicated the presence of Mn-54, Cs-134, and Cs-137 above detection limits.

In case of Sample 10, an approximately 0.25 g of ‘as-received’ sample was accurately taken, counted by gamma-spectrometry and then subject to a Fenton’s reagent-based dissolution technique, however the material appeared to be insoluble under these conditions. The treated resin was filtered off and digested in hot concentrated nitric acid. Following further filtration, the solutions were combined and diluted to 250 ml with de-ionised water. Gamma spectrometry was carried out on the filtrate and filter papers to check the extent of radionuclide solubilisation. Gamma spectrometry on the solution was carried out on an accurately measured volume (100 ml) in a calibrated geometry (calibrated over the range 59 keV to 1836 keV using a mixed radionuclide standard traceable to National Standards) for a count time of ~56 hours. Gamma spectrometry was carried out using an Ortec® GMX n-type high purity germanium photon detector coupled to an Ortec® D-SPEC 502 digital signal processing gamma-ray spectrometer. Spectra were processed and corrected for environmental background using a library based analysis engine (WAN32) within Ortec® GammaVision software application. It was not possible to quantify Am-241 by gamma-spectrometry due to <MDA Am-241 results arising from the low Am-241 activity present and the high Compton background from beta gamma emitters present in the sample, notably Co-60 and Cs-137.

## **8. Preliminary results**

A project meeting was held to discuss the radioanalytical procedures and preliminary results. The radiochemical analysis yields of initial results are presented in Table 7. The results show that the uranium yields vary from 62 to 83%, plutonium yields from 18 to 107%, Americium/curium yields from 12 to 114%, and neptunium yields from 20 to 28%.

**Table 7. Chemical yields of preliminary U, Pu, Am, Cm and Np results.**

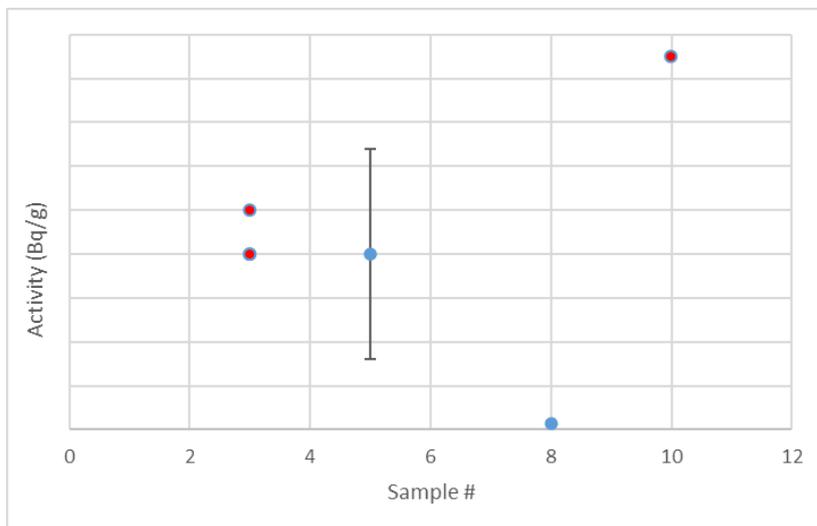
Sample	Mass (g)	Yield (%) (uncertainties are stated with $k = 2$ )			
		Uranium isotopes	Plutonium isotopes	Americium and curium isotopes	Np-237
2	0.1083	-	$19 \pm 1$	$55 \pm 6$	-
	0.1764	-	$18 \pm 1$	$52 \pm 6$	-
3	0.0446	$72.7 \pm 2.4$	$27.9 \pm 3.2$	$12.0 \pm 0.42$	$27.9 \pm 3.2$
	0.0541	$77.4 \pm 2.5$	$19.6 \pm 0.89$	$13.4 \pm 0.43$	$19.6 \pm 0.89$
	0.0532	$71.1 \pm 2.3$	$26.1 \pm 1.8$	$12.7 \pm 0.47$	$26.1 \pm 1.8$
4	0.0283	-	$66.1 \pm 8.3$	$65.7 \pm 11.1$	-
	0.0094	-	-	-	-
5	0.0090	62	102	112	-
	0.0203	83	107	114	-
6	0.1021	-	<1%	-	-
	0.0970	-	<1%	-	-
	0.0618	-	<1%	-	-
7	0.1251	-	-	-	-
8	0.1010	$83 \pm 3$	-	-	-

	0.2900	-	88.8±2.5	82.6±3.2	-
9	0.0101	Not calculated	-	-	-
	0.0049	Not calculated	-	-	-
10	0.2522	82.1	89.9	20.5	-

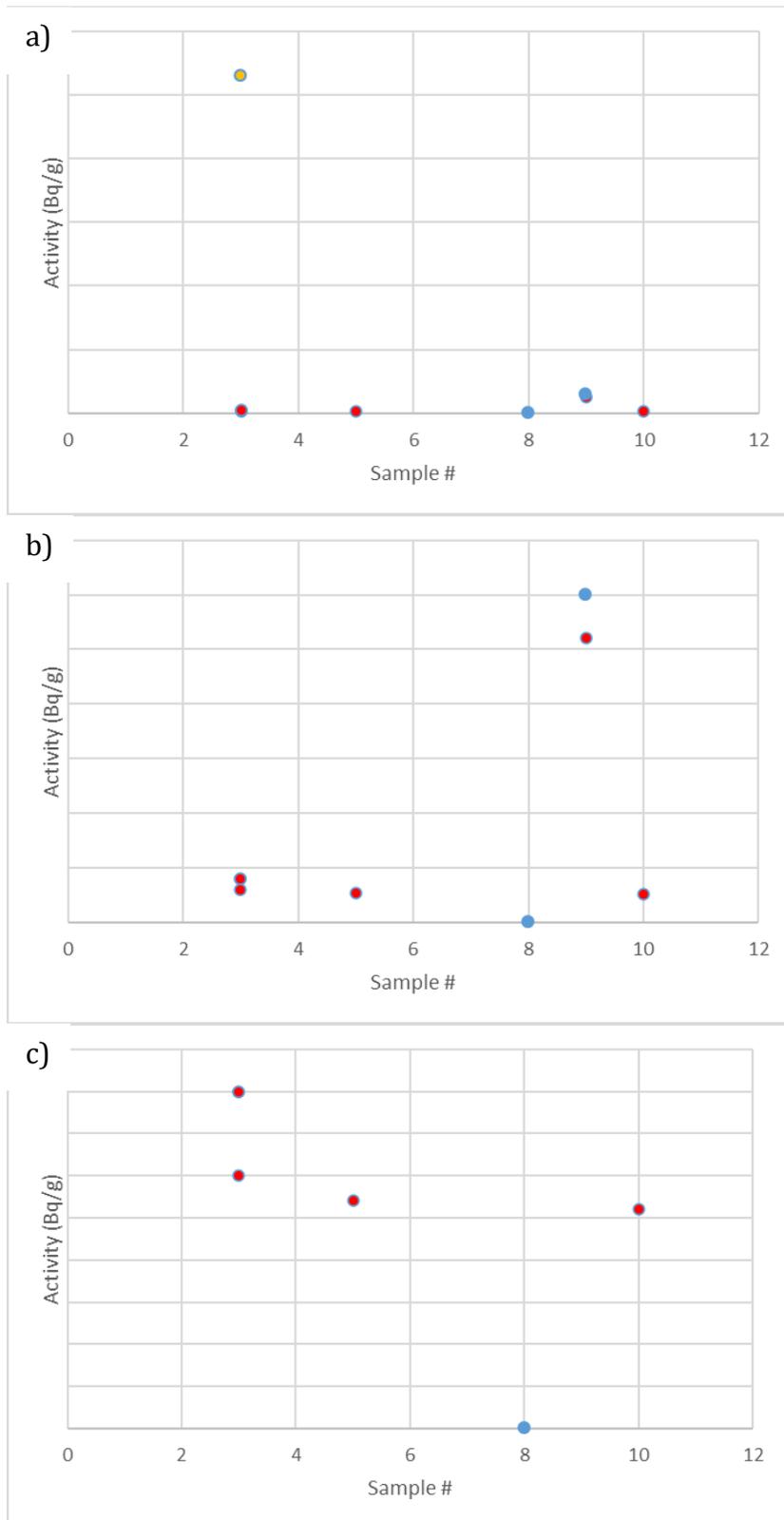
The preliminary results in Figure 2 to Figure 12 are shown as they were discussed in the preliminary meeting i.e. without scale to demonstrate trends and to give an alert to possible deviations.

The preliminary U-234 results in Figure 2 show that four sets of results were submitted. Samples 3, 5 and 10 were analysed using alpha spectrometry and Sample 8 using ICP-MS. However, Sample 5 and 8 were the only results above limit of detection.

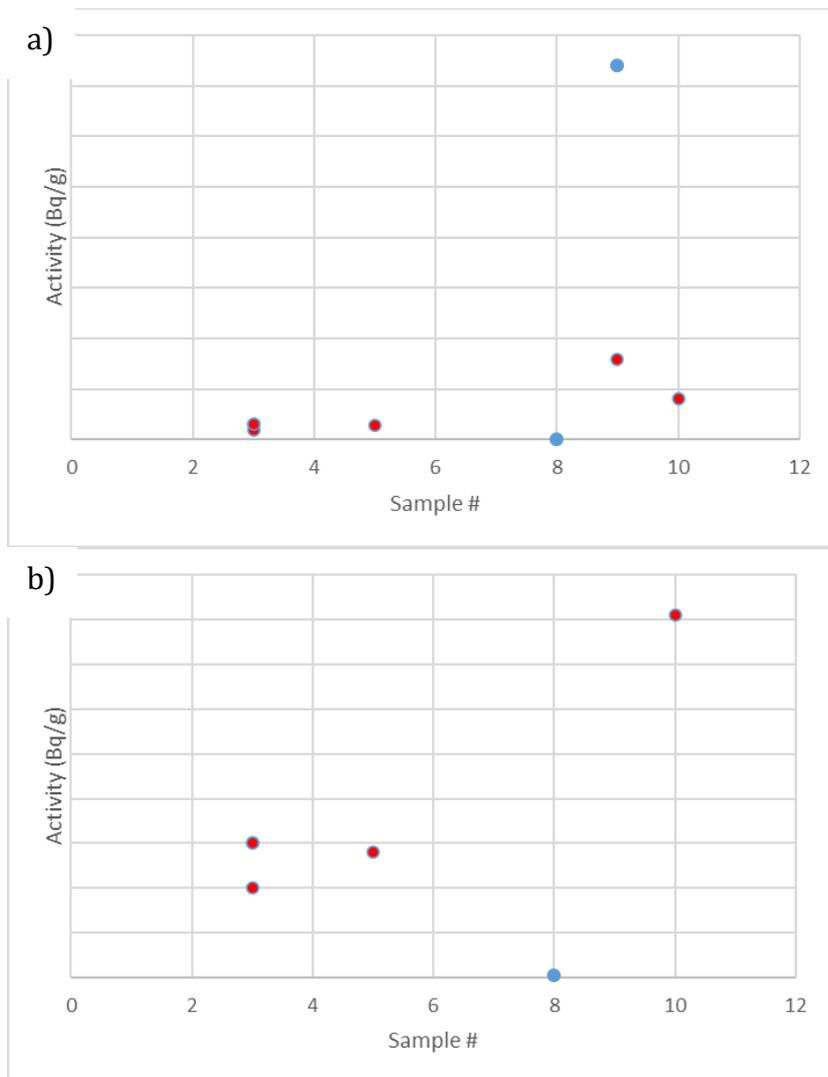
The preliminary U-235 results in Figure 3 show that five sets of results were submitted. Sample 3 was measured with both alpha and gamma spectrometry and the results were below limit of detection. Samples 5, 9 and 10 were measured using alpha spectrometry and Sample 8 using ICP-MS. The results show inconsistencies in Sample 9 the high result was thought to be due to some contamination in the detector. The only reliable result above limit of detection was produced was Sample 8 using ICP-MS. The same trend is also seen in preliminary U-238 results (Figure 4) in which reliable above limit of detection results were produced only using ICP-MS (Sample 8).



**Figure 2. Preliminary U-234 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . Samples 3, 5 and 10 by alpha spectrometry. Sample 8 by ICP-MS. Red dots indicate alpha spectrometry results under limit of detection.**



**Figure 3. Preliminary U-235 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) zoomed in results without gamma spectrometry results, c) zoomed in results. Samples 5, 9 and 10 with alpha spectrometry. Sample 3 with gamma and alpha spectrometry. Sample 8 with ICP-MS. Red dots indicate alpha spectrometry results and yellow gamma spectrometry results under limit of detection.**

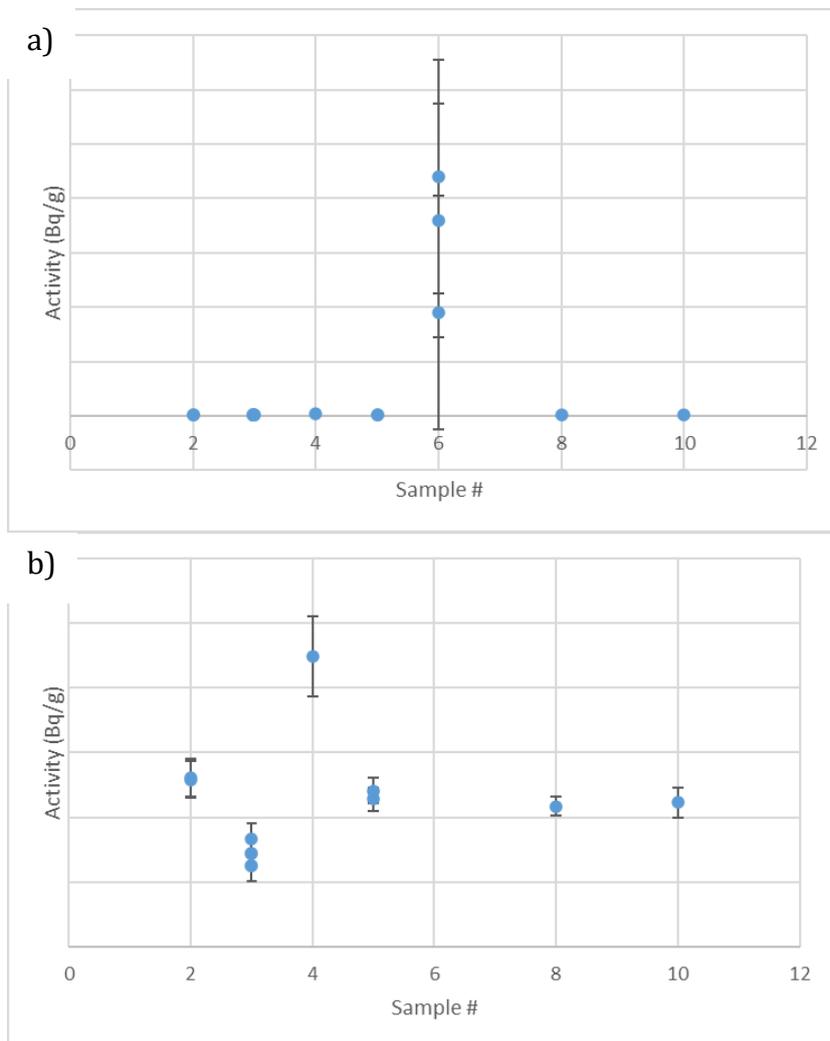


**Figure 4. Preliminary U-238 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) zoomed in results. Samples 3, 5, 9 and 10 by alpha spectrometry. Sample 8 by ICP-MS. Red dots indicate alpha spectrometry results under limit of detection.**

The preliminary Pu-238 results in Figure 5 show that Sample 6 results are clear outliers. Significant difficulties with the radiochemical analysis, yield determinations, activity calculations, and uncertainty calculations were reported for Sample 6. As the outliers were removed, the remaining six sets of results showed a relatively consistent results even though Sample 3 was a little lower and Sample 4 a little higher of the general trend.

The preliminary Pu-239,240 results in Figure 6 show that Sample 6 is a clear outlier and Sample 9 show inconsistencies in the replicate results. The remaining six sets of results show a

relatively consistent trend even though Sample 4 seems to be little higher compared to the other results.



**Figure 5. Preliminary Pu-238 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) Sample 6 results excluded.**

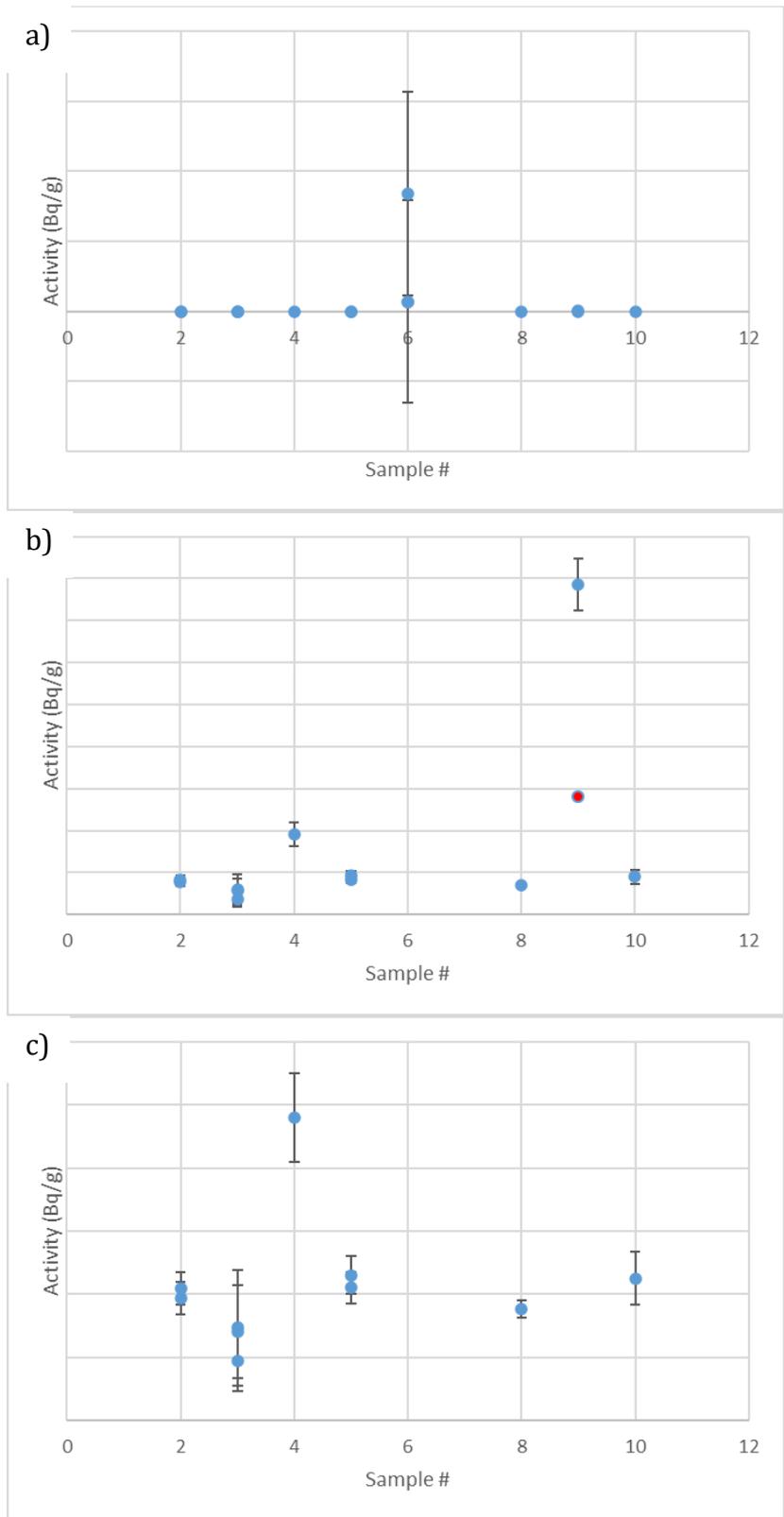
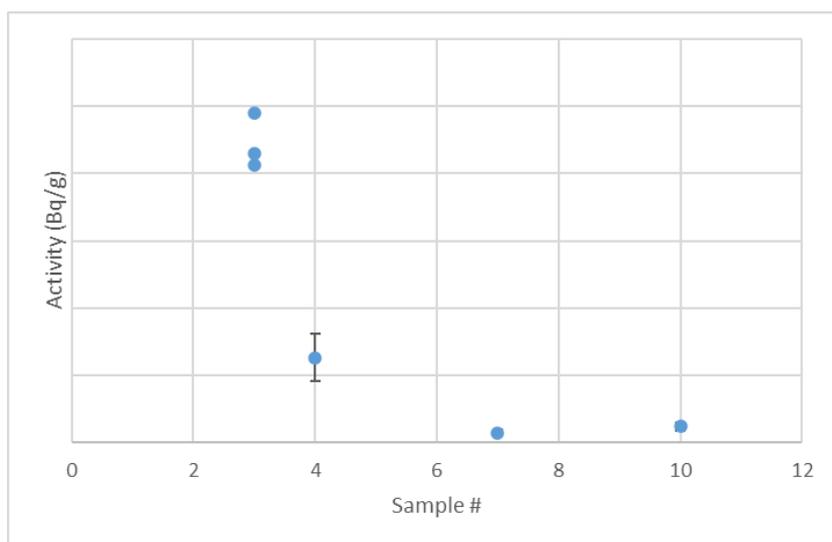


Figure 6. Preliminary Pu-239,240 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) Sample 6 results excluded, c) Sample 6 and 9 excluded. Red dots indicate alpha spectrometry results under limit of detection.

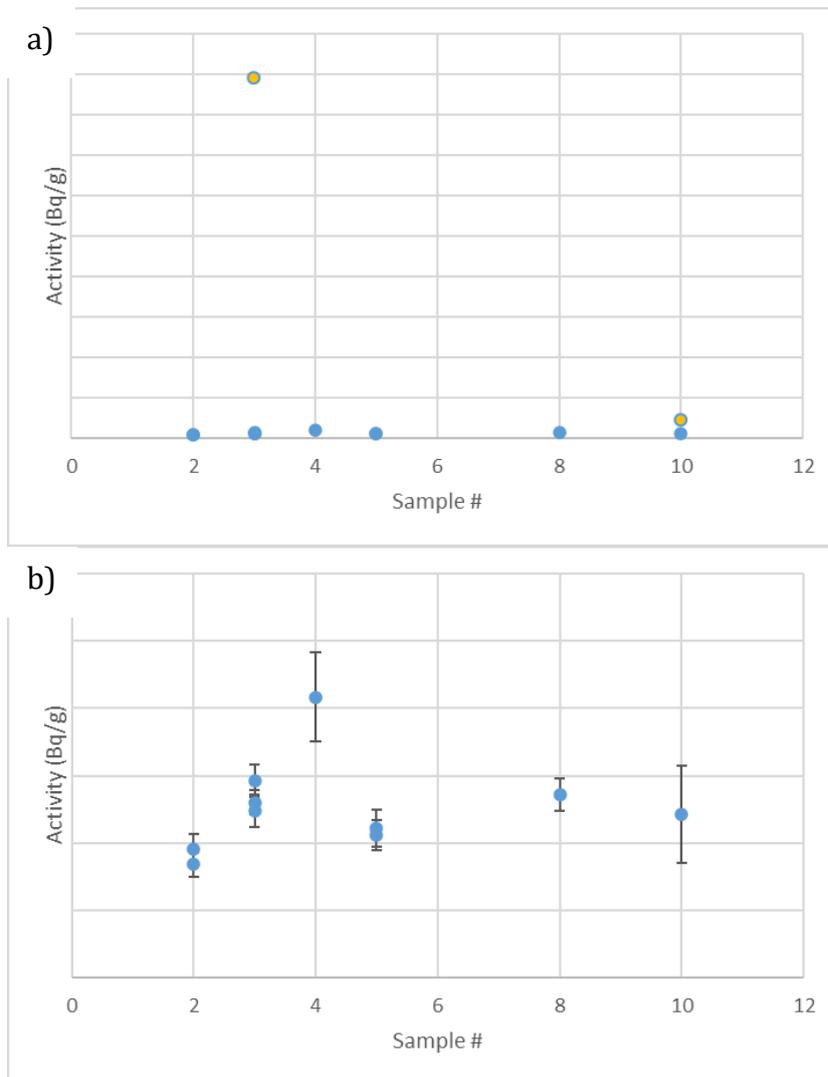
The preliminary Pu-241 results in Figure 7 show significant differences between the submitted four sets of results. Sample 10 result was almost twice the result of Sample 7. Sample 3 replicates were significantly higher compared to Samples 7 and 10 whereas Sample 4 was between them. The preliminary meeting discussions included suggestions that the deviations could be contributed to LSC efficiency calibration or spectral interferences. The common practice to use H-3 as an efficiency calibration standard may not be justified due to differences in the shape of Pu-241 and H-3 LSC spectra. The spectral interferences could include Co-60 interference or color quenching due to acid stripping of Pu-plate samples.



**Figure 7. Preliminary Pu-241 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

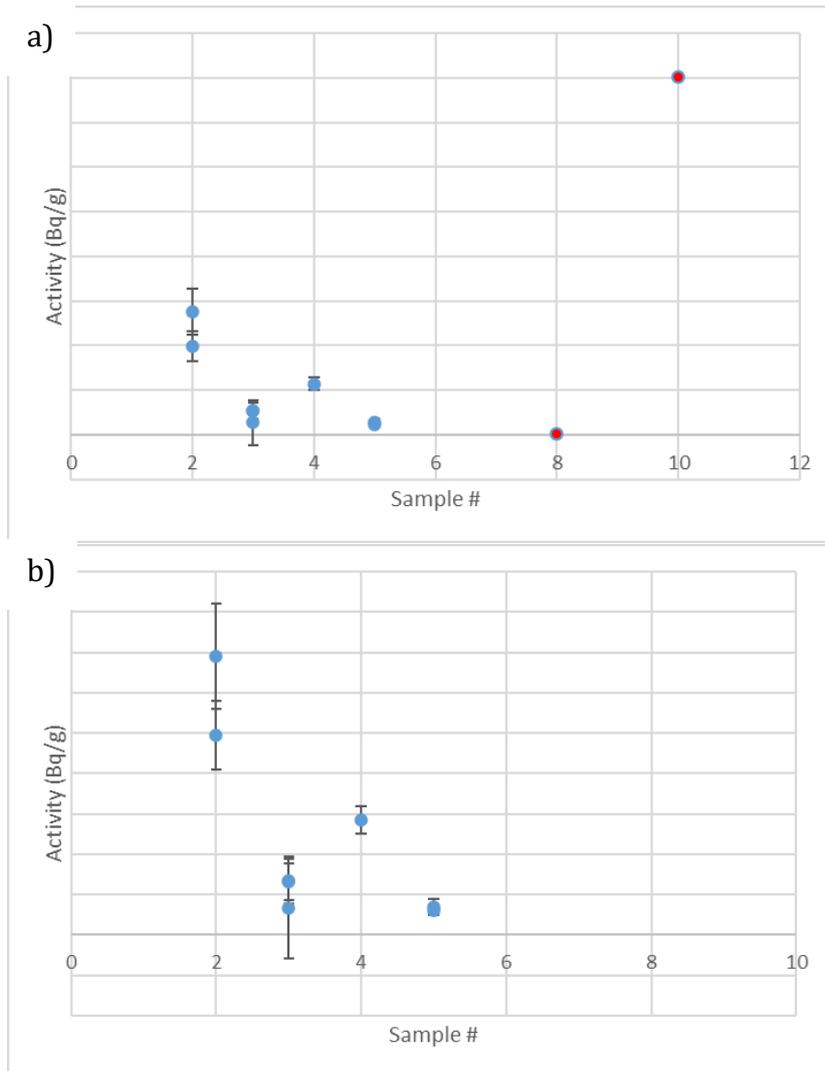
Figure 8 show the preliminary Am-241 results. Even though Am-241 can be measured also using gamma spectrometry, it was not detected in DTM Decom III exercise due to complex gamma spectrum [Leskinen et al. 2022a]. However, two partners carried out gamma spectrometric measurements in the purified Am-241 fractions. As the results in Figure 8 show, the limits of detection using gamma spectrometry are significantly higher compared to the

corresponding results with alpha spectrometry. The Am-241 alpha spectrometry results show a relatively good trend with Sample 4 a little higher to others.



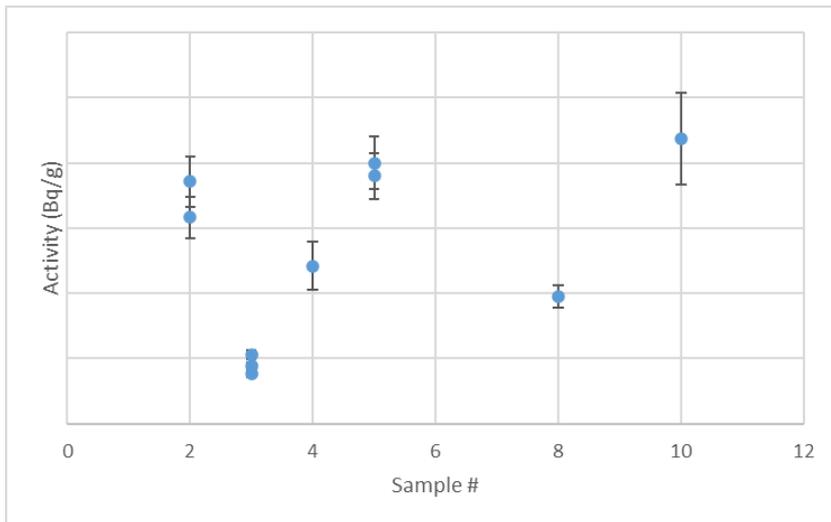
**Figure 8. Preliminary Am-241 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) gamma spectrometry results excluded. Yellow dot indicates gamma spectrometry results under limit of detection.**

Figure 9 shows the preliminary Cm-242 results in which two out of six results were below limit of detection. The critique given in the preliminary meeting concluded that due to the short half-life (163 d) the confidence in the results was low.



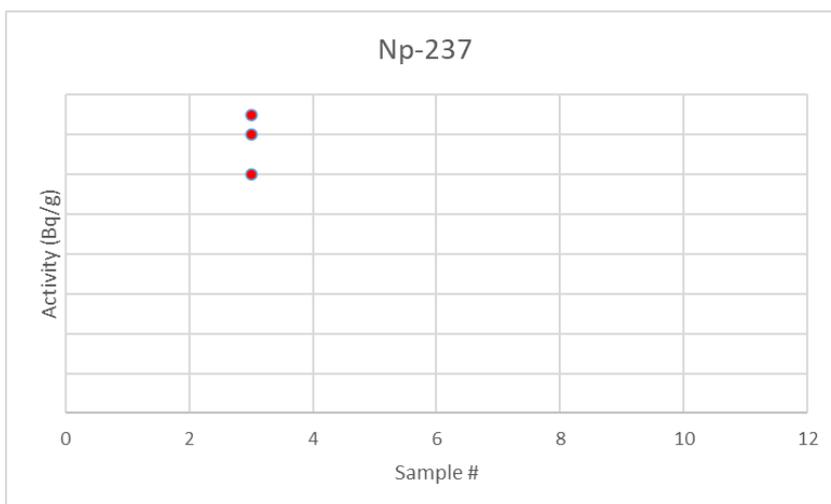
**Figure 9. Preliminary Cm-242 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) below limit of detection results excluded. Red dot indicates alpha spectrometry results under limit of detection.**

Figure 10 shows the preliminary Cm-243,244 results having variance, which was suggested in the preliminary meeting to originate from decay correction. Therefore, it was decided that a reference date nearer to the analysis time (summer 2022) would be used in the final results.



**Figure 10. Preliminary Cm-243,244 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

Figure 11 shows the preliminary Np-237 results which had been calculated using Plutonium isotope yields. However, the critique given in the preliminary meeting concluded that the chemical behaviour of neptunium and plutonium isotopes are not necessarily the same due to the effect of oxidation states, for example. A recommended reference to study the differences in behaviour of Pu and Np was given [Strisovska et al. 2013].



**Figure 11. Preliminary Np-237 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . Red dot indicates alpha spectrometry results under limit of detection.**

Figure 12 shows the preliminary gross alpha results. Only three sets of results were submitted and visually Sample 3 clearly deviates from the Sample 7 and 10 results. The preliminary meeting discussions concluded that use of LSC in gross alpha measurements can be troublesome due to beta and alpha signal spill overs. Especially in this case, there are orders of magnitude higher amounts of beta emitters compared to the alpha emitters in spent ion exchange samples and consequently even low levels of spill over betas to alpha side can cause a significant error.

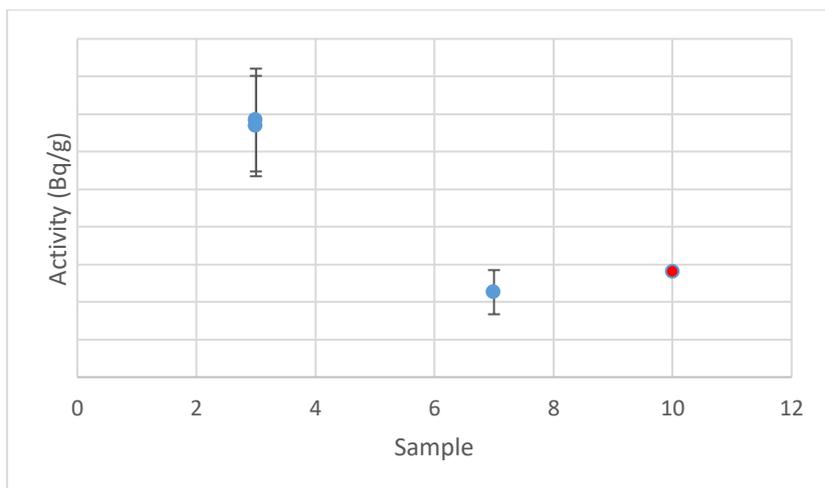


Figure 12. Preliminary gross alpha results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . Red dot indicates alpha spectrometry results under limit of detection.

## 9. Methodology for statistical analysis of the reported results

### 9.1 Statistical analysis according to ISO 13528

The statistical analyses of the submitted results were carried out using the ISO 13528 standard [International Standard 2015] similarly to the DTM Decom projects I-III [Leskinen et al. 2020a, 2020b, 2021a, 2021b, 2022a, 2022b]. A robust statistical method was utilised for calculation of assigned values based on the participants' results [International Standard 2015]. Robust mean and robust standard deviation were calculated using Algorithm A, which is robust for outliers, when the expected proportion of outliers is less than 20% [International Standard 2015]. Performance assessment was carried out using z score (Eq. 26) [International Standard 2015]. The analysis results with z score were acceptable when  $|z| \leq 2.0$ , a warning signal was given for results with  $2.0 < |z| < 3.0$ , and results were unacceptable when  $|z| \geq 3.0$  [International Standard 2015].

$$z_i = \frac{(x_i - x_{pt})}{\sigma_{pt}} \quad (26)$$

Where

$x_{pt}$ : the assigned value

$\sigma_{pt}$ : standard deviation for the proficiency assessment

In cases where the robust standard deviation is large, another value for  $\sigma_{pt}$  can be used so that the results that are not fit for purpose will receive an action signal [International Standard 2015]. In cases where the robust standard deviation was large ( $1\sigma > 20\%$ ), the uncertainty of the assigned value (Eq. 27) was used as  $\sigma_{pt}$  [International Standard 2015].

$$u(x_{pt}) = \frac{1.25 \cdot s^*}{\sqrt{p}} \quad (27)$$

Where

$s^*$ : robust standard deviation of the results

$p$ : number of samples

## 9.2 Extended statistical analysis

The results for Am-241 were analysed using a combination of  $\zeta$ -score, z-score and relative uncertainty test [Jerome and Harms, 2022] with the value of  $\sigma_{pt}$  derived from the data submitted by all participants. The approach is as follows:

Results with no reported uncertainty are rejected. The  $\zeta$ -score is calculated and  $\zeta$ -scores  $> 5,026$  are flagged as improbable deviations. The z-score is calculated as usual, where  $\sigma_p = A \cdot u_{rel}(med)$  and  $u_{rel}(med)$  is determined *after* rejection of outliers according to the Pierce criterion. Finally, the R-score is calculated as follows:

$$R_i = \frac{\ln u_{rel}(L_i) - \ln u_{rel}(med)}{\sigma_{\ln u_{rel}(med)}}$$

The R-test is passed if  $R_{lower} < R_i < R_{upper}$ .

The outcomes from the three tests may be used to assign an overall score to a particular laboratory's reported result. If the tests are assigned priorities in this order  $\zeta$ -test  $>$  z-test  $>$  R-test, and then the z- and R-tests are subdivided into pass or fail at the lower limit and pass and fail at the upper limit, then each test returns a simple binary result. The score may be constructed as follows:

Set the value of the score to 0

Pass  $\zeta$ -test (ie  $-2.576 < \zeta_i < +2.576$ ): add 16

Pass z-test (at the higher level, ie  $z_i < +2.576$ ): add 8

Pass z-test (at the lower level, ie  $z_i > -2.576$ ): add 4

Pass R-test (at the higher level ie  $R_i < R_{upper}$ ): add 2

Pass R-test (at the lower level ie  $R_i > R_{lower}$ ): add 1

It is impossible to score 0 or 1, and so:

Results without uncertainties: set score to 0

Results flagged as improbable deviations: set score to 1

A score of 31 (all three tests passed) indicates an acceptable result. Scores between 12 and 30 indicate that either the  $\zeta$ -test *or* the z-test has been failed, and the result is labelled as questionable. A score of 11 or less indicate that the  $\zeta$ -test and the z-test has been failed and the result is labelled as discrepant.

Additionally, one should note that scores of 2, 3, 4, 8, 12, 16, 17, 18, 19, 20, 24 and 28 cannot be achieved since it is impossible to fail the z-test (high) and the z-test (low) at the same time, neither is it possible to fail the R-test (high) and the R-test (low) at the same time.

These scores can be used to rapidly identify opportunities for improvement at individual laboratories and may be used to identify trends associated with their performance within a particular exercise or ongoing performance across several exercises. From the organiser's perspective, it enables the identification of measurement issues across the user community, or for specific measurement problems with a particular nuclide.

## 10. Final results

After the preliminary meeting, each partner was requested to submit one analysis result per radionuclide. Additionally, any iterations or new data entries were requested to be clearly defined in submission of the final results. All partners were requested to submit one Cm-243,244 result with the updated reference date. New data entries were submitted for Sample 3 i.e., ICP-MS results for uranium isotopes and remeasured Pu-241 and gross alpha results.

Calculation corrections were made for the Sample 4 Pu-238, Pu-239,240, Pu-241 and Am-241 results as impurities had been detected in the Pu-242 source.

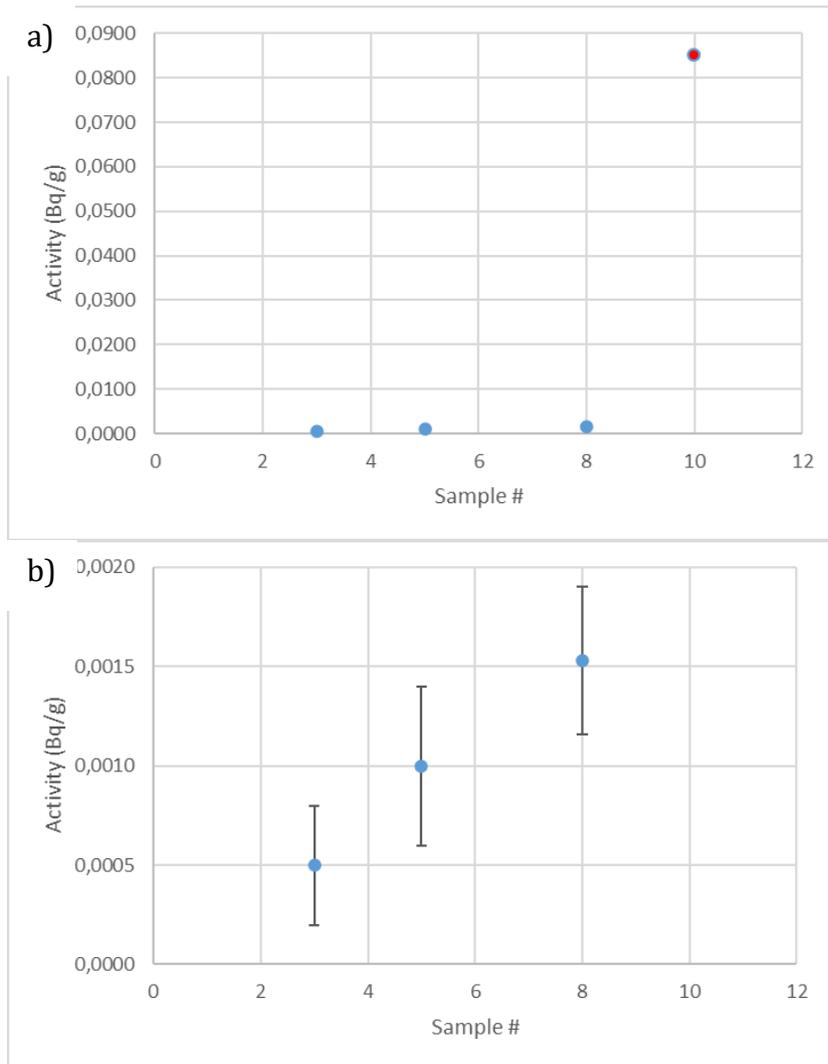
The final results were analysed with ISO 13528 standard when i) there were  $\geq 5$  above limit of detection data entries per radionuclide, and ii) only 1 result per radionuclide per sample (i.e., no replicate results). The final results with less than 4 data entries above limit of detection are presented in trend figures in section 8.1. The final results with ISO 13528 based statistical analysis are presented in section 8.2. The complementary statistical analysis of Am-241 results are presented in section 8.3.

### **10.1. DTM results with less than 4 data entries**

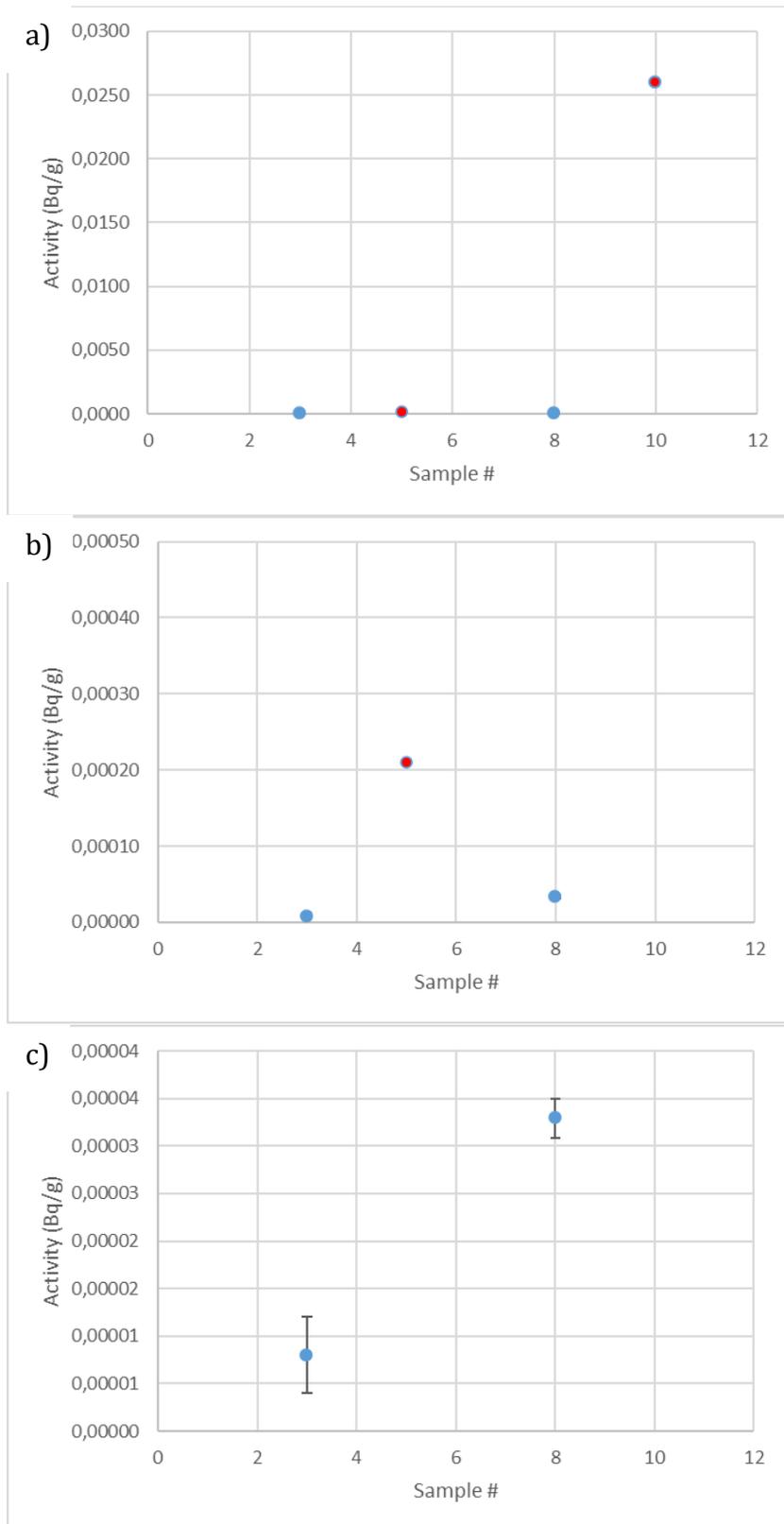
The final U-234 results in Figure 13 show that in total four data entries (1 result/radionuclide/partner) were submitted. Sample 3, 4 and 8 results were above limit of detection whereas Sample 10 was below limit of detection. Samples 5 and 10 were measured using alpha spectrometry whereas Samples 3 (new entry) and 8 were measured using ICP-MS. The results show that both alpha spectrometry and ICP-MS techniques were able to detect the mBq/g level U-234 activity concentrations.

The final U-235 results in Figure 14Figure 13 show that in total four data entries were submitted. One set of results (Sample 9) were excluded as replicate results were submitted. Sample 3 (new entry) and 8 results were above limit of detection whereas Samples 5 and 10 were below limit of detection. Samples 5 and 10 were measured using alpha spectrometry whereas Samples 3 and 8 were measured using ICP-MS. The results show that contrary to U-234 results only ICP-MS technique was able to detect the tens of  $\mu\text{Bq/g}$  level U-235 activity concentrations. Even though the Sample 3 and 8 results deviate from each other, the measured activity concentrations are very low.

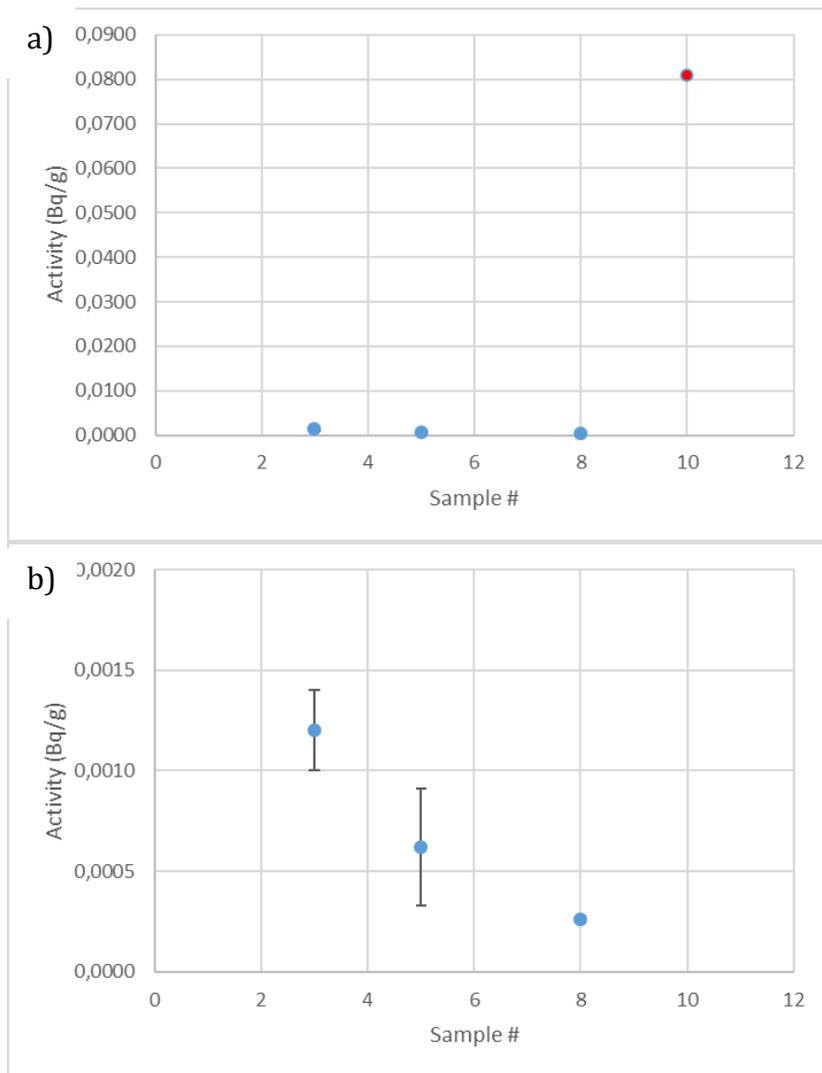
The final U-238 results in Figure 15Figure 13 show that in total four data entries were submitted. One set of results (Sample 9) were excluded as replicate results were submitted. Sample 3 (new entry), 5 and 8 results were above limit of detection whereas Sample 10 was below limit of detection. Samples 5 and 10 were measured using alpha spectrometry whereas Samples 3 and 8 were measured using ICP-MS. The results show that similarly to U-234 results both alpha spectrometry and ICP-MS techniques were able to detect the mBq/g level U-238 activity concentrations.



**Figure 13. The final U-234 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) results above limit of detection. Red dot indicates alpha spectrometry results under limit of detection.**

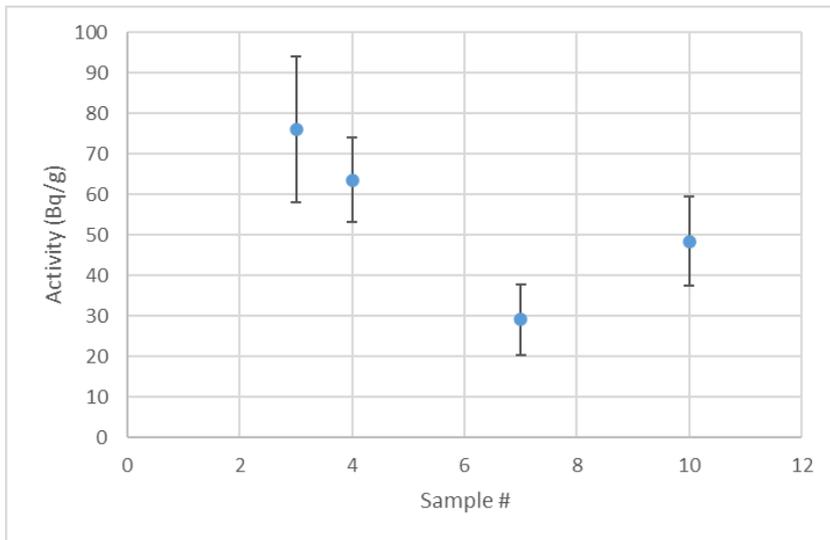


**Figure 14. The final U-235 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) zoomed in results, c) zoomed in results with only above limit of detection results. Red dot indicates alpha spectrometry results under limit of detection.**



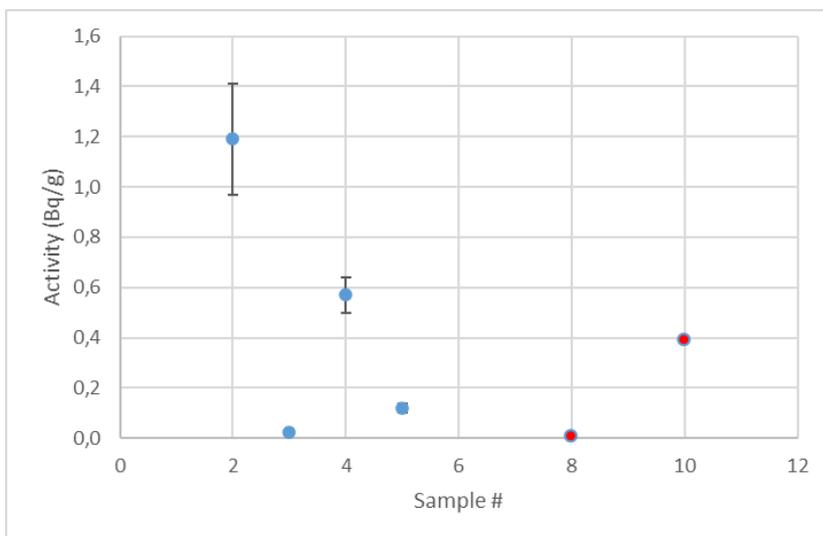
**Figure 15. The final U-238 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . a) all results, b) results above limit of detection results. Red dot indicates alpha spectrometry results under limit of detection.**

The final Pu-241 results in Figure 16 show significantly more consistent results compared to the preliminary results (see Figure 7). Sample 3 had been remeasured after acid stripping of two Plutonium measurement targets (preliminary results taken as an aliquot prior to electrodeposition) and the yield was determined by repetition of alpha spectrometric measurements after the acid stripping. Additionally, an improved Hidex SL300 measurement protocol was utilised e.g. better care was taken in limitation of spillover of alpha signals into the beta channel. The recalculation of the Sample 4 results included corrective actions due to impurities reported in the Pu-242 source. In general, the Pu-241 results are within order of magnitude between 30 to 75 Bq/g.



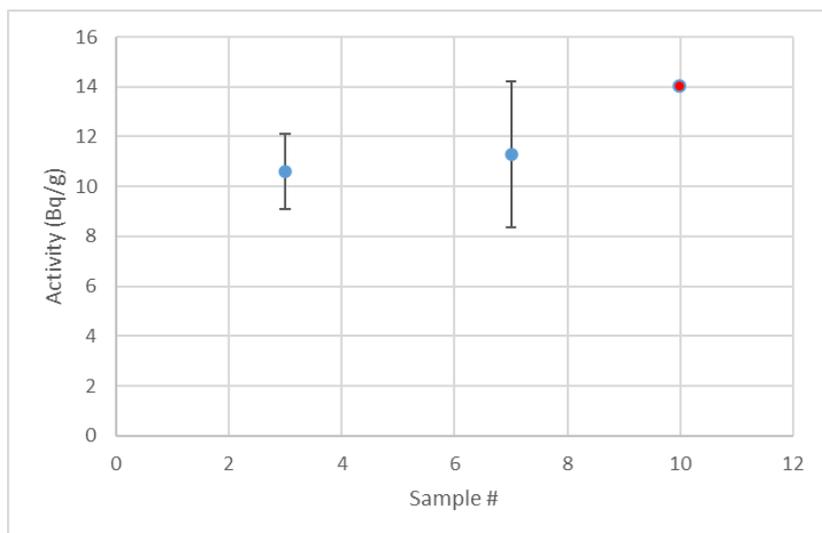
**Figure 16. The final Pu-241 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

The final Cm-242 results in Figure 17 show that four out of six data entries were above limit of detection. The results also show a scatter from 0,020 to 1,2 Bq/g. The final meeting discussions included a comment that there has been evidence in a large set of data that there is a 5% low bias for Cm due to different chemical behaviour compared to Am [Jerome and Skipperud, 2022].



**Figure 17. The final Cm-242 results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . Red dot indicates alpha spectrometry results under limit of detection.**

preliminary results in Figure 12. The corrective actions in Sample 3 results were carried out in the LSC measurements as a closer look at the LSC spectrum showed significant spillover of beta events to the alpha channel. Therefore, spill of counts were lowered with utilisation of “spill to beta” parameter in the LSC measurement and lowering of quenching was achieved with addition of more liquid scintillation cocktail. The efficiency of Sample 3 measurement was assumed to be equal to TDCR i.e. 100%. Even if only three data entries were submitted, the results are well aligned between the LSC (Sample 3), alpha spectrometry planchet (Sample 7), and twin channel LSC (Sample 10) results.



**Figure 18.** The final gross alpha results in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ . Red dot indicates results under limit of detection.

## 10.2. DTM results with ISO 13528 statistical analysis

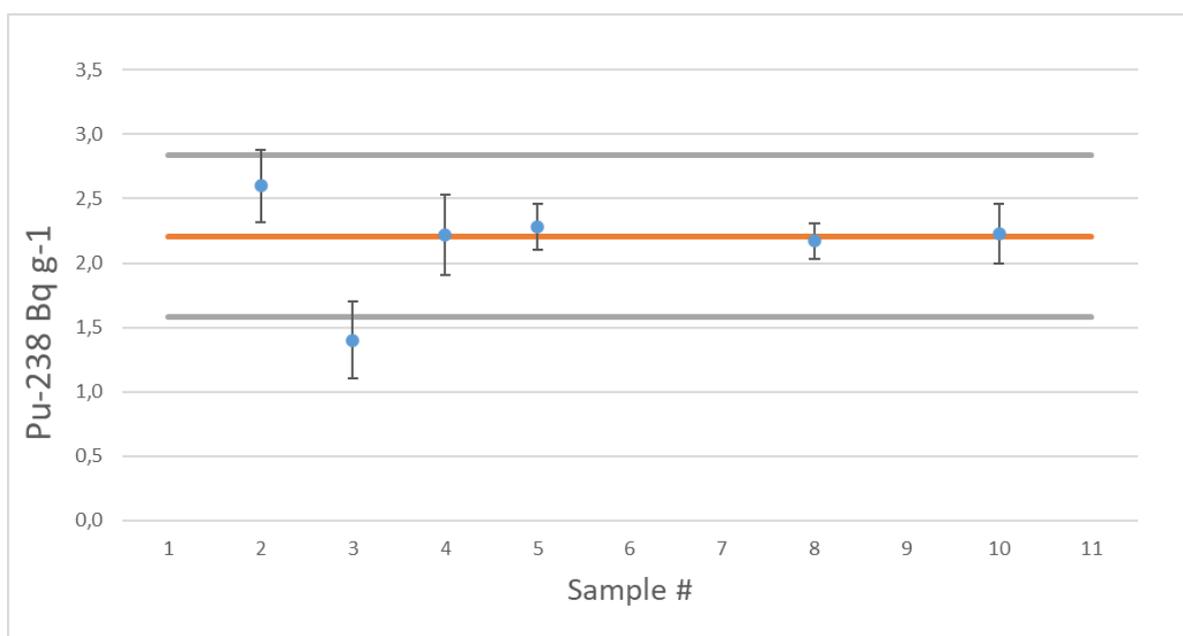
Statistical analysis according to ISO 13528 standard was carried out for Pu-238, Pu-239/240, Am-241, and Cm-243/244 results as at least five individual result entries were submitted. Table 8 shows the statistical analysis results including number of data entries, number of iterations, assigned values, robust standard deviations, and standard uncertainties of assigned values.

**Table 8.** Sample numbers, number of iterations, assigned value, robust standard deviation and standard uncertainty of assigned value of Pu-238, Pu-239/240, Am-241, and Cm-243/244 results. The uncertainties of assigned values are presented with a coverage factor of  $k = 2$ , and calculated from robust standard deviation when it was  $\leq 20\%$ , otherwise standard uncertainty of assigned value used.

	<b>Pu-238</b>	<b>Pu-239,240</b>	<b>Am-241</b>	<b>Cm-243,244</b>
Number of data entries in calculations	6	6	6	6
Number of iterations	22	13	4	2
Assigned value $\pm 2k$ uncertainty	$2,2 \pm 0,6$ Bq/g	$418 \pm 145$ mBq/g	$1,2 \pm 0,4$ Bq/g	$5,4 \pm 2,9$ Bq/g
Robust standard deviation (%)	14.2	34.0	18.3	52.5
Standard uncertainty of	7.3	17.4	9.3	26.8

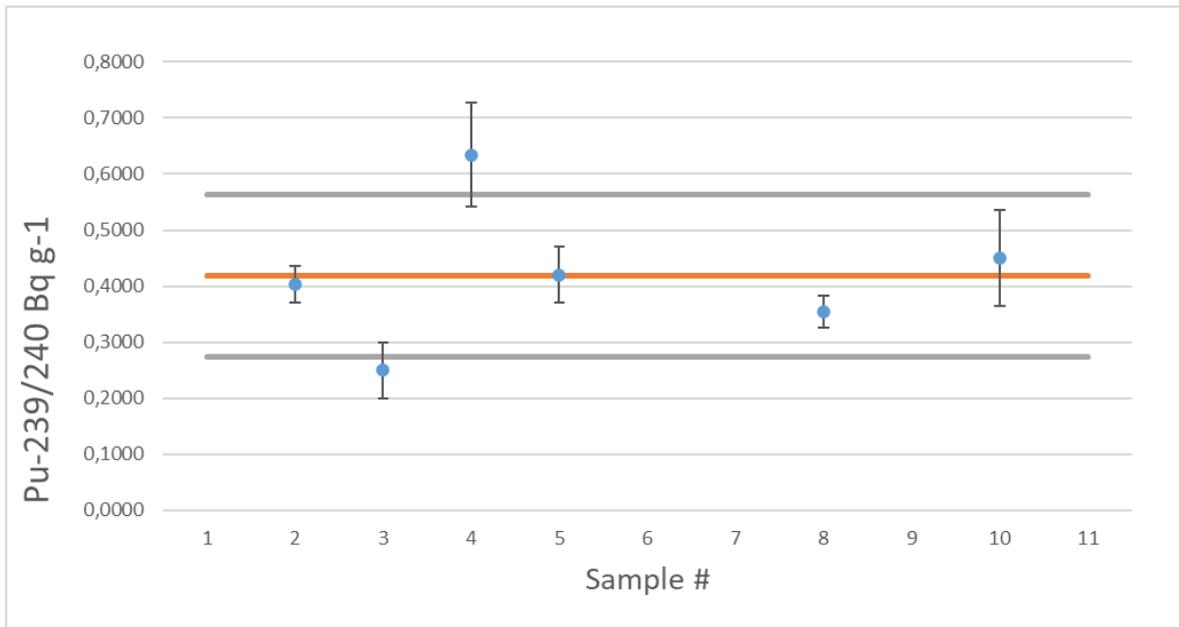
assigned value (%)				
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The statistical analysis of Pu-238 results (Table 8, Table 9, Figure 19) were carried out using 6 data entries and 22 iterations. The assigned value for the Pu-238 activity concentration was calculated to be  $2,2 \pm 0,6$  Bq/g ( $k=2$ ). The robust standard deviation of the assigned value was 14,2% and therefore it was used in calculation of the z score. The Table 9 and Figure 19 results show that all other data entries were in acceptable range ( $z \leq 2$ ) except Sample 3 which is in warning signal range ( $2 < z < 3$ ).



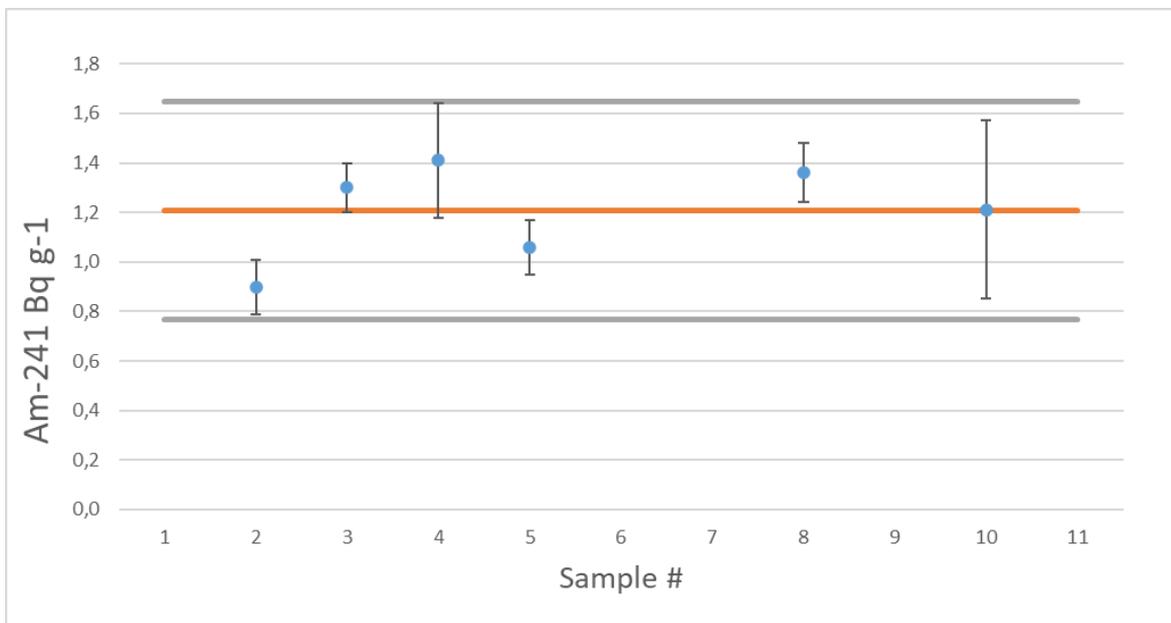
**Figure 19. Final Pu-238 results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

The statistical analysis of Pu-239,240 results (Table 8, Table 9, Figure 20) were carried out using 6 data entries and 13 iterations. The assigned value for the Pu-239,240 activity concentration was calculated to be  $418 \pm 145$  mBq/g ( $k=2$ ). The robust standard deviation of the assigned value was 34,0 % and therefore standard uncertainty of assigned value (17.4%) was used in calculation of the z score. The Table 9 and Figure 20 results show that four out of six data entries were in acceptable range ( $z \leq 2$ ) whereas Sample 3 was warning signal range ( $2 < z < 3$ ) and Sample 4 in unacceptable range ( $z \geq 3$ ).



**Figure 20. Final Pu-239,240 results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

The statistical analysis of Am-241 results (Table 8, Table 9, Figure 21Figure 20Figure 19) were carried out using 6 data entries and 4 iterations. The assigned value for the Am-241 activity concentration was calculated to be  $1.2 \pm 0.4$  Bq/g ( $k=2$ ). The robust standard deviation of the assigned value was 18.3 % and therefore it was used in calculation of the z score. The Table 9 and Figure 21 results show that all the data entries were in acceptable range ( $z \leq 2$ ).



**Figure 21. Final Am-241 results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .**

The statistical analysis of Cm-243,244 results with changed reference date (Table 8, Table 9, Figure 22Figure 21Figure 20Figure 19) were carried out using 6 data entries and 2 iterations. The assigned value for the Cm-243,244 activity concentration was calculated to be  $5.4 \pm 2.9$  Bq/g ( $k=2$ ). The robust standard deviation of the assigned value was 52,5 % and standard uncertainty of assigned value was used in calculation of the z score. However, the standard uncertainty of the assigned value was also large (26.8%)

signalling scattering of the results. The Table 9 and Figure 22 results show that only one result (Sample 2) is in an acceptable range ( $z \leq 2$ ) whereas all the other five results are given a warning signal ( $2 < z < 3$ ). Comparison of the preliminary (Figure 10) and final Cm-243,244 results (Figure 22), which were calculated to different reference dates, do not seem to differ in general trend. Therefore, calculation of the Cm-243,244 in closer to the analysis time reference date does not seem to have a significant effect on the result. As the Am-241 results were well comparable whereas Cm-243,244 results were not, there can be other parameters affecting the results. One reason could be the difference in chemical properties and different radiochemical procedures of the participating laboratories. As there is a lack of a good Cm tracer (e.g., price and purity) laboratories are forced to use Am as the tracer. Additionally, decay corrections may have affected the results to some extent. The decay correction information is given in Table 10.

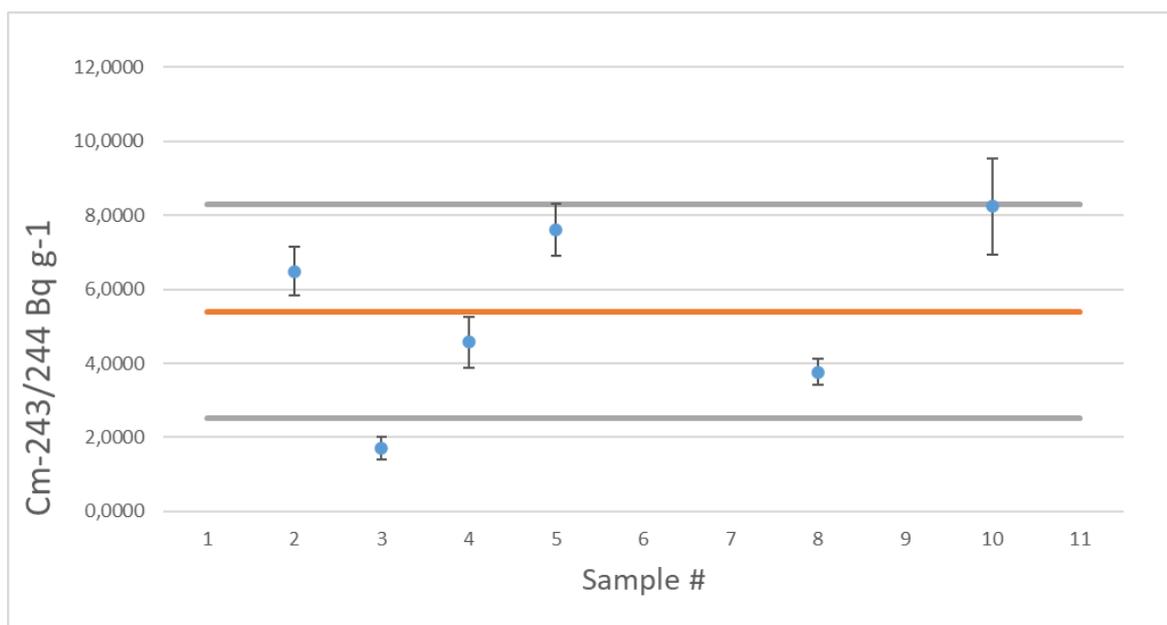


Figure 22. Final Cm-243,244 results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of  $k = 2$ .

Table 9. z scores of Pu-238, Pu-239,240, Am-241, and Cm-243,244. Acceptable  $z \leq 2.0$  in green, warning signal  $2.0 < z < 3.0$  in orange, unacceptable  $z \geq 3.0$  in red.

Sample	z score			
	Pu-238	Pu-239,240	Am-241	Cm-243,244
2	1.3	0.2	1.4	1.9
3	2.6	2.3	0.4	2.8
4	0.0	3.0	0.9	2.2
5	0.2	0.0	0.7	2.2
6	-	-	-	-
7	-	-	-	-
8	0.1	0.9	0.7	2.2
9	-	-	-	-
10	0.1	0.4	0.0	2.2

Table 10. Decay correction calculation of Cm-243,244 results.

Sample	Decay correction calculation

2	Decay-corrected using the half-life of $^{244}\text{Cm}$ only
3	Not reported
4	Decay-corrected using the half-life of $^{244}\text{Cm}$ only
5	Decay-corrected using the half-life of $^{244}\text{Cm}$ only
6	-
7	-
8	Decay-corrected using the half-life of $^{244}\text{Cm}$ only
9	-
10	Decay-corrected using the half-life of $^{244}\text{Cm}$ only

### 10.3. Extended statistical analysis results

The results for Am-241 were analysed using a combination of  $\zeta$ -score, z-score and relative uncertainty test [Jerome and Harms, 2022]. This approach identifies improbable deviations from the assigned value where the  $\zeta$ -score is greater than 5.026 and bases the value of  $\sigma_{pt}$  on the data submitted by all participants. However, the dataset is too small to make this approach meaningful although some useful information can be extracted.

If the means of the results for Am-241 are computed, the results are shown in Table 11.

**Table 11. Complementary analysis of all Am-241 results.**

NKS Am-241 (all)	y	u(y)	$\pm$ %	$\frac{\chi^2}{n-1}$
<b>Mandel-Paule mean</b>	1.198	0.082	6.9%	1.00
<b>Weighted mean</b>	1.169	0.026	2.3%	9.86
<b>Arithmetic mean</b>	1.21	0.20	16.2%	10.27

The result of Sample 2 *might* be considered an outlier, but rejection of this data point from a dataset of only six results is questionable. However, if this is done, the results are shown in Table 12.

**Table 12. Complementary analysis of Am-241 results without a suggested outlier.**

NKS Am-241 (Sample 2 rejected)	y	u(y)	$\pm$ %	$\frac{\chi^2}{n-1}$
<b>Mandel-Paule mean</b>	1.263	0.064	5.1%	1.00
<b>Weighted mean</b>	1.249	0.030	2.4%	4.57
<b>Arithmetic mean</b>	1.27	0.14	10.9%	4.67

The outcome of this analysis is to shift the means slightly, and in the case of the Mandel-Paule mean to expand the uncertainty by forcing the reduced  $\chi^2$  value to 1 by adding additional uncertainty to each of the contributing values and so the Mandel-Paule mean and uncertainty are reasonable estimates for the assigned value and uncertainty.

## 11. Summary

DTM alpha emitters and gross alpha were determined in the spent ion exchange resin, which was also analysed for betas and gammas in the previous project (DTM-Decom III project) [Leskinen et al. 2022a, 2022b]. The focus was on the Am-241 and uranium, plutonium, curium isotope analysis with optional gross alpha, Pu-241, and Np-237 analyses. The radiochemical separation of actinides was implemented mainly using ion exchange and extraction chromatography with different resins combination. For alpha spectrometric measurements, the measurement targets were mainly prepared using electrodeposition, while micro-precipitations on filters were also used. Measurements of actinides radionuclide were carried out using by alpha- and gamma spectrometry and ICP-MS. The preliminary results were discussed to see trends and also suggest possible correction actions. The final results were analysed according to the ISO 13528 standard when at least 5 individual data entries (above detection limit) were submitted. The assigned values, to which results were comparable, were calculated from the submitted results and the performance was assessed using z score which indicates result's deviance from the assigned value.

The results of uranium isotopes showed that ICP-MS technology was needed for detection because of the low concentration of uranium isotopes in this resin sample. Neither gamma nor alpha spectrometry method are sufficient good for the measurement, especially for U-234 and U-235, among it, the limit of detection for gamma spectrometry is the highest one. However, not enough data entries of uranium isotopes (i.e.,  $\geq 5$ ) above limit of detection were submitted for statistical analysis.

The assigned value for Pu-238 calculated from the reported results was  $2.2 \pm 0.6$  Bq/g ( $k=2$ ) and 5 of 6 reported results were within the acceptable range of z score. The assigned value for Pu-239,240 was  $418 \pm 145$  mBq/g ( $k=2$ ) and four out of six results were in acceptable range of z score.

The final Pu-241 results were significantly improved with careful selection of LSC measurement parameters and corrective calculations due to impurities in the yield standard. However, the four data entry results varied even though they were in same order of magnitude.

The assigned value for Am-241 calculated from the reported results was  $1.4 \pm 0.4$  Bq/g ( $k=2$ ) and all six results were within the acceptable range of z score.

No final Np-237 result was reported, although the preliminary Np-237 results were submitted because yield of Np calculated from Pu-242 was considered not appropriate due to significantly different chemical behaviours of two elements in the separation procedure.

The curium isotope results indicated that use of Am-243 tracer for yield monitoring may cause scattering of results due to their possibly different chemical behaviours. A large uncertainty was seen in the Cm-243,244 assigned value of  $5.4 \pm 2.9$  Bq/g ( $k=2$ ). Additionally, only one out of six z scores were in acceptable range whereas all the others were in warning signal range.

The final gross alpha results were significantly improved with careful selection of LSC measurement parameters as a clear outlier of preliminary results (one out of three) was remeasured to correspond the other results. Significantly higher amount of beta emitters in the sample had increased the alpha signal in the LSC spectrum of the outlier.

As a conclusion, the RESINA project has further strengthened collaboration between radiochemistry laboratories. Similarly to DTM Decom I to III projects, RESINA project produced interesting set of results, which will be further analysed and discussed in a peer reviewed publication.

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## 13. References

American National Standard (1996) Performance Criteria for Radiobioassay, HPS N13.30: Health Physics Society

Atomic and Nuclear Data Online application Nucléide - Lara, provided by National Laboratoire Henri Becquerel, <http://www.lnhb.fr/nuclear-data/module-lara/>

Calin, M. R., Saizu, M. A. and Radulescu, I., Assets on energy and efficiency calibration of an alpha spectrometry system using standard sources, J Radioanal Nucl Chem (2013) 298: 55 - 66, 2013

Chen, Q.J., Aarkrog, A. Nielsen, S.P., Dahlgaard, H., Nies, H., Yu, Y., Mandrup, K. (1991) Determination of plutonium in environmental samples by controlled valence in anion exchange. Risø National Laboratory Report Risø-M-2856

Currie, L. A., (1968). Limits for qualitative detection and quantitative determination. Application to radiochemistry. Anal Chem 40(3): 586-593

Eichrom Technologies (2014) AMERICIUM IN WATER, Analytical Procedure, Method No: ACW04

Harms, A.V. (2009) A New Approach for Proficiency Test Exercise Data Evaluation. Accreditation and Quality Assurance, 14:253-261. DOI: 10.1007/s00769-009-0511-1

Hou, X., Anderot, M., Ekerljung, L., Salminen-Paatero, S., Olszewski, G., Öhlin, H., Davidsson, M., Bruzell, F., Tovedal, A., Rautio, S., Allard, S., Hatakka, A., Wijk, S., Eriksson, M., Åberg, H., Settervik, E., Suutari, T., Vesterlund, A., Lindahl, P., Kangas S., Hovi, P. (2020) Determination of important alpha emitters in nuclear and environmental samples – OptiMethod 2019 project report. NKS-436, Roskilde, Denmark.

Ikäheimonen (2000) Measurement of Pu-241 in environmental samples, JRNC 243(2):535-541

International Standard ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison.

Jerome, S.M and Harms, A.V. (2022) Proficiency Test Data Interpretation and Data Rejection. Applied Radiation and Isotopes, *In press*

Jerome, S.M. and Skipperud, L., (2023?) Unpublished data

Kressin, I.K., (1977) Electrodeposition of plutonium and americium for high resolution  $\alpha$ -spectrometry. Anal Chem 49(6):842-846 DOI <https://doi.org/10.1021/ac50014a044>

Leskinen, A., Tanhua-Tyrkkö, M., Kekki, T., Salminen-Paatero, S., Zhang, W., Hou, X., Stenberg Bruzell, F., Suutari, T., Kangas, S., Rautio, S., Wendel, C., Bourgeaux-Goget, M., Stordal, S., Fichet, P., Gautier, C., (2020a) Intercomparison exercise in analysis of DTM in decommissioning waste, NKS-429 report ISBN 978-87-7893-519-9

Leskinen, A., Salminen-Paatero, S., Gautier, C., Rätty, A., Tanhua-Tyrkkö, M., Fichet, P., Kekki, T., Zhang, W., Bubendorff, J., Laporte, E., Lambrot, G., Brennetot, R., (2020b) Intercomparison exercise on difficult to measure radionuclides in activated steel: statistical analysis of radiocanalytical results and activation calculations, J Radioanal Nucl Chem, 324:1303-1316

Leskinen, A., Tanhua-Tyrkkö, M., Salminen-Paatero, S., Laurila J., Kurhela C., Hou, X., Stenberg Bruzell, F., Suutari, T., Kangas, S., Rautio, S., Wendel, C., Bourgeaux-Goget, M., Stordal, S., Isdahl, I., Gautier, C., Laporte, E., Giuliani, M., Bubendorff, J., Fichet, P., (2021a) DTM-Decom II Intercomparison exercise in analysis of DTM in decommissioning waste NKS-441 report ISBN 978-87-7893-533-5

Leskinen, A., Gautier, C., Rätty, A., Kekki, T., Laporte, E., Giuliani, M., Bubendorff, J., Laurila J., Kurhela C., Fichet, P., Salminen-Paatero, S. (2021b) Intercomparison exercise on difficult to measure radionuclides in activated concrete - statistical analysis and comparison with activation calculations, J Radioanal Nucl Chem, 329:945-958

Leskinen, A., Dorval, E., Salminen-Paatero, S., Hou, X., Jerome, S., Jensen, K.A., Skipperud, L., Vasara, L., Rautio, S., Bourgeaux-Goget, M., Moussa, J., Stordal, S., Isdahl, I., Gautier, C., Baudat, E., Lambrot, G., Giuliani, M., Colin, C., Laporte, E., Bubendorff, J., Brennetot, R., Wu, S.-S., Ku, Y.H., Wei, W.C., Li, Y.C., Luo Q.T. (2022a) DTM-Decom III Intercomparison exercise in analysis of DTM beta and gamma emitters in spent ion exchange resin, NKS-report NKS-457, ISBN 978-87-7893-550-2

Leskinen, A., Dorval, E., Baudat, E., Gautier, C., Stordal, S., Salminen-Paatero, S. (accepted 2022b) Intercomparison exercise on difficult to measure radionuclides in spent ion exchange resin J Radioanal Nucl Chem

López-Lora, M., Levy, I., Chamizo, C., (2019) Simple and fast method for the analysis of  $^{236}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  from seawater samples by Accelerator Mass Spectrometry. Talanta, 200:22–30. DOI <https://doi.org/10.1016/j.talanta.2019.03.036>

Mercedes López-Lora, M., Chamizo, E., Villa-Alfagem, M., Hurtado-Bermúdez, S., Casacubert, N., García-León, M. (2018) Isolation of  $^{236}\text{U}$  and  $^{239,240}\text{Pu}$  from seawater samples

and its determination by Accelerator Mass Spectrometry. *Talanta*, 178, 202–210 DOI <https://doi.org/10.1016/j.talanta.2017.09.026>

Salminen-Paatero, S., Meriläinen, V., Hou, X., Kaipainen, M., Vaaramaa, K., Lindahl, P., Rautio, S., Kangas, S., Jortikka, S., Vasara, L. (2021) Intercomparison for separating Pu and Am from environmental samples by a joint radioanalytical method. NKS-442, Roskilde, Denmark.

Sidhu, R.S., Østmo, K., and Ruud, A.B. (2004) Sequential extraction chromatographic separation of Pu, Am, Cm and Sr in soil, sediment and urine samples in “Extraction Chromatographic Separation of Sr, Pu and Am in Environmental Samples” PhD Thesis Unipub AS, Oslo

Sidhu, R. (2004) Extraction Chromatographic Separation of Sr, Pu and Am in Environmental Samples, PhD Thesis Unipub AS, Oslo

Sidhu, R.S. (2002) Sequential analysis of Sr, Pu, Am and Cm in low-level liquid radioactive effluents, *Radioprotection – Colloques*, Vol. 37, C1, 917-920

Strisovska, J., Drabova, V., Kuruc, J. (2013) The preparation of the Np-239 tracer from Am-243 and the purification of the stock solution *J Radioanal Nucl Chem* 298:1179-1183.

Talvitie, N.A. (1972) Electrodeposition of actinides for  $\alpha$ -spectrometric determination. *Anal Chem*, 44(2), 280–283 DOI: <https://doi.org/10.1021/ac60310a013>

UKNNL internal procedures WRC-SOP-0401 v21, *Operation of gamma spectrometers*, WRC-SOP-0409 v14 *Analysis of Pu alpha, Cm and Am in Aqueous Waste Samples*, WRC-SOP-0415 v11, *Analysis of Pu-241 in Aqueous Waste Samples*, WRC-SOP-0414 v8, *Determination of Uranium Isotopes*, WRC-SOP-0403 v16, *The Analysis of Dissolution Liquor for Total Alpha and Beta*, WRC-SOP-0459 v18, *Dissolution of Radioactive Waste Samples*

Wang, Y., Hou, X., Zhang, W., Zhang, L., Fan, Y. (2021) Determination of ultra-low  $^{236}\text{U}$  in environment samples using ICP-MS/MS measurement and chemical separation, *Talanta*, 224:121882

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Key words

Decommissioning, Difficult-to-measure alpha radionuclides,  
intercomparison exercise, spent ion exchange resin