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Intercomparison exercise on difficult to measure alpha radionuclides in spent ion exchange resin

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Abstract

In radiochemical analysis of decommissioning waste, reference materials are not commercially available and consequently intercomparison exercises are needed for method validations. This paper reports the results from an intercomparison exercise focusing on analyses of α-emitter radionuclides in spent ion exchange resin. The exercise and statistical analysis of the submitted results were carried out based on ISO 13528 standard according to which the assigned values were calculated from the participant's results and the performances were assessed using z-scores, which showed excellent performance for all ^{241}Am analyses, good performance for ^{238}Pu analyses, tolerable performance for ^{239,240}Pu analyses, and questionable ^{243,244}Cm analyses.

Keywords Difficult to measure alpha radionuclides · Intercomparison exercise · Decommissioning waste · Operational waste · Spent ion exchange resin · ISO 13528

Introduction

Characterisation of radioactive decommissioning waste may be divided into (i) easy to measure (ETM), and (ii) difficult to measure (DTM) radionuclides. The ETMs are analysed using γ-spectrometry, which is a non-destructive characterisation method for γ-emitters. The DTMs, which may be further divided to α- and β-emitters, require destructive radiochemical characterisation methods which include separation of the DTMs from the matrix and from other interfering radionuclides or elements. Even though α- and β-emitting radionuclides are radiochemically separated and purified using similar methods (including ion exchange chromatography, extraction chromatography and precipitation), the measurement techniques generally are α-spectrometry for α-emitters and liquid scintillation counting (LSC) for β-emitters. The measurement source in α-spectrometry is ideally a very thin layer of the purified DTM fraction on a smooth surface. Preparation of the measurement source can be carried out using micro-coprecipitation on a filter or electrodeposition on a metal disc. The measurement source is measured in vacuum at a set distance from the detector. The thin layer minimises self-absorption of α-particles and consequently the α-spectrum can exhibit discrete energy specific peaks. Widening of the peaks is linked with self-absorption of the α-particles and the limitations of the detector system that lowers the resolution of the measured α-spectrum and can make the interpretation of the spectrum more complex. In LSC measurements of β-emitters, an aliquot of purified fraction is mixed with a scintillation cocktail prior to measurement. Ideally, the chemical and colour quenching from the separated material should be minimised. In addition to α-spectrometry and LSC measurements, measurement of DTMs can be carried out using mass spectrometric techniques, such as inductively coupled plasma mass spectrometry (ICP-MS); both techniques provide isotopic information

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on the sample and ICP-MS may provide information about the sample that is inaccessible by radiometric techniques, such as the determination of ^{239}Pu and ^{240}Pu. The mass spectrometric analyses are challenged by isobaric and polyatomic interferences from isotopes and molecules with similar masses, complicating the determination of DTM content in the sample. However, significantly lower detection limits at µBq levels may be reached using ICP-MS compared to LSC, which detection limits are typically at the mBq level [1].

Characterisation of decommissioning waste relies on application of material specific scaling factors which link a key ETM (e.g., ^{60}Co in steel) to DTMs (e.g., ^{55}Fe and ^{63}Ni in steel). Scaling factors are determined preferably before dismantling to measure only the ETMs and calculate the DTMs when large number of waste packages are characterised during dismantling. As with any analytical method, method validation is required for reliable results and to demonstrate confidence in such results. Commercial reference materials can be analysed using the analytical method and satisfactory results strongly support validation of the method. Participation in intercomparison exercises supports method validation.

Four years of intercomparison exercises within the Nordic Nuclear Safety Research (NKS) community on radiochemical analysis of DTM radionuclides in decommissioning waste were organised between 2019 and 2022 [2–5]. The capabilities of the participants from Nordic and non-Nordic countries ranged from status of building up the capabilities to advanced laboratories with routine analysis services. The studied materials were activated steel [2, 6], activated concrete [3, 7] and spent ion exchange resin [4, 5, 8]. The exercises were organised, and the results were statistically analysed according to the requirements of the ISO 13528 standard [9]. The coordinator carried out the homogeneity studies of the materials used with γ-spectrometric analysis of a key ETM, which consistently showed < 2% relative standard deviation (RSD) [2–5]. Additionally, the homogeneities of individual materials were calculated and confirmed according to the ISO 13528 standard.

Individual partners had several months to carry out the analyses; discussions on the challenges and exchange of information were encouraged. The coordinator collected the analysis results calculated on a reference date and organised a preliminary meeting, in which the preliminary results were discussed and possible reasons for deviations from the general trends were suggested. Where a result seemed to be a clear outlier (e.g., an order of magnitude difference to the general trend), the partner was contacted in advance and advised to check the results for possible calculation errors and similar errors, referred to as 'blunders' in ISO 13528. After the preliminary meeting, each partner had about a month to re-check their results (e.g., update of quenching curves) and submit the final results. The project reports include both the preliminary and final results [2–5] whereas the peer-reviewed articles include the final results with more detailed statistical analysis and critical considerations regarding the analysis methods and radionuclides [6–8].

This paper reports the analysis of α-emitting DTM nuclides in the spent ion exchange resin, which β-emitting DTM nuclides and ETMs were studied in the previous project [5]. Nine laboratories participated in the exercise named RESINA. The main α-emitting DTM nuclides analysed were ^{241}Am, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, ^{239,240}Pu, ^{242}Cm, and ^{243,244}Cm with gross α-activity measurements and ^{241}Pu (β-emitter) as optional analyses. Additionally, preliminary ^{237}Np results were also submitted but not reported in the final results as measurement is compromised by the lack of a suitable yield tracer [5]. Statistical analyses according to the ISO 13528 standard were carried out for sets of results for which at least five above limit of detection results (one result per partner) were submitted. Additionally, an example of an extended data analysis is shown for ^{241}Am results.

Sample history, homogeneity and stability

The spent ion exchange resin, which had already been studied in the previous intercomparison exercise named DTM Decom III [4], was a nuclear grade FINEX C/A 850 H mixed exchanger with 1:1 ratio of cation and anion exchange capacity. The resin particle sized was between 10 to 200 µm. The resin had been used for cleaning of a primary circuit of a nuclear power plant and it was relatively fresh as short-lived radionuclides, such as ^{54}Mn, were detected [4]. Homogeneity and stability of the samples were established in the DTM Decom III project according to the ISO 13528 standard [4].

Origin of α-emitting DTM nuclides in spent ion exchange resin

The ETMs and DTMs in the primary circuit of a nuclear reactor are divided into fission products, coolant activation products, and corrosion products [10]. The ETMs and DTMs in the coolant are removed from circulation via cleaning loops with ion exchange resins. The α-emitters originate from the nuclear fuel. For example, a light water reactor spent fuel with a burnup of 50 GWd/tHM consists of approximately 93.4% uranium (approximately 0.8% ^{235}U), 5.2% fission products, 1.2% plutonium, and 0.2% minor transuranium elements, mainly neptunium, americium and curium [11]. Although the fuel is in the form of low solubility UO_2 and the fuel cladding is relatively inert, some activity does originate from the fuel, although most of the radionuclides in the primary circuit originates from corrosion and consequently there are overwhelmingly more β-emitting radionuclides than α-emitters in the spent ion exchange resin.

Methodology for statistical analysis

The intercomparison exercises and statistical analyses in the DTM Decom I-III and RESINA projects were performed according to the ISO 13528 standard on proficiency testing by interlaboratory comparison [9]. As noted before, the spent ion exchange resin came from an operating nuclear power plant and thus the reference values of α-emitting DTM nuclides were not known in advance. Therefore, the assigned values, against which the performances were assessed, were calculated from the reported results as recommended in the ISO 13528 [9]. The assigned values, robust mean values and robust standard deviations, were calculated using Algorithm A, which is robust for outliers up to 20% [9]. The iterations of the robust mean and standard deviations were carried out until there was no change in the third significant figure [9]. The performance assessments were carried out using z-score of Eq. (1), which is the recommended method when the assigned value is calculated from the submitted results [9]. When the robust standard deviation was large ($> 20\%$), the uncertainty of the assigned value from equation was used as σ_{pt} [9]. The submitted results (x_i) were assessed against the assigned values derived from the participants' results [9]. The z-score results were acceptable when $|z| \leq 2.0$, a warning signal was given for results with $2.0 < |z| < 3.0$, and $|z| \geq 3.0$ results were unacceptable [9].

$$z_i = \frac{(x_i - x_{\text{pt}})}{\sigma_{\text{pt}}} \tag{1}$$

where.

x_{pt}:the assigned value.

σ_{pt}:standard deviation for the proficiency assessment

$$u(x_{\text{pt}}) = \frac{1.25 \bullet s^*}{\sqrt{p}} \tag{2}$$

where.

s^*:robust standard deviation of the results.

p:number of samples

In addition to the previous exercises, an extended data analysis was carried out for the ^{241}Am results. If the dataset is large enough, the data analysis may be extended, and outliers from the dataset identified using the Pierce criterion [12, 13]; note that this does not necessarily establish an assigned value, although it may be used to do so if the intercomparison exercise organiser is confident that there are no systematic biases within the dataset. Using the culled dataset allows the establishment of σ_{pt}, based on the results submitted by participants. Additionally, the quality of reported uncertainties may be established through means of an R-score which is calculated using Eq. (3).

$$R_i = \frac{\ln u_{\text{rel}}(L_i) - \ln u_{\text{rel}}(\text{med})}{\sigma_{\ln u_{\text{rel}}(\text{med})}} \tag{3}$$

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

Having set the pass fail criteria for the ζ-score, z-score and relative uncertainty tests, the outcomes may be combined [14] and the dataset may be analysed as follows:

- Results with no reported uncertainty are rejected.
- The ζ-score is calculated and ζ-scores > 5.026 (a different limit may be used) are flagged as improbable deviations, where:

$$\zeta = \frac{\left| x_i - x_{\text{pt}} \right|}{\sqrt{u^2(x_i) + u^2(x_{\text{pt}})}}$$

- The z-score is calculated as usual, where $\sigma_p = A \bullet u_{\text{rel}}(\text{med})$ and $u_{\text{rel}}(\text{med})$ is determined after rejection of outliers according to the Pierce criterion.
- Finally, the R-score is calculated as above.

The outcome from the three tests may be interpreted as explained in Table 1. The combination of these tests allows the participant result to be assessed against the assigned value, and comparison with the general performance of the participants in the intercomparison exercise.

Experimental

The radiochemical analysis methods for α-emitting DTM nuclides included utilisation of acid digestion or leaching, precipitations, and ion exchange and chromatographic column separations prior to measurement of the separated and purified actinide fractions (Table 2). In previous exercises, the β-emitting DTM nuclides were mainly analysed using LSC and in one case using ICP-MS (^{90}Sr in spent ion exchange resin) [4]. However, in this exercise four measurement techniques were implemented.

Table 1 ζ-, z- and R-test data interpretation

ζ-test	z-test	R test	Interpretation
Pass	Pass	Pass	Reported result is acceptable
Pass	Pass	Fail	Reported result is questionable
Pass	Fail	Pass or fail	
Fail	Pass	Pass or fail	
Fail	Fail	Pass or fail	Reported result is discrepant

Table 2 Overview of radiochemical analysis methods for Samples 2–10

Sample			2	3	4	5	6	7	8	9	10
Mineralisation	Pre-treatment		-	-	-	×	-	-	-	-	-
	Acid digestion		×	×	×	×	×	×	×	×	×
	Complete destruction of the matrix		-	×	×	×	-	×	×	×	-
Precipitation	Coprecipitation		×	-	-	-	-	-	×	-	-
Resin	TEVA®		×	-	-	-	-	-	×	-	-
	UTEVA®		-	-	×	-	×	×	-	×	×
	TRU®		-	-	×	×	×	×	-	-	×
	DGA®		×	-	-	-	-	-	×	-	-
	AG1×8® / anion exchange		-	-	-	-	-	×	-	×	×
Source preparation	Micro-coprecipitation		×	-	-	-	-	-	-	-	-
	Resolve-filter		-	-	-	-	×	×	-	-	-
	Evaporation on planchet		-	-	-	-	-	-	×	-	-
	Electrodeposition		-	×	×	-	-	-	×	×	×
Measurement	α-spectrometry	^{234}U, ^{235}U, ^{238}U	-	×	-	×	×	-	-	×	×
		^{238}Pu, ^{239,240}Pu	×	×	×	×	×	-	×	×	×
		^{241}Am	×	×	×	×	×	-	×	×	-
		^{242}Cm, ^{243,244}Cm	×	×	×	×	×	-	×	×	×
		Gross α	-	-	-	-	-	-	×	-	-
	γ-spectrometry	^{241}Am	-	×	-	-	-	-	-	-	×
		^{235}U	-	×	-	-	-	-	-	-	-
	Mass spectrometry	^{234}U, ^{235}U, ^{238}U	-	×	-	-	-	-	-	×	-
	Liquid scintillation counting	^{241}Pu	-	×	×	-	-	-	×	-	×
		Gross α	-	×	-	-	-	-	-	-	×

- α-spectrometry for the measurement of gross α-activity measurements, ^{241}Am, uranium, plutonium, curium isotopes,
- γ-spectrometry for measurement of ^{241}Am and ^{235}U,
- mass spectrometry for measurement of uranium isotopes, and
- LSC for the measurement of gross α-activity and ^{241}Pu.

The detailed account of preliminary (replicate results included) and final results are presented by Leskinen et al. [4] whereas general descriptions are given in following subchapters and Table 2. The statistical analysis of the final results was carried out when at least 5 above limit of detection data entries per radionuclide and only one data entry per sample (no replicate results) were available.

Overview of the radiochemical methods

The published radiochemical methods [15–28] used for the α-emitting DTM nuclide analyses were presented by Leskinen et al. [5]. Resin samples from 10 to 250 mg were acid digested in different mixtures of acids (e.g., HNO_3, HCl, H_2SO_4) and oxidising agents (e.g., H_2O_2, Fenton's reagent) with addition of heat on a hotplate, microwave, sand bath or under reflux. Pre-treatment with drying at 150 °C and ashing at 500 °C was carried out for Sample 4. Radioactive tracers were used in yield determinations in all Samples (Samples 2–10) and additionally carriers and hold-back carriers, such as Fe, Co, Ni, Eu, Cs, Sb and Sr, were added in Samples 2 and 8. The separation techniques included precipitation including actinide coprecipitation with iron hydroxide and lanthanum coprecipitation in ammonia, the use of ion exchange resin (AG1×8®) and extraction chromatography media (TEVA®, TRU®, UTEVA® and DGA®). The purified fractions contained:

- uranium isotopes,
- plutonium isotopes and possibly neptunium, and
- ^{241}Am and curium isotopes.

The measurement sources for the α-spectrometry analyses were prepared using precipitation (Samples 2 and 5) and electrodeposition (Samples 3, 4, 8, 9, and 10).

Overview of gross α determination

The gross α methods included complete destruction of the matrix, evaporation and measurement using α-spectrometry (Sample 7), acid leaching and direct mixing of the resin

residue in acid with liquid scintillation cocktail (Sample 3), and acid leaching, filtration, evaporation of aliquot and mixing with liquid scintillation cocktail (Sample 10). Some of these techniques have been published as ISO standards [29–31].

Overview of the measurement techniques

Measurement of ^{241}Am, uranium, plutonium, and curium isotopes were carried out using α-spectrometry. Additionally, uranium isotopes in Samples 3 and 8 were also analysed using HR-ICP-MS and ICP-MS/MS, respectively. Gamma spectrometry was also utilised in measurement of ^{241}Am and ^{235}U. The γ-spectrometric analysis results in the previous exercise [4] did not detect these radionuclides most likely due to masking of the low energy signals, such as ^{241}Am (γ-rays with 59.5 keV energy and 35.8% emission probability [32]) by the large number of γ-emitters or due to limit of detection. Nevertheless, γ-spectrometric measurements were carried out for detection of ^{235}U and ^{241}Am in purified fractions (Sample 3) and ^{241}Am in the original and acid digested sample (Sample 10). LSC was utilised in measurement of gross α-activity and ^{241}Pu.

Results and the statistical analyses

The masses taken for the radiochemical analyses varied from 10 to 250 mg (Table 3). Small sample sizes are appropriate in cases when the samples are homogenous and activity concentrations are high enough for quantitative analysis. In this study, the particle size of the sample ranged from 10–200 um. Whether small subsamples of < 100 mg can be considered to be representative is dependent on the homogeneity of the material at the sample size used, and must be considered on a case-by-case basis, since the homogeneity measurements described earlier were carried out with samples of approximately 0.8 g, and are not strictly applicable to smaller sample sizes. Furthermore, the relative uncertainty of mass measurements at low sample masses may become comparable to other contributing uncertainties.

The acid digestions resulted in total destruction of the matrix in all cases except for Samples 2, 6 and 10, which were filtered prior to radiochemical separations. Sample 2 had been treated with *aqua regia* and H_2O_2 on a hot plate. Sample 6 had been treated with mixture of H_2SO_4, HNO_3 and $HClO_4$ on a sand bath. Sample 10 had been treated with Fenton's reagent and after filtration, the residue was treated with HNO_3. The complete destruction of the matrix was achieved with HNO_3 and H_2O_2 mixture in a microwave oven (Sample 3), HCl, HNO_3 and H_2O_2 mixture on a hot plate (Sample 4), HNO_3 treatment in a microwave oven (Samples 5 and 9), HNO_3 and HCl mixture in a microwave

Table 3 Uranium, plutonium, and americium chemical yields and masses (preliminary results with replicates)

Sample	Mass (mg)	Yield (%) (uncertainties are stated with $k=2$)		
		Uranium	Plutonium	Americium
2	110	-	19 ± 1	55 ± 6
	180	-	18 ± 1	52 ± 6
3	40	73 ± 2	28 ± 3	12 ± 0
	50	77 ± 3	20 ± 1	13 ± 0
	50	71 ± 2	26 ± 2	13 ± 1
4	30	-	66 ± 8	66 ± 11
	10	-	-	-
5	10	62	102	112
	20	83	107	114
6	100	< 1	< 1	< 1
	100	< 1	< 1	< 1
	60	< 1	< 1	< 1
7	130	-	-	-
8	100	83 ± 3	-	-
	290	-	89 ± 3	83 ± 3
9	10	Not calculated	-	-
	10	Not calculated	-	-
10	250	82	90	21

oven (Sample 7), and HNO_3, HCl, and H_2O_2 mixture under reflux (Sample 8). The success of complete destruction of the matrix does not seem to be linked with sample masses (Table 3) nor acids whereas a link can be drawn with use of a microwave oven in which temperature, pressure, acid and time contribute to the decomposition process. Complete destruction of the matrix had been also achieved without a microwave oven when the sample had been pre-treated with drying and ashing (Sample 4) and under a reflux (Sample 8). The ashing had been carried out at 500 °C in order to destroy the organic matter through combustion of the styrene–divinylbenzene copolymer structure of the resin prior to the acid digestion. At the above-mentioned temperature, loss of actinides or formation of difficult to dissolve species should not occur. However, complete destruction of the matrix is not necessary when the studied radionuclides are quantitatively extracted using acid leaching. For example, weak acid resins have a high affinity for the H^+ and are consequently easily regenerated with strong acids whereas strong acid resins retain their ability to exchange cations across the entire pH range. Use of oxidising acids such as HNO_3 attack the resin structures causing degradation of the matrix and consequently both regeneration and degradation of the resin occurs. Therefore, the resin specifications should be considered in selection of the acid treatment method. In this study, the resin was a mixture of strong acid cation and strong base anion exchange resins and consequently

complete destruction of the matrix is advisable even though no causation can be seen between the activity concentration results of the samples with complete and incomplete acid digestions. Complete destruction of the matrix could be also carried out using alkali fusion, which is an efficient method for treatment of large sample sizes (e.g., in analysis of low activity samples).

Table 3 summarises the preliminary uranium, plutonium, and americium yield results. The results show that the uranium yields were mainly good varying between approximately 60% to 80% whereas wide range of yields were reported for plutonium (from estimated < 1% to approximately 100%) and americium (from < 1% to 110%). The Sample 6 yield results suffered from significant challenges in their determinations and consequently the yield were estimations. The curium results were calculated from the americium yields, as ^{243}Am was used as a tracer for Cm isotopes as well. Longer lived curium isotopes are not available as tracers for radiochemical analysis of ^{242,243,244}Cm, and therefore ^{243}Am is commonly used as a tracer isotope in analysis of both ^{241}Am and ^{242,243,244}Cm, due to adequately similar chemical behaviour [33] of these two elements.

Uranium isotopes

The final uranium isotope analysis results were not statistically analysed as only four data entries above limit of detection for each radionuclide, ^{234}U, ^{235}U and ^{238}U, were available. However, an interesting phenomenon in the uranium isotope measurement capabilities were seen in the preliminary and final results when comparing γ-, α- and mass spectrometry. Mass spectrometry determinations of uranium isotopes return lower detection limits than radiometric techniques, as demonstrated in Sample 3, where ^{235}U results by γ-and α-spectrometry were below limits of detection, 5.3 Bq g^{-1} and 40 mBq g^{-1}, respectively, although it was possible to detect ^{235}U quantitatively by mass spectrometry, where the activity concentration was determined to be 8 μBq g^{-1}. However, quantitative ^{234}U and ^{238}U results were achieved both with α-(Sample 5) and mass (Sample 3 and 8) spectrometry at mBq g^{-1} level.

Plutonium isotopes

Statistical analysis was carried out for the final ^{238}Pu and ^{239,240}Pu results (Table 4). Sample 6 results were not included in the assigned value calculation as they were reported late. Therefore, the ^{238}Pu and ^{239,240}Pu assigned values, 2.2 ± 0.6 Bq g^{-1} and 420 ± 150 mBq g^{-1} respectively, were both calculated from six data entries. The robust standard deviation of ^{238}Pu results was 14% and this value was used in the z-score assessments. The corresponding ^{239,240}Pu result was 34% and consequently standard uncertainty of assigned value in the z-score assessments (Eq. 2). The final ^{238}Pu results with the assigned value in Fig. 1 show a good general trend even though sample 3 has been given a warning signal, where 2.0 < |z| < 3.0, and sample 6 is unacceptable, where |z| ≥ 3.0, as seen in Table 5. The final ^{239,240}Pu results in Fig. 2 and Table 5 show that sample 3 and 4 deviate a little from the general trend whereas sample 6 also deviates from the general trend and has very large uncertanties. Sample 3 has been given a warning signal whereas sample 4 and 6 results are in the unacceptable range with |z| ≥ 3.0.

Statistical analysis was not carried out for the final ^{241}Pu results as only four data entries were available. The comparison of preliminary and final ^{241}Pu results in Fig. 3, however, show significant improvement in the general trend after the Sample 3 and 4 results had been re-assessed. The preliminary Sample 3 result was an order of magnitude greater than the final result whereas the preliminary Sample 4 results were approximately four times higher than the final result. Possible reasons for the deviations of the preliminary Sample 3 and 4 results were suggested to originate from the LSC efficiency calibrations or spectral interferences. A general practice in ^{241}Pu LSC measurements is to use ^{3}H in LSC efficiency calibrations due to difficulties in procurement of ^{241}Pu standard solutions. Although the β-energy maxima for ^{241}Pu and ^{3}H are similar, it should be noted that this approach only approximates the efficiency calibration for ^{241}Pu, due to significant differences between the shapes of the β-spectra, and hence detection efficiency, for ^{241}Pu and ^{3}H. Additionally, it was suggested that the spectral interferences may rise from ^{60}Co contamination or color quenching

Table 4 Sample numbers, number of data iterations, assigned value, robust standard deviation and standard uncertainty of assigned value of ^{238}Pu, ^{239,240}Pu, ^{241}Am, and ^{234,244}Cm results. The uncertainties of assigned values are presented with a coverage factor of k = 2, and calculated from robust standard deviation when it was ≤ 20%, otherwise standard uncertainty of assigned value used

	^{238}Pu	^{239,240}Pu	^{241}Am	^{243,244}Cm
Number of data entries used	6	6	6	6
Number of data iterations	22	14	4	2
Assigned value Bq g^{-1} (uncertainty at k=2)	2.2 ± 0.6	0.42 ± 0.15	1.2 ± 0.4	5.4 ± 2.9
Robust standard deviation	14%	34%	18%	53%
Standard uncertainty of assigned value	7%	17%	9%	27%

Fig. 1 Final ^{238}Pu results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of $k=2$
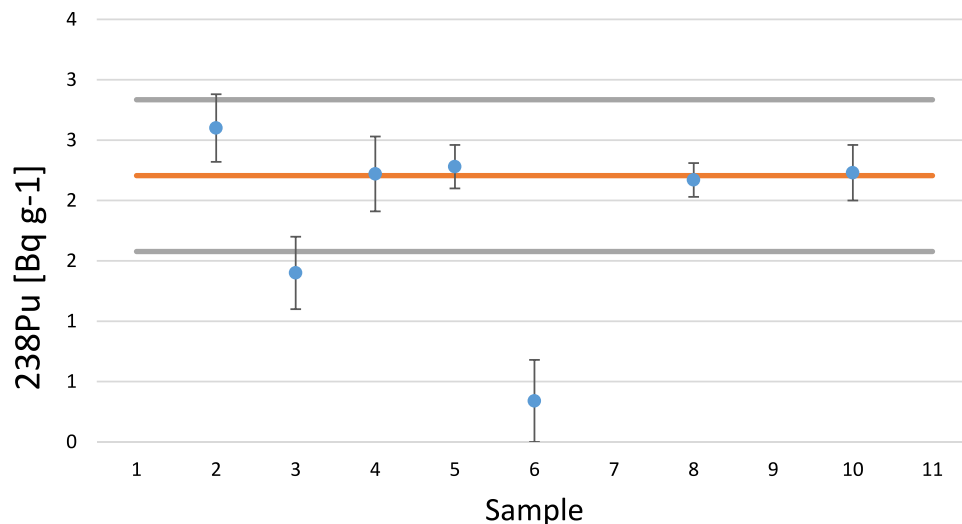

Table 5 z-scores of ^{238}Pu, ^{239,240}Pu, ^{241}Am, and ^{243,244}Cm final results

Sample	z-score			
	^{238}Pu	^{239,240}Pu	^{241}Am	^{243,244}Cm
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	5.9	3.8	4.7	3.0
7	-	-	-	-
8	0.1	0.9	0.7	2.2
9	-	-	-	-
10	0.1	0.4	0.0	2.2

due to acid stripping of plutonium measurement sources after α-spectrometric measurements. However, ^{241}Pu measurements of Sample 3 were carried out in aliquots taken prior to electrodeposition and consequently it was proposed that the yield determination in the electrodeposited measurement source using α-spectrometry was not necessarily the same as in the ^{241}Pu aliquot. Therefore, the final ^{241}Pu results of Sample 3 were measured after acid stripping of two plutonium measurement sources and the yields were re-calculated after α-spectrometry measurement of the acid stripped measurement sources. The same LSC ^{3}H measurement protocol was used but an improved feature to limit spillover of α-signal into the β-channel was implemented. Consequently, the ^{241}Pu results for sample 3 were reduced to a comparable level. The improvement in the ^{241}Pu result for sample 4 originated from a re-calculation of the result after discovery of impurities in the ^{242}Pu source. The partner had

Fig. 2 Final ^{239,240}Pu results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of $k=2$
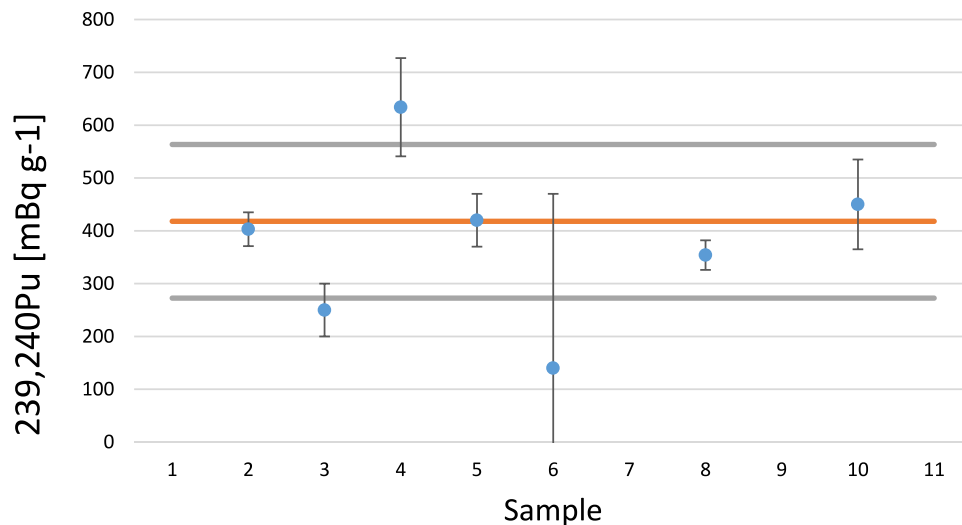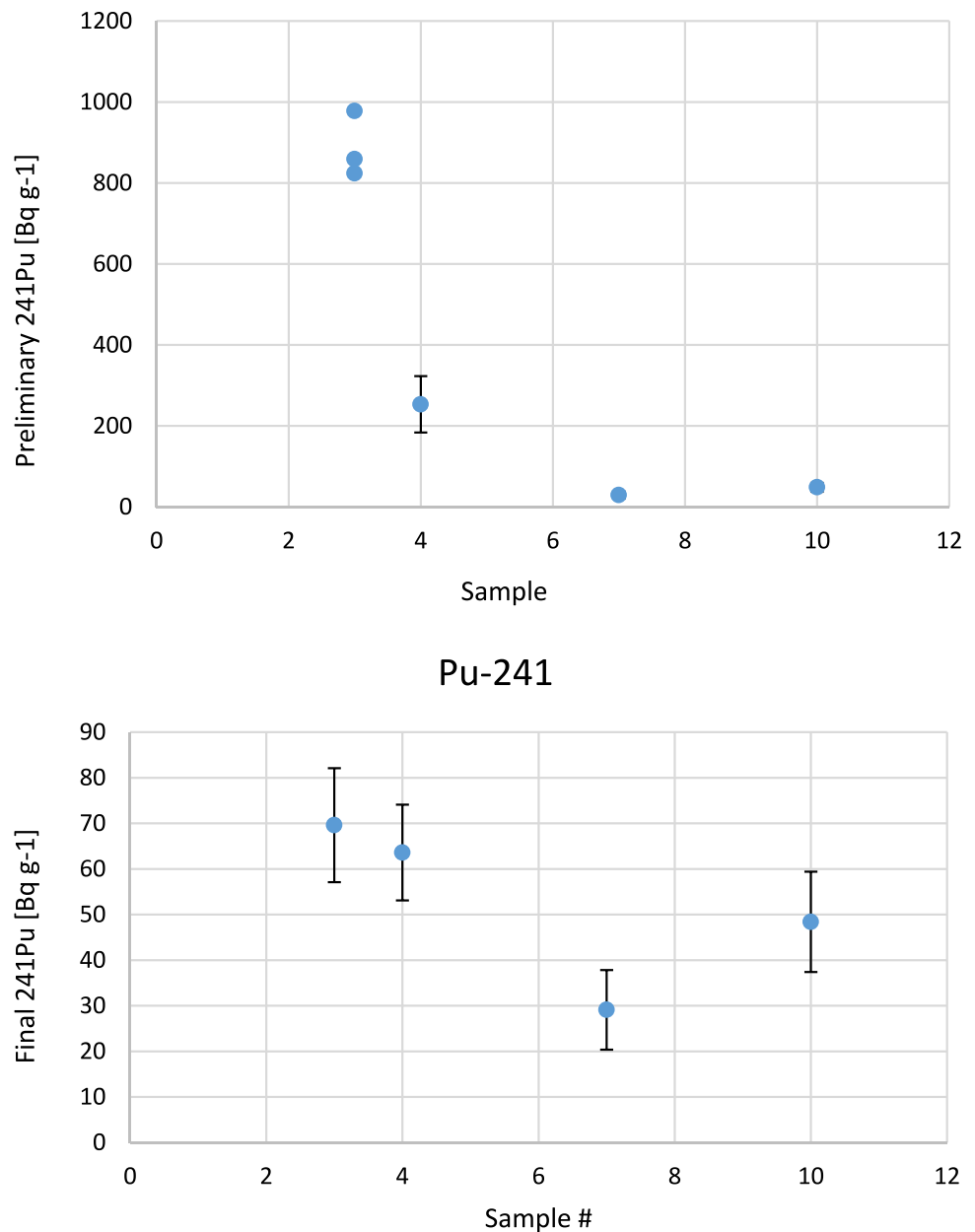
Fig. 3 Preliminary and final ^{241}Pu results in spent ion exchange resin with uncertainties stated with a coverage factor of $k=2$

concluded that their preliminary results were systematically above the general trends and after inspection of their procedures noticed that the ^{242}Pu tracer included ^{238}Pu, ^{239,240}Pu, ^{241}Am and ^{241}Pu impurities. Consequently, the partner recalculated all their Sample 4 results taking into consideration the effect of the impurities.

^{241}Am

Two types of statistical analyses were carried out for ^{241}Am results, namely statistical analysis according to the ISO 13528 standard and the extended data analysis. First, the statistical analysis was carried out for the final ^{241}Am results according to the ISO 13528 standard. The ^{241}Am assigned

value of 1.2 ± 0.4 Bq g^{-1} was calculated from six data entries (Table 4). Sample 6 result were not included in the assigned value calculation as it was reported late. The robust standard deviation was 18% and therefore it was used in the z-score assessments. The final ^{241}Am results with the assigned value in Fig. 4 show good consistency and consequently all z-score results (except sample 6) are in acceptable range (Table 5).

Preliminary ^{241}Am results measured using γ-spectrometry were submitted for Samples 3 and 10. In both cases, the results were below limit of detection of 89 Bq g^{-1} and 5 Bq g^{-1}, respectively. Sample 3 measurements were carried out in the purified americium fraction, which benefit is in the elimination of interfering radionuclides. However, in the Sample 3 measurements,

Fig. 4 Final [241]Am results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of $k = 2$
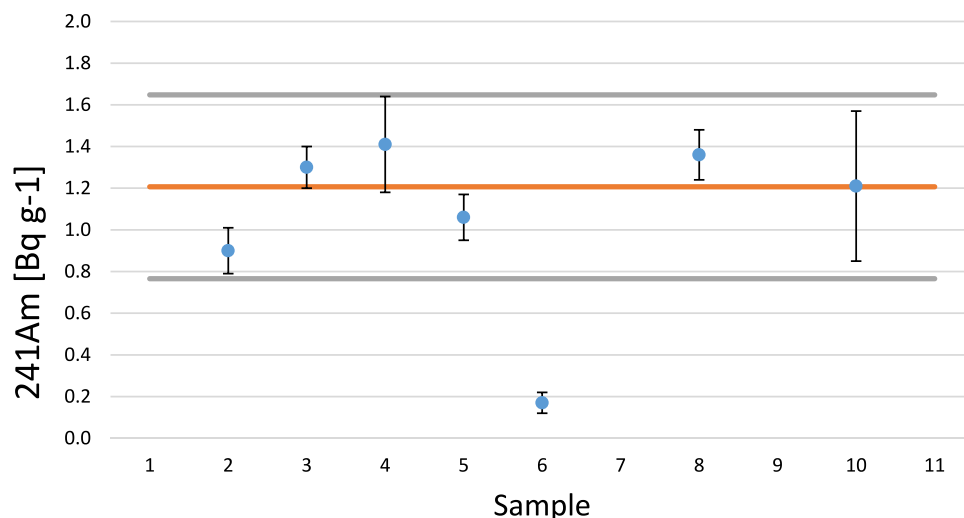

Table 6 Complementary analysis of all [241]Am results

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

Table 7 Complementary analysis of [241]Am results excluding a possible outlier

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

the sample size was small (50 mg) and [54]Mn, [134]Cs and ^{137}Cs were seen in the γ-spectrum. Additionally the yield calculations were carried out based on the electrodeposited tracer and, as discussed earlier for [241]Pu sample 3 measurements, the yield prior and after electrodeposition is not necessarily the same. The limit of detection for the Sample 10 measurements using γ-spectrometry was significantly lower than Sample 3. Sample 10 measurements were carried out in the acid digested solution in which 0.25 g of resin had been partially decomposed. However, the γ-spectrometric [241]Am quantification was challenged by low [241]Am activity and the high Compton background arising notably from presence of ^{60}Co and [137]Cs.

Second, the extended data analysis for the [241]Am results were analysed using a combination of ζ-score, z-score and relative uncertainty test as described earlier. Sample 6 result was a clear outlier. However, the dataset was too small to make this approach meaningful although some useful information can be extracted. If the means of the results for [241]Am are computed, the results are shown in Table 6.

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 outcome is shown in Table 7.

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 χ^2 value to 1 by adding additional uncertainty to each of the contributing values

and so the Mandel-Paule mean [34, 35] and uncertainty are reasonable estimates for the assigned value and uncertainty.

Curium isotopes

Statistical analysis was carried out for the final [243,244]Cm results (Table 4). The [243,244]Cm assigned value of 5.4 ± 2.9 Bq g^{-1} was calculated from six data entries. Sample 6 result was not included in the assigned value calculation as it was reported late. Both the robust standard deviation and standard uncertainty of assigned value were significantly large −53% and 27%, respectively. However, for the sake of the exercise, the standard uncertainty of assigned value was used in the z-score assessments. The final [243,244]Cm results with the assigned value in Fig. 5 show a scattered trend. Consequently, only one z-score result (Sample 2) was in the acceptable range, where $|z| \leq 2.0$, whereas one result was unacceptable and all the other results were given a warning signal (Table 5). The scatter was postulated to originate from slightly different chemical behaviour of the americium and curium, because even though the same americium tracer was used in the yield calculations, the [241]Am results were well comparable whereas [234,244]Cm results were not. Several different types of radiochemical methodologies were utilised in this exercise and consequently different chemical behaviour of americium and curium can result in significantly different

Fig. 5 Final ^{243,244}Cm results and assigned value in spent ion exchange resin with uncertainties stated with a coverage factor of $k=2$
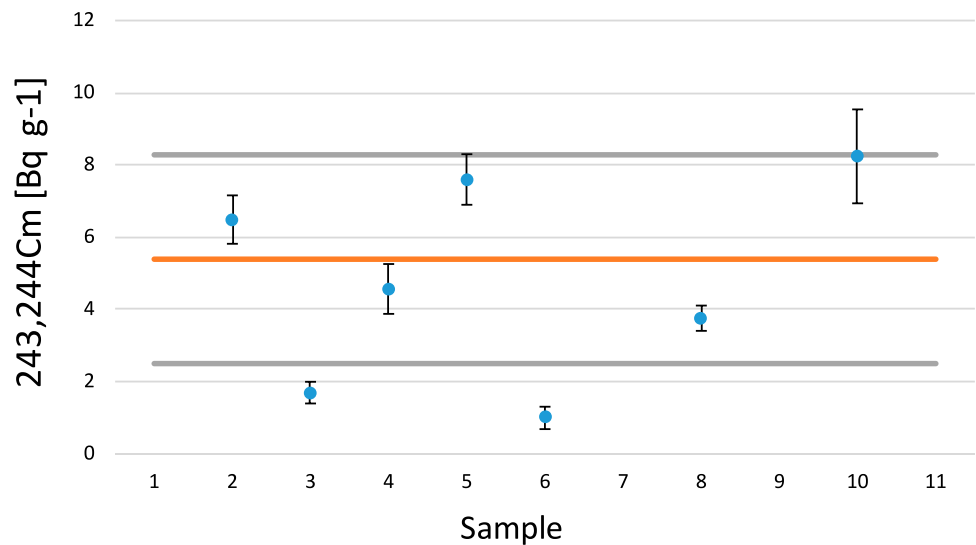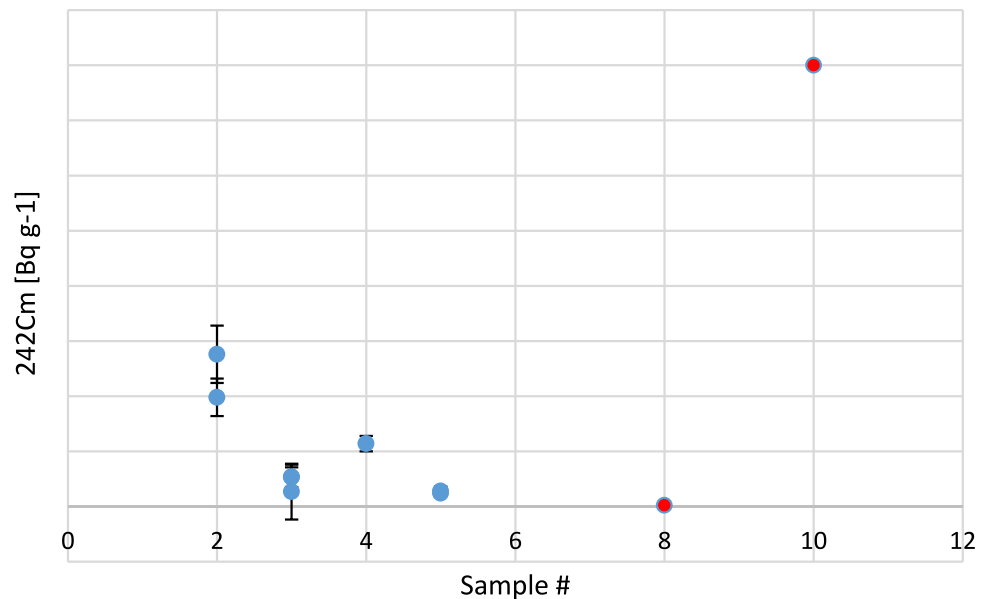

Fig. 6 Preliminary ^{242}Cm results in spent ion exchange resin with uncertainties stated with a coverage factor of $k=2$. Red dot indicates limit of detection result

outcomes. However, the results were in same order of magnitude between 2 and 8 Bq g^{-1}.

Statistical analysis of the final ^{242}Cm results were not carried out as only four results above limit of detection were available. However, the preliminary ^{242}Cm results (Fig. 6) show inconsistencies similarly to the ^{243,244}Cm results. For example, the highest and lowest ^{242}Cm results were below limit of detection. Critique was given to the reliability of the results due to the short half-life of ^{242}Cm, 162.9 d [36]. It was found in a previous NKS intercomparison exercise, that decay corrections for ^{242}Cm might be problematic, leading to highly varying results among laboratories, not only due to the half-life of ^{242}Cm, but also because of unknown activity content of its parent nuclide ^{242m}Am (half-life 141 a) in a nuclear power plant sample [23, 37]. Additionally, the use

of americium tracer in the yield calculations needs to be considered as previously discussed.

Gross α activity measurements.

Statistical analysis of the gross α-activity results was not carried out as only three analysis results were available. However, a significant improvement in the gross α-activity results can be seen between the preliminary and final results in Fig. 7. The preliminary results show that Sample 3 gross α-activity is approximately three times higher than the Sample 7 and 10 results. It was suggested the Sample 3 measurement results may have suffered from spillover of the β-signal to the α-side. The presence of much higher levels of β-emitters compared to α-emitters may be present in spent primary circuit ion exchange resins due to the source of the radionuclides in that β-emitting radionuclides is mainly from corrosion of primary circuit steel

Fig. 7 Preliminary and final gross α-results in spent ion exchange resin with uncertainties stated with a coverage factor of k = 2. Red dot indicates limit of detection result
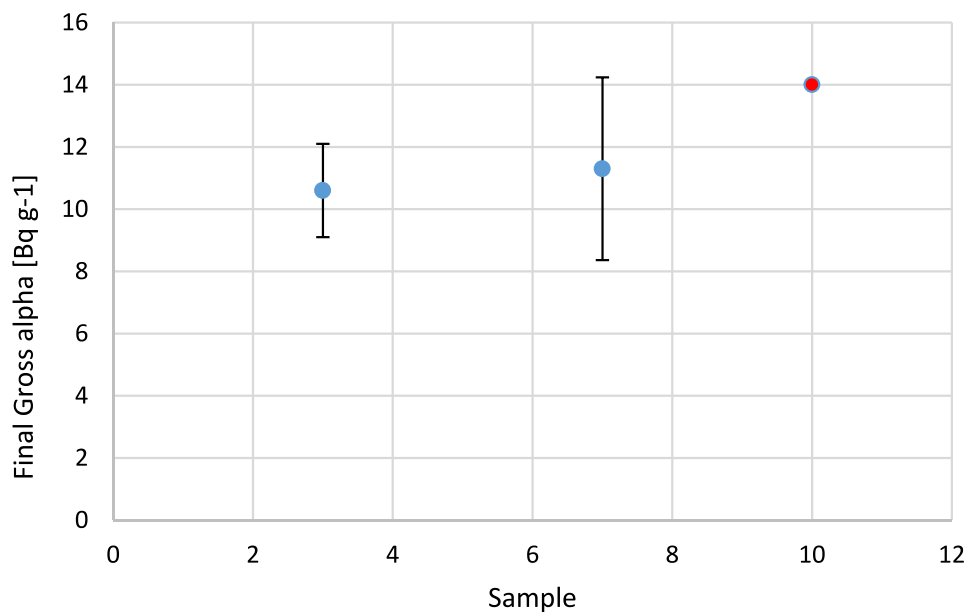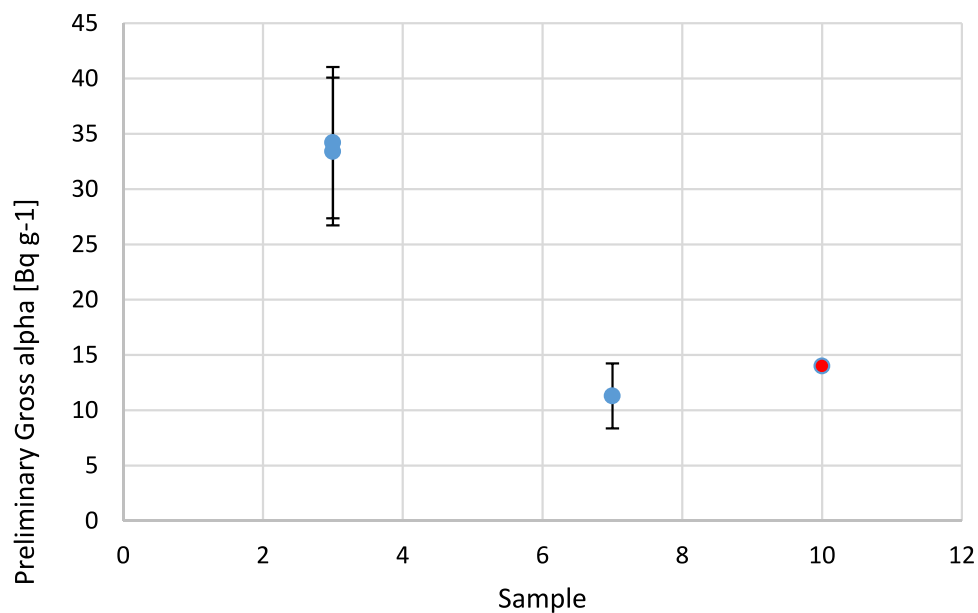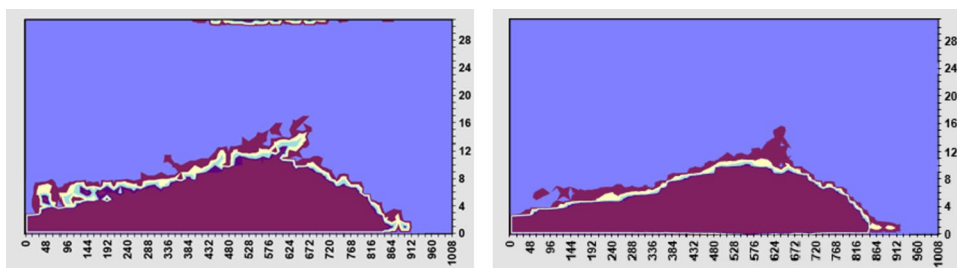

Fig. 8 Preliminary and final 2D plots of gross β-activity measurement of Sample 3. The x-axis is channel and y-axis is pulse length index

piping internals and α-emitting radionuclides from spent fuel leakage. Therefore, even low levels of spillover from the β-channel to the α-channel can cause a significant bias. The LSC spectrum of the Sample 3 gross α-activity results were re-studied and a 2D plot (Fig. 8) revealed the erroneous

counting of β-coincidence signal as α-particle signal shown as pulses on the upper edge of the spectrum. The coincidence phenomenon was counteracted by lowering quenching with addition of more liquid scintillation cocktail and the Sample 3 was remeasured using a 'spill to beta' parameter

in the Hidex 300SL counter. The pulse length index (PLI) parameter, which discriminates between α- and β-signals, was kept as default setting and the triple to double coincidence ratio (TDCR) was directly used as measurement efficiency of 100% even though more reliable results would have needed a more exhaustive efficiency correction. However, with these corrective actions, the final Sample 3 results were well aligned with the other data entries.

An additional study was carried out after the intercomparison exercise to test the significance of removal of the overwhelming number of β-emitters in the gross α-LSC measurement. An α-PSresin is a new plastic scintillation resin which has been reported for an analysis of gross α-activity in drinking and river waters [38]. A set of α-PSresin was kindly provided as pre-packed columns, which were first tested for yield and determination α- and β-separation parameter (PLI) using ^{233}U and ^{90}Sr/^{90}Y standards. The columns were treated in a vacuum box and flowrate was preferably kept below 1 ml per minute. Stable europium (1 mg) was used for the yield determination, which was 100% in all cases. Two α-PSresin columns were treated with known amounts of ^{233}U and ^{90}Sr/^{90}Y standards (^{90}Y retained in the column) to determine the PLI level. After establishment of the PLI level, two 10 mg resin samples were first acid digested with 1 mg Eu using 8 M HNO$_3$ for 2 h at 200 °C. The samples were filtered through Whatman glass microfibre filters and diluted to 6 M HNO$_3$ using deionised water prior to β-emitter removal in pre-treated α-PSresins. The α-PSresin separation consisted of pre-treatment of the pre-packed colums with 6 M HNO$_3$, introduction of the sample, and washing of the columns using 6 M HNO$_3$ and deionised water. Drying of the columns were carried out by reducing the pressure inside the vacuum box for 10 min. The yield determinations were carried out by taking ICP-OES samples from the flow through solution and measurement of Eu. The gross α-activity measurements were carried out by placing the α-PSresin columns inside plastic LSC vials and measured using pre-determined gross α-activity measurement parameters. The initially measured averaged gross α-activity result was 36 Bq g^{-1}, which was approximately three times higher than the previously determined Sample 3 results. The samples were re-measured every few days and a decrease in activity was observed and contributed to ingrowth and decay of ^{90}Y decay. The measurement results stabilised to 9 Bq g^{-1} after couple of weeks giving comparable results (see Fig. 7).

Discussion

The radiochemical analyses of α-emitting radionuclides are as challenging as analyses of β-emitting radionuclides. In both cases, interfering radionuclides and stable elements must be preferably removed or at least minimised using precipitations, ion exchange and chromatographic column separations. However, many of the α-emitting radionuclides can be present in several oxidation states causing an additional challenge in management of their chemical behaviour. Similar to the detection of the β-emitters, α-emitter measurement sources require careful preparation based on the detection technique. The following sub-sections present critical considerations in the measurement source preparation, analysis of americium and uranium, plutonium, curium isotopes, gross α-activity analysis, and intercomparison exercises and statistical analysis.

Critical considerations in the measurement source preparation

Alpha particles are relatively large and strongly ionising particles with a short travel range in material and air. Therefore, they are prone to self-absorption, which means that their α-decay energy is absorbed by collisions with surrounding material. In the case of α-spectrometric measurements, the α-particle self-absorption hinders the signal travel from the sample surface to the detector. Therefore, the most important part in preparing a counting source for α-spectrometric measurement is to have a smooth and as thin as possible, almost massless, measurement source. Otherwise, high resolution, derived from the full width at half maximum (FWHM), spectrum peaks cannot be obtained. The resolution is very sensitive to the source mass, for example increasing from 40–50 keV to around 70 keV, when the solid deposition is increased from < 100 μg to 100–200 μg [39]. Sample purity is important as well, since any impurities present in the sample will increase the source thickness, causing tailing and degradation of the resolution.

Before the measurement source preparation, it is essential to separate the analyte of interest from other radionuclides. Otherwise, the energy peaks of the different radionuclides will overlap, and the activity of a certain radionuclide cannot be reliably determined. Another thing to consider in the source preparation is the deposition yield—the fraction of the tudied analyte that is deposited from the solution onto the measurement source [40] Deposition yields vary between different source preparation methods in that one method can be more suitable for some analytes but give poor yields for another [27, 40].

The most common methods for α-spectrometry source preparation are micro-coprecipitation and electrodeposition, both used in this intercomparison project. For micro-coprecipitation, a lanthanide carrier is added to the actinide solution, and both the radionuclide of interest and the carrier are precipitated as fluorides with addition of concentrated HF [41]. Actinides with higher oxidation states, including uranium and plutonium, require the use of a reducing agent, such as TiCl$_3$, for a more complete precipitation. The precipitate is left to form at a low temperature for at least 20 min

[42] before filtration on to a membrane or micro-pore filter paper. During the filtration, a substrate solution of the lanthanide is filtered first to form a base layer for the actinide precipitation. This produces a more even deposition and prevents the actinides entering the pores of the filter, resulting in a higher resolution [42]. If filtration is performed under a vacuum, instead of a syringe filtration, the actinides are likely to be retained deeper in the pores of the filter, causing peak tailing in the spectrum [43]. Care should be taken in the removal of impurities, such as iron and carbon, since microcoprecipitation is not a specific method, and any impurities present can precipitate on the source as well [44, 45].

In electrodeposition, the analyte deposited from solution on a stainless-steel disk with the use of an electrical current. The method is more time-consuming than micro-coprecipitation, one sample taking around 1–3 h [20, 27]. The dry actinide samples are usually dissolved in a H_2SO_4 solution, and the solution is transferred into the electrodeposition cell [27]. No HCl should be present in the deposition cell, as it can corrode the electrodes and thus affect the quality of the deposition [20]. The pH of the system needs to be carefully adjusted and maintained during the electrodeposition, typical pH being around 2–3 [27]. The discs are rinsed after the deposition and dried. The method is very sensitive for changes in the electric current and the pH, as well as any impurities present in the sample solution. The impurities, such as metal ions and carbon, are competing for deposition sites with the actinides and can lead to lower deposition yields or peak tailing [20, 44, 46]. Adjustment of the pH and keeping it steady can be time-consuming, and it requires skill [27, 40]. An $NaHSO_4$-Na_2SO_4 solution has been used as an electrolyte since it is self-buffering at pH ~ 2 and remains stable during the deposition [20]. Sodium hydrogen sulphate is also useful in evaporation steps prior to electrodeposition because it prevents actinides from adsorbing on beaker walls, increasing the radiochemical yield [20].

Electrodeposition usually gives better resolution than micro-coprecipitation, however, the latter still has sufficient resolution to distinguish between ^{244}Cm and ^{241}Am peaks in the same spectrum [43]. In addition, electrodeposition has a lower reproducibility for high deposition yields [43]. Micro-coprecipitation may be a more practical option if a large number of samples are measured [44].

In this study, the sample preparation was discussed but no discussions were carried out for visual inspections of spectra. Therefore, no assessments on the success of the sample preparations using FWHM were carried out.

Critical considerations in the uranium isotope analysis

Uranium-234, ^{235}U and ^{238}U can be quantified by α-spectrometry or ICP-MS. Alpha spectrometry has been successfully utilised in determination of uranium isotopes from environmental and mining samples [25, 47, 48] and nuclear power plant and nuclear reactor waste samples [26, 49–51] during the past decades. As it was mentioned in the previous section, a thin α source is essential in determination of uranium isotopes by α-spectrometry. Besides separating uranium efficiently from stable elements which are often abundant in decommissioning and environmental samples in much higher concentrations than actinides, it is also necessary to separate actinide elements efficiently from each other, due to their similar α-energies [49–52]. An adequately pure uranium sample for α-spectrometric purposes may be achieved by ion exchange, extraction chromatography and precipitation, and usually a combination of these techniques is employed.

Uranium has two main oxidation states, U(IV) and U(VI), in environment. In oxygen-rich environment and in acidic solutions, uranium is predominantly in U(VI) form. However, during radiochemical separations and as already mentioned in α source preparation by lanthanide fluoride coprecipitation, U(VI) can be converted to U(IV) by adding a suitable reductant, such as $TiCl_3$, ascorbic acid, and Fe(II) compounds to the sample solution. Usually, the oxidation state of reduced uranium returns quickly to an oxidised form, being U(VI) in radiochemical separations. Despite the advantages of α-spectrometry, ICP-MS can be considered superior for analysis of long-lived uranium isotopes, although one should note that elemental purity requirements are quite different for both measurement techniques. ICP-MS enables to achieve a better sensitivity in a shorter counting time in comparison to α-spectrometry, and is used widely for the routine analysis of uranium [1]. As for α-spectrometry, a radiochemical purification must be applied before ICP-MS measurement, especially to remove plutonium for accurate ^{238}U analysis, when excessive quantities of ^{238}Pu is present. Otherwise, presence of isotope ^{238}Pu in the sample causes isobaric interference on ^{238}U in mass spectrum. For that purpose, the purification step is nowadays often based on extraction chromatography with UTEVA® resin [28, 28, 50, 54] since it separates efficiently uranium from other actinides with lower oxidation states. Also, the column separation with UTEVA® resin is relatively fast compared to ion exchange. However, other extraction chromatography resins as well as ion exchange are also used for separating uranium for mass spectrometric measurements. Recently, new developments to simplify the radiochemical procedures have been carried out by reducing isobaric interferences with the implementation of collision/reaction cells available in ICP-MS devices [53] or the use of ICP-MS/MS instruments [28, 54].

Regardless of the detection method, the radiochemical separation methods are still needed to achieve unbiased results for uranium analysis. In the present intercomparison

exercise, the majority of the laboratories used ^{232}U as tracer and UTEVA® and/or TRU® resins to purify a uranium fraction. All laboratories (except Sample 6) obtained separation yields higher than 50% which demonstrated their competence in implementing the radiochemistry method dedicated to uranium purification. The measurements of uranium isotopes were mainly performed by α-spectrometry. Sample 3 and Sample 8 were analysed in the purified uranium fractions respectively by HR-ICP-MS and ICP-MS/MS and obtained better detection capabilities in comparison to α-spectrometry, which was very interesting in characterisation of all uranium isotopes in the studied resin sample.

Critical considerations in Pu isotopes analysis

All plutonium isotopes are radioactive, and for environmental and nuclear waste samples, the main nuclides of interest are ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu [1, 52]. Plutonium isotopes have been characterised in various types of radioactive waste, such as resins [50, 55–58], charcoal beds [50], metals [59], evaporator concentrates [55, 57, 60] and effluents [58, 61], noting that ^{241}Pu is a β-emitter while other plutonium isotopes are α-emitters. For all plutonium isotopes, a radiochemical purification procedure must be applied before measurement. Coprecipitation, liquid–liquid extraction, ion exchange chromatography and extraction chromatography are often used for plutonium purification, although liquid–liquid extraction is rarely used in analysis[59]. Anion exchange resin has been particularly applied in HCl or HNO$_3$ medium [55–59, 62]. Different extraction chromatographic resins can be implemented, such as TRU® [55, 61], TEVA® [61] and DGA® [60] resins. The radiochemical procedure used for α-emitting isotopes of plutonium determination can be implemented for ^{241}Pu analysis but adaptations can be carried out depending on the detection technique (for example, LSC or ICP-MS). In the present work, only two laboratories (Sample 2 and Sample 7) performed a coprecipitation step based, respectively, on iron hydroxide in NaOH medium and lanthanum hydroxide in ammonia medium to isolate plutonium isotopes. Sample 2 was prepared with a micro coprecipitation with neodymium trifluoride to prepare an appropriate source for α-spectrometry. Anion exchange chromatography was implemented for Sample 7, Sample 9 and Sample 10. Most of the laboratories carried out separations based on extraction chromatography and combined different types of resins (TRU®, TEVA® and DGA®) to achieve high decontamination factors.

Furthermore, the activity concentrations of natural α-emitting radionuclides (uranium, thorium, polonium) are often orders of magnitude higher compared to the activity concentration of artificial α-emitters especially in environmental samples. Therefore, it is crucial to reduce the concentration of natural α-emitters to a tolerable level prior to

determining plutonium isotopes by α-spectrometry. It is even more important in ICP-MS determination of plutonium isotopes, because ^{238}U and its hydrides are isobaric interferences in determination of ^{239}Pu, ^{240}Pu and especially ^{238}Pu with ICP-MS.

It must be noted that plutonium chemistry is complex due to the existence of various oxidation states, which complicates the overall separation process [63]. Plutonium can be encountered in four oxidation states (III, IV, V, VI) in solution, which affects its behaviour during the different purification steps. For example, Pu(III) is not retained on anion exchange resin in HCl medium whereas Pu(IV) and Pu(VI) are strongly fixed in the same conditions. Pu(IV) can polymerise in nitric acid depending on plutonium and nitric concentrations. Consequently, the main challenge is the adjustment of oxidation state during the radiochemical separation method. Success or lack of it affects the overall radiochemical yields and thus the sensitivity. Different chemical reagents have been applied in the literature. The main reagent used for plutonium oxidation is sodium nitrite [55, 56, 58, 59, 61, 64]. Plutonium reduction is often performed with sodium sulphite, hydroxylamine hydrochloride [50, 55], oxalic acid [61], ascorbic acid [50, 65] and hydroiodic acid [55, 56, 62]. The completion of the redox cycle is a key step in successful radiochemistry for plutonium. A failure of this process can induce low separation yields, as it might be the case for Sample 5 and Sample 6. In the present work, Sample 2, Sample 3 and Sample 7 used sodium nitrite and hydroxylamine hydrochloride for plutonium redox cycle.

In this intercomparison exercise, ^{239}Pu and ^{242}Pu tracers were used to determine plutonium separation yields. As mentioned in the previous sections, special care has to be taken towards the choice of tracers to avoid errors in determining the purification yield. Sample 4 highlighted that the tracer purity is essential to garantee accurate results. Actually Sample 4 observed ^{238}Pu, ^{239,240}Pu, ^{241}Am and ^{241}Pu impurities in ^{242}Pu tracer which induced unacceptable results when no correction was applied to take into account of the impurities.

As α-emitters, ^{238}Pu, ^{239}Pu and ^{240}Pu can be determined by α-spectrometry. The same critical considerations as for uranium analysis by α-spectrometry can be applied towards the preparation of thin sources for plutonium isotopes and other α-emitting radionuclides (uranium, thorium, polonium). It must be noted that α-decay energies of ^{239}Pu (5106 keV, 11.9%; 5144 keV, 17.1%; 5157 keV, 70,8%) [66] and ^{240}Pu (5124 keV, 27.2%; 5168 keV, 72.7%) [32] are so close that they cannot be resolved from each other in routine α-spectrometry, and so usually only the sum activity of ^{239}Pu and ^{240}Pu can be measured. However, from a thin electrodeposited source and by using spectral deconvolution programs, it is possible to resolve the α-peaks of ^{239}Pu and ^{240}Pu from each other [52], although this technique might

not be suitable for routine analysis. A more common method for determining separate concentrations of ^{239}Pu and ^{240}Pu is to measure them by ICP-MS. This technique does not only enable separate detection of ^{239}Pu and ^{240}Pu and their mass ratio ^{240}Pu/^{239}Pu, but also it has a much lower detection limit for long-lived plutonium isotopes and much shorter measurement time, compared to α-spectrometry. However, ^{238}U and its hydrides can generate isobaric interferences towards ^{239}Pu and ^{240}Pu. The presence of ^{238}U highly hinders ^{238}Pu quantification by ICP-MS through direct isobaric interferences. Therefore, α- and mass spectrometry can be considered complementary in analysis of plutonium isotopes [1]. For both techniques, a highly selective purification method is required before plutonium measurement. As for uranium analysis, the application of collision/reaction cells available in ICP-MS instruments [67] or ICP-MS/MS [86] systems can be considered to simplify the purification methods, but those approaches are still not widespread for plutonium analysis in nuclear waste. In the present work, only α-spectrometry was used for determination of α-emitting isotopes of plutonium. It can be noticed that despite the variety of purification methods, the results related to plutonium α-emitters are relatively consistent (robust standard deviation percentages of 14% for ^{238}Pu and 34% for ^{239,240}Pu), which highlighted the validity of the results obtained by the laboratories that worked on α plutonium characterisation. Radioanalytical problems in plutonium separations due to natural radionuclides and oxidation state adjustment has been also discussed in connection with a previous NKS intercomparison exercise [44].

Plutonium-241 is an isotope of plutonium formed when ^{240}Pu captures a neutron. It is a β-emitter (half-life 14.33 years, β_{max} 20.8 keV) [66] decaying to ^{241}Am. This radionuclide has a short half-life contrary to ^{241}Am (432.6 years) [32]. Plutonium-241 can be indirectly determined by measuring its decay product ^{241}Am by γ-spectrometry. For its direct measurement, ^{241}Pu must be isolated from the matrix and all the other interfering radionuclides, in particular β-emitters, before LSC measurement. As ^{241}Pu is a low β-emitter, it is possible to use ^{3}H to establish the efficiency curve for ^{241}Pu quantification [68] to avoid the supply of ^{241}Pu sources. In the RESINA project, the separated plutonium used for determination of ^{238}Pu and ^{239,240}Pu is also analysed by LSC for ^{241}Pu measurement after the α-spectrometric analysis. The present intercomparison exercise demonstrated that ^{241}Pu analysis is more difficult than ^{238}Pu and ^{239,240}Pu quantification. During the preliminary meeting, the four results submitted initially were scattered and two laboratories (Sample 3 and 4) obtained much higher values. The latter two conducted investigations to understand where the difference in results came from. As mentioned above, Sample 4 had been analysed with a tracer containing impurities at significant level which introduced a bias.

Sample 3 had been initially analysed by taking an aliquot prior to electrodeposition. Sample 3 was re-analysed using acid stripping of the plutonium measurement source and re-measurement of the acid stripped measurement source for yield corrections. Additionally, the LSC measurement parameters using ^{3}H efficiency correction was modified to accommodate interference from α decay. After those investigations, the four results were found to be in the same order of magnitude, which is reassuring for future ^{241}Pu analyses.

Critical considerations in the americium and curium isotope analysis

Americium and curium isotopes in the spent nuclear fuel originate from the neutron activation of uranium or plutonium isotopes. The main americium and curium isotopes in spent fuel and found in spent ion exchange resins are ^{241}Am (432.6 a) [32], ^{242}Cm (162.9 d) [36], ^{243}Cm (28.9 a) [36] and ^{244}Cm (18.1 a) [36]. Americium-241 is the main contributor of decay heat in spent fuel after the first 100 year of cooling [11]. Curium-242 and ^{244}Cm comprise of 90% of all curium isotopes in spent fuel and they have significant contribution to the radiotoxicity [69].

Alpha particle energies of americium and curium isotopes are mostly separated enough for simultaneous measurement with the α-spectrometry. However, ^{243}Cm and ^{244}Cm α-particle energies overlap within about 80 keV energy interval, therefore it is impossible to separate them in conventional α-particle spectrometry. Due to the higher combined activation and fission cross section for ^{243}Cm, the most (< 90%) of the ^{243,244}Cm activity is in fact produced by ^{244}Cm in high burn-up fuels. In addition, ^{243}Cm has also low probability (12.5%) contribution to ^{242}Cm emission at 5992–6067 keV. Therefore, completely accurate quantification of ^{242}Cm would require known concentration of ^{243}Cm. [70].

Americium-243 is often assumed to be a suitable yield tracer for curium isotopes and therefore used as radiochemical yield tracer for their analysis. Both americium and curium are chemically similar and are comparable in ionic size. They both have strong thermodynamic preference to trivalent oxidations state and they are in trivalent state in aqueous solutions. Habibi et al. [69] conducted speciation computations of different separation steps of americium and curium separation procedure and found out that pH of the solution has significant effect on their speciation during the separation. Even small variations in pH ($\pm$ 0.5) may result in conditions where americium and curium do not form similar precipitates or complexes, which may induce loss of radionuclide of interest and further biased yields. Hence, pH adjustments during separation and purification procedures should be considered as critical points.

With increasing atomic number in the actinoid series, higher charge of nucleus attracts more 5f electrons and therefore they seldom participate in the bonding processes. Therefore, chemical behaviour of heavier actinides, such as americium and curium, and lanthanides is similar and their prevailing oxidation state is +III. Presence of lanthanides in the sample hinders especially the electrodeposition of americium and curium, leading to a thick α-spectrometry source and further self-absoption and poor quality of measurement source. Problems with deposition quality has been reported previously with americium and curium fractions in intercomparison exercise with samples of nuclear power plant origin [44]. Even though no discussions on the α-spectra were carried out in RESINA project, in some cases of both black and white residues on the metal discs were encountered resulting in poor resolution by tailing to lower energies.

Many of the participants used TRU® extraction chromatography resin for americium and curium and plutonium separation in this exercise. Tri-, tetra- and hexavalent actinides and lanthanides are retained strongly on TRU® in HNO_3 media with concentration higher than 0.5 M [71]. Slightly different behavior of americium and curium in the TRU® resin has been demonstrated previously [72]. The heavier neighboring element, curium, has been reported to have lower retention factor to TRU® compared to the lighter neighbor, americium, and a similar phenomenon has been observed in lanthanoid series between Eu(III) and Gd(III) as well [69]. Salminen-Paatero et al. also detected below reference value result for ^{244}Cm, when in the same sample the ^{241}Am results where more evenly distributed below and above the reference value [44]. The use of ^{243}Am as yield tracer can overestimate the curium yields due to the phenomenon where americium retention to TRU® resin is higher than the retention of curium [55, 73, 74].

Also, DGA® resin was used for the americium and curium separation by two of the participants in this exercise. Separation with DGA® resin is less sensitive for Fe(II), Fe(III) competition and retention coefficients greater by factor ≥ 10 compared to TRU® has been reported for americium and curium [75]. However, small differences in the retention behavior have been identified in DGA® resin as well. In nitric acid media the major differences in retention to DGA® are at lower HNO_3 concentration ranges (0.01 to 0.1 M) [72] and the use of DGA® resin in higher nitric acid concentration ranges (< 1 M) could result in more uniform americium and curium results compared to TRU®.

Yields for the americium and curium fraction varied significantly (from < 1% to 110%). A poor yield may derive from the competition of Fe(III) and trivalent lanthanides in the TRU® separation step. The yields for DGA® separated americium and curium fraction were both in acceptable range, which could result from the lower sensitivity to competition with Fe(III). Plutonium isotopes may cause spectral

interferences, if they are carried over in the americium and curium fraction due to the incomplete oxidation of Pu(III) in the TRU® column. Traces of plutonium in americium and curium spectrum will broaden the α-peaks and will lead to inaccurate results. Habibi et al. [69] tested the use of ^{248}Cm as a yield tracer for curium isotopes successfully. However, the use of ^{248}Cm as a yield tracer may be difficult due to the poor commercial availability.

Critical considerations in the gross α-activity analysis

Even though gross α- and β-activity measurements can be used as a fast screening tool in environment monitoring, radioecology and industrial applications, it has limitations such as loss of volatile radionuclides (e.g., ^{3}H, ^{14}C, radon, ^{210}Po, ^{137}Cs) in cases when heat is included in the sample preparation, changes in sample composition such as total dissolved solids and chemical composition, affect the counting efficiency, and establishment of representative α- and β-particle discrimination where differences between standard solutions and radionuclides in the sample may affect this parameter [76, 77]. Additionally, gross α- and β-activity measurement cannot be used as an absolute determination of the radioactive content in a sample [78]. However, coupled with detailed knowledge of the specific radionuclides present in the sample and their fractional relationship to each other, gross α- and β-activity measurement can be used to calculate the specific content of a radionuclide in a sample of same origin. Gross α- and β-activity analysis is, on the other hand, a quite quick and reliable way to determine the gross level of activity in a sample.

Gas proportional counting (GPC) and LSC are commonly used methods in gross α- and β-activity analysis. The GPC method consists of evaporation of the liquid on a planchet and measurement whereas the LSC method consists of either an evaporation of the liquid into a smaller volume and mixing it with a liquid scintillation cocktail or a direct mixing of a liquid aliquot with the cocktail. Some of the above-mentioned limitations have been counteracted in GPC and LSC analyses for example by preparation of a thin measurement source using a source spraying method [79] and pretreatment and concentration of the sample solution without heating and removal of β-emitters [38].

Measurement of the gross α-activity with LSC has advantages over specific α nuclide counting [80] as there is a little to no self-absorption in the liquid sample, there are less demands for pre-treatment, sample preparation is less complex, and it is less time consuming. However, the challenges in gross α-activity measurement using LSC are chemical and physical quench, the presence of β-emitters and other interfering nuclides and chemical and physical behaviour of the sample [78, 80]. Quench agents, either chemical or physical,

in the sample decrease the counting efficiency and shift the α-spectrum towards the left [81]. The shift in the spectrum due to quench, has the most impact if the sample simultaneously contains both α- and β-emitters. While quenching also leads to a shift in the β-spectrum, the shift in the α-spectra is more pronounced. With both α- and β-emitters present, the spill over of α-signal into the β-spectrum, or vice versa, will cause misclassification and consequently bias in the analysis results.

Other parameters affecting the LSC measurements are for example type of vial and type of scintillation cocktail [77]. The detection efficiency of α-particles in LSC is approximately 100% since α-particles have a short range and display a line spectrum. The pulse height resulting from α decay is a peak at 1/10 of the α particle's actual energy [82]. The detection efficiency of β decay is less than 100% due to β decay resulting in a continuous spectrum from zero to a maximum energy [83].

The intensity of photons from a scintillation event as a function of time, can be divided into a fast or a prompt component and in a slow or a delayed component. Alpha particles cause a slow delayed component with a decay time of 200–300 ns, while a β-particle causes a fast and prompt component with decay time of a few nanoseconds [83]. The relative amounts of light in the prompt and delayed components are dependent on the specific ionisation of the scintillator and thus is specific to the particle that caused the ionisation. Consequently, differentiation between α- and β-emission by LSC can be carried out and some scintillation cocktails have been designed for enhanced α- and β-particle discrimination. The differentiation between α- and β- pulses is carried out for example using a pulse shape analyser (PSA) or pulse length index (PLI) parameters. However, care should be taken to use the optimal parameter settings, as the analysis is affected by the activity concentrations in a sample, the α- and β- energies and both chemical and color quench level [81, 84]. The optimal parameter setting enables a sufficient discrimination of the α- and β- spectrum and the background effects are reduced. When simultanous measurement of both gross α-activity and gross β-activity in a sample is carried out, care must be taken in the calibration process of the detector to ensure good enough separation of β-signals and α-signals [85]. Additionally, samples containing amounts of higher energy β-particles, can cause spill over into the α-spectrum [81] and thus overestimating the α-activity. The gross α-activity analysis can be carried out without a pulse shape analyser, but more emphasis is needed on elimination of β-emissions [82]. However, real samples may contain several α- and β-emitters with different energies than utilised in the calibrations and different quench properties. Consequently, the optimal parameter settings may not be as precise as desired.

Three of the participants in the RESINA intercomparison exercise performed the gross α-activity measurement. The sample 7 analysis using evaporation and α-spectometry did not suffer from analytical difficulties whereas sample 10 result was comparable with the other results even though it was reported with a limit of detection. The sample 3 analysis initially suffered from significant overestimation of the gross α-activity measurement due to missclassification of overwhelming amount of β-emitters as α-emitters. The missclassification was corrected by lowering quenching with addition of more scintillation cocktail and utilisation of the '*spill to beta*' measurement parameter. These two simple modifications enabled a comparable result. Consequently, gross α-activity measurements carried out using LSC (samples 3 and 10) and α-spectrometry (sample 7) produced comparable results. The additional study, in which the α-PSresin was utilised in the removal of overwhelming amount of β-emitters, showed initially a higher gross α-activity due to retained ^{90}Y. However, the result became comparable after decay of ^{90}Y. It can be concluded that some knowledge on which radionuclides may be present in a sample and on what activity level is of importance as the operator can be aware of possible spill overs. Additionally, as increasing quench increases the chances of an α-pulse to be misclassified as a β-pulse, the quench level should be monitored.

Critical considerations in the intercomparison exercises and statistical analysis

The data has been analysed in accordance with the requirements of ISO 13528, with an extended data analysis also used for analysing the data arising from ^{241}Am measurements.

Central to the assessment of the reported data is the selection of a reference or assigned value for each nuclide, since the activity concentration was unknown before these samples were analysed. This may be mitigated by the use of robust values for activity concentrations and uncertainties, but (as an example) the assigned value for ^{241}Am shifts by at least 5% if a suspected outlier is removed. Nevertheless, the assigned values allow an assessment of the data reported.

Determination of assigned values is possible for uranium isotopes, plutonium isotopes (including ^{241}Pu), ^{241}Am and ^{242}Cm. However, knowledge of the ratio between ^{241}Pu and ^{241}Am at a given time better informs the variation of the ^{241}Am activity concentration over time, which will be subject to radioactive decay of ^{241}Am, as well as ingrowth of ^{241}Am from ^{241}Pu decay, although this may not be significant over the duration of this work.

The analysis of gross α-activity and $^{243/244}Cm$ is complicated by the differing decay rates of the constituent radionuclides, although an approximation can be made for $^{243/244}Cm$.

In short, this exercise has provided useful information on the determination of actinide measurement in a challenging matrix, and the outcomes of the data analyses provide good insight if the complexities of such analyses. It would be beneficial to organise a similar comparison exercise involving a wider participation base to allow a more detailed analysis of the measurement data. Additionally, given the importance of the measurements of actinides in radioactive waste, there may be some scope in proposing an extended exercise as a supplementary Bureau international des poids et mesures (BIPM) comparison.

Summary and conclusions

The α-emitting DTM nuclide intercomparison exercise in spent ion exchange resin was carried out using the same methodology as in the previous exercises [2–5]. The radiochemical procedures in separation and purification of α-emitters consisted of similar techniques as for β-emitters, namely precipitations and different ion exchange and chromatographic resins. However, as majority of the measurements were carried out using α-spectrometry, the preparation of a thin measurement source was of a great importance. Additionally, several α-emitters studied in this exercise can be present in several oxidation states and their control can be concluded to be crucial as they affect both the separation and purification behaviour and measurement source preparation.

The analyses of uranium isotopes were carried out using α- and mass spectrometry. The purification procedures to eliminate interferences were needed prior to both α- and mass spectrometry measurements. In majority of cases good (higher than 50%) yields were obtained. Statistical analyses of uranium isotope results were not carried out as only four data entries above limit of detection were available. However, the results showed that the sensitivity of mass spectrometry is superior to α-spectrometry in uranium isotope detection.

The results related to plutonium α-emitters are relatively consistent, which demonstrates the analytical capabilities of the laboratories towards plutonium analysis by α-spectrometry after radiochemical purification. However, the separation yields need improvement by some laboratories. A poorly controlled redox cycle process applied to control plutonium oxidation state might be the cause of low plutonium recovery yields. Statistical analyses were carried out for the ^{238}Pu and ^{239,240}Pu results, which assigned values were 2.2 ± 0.6 Bq g^{-1} and 420 ± 150 mBq g^{-1}, respectively. The z-score determinations showed that majority of the reported results were acceptable.

This intercomparison exercise also showed that ^{241}Pu analysis using LSC is much more complicated to manage and is still challenging for some laboratories in comparison

to the characterisation of plutonium α-emitters. In particular, special care must be taken towards the establishment of efficiency calibration in LSC, notably when ^{3}H is used instead of ^{241}Pu. The ^{241}Pu counting window has also to be optimised to limit the impact of α-signal and avoid overestimation of ^{241}Pu activity. Moreover, the present intercomparison exercise showed that the purity of the plutonium tracer used must be checked carefully to avoid measurement bias. From those results, significant progress was achieved for ^{241}Pu determination in nuclear waste, which is reassuring for future analysis.

The ^{241}Am results were analysed using statistical analysis according to the ISO 13528 standard and the extended data analysis. The assigned value of ^{241}Am was 1.2 ± 0.4 Bq g^{-1} and all results (except one) were in acceptable range. The radiochemical purifications of ^{241}Am and curium isotopes are carried out simultaneously and the ^{234}Am tracer is often also allocated for curium yield calculations. However, the results obtained in this exercise clearly demonstrated that use of ^{243}Am tracer is not optimal, due to the slightly different chemical behavior of americium and curium, for curium isotopes since the ^{243,244}Cm results showed large scattering (assigned value 5.4 ± 2.9 Bq g^{-1}) whereas ^{241}Am results were well aligned.

The extended ^{241}Am analysis revealed some interesting information, in that one result was identified as an outlier by the Peirce criterion [12, 13]. However, given the small size of the data set, it is questionable whether outlier rejection can be justified. Use of the Mandel-Paule mean [34, 35] allowed an improved estimate of the assigned value to be made as this mean is weighted by the reported uncertainties with additional uncertainty added to the final value to force the reduced chi squared value to 1. Analysis of the reported uncertainties via the R-test [14] revealed no additional information about uncertainty estimation by the participants. A larger data set would allow more meaningful analysis.

The gross α-activity analyses were carried out using acid digestion/leaching and measurement of evaporated sample on planchet using α-spectrometry or mixing with the leachate or concentrated leachate with liquid scintillation cocktail and measurement using LSC. The results highlighted the significance of careful setting of LSC measurement parameters as the overwhelming quantity of β-emitters in a spent ion exchange resin was causing misclassification of β-signal as α-signal. The additional study with the α-PSresin showed comparable results after removal of β-emitters and decay of ^{90}Y.

As a conclusion, the RESINA intercomparison exercise introduced a new set of challenges in the DTM analyses. Firstly, many of the α-emitters and their interferences can be present in several oxidation states and their control is directly linked with success of the radiochemical purifications and measurement source preparations. Secondly, α and

β discrimination settings in LSC measurements are crucial in minimisation of α and β signal misclassifications. Thirdly, radiochemical behaviours of americium and curium isotopes are not necessarily identical and consequently use of ^{243}Am tracer in ^{243,244}Cm analysis may be problematic.

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