Analyzing alpha emitting isotopes of Pu, Am and Cm from NPP water samples: an intercomparison of Nordic radiochemical laboratories

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Abstract

Radioanalytical methods for the determination of isotopes of Pu, Am and Cm in water samples from nuclear power plants were compared and further developed in a Nordic project (Optimethod) through two intercomparison exercises among Nordic laboratories. With this intercomparison, the analytical performance of some laboratories was improved by modification of the analytical method and adopting new techniques. The obtained results from the two intercomparisons for alpha emitting transuranium isotopes are presented, and the lessons learnt from these intercomparison exercises are discussed.

Keywords Actinides · Radioanalytical methods · Extraction chromatography · Nuclear power plant samples · Water samples · Alpha spectrometry

Introduction

Nordic co-operation has been continuing among institutes in the fields of radiochemistry and nuclear safety via Nordic nuclear safety research (NKS) programs for over 40 years.

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In many of the past NKS-funded projects, intercomparison exercises have been performed for evaluating the performance of different separation and detection methods used in Nordic radiochemistry laboratories, as well as for developing new advanced methodologies [1–5]. In a recent two-year NKS project called Optimethod, two intercomparison campaigns were organized with the aim to analyze alpha emitting isotopes of transuranium elements in different NPP (nuclear power plant) water samples [6, 7]. In both intercomparisons, transuranium isotopes ^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm and $^{243+244}$Cm were radiochemically separated and measured by alpha spectrometry. In some participating laboratories, ICP-MS was also utilized for measurement of ^{239}Pu and ^{240}Pu individually. In total 12 partners, including all Swedish and Finnish nuclear power plants, some Nordic academic research institutes and radiation safety authorities participated in this project focusing on the intercomparison of transuranium isotopes by alpha spectrometry. These laboratories normally work on radiochemical analysis of either NPP samples and/or with environmental and food samples, as well as with method development for radiological preparedness. In general, the Optimethod project (2018–2019) aimed to improve the analytical quality for the determination of alpha-emitting radionuclides in various samples, especially in the samples from a nuclear power reactor. This goal was achieved by validation and optimization of the analytical method used in the Nordic laboratories through

inter-comparison exercise for the determination of isotopes of Pu, Am and Cm in a spiked artificial water sample and a real reactor water sample collected from Nordic NPPs. Two intercomparison exercises were organized in 2018 and 2019 for the analysis of Pu, Am and Cm isotopes in the spiked water, reactor coolant water and spent fuel pool water sample. In the first intercomparison exercise, spiked water and reactor water with relatively high concentration of transuranic isotopes of ≤ 2 Bq kg^{-1} were analyzed. In the second intercomparison exercise, spent fuel coolant water with lower concentrations of transuranic isotopes of ≤ 50 mBq kg^{-1} were analyzed.

Alpha spectrometry is often used for measuring activities of alpha emitting isotopes of e.g. Pu, Am, and Cm [8–20]. Alternatively, ICP-MS is an attractive method for measurement of long-lived transuranic element radioisotopes, especially to measure ^{239}Pu and ^{240}Pu individually [2, 4, 5, 21–30]. Due to similar alpha decay energies of ^{239}Pu and ^{240}Pu, these nuclides are difficult to be discriminated in alpha spectrometry, although it is possible to resolve ^{239}Pu from ^{240}Pu in an alpha spectrum by using thin target prepared by electrodeposition [31–35]. A high resolution (low tailing on the low-energy side of a peak) detector setup and good counting statistics are required, as well as a fairly long distance between the sample and the detector in order to reduce coincidences between conversion electrons and alpha particles [36]. Increasing source-detector distance also reduces tailing in alpha spectrum, as the angle of incidence for alpha particles becomes more uniform. Then the track of alpha particles from sample to detector, through the deposited sample and the dead layer of the detector, is as coherent as possible. In addition, the detection limits of ICP-MS for long-lived radionuclides such as ^{239}Pu, ^{240}Pu, ^{237}Np, ^{235}U, ^{238}Pu are lower than of radiometric methods, and the measurement time (10–20 min) is much shorter than in alpha spectrometry (often a few hours to days). However, with ICP-MS it is usually hard to measure low-level ^{238}Pu due to the isobaric interference of high background ^{238}U present in separated samples as well as shorter-lived radionuclides (e.g. ^{242}Cm, ^{210}Po), and therefore both techniques are complementary in the analysis of radioisotopes of transuranic elements [37].

In nuclear power plants, the isotopes of Pu, Am and Cm are produced mainly in the nuclear fuel. Small amounts might also exist in the reactor materials (through the reactions of impurity uranium with neutrons). Monitoring and reporting of these alpha emitters in atmospheric releases and liquid effluents in the nuclear power plants are recommended by the European Union [38]. Process water (reactor coolant and spent fuel pool water) is often analyzed in the NPPs to monitor the possible leakage of the nuclear fuel (together with gamma spectrometry), to investigate the dispersion and deposition of alpha emitters in the nuclear reactor system,

and for determining activities in operational waste. In the Nordic nuclear industry laboratories such as all Nordic NPPs, the Swedish Nuclear Fuel and Waste Management Company (SKB), etc., different methods have been developed and applied for the determination of artificial alpha emitters in reactor water, fuel pool water and filters, including direct electrodeposition and extraction chromatographic separation followed by alpha spectrometry. However, these analytical methods were not always validated for all kinds of sample types. Suitable standard reference materials and inter-laboratory comparisons for relevant sample matrix are not available. Consequently, the NPPs laboratories have a strong requirement to validate, improve and optimize their analytical methods for determination of alpha emitters in their routine samples. Nordic research institutes and authorities have a long history of determining alpha emitters in nuclear, environmental and food samples. Several methods for the determination of anthropogenic alpha emitters in various nuclear, environmental and decommission samples have been developed and applied in these laboratories [13, 20, 25, 27, 39–41]. In many laboratories, different alpha emitters are separated and measured individually, but a sequential separation and simultaneous determination of all isotopes of Pu, Am and Cm is still not well established and validated in most of laboratories.

This work aims to present the findings and lessons learned from the two intercomparison exercises, in order to improve and optimize the analytical methods for the determination of alpha emitting radionuclides of transuranium elements in NPP water samples.

Experimental

Water samples for intercomparison exercise

Information of the three water samples used for the intercomparison exercises in 2018 and 2019 is presented in Table 1. A simulant water sample was prepared at Chalmers University of Technology by spiking ^{238,239,240,241,242}Pu and ^{244}Cm standard solutions in 1 M HNO$_3$ solution [6]. The activity concentrations of the radionuclides (standard values) in the spiked water were calculated by the amount of the spiked standards and the total mass of the solution. Subsamples of 200 ml of each in PE bottle were delivered to partner laboratories for analysis.

Reactor coolant water was collected in Olkiluoto NPP. The water was acidified to pH 1 with HNO$_3$, transferred to 200 ml PE bottles and sent to partner laboratories for analysis [6]. This water sample contained a variety of radionuclides, both fission products from fuel leakages and activation products of the construction materials in the reactor.

Table 1 Information of the intercomparison samples used in Optimethod project

Sample	Reference value or estimated range of radionuclides in the sample (mBq kg^{-1})			Preparation or sampling date	Other information
	Pu-isotopes	Am	Cm-isotopes		
Spiked water 2018	^{238}Pu 38 ± 31*, ^{239}Pu 77 ± 1, ^{240}Pu 50 ± 1, ^{241}Pu 9 ± 11, ^{242}Pu 0.2*	^{241}Am 71 ± 11	^{244}Cm 195 ± 6	March 2018	The uncertainty of the activities is for $k = 1$
Reactor coolant water (Olkiluoto 2018)	^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu 100–2000	^{241}Am, ^{243}Am 100–2000	^{242}Cm, ^{243}Cm, ^{244}Cm 100–2000	April 2016	Also contains activation and fission products
Spent fuel pool water (SKB Clab 2019)	^{238}Pu 5–50 $^{239,\,240}$Pu 1–10	^{241}Am 1–10	^{244}Cm 1–10	December 2018	Total activity ~ 50 Bq kg^{-1} (mainly from ^{60}Co)

*Estimated from the atomic ratio in the Pu standard solution after decay correction

In the second intercomparison exercise in 2019, a water sample was collected from a spent fuel storage pool by SKB [7]. The water sample was acidified to pH 2 with HNO_3, and two litres of water sample in PE bottle was delivered to partner laboratories for analysis. This water sample contained more than a 1000-fold activity of ^{60}Co compared to the actinide isotopes, as well as other fission and activation products.

Aliquots of 10–100 ml were used as subsamples for the radiochemical determinations of Pu, Am and Cm isotopes from spiked water and Olkiluoto reactor coolant water in 2018, while larger aliquots (500–1000 ml) or whole 2 l sample of spent fuel pool water were used for analysis in partners' laboratories in 2019.

Radiochemical methods for the separation of Pu, Am and Cm and the determination of their radioisotopes in the Nordic intercomparisons

Overview of the separation methods used by Nordic partners in 2018

In the first intercomparison in 2018, eleven out of twelve participants determined isotopes of Pu, Am and Cm in water samples by applying their commonly used radiochemical methods. These methods are described briefly in Table 2. About half (5 of 11) of the participating laboratories used the method procedure based on UTEVA + TRU extraction chromatography modified from the method published by Eichrom [42]. Other laboratories used combinations of different extraction chromatography resins (TEVA + DGA, TEVA + TRU, TEVA + UTEVA + TRU), the combination of extraction chromatography and ion exchange (Dowex 1×4 + TRU), or liquid–liquid extraction. One laboratory did not separate transuranic elements from each other,

but prepared the alpha target by direct electrodeposition after acid digestion and pre-concentration by evaporation. Therefore, ^{238}Pu ($E\alpha$ 5.456–5.499 MeV) and ^{241}Am ($E\alpha$ 5.443–5.485 MeV) could not be discriminated and were reported as the sum activity of ^{238}Pu and ^{241}Am).

^{242}Pu and ^{243}Am (0.02–0.08 Bq) were used as chemical yield tracers for Pu and Am/Cm, respectively, in most of the laboratories. For the method without chemical separation of transuranic elements, only ^{233}U (0.1 Bq) was used to estimate the chemical yield of all transuranics. In most of the laboratories, the samples were first treated by evaporation followed by acid digestion of the residue. Two laboratories used $Ca_3(PO_4)_2$ co-precipitation to pre-concentrate transuranium elements from water samples, instead of evaporation. The majority of the participating laboratories (10 of 11) used electrodeposition for preparing alpha counting sources and only one laboratory used micro-co-precipitation with lanthanide fluorides for preparing the alpha counting samples. A more detailed description of the analytical methods used by each participating laboratory was reported elsewhere [6].

Preparation of alpha measurement target by electrodeposition and micro-co-precipitation

Electrodeposition is a traditional method in preparing an alpha measurement target for obtaining a thin layer of actinides, and it was also used predominantly among the participants of the Optimethod project. The separated transuranium element fraction (often in HCl or HF medium) was first evaporated to dryness after adding 0.5 g of NaCl or Na_2SO_4. The residue was then dissolved in diluted H_2SO_4, and the solution was evaporated to dryness to remove all Cl$^-$ and NO_3^-. The solution was then dissolved in 10 ml of 0.2 M H_2SO_4 and transferred to the electrodeposition cell. Ammonia was added to the cell to achieve pH 2.5. One laboratory

Table 2 Methods used in participating laboratories for radiochemical separation and target preparation [6]

Lab code	Separation method	Target preparation	Yield tracers	Problems with the radio-analytical method in 2018	Changes in the procedure between the intercomparisons of 2018 and 2019
1	TEVA-DGA	Electrodeposition for alpha spectrometry/in 0.5 M HNO_3 medium for ICP-MS	^{242}Pu, ^{243}Am		
2	TEVA-TRU	Electrodeposition/ $Na_2SO_4 + H_2SO_4$	^{242}Pu, ^{243}Am	Sometimes low Pu recovery	
3	No	Electrodeposition/sulfuric media	^{242}Pu, ^{243}Am	Only total alpha activity is obtained	
4	Dowex 1×4-TRU	Electrodeposition/ $Na_2SO_4 + H_2SO_4$	^{242}Pu, ^{243}Am		TEVA-TRU-TEVA
5, 7, 10, 11	UTEVA-TRU	Electrodeposition/ $Na_2SO_4 + H_2SO_4$	^{242}Pu, ^{243}Am	Incomplete separation of Pu from Am + Cm. Black residue in the Am + Cm fraction	H_2SO_4 was added to eluate only after evaporation to near dryness. Am yield was improved, and no black residue occurred
6	TEVA-UTEVA-TRU	Electrodeposition/ $Na_2SO_4 + NaHSO_4$	^{242}Pu, ^{243}Am	Sometimes low recovery or low resolution in the alpha spectrum	
8	No	Electrodeposition/ $Na_2SO_4 + H_2SO_4$	^{233}U	Only sum concentration of $^{238}Pu + ^{241}Am$ is obtained	
9	No results for the inter-comparison samples due to unknown analytical failure	Micro-co-precipitation	^{242}Pu, ^{243}Am	The method used in 2018 was designed for spent resin and it was not suitable for water samples	TRU + TEVA with micro-co-precipitation was used for the intercomparison samples
12	UTEVA-TRU	Micro-co-precipitation	^{242}Pu, ^{243}Am	Varying recoveries of Pu, Am and Cm. Sometimes low Pu recoveries	

used sulphate buffer solution ($Na_2SO_4 + NaHSO_4$) for the deposition, instead of H_2SO_4 and ammonia [43]. Electrodeposition of Pu, Am and Cm on stainless steel discs was carried out using electric current of 0.25–1.5 A for 1–3 h [44–46]. As a result, a layer of transuranium elements was deposited on the middle of the stainless steel disc, which was washed by dipping in deionized water to remove the salt residues. After drying in air, the disc was most often heated at 90 °C for 10 min to stabilize the deposited layer of the transuranic element.

Besides electrodeposition, tri- and tetravalent actinides can also be co-precipitated from a solution with lanthanide fluorides, e.g. with NdF_3 or CeF_3 [47–49] for alpha spectrometry measurement. Typically a few tens of micrograms of lanthanides are added to sample as a carrier, and about one milliliter of concentrated HF is then added to co-precipitate transuranic fluoride with lanthanide fluorides. Precipitation is usually carried out in an ice bath or a fridge, and the minimum required time for completing the precipitation is about 20 min. The fine precipitate is filtered through a membrane filter or micro-pore filter paper, aiming to produce as much as possible even and thin precipitate layer onto the filter surface. The resulting co-precipitate on filter containing the radionuclides of interest is glued, for example, on a plastic disc and measured by alpha spectrometry.

In this project, two laboratories used micro-co-precipitation of Pu, Am and Cm with NdF_3 for preparing alpha counting samples. 50 μg Nd as a carrier was added and the precipitate was filtered through a membrane filter having 0.10 μm pore size.

Alpha spectrometric measurements

All laboratories used PIPS (Passivated Implanted Planar Silicon) detectors for the measurements of alpha emitting isotopes. The counting time varied between 3 and 7 days, depending on the laboratory and the activity level. Each laboratory performed efficiency and energy calibrations and background measurements of the alpha measurement chambers by their own protocols. Also, the quality assurance samples—reference and blank samples—were prepared according to the participants' own quality assurance program. A detection limit of 0.05–0.10 mBq is often obtained for alpha spectrometry depending on the counting time and the background level.

Intercomparison in 2019—changes of the analytical method compared to the first intercomparison in 2018

In the second intercomparison in 2019, 10 participants provided analytical results. The water sample analyzed in this test contained a much lower concentration of transuranic isotopes compared to the first intercomparison. Due to the lower radioactivity level of the separated Pu, Am and Cm isotopes, the resulted measurement time of the alpha samples was relatively longer, up to one month, compared to the samples analyzed in 2018.

As an effect of the findings from the first exercise, some changes were made to the radioanalytical methods in the participating laboratories between the intercomparisons in 2018 and 2019 (Table 2). One participant adopted the modified Eichrom method [50] using TRU and TEVA resins for the separation of Pu, Am and Cm in the intercomparison in 2019. Another laboratory changed the method from Dowex 1×4 and TRU resin to TEVA-TRU-TEVA extraction chromatography combination. One more partner added H_2SO_4 at the later stage of alpha target preparation, after evaporating the residue to near dryness.

Results

Problems in the chemical separation and the alpha target preparation during the intercomparison analysis in 2018

Some problems were recognized during the intercomparison in 2018 (Table 2). The methods as well as the results in detail can be found in the project report [6]. The recoveries of Pu, Am and Cm analyses varied both between the laboratories and the sample types. Additionally, low recoveries of the transuranium elements were reported by some laboratories that resulted in higher measurement uncertainty of the radionuclide concentration and a higher detection limit. The reason for the low and varying recovery is difficult to track, due to several steps in the radiochemical separation procedure, and the loss of transuranium nuclides might occur in any step of the procedure, e.g. pre-concentration, radiochemical separation, or target preparation for alpha spectrometry measurement. A possible reason for the low recovery of Pu might also be the unsuccessful adjustment of its oxidation state before chromatographic separation. Incomplete separation of Pu from Am + Cm has also been reported in some laboratories using combined UTEVA + TRU chromatographic separation.

Another reoccurring problem is the quality of the deposition. In some laboratories, black residues occurred in the Am + Cm fractions after the radiochemical separation that significantly worsened the quality of the alpha spectrum,

causing tailing on the low-energy side of a peak. The radioanalytical method used for separating transuranium elements has an obvious impact on the purity of the separated fraction to be deposited, and the amount of added H_2SO_4 and pH of the final solution are also critical factors in the electrodeposition [45]. Electrodeposition is a matrix-sensitive method, impurities in the sample solution will compete with transuranium elements or prevent transuranium elements from depositing onto the metal disc.

Besides problems described above and in Table 2, there was an issue of impure tracer solutions in two laboratories. One laboratory used ^{242}Pu tracer solution containing ^{238}Pu as an impurity during the first intercomparison. The tracer solution was later replaced with a newer one without impurities. Another laboratory noticed that the activity concentration had been overestimated for their ^{243}Am tracer. This shows the importance of using adequate quality control.

Results from the first intercomparison in 2018

The results of the intercomparison analyses in 2018 are presented in Figs. 1, 2, 3, 4, 5, 6, 7, 8 and 9. All the uncertainties of the measured activity concentrations are presented for $k = 1$ for spiked water, while the rest of the results are given with 1σ uncertainty. For the results in spiked water (Figs. 1, 2, 3, 4), the red lines are the reference values which were calculated from the certified concentrations of each radionuclide in the standard solution used for spiking, and the orange lines represent the standard uncertainty ($k = 1$) of radionuclides concentration in the spiked water. It can be noted, that the uncertainty of the reference concentration of ^{238}Pu in the spiked sample is relatively high, this value was calculated based on known isotopic composition of the
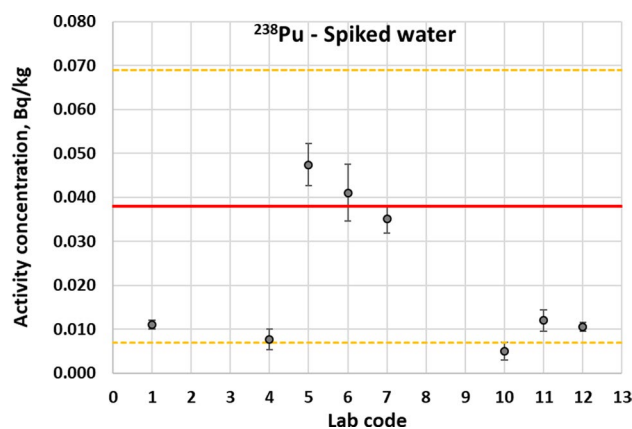

Fig. 1 The activity concentration of ^{238}Pu in the simulant water sample of intercomparison 2018—the red line is the calculated activity concentration based on added spike activity, and orange lines are the uncertainty range ($k = 1$) for the calculated value. (Color figure online)
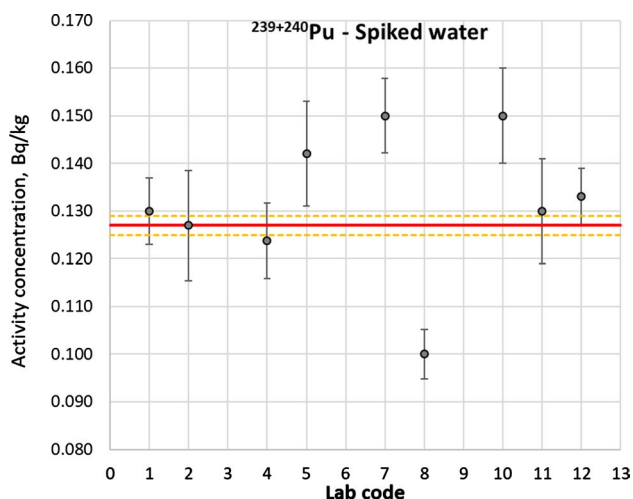
Fig. 2 The activity concentration of $^{239+240}$Pu in the simulant water sample of intercomparison 2018. The red line is calculated activity concentration based on added spike activity, and orange lines are the uncertainty range ($k=1$) for the calculated value. One extreme outlier is excluded from the data
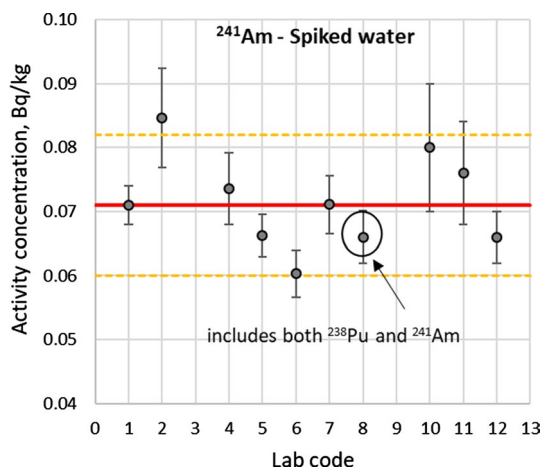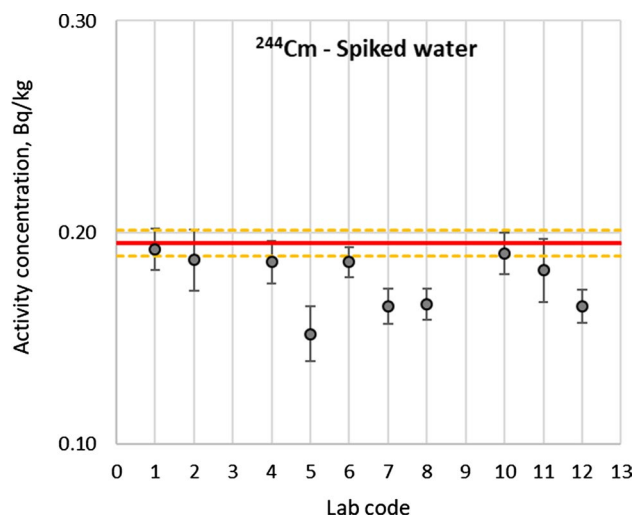

Fig. 4 The activity concentration of ^{244}Cm in the simulant water sample of intercomparison 2018

Fig. 3 The activity concentration of ^{241}Am in the simulant water sample of intercomparison 2018—the red line is calculated activity concentration based on added spike activity, and orange lines are the uncertainty range ($k=1$) for the calculated value. (Color figure online)
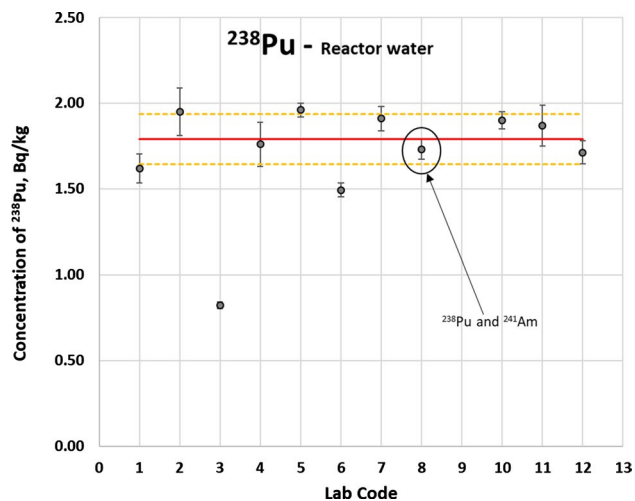
Fig. 5 The activity concentrations of ^{238}Pu in the reactor coolant water sample of intercomparison 2018—the red line is an average of the participants' results excluding two outliers, and orange lines are uncertainty range ($\pm 1\sigma$) for the average value. (Color figure online)

spike solution and the measurements of other Pu isotopes by ICP-MS and gamma spectrometry.

The reported activity concentration values of ^{238}Pu in the spiked water were within or close to the given uncertainty range, 38 ± 31 mBq kg^{-1} (Fig. 1). However, the reported results seem to fall into two groups, one with a concentration around 10 mBq kg^{-1} and the other around 40 mBq kg^{-1}. The activity concentration of ^{238}Pu in this sample is very low and the reference value of ^{238}Pu has a high uncertainty. Five reported activity concentrations of $^{239+240}$Pu were adequately

close to the reference value, 127 ± 2 mBq kg^{-1}, taking into account reported uncertainty intervals, whereas other five values were more scattered (Fig. 2). It has to be noted, that the given uncertainty of the reference value is relatively narrow in this case.

The reported results of both ^{241}Am (Fig. 3) and ^{244}Cm (Fig. 4) had similar variation as for the Pu isotopes. All except one reported values corresponded to the reference value for ^{241}Am, 71 ± 11 mBq kg^{-1}. For ^{244}Cm, all reported values were more or less below the reference value, 195 ± 6 mBq kg^{-1}, and six of ten values with their reported uncertainties reached the uncertainty range of the reference

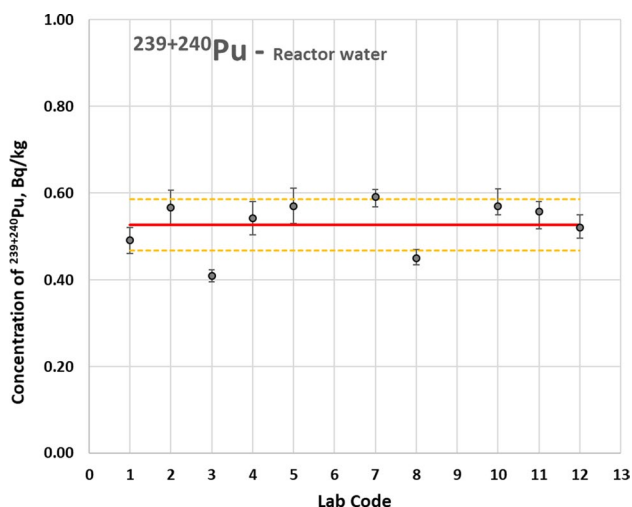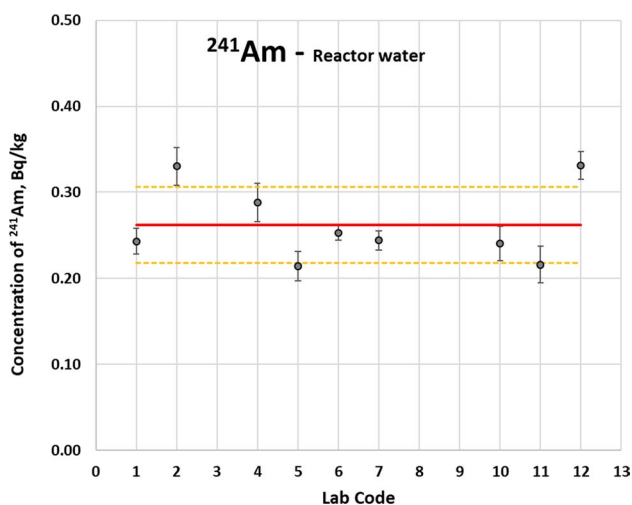**Fig. 6** The activity concentration of $^{239+240}$Pu in the reactor coolant water sample of intercomparison 2018—the red line is an average of the participants' results excluding one outlier, and orange lines are uncertainty range ($\pm 1\sigma$) for the average value. (Color figure online)

Fig. 8 The activity concentration of $^{243+244}$Cm in the reactor coolant water sample of intercomparison 2018

Fig. 7 The activity concentration of ^{241}Am in the reactor coolant water sample of intercomparison 2018
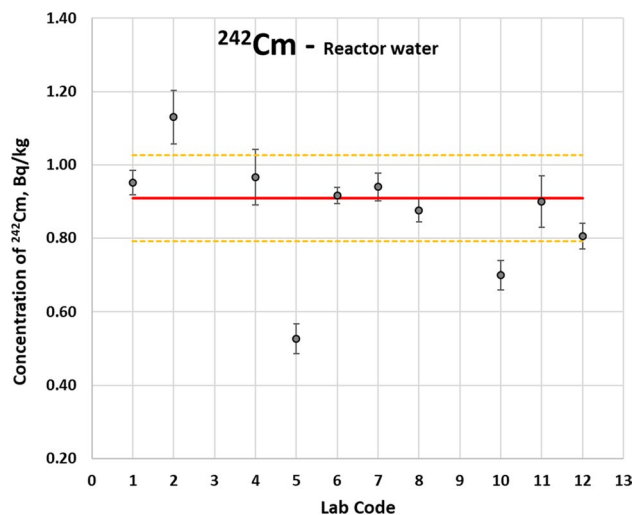
Fig. 9 The activity concentration of ^{242}Cm in the reactor coolant water sample of intercomparison 2018

value. The reason for generally lower values for ^{244}Cm is unknown, but it has to be taken into account again that the uncertainty range of the reference value for ^{244}Cm is narrow, and the activity concentrations of the investigated transuranium isotopes are low.

For the reactor coolant water used for the intercomparison in 2018, the true concentration values of transuranic isotopes are unknown. The averages and 1σ of the reported values by the participating laboratories excluding outliers are represented as red and orange lines, respectively, in Figs. 5,6,7,8and9. The concentrations of transuranic isotopes in this sample are higher compared to the spiked water (Table 1), and it also contains relatively high levels
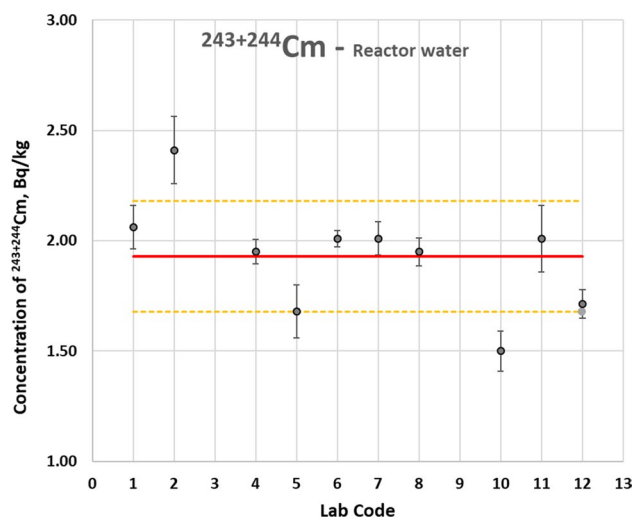
of other radionuclides. The reported activity concentrations for ^{238}Pu (Fig. 5), $^{239+240}$Pu (Fig. 6), ^{241}Am (Fig. 7), and $^{243+244}$Cm (Fig. 8) agree quite well, with only one or two reported data for each radionuclide that deviated and which was excluded from the calculation of the average and standard deviation. The reported activity concentrations of ^{242}Cm in the reactor coolant water (Fig. 9) are more fluctuating, having three outlying values; this might be attributed to different ^{242}Cm decay corrections performed in the laboratories due to its relatively complicated production model [6]. ^{242}Cm is a relatively short-lived ($T_{1/2} = 162$ d) isotope of curium. In a nuclear reactor, ^{242}Cm is produced mainly from the short-lived ^{242}Am

$(T_{1/2} = 16$ h) through the beta minus decay and ^{242m}Am $(T_{1/2} = 141$ a) that decays through isomeric transition to short-lived ^{242}Am that undergoes β-decay to ^{242}Cm.

After removing water from the reactor, the only possible source of ^{242}Cm is the decay of long-lived ^{242m}Am. If the storage time of reactor coolant water after the collection is not very long (< 2 a) compared to the half-life of ^{242}Cm (162 d), the ^{242}Cm concentration in the sample will be related to the decay of ^{242}Cm and the production from the decay of ^{242m}Am in the water sample, and the correction depending on the concentrations of both ^{242}Cm and ^{242m}Am in the samples. If the sample is stored for a sufficiently long time (> 5 a), the ^{242}Cm will be almost in secular equilibrium with ^{242m}Am in the sample. Since the reactor coolant water sample used in this intercomparison was only stored for 1–2 years before analysis, the decay correction becomes more difficult in consideration of unknown ^{242m}Am concentration in the sample. This is why discrepancies in ^{242}Cm results are noticed between the participating laboratories in which the sample was analyzed at different dates during half a year [6].

The results from intercomparison 2019 and lessons learned from the intercomparison 2018

The reported activity concentrations for ^{238}Pu (Fig. 10), $^{239+240}$Pu (Fig. 11), ^{241}Am (Fig. 12), and ^{244}Cm (Fig. 13) in the spent fuel storage pool water sample by the participating laboratories were even more uniform and mostly between the uncertainty ranges in the second intercomparison in 2019. The outliers, although still present were deviating less from the average values than in the first intercomparison in 2018
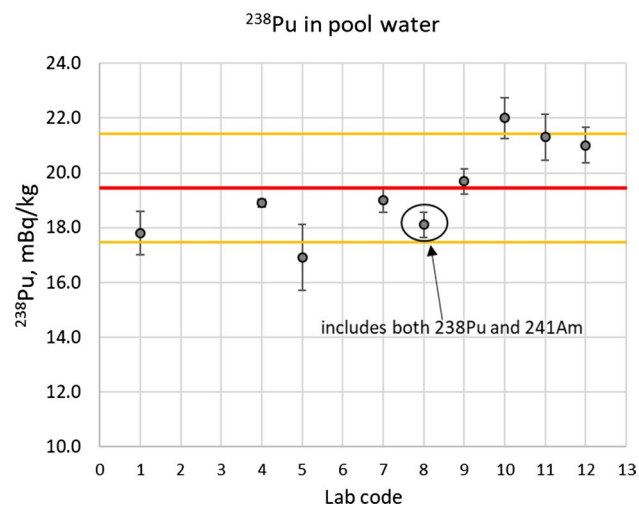
even though activity concentrations of the investigated transuranium isotopes in the spent fuel pool water sample in 2019 were lower compared to the reactor coolant water used in the inter-comparison in 2018. The accuracy and precision of the obtained results were improved from the first project year. One possible reason for this improvement is the modification of the sample treatment before electrodeposition in some laboratories based on the lessons learned from the intercomparison exercise in 2018. There were no longer problems with the black residue observed in the Am+Cm fraction prior to electrodeposition.

Fig. 11 The activity concentration of $^{239+240}$Pu in the pool water sample of intercomparison 2019—the red line is an average of the participants' results and orange lines are uncertainty range ($\pm 1\sigma$) for the average value. (Color figure online)
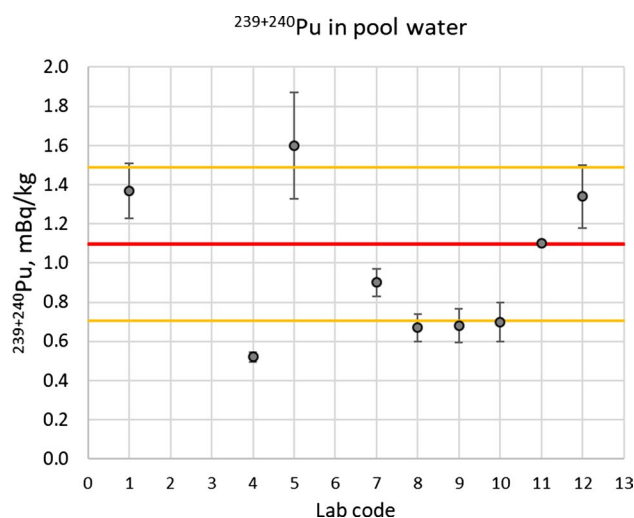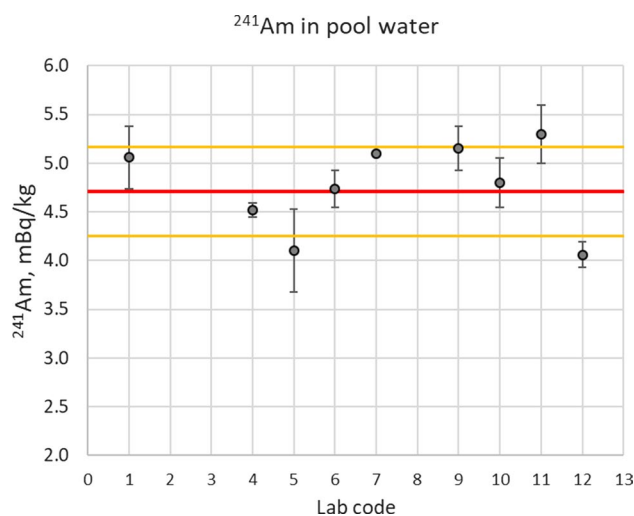

Fig. 10 The activity concentration of ^{238}Pu in the pool water sample of intercomparison 2019—the red line is an average of the participants' results and orange lines are uncertainty range ($\pm 1\sigma$) for the average value. (Color figure online)

Fig. 12 The activity concentration of ^{241}Am in the pool water sample of intercomparison 2019
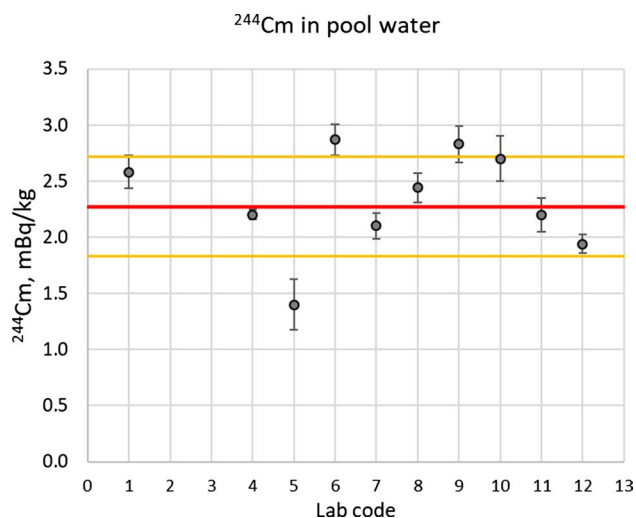
Fig. 13 The activity concentration of ^{244}Cm in the pool water sample of intercomparison 2019

In the analysis of such a low-level sample, the blank or background level of the detector becomes more important. Some participants observed a high background in their alpha detector (probably due to the long-term deposition of some radionuclides recoiled or emitted as gas from a high-level target), which prohibited precise measurement of low-level radionuclides in the intercomparison samples. Some reported results are close to the detection limit, and longer measurement time was needed for obtaining a result with a lower measurement uncertainty. Due to the very low level of ^{242}Cm in the spent fuel pool water sample and relatively short half-life, the ^{242}Cm concentrations were below the detection limits in almost all participating laboratories, and only a few laboratories reported the analytical results above the detection limit.

Discussion

Electrodeposition versus micro-co-precipitation in preparation of alpha counting samples

In general, electrodeposition is considered a less time-efficient method for preparation of alpha spectrometry measurement target compared to micro-co-precipitation [47], especially for the analysis of a large number of samples. Electrodeposition is thought to produce thinner alpha target and therefore a better resolution of the alpha spectrum. However, electrodeposition is more sensitive to impurity elements present in the sample solution (e.g. rare earth elements in the separated Am/Cm solution or Fe residues in Pu fraction) compared to micro-co-precipitation, leading to decreased radiochemical yield in this step. Sometimes

micro-co-precipitation produces thick alpha counting target, causing peak broadening in the spectrum because the method is not specific and other elements than the target radionuclides may co-precipitate as well [48]. Thick alpha counting samples may also be due to mixing the analyte (actinides) with NdF_3, producing precipitate where actinide ions are incorporated to NdF_3 matrix. This problem can be overcome by e.g. preparing NdF_3 precipitate first, filter the precipitate and then produce AmF_3 which is sorbed on top of the NdF_3 layer [49]. According to the comparison made by Luskus [46], both electrodeposition and micro-co-precipitation work satisfactorily for alpha target preparation giving adequately good radiochemical yields and producing sufficiently high resolution in the alpha spectrum (thin counting sample). In case that a high sample throughput is required, micro-co-precipitation is more efficient method compared to electrodeposition. The success of the alpha sample preparation is highly dependent on the original sample matrix and the chemical treatments performed before preparing the alpha counting source.

Some participating laboratories reported a problem with a black residue in the separated and evaporated Am + Cm fraction after column separation by UTEVA + TRU resins. During the first intercomparison, it was suggested that it might result from organic substances in TRU resin, eluted within the separated Am + Cm fraction. It is possible to destroy the organic remaining in the separated solution by wet digestion using *aqua regia* or nitric acid plus hydrogen peroxide before electrodeposition.

Experiences from the second intercomparison in 2019

One laboratory used a direct electrodeposition method for determining all transuranium isotopes in the water samples. The activity concentrations of $^{239+240}$Pu, $^{243+244}$Cm and ^{242}Cm determined by this laboratory agreed well with the reference values of the spiked water and average values in the reactor coolant and fuel pool waters. Therefore, this simpler determination method is suitable for determining the fore mentioned transuranium isotopes from NPP water samples. The method cannot be used to determine individual activity levels of ^{238}Pu and ^{241}Am due to their similar energies. As for ^{239}Pu and ^{240}Pu, the sum of both nuclides are measured.

In the second intercomparison, one participating laboratory adopted successfully the separation method based on TRU and TEVA extraction chromatography resins for the determination of Pu, Am and Cm isotopes in these types of water samples, while no analysis of transuranic isotopes was performed at that laboratory before the intercomparison was started. The obtained results in the second intercomparison for that laboratory were also in a good agreement with the

average values, and therefore the newly adopted separation method was taken into practice in their routine analysis.

One participating laboratory changed chromatographic resin for Pu separation from Dowex 1 × 4 to TEVA and the reagents for oxidation state adjustment of Pu from H_2O_2/$NaNO_2$ to $Fe(NH_2SO_3)_2$/$NaNO_2$. With this change, much higher Pu recoveries were obtained. In addition, the Am/Cm fraction separated using TRU resin was further purified using TEVA chromatography in NH_4SCN-formic acid solution to remove REE, in order to analyze samples with high REE content in the future.

Another participating laboratory changed the alpha target preparation procedure by addition of H_2SO_4 to the evaporated residue from the separated transuranic solution, instead of adding it directly to the separated solution in the previously used procedure. The electrodeposition disc prepared from this solution had a lighter color and thinner layer of the deposited sample. Additionally, the problem with black residues in electrodeposition and low-quality alpha spectra was also solved when this change was applied.

Overall, the second intercomparison was successfully implemented by the modification of the analytical methods based on the lessons learned from the first intercomparison exercise. It would be extremely useful to continue these intercomparisons with more challenging sample matrices, which will be discussed in the next section.

Future aims for the radioanalytical development

There are several points that should be developed in the radioanalytical methods used for determining transuranium elements in these intercomparisons and beyond. Although radiochemical recovery is an important factor considering performance of the separation method and detection limit, and recovery below 30% is often considered as non-quantitative, even low recovery should not affect the analytical accuracy. In these two intercomparisons, only few participants reported their radiochemical recoveries, so no comparison can be done between different methods. Varying and low radiochemical recovery shadowing some separation methods should be improved for obtaining robust and stable methods. The reason for this effect could not be tracked during these intercomparisons and the development work will continue in the laboratories for finding out the reasons.

The radioanalytical methods used for determining transuranium isotopes in NPP water samples in the participating Nordic laboratories provided generally satisfactory results. However, there are some needs to analyze more challenging sample matrices, for example low level water samples and solid samples as air filter, soil, sediment and spent resins. Many of the currently used separation methods need modification throughout the separation procedure, from the sample decomposition steps to column separation steps and finally in the preparation of the alpha measurement source. High amounts of both inorganic and organic components are often present in environmental samples combined with commonly low level radionuclides in the environmental samples and this creates an analytical challenge to remove excessive amounts of disturbing matrix elements.

One central problem in analysis of environmental samples and air filters for transuranic isotopes is the interference of natural radionuclides present in high levels in the samples. For example, ^{210}Po activity is normally a few orders of magnitude higher than the activity of artificial transuranium isotopes in air filter samples and environmental samples. High levels of ^{210}Po ($E\alpha = 5.30$ MeV) interferes in the measurement of ^{241}Am due to its similar alpha energy with ^{243}Am ($E\alpha = 5.28$ MeV), which is typically used as the yield tracer of ^{241}Am and Cm isotopes. Besides ^{241}Am, ^{210}Po can interfere with the measurement of Pu isotopes as well, if ^{210}Po is not well removed from Pu. With selection of proper purification steps and reagents, the presence of ^{210}Po in the separated Pu or Am + Cm fractions can be eliminated or minimized to an acceptable level. $^{210}Po^{4+}$ adsorbed to extraction chromatography resin together with the transuranium isotope ions can be removed before eluting Pu, Am and Cm. For example, ^{210}Po can be removed using 8 M HNO_3 from TRU column before eluting Am + Cm [51] and also with 8 M HNO_3 from TEVA column [52]. It is also possible to elute Pu from a TRU column with a solution containing the reducing reagent $TiCl_3$, instead of more commonly used ammonium oxalate solution, for keeping any residual tetravalent $^{210}Po^{4+}$ in the resin column while eluting trivalent Pu^{3+} [53].

One promising separation medium, which is not yet commonly used among Nordic laboratories, is DGA extraction chromatography resin. One laboratory used a separation method based on the combination of TEVA and DGA resins in both intercomparisons. This separation method gave representative results compared to reference and average values of Pu, Am and Cm isotopes, good radiochemical yields for Pu, Am and Cm, and it was also quite rapid. The method has a potential to be used for more challenging sample matrices as well, after some adjustments.

A concept of the optimized separation method is not unambiguous among different laboratories having different resources and needs. There is a consensus among the participating Nordic laboratories that the separation methods in use should be further optimized, especially if the methods are planned to be applied for a more complicated sample matrices. Some criteria presented for an optimized separation method in the project discussions include: improved environmental friendliness (avoid the use of HF and high volumes of concentrated acids), increased safety, faster, lower costs, better radiochemical recovery, and better separation between different radionuclides, including natural

ones. However, there are varying financial and workforce resources available for method development among the different laboratories. Although some problems exist, there might not be enough time and funding for solving the problems and if the methods are fit-for-purpose, convenient and safe to use, they might be still utilized despite of the certain lacks.

Conclusions

Radioanalytical methods for different purposes are needed since the objectives may be different in the research institutes, often having various short-term projects, and NPPs where routine analyses are performed more permanently. Most of the Nordic laboratories use alpha spectrometry for measuring alpha emitting radionuclides of Pu, Am and Cm, but ICP-MS is also used in some laboratories for completing the characterization of the sample, providing individual results of both ^{239}Pu and ^{240}Pu.

In addition to NPP water samples analyzed in these intercomparisons, most of the Nordic radiochemistry laboratories analyze solid NPP and/or environmental samples as well. Development, verification and validation of the radioanalytical separation methods for the alpha emitting transuranium isotopes will be further continued with solid sample matrices in on-going and future collaboration projects among the Nordic partners.

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