Determination of important alpha emitters in nuclear and environmental samples : OptiMethod 2019 project report

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Abstract

This report presents the achievement of the NKS-B OptiMethod 2019 project which was conducted in 2019. An intercomparison was organized on determination of important alpha emitters in two real samples collected from Swedish nuclear power plants, one is nuclear fuel pool water and another is aerosol filter sample. Ten Nordic labs participated in this exercise and reported the analytical results of ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm and ^{243,244}Cm and ^{210}Po. For the nuclear fuel pool water sample, the analytical results of ^{238}Pu, $^{239, 240}$Pu, ^{241}Am and $^{243, 244}$Cm reported by all participating labs agree with each other very well, and the performance of all participating labs is much better than the intercomparison in 2018. Meanwhile the problems occurred in the intercomparison analysis in 2018, such as low chemical yields of Pu and Am/Cm, black residues in the prepared samples, and black and low quality of electrodeposition alpha source in some samples and in some labs were not observed in the analysis in 2019, all these indicate a significantly improved quality of the radiochemical analysis of these radionuclides in all partners' labs through this project. For the aerosol filter sample, the reported analytical results of alpha emitting radionuclides are lower than the detection limits of the methods in most of partners' labs, and a few reported data vary largely. This is mainly attributed to the very low concentrations of target radionuclides in the aerosol filter and relative small sample size used for this intercomparison analysis. The strategies for the analysis of alpha emitters in the samples with very high ^{210}Po content and the problem solution in the Nordic labs are also discussed in this report.

Key words: radioanalysis; nuclear power plant;pool water, aerosol filter, inter-comparison; plutonium; americium; curium

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Content

1. Introduction

Isotopes of plutonium ($^{238, 239, 240}$Pu), americium (^{241}Am) and curium (^{242}Cm, ^{243}Cm and ^{244}Cm) are the most important anthropogenic radionuclides in radiation protection, environmental radioactivity, decommissioning of nuclear facilities and repository of nuclear waste, due to their relatively high production rates in the nuclear activities and high radiological toxicity of the alpha emitters.

Isotopes of Pu, Am and Cm are produced mainly in the nuclear fuel in the nuclear reactors and nuclear weapons tests. Some small amount of them might also be present in the reactor materials (through the reactions of impurity uranium with neutrons). Monitoring and reporting of these alpha emitters in atmospheric and liquid effluents from nuclear power plants are recommended by European Union (Euratom, 2004). This is also required by some authorities in Nordic countries in order to estimate the amount of these alpha emitters released to the environment and its impact to the publics and environment. Meanwhile, process water (reactor coolant and nuclear fuel pool water) and ion exchange resin are often analyzed in the NPPs to monitor the possible leakage of the nuclear fuel, to investigate the dispersion and deposition of alpha emitters in the nuclear reactor system, and to estimate the inventory of alpha emitters in the waste.

Fuel leakage has occurred during the operation of many nuclear power reactors, including those in the Nordic nuclear power plants such as Loviisa, Olkiluoto, Forsmark, Ringhals and Oskarshamn NPPs. It is essential to understand how the radionuclides were released from the fuel and to know the age of the leaked fuel, as well as to understand the behavior of the released radionuclides in the reactor system. Determination of the artificial alpha emitters is important for understanding of their behavior in the reactor water and their distribution in the reactor system, possible discharges to the environment and exposure to the operation staff and potentially to the public. These measurements can be also used to verify the simulation model currently used in the NPPs and to provide the important and critical information for decision-making. Therefore, the most Nordic NPPs have established radioanalytical laboratory for the determination of the alpha emitting radionuclides besides the beta and gamma emitters.

In the investigation of environmental radioactivity and radioecology, isotopes of Pu and Am in the environment and food are often determined to evaluate radiation exposure to the public and consequent radiation impact. Determination of alpha emitters is also an essential requirement in the nuclear and radiological emergency preparedness. In this case, a rapid analysis has to be implemented to meet the requirement of quick decision. For these purposes, sequential chemical separation and quick measurement are important. The Nordic authorities such as SSM, NRPA and STUK, and institutions such as DTU, University of Helsinki, FOI, etc. are heavily involved in these works.

Different methods have been developed and applied for determination of artificial alpha emitters in Nordic laboratories (Hou et al. 2016, 2019). In the Nordic nuclear industry laboratories such as all Nordic NPPs, SKB etc., two major methods are applied. One method is based on directly electrodeposition of metals on metal discs from the water sample and measurement by alpha spectroscopy. The major drawback with this method is that all alpha emitters with similar alpha energies (e.g. ^{241} Am and ^{238} Pu, ^{210}Po and ^{243}Am), cannot be discriminated, and the results are normally not radionuclide specific. For samples with high ^{210}Po, ^{243}Am cannot be used as tracer for the determination of isotopes of Am and Cm. Another method is based on the chemical separation using Eichrom procedures, followed by electrodeposition and alpha spectrometry measurement. This method enables to separate each element and measure individual radionuclides, e.g. ^{241} Am and ^{238} Pu. But it is high labor intensive and often associated with some problems, such as low separation efficiency, black residue occurring in the electrodeposition, white residue formed in the separated solution, causing bad resolution in the prepared alpha source, unsuitable chemical yield tracers, no precise adjustment of the electrodeposition solution. The major problem is lack of the validation of the analytical method and verification of the analytical results for different samples, because suitable standard reference materials and inter-laboratory comparisons for relevant sample matrix are not available. Consequently, the NPPs labs have a strong requirement for validation and improvement of their analytical methods for determination of alpha emitters in their routine analysis. In addition, the behavior of alpha emitters released during the leakage in the reactor is still not well understood.

The OptiMethod project was initiated in 2018, aims to summarize and improve the analytical methods used in Nordic labs for the determination of alpha emitting radionuclides. The analytical capacity and methods used in Nordic labs for determination of alpha emitters have been reviewed and summarized (Hou et al. 2019). 11 Nordic labs in Denmark, Finland and Sweden have capacities to determine individual alpha emitters including ^{238}Pu, $^{239, 240}$Pu, ^{241}Am, ^{242}Cm and $^{243, 244}$Cm in nuclear (reactor and spent fuel pool water) and/or environmental samples. Alpha spectrometry is used in most of labs for the measurement, sequential separation using different combination of ion exchange and extraction chromatography, e.g. UTEVA-TRU, TEVA-UTEVA-TRU, Dowex-TRU and TEVA-DGA columns are used for separation of Pu, Am and Cm from matrices and each other. These methods were summarized in the project report (Hou et al. 2019). An inter-comparison exercise for analysis of a spiked water and a real reactor water was organized in 2018, 11 Nordic labs participated in this inter-comparison exercise and reported the analytical results of isotopes of plutonium, americium and curium. The results reported by the most labs agree with each other with only 1-2 outlying data for each radionuclide (Hou et al. 2019). Some problems were recognized in this inter-comparison exercise:

1) The direct electrodeposition followed by alpha spectrometry method was used in one Nordic lab for the determination of alpha emitters. In this case, it is not possible to report the individual activity

concentrations of ^{238}Pu and ^{241}Am because of the similar energies of alpha particles emitted from these two radionuclides. For the analysis of samples with complicated matrices (e.g. discharge water, environmental samples), this method might be not usable.

2) Variable and low recovery of Am and Cm (down to 18-50%) in the analytical procedure was observed in some labs for some samples. Meanwhile, low recoveries of Pu (10-20%) in the analytical procedure in some labs were also reported. Besides the chemical separation procedure, electrodeposition step might be another reason.
3) It was reported that the prepared source using electrodeposition is not always good, sometimes a black source was obtained, causing a bad energy resolution in alpha spectra in some samples. Besides the electrodeposition condition, the purity of the separated sample solution might be another reason, which might be also a reason causing low recovery of the radionuclides measured in the alpha sources. A further investigation and optimization to overcome this problem is needed.
4) A black residue was found in the separated Am-Cm fraction after evaporation in some lab using UTEVA-TRU separation procedure, it was not clear how the residue was formed and if it contains Am and Cm. Organic residues eluted from the UTEVA and TRU resin might be the possible source of this black residue. A further investigation is needed to clarify it, and to assess its effect in the separation of Am and Cm.
5) Different separation procedures are used in the Nordic labs for the separation of alpha emitters, all of them work well for the analysis of reactor water samples with simple matrices. However, the suitability of these procedures for analysis of samples with complicated matrices, such as filter paper and discharge water from nuclear power plants, environmental samples such as soil, sediment, seawater and fresh water is not known. One challenge might be the removal of ^{210}Po interference in the analysis of filter and environmental samples. The concentration of ^{210}Po in filter sample might be a few orders of magnitude higher compared to the measured alpha emitters, the similar energy of alpha particles with ^{210}Po (5.30 MeV), namely ^{243}Am (5.28 MeV) which was used as a yield tracer of Am and Cm isotopes makes the analytical results questionable if ^{210}Po was not well eliminated. Another challenge will be the sufficient removal of the large amount of matrix elements in the environmental samples. A further improvement and investigation for optimization of the analytical method for isotopes of U, Pu, Am and Cm is needed.

The OptiMethod2019 project is a continuation of the work in 2018, it aims to solve the problem recognized in the last stage of the project, to improve the analytical quality of the Nordic laboratories for radiochemical analysis of artificial alpha emitters in NPP, waste and environmental samples by organizing the second inter-comparison exercises, in order to evaluate and optimize method used in participating labs.

2. Inter-comparison exercise on determination of isotopes of Pu, Am and Cm in nuclear fuel pool water and aerosol filter of a nuclear power plants

The second inter-comparison exercise was organized in this project in 2019 for the determination of isotopes of Pu, Am and Cm in a nuclear fuel pool water sample and an aerosol filter samples collected from one Nordic NPP. Ten Nordic labs participated in the inter-comparison exercise. The analytical results of this inter-comparison exercise are presented and discussed below.

2.1 Samples

One nuclear fuel pool water and one aerosol filter sample collected from one NPP were prepared for this exercise.

(1) Nuclear fuel pool water was collected from one of Swedish Nuclear fuel storage pools in Oct. 2018, and provided by SKB. This sample was pure water without addition of boric acid or other chemicals. The sample was acidified to about pH2 using HNO_3 immediately after sampling. 2 liters of water sample in a plastic container were sent to partner laboratories for inter-comparison exercise. This sample contains some activation and fission product radionuclides, with total gamma activity of about 100 Bq/L. The concentrations of ^{239,240}Pu, ^{241}Am and ^{243,244}Cm were estimated to be 0.1-10 mBq/L of each radionuclide, and 1-50 mBq/L for ^{238}Pu.

(2) Aerosol was collected on 0.45μm membrane filters of 47 mm in diameter at different parts of the ventilation systems in a Swedish nuclear power pant, more than 30 filters were collected in 2018, which were used for this inter-comparison exercise. To avoid the problem of inhomogeneity of radionuclides among filters and in each filter, all collected filters were combined to one sample and cut into small pieces. The filters were leached using 1M H_2SO_4 solution for 3 times by heated on a hotplate. All leachates were combined and filtered through a 0.45 micrometer filter, in total 1500 ml leachate was obtained. After well mixed, the leachate was divided into aliquots of 100 ml (equivalent to 2 filters), sealed into plastic bottle, and delivered to each partners lab for inter-comparison exercise. The concentrations of 1-10 mBq/100 ml for each isotope of Pu, Am and Cm and 0.1-2.0 Bq/100ml for ^{210}Po were estimated.

Table 1 Two inter-comparison water samples for determination of alpha emitters

Sample code	Sample description	Matrix	Preparation/ collection date	Alpha radionuclides to be determined and major radionuclides, activation and small fission products
Pool water	Nuclear fuel pool water from SKB	2.0 L, acidified to pH2 with HNO_3	Oct. 2018	^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, $^{243,244}Cm$
Filter	Leachate of aerosol filter collected from Forsmark NPP	100 ml leachate of 1M H_2SO_4, filtered through 0.45 μm filter	March - Nov. 2018	^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, ^{243}Am, ^{242}Cm, ^{243}Cm ^{244}Cm, other activation and fission product radionuclides, relative high ^{210}Po level.

3.2 Analytical methods applied for the determination of alpha emitters by the participants

In this inter-comparison exercise, the measurement of alpha emitters was implemented by alpha spectrometry in all participating partner labs. The alpha sources were mainly prepared by electrodeposition on stainless steel disc in most of labs, but a few labs also used micro-precipitation method by forming co-precipitation of actinide fluoride with LnF_3, the precipitates was transferred to a small filter paper by filtration and used for alpha measurement. For the chemical separation, 4 different procedures were used by the 10 participating labs. Among them, 6 labs used UTEVA-TRU method (Fig. 1), 4 of them used electrodeposition for alpha source preparation and two labs used micro-precipitation (NdF_3) for source preparation. One lab directly electrodeposited actinide on stainless steel disc for alpha measurement of the radionuclides without chemical separation. The sample solution was simply evaporated to dryness and the residue was dissolved into H_2SO_4 solution and then adjust to pH2.1-2.4 for electrodeposition of all actinide on to disc. Other 3 labs used different chemical separation procedures, including TEVA-UTEVA-TRU-Ln method (Fig. 2), TEVA-DGA method (Fig. 3), and TEVA-TRU-TEVA method. The detailed procedures of these methods have been reported elsewhere (Hou et al. 2019). ^{242}Pu and ^{243}Am purchased from different organizations (e.g. NIST, NPL, Eckert & Ziegler) were used as yield tracers for plutonium isotopes and isotopes of Am and Cm, respectively in the chemical separation in all labs who did the chemical separation. 0.01-0.08 Bq of ^{242}Pu and ^{243}Am were spiked to sample solution before chemical separation. In the direct measurement method (no chemical separation was applied), ^{233}U (0.1 Bq) was spiked as yield tracer for estimation of the recoveries of all alpha radionuclides during sample preparation and electrodeposition processes, and for correcting the activity

of all other radionuclides in alpha spectrometry measurement. Table 2 summarizes the methods used in this comparison by participating labs.

Table 2 Analytical methods applied in partners' lab for inter-comparison exercise

Lab code	Separation method	Source preparation	Tracer(s)	Measurement methods
1	TEVA-DGA	Electrodeposition	^{242}Pu, ^{243}Am	α-spectrometry
4	TEVA-TRU-TEVA	Electrodeposition	^{242}Pu, ^{243}Am	α-spectrometry
5, 7, 10, 11	UTEVA-TRU	Electrodeposition	^{242}Pu, ^{243}Am	α-spectrometry
6	TEVA-UTEVA-TRU-Ln resin	Electrodeposition	^{242}Pu, ^{243}Am	α-spectrometry
8	no	Electrodeposition	^{233}U	α-spectrometry
12, 9	UTEVA-TRU	Micro-coprecipitation	^{242}Pu, ^{243}Am	α-spectrometry

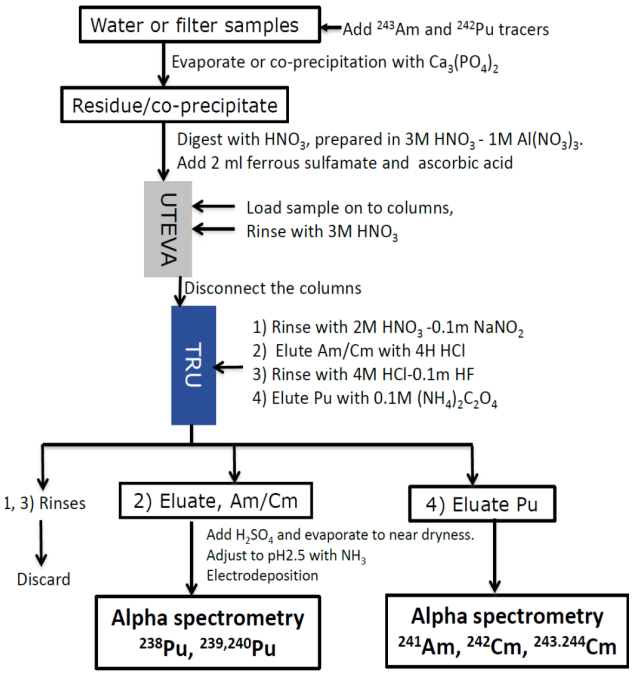

Fig. 1 Diagram of an analytical procedure for determination of Pu, Am and Cm with a combination of UTEVA and TRU columns used in 6 partner labs.

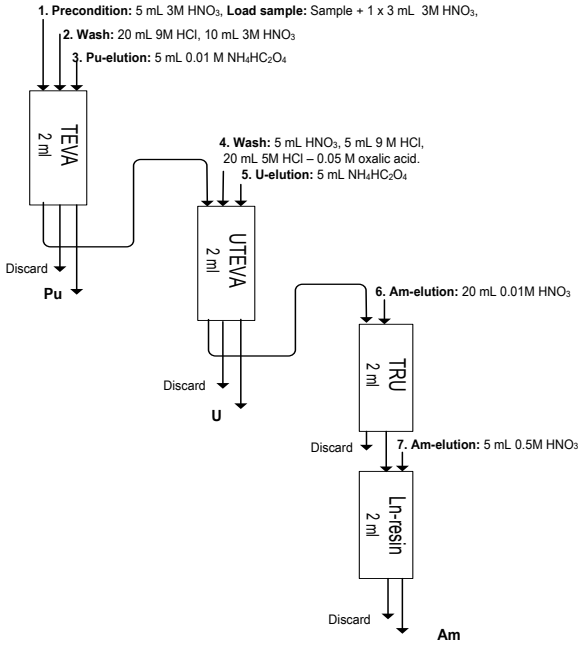

Fig.2 Diagram of an analytical procedure for determination of Pu, Am and Cm with a combination of TEVA, UTEVA, TRU and Ln columns used in a Nordic lab.

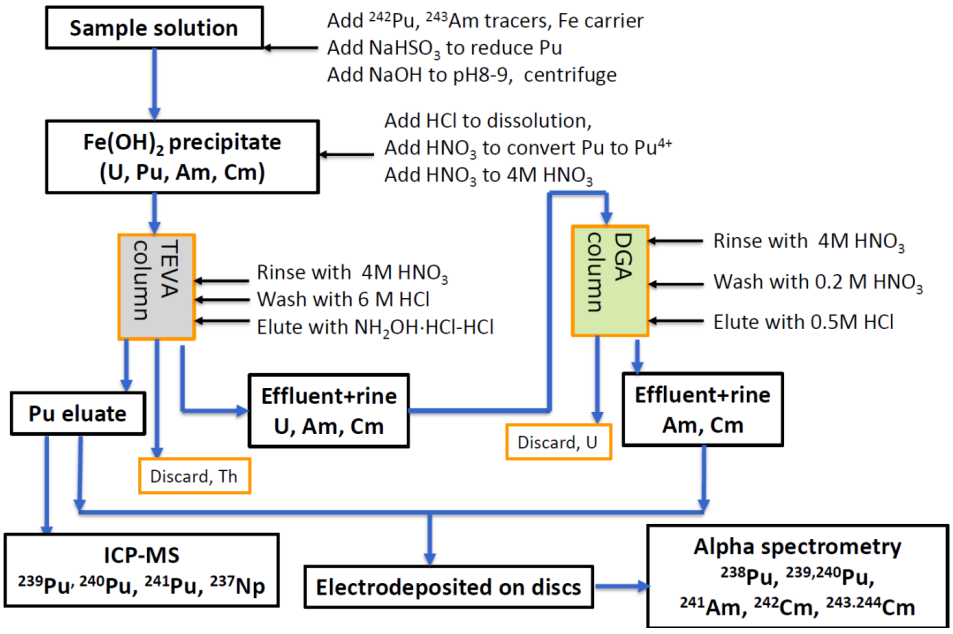

Fig. 3 Diagram of chromatographic separation procedure for sequential separation of Pu, Np, Am and Cm and measurement of their isotopes.

2.3 Analytical results of inter-comparison exercise

(1) Nuclear fuel pool water

Overall 10 labs participated in the inter-comparison analysis of the nuclear fuel pool water sample, among them, 10 labs reported analytical results of the isotopes of Am and Cm, 9 labs reported the results of ^{238}Pu and ^{239,240}Pu. The analytical results with uncertainties (k=2) of each lab are presented in Fig. 4. All results were decay corrected to 1st Jan. 2019. The values of average (red line) and 2SD (yellow lines) of all reported data are also presented in the figures.

The reported ^{238}Pu concentrations in this sample range from 16.9 to 21.3 mBq/kg with an average and 1SD of 19.4±2.0 mBq/kg, The variation of the analytical results among all participating labs is relative small with a relative standard deviation of only 10%. These results are much better than the inter-comparison in 2018 although the concentration of ^{238}Pu in this sample is 2 times lower than that in the reactor water used in the inter-comparison in 2018.

The reported concentrations of ^{239,240}Pu in the pool water range from 0.52 to 1.60 mBq/L with an average and 1SD of 1.10±0.39 mBq/kg. A relative bigger variation among participating labs with a relative standard deviation of 36% was obtained. This is mainly attributed to the low concentration of ^{239,240}Pu in this sample, more than 10 times lower than that of ^{238}Pu. However, there is no exceptional

value which are far from the most of data in this inter-comparison for ^{239,240}Pu, indicating the performance on the determination of $^{239, 240}$Pu also better than that in 2018, especially in consideration of more than 2 orders of magnitude lower ^{239,240}Pu in this sample compared to the reactor water samples (527±59 mBq/kg in average and 1SD) used in the inter-comparison in 2018.

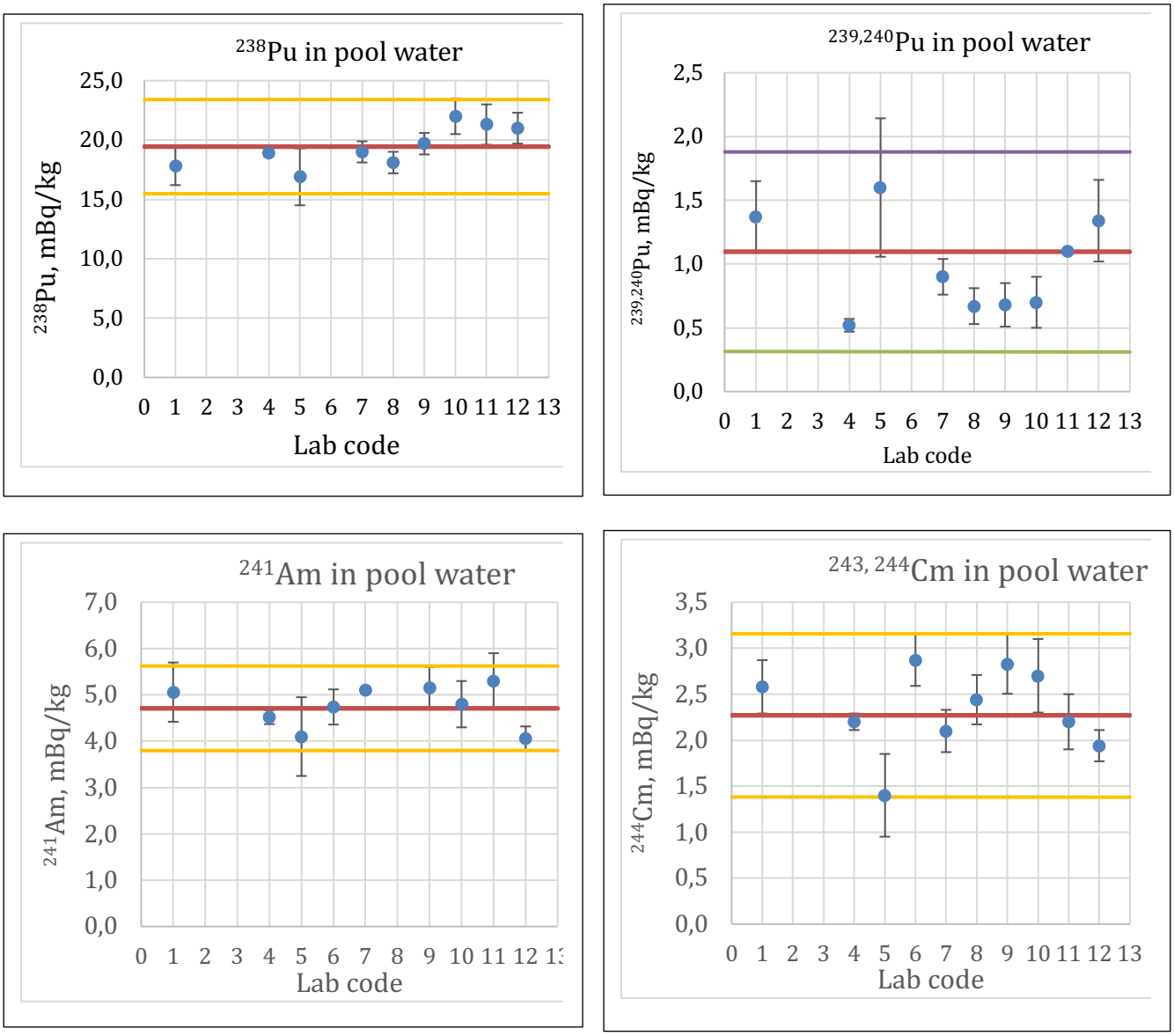

Fig. 4 Inter-comparison results of nuclear fuel pool water sample for ^{238}Pu, ^{239,240}Pu, ^{241}Am and ^{244}Cm in Nordic labs.

The reported concentrations of ^{241}Am in the pool water sample range from 4.06 to 5.30 mBq/kg with an average and 1SD of 4.71±0.46 Bq/kg. The variation of the analytical results among all participating

labs is relative small with a relative standard deviation of only 10%. These results are also much better than in the inter-comparison in 2018 although the concentration of ^{241}Am in this sample is 40 times lower than that in the reactor water (254±39 mBq/kg) used in the inter-comparison in 2018.

The reported concentrations of ^{243,244}Cm in the pool water range from 1.40 to 2.87 mBq/kg with an average and 1SD of 2.27±0.44 mBq/kg. The variation of the results among all participating labs is 20%, which is comparable with the results of $^{243,\ 244}$Cm of the inter-comparison in 2018 (1500-2400 mBq/kg), although the concentration of ^{243,244}Cm in the pool water in this inter-comparison is nearly 3 orders of magnitude lower than that in the reactor water used in the inter-comparison in 2018.

In general, the analytical results of all participating labs for ^{238}Pu, ^{239,240}Pu, ^{241}Am and $^{243,\ 244}$Cm in the nuclear fuel pool water agree very well. Although the concentrations of these radionuclides in the pool water samples are 2 times to 3 orders of magnitude lower than those in the reactor coolant water used in the inter-comparison in 2018, the performance of all participating labs is better than that in 2018, indicating a significantly improved performance of the radiochemical analysis in the Nordic labs. This should be attributed to the activities of organized in this project, which help the participants to solve the problems and to improve the analytical method and the operation skills in the radiochemical analysis.

For ^{242}Cm, the most of the reported results are below the detection limit of the methods used by the partners (0.5 mBq/kg), only a few labs reported values (e.g. 0.06 mBq/kg) above the detection limits of their methods. Therefore it is difficult to make a comparison for this radionuclide in this sample, and the results are therefore not presented in the figure. ^{242}Cm is a relative short-lived (162 days) radionuclide, which is produced mainly through the beta decay of the short-lived ^{242}Am (16 h) and internal conversion followed by beta decay of relative long-lived ^{242m}Am (141 years) (Fig. 5). The nuclear fuel pool water used in this inter-comparison was collected in Oct. 2018, and the sample was analyzed in each participating lab in July - Sept. 2019, i.e. more than 240 days after collection. The spent fuels stored in the pool might has already been taken out from the reactor for a few years. Therefore, the contribution from ^{242}Am should be negligible, and the dominant source of ^{242}Cm should be ^{242m}Am. The decay correction for ^{242}Cm (about half year) might not have a significant contribution to the variation of the results.

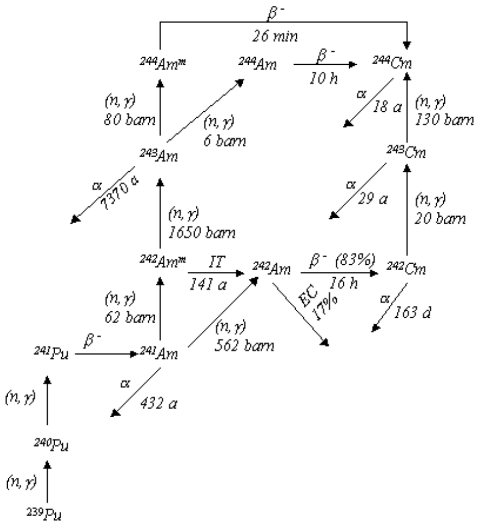

Fig. 5 Production routes of isotopes of Am and Cm in the nuclear reactor (Holm et al. 2002)

The undetectable level of ^{242}Cm in the nuclear fuel pool water indicates that its production and reservation in the nuclear fuel pool is very small. The concentrations of alpha emitting isotopes of plutonium, americium and curium in the fuel pool water analyzed in this inter-comparison are significantly lower than those in the reactor water analyzed in the inter-comparison in 2018, indicating that no leakage of the fuel elements might be occurred in this nuclear fuel pool, the trace amounts of these alpha emitting actinides might originate from the impurities of uranium presented on the surface of the fuel elements, which was exposed to the neutrons during the utilization of the fuel in the power reactor.

(2) Aerosol filter from nuclear power plant

The aerosol filters collected from different parts of ventilation system in a Swedish nuclear power plant was used in the inter-comparison in this work. To avoid the homogeneity problem, all 30 filter samples were cut and leached using H_2SO_4, and the leachate was filtered and divided into 100 ml aliquots to be distributed to the partners' labs. The analytical results of the radionuclides were reported in mBq/kg of leachate.

Table 2 shows the analytical results of ^{238}Pu, $^{239,240}Pu$, ^{241}Am, ^{242}Cm and $^{243,244}Cm$. It can be seen that the reported results are lower than the detection limits in the most of the labs. This is mainly attributed to the very low concentrations of these radionuclides in the air released through the ventilation system from the nuclear power plant. Meanwhile, the sample size used for inter-comparison exercise was too small to be capable of measuring the very low concentrations of alpha emitting radionuclides. The relative high detection limits of these radionuclides in the analysis of this sample compared to those for the nuclear fuel pool water sample is mainly attributed to the small size of filter leachate of only 30 -100 g compared to 1000 g for the pool water sample. This results in a much less amount of radionuclides on the electrodeposited disc. For a 50 g filter leachate sample, with 90% chemical yield, 25% counting efficiency of alpha spectrometry, and a detection limit of 0.1 counts/h of the alpha spectrometry, the detection limit of the method will be 2.5 mBq/kg. Fig. 6 shows the alpha spectra of plutonium fraction and Am/Cm fraction with ^{242}Pu and ^{243}Am as yield tracers, respectively. It can be seen that no ^{238}Pu and $^{239,240}Pu$ peaks in the plutonium fraction and no ^{241}Am, ^{242}Cm, $^{243,244}Cm$ peaks in the Am/Cm fraction were measureable, and only the peaks of ^{242}Pu and ^{243}Am (which were spiked to the sample as yield tracers) in the spectra were visible, even when the sources were measured for 7 days.

Table 2 Results of inter-comparison analysis for isotopes of Pu, Am and Cm in filter leachate

Lab code	^{238}Pu, mBq/kg		^{239,240}Pu, mBq/kg		^{241}Am, mBq/kg		^{242}Cm, mBq/kg		^{243,244}Cm, mBq/kg	
	Value	Uncert	Value	Uncert	Value	Uncert	Value	Uncert	Value	Uncert
1	<5.2		<5.2		<3.0		<2.5		<2.8	
4	<2		<2		0.85	0.17	0.98	0.18	0.58	0.13
5	29.40	8.30	<6.7		9.20	0.75	32.9	10.6	<3.3	
6										
7	<1.9		<1.9		2.70	0.71	1.90	1.30	<0.71	
8	45.20	3.62	4.70	1.03	with ^{238}Pu			9.30	1.488	
10	<25.6		<8.8		12.60	4.80	<6.9		<2.6	
11	<14		<14		<21		<15		<11	
12	<12.8		<8.5		<6.9		<13.0		<3	

*The data presented as "< xx " are the detection limits of the methods used in the partner's labs. The analytical uncertainties presented are extended uncertainty with k=2.

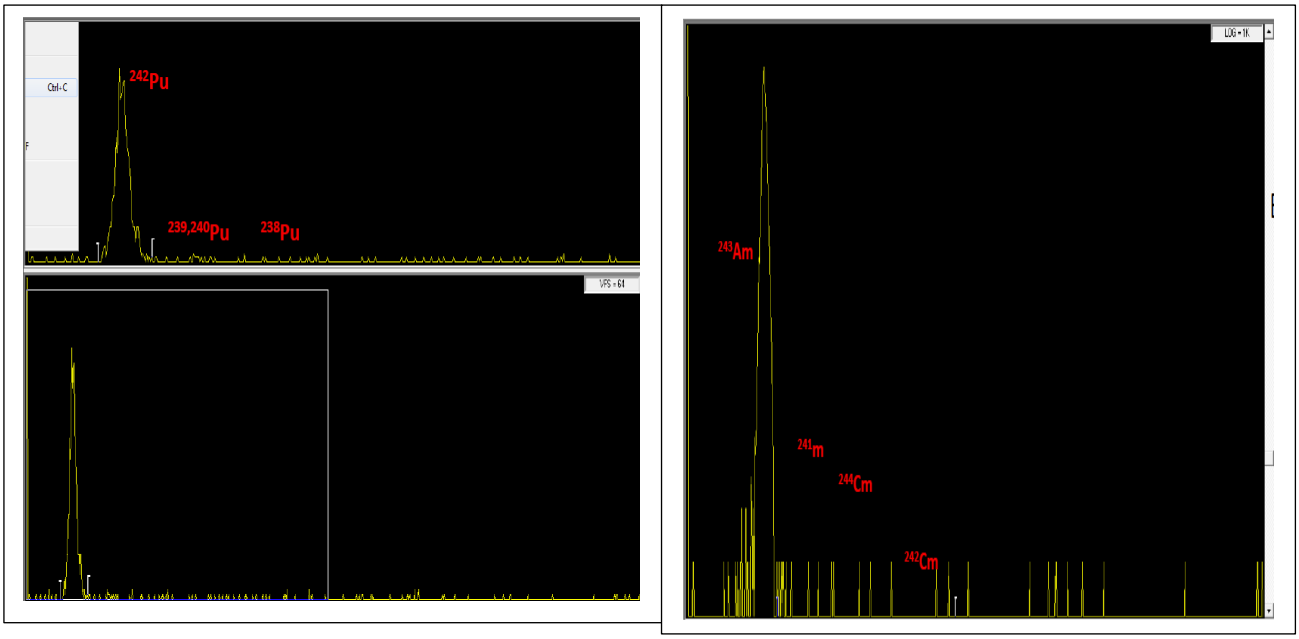

Fig. 6 Alpha spectra of plutonium fraction and Am and Cm fraction determined in the nuclear fuel pool water samples for inter-comparison 2019.

The very low concentrations of isotopes of Pu , Am and Cm in the aerosol filter should be attributed to the refractory features of the actinides, which are stable in the circumstances in the nuclear reactor, not volatile, and which doesn't easily form aerosol even presented in the reactor water. These results also indicate that the atmospheric releases is not a significant pathway for the isotopes of Pu, Am and Cm.

A few labs reported the analyzed values for some radionuclides, but showed a very large variation (Table 2). This might be attributed to the small size of the sample used for the analysis and the efficiency for decontamination of the interference radionuclides might be not sufficiently high. It was observed that ^{210}Po concentration in the aerosol sample is quite high. Three labs have analyzed the ^{210}Po concentration in the filter leachate, the reported concentrations of ^{210}Po ranged in 2530-3370 mBq/kg with an average and 1SD of 2870±440 mBq/kg. This is 2-3 orders of magnitude higher than those of alpha isotopes of Pu, Am and Cm. The chemical properties of ^{210}Po are very complicated, and ^{210}Po might enter to the fractions of plutonium and Am/Cm fraction, and cause a high interference, especially for the determination of isotopes of Am and Cm, because the alpha energy of ^{210}Po (5.30 MeV) is close to that of ^{243}Am (5.23-5.28 MeV), and the alpha spectrometry could not discriminate these two radionuclides. Since ^{243}Am was employed as yield tracer for Am and Cm, the contamination of ^{210}Po in the Am/Cm fraction will cause an overestimated values of ^{241}Am, ^{242}Cm and $^{234,\,244}$Cm.

4. Problems and strategies in the analysis of alpha emitters

1) ***Challenge and strategies in the analysis of filter samples from a nuclear power plant***

The selection of the aerosol filter samples from the nuclear power reactor for the inter-comparison exercise in this work was based on the following considerations: 1) atmospheric releases of radionuclides in the nuclear power plants is an important issue in view of radiation protection, and the monitoring of the radioactivity level in the effluents including atmospheric releases is required by the authorities of radiation protection; 2) The Nordic labs have demonstrated a good capacity in the analysis of alpha radionuclides of Pu, Am and Cm in the inter-comparison exercise in 2018 by analysis of spiked water and the reactor coolant water, which allows to plan a more challenging work for determination of low level alpha emitting isotopes of Pu, Am and Cm in the second stage of the project in 2019; 3) Some labs of Nordic nuclear industry had started and planned for the analysis of filter samples for alpha emitting isotopes of Pu, Am, and Cm. It was known that the concentrations of alpha emitting radionuclides in the aerosol filters are very low, and the activity concentration of ^{210}Po in this type of filter is a few orders of magnitude higher than the isotopes of actinides. Therefore, an investigation was implemented for better elimination of the interferences of ^{210}Po in the determination of these radionuclides, especially in the Am/Cm fraction. Meanwhile, the analytical

procedures used for the routine analysis were modified to eliminate polonium in the chemical separation procedure.

In the chemical procedure with UTEVA-TRU chromatographic columns (Fig. 1) which was used by 6 partner's labs, polonium can be removed in the TRU column separation step. Po^{4+}, Pu^{3+}, Am^{3+} and Cm^{3+} do not adsorb on the UTEVA column at 3-4 M HNO_3 media. The prepared sample solution in 3M HNO_3 is loaded to a UTEVA column, where Po^{4+}, as well as Pu^{3+}, Am^{3+} and Cm^{3+} pass through the UTEVA column and load to the TRU column. Po^{2+} could not be adsorbed in the TRU resin in HNO_3 solution, but is highly adsorbed in HCl media (Fig. 7). On the contrary, Pu^{3+}, Am^{3+} and Cm^{3+} have a relatively high adsorption on TRU resin in high concentrations of HNO_3 (>1M) media (Fig.7). After loading the sample solution in 3M HNO_3 media to the TRU column, the TRU column was rinsed with high concentration of HNO_3 (e.g. 4-8 M) with addition of $NaNO_2$ to on-column oxidizing Pu^{3+} to Pu^{4+} to be strongly adsorbed on TRU resin, then extensively rinsing the TRU column with 8 M HNO_3 to highly eliminate Po^{4+} remaining on the column. Afterwards, Am/Cm and Pu were sequentially eluted using 4M HCl and complexing reagent $(NH_4)_2C_2O_4$, respectively. Since the Am/Cm was eluted with 4M HCl and high adsorption of Po^{4+}on TRU resin occurs at HCl media, a high decontamination factor of Po^{4+} in the Cm/Am fraction is expected by this modification.

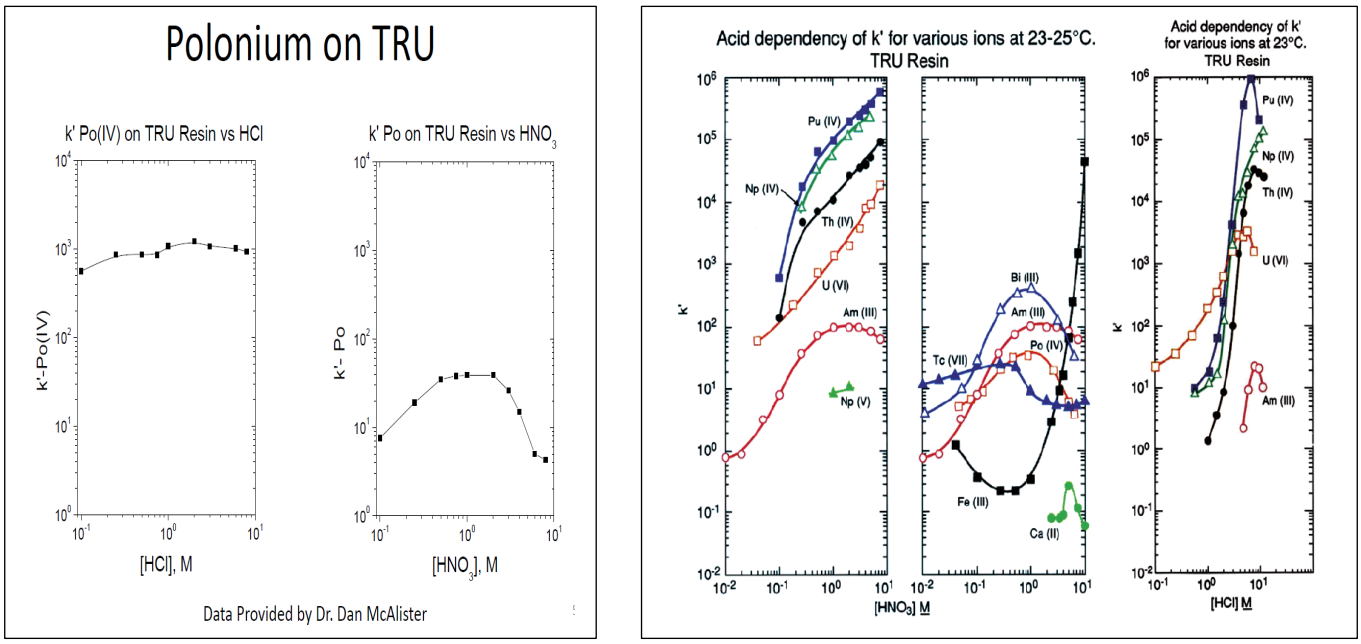

Fig. 7 Distribution factor of Po^{4+} Pu^{3+}, Am^{3+} and Cm^{3+} on TRU resin (Maxwell et al. 2013; Triskem 2020).

In the TEVA-DGA procedure used in one partner lab (Fig. 3), the procedure was modified to remove Po^{4+} in both TEVA and DGA chromatographic separation steps. Po^{4+} has a relative high distribution factors on TEVA resin in low concentrations of HNO_3 and HCl media, especially in HCl medium (Fig. 8). However, the distribution factors of Po^{4+} on the TEVA decrease with the increased concentrations of the HCl and HNO_3, 1-2 orders of magnitude lower distribution factor of Po^{4+} on the TEVA resin could be obtained in 8 M HNO_3 media. Based on this feature, the prepared sample solution in 4M HNO_3 media is loaded onto the TEVA column, followed by rinsing with 4M HNO_3. In this case Pu^{4+} and Po^{4+} are highly retained on the TEVA column, while Am/Cm pass through the TEVA column and enter to the effluent and rinse solution for further purification. Additional step rinsing using 8M HNO_3 was added in the modified procedure after the loading and rinsing TEVA column (Fig. 9), in order to get a better removal of Po^{4+} from the Pu fraction.

In the DGA resin, Po^{4+} has a high adsorption in HCl media, but relatively low and increasing distribution factor on the DGA resin with increasing concentrations of HNO_3. The distribution factor of Po^{4+} is about 2 at 0.1M HNO_3 media (Fig. 10). The Am/Cm fraction loaded in a DGA column was further rinsed with 0.2 M HNO_3 to remove any remaining Po^{4+} in the effluent from the TEVA column before eluting Am/Cm with HCl solution, to ensure a high decontamination factor for ^{210}Po in the separated Am/Cm solution, and eliminate the interference of ^{210}Po to the measurement of ^{243}Am (tracer).

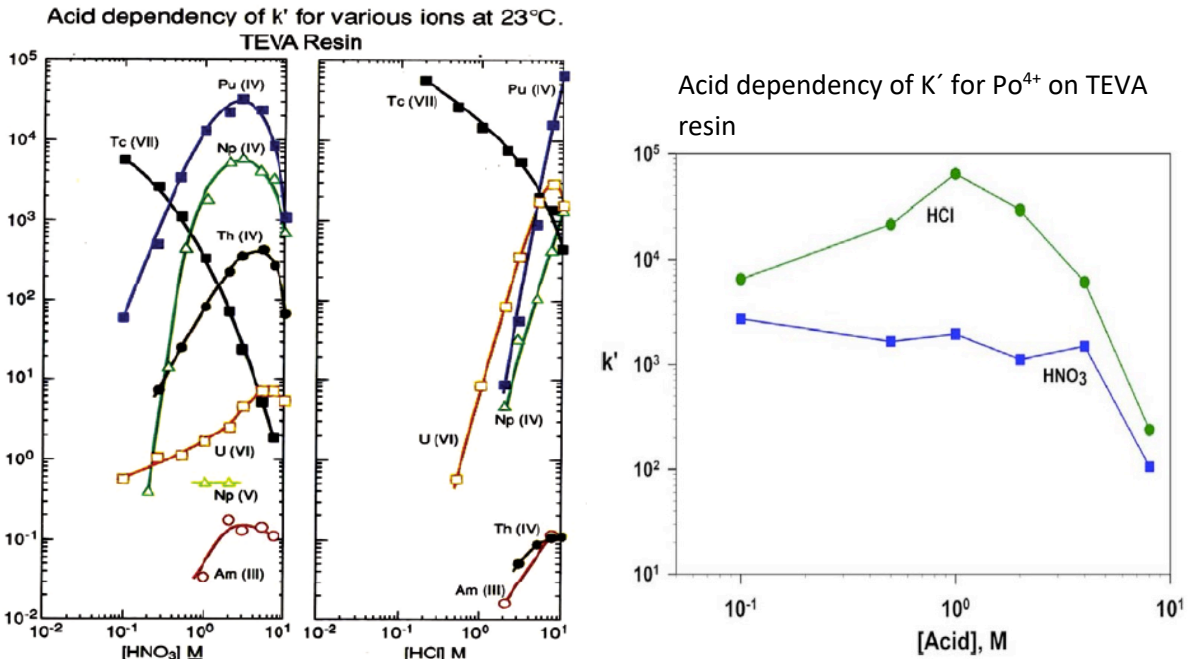

Fig. 8 Variation of k' values of Po^{4+} and other ions with the concentration of HNO_3 and HCl in TEVA resin (Triskem 2020, Khaing & Thakur, 2017)

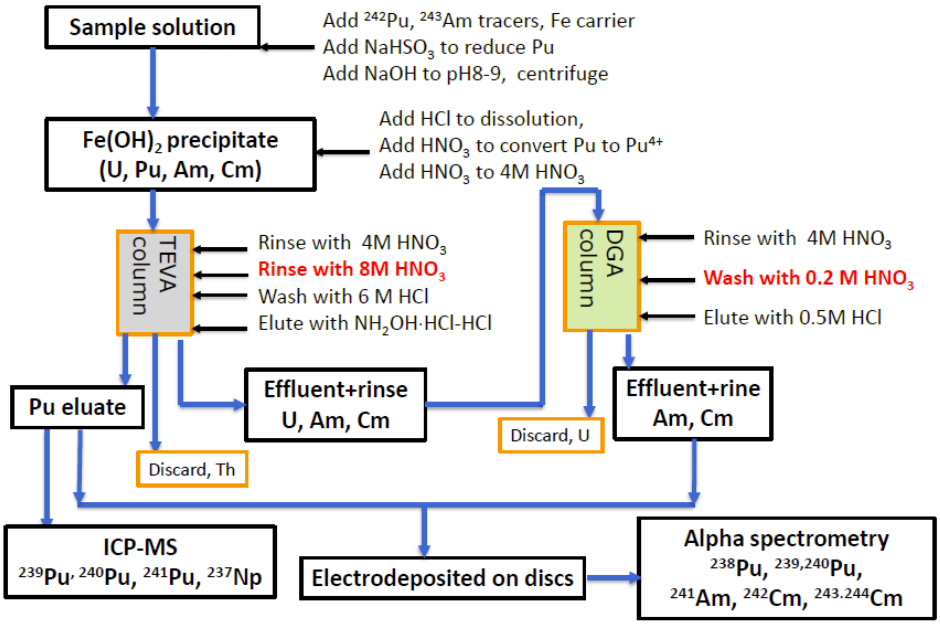

Fig. 9 Modified procedure for the separation of Pu, Am and Cm from aerosol filter samples with high ^{210}Po content

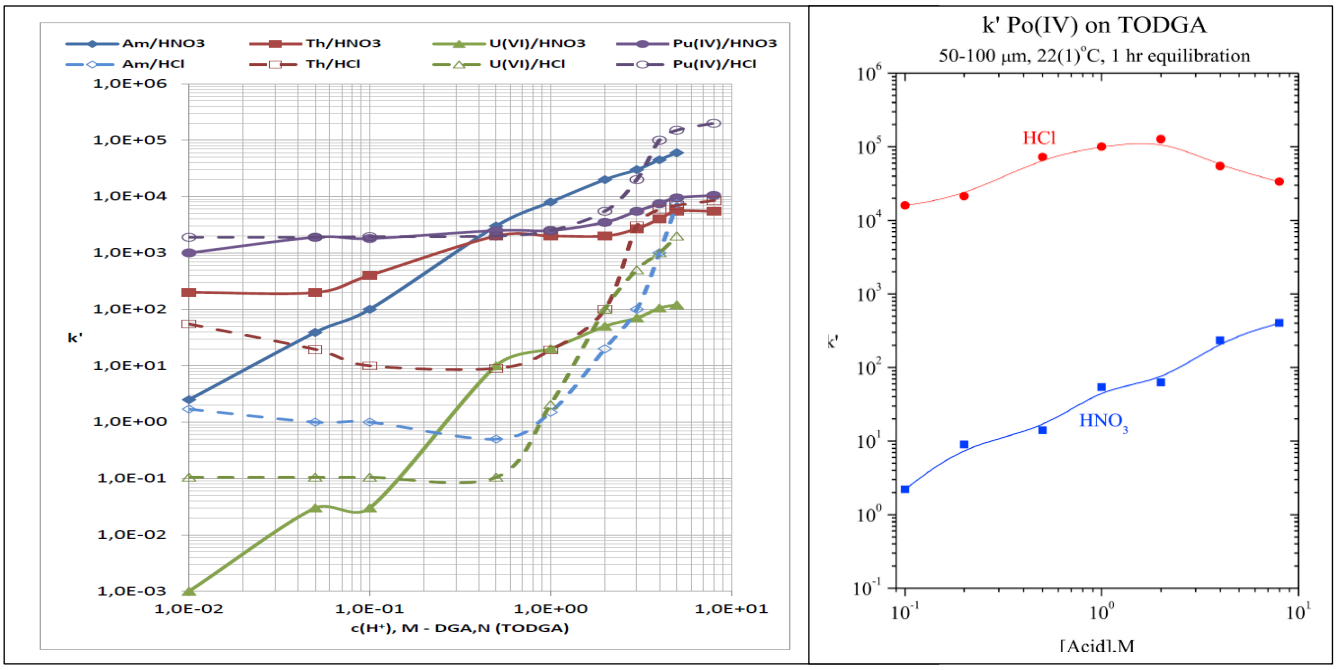

Fig. 10 Fig. 8 Variation of k' values of Po^{4+} and other ions with the concentration of HNO_3 and HCl in DGA resin (Triskem, 2020; Maxwell et al. 2019)

2) ***Improvement of the preparation of alpha sources for the measurement of Am and Cm isotopes.***

In the inter-comparison exercise in 2018, some labs reported that a black residue was observed in the separated Am-Cm fraction after addition of H_2SO_4 and evaporation to dryness using UTEVA-TRU separation procedure, It was proposed that the black residue might be organic residues from the TRU or/and UTEVA resin. A modified procedure was used in this lab by evaporation of the Am/Cm fraction to dryness without addition of H_2SO_4. The formed residue was dissolved with 0.05M H_2SO_4 solution for electrodeposition. By modification, no black residue was observed anymore, and the chemical yield of Am/Cm monitored by ^{243}Am was not significantly changed. This might confirm that the black residue is the organic substance from the resin, which could be burned to blank carbon by concentrated H_2SO_4 at high temperature during evaporation step, after HCl and H_2O were removed from the eluate. However, it should be mentioned that the complete removal of HCl and HNO_3 is necessary before electrodeposition, otherwise it might interfere with the electrodeposition of Am/Cm on the stainless steel.

It was also reported in the inter-comparison in 2018 that a black disc was observed ~~on~~ in some lab during electrodeposition and consequently a bad energy resolution in alpha spectra in these samples occurred. This was attributed to the possible impurities in the separated Am/Cm fraction, including organic substances which might be burned during electrodeposition at high electric current (1.0-1.5 A). In the inter-comparison in 2019, no such ~~as~~ black alpha source was observed, meanwhile, the chemical yields of Am/Cm and Pu in the corresponding fraction were also sufficiently high (> 60%), no recovery of less than 20% was observed. This demonstrated that the investigation and discussion through the implementation of the project practically helped the partners for improvement of their analytical procedure and experimental skills. With the effort of the participating labs in the operation of the chemical separation procedure, a better removal of the impurities and improved chemical yield of Pu and Am/Cm were ensured.

5. Summary and Remarks

This project is a continuation of the work in 2018. Based on the achievement and knowledge obtained during the operation of the project in 2018, the second run inter-comparison analysis of two real samples was organized, ten Nordic labs participated in this inter-comparison exercise and reported the results of isotopes of plutonium, americium and curium. The problems and strategies identified in 2018 were investigated for improvement of the performance of the radiochemical analysis in the Nordic labs for reliable determination of these radionuclides. The major achievements are summarized below:

1) All 12 partner labs of this project in Denmark, Finland and Sweden have established the capability for the determination of alpha emitters ^{238}Pu, $^{239, 240}$Pu, ^{241}Am, ^{242}Cm and $^{243, 244}$Cm in nuclear (reactor and spent fuel pool water) samples. In most of the labs, alpha spectrometry is used for the measurement

of these alpha emitting radionuclides. ICP-MS is only used in a few labs for measurement of ^{239}Pu, ^{240}Pu and isotopes of uranium (^{234}U, ^{235}U, ^{238}U), mainly in the labs of universities and institutes.

2) All reported results of ^{238}Pu, $^{239,\ 240}$Pu, ^{241}Am and $^{243,\ 244}$Cm by the participating labs in the inter-comparison exercise of the nuclear fuel pool water samples agree very well, although the activity concentrations of these radionuclides are significantly lower by a factor of up to 3 orders of magnitude than that in the reactor coolant water used in the inter-comparison in 2018. This indicates a significantly improved performance in the Nordic labs in the radiochemical analysis.
3) The problems of black residue and black electrodeposition sources occurred in the inter-comparison analysis in some partners' labs in 2018 did not occur in the analysis in 2019. Besides the modification of the analytical procedure, the experimental skills in the separation were also significantly improved. This was also confirmed by the high chemical yields of Pu and Am/Cm in all participating labs.
4) An aerosol filter sample collected from the ventilation system in a Swedish nuclear power plant was also used for the inter-comparison exercise. Unfortunately, the reported concentrations of ^{238}Pu, $^{239,\ 240}$Pu, ^{241}Am, ^{242}Cm and $^{243,\ 244}$Cm are lower than the detection limits of the method used in most of the participating labs. This is mainly attributed to the very low concentrations of these radionuclides in the air in the nuclear power plant, and the relative small size of the sample used for the analysis.
5) Although the concentrations of the interesting radionuclides in the filter sample were not measurable, however, the main challenge of very high ^{210}Po content compared to the interesting alpha emitter in this type of samples was well recognized in the partners' labs, and the analytical procedures were modified to improve the elimination of the ^{210}Po interference to the measurement of isotopes of Am and Cm.
6) Besides water and filter samples from nuclear power plants, various environmental samples (soil, sediment, seawater, vegetation, and animal tissues) and waste samples from decommissioning of nuclear facilities are also being analyzed in many Nordic labs. Therefore validation, verification and improvement of the analytical methods for these sample types in the Nordic labs are also highly needed. A continuation of this project is expected to increase the reliability of the present applied analytical method for alpha emitting radionuclides in these types of samples in the Nordic labs. A new NKS project of RAD-MERDE was proposed and launched in 2020. In this project, the improved analytical method achieved in the OptiMethod project for sequentially analyzing Pu, Am, and Cm in NPP water samples will be expanded to facilitate the analysis of different solid environmental and decommissioning samples.

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Abstract max. 2000 characters	This report presents the achievement of the NKS-B OptiMethod 2019 project which was conducted in 2019. An intercomparison was organized on determination of important alpha emitters in two real samples collected from Swedish nuclear power plants, one is nuclear fuel pool water and another is aerosol filter sample. 10 Nordic labs participated in this exercise and reported the analytical results of isotopes of plutonium, americium, curium and ^{210}Po. For the nuclear fuel pool water sample, the analytical results of ^{238}Pu, $^{239,\,240}$Pu, ^{241}Am and $^{243,\,244}$Cm reported by all participating labs agree with each other very well, and the performance of all participating labs is much better than in the intercomparison in 2018. Meanwhile the problems occurred in the intercomparison analysis of 2018, such as low chemical yield of Pu and Am/Cm, black residues in the prepared samples, and black and low quality of

electrodeposition alpha source were not observed in the analysis in 2019. All these indicate a significantly improved quality of the radiochemical analysis of these radionuclides through this project. While, for the aerosol filter sample, the reported analytical results of alpha emitting radionuclides are lower than the detection limits of the method used in the partners' lab, and a few reported data also vary largely, this is mainly attributed to the very low concentrations of target radionuclides in the aerosol filter and relatively small sample size for the analysis. The strategies for the analysis of alpha emitters in sample with very high 210Po content and the problem solution in the Nordic labs are also discussed in this report.

Key words Alpha emitter; Radioanalysis; reactor water; Inter-comparison; Plutonium; Americium; Curium

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