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**Simultaneous Determination of Isotopes of Pu,  
Am and Cm in Reactor Water Samples –  
Report of OptiMethod 2018 project**

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## Abstract

This report presents the progress on the NKS-B OptiMethod project which was conducted in 2018, aiming to establish a Nordic optimal method for the determination of isotopes of plutonium, americium and curium in nuclear and environmental samples. The capacity and the analytical methods used in Nordic labs for determination of alpha emitters were reviewed and summarized. 11 Nordic labs in Denmark, Finland and Sweden can determine individual alpha emitters including  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  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 often used for separate Pu, Am and Cm from matrices and each other. An inter-comparison exercise for analysis of a spiked water and a real reactor water was organized, 11 Nordic labs participated in this 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. The problems and strategies in the analysis of alpha emitters in the Nordic labs were summarized and discussed, a further investigation for solving these problems and establishment of an optimal method for determination of alpha emitters in nuclear and environmental samples was proposed.

**Key words:** Alpha emitter; radioanalysis; reactor water; inter-comparison; plutonium; americium; curium

# **Progress report on the NKS-B OptiMethod project: Optimization of analytical methods for simultaneous determination of important alpha emitting radionuclides in nuclear and environmental samples**

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## 1. Introduction

Due to the high radiological toxicity, alpha emitters are key radionuclides in radiation protection, environmental radioactivity, decommissioning of nuclear facilities and repository of nuclear waste. Among artificial radionuclides, isotopes of Plutonium ( $^{238}$ ,  $^{239}$ ,  $^{240}\text{Pu}$ ), Americium ( $^{241}\text{Am}$ ) and Curium ( $^{242}\text{Cm}$ ,  $^{243}\text{Cm}$  and  $^{244}\text{Cm}$ ) are the most important ones due to their relatively high production rates in nuclear activities.

In nuclear power plants, the isotopes of Pu, Am and Cm are produced mainly in the nuclear fuel. Some small amount of them might also exist in the reactor materials (through the reactions of impurity uranium with neutrons). Monitoring and report of these alpha emitters in atmospheric releases and liquid effluents in the nuclear power plants are recommended by European Union (Euratom, 2004). This is also required by the authorities in the Nordic countries in order to estimate the amount of these alpha emitters released to the environment and their impact to the publics and environment. Meanwhile, process water (reactor coolant and spent 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.

In many Nordic nuclear power reactors, including Loviisa, Olkiluoto, Forsmark, Ringhals and Oskarshamn NPPs, fuel leakage has occurred during their operation. It is essential to understand how different 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 isotopes of the artificial alpha emitters is important for understanding their behavior in the reactor water and spent fuel pool 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 also be used to verify the simulation model presently used in the NPPs and to provide the important and critical information for decision-making.

In nuclear decommissioning, it is required to determine alpha emitters for radiological characterization, which is essential for classification of the waste for their final repository. Various sample matrix might be involved, such as water, metals, exchange resin, graphite, concrete, etc., in which these alpha emitters can be in-situ produced from the uranium impurity, or contaminated through other media (e.g. reactor water). Because the activity level of alpha emitting nuclides normally

is much lower than that of gamma and beta emitters, chemical separation with high decontamination factors to these high-level radionuclides from a big size sample is the critical step to avoid spectral interferences from other alpha-emitters as well as interferences from the matrices and ensure reliable determination of these alpha emitters.

Determination of isotopes of Pu and Am in the environment and food is one of the major requirements in investigation of environmental radioactivity and radioecology in view of radiation protection, environmental behavior and radiation exposure to the public. Determination of alpha emitters is also an important requirement in the nuclear and radiological emergency preparedness. In this case, a rapid analysis has to be done to meet the requirement of quick decision. For this purpose, a sequential chemical separation procedure and quick measurement is important. The Nordic authorities such as SSM and STUK, and institutions such as DTU Nutech and FOI are heavily involved in these works.

In Nordic laboratories, different methods have been developed and applied for determination of artificial alpha emitters and for different purposes. In the Nordic nuclear industry laboratories such as all Nordic NPPs, SKB etc., different methods including direct electrodeposition and extraction chromatographic separation followed by alpha spectrometry have been applied for the determination of alpha emitters in reactor water, fuel pool water and filters. However, these analytical methods were not validated for the analysis of these types of samples and the analytical results were not well verified. Suitable standard reference materials and inter-laboratory comparisons for relevant sample matrix are not available. Consequently, the NPPs labs have a strong requirement for validate and improve their analytical methods for determination of alpha emitters in their routine samples. In addition, the behavior of alpha emitters released during the leakage in the reactor is still not well understood.

Nordic institutes and authorities such as DTU Nutech, FOI, STUK, UH and SSM have a long history on determination of alpha emitters in nuclear, environmental and food samples. A number of methods for determination of artificial alpha emitters in various nuclear, environmental and decommission samples have been developed and applied in these labs. (Chen et al. 1993; Chen et al. 2001; Qiao et al. 2009; Nygren et al. 2007; Ikäheimonen and Saxén 2002; Salminen et al. 2005; Lehto et al. 2013, Olszewski et al. 2018). However, there is very little collaboration in the determination and studies related to the artificial alpha emitters among Nordic labs, and no Nordic inter-comparison has been organized on determination of artificial alpha emitter. In many labs, 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 labs.

The Optimethod project aims to build up a Nordic network for strengthening collaboration of Nordic labs in the investigation of alpha emitters in nuclear power reactor, nuclear waste and repository, as well as in the environment. This will help to improve the analytical quality of alpha emitting radionuclides in various samples, especially in the samples from nuclear power reactor. Firstly, the analytical capacity and analytical methods using in the partners' laboratories including the separation procedure and measurement techniques for determination of isotopes of Pu, Am and Cm were reviewed in 2018. Then, an inter-comparison was organized for the determination of isotopes of Pu, Am and Cm in a spiked artificial water sample and a real reactor water sample collected from one of the Nordic NPP. The outcomes of these activities are summarized and discussed in this report. Meanwhile, the problems and challenges are highlighted.

## **2. Present status on the analysis of alpha emitters in nuclear and environmental samples in Nordic labs**

Many Nordic labs analyze alpha emitters. Table 1 summarizes the major activities of alpha emitter analysis in the labs of the partners of NKS OptiMethod project, which covers most of labs in Denmark, Sweden and Finland. The labs in Norway, which might also analyze artificial alpha emitters in nuclear and environmental samples, are not included in this summary. In all these labs listed in Table 1, the analysis of alpha emitters can be classified into two groups, one group mainly works on the analysis of samples from nuclear power plants, and another groups mainly works on the analysis of environmental and food samples. The analysis in the labs of all 5 Nordic nuclear power plants and SKB mainly focus on the analysis of reactor coolant water, spent fuel pool water, aerosol filter from the nuclear power plants, and liquid effluents from the nuclear power plants, and the isotopes of Pu ( $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ), Am ( $^{241}\text{Am}$ ) and Cm ( $^{242}\text{Cm}$ ,  $^{243,244}\text{Cm}$ ) are routinely determined. While the analysis in the labs of universities, institutes and authorities mainly focus on the analysis of environmental and biological samples for isotopes of U ( $^{236}\text{U}$ ), Pu ( $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ), Np ( $^{237}\text{Np}$ ) and Am ( $^{241}\text{Am}$ ). The isotopes of Cm ( $^{242}\text{Cm}$ ,  $^{243,244}\text{Cm}$ ) were not often determined in these labs, because of their very low concentration in the environment and relative short half-lives (162 days for  $^{242}\text{Cm}$ , 28.5 years for  $^{243}\text{Cm}$  and 18.2 years for  $^{244}\text{Cm}$ ). In addition, a few labs also analyze samples from the decommissioning of nuclear facilities for the determination of isotopes of Pu, Am and Np.

For the determination of small volume of water (< 5 L) from the nuclear power plants (reactor coolant water, spent fuel pool water and liquid effluent from nuclear power plants), evaporation and co-precipitation of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Fe}(\text{OH})_3$  are often used to pre-concentration followed by acid digestion or dissolution. While, the air filter from the nuclear power plant is often digested using mixed acids including  $\text{HNO}_3$  and  $\text{HCl}$ , as well as  $\text{HF}$  and  $\text{H}_2\text{O}_2$  for decomposition of silica and organic substances. In the most of labs of Nordic nuclear power plants, the separation of Pu, Am and Cm in the prepared sample from the water and filter from nuclear power plant was often implemented by a sequential extraction chromatography using UTEVA and TRU proposed by Eichrom (2014). Fig. 1 shows the diagram of the chemical separation procedure. The sample is prepared in 3 M  $\text{HNO}_3$  solution and reductants (e.g. ferrous sulfamate and ascorbic acid) are added to reduce plutonium to  $\text{Pu}^{3+}$ . The prepared sample solution is loaded to a sequentially connected two extraction chromatographic columns of UTEVA and TRU, followed by rinsing the columns using 3M  $\text{HNO}_3$ . Uranium (as  $\text{UO}_2^{2+}$ ) is adsorbed on the UTEVA column, while tri-valent  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  pass through the UTEVA column, and they are adsorbed on the TRU column. The TRU column is dis-connected from the UTEVA for further separation of Pu and Am. The TRU column is first rinsed with 2M  $\text{HNO}_3$  -0.1M  $\text{NaNO}_2$  solution to oxidize  $\text{Pu}^{3+}$  to  $\text{Pu}^{4+}$  on column to enhance the affinity of Pu on the TRU column. Then Am/Cm is eluted from the TRU column using 4M  $\text{HCl}$  while  $\text{Pu}^{4+}$  still strong adsorbed on the column, based on the high affinity of  $\text{Pu}^{4+}$  on the TRU column in 4M  $\text{HCl}$  media.  $\text{Pu}^{4+}$  on the TRU column is finally eluted using 0.1M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  based on the strong complex formation of oxalate with  $\text{Pu}^{4+}$ . Uranium adsorbed on the UTEVA column can be further purified by rinsing with 9M  $\text{HNO}_3$  and 5M  $\text{HCl}$  to remove Po and Th, and finally eluted with 1 M  $\text{HCl}$ . One of the major advantage of this procedure is the sequential separation of U, Pu, Am and Cm for the simultaneous determination of the isotopes of these alpha emitters. While, Pu could not be completely separated from Am/Cm as reported in some labs (Table 1), causing the interference of  $^{241}\text{Am}$  (5.48 MeV) on the measurement of  $^{238}\text{Pu}$  (5.45-5.50 MeV). Low recovery of Am/Cm was also reported in some samples.

Some Nordic labs analyze the isotopes of Pu, Am and Cm in the reactor coolant and fuel pool water by direct electro-depositing all radionuclides on metal disk after a simple evaporation and acid digestion. Although this method works for determination of the most of isotopes of Pu, Am and Cm in such water samples with much less salt and other metals. However,  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  cannot be discriminated and only a sum concentration of  $^{238}\text{Pu}+^{241}\text{Am}$  could be measured.

Table 1. Summary of the methods used in Nordic labs for analysis of alpha emitters

Nordic lab	Type of samples	Radionuclides	Pretreatment method	Separation method	Measurement method	Challenges
DTU	Environmental sample (water, soil, sediment, plants, filter). decommissioning waste	Isotopes of U, Pu, Np, Am and Cm, <sup>226</sup> Ra, <sup>210</sup> Po	Acid leaching, co-precipitation	Ion exchange and extraction chromatography (TEVA, UTEVA, TRU, DGA)	Electrodeposition- $\alpha$ -spectrometry, ICP-MS, AMS	
Univ. Helsinki	Environmental sample (water, soil, sediment, plants, tissues, filter)	Isotopes of U, Pu, Np, Am and Cm	Acid leaching, co-precipitation	Anion exchange-TRU-TEVA for Am, Cm; UTEVA-TRU for Pu, Am	Micro-coprecipitation- $\alpha$ -spectrometry, ICP-MS	Varied chemical yield for complex samples
FOI	Environmental water, soil, vegetation, biological and forensic samples	Isotopes of U, Pu, Am, Cm, and <sup>230</sup> Th, <sup>226</sup> Ra, <sup>210</sup> Po	Microwave digestion, fusion	Extraction chromatography, TEVA-UTEVA-TRU	Electrodeposition- $\alpha$ -spectrometry, ICP-MS	Low recoveries for some element, low resolution of alpha spectroscopy for some samples
SSM	Environmental sample (soil, sediment, etc.)	Isotopes of U, Pu, Np, Am and Cm	Fusion, co-precipitation	extraction chromatography (UTEVA-TEVA, TRU-TEVA)	Electrodeposition- $\alpha$ -spectrometry, ICP-MS	
Cyclife	Environmental water, soil, filter, decommissioning waste samples	Isotopes of U, Th, Pu, Am and Cm	Acid digestion, evaporation	Extraction chromatography, (UTEVA-TRU)	Electrodeposition- $\alpha$ -spectrometry	
SKB	Nuclear samples (liquid effluent, reactor and fuel pool water, filter)	Isotopes of Pu, Am and Cm	Acid digestion, evaporation	Extraction chromatography (UTEVA-TRU)	Electrodeposition- $\alpha$ -spectrometry	Insufficient separation of Pu from Cm and low resolution of $\alpha$ -spectrometry for some samples

Table 1 Summary of the methods used in Nordic labs for analysis of alpha emitters (Continued)

Nordic lab	Type of samples	Radionuclides	Pretreatment method	Separation method	Measurement method	Challenges
Oskarshamn NPP, OKG	Nuclear samples (reactor and fuel pool water, waste water, filter)	Isotopes of U, Pu, Am and Cm	Acid digestion, evaporation	Extraction chromatography (UTEVA-TRU)	Electrodeposition- $\alpha$ -spectrometry	Insufficient separation of Pu from Am/Cm, Low recovery of Am/Cm; low resolution of $\alpha$ -spectrometry, black residue in Am fraction
Ringhals NPP	Nuclear samples (liquid effluent, reactor and fuel pool water, filter)	Isotopes of Pu, Am and Cm	Acid digestion, evaporation	Extraction chromatography (UTEVA-TRU)	Electrodeposition- $\alpha$ -spectrometry	Low resolution of $\alpha$ -spectrometry, black residue in Am fraction
Forsmark NPP	Nuclear samples (liquid effluent, reactor and fuel pool water)	Isotopes of Pu, Am and Cm	Acid digestion, evaporation	No chemical separation	Electrodeposition- $\alpha$ -spectrometry	$^{238}\text{Pu}$ and $^{241}\text{Am}$ could not be discriminated because no chemical separation, black residue in the electrodeposition
Olkiluoto NPP	Nuclear samples (reactor and fuel pool water, filter)	Isotopes of U, Pu, Am and Cm	Acid digestion, $\text{Ca}_3(\text{PO}_4)_2$ co-precipitation, Acid dissolution	Extraction chromatography (TEVA-TRU)	LSC for effluent Proportional counter for filter	Low recovery for Pu fraction for some samples. Decomposition of filter is not completed using mixed acids
Loviisa NPP	Nuclear samples (liquid effluent, filter)	Gross alpha	Evaporation	No separation	LSC or proportional counter	Analysis of specific alpha emitters is under development
Chalmers Uni. Techn.	Environmental water, soil, sediment, plants, and tissues	Isotopes of U, Pu, Am, Cm	Acid dissolution, evaporation	Liquid-liquid extraction	$\gamma$ - and $\alpha$ -spectrometry, LSC, ICP-MS	

Determination of isotopes of Pu, Am and Cm in air filter samples from the nuclear power plants (Table 1) are also routinely implemented in the labs of Nordic NPPs. The major problem in the analysis of this type of sample is the serious interference of  $^{210}\text{Po}$ .  $^{210}\text{Po}$  is a decay daughter of  $^{222}\text{Rn}$  and a volatile radionuclide, it is released to the atmosphere by natural process of diffusion of gaseous  $^{222}\text{Rn}$  from soil and direct emission of  $^{210}\text{Po}$  from human activities during combustion of fuels and industrial activities (Persson & Holm, 2011). Due to its relative high concentration in the atmosphere (0.03-0.3 Bq/m<sup>3</sup>) (Persson & Holm, 2011), the concentration of  $^{210}\text{Po}$  might be much higher than that of the isotopes of Pu, Am and Cm in the filters from the NPPs, and therefore interfering the alpha measurement of other radionuclides.

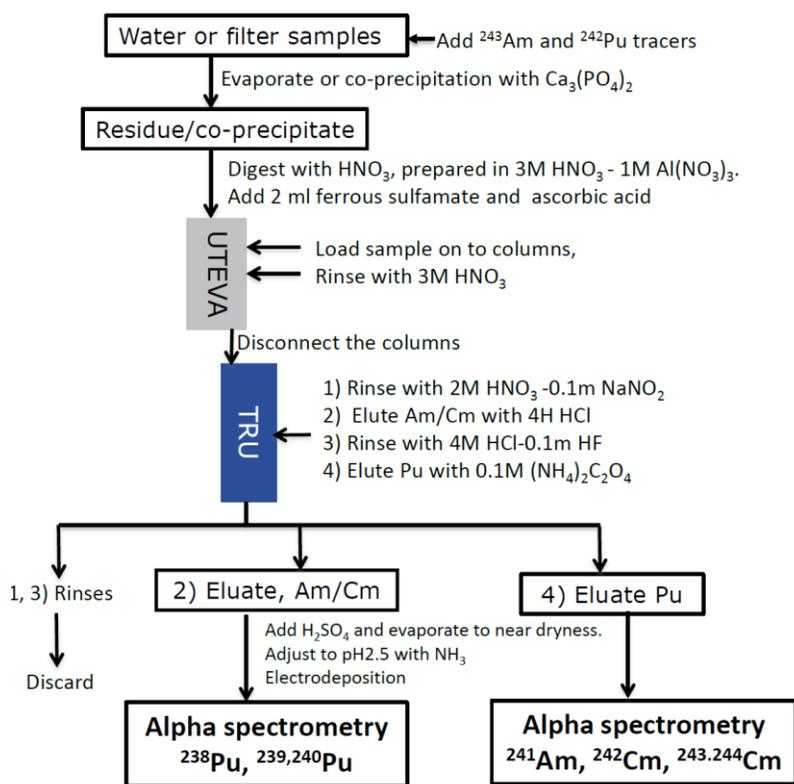


Fig. 1 Diagram of an analytical procedure for determination of Pu, Am and Cm in Labs of Nordic NPPs

The alpha energy of  $^{210}\text{Po}$  (5.30 MeV) is similar as the  $^{243}\text{Am}$  (5.28 MeV), the alpha spectrometry cannot discriminate these two radionuclides. Therefore,  $^{210}\text{Po}$  could cause a serious interference in the measurement of  $^{243}\text{Am}$  if  $^{210}\text{Po}$  is not completely removed before the measurement. Since  $^{243}\text{Am}$  is

often used as yield tracer of  $^{241}\text{Am}$  and isotopes of Cm. The inaccurate measurement of  $^{243}\text{Am}$  makes the accurate measurement of  $^{241}\text{Am}$  and isotopes of Cm difficult. The separation using the combined UTEVA and TRU resin can in principle separate  $^{210}\text{Po}$  from Pu, Am and Cm. However, it was reported in some Nordic labs that  $^{210}\text{Po}$  was observed in the separated Am/Cm fraction in some samples. It might be attributed to the complex behavior of Po on the column separation, causing a worse decontamination of Po in some samples. A further investigation is highly needed to overcome this problem. If chemical separation was not applied before measurement of alpha emitters, the activity of  $^{210}\text{Po}$  might overwhelm the total activity of the alpha source prepared, and therefore cause a serious interference for the measurement of other alpha emitters, even no  $^{243}\text{Am}$  is used as a yield tracer.

A white residue in the separated Pu and Am/Cm fractions before electrodeposition and low resolution of alpha spectrometry were observed in many labs, this might be attributed to the less pure ~~of the~~ separated Am/Cm or Pu solution, causing deposition of other elements on the disk and therefore producing a thick alpha counting source. Therefore a further improvement of separation procedure is still needed. In addition, a black disk during the electrodeposition for alpha source preparation was observed for some samples. This might be attributed to the impurity of the solution, and the condition of the electrodeposition setup and parameters. Black residue was also observed in the Am/Cm fraction from the column separation before electrodeposition, this might be caused by some organic matter presented in the eluate, which was converted to the black carbon during treatment of evaporation and digestion. All these observations indicate that a further improvement of the analytical methods is highly needed in the Nordic labs in the nuclear industry.

In the Nordic labs of universities, institutes and authorities, artificial alpha emitters are often determined in environmental samples, such as soil, sediment, aerosol filter, seawater, vegetation and tissues (Table 1). Due to the very low concentration of the isotopes of Pu, Np, Am and Cm, a large sample (e.g. >100 L seawater, >5 g soil and sediment, > 50 g vegetation) has to be used. All sample matrices and other radionuclides have to be separated before the measurement of these artificial alpha emitters. A pre-concentration combined with a comprehensive chemical separation is often applied for their determination. Fig. 2 shows a diagram of pre-concentration procedure for separation of U, Np, Pu, Am, Cm from environmental water and solid samples used in DTU Nutech. The pre-concentration and pre-separation of the alpha emitters is mainly based on the formation of co-precipitation of hydroxides of actinides with  $\text{Fe}(\text{OH})_3$ . Before pre-separation, actinides are first separated from solid samples (soil, sediment, filter, ashes of vegetation, etc.) by acid leaching using *aqua regia*. It should be mentioned that the actinides in these sample are not present as refractory oxides. For the samples containing hot

particles (present as refractory oxides of actinides), a fully dissolution or fusion method should be applied. The solid sample is first ashed at 450 °C for over night to decompose organic substance, which is difficult to be decomposed using acid leaching. Addition of reductants (e.g. Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) in the large volume of water samples before pre-concentration can improve the recovery of Pu and Np in the hydroxide co-precipitation step.

## Preconcentration of U, Pu, Np, Am, Cm

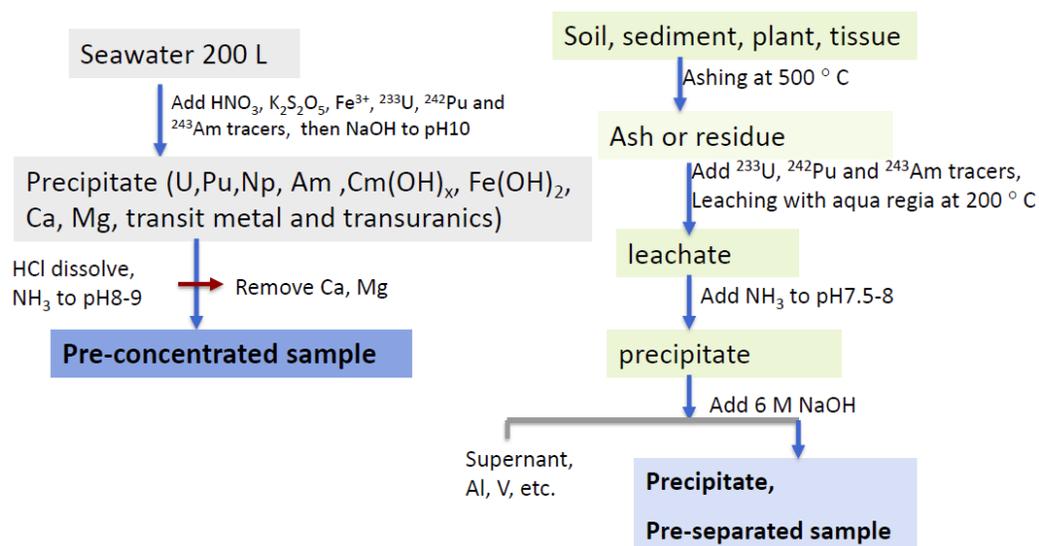


Fig. 2 Diagram of pre-concentration for determination of isotopes of U, Pu, Np, Am and Cm.

Anion exchange chromatography has been widely used for separation of Pu, Np, Am and Cm, Fig. 3 and Fig. 4 shows a sequential procedure for separation of Pu/Np and Am/Cm for the measurement of their isotopes in DTU Nutech. This is based on that Pu<sup>4+</sup> and Np<sup>4+</sup> can be highly adsorbed on strong anion exchange resin in high concentration of HNO<sub>3</sub> and HCl, and trivalent Am<sup>3+</sup> and Cm<sup>3+</sup> can only be adsorbed in non-aqueous media, i.e. 93% CH<sub>3</sub>OH-HNO<sub>3</sub> media. The sample solution is first prepared to convert Pu and Np to tetravalent states (Pu<sup>4+</sup>, Np<sup>4+</sup>), and loaded to an anion exchange column (e.g. AG 1x-4), Pu and Np are adsorbed on the column, while uranium (UO<sub>2</sub><sup>2+</sup>) and Am<sup>3+</sup>, Cm<sup>3+</sup> pass through the column and they are collected in the effluent and rinse solution of 8M HNO<sub>3</sub>. Pu and Np are finally eluted from the column using NH<sub>2</sub>OH·HCl-HCl solution by reducing it to Pu<sup>3+</sup> and depending on their

less affinity on the column in low concentration of HCl. The eluate is then prepared for measurement of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  using alpha spectrometry and  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  using ICP-MS.

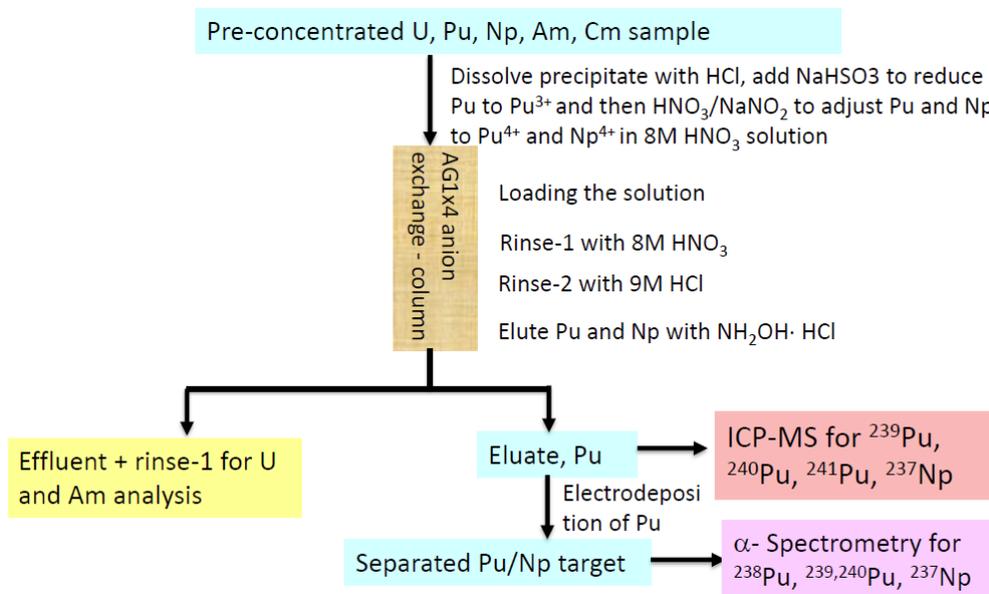


Fig. 3 Procedure for separation of Pu/Np using anion exchange chromatography

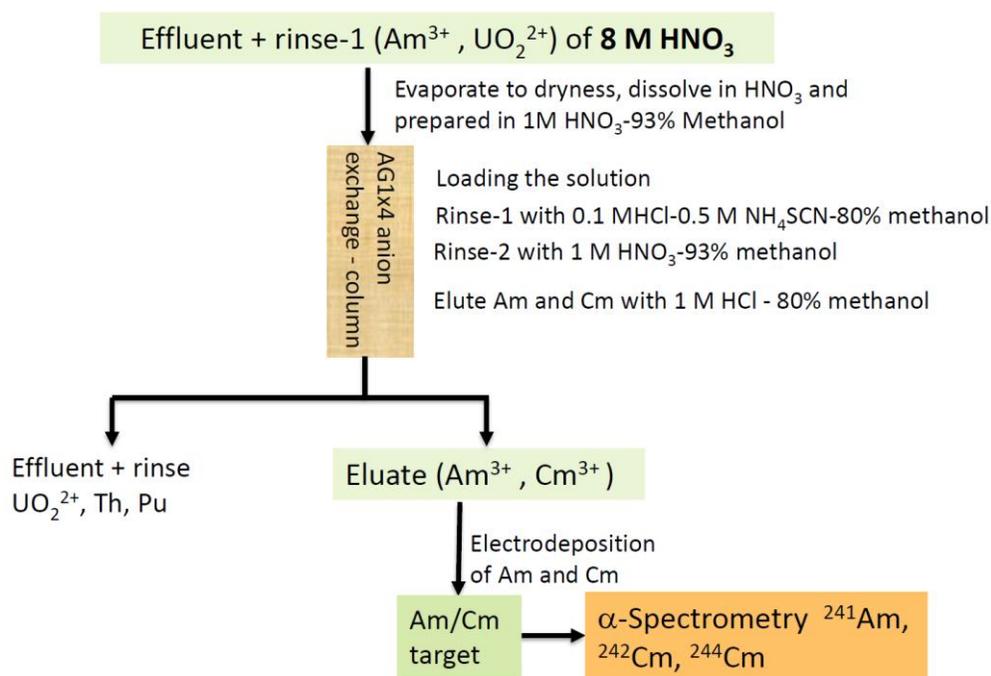


Fig. 4 Procedure for separation of Am/Cm using anion exchange chromatography

The effluent and rinse solution from the first anion exchange column is evaporated to dryness and prepared in 93%-1M HNO<sub>3</sub> solution and loaded to a new anion exchange column. In this case, Am<sup>3+</sup> and Cm<sup>3+</sup> are adsorbed on the column by forming anion complex with HNO<sub>3</sub> in such a non-aqueous media. Rare earth elements are removed from the column by rinsing using 0.1 M HCl-0.5 M NH<sub>4</sub>SCN-80% CH<sub>3</sub>OH solution, based on the formation of anion complex of Am<sup>3+</sup> and Cm<sup>3+</sup> with SCN<sup>-</sup>, but not rare earth elements. The Am<sup>3+</sup> and Cm<sup>3+</sup> are finally eluted from the column using a 1M HNO<sub>3</sub>-90% CH<sub>3</sub>OH based on the decomposition of the anion complex of Am<sup>3+</sup> and Cm<sup>3+</sup> with HNO<sub>3</sub> in low concentration of CH<sub>3</sub>OH due to the formation of the hydrates of Am<sup>3+</sup> and Cm<sup>3+</sup>. The separated Am and Cm are then prepared for alpha spectrometry measurement of their isotopes.

In recent years, extraction chromatography has been widely used for the separation of actinides, and the often applied resins ~~are~~ are TEVA, UTEVA, TRU, Ln, and a combination of these resins. TEVA has similar functional group as the strong acidic anion exchange resin, therefore it is often applied for the separation of plutonium and neptunium due to their high affinities on this resin at tetravalent state. Fig. 5 shows a procedure for the separation of plutonium using TEVA column. Plutonium and neptunium are first adjusted to Pu<sup>4+</sup> and Np<sup>4+</sup>, and the prepared solution is loaded to the column. Uranium does not adsorb on the column in 3M HNO<sub>3</sub> and it is removed during loading and rinsing using 3M HNO<sub>3</sub>, Th<sup>4+</sup> is removed by rinsing using 6M HCl. Plutonium and neptunium are eluted using NH<sub>2</sub>OH·HCl-HCl solution or 0.1M HCl. The eluate is then prepared in suitable media for the measurement of these isotopes. (e.g. 0.5 M HNO<sub>3</sub> for ICP-MS). This procedure has been successfully applied for the determination of the isotopes of Pu and Np in various environmental samples (Qiao et al. 2009; Xu et al., 2014, 2018; Wang et al. 2017).

UTEVA resin is often applied for the separation of uranium based on the high affinity of uranium to UTEVA at high concentration of HNO<sub>3</sub> and HCl media compared to many other resins. Uranium adsorbed on the column is eluted using low concentration of HCl (e.g. 0.025 M) after rinsing with 6 M HCl to remove thorium. Fig. 6 shows a procedure for separation of uranium from large volume of seawater for determination of <sup>236</sup>U using AMS (Qiao et al. 2015).

TRU resin has high affinity to most of actinides in high concentration of HNO<sub>3</sub> and/or HCl media; it has been used for the separation of Pu and Am in combination with UTEVA (e.g. Fig. 1) for removal of uranium and thorium. Only TRU resin can be also used for separation of plutonium. In this case, Pu is converted to Pu<sup>4+</sup> and prepared in 3M HNO<sub>3</sub> solution to be loaded to the TRU column. After removing Am/Cm using 4M HCl, Pu is eluted with 0.1M NH<sub>2</sub>OH·HCl-4M HCl solution (Fig. 7). In this case, uranium

and thorium are still adsorbed on the column due to their high affinities to the TRU column in high concentration of HNO<sub>3</sub> and HCl media.

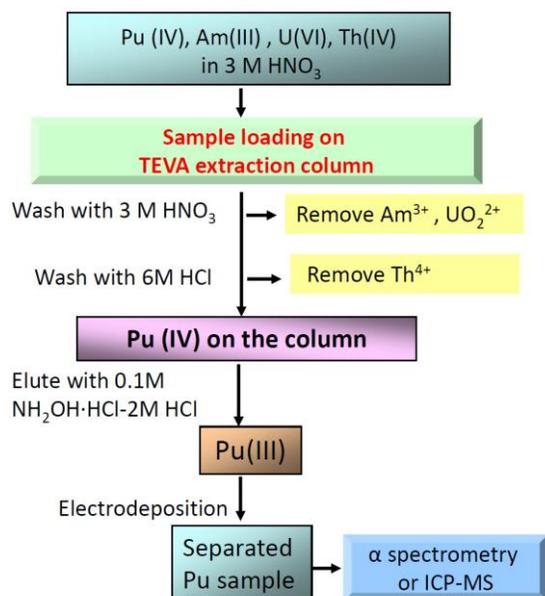


Fig. 5 Separation of Pu using extraction chromatography with TEVA column

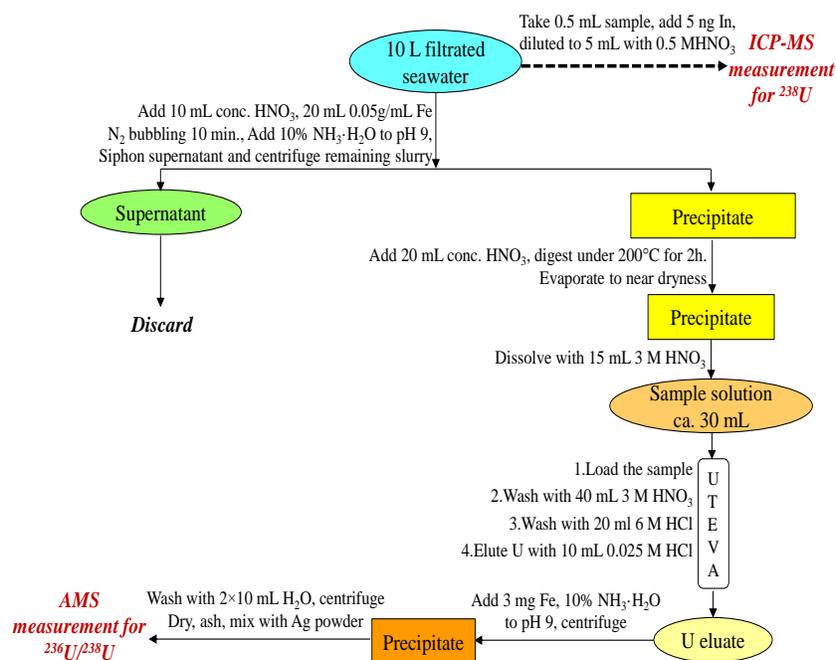


Fig. 6 Separation of uranium from seawater for the determination of <sup>236</sup>U

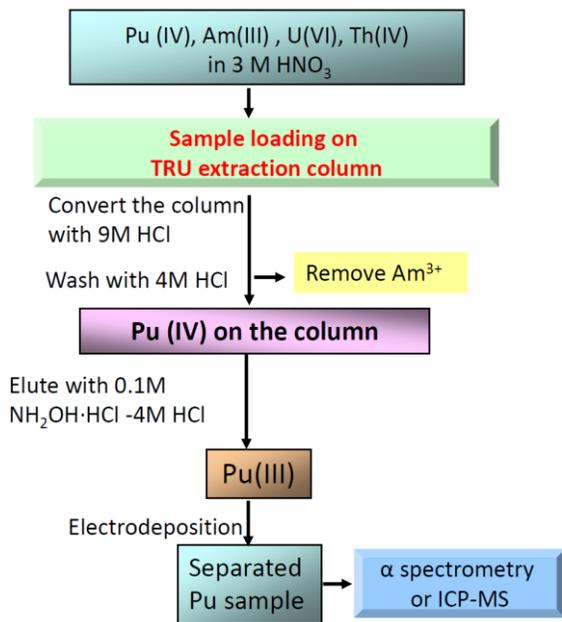


Fig. 7 Separation of Pu using extraction chromatography with TRU column

Due to the extremely high affinity of Am/Cm in DGA resin compared to other extraction chromatographic resins in high concentration of HCl and HNO<sub>3</sub> (Fig. 8), chromatographic separation using DGA resin has been used for separation of Am/Cm from the matrix and other actinides (Eikenberg et al. 2009; Groska et al. 2016).

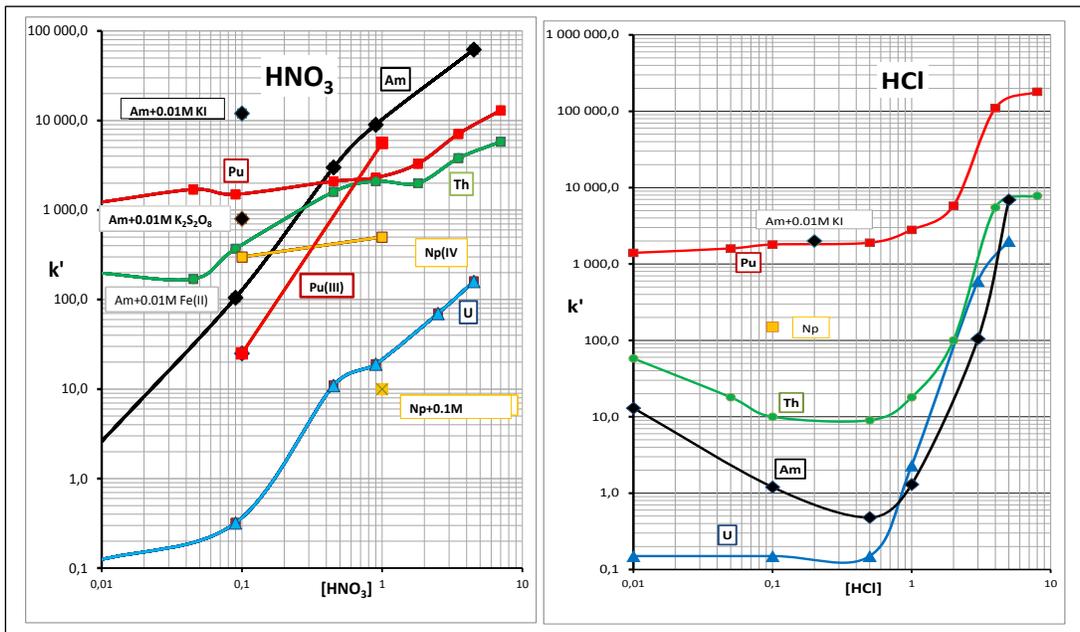


Fig. 8 Affinities of actinides on DGA resin in different concentration of HNO<sub>3</sub> and HCl

Fig. 9 shows a diagram of analytical procedure for determination of isotopes of Pu, Np, Am and Cm by a sequential separation using a connected TEVA and DGA chromatographic columns used in DTU Nutech. In this procedure, plutonium and neptunium in the sample solution is converted to tetravalent states and the sample is loaded to a TEVA column after prepared in a 4M HNO<sub>3</sub> solution, followed by rinse with 4M HNO<sub>3</sub>. Am<sup>3+</sup> and Cm<sup>3+</sup> pass through the TEVA column are adsorbed in the DGA column. Then, the two columns are disconnected. Plutonium and Neptunium adsorbed in the TEVA column are eluted using 0.1 NH<sub>2</sub>OH·HCl-2M HCl solution after rinsing the column with 6M HCl to remove Th<sup>4+</sup> on the column. The DGA column is rinsed with 0.2 M HNO<sub>3</sub> solution to remove uranium. Am<sup>3+</sup> and Cm<sup>3+</sup> are still remained on the column and finally eluted using 0.5 M HCl solution. This is based on the low affinity of UO<sub>2</sub><sup>2+</sup> in the DGA resin at low concentration of HNO<sub>3</sub>, and low affinity of Am<sup>3+</sup>/Cm<sup>3+</sup> in the DGA resin. With this procedure, the recoveries of more than 90% was observed for Pu, Am and Cm, and the decontamination factors of other radionuclides in the Pu/Np fraction and Am/Cm are higher than 10<sup>4</sup>. Fig. 10 shows the alpha spectra of two fractions using this method.

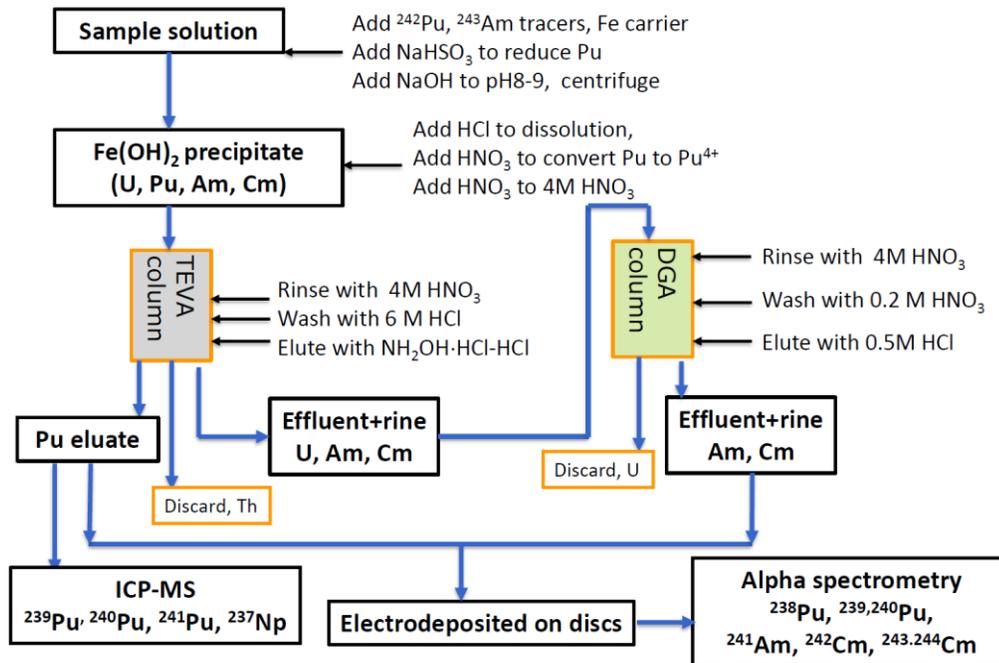


Fig. 9 Diagram of chromatographic separation procedure for sequential separation of Pu, Np, Am and Cm and measurement of their isotopes.

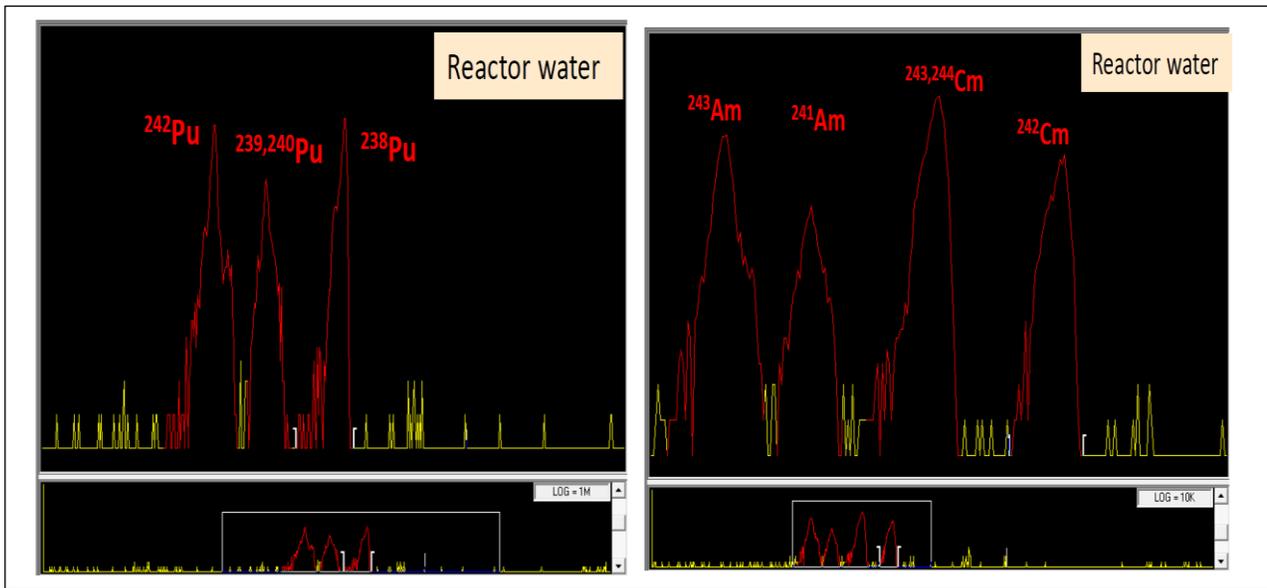


Fig. 10 Alpha spectra of Pu fraction and Am/Cm fraction separation using TEVA-DGA columns from reactor coolant water samples.  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  are spiked yield tracers.

A sequential connected extraction chromatographic columns of TEVA-UTEVA-TRU have been proposed for separation of Pu, U, Am and Cm by FOI (Fig. 11). In this case, the sample solution was prepared in 3M  $\text{HNO}_3$  and Pu was first reduced to  $\text{Pu}^{3+}$  using  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and then oxidized to tetravalent state using  $\text{NaNO}_2$  under heating. The prepared sample solution was loaded to three connected columns followed by rinse with 3M  $\text{HNO}_3$ .  $\text{Pu}^{4+}$  is adsorbed in the TEVA column,  $\text{UO}_2^{2+}$  passed through the TEVA column in the effluent and rinse solution is adsorbed in the UTEVA column, and the  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  which are not retained in the TEVA and UTEVA columns are adsorbed in the TRU column. Afterwards, the three columns are disconnected. Plutonium in the TEVA column is eluted using 0.01M  $\text{NH}_4\text{HC}_2\text{O}_4$  after rinsing with 9M  $\text{HCl}$  and 3M  $\text{HNO}_3$  and to remove the thorium. Uranium in the UTEVA column is then eluted also using 0.01M  $\text{NH}_4\text{HC}_2\text{O}_4$  after rinsing with 3M  $\text{HNO}_3$ , 9M  $\text{HCl}$ , and 5M  $\text{HCl}$ -0.05M  $\text{H}_2\text{C}_2\text{O}_4$  to remove the matrix elements and other interfering radionuclides.  $\text{Am}^{3+}/\text{Cm}^{3+}$  adsorbed on the TRU column was eluted with 0.01M  $\text{HNO}_3$  after rinsing with 10M  $\text{HNO}_3$  to remove  $^{210}\text{Po}$  if present. However, recovery of plutonium varied greatly in 15-80%. This might be attributed to unstable adjustment of plutonium to tetravalent state before loading the sample solution to the columns. In addition, the recovery of uranium is only 50-70%, this might be attributed to the uncompleted rinse of the TEVA column after loading.

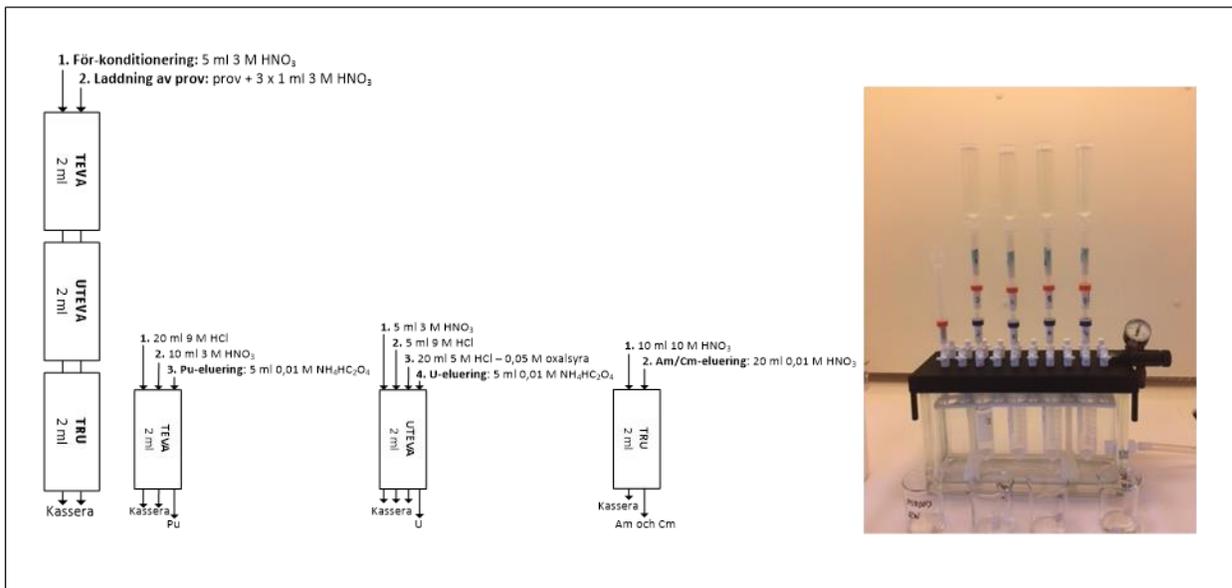


Fig. 11 Diagram of sequential separation of Pu, U, Am and Cm using TEVA-UTEVA-TRU columns

A combined procedure using anion exchange chromatography (Dowex 1x-4) and extraction chromatography using TRU resin is used for the separation of Pu, Am and Cm by SSM. In this procedure, the sample is prepared in 8M HNO<sub>3</sub> solution, and plutonium is adjusted to tetravalent state using H<sub>2</sub>O<sub>2</sub> and NaNO<sub>2</sub>. The prepared sample solution is first loaded to Dowex 1x-4 column followed by rinsing with 8M HNO<sub>3</sub>, Pu<sup>4+</sup> is adsorbed on the column, while Am<sup>3+</sup> and Cm<sup>3+</sup> pass through the column and they are collected in the effluent and rinse solution. After rinsing the Dowex column with 9M HCl to remove thorium, Pu on the column is eluted with 0.1M NH<sub>4</sub>I-9MHCl by reducing Pu<sup>4+</sup> to Pu<sup>3+</sup>. The effluent and rinse solution is evaporated to dryness and then prepared in 3M HNO<sub>3</sub>-1M Al(NO<sub>3</sub>)<sub>3</sub> solution and loaded to an TRU column. Am<sup>3+</sup> and Cm<sup>3+</sup> are adsorbed on the column. After rinsing the column, Am and Cm are eluted using NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> solution.

Alpha spectrometry is applied for the measurement of <sup>238</sup>Pu, <sup>239,240</sup>Pu, <sup>241</sup>Am, <sup>242</sup>Cm and <sup>243,244</sup>Cm in the Nordic labs, ICP-MS is also used for the determination of <sup>240</sup>Pu/<sup>239</sup>Pu ratio or <sup>239</sup>Pu and <sup>240</sup>Pu concentrations. The electrodeposition is the often applied technique in the Nordic labs for preparation of the measurement source of alpha spectrometry. This method enables to obtain a stable and thin source, and therefore a high resolution of the spectra. However, a low resolution of the spectra was observed in some samples, this might be attributed to the presence of some impurities in the sample

solution, which might be also deposited on the electrodeposition disk to worsen the resolution. The black source was sometimes obtained in the electrodeposition due to presence of organic substance in the sample solution, and unsuitable conditions of electrodeposition (e.g. pH, temperature) might be another reason.

$^{242}\text{Pu}$  is used as a tracer for monitoring chemical yield of plutonium, and  $^{243}\text{Am}$  is used as tracer for monitoring chemical yields of Am and Cm, due to the similar chemical properties and the same behavior in the chemical separation procedure. It should be mentioned that  $^{243}\text{Am}$  and  $^{242}\text{Pu}$  might be present in some samples, such as reactor coolant water and spent fuel pool water. Analysis of the sample without spike  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  tracers should be conducted to confirm the presence of these two radionuclides in the sample. In general, the concentrations of  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  in the sample is very low if it is measurable. A sufficient high amount of  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  tracers (more than 50 times higher) should be added as tracer to overcome this problem.

### **3. Inter-comparison exercise on determination of isotopes of Pu, Am and Cm in water samples**

An inter-comparison exercise was organized in this project in 2018 for the determination of isotopes of Pu, Am and Cm in two water samples. Eleven Nordic labs participated in the inter-comparison exercise. The analytical results of this inter-comparison exercise are presented and discussed below.

#### **3.1 Inter-comparison samples**

Two water samples were prepared for this exercise. (1) spiked water was prepared by Chalmers University of Technologies by mixing a plutonium standard solution (including  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{242}\text{Pu}$  with atomic percentage of 0.13%, 84.02%, 14.45%, 0.73% and 0.34%, respectively dated to 20<sup>th</sup> Oct. 1992) and  $^{244}\text{Cm}$  standard solution in 1M  $\text{HNO}_3$  solution. The mixed solution was analyzed using ICP-MS, alpha spectrometry and HPGe gamma spectrometry. This solution was spiked to 1M  $\text{HNO}_3$  solution and used for inter-comparison. The concentrations of each radionuclide are presented in Table 2. (2) reactor water is reactor coolant water collected from Olkiluoto NPP on 5th April 2016, the water was acidified to pH using  $\text{HNO}_3$ . This sample also contains various activation and fission product radionuclides due to the leakage of fuel in this reactor occurred before.

200 ml of the spiked water and the reactor water respectively in PE bottles were sent to partners' labs in April 2018 for inter-comparison analysis. Table 3 summarizes the features of the two inter-comparison samples.

Table 2. The standardized concentration of radionuclides in the spiked water samples (Chalmers University of Technologies)

<i>Nuclide</i>	<i>Activity (Bq/L)</i>	<i>Uncertainty (2 sigma)</i>
Pu-238 *	0.038	0.031
Pu-239	0.077	0.002
Pu-240	0.048	0.004
Pu-241	0.009	0.022
Cm-244	0.195	0.012
Am-241	0.071	0.002
Pu-242 *	$2.0 \times 10^{-4}$	

\*Estimated from the atomic ratio in the plutonium solution and decay correction

Table 3 Two inter-comparison water samples for determination of alpha emitters

Sample code	Sample description	Matrix	Preparation/ collection date	Major radionuclides contained
Spiked water	Plutonium and <sup>244</sup> Cm solution was spiked to 1M HNO <sub>3</sub>	200 ml in 1M HNO <sub>3</sub>	March 2018	<sup>238</sup> Pu, <sup>239</sup> Pu, <sup>240</sup> Pu, <sup>241</sup> Pu, <sup>242</sup> Pu, <sup>241</sup> Am, <sup>244</sup> Cm
Reactor water	Reactor coolant water from Olkiluoto NPP	200 ml water acidified to pH1 with HNO <sub>3</sub>	April 2016	<sup>238</sup> Pu, <sup>239</sup> Pu, <sup>240</sup> Pu, <sup>241</sup> Pu, <sup>242</sup> Pu, <sup>241</sup> Am, <sup>243</sup> Am, <sup>242</sup> Cm, <sup>243</sup> Am, <sup>244</sup> Cm, other activation and fission product radionuclides

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

In this inter-comparison exercise, the measurement of alpha emitters was mainly implemented by alpha spectrometry, only one lab did perform ICP-MS measurement for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . For the chemical separation, 4 different methods were used by the 11 participating labs. Among them, 6 labs used UTEVA-TRU method (Fig. 2), 5 of them use electrodeposition for alpha source preparation and one lab used micro-precipitation ( $\text{NdF}_3$ ) for source preparation. Two labs directly measure the radionuclides without chemical separation. Other 3 labs used different chemical separation method, including TEVA-UTEVA-TRU method (Fig. 11), TEVA-DGA method (Fig. 5), and Dowex1-x4 - TRU method. The detailed procedures of these methods have been presented and discussed above.  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  are 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 before measurement. 0.02-0.08 Bq of  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  were added to 25-100 ml samples before the treatment of the sample. In the direct measurement method (no chemical separation was applied) used in some labs,  $^{233}\text{U}$  (0.1 Bq) was spiked as standard addition tracer for calculating the activity of other radionuclides in alpha spectrometry measurement. Table 4 summarizes the methods used in this comparison by participating labs.

Table 4 Analytical methods applied in partners' lab for inter-comparison exercise

Lab code	Separation method	Source preparation	Tracer(s)	Measurement methods
1	TEVA-DGA	Electrodeposition/0.5M $\text{HNO}_3$	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry, ICP-MS
2	TEVA-TRU	Electrodeposition	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry
3	no	Electrodeposition	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry
4	Dowex1-x4-TRU	Electrodeposition	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry
5, 7, 10, 11	UTEVA-TRU	Electrodeposition	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry
6	TEVA-UTEVA-TRU	Electrodeposition	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry
8	no	Electrodeposition	$^{233}\text{U}$	$\alpha$ -spectrometry
12	UTEVA-TRU	Micro-coprecipitation	$^{242}\text{Pu}$ , $^{243}\text{Am}$	$\alpha$ -spectrometry

### 3.3 Analytical results of inter-comparison exercise

#### (1) Spiked water sample

11 labs participated in the inter-comparison analysis of the spiked water samples, and 10 labs reported the analytical results for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ . The analytical results with uncertainty ( $k=2$ ) are presented in Fig. 12. Meanwhile, the spiked values of radionuclides with uncertainty (2 sigma) are also presented. All results presented are decay corrected to 1<sup>st</sup> April 2018.

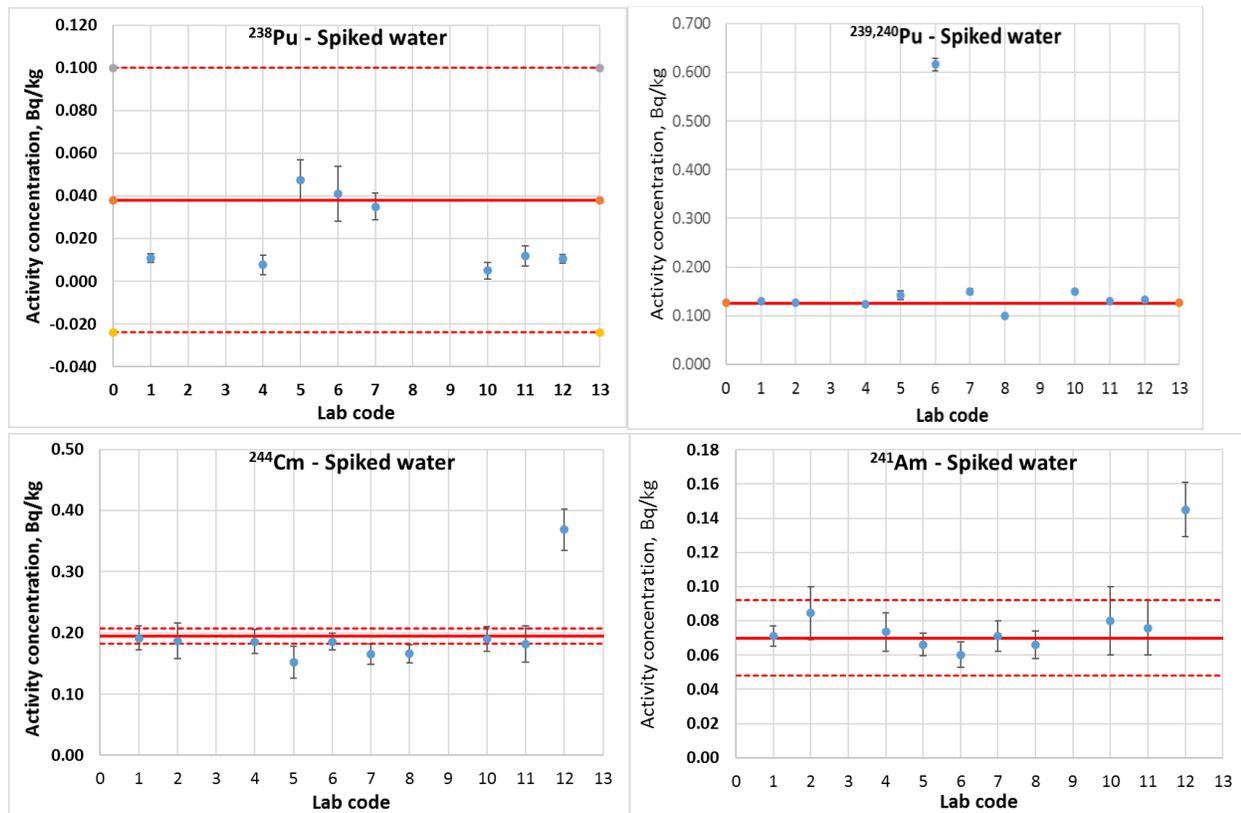


Fig. 12 Inter-comparison results of spiked water sample for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$

From the results in Fig. 12, it can be seen that: (1) for  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ , most of the analytical results agree well with the spiked values and each other, except only 1-2 data; (2) for  $^{238}\text{Pu}$ , the results are divided into two groups 0.01 Bq/kg and 0.04 Bq/kg, respectively.

The two groups of data of  $^{238}\text{Pu}$  could not be attributed to the differences between the chemical separation methods. The different results for  $^{238}\text{Pu}$  are mainly result from the low concentration of  $^{238}\text{Pu}$  in this sample ( $<0.04\text{ Bq/L}$ ). Considering the large uncertainty of  $^{238}\text{Pu}$  concentration in the spiked value (calculated from the original data, not measurable in the original concentration by the sample provider), all reported results agree with the spiked value ( $0.038 \pm 0.031\text{ Bq/L}$ ). For  $^{239, 240}\text{Pu}$ , if the outlying data was excluded, all other analytical results agree very well with the spiked value and each other (Fig. 13). The reason for the extremely high value of  $^{239, 240}\text{Pu}$  reported by one lab is unknown and is under investigation.

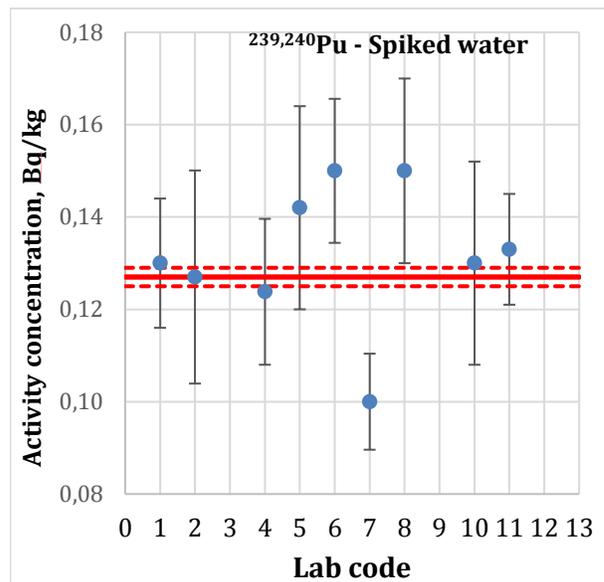


Fig. 13 Inter-comparison results for  $^{239, 240}\text{Pu}$  in spiked water excluding the one outlying data.

For  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ , except one outlying data, the results of all other 9 labs agree very well. The outlying data are about 2 times higher than the spiked values. A further investigation shows that this outline data is attributed to the mis-calibrated  $^{243}\text{Am}$  tracer for this analysis. The  $^{243}\text{Am}$  used in this lab was an old source of  $^{243}\text{Am}$  and has been not calibrated for many years. The total activity of this source was measured by LSC and supposed to be only  $^{243}\text{Am}$ . However, the further investigation found that this  $^{243}\text{Am}$ -tracer contains equal amount of  $^{239}\text{Np}$  activity ( $t_{1/2} = 2.35\text{ days}$ , the decay daughter of  $^{243}\text{Am}$ ) and possibly also small amount of  $^{239}\text{Pu}$  (granddaughter of  $^{243}\text{Am}$  and directly decay daughter of  $^{239}\text{Np}$ ). Because all these alpha radionuclides ( $^{243}\text{Am}$ ,  $^{239}\text{Np}$  and  $^{239}\text{Pu}$ ) occurred as a single alpha peak and could not be discriminated in LSC spectrum, the activity of  $^{243}\text{Am}$  was overestimated by more than 2 times, causing an overestimated activity concentration of  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  when they were calculated against the activity of  $^{243}\text{Am}$  tracer spiked to the samples. After re-calibration of  $^{243}\text{Am}$  concentration in the  $^{243}\text{Am}$  tracer using both gamma and alpha spectrometry, the  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  concentrations analyzed in this lab were re-calculated. The results (Fig. 14) show that the corrected results agree well with the spiked value and all other reported data. From this inter-comparison exercise, a lesson was learned that re-calibration and confirmation of the activity of the tracer isotope in the tracer solution is important,

especially when the tracer solution was not used for a long time. In addition, more than one method should be applied for calibration/confirmation of the concentration of the tracer radionuclides.

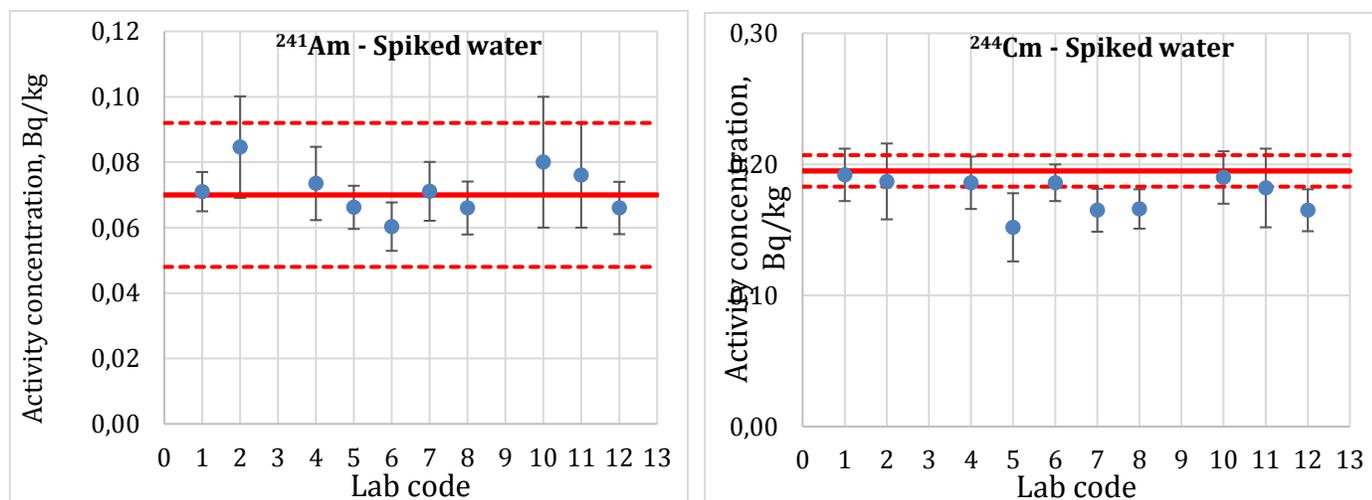


Fig. 14 Inter-comparison results of spiked water sample for  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  after correction for the mis-calibrated  $^{243}\text{Am}$  tracer in one reported data.

## (2) Reactor water sample

Eleven Nordic labs participated in the inter-comparison analysis of reactor water sample, all of them reported analytical results. The analytical results are presented and compared in Fig. 15, the average of the measurement results except the outlying data (red concrete line) with 2SD (dash red lines) are also showed in the figure. It can be seen from these results: (1) most of analytical results agree well with each other, except 1-2 outlying data for each radionuclide; (2) for some outlying data, the difference to the average is about 10 times. (3) the outlying cannot be attributed to the analytical procedure used; (4) the reported  $^{242}\text{Cm}$  results are scattered, this might be associated with its production and decay correction.

Compared with the results of spiked water, the analytical results of  $^{238}\text{Pu}$  agree very well with each other except the result of one lab (because of no chemical separation was used), this should be attributed to the high concentration of  $^{238}\text{Pu}$  in the reactor water sample (1.8 Bq/L) compared to the spiked water (0.04 Bq/L). For  $^{239,240}\text{Pu}$ , one lab reported a 10 times higher value compared to other labs. The same high  $^{239,240}\text{Pu}$  value was also been reported in the spiked water samples by the same lab. Therefore, this outlying data should be attributed to the analytical method of this lab, not the sub-sample (e.g. hot particle in the sub-sample). The precise reason for the extremely high value of  $^{239,240}\text{Pu}$  reported by one lab is unknown

and needs to be further investigated. Excluding this data, all other analytical results agree well with each other with an average and 2SD of  $0.53 \pm 0.06$  Bq/L (Fig. 16a).

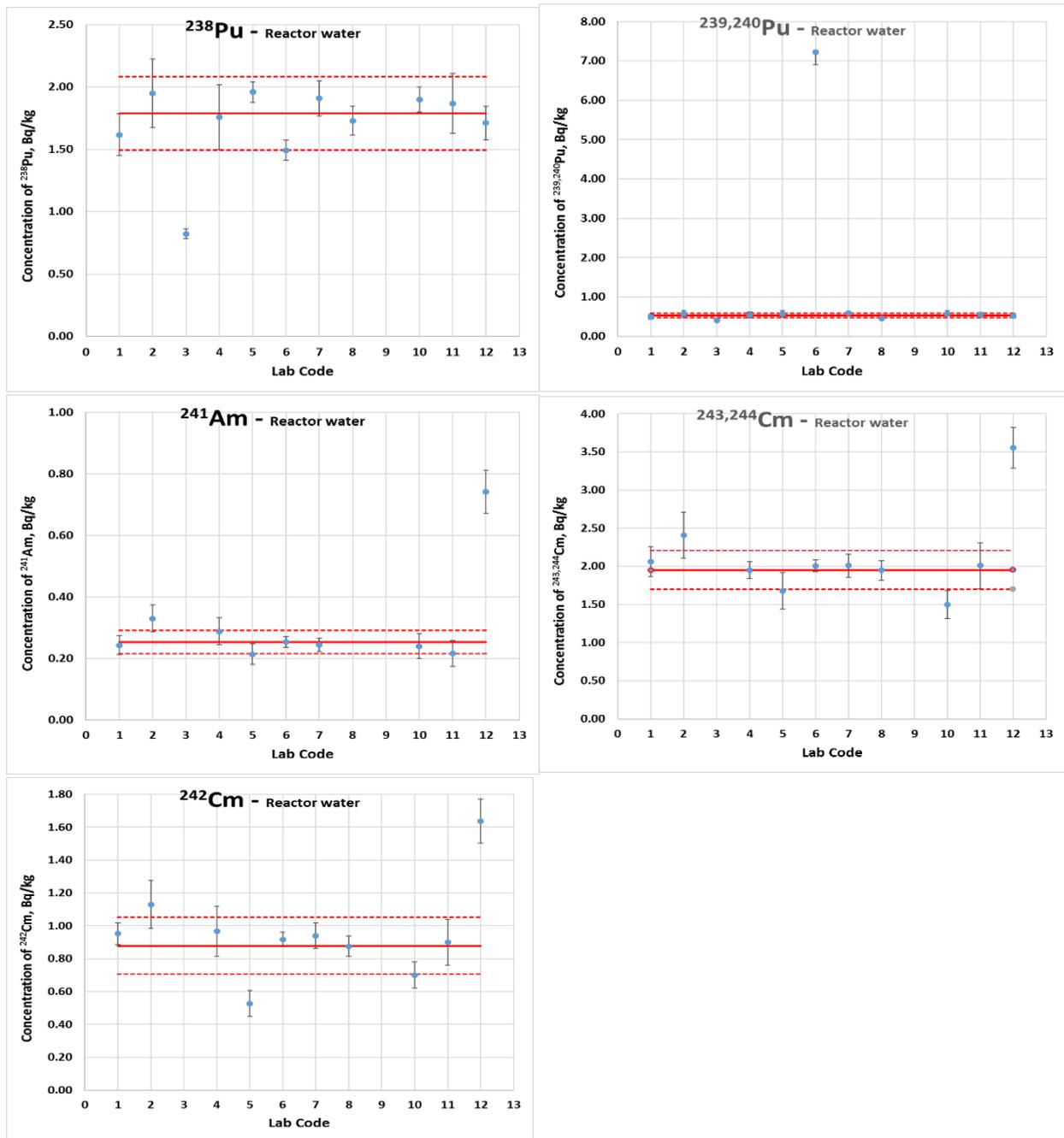


Fig. 15 Inter-comparison results of reactor water sample for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$

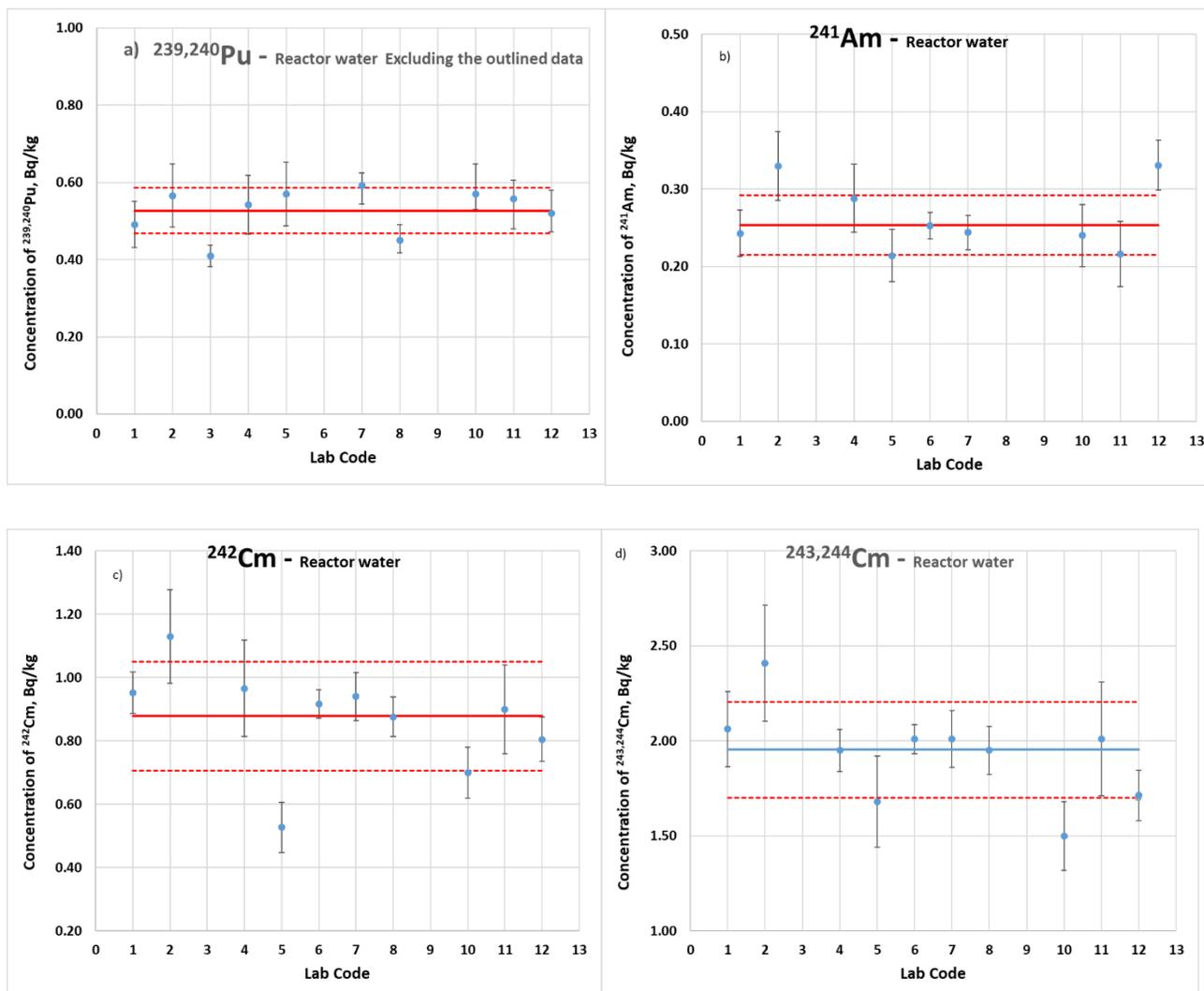


Fig. 16 Inter-comparison results of reactor water sample for  $^{239,240}\text{Pu}$  excluding the outlying data and  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  with the corrected values of one lab.

The outlying data on  $^{243,244}\text{Cm}$  and  $^{241}\text{Am}$  reported by one lab have been investigated by this laboratory, and found that the values of  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  were overestimated, this is attributed to the mis-calibration of  $^{243}\text{Am}$  tracer (see the discussion above). After re-calibration of  $^{243}\text{Am}$  concentration in the  $^{243}\text{Am}$  tracer using both gamma and alpha spectrometry, the  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  concentrations were re-calculated. The results (Fig. 16 b, c, d) show that the corrected results agree well with the spiked value and all other reported data.

Relatively scattered results of  $^{242}\text{Cm}$  ranging from 0.53 to 1.13 Bq/L in the reactor water sample were reported (Fig. 16c). Besides the different methods used in the participating labs, the analysis in different time by each lab and decay correction might be another reason.  $^{242}\text{Cm}$  is a relative short-lived (162 days) isotope of curium. In the nuclear reactor,  $^{242}\text{Cm}$  is produced mainly through the beta decay of the short-lived  $^{242}\text{Am}$  (16 h) and internal conversion followed by beta decay of relative long-lived  $^{242\text{m}}\text{Am}$  (141 years) (Fig. 17).

The reactor water sample used for this inter-comparison analysis was collected in April 2016 from the coolant water in the reactor unit 1 of the Olkiluoto NPP, more than 2 years reservation time before analysis makes most of original  $^{242}\text{Cm}$  (> 95%) and its direct parent  $^{242}\text{Am}$  (> 99.9%) have decayed away. Therefore,  $^{242}\text{Cm}$  measured in the reactor water should be mainly decayed from its grandparent  $^{242\text{m}}\text{Am}$ . Considering a long reservation time of more than 2 years and the long half-life of  $^{242\text{m}}\text{Am}$  (141 years) and the short half-lives of  $^{242}\text{Am}$  (16h) and  $^{242}\text{Cm}$  (161 days), the  $^{242}\text{Cm}$  present in the sample during the analysis by participating labs was nearly in equilibrium with  $^{242\text{m}}\text{Am}$  in the reactor water, i.e. the  $^{242\text{m}}\text{Am}$  supported  $^{242}\text{Cm}$ . Therefore, the analytical results of  $^{242}\text{Cm}$  should not be decay corrected using the half-life of  $^{242}\text{Cm}$  (162 days) in this inter-comparison analysis.

However, the routine analysis of isotopes of Pu and Cm in the reactor water is often implemented within a short time after sampling from the reactor coolant water (<3 months), a decay correction for  $^{242}\text{Cm}$  has to be considered for this situation. In the case of spent fuel pool water analysis, the age of the spent fuel took from the nuclear reactor needs to be considered when calculating  $^{242}\text{Cm}$  concentration from the measured  $^{242}\text{Cm}$  activity in the sample. For the discharge water from nuclear facilities (e.g. NPP), the decay correction might be not needed, since it is not easy to know the age of the radioactive sources.

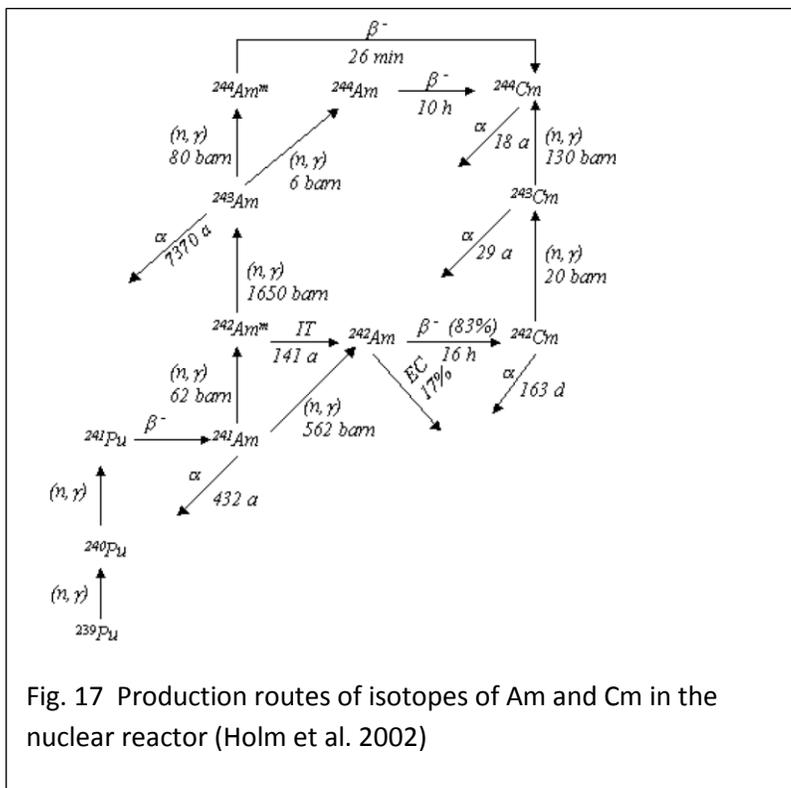


Fig. 17 Production routes of isotopes of Am and Cm in the nuclear reactor (Holm et al. 2002)

#### 4. Problems and strategies on the analysis of alpha emitters in nuclear and environmental samples

Different methods were used in Nordic labs for determination of alpha emitters in the nuclear and environment sample. The inter-comparison exercise organized in this project by analysis of a spiked water and a reactor water shows that the most of Nordic labs performed very good, but some problems were also observed, and some further investigations have been implemented to solve these problems. Meanwhile, some strategies are needed to face the analysis of low-level environmental samples and samples with complicated matrices. The major problems observed in the participating labs and the strategies are summarized below.

- 1) A direct electrodeposition followed by alpha spectrometry method was used in one Nordic lab for the determination of alpha emitters. The results show that the analytical results of  $^{239,240}\text{Pu}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  in spiked water and reactor water samples agree with the spiked value and average values of all labs, indicating that this method is valid for the analysis of reactor water with pure matrices for these radionuclides. However, it is not possible to report the results for  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  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 used.
- 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 recovery 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) Alpha spectrometry is normally applied in the Nordic labs for determination of  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ , and  $^{243,244}\text{Cm}$ , although ICP-MS is also used in a few labs for determination of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . The electrodeposition is often used to prepare an alpha source for measurement in the Nordic labs, although micro-precipitation is also used in some Nordic labs for this purpose. It was reported that the prepared source using electrodeposition is not always good, sometimes a black source was obtained (Fig. 18) and a bad energy resolution in alpha spectra in some samples is observed (Fig. 18). Besides the electrodeposition condition, the purity of the separated sample solution might be another reason, which might be also a reason causing a low recovery of the radionuclides measured in the alpha sources. Electrodeposition of Pu, Am and Cm is often implemented in a current of 0.5-1.5 A for 1-3 hours. Due to the high current, the sample solution was heated to a high temperature

(>80°C) in a short time (<20 min.). While the electrodeposition cell is not cooled in many labs, it causes a quick evaporation of the sample solution, and the volume of the solution is significantly reduced in the end of the electrodeposition. The black alpha counting source and low recovery of Pu, Am and Cm might be also attributed to this step. In addition, the electrodeposition should be conducted in a slightly acidic media (preferred in sulfuric acid medium), the pH and the composition of the media are critical for the recovery of radionuclides and the quality of the electrodeposited disk in the electrodeposition step. A further investigation and optimization might be needed in some Nordic labs to improve their performance in the analysis of alpha emitters.

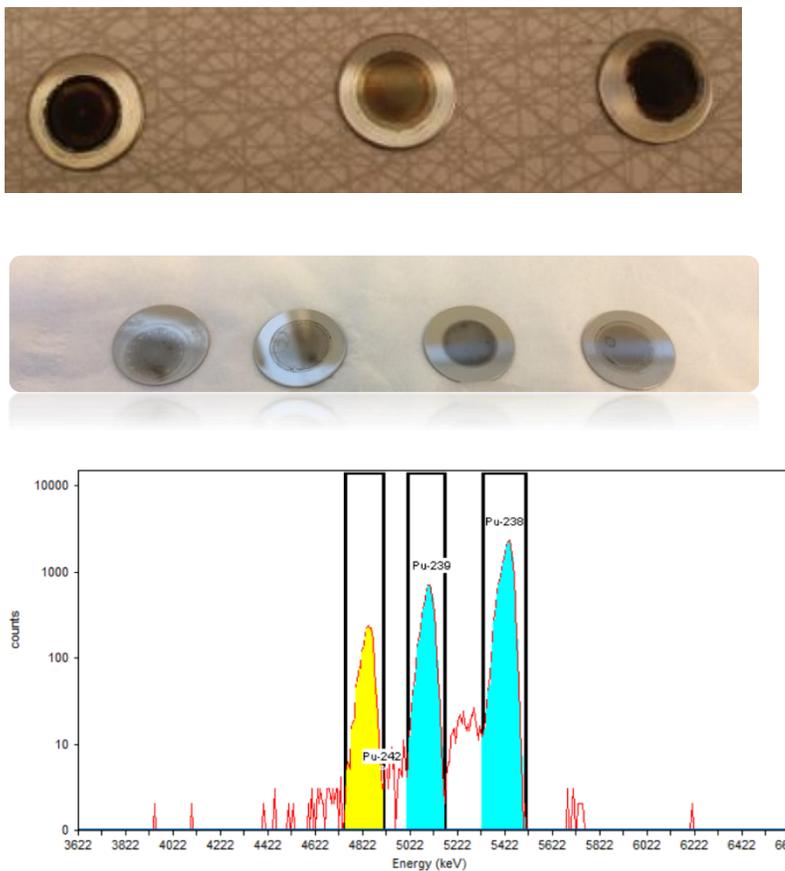


Fig. 18 Alpha source prepared in some labs for inter-comparison analysis, and the alpha spectra of some sample in some labs.

- 4) A black residue was found in the separated Am-Cm fraction after evaporation in some lab using UTEVA-TRU separation procedure, it is not clear how the residue was formed and if it contains Am

and Cm. Am and Cm was eluted from the TRU column using 4M HCl after loading the effluent from the UTEVA column and rinsed with 2M HNO<sub>3</sub>-NaNO<sub>2</sub> solution. Some organic residues 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 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 well known. One challenge might be the removal of <sup>210</sup>Po interference in the analysis of filter and environmental samples. The concentration of <sup>210</sup>Po might be a few orders of magnitude higher in these samples compared to the measured alpha emitters and the similar energy of alpha particles with <sup>210</sup>Po (5.30 MeV), namely <sup>243</sup>Am (5.28 MeV) which was used as a yield tracer of Am and Cm isotopes. Another challenge will be the sufficient removal of the large matrices elements in the environmental samples. A further improvement and investigation for an optimal method for isotopes of U, Pu, Am, Cm is needed.

## 5. Summary and Remarks

This project reviewed the capacity and analytical methods used in Nordic labs for determination of artificial alpha emitters. An inter-comparison analysis of two water samples with one spiked and a real reactor water samples was organized, eleven Nordic labs participated in this analysis and reported the results of isotopes of plutonium, americium and curium. The problems and strategies were investigated for reliable determination of these radionuclides in order to establish an optimal method for determination of alpha emitters in nuclear and environmental samples. The major achievements are summarized below:

- 1) Among 12 partner labs of this project, 11 labs in Denmark, Finland and Sweden can determine individual alpha emitters including <sup>238</sup>Pu, <sup>239, 240</sup>Pu, <sup>241</sup>Am, <sup>242</sup>Cm and <sup>243, 244</sup>Cm in nuclear (reactor and spent fuel pool water) and/or environmental samples. In most of labs, alpha spectrometry is used for the measurement of these alpha radionuclides, ICP-MS is used in a few labs for measurement of <sup>239</sup>Pu, <sup>240</sup>Pu and isotopes of uranium (<sup>234</sup>U, <sup>235</sup>U, <sup>238</sup>U).

- 2) For the determination of isotopes of Pu, Am and Cm, 4 procedures/methods are used in the Nordic labs, i.e. no chemical separation, separation for individual element, sequential separation using Eichrom method and sequential separation using own developed method. Method of no chemical separation is only used for analysis of nuclear water samples (reactor coolant and fuel pool water) with less matrices with a simple evaporation plus acid digestion. This method could not provide the information of  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  due to similar alpha energy.
- 3) Of the chemical separation methods used in Nordic labs, the Eichrom method using UTEVA-TRU resin is the most popular one used in the nuclear power plants and other nuclear industry labs. Other sequential separation methods using different combination of ion exchange and extraction chromatographic columns, e.g. TEVA-UTEVA-TRU, Dowex-TRU and TEVA-DGA are used in other Nordic labs, especially in the Nordic universities, institutes and authorities for the analysis of environmental samples with complicated matrices.
- 4) The reported results of the first inter-comparison analysis of two water samples from the participating labs are good, only 1-2 outlying data for each radionuclide. The outlying data of  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  was reported by one lab. A further investigation shows that is due to the mis-calibration of the  $^{243}\text{Am}$  yield tracer, and after re-calibration, the results agree with other labs. It is learned that regular calibration of the tracer/standard using two different method or compared with other standard is necessary for the control of the analytical quality. This inter-comparison exercise also validated the methods used in many Nordic labs, which is important for the reliability of the reported data in their routine analysis. An outlying data of  $^{239,240}\text{Pu}$  was reported by one lab in the two inter-comparison samples, indicating that this might be attributed to the method or procedure used in this lab. The precise reason is unknown but under investigation.
- 5) Besides water samples (reactor water and spent fuel pool water), filter, exchange resin, environmental water (effluent water), and environmental solid samples (soil, sediment, seawater, vegetation) are analyzed in many Nordic labs, therefore validation and verification of analytical methods for these sample types are highly needed. A continuation of this project is proposed, the second inter-comparison exercise for analysis of sample with complicated matrices (air filter) will be organized and an investigation on the problems occurred in the partners' labs and establish an optimized method for determination of individual alpha emitters is going to be implemented.

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Title	Simultaneous Determination of Isotopes of Pu, Am and Cm in Reactor Water Samples –Report of OptiMethod 2018 project
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Abstract max. 2000 characters	This report presents the progress on the NKS-B OptiMethod project which was conducted in 2018, aiming to establish Nordic optimal method for the determination of alpha emitters in nuclear and environmental samples. The capacity and the analytical methods used in Nordic labs for determination of alpha emitters were reviewed and summarized. 11 Nordic labs in Denmark, Finland and Sweden can determine individual alpha emitters in nuclear and/or environmental samples. Alpha spectrometry are used in most of labs for the measurement, sequential separation using different combination of ion exchange and extraction chromatography are often used for separate Pu, Am and Cm from matrices and each other. An inter-comparison analysis of a spiked water and a real reactor water was organized, 11 Nordic labs participated in this analysis and reported the analytical results of <sup>238</sup> Pu, <sup>239, 240</sup> Pu, <sup>241</sup> Am, <sup>242</sup> Cm, <sup>243, 244</sup> Cm. The results reported by the most labs are good, and only 1-2 outlying data for each radionuclides were observed. The problems and strategies in the analysis of alpha emitters in the Nordic labs were summarized and discussed.
Key words	Alpha emitter; Radioanalysis; reactor water; Inter-comparison; Plutonium; Americium; Curium

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