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Application of Rapid and Automated Techniques in Radiochemical Analysis

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April 2015

Abstract

NKS Rapid-Tech project 2014 aims to explore the application of different rapid techniques in determination of radionuclides, thus to improve the analytical efficiency and capacity of present radioanalytical methodologies used for different purposes in the areas of E, W and R. Specific tasks are described as follows:

- Identification of current needs and problems in methodology development for rapid determination of radionuclides (e.g., ^{90}Sr , actinides).
- Identification of individual processes/operations wherein rapid techniques can be potentially applied to improve the analytical efficiency.
- Establishment of practical solutions/suggestions in the application of rapid techniques in radiochemical procedures.
- Development and optimization of rapid methods for determination of radionuclides (e.g., ^{90}Sr , actinides) in environmental samples using automation and effective sample treatment techniques.
- Assessment of analytical performance and summarization of successes/failures, challenges and future attempts.

In 2014, Rapid-Tech project gathered scientists working in radiochemistry among Nordic countries and oversaw the problems and needs in developing effective radiochemical methods. Based on screening the current analytical methods for common radionuclides (e.g., Sr, actinides) assays in individual institute, challenges and future development needs were identified by each institute and presented in this report.

Experiments in applying distinct novel techniques in each institute were also performed: 1) DTU Nutech (Denmark) improved method applicability for different matrix content in Pu determination by exploring oxalate co-precipitation, and improved Sr seawater procedure; 2) STUK (Finland) improved Pu/Am source preparation technique and Pu procedure in air filter analysis for emergency preparedness; 3) IFE (Norway) improved ^{90}Sr seawater method in terms of reducing the use of fuming nitric acid and testing the application of Sr resin to ^{210}Pb analysis in water samples; 4) FOI (Sweden) tested new redox reagents for improving the stability of Pu analytical method and investigated the matrix effect on TEVA resin to improve the chemical yield of Pu. The preliminary results obtained in each institute are assessed and summarized in this report.

Key words

Rapid determination, Pu, Sr, Tc, environment analysis, emergency preparedness

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Final report from the NKS-B Rapid-Tech activity

(Contract: AFT/B(14)7)

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- Development and optimization of rapid methods for determination of radionuclides (e.g., ^{90}Sr , actinides) in environmental samples using automation and effective sample treatment techniques.
- Assessment of analytical performance and summarization of successes/failures, challenges and future attempts.

In this report, the state-of-art on analytical methods for common radionuclides (e.g., Sr, actinides) in environmental assays and emergency preparedness among Nordic countries are screened and summarized. Practical problems, challenges and future needs in developing effective radiochemical methods are identified.

Within Rapid-Tech 2014 project, experiments in applying rapid techniques and improving analytical efficiency were performed in each participating institute: 1) DTU Nutech (Denmark) improved method applicability for different matrix content in Pu determination by exploring oxalate co-precipitation, and improved Sr seawater procedure by investigating different affecting parameters; 2) STUK (Finland) improved Pu/Am source preparation technique and Pu procedure in air filter analysis for emergency preparedness; 3) IFE (Norway) improved ^{90}Sr seawater method in terms of reducing the use of fuming nitric acid and tested the application of Sr resin to ^{210}Pb analysis in water samples; 4) FOI (Sweden) studied new redox reagents for improving the stability of Pu analytical method and investigated the matrix effect on TEVA resin to improve the chemical yield of Pu. The preliminary results obtained within the project are assessed and summarized in this report.

Key words

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1. Introduction

Rapid sample processing techniques are desirable in radionuclide determination for emergency preparedness, environmental monitoring, nuclear decommissioning and waste management to achieve fast analysis, and high sample throughput with low labor intensity and cost. Within the Nordic countries, a few laboratories working with radiochemistry have initiated R&D in developing rapid radiochemical methods using different rapid and effective sample treatment techniques. However, the exploration of rapid techniques is still a fresh area, and very little has been done to share experiences and knowledge on this topic among the Nordic countries.

In 2014, within NKS-B Rapid-Tech project [AFT/B(14)7], Nordic scientists gathered together and screened the current analytical methods for common radionuclides (e.g., Sr, actinides). Problems and needs in developing rapid radiochemical methods were identified and applications of distinct rapid sample processing techniques to improve the simplicity and analytical efficiency in radioassays for determination of the most common radioisotopes were assessed. Based on the screening, several consensuses through the screening have been reached: 1) Current application of novel automated techniques in Nordic countries is very limited, many of them have only been exploited for research purpose while most routine analysis are still operated in batch-wised manual fashion. 2) Analytical techniques used for Sr determination vary significantly from lab to lab. Especially for low-level environmental samples, several Nordic labs are still using very traditional methods developed in 1960-70s. These methods are not only problematically slow and labor intensive but also based on the use of harmful chemicals (e.g., fuming nitric acid) wherein laboratory safety issues are worth of concern. 3) There is a need for end users to become more aware of the advantages of improved techniques for radiochemical assays, so that they can become more active in driving the long-term development. Identification of concrete analytical benefits and experience sharing are necessary for selecting purpose-fit novel techniques.

2. Overview of Current Status on Radiochemical Analysis in Nordic Countries

A kick-off meeting for NKS-B Rapid-Tech project was held on 9th April 2014. During the meeting, project participants shared experiences in analytical methods for important radionuclides (mainly Sr and Pu). A concrete work program was made wherein detailed experimental plan were structured in each institute to improve the efficiency of specific analytical protocols used for different sample matrix and radioactivity levels.

To better understand the state-of-art radiochemical analysis for Sr, actinides and other radionuclides among Nordic countries, an overview of current radiochemical procedures used in each institute for different situation and samples are given in the following context. Advantages, problems and challenges demonstrated in current analytical methods are pinpointed and future optimization and development are identified.

2.1 Environmental Analysis for ^{90}Sr , $^{239,240}\text{Pu}$, ^{237}Np and ^{99}Tc in DTU Nutech

Strontium-90 and technium-99 as important beta-emitting fission products, along with plutonium-239, 240 and neptunium-237 as important alpha emitters need to be determined for environmental risk assessment and monitoring, remediation, nuclear security and radioecology studies. In DTU Nutech, low level ^{90}Sr , ^{99}Tc , $^{239,240}\text{Pu}$ and ^{237}Np are routinely analyzed for large volume aqueous and solid environmental samples in many types. Thorough chemical purification is required for all these radionuclides to eliminate the interferences including any other beta or alpha emitters and natural matrix elements. This section summarizes the current radiochemical methods used in DTU Nutech for ^{90}Sr , ^{99}Tc , $^{239,240}\text{Pu}$ and ^{237}Np determination in different environmental samples, critically evaluates the advantages and disadvantages of these methods, and points out possible solutions/perspectives to overcome the potential problems existed in the analytical procedures.

2.1.1 Procedures for Sr determination

The current method for Sr determination in DTU Nutech is designed for measuring ^{90}Sr through its daughter ^{90}Y in-growth by low background gas flow Geiger Müller beta counter. Samples analyzed for ^{90}Sr include seawater, freshwater, air filter, soil, sediment and food (milk, vegetable, fruit, etc.). ^{85}Sr is spiked as chemical yield monitor for Sr, and stable yttrium (^{89}Y) is used to monitor the chemical yield of ^{90}Y in the Sr-Y separation step and quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). The limits of detection are 0.1 Bq/m³ for seawater, 0.1 Bq/kg for air filter ash and 0.5 Bq/kg for soil, sediment or food ash, based on the sample size of 45 L seawater, 50 g filter ash and 10 g soil, sediment or food ash, respectively. Typical chemical yields for Sr are in the range of 60-85% and the analytical turnover time for one sample is about 5 days excluding the 3-week waiting for the in-growth of ^{90}Y and the beta counting (ca. 1-2 weeks).

(1) Sr in seawater

For ^{90}Sr seawater analysis, normally 45 L sample is processed through three stages: sample pre-concentration, chemical purification and ^{90}Y source preparation (*Figure. 1*). For pre-concentration, calcium carbonate is used to scavenge most Sr into the residue. A hydroxide precipitation is then performed in 0.2 M NaOH to remove large amount of Ca as well as other interfering radionuclide (actinides, Po and rare elements), whilst Sr remains in the supernatant. Afterwards, another carbonate precipitation is performed to concentrate Sr. The chemical

purification is then carried out to further remove Ca and other impurities. For this purpose, strontium nitrate precipitation is repeatedly performed with the use of fuming nitric acid, wherein only Sr forms precipitate and most of impurities will be dissolved in the supernatant. After an iron hydroxide co-precipitation, the supernatant containing ^{90}Sr will be kept for 3 weeks for the in-growth of its daughter ^{90}Y . For the ^{90}Y source preparation and detection, ^{90}Sr and other interfering elements such as Ba and Ra should be separated. Yttrium hydroxide precipitation is repeatedly performed to remove ^{90}Sr , in combination with barium sulphate precipitation to remove Ba and Ra as BaSO_4 and RaSO_4 , respectively. The ^{90}Y source is finally precipitated as yttrium oxalate which is embedded on a paper filter for the beta counting.

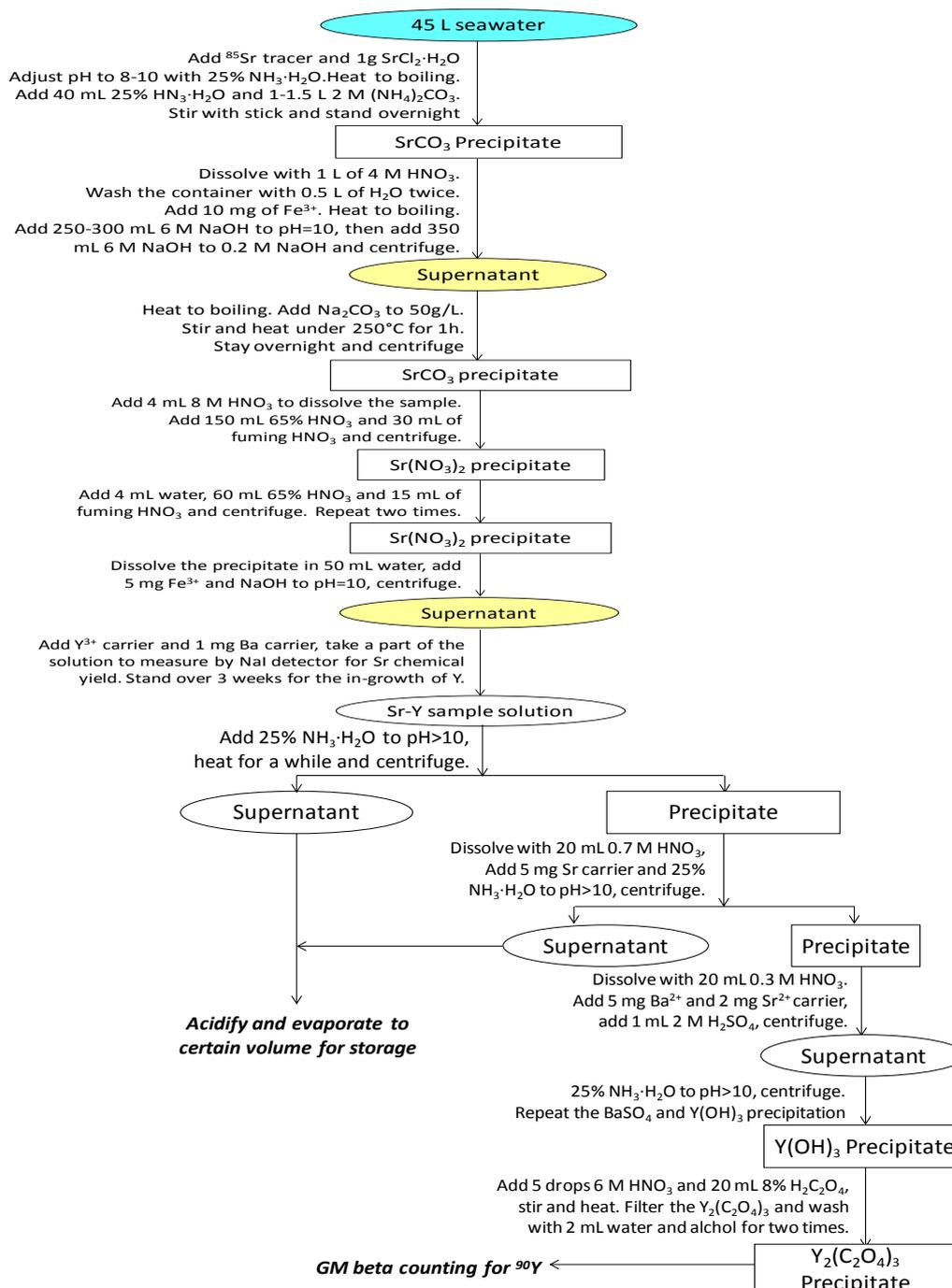


Figure. 1 The analytical procedure for ^{90}Sr determination in 45 L seawater

(2) Sr in air filter, soil, sediment and food

For ^{90}Sr air filter, soil, sediment and food analysis, samples are processed following similar three analytical stages as for seawater, but different in sample pre-concentration depending on the sample type (Figure. 2). In the pre-concentration stage, typically 30-50 g filter ash, 10 g soil/sediment, or 10 g food ash is digested with aqua regia to extract Sr into liquid phase. Iron hydroxide precipitation is employed to remove metal elements for air filter and soil/sediment samples, while calcium oxalate precipitation is used for food samples. Finally, a carbonate precipitate is carried out for all type of solid samples prior to the chemical purification using fuming nitric acid and ^{90}Y source preparation as indicated in the Sr seawater analysis.

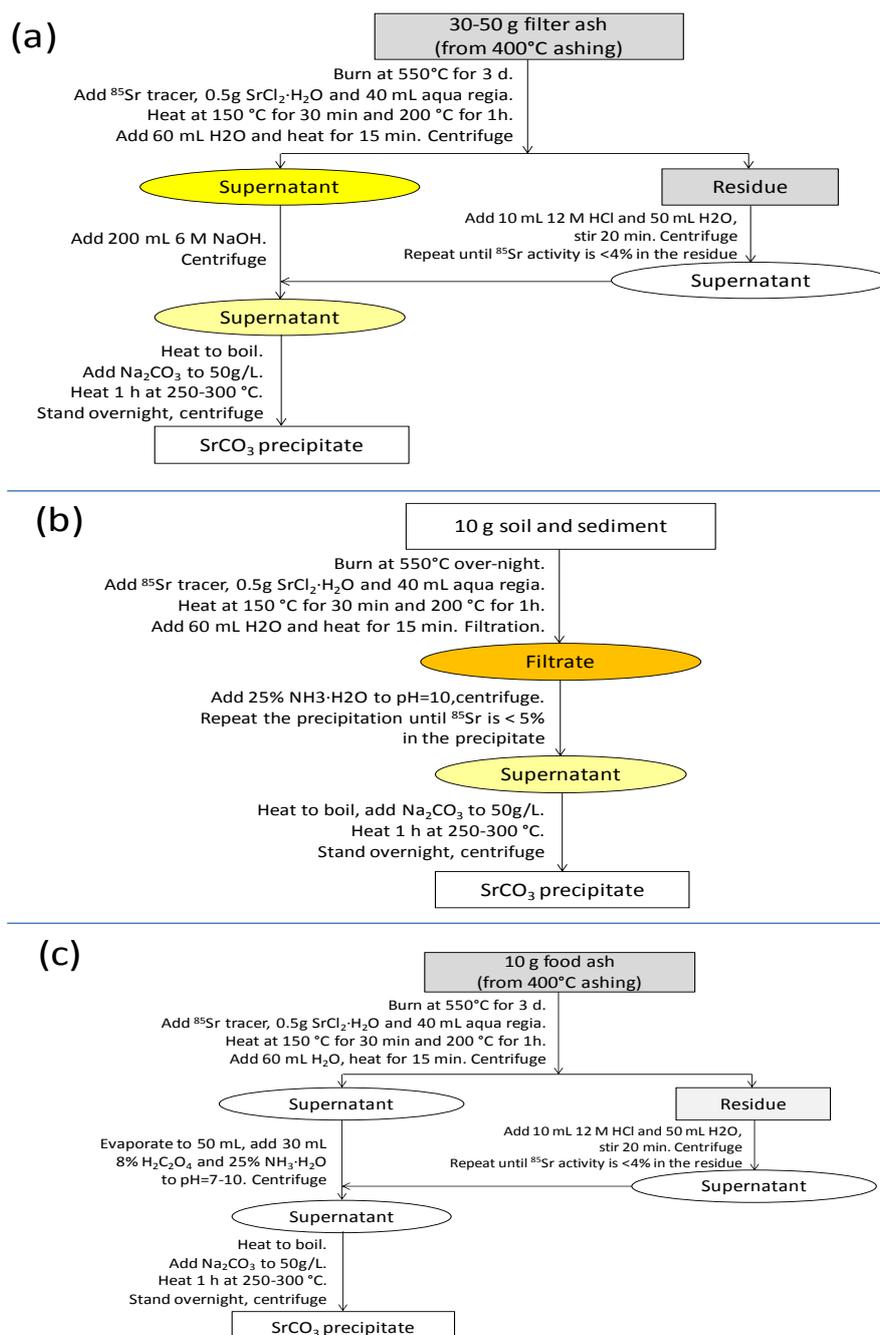


Figure. 2 Sample pre-concentration procedures in ^{90}Sr air filter, soil, sediment and food analysis

2.1.2 Procedures for ^{99}Tc , ^{237}Np and $^{239,240}\text{Pu}$ determination

Traditionally, the determination of ^{99}Tc is performed separately from Pu and Np in DTU Nutech. Samples routinely analyzed for ^{99}Tc are mostly seawater, freshwater and seaweed. For ^{99}Tc water sample analysis, anion exchange chromatography is used by pumping the large volume (100-200L) water directly through a big anion exchange column, wherein Tc will be absorbed and pre-concentrated (Chen et al. 1990, 1994). ^{99}Tc is further purified with $\text{Fe}(\text{OH})_3$ precipitation and TIOA-xylene solvent extraction. For ^{99}Tc seaweed analysis, a wet ash using concentrated H_2SO_4 and HNO_3 is employed followed by chemical purification using anion exchange chromatography and TIOA-xylene solvent extraction. For all samples analysis, short-lived $^{99\text{m}}\text{Tc}$ is spiked as a chemical yield monitor, which restricts the analytical process to be finished within 5 days. ^{99}Tc after purification is electrodeposited on a stainless steel disc and then counted using low background gas flow beta counter. Typical chemical yields for Tc are 60-80% for seawater and 70-90% for seaweed. The analytical turnover time is about 3-4 days for seawater and 2-3 days for seaweed, except the counting time.

The routine based determination of ^{237}Np and Pu isotopes in DTU Nutech is mostly carried out for seawater, soil and sediment samples. For seawater samples, a series $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$ co-precipitation is used to scavenge Np and Pu from the seawater, followed by anion exchange chromatography using macro-porous resin (AGMP-1M). For soil and sediment samples, acid digestion using aqua regia is used to leach Np/Pu into the aqueous phase followed by similar $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$ co-precipitation and anion exchange chromatography as for seawater (Qiao et al. 2009, 2011). ^{242}Pu is spiked as a chemical yield tracer for both ^{237}Np and Pu isotopes, which avoids the difficulties in obtaining Np isotopic tracers. The Np and Pu eluate after final column separation is evaporated to dryness and re-dissolved in 0.5 M HNO_3 and measured by inductively coupled mass spectrometry (ICP-MS). The limits of detection for ^{237}Np , ^{239}Pu and ^{240}Pu are $0.25 \mu\text{Bq}/\text{m}^3$, $20 \mu\text{Bq}/\text{m}^3$, $80 \mu\text{Bq}/\text{m}^3$, respectively, for 200 L seawater and $5 \mu\text{Bq}/\text{kg}$, $0.4 \text{ mBq}/\text{kg}$, $1.6 \text{ mBq}/\text{kg}$, respectively, for 10 g of soil/sediment. The analytical turnover times for Np and Pu are about 3-4 days for seawater and 2-3 days for soil/sediment, respectively.

Recently, a new analytical method is developed, which is targeted for simultaneous determination of ^{99}Tc , Np and Pu in 200 L seawater (Qiao et al. 2014). The method is based on the effective co-precipitation of Tc(IV) along with Pu and Np in alkaline condition via $\text{Ca}(\text{OH})_2\text{-Mg}(\text{OH})_2\text{-Fe}(\text{OH})_2$. After the simultaneous pre-concentration, Tc is separated from Np and Pu fraction by oxidizing Tc(IV) to Tc(VII) prior to the $\text{Fe}(\text{OH})_3$ co-precipitation, whereupon Tc(VII) will remain in the supernatant whilst Np/Pu remain in the precipitate. The further purification of Tc and Np/Pu is then performed separately using extraction (TEVA) and anion exchange (AGMP-1M) chromatography, respectively. Similar to the traditional method, beta counter is used for the quantification of ^{99}Tc and ICP-MS for ^{237}Np and Pu isotopes with comparable limits of detection to the traditional methods for all target radionuclides.

(1) Tc, Np and Pu in seawater

The traditional analytical method for ^{99}Tc seawater analysis has been reported in Risø-R-1263 report. Herein the new method for combined ^{99}Tc , ^{237}Np and Pu isotopes determination is detailed following the stages of sample pre-concentration, Tc purification, Np and Pu purification, source preparation and detection. In the pre-concentration stage, Tc is co-

precipitate along with Np and Pu via $\text{Ca}(\text{OH})_2\text{-Mg}(\text{OH})_2\text{-Fe}(\text{OH})_2$ (pH=10-11) from 200 L sample based on the redox control of Tc(IV) (*Figure.3*). Ca and Mg is then removed via $\text{Fe}(\text{OH})_2$ co-precipitation through controlling the pH to 9-10. After that, the separation of Tc from Np and Pu is performed by oxidizing Tc(IV) to Tc(VII) prior to another $\text{Fe}(\text{OH})_3$ co-precipitation, whereupon Tc(VII) becomes soluble in the supernatant while Np and Pu remain in the precipitate.

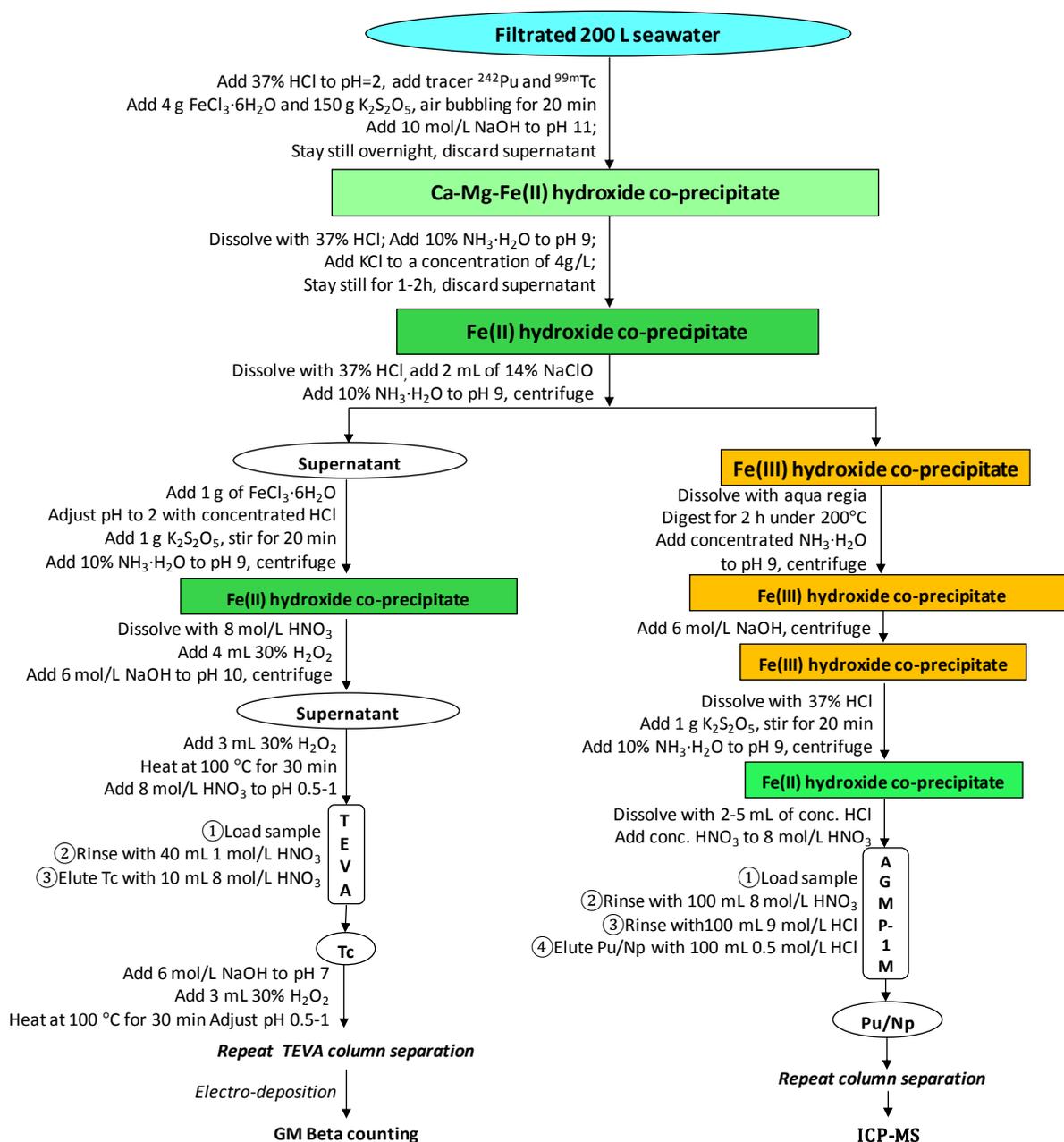


Figure. 3 Analytical procedure for simultaneous determination of ^{99}Tc , ^{237}Np and $^{239,240}\text{Pu}$ in 200 L seawater

For Tc purification, a $\text{Fe}(\text{OH})_2$ co-precipitation is performed again to reduce the sample volume followed by a $\text{Fe}(\text{OH})_3$ precipitation to transfer Tc(VII) into aqueous phase meanwhile remove Fe in the residue. The interfering radionuclide such as Mo, Ru, U, Th, Po is further removed through 30% H_2O_2 treatment in combination of extraction chromatography (TEVA). In the chromatographic separation, the sample is prepared in 0.1 M HNO_3 and loaded onto a 2-mL TEVA column. The column is then rinsed with 1 M HNO_3 to remove Ru and Mo, and Tc is finally eluted with 8 M HNO_3 . The TEVA column separation is repeated two times to ensure sufficient decontamination of interfering nuclides. The final Tc eluate is evaporated under lower temperature (100 °C) to near-dryness for source preparation and detection.

For Np and Pu purification, acid digestion using aqua regia is carried out to decompose potential organic matter wrapped in the $\text{Fe}(\text{OH})_3$ precipitate, followed by repeated $\text{Fe}(\text{OH})_3$ co-precipitation in ammonia and NaOH medium to further remove matrix elements (Ca, Mg) and amphoteric elements (Al, V, U), respectively. After valence adjustment of Pu(IV) and Np(IV) using a redox pair $\text{K}_2\text{S}_2\text{O}_5$ -conc. HNO_3 , automated anion exchange chromatography (AGMP-1M) assembled in a flow injection (FI) system is employed to further remove matrix elements (e.g., Fe, Mn) and other interfering radionuclides (e.g., U, Am, Th), see *Figure 4*. Four samples can be processed simultaneously in the FI system. In the anion exchange chromatographic separation, the sample prepared in 8 M HNO_3 is loaded onto a 4-mL AGMP-1M column, the column is rinsed with 8 M HNO_3 followed by 9 M HCl , Np and Pu is finally eluted with 0.1 $\text{NH}_2\text{OH}\cdot\text{HCl}$ -2 M HCl and evaporated to dryness. The column separation is also repeated two times to ensure sufficient decontamination of interferences, especially for U. But for the second chromatographic separation, a 2-mL column is used instead of a 4-mL column to reduce the consumption of the anion exchange resin.

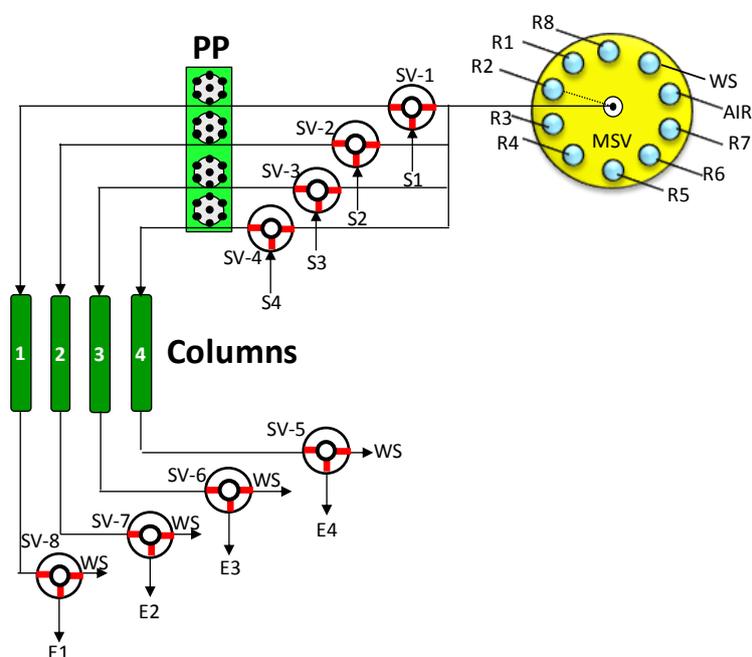


Figure. 4. Schematic illustration of the multi-sample processing FI system for simultaneous determination of Tc, Np and Pu in large volume seawater (PP: Peristaltic pump, S1-S4: ports for sample loading, E1-EF4: ports for eluate collection, WS: waste, AIR: port for air aspiration/dispense, SV-1-SV-8: selective valves, R1-R8: reagents for column separation)

In the source preparation and detection, the evaporated Tc eluate is re-dissolved with 2 M NaOH and electrodeposited onto a stainless steel disc under a current of 150 mA for at least 5 hours. After dry, the Tc disc is counted for about 3-5 days (10 hours/run, 8-12 runs). For the detection of Np and Pu, the evaporated eluate is re-dissolved with 0.5 M HNO₃ (containing 1 ng/g of In as internal standard), and measured under hot plasmas condition using X^{II} series quadruple ICP-MS connected to ultrasonic nebuliser.

(2) Pu in environmental solid

Sequential injection (SI) based automated analytical methods have been developed in DTU Nutech for determination of Pu in different environmental solid samples including soil, sediment and seaweed. These methods have been successfully used for Pu tracer applications in radioecology studies in different research projects. The detailed analytical procedure for Pu environmental solid analysis is demonstrated in *Figure. 5*. Typical sample size is 5-10g of soil and sediment, and 10-20 g of seaweed. The sample material, after grinding, sieving, freeze drying and ashing, is digested with aqua regia to leach Pu into the solution. A series Fe(OH)₃ co-precipitation is used to pre-concentrate Pu and remove most of the matrix elements. After valence adjustment with a redox pair K₂S₂O₅-conc. HNO₃, the sample is prepared in 1 M HNO₃ solution and loaded onto a 2-mL TEVA column. The column is rinsed with 1 M HNO₃ followed by 6 M HCl. Pu is finally eluted with 0.1 NH₂OH·HCl in 2 M HCl solution. It should be noted that, in case of processing high matrix elements (e.g., Fe, Mn, Ni) or U content samples (such as soils from areas with heavy industrial pollution), anion exchange column is normally used before the TEVA column to perform the preliminary purification of Pu as well as to avoid a breakthrough on TEVA column.

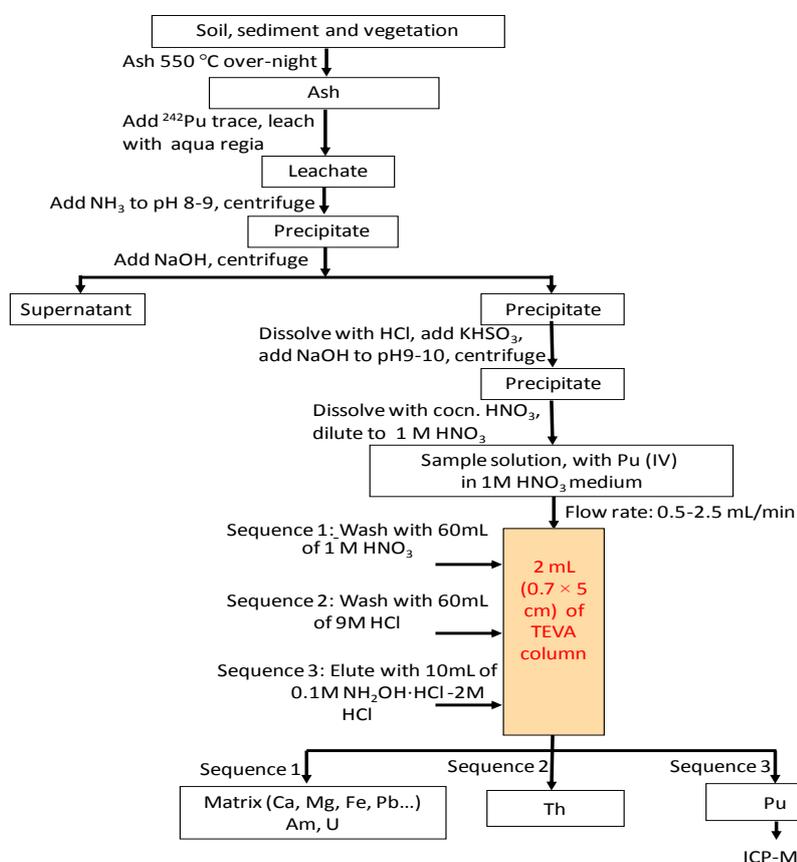


Figure. 5 Analytical procedure for Pu determination in environmental solid samples

2.1.3 Performance evaluation for current analytical methods

(1) Sr analytical methods

i) High accuracy, precision and applicability

Current Sr analytical methods used in DTU Nutech is very robust and has high decontamination factor for interfering nuclides, providing high resolution and precision in the analytical results. The methods have been successfully applied to the intentional inter-comparison exercises and professional tests. The analytical results obtained from these exercise or tests agree very well with the reference/recommended values, which further indicates the satisfactory accuracy of the current methods. These methods are relatively easy to handle and suitable to samples with varying matrix composition, thus have high applicability.

ii) Low safety factor

In the current Sr analysis, potential safety issues exist. In the Sr seawater pre-concentration, highly toxic chemical $(\text{NH}_4)_2\text{CO}_3$ is used for the CaCO_3 co-precipitation operation. This operation is operated under relatively high temperature (90-100°C), which accelerates the evaporation or dispersion of $(\text{NH}_4)_2\text{CO}_3$ in the atmosphere and consequently the analyst is exposed to relatively high toxicity during the operation.

In the Sr seawater analysis, the separation of Ca from Sr is very important to ensure the analytical quality, since seawater contains very high level of Ca which behaves very similarly as Sr. In the current method, Ca is pre-separated with the NaOH treatment, which is based on the high solubility of Sr in 0.2-0.5 M NaOH while Ca forms insoluble hydroxide and precipitates in the residue. However, the further separation of Ca and purification of Sr from other interference elements is performed with the use of fuming nitric acid, which gives off noxious and offensive fumes and is very corrosive. Even though the current method has significantly reduced the consumption of fuming acid compared to the previous methods reported in literature, analysts still could not completely avoid to handle fuming nitric acid and face any potential risk associated with the use of this chemical.

iii) Low analytical efficiency

The Sr analytical procedure in general is very tedious and time consuming due to the repeated precipitation or co-precipitation. For example, in the Sr purification using fuming nitric acid where the $\text{Sr}(\text{NO}_3)_2$ precipitation is repeated at least three times for each samples, and in the Y source preparation, $\text{Y}(\text{OH})_3$ and BaSO_4 precipitation are also repeated several times to ensure the purity of Y source. This leads to relatively low sample throughput and thus high analytical cost.

(2) Combined Tc and Pu, Np analytical procedure

i) Reduced sampling cost and Np/Pu analytical time

Important advantages of combining determination of Tc, Np and Pu in one analytical procedure include reducing sample volume needed for analysis so as to relieve the workload in

transporting very large volumes of seawater over long distances, as well as shortening analytical time and thus saving analytical cost and improving sample throughput.

To our experience, the application of automation is important to obtain good analytical repeatability and constant sample throughput, especially for Np and Pu column separations, since the density/viscosity of the column loading solutions for Np and Pu are very high (containing a large amount of matrix elements, such as Fe and Mn), often inducing blockage of the column or fluctuation of flow rate whenever manual operations are performed.

ii) High complexity

In the combined Tc, Pu and Np procedure, $\text{Fe}(\text{OH})_2$ is used for the pre-concentration of target radionuclide. Even though the co-precipitation efficiency is satisfactory, the selectivity is not very high since a lot of interfering matrix (Mn, Co, Ni) and radionuclide (U, Th, Mo, Ru) will be scavenged along with Tc, Pu and Np. This impose relatively high burden in the chromatographic column separation, which require repeated operation for column separation to ensure high resolution and decontamination of interferences. Consequently, this renders the analytical process somehow complicated and time-consuming. Especially in the case for Tc determination, the analyst is frustrated with time-constrain of the short half-life of $^{99\text{m}}\text{Tc}$, and the repeated and complicated operation may cause more human error in the operation.

iii) Low analytical efficiency for ^{99}Tc

At present, the Tc column separation is performed manually and the flow rate is sometime very slow due to the high density of the sample loading solution, which possibly decreases the analytical efficiency. Moreover, in the ^{99}Tc source preparation, the Tc eluate has to be evaporated to near dryness in order to be able to reconstitute in 2 M NaOH. However, due to the readily volatile behaviour of Tc, the evaporation operation cannot be operated under high temperature which slows down the sample process and also bring more stress to the analysis with the analytical time. The Tc electro-deposition is also time-consuming which takes at least 6 hour to get quantitative Tc source, which again prolong the analytical processes.

(3) Pu solid analytical procedure

i) High simplicity and analytical efficiency

The current Pu method developed for environmental solid samples is simple and straightforward, and the chromatographic separation can be performed in a sequential injection system for automated operation (*Figure. 6*). With the application of automated sequential injection system, sample throughput is improved and labor intensity is reduced.

ii) Low applicability

However, the current method used for Pu solid analysis is not suitable for sample containing refractory Pu oxides, since acid leaching is not able to extract Pu from refractory oxides. As mentioned in the method description, in the case of analyzing samples containing high amount of matrix elements, a guard anion exchange column is needed to avoid the breakthrough of the TEVA column, since TEVA column is sometimes very sensitive to matrix content in the sample loading solution. Consequently, the chemical yields of Pu from TEVA column vary significantly with the matrix composition of the sample. Besides, with the

used of $\text{Fe}(\text{OH})_3$ co-precipitation, U will be co-precipitated with Pu, thus one TEVA is sometime not sufficient to get satisfactory decontamination of U. We recently observed that NaOH treatment of $\text{Fe}(\text{OH})_3$ could improve the decontamination of U since U behave as amphoteric element and will be dissolved in the relatively high concentration of alkaline solution (Qiao et al. 2014). But even with the NaOH treatment, the decontamination of U with the use of only one TEVA column is still not satisfactory, especially for the samples with high matrix content.

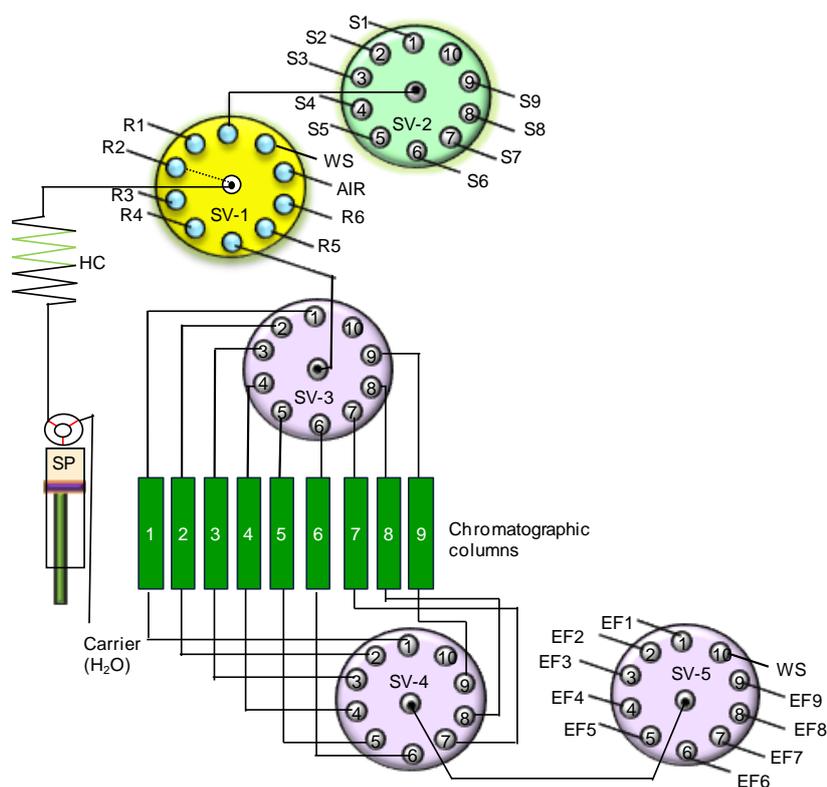


Figure. 6 Sequential injection network for Pu determination in environmental solid samples (SP: syringe pump, HC: holding coil, S1-S9: ports for sample loading, EF1-EF9: ports for eluate collection, WS: waste, AIR: port for air aspiration to isolation the carrier from the solution drawn into the holding coil, SV-1-SV-5: selective valves, R1-R6: reagents for column separation)

2.1.4 Potential solutions and perspectives

(1) Sr analytical methods

The safety issue involved in Sr analytical procedure might be solved by changing to use chemicals with similar performance as $(\text{NH}_4)_2\text{CO}_3$ but lower hazards, e.g., Na_2CO_3 . Another alternative solution is to completely change the technique used for co-precipitation., e.g., using CaC_2O_4 co-precipitation under lower pH (5) which could also improve the selectivity against many metal ions. Bojanowski and Knapinska-skiba (1990) have reported the application of oxalate co-precipitation for Sr large volume seawater analysis.

In the separation of Ca from Sr, NaOH treatment can be repeatedly used instead of using fuming nitric acid. The application of NaOH in separating large amount of Ca from Sr for

seawater analysis have been investigated by Popov et al. (2006, 2009) and successfully used in large volume seawater analysis. This will improve the safety factor of the analytical procedure as well as reduce the analytical cost since the price of fuming nitric acid is much higher compared to NaOH.

Besides, many researchers have used Sr resin for determination of Sr in different environmental and biological samples. The Sr extraction chromatography method is rather straightforward and simple, which significantly reduce the analytical turnover time. In the separation of ^{90}Y from Sr, Ln resin has also been applied to achieve a rapid separation which can be considered in the future method improvement for DTU Nutech.

(2) Tc analytical methods

In Tc determination, beta counting is used which requires time-consuming source preparation, since the ^{99}Tc eluate in 8 M HNO_3 medium has to be evaporated slowly and then re-dissolved in 2 M NaOH and electrodeposited for at least 5 hours. With the development of mass spectrometry, more and more researcher started to use ICP-MS for ^{99}Tc determination (Shi et al. 2012). The measurement normally takes less than 10 minutes and does not require complicated source preparation. The only challenge is the external (e.g., from lab wares and atmosphere) contamination of stable Mo and Ru at the mass 99, but this can be controlled via careful clean-up the lab ware and using inflammation box to avoid contamination from air.

For the column separation, vacuum box is a good choice due to its relative low cost and easy handle-ability for analyst. But the drawback is that the vacuum box system is not fully automated and human attention is needed throughout the whole operational process. Flow/sequential injection techniques have been used in many labs for fully automated column separation. In DTU Nutech, these techniques have been successfully used for routine Np and Pu seawater analysis, which improve the analytical efficiency and reduce the labor insensitivity. However, these techniques require to analyst to have more intensive training and knowledge for handling and the instrumental cost is relatively high compared to vacuum box.

(3) Pu analytical methods

For Pu environmental solid analysis, method development is needed to explore the analytical method to be applied for samples with different origins and matrix composition. For example, alkaline fusion will be developed for the pre-treatment of samples containing refractory Pu oxides and possibly boric fusion could be a technique of choice according to its successful application in many Pu studies for geological samples (Croudace et al. 1998). To overcome the high susceptibility of TEVA to matrix content, development of an alternative co-precipitation technique using CaC_2O_4 could be considered to eliminate the scavenge of most metal elements contained in the samples (Fe, Mn, Ni, Co), since the CaC_2O_4 co-precipitation is normally operated in low pH (1-2). As a consequence, one TEVA column separation might be sufficient to remove the remaining interfering nuclides. Thus the analytical time will be reduced comparing to the one using an extra anion exchange column before the TEVA column separation.

2.2 Nuclear emergency preparedness methods for $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ at FOI Umeå

At FOI CBRN Defence and Security, $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ are routinely measured in different sample matrices. The sample dissolution technique used is chosen depending on the sample matrix and after dissolution, solid phase extraction (SPE) is performed to separate the analyte from concomitants. After the whole sample preparation procedure, nuclide specific measurement is performed with techniques suitable for the nuclide of interest. In this section the actual nuclear emergency preparedness methods for $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ are described.

2.2.1 Procedure for Sr

The current method for Sr determination at FOI is designed for measuring $^{89,90}\text{Sr}$. Samples types measured for Sr include air filter, ash, sludge, soil, sediment, vegetation and milk. To ensure proper separation between Sr and any possible interfering radionuclides, two consecutive separations are performed. In this report the sample dissolution methods are not described. The full description of the method is published by Holmgren et al. (2014)

For the chemical purification of Sr, a Sr-resin cartridge is mounted on a vacuum box, with a column reservoir on top of the cartridge and thereafter preconditioned with 8 M HNO_3 . The sample solution prepared in 8 M HNO_3 is loaded and the column is rinsed in three consecutive steps with 8 M HNO_3 , 3 M HNO_3 /0.05 M $\text{H}_2\text{C}_2\text{O}_4$ and 8 M HNO_3 , respectively. Sr is thereafter eluted using 0.05 M HNO_3 . The Sr eluate is adjusted to 8 M HNO_3 and the separation procedure is repeated once. In order to avoid interferences from the ingrowth of ^{90}Y from ^{90}Sr , an immediate (within 3 h) 15-min Cherenkov counting of ^{89}Sr is performed.

After allowing the ingrowth of ^{90}Y for about 24 h, reaching a ^{90}Y activity of about 25% of the original ^{90}Sr activity, the sample is transferred from the scintillation vial used in the Cherenkov counting to a beaker. The scintillation vial is rinsed with Milli-Q water and the washing solution is combined to the sample. The sample is evaporated to dryness and then dissolved in 8 M HNO_3 . A Sr-resin cartridge is mounted on a vacuum box, with a column reservoir on top and thereafter pre-conditioned with 8 M HNO_3 . The sample is loaded onto the column and the sample vessel is rinsed with 8 M HNO_3 . The collected effluent is measured for its ^{90}Y activity by means of Cherenkov counting. The measurement time for ^{90}Y is 240 min.

The detection limit for the double separation is 0.2Bq/kg for ^{90}Sr and 0.4Bq/kg for ^{89}Sr . The analytical turnover time for one sample is roughly two days for the separation method described above.

2.2.2 Procedure for $^{239,240}\text{Pu}$

The determination of Pu isotopes at FOI is most often carried out for soil and sediment samples. The full description of the method has been published by Nygren et al. (2007). The sample is mixed with lithium metaborate and spiked with ^{242}Pu for chemical yield determination. Thereafter the sample is fused and, after cooling, dissolved in 1.4 M HNO_3 . In order to prevent precipitation of silicic acids during the following separation procedure, 2 mM PEG2000 is added to flocculate the dissolved Si. The precipitate is removed by filtration and the resulting filtrate is suitable for the following solid phase extraction (TEVA) procedure.

Before the separation of Pu from concomitant elements using solid phase extraction, a redox procedure is used to adjust Pu to Pu(IV) while Am is kept as trivalent. First, Pu is reduced to the trivalent state by adding $\text{NH}_2\text{OH}\cdot\text{HCl}$ (375 mg ml^{-1}) and heating at 90°C for 5 minutes. After cooling to approximately 40°C , NaNO_2 (450 mg ml^{-1}) is added to oxidise Pu(III) to Pu(IV). A column containing TEVA is conditioned with 3 M HNO_3 and thereafter the sample is loaded onto it. Under these conditions, Pu (IV) is retained on the TEVA resin and U and Am pass through the column. The TEVA column is rinsed with 9 M HCl to remove Th, followed by 3 M HNO_3 to remove remaining U. Pu is then eluted using 0.01% HEDPA and the sample is ready for measurement on ICP-MS.

The detection limits for ^{239}Pu and ^{240}Pu are 0.7 Bq/kg and 2.5 Bq/kg, respectively, for 1 g of soil/sediment. The analytical turnover time for Pu is one day for soil/sediment.

2.2.3 Performance evaluation for current analytical methods

Current Sr and Pu methods have been successfully applied to international inter-comparison exercises and the analytical results obtained agree very well with the reference or recommended values, which indicate satisfactory accuracy of current methods. These methods are easy to handle and suitable to samples with varying matrix composition, thus having high applicability.

2.2.4. Potential improvements and perspectives

(1) Sr method

FOI has recently purchased an inductively coupled plasma optical emission spectrometer (ICP-OES). Up until now, an atomic absorption spectrometer (AAS) has been used for the chemical yield determinations of ^{90}Sr and ^{90}Y . The ICP-OES will be tested for robustness and the plan is to move the yield determination measurements from AAS to ICP-OES at the end of 2014.

Double separation of Sr is needed when dealing with samples of high $^{89}\text{Sr}/^{90}\text{Sr}$ activity ratios, as well as samples containing high interferences. It is believed that double separation using Sr-resin will be useful when dealing with samples in situations of emergency preparedness. Further work regarding validation on different matrixes, *e.g.* milk or urine is needed.

(2) Pu method

FOI is using TEVA for the chemical separation of Pu. There have been problems with low Pu chemical yields using this resin in pre-packed cartridges, and thereafter the resin is used in an open column but without the possibility to use vacuum boxes for the separation. The problem with low chemical yields is most likely due to flow restrictions within the cartridge. Alternative resin packing methods may be tested to find a solution where the vacuum box system can be used, thus leading to faster separations.

FOI uses a redox scheme that first reduces Pu to Pu (III) followed by an oxidization step that transfers Pu to Pu(IV). This redox step is very sensitive and small changes in temperature during the procedure will drastically change the chemical yields during the separation step. Alternative redox methods will be tested to find a more robust method.

2.3 Environmental analysis and emergency preparedness methods for $^{89,90}\text{Sr}$, $^{238,239,240,241}\text{Pu}$ and ^{241}Am in STUK

At STUK $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ are routinely measured in various environmental samples. STUK measures also other radionuclides routinely from environmental samples but this section concentrates only on Sr and Pu isotopes. The routine analysis of $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ carried out in STUK consist of several steps and requires several weeks to be completed. STUK has also developed emergency preparedness methods for $^{89,90}\text{Sr}$ and $^{239,240}\text{Pu}$ that can be used in emergency situations when results are needed within a short time.

2.3.1 Routine analytical procedures for $^{89,90}\text{Sr}$, $^{238,239,240,241}\text{Pu}$ and ^{241}Am in STUK

(1) Procedures for ^{90}Sr analysis from environmental samples

^{90}Sr is routinely analyzed from various environmental matrices (e.g. milk, vegetation, seawater, surface water, fish, soil and sediment, meat, air filter, deposition, urine). The method used for ^{90}Sr determination in STUK is based on various precipitations (carbonate, oxalate, iron, and chromate precipitations) followed by extraction chromatography with Sr-resin. Purified samples are counted with liquid scintillation counter or with low proportional counting. For ^{90}Sr both counters can be used, but if ^{89}Sr is to be determined proportional counter should be used preferably. The sample dissolution technique selected depends on the sample matrix. Typical size of the sample for ^{90}Sr analysis from milk is 5-10 L and associated minimum detectable activity (MDA) is about 0.002 Bq/L. ^{90}Sr analysis is normally carried out within 1-2 months. Detailed description of ^{90}Sr analysis from vegetation samples is given as an example below.

Example I: Analysis of ^{90}Sr from vegetation sample

Dissolving the sample

1. Ash is used in the analysis as follows:
2. a) Kelp (*Fucus vesiculosus*) and bear moss (*Polytrichum*) 5 g.
b) Other type of samples 10 g. Additional ashing is done at 600 °C (1- 2 h), if sample contains too much carbon.
3. Two alternative methods can be used to convert the ashed samples into liquid samples:
 - a. microwave digestion or b. melting with sodium carbonate.
- a. Mars5-burn: Choose “sample specific burn” from the “MARS-cookbook”. After digestion, transfer the liquid to a beaker (liter volume) or to a Teflon covered beaker in case of using HF. Evaporate the residue to dryness with care. Centrifuge if needed, and wash the precipitate with HCl in ratio of 1:4. If the sample is rich in silicate, follow the instructions given in point 4.
- b. Melting: Place/put anhydrous Na_2CO_3 on the bottom of a platinum bowl and on top of it, put about 90 mg $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$, and add ashed sample mixed with Na_2CO_3 ; ratio is 1:4 (weight ratio). Add another thin layer of sodium carbonate. Melt the mixture in muffle furnace at 900 °C for 30 minutes (Remember fiberglass gloves and calf-length tongs!)
4. Stir and cool the melt by dipping the bowl bottom into ice-water. Place the cooled bowl (outer side rinsed with distilled water) in a 600-mL beaker. Add about 200-mL distilled water. Extract the sample with a heating magnetic stirrer until the precipitate unstuck the bowl. Centrifuge the sample and discard the liquid.

5. Dissolve the carbonate precipitate with 50 mL 37% HCl and 150 mL H₂O (HCl ratio 1:4) and transfer the solution to a beaker (volume of 1 litre) Mix and evaporate the sample with care to dry in a beaker on a hot plate. Add a further 37% HCl and evaporate to dryness. Add about 50 mL of 37% HCl and 150 ml H₂O. Heat the sample in water bath, centrifuge and transfer it to a beaker (volume 1 litre). Wash the residual precipitate two times with 50 mL of 37% HCl and 150 ml H₂O (HCl ratio 1:4), centrifuge and add it to the previous solution.

Oxalate precipitation

1. Add 25 mL of 25% ammonium acetate (CH₃COONH₄) and 30 g of oxalic acid (C₂H₂O₄·2H₂O) to the solution. Heat the solution on a hot plate and adjust the pH to 5-6 with aid of 25% of ammonia (checked with pH paper) (*Figure. 7*). Dilute the solution to 900 mL, boil it and leave the solution to stand for at least 4 hours in order to descent the precipitate (*Figure. 8*).



Figure. 7 Oxalate precipitation for soil sample



Figure. 8 Oxalate precipitation has settled (deposition sample)

2. The liquid is then sucked into drains and the sediment is transferred to a 250-mL centrifuge tube with water. Centrifuge and suck the solution into the drain. Wash the precipitate once with water and centrifuge it.
3. Transfer the oxalate precipitation to a quartz beaker with a small amount of water, dry it with an infrared lamp and ash the oxalates to carbonates in a muffle furnace at 600 - 700 ° C for about a half hour (*Figure. 9*).



Figure. 9 Ashed oxalate precipitation in crucibles

Iron precipitation and chromate precipitation

1. If the sample does not contain ^{210}Pb , dissolve the carbonate precipitate in 20 mL of 8 M HNO_3 and follow the instructions given in section 'Extraction chromatography with Sr resin'.
2. If the sample contains ^{210}Pb , proceed as follows: add 60 mL of distilled water and 65% HNO_3 to the cooled silica crucible until no dissolution of carbonates can be detected. Boil for at least 10 min. covered with a watch glass.
3. Heat the solution well. Precipitate iron with carbonate free ammonia (pH 8-9), heat the solution for a few minutes and filter while hot (Whatman 41 filter paper). Wash the precipitate with hot water containing ammonia. Add 10 mg of lead carrier and a few drops of methyl red indicator, adjust pH by addition of 6 M HNO_3 until the solution turns red and then add 6 M NH_4OH until the solution turns from back to yellow. Add 1 mL of 30% acetic acid and 2 mL of 25% ammonium acetate solution.
4. Heat the solution well and precipitate lead by adding 1 mL of 30% Na chromate. Heat, cool and centrifuge the solution. Filter through the Whatman paper (no. 40). Solution is adjusted to basic with ammonia (lemon yellow color change). Precipitate Sr with ammonium carbamate (3.5 to 4 g), heat, cool and centrifuge. Dissolve the precipitate in 20 mL of 8 M HNO_3 . Chromate filtrate and lead chromate precipitate is treated as hazardous waste/ toxic waste

Extraction chromatography with Sr resin

1. Prepare a Sr-Spec column (*Figure. 10*). Add glass wool on the bottom of the column. Add distilled water to the column (half full). Weigh 3 g of Sr resin (100 - 150 μm) and mix it with small amount of distilled water. Transfer the resin into the column. Add glass wool on the top of the resin bed. Condition the column with 30 mL of 3 M HNO_3 . (*Resin can be used 10 times but it must be reconditioned after each use by washing it with 30 mL of distilled water followed by 30 mL of 3 M HNO_3 . If removal of Pb and its daughters is needed, resin is washed with 30 mL of 8 M HCl , followed by 30 mL of water and then 30 mL of 3 M HNO_3*)
2. Transfer the sample to the column and allow it to drip freely into a clean beaker. Rinse a quartz beaker or centrifuge tube with 10 mL of 8 M HNO_3 and transfer the rinsing solutions to the column.
3. Wash the column twice with 20 mL of 8 M HNO_3 followed by 20 mL of 3 M HNO_3 . Record the exact time when washing was completed (*yttrium ingrowth starts*)
4. Elute Sr from the resin with 70 mL of 0.05 M HNO_3 and collect the eluate into a 250-mL centrifuge tube.

5. Add 25 % $\text{NH}_3 \cdot \text{H}_2\text{O}$ to adjust the pH to 8-9 and add 3.5 - 4 g of solid ammonium carbamate ($\text{NH}_4\text{CO}_2\text{NH}_2$) to the solution. Heat in water bath until precipitate settles in the bottom of the tube. Cool in ice water bath.



Figure. 10 Preconditioned Sr-resin columns ready to be used

Measurement of ^{90}Sr with liquid scintillation counter

1. Filter the sample solution on pre-weighed Whatman 42 filter paper (diameter 3 cm) that has been dried at 105 °C for 30 min. Wash the precipitate 5 mL of distilled water for 3 times and then with 5 mL of technical alcohol for three times. Dry the sample at 105 °C for 30 min. and weigh the precipitate.
2. Transfer the precipitate into a pre-weighed 20-mL liquid scintillation (LS) bottle and dissolve it with 1.7 mL of 1M HCl. Shake well.
3. Weigh the scintillation bottle. To determine the Sr yield with AAS, take an aliquot of 0.15 ml with pipette and transfer it into a pre-weighed 50-mL measuring bottle and weigh. Add 1 mL of 6 M HCl and fill the measuring bottle with distilled water. Weigh the LS bottle and determine the weight of the final solution.
4. Add 6 mL of Ultima Gold uLLT scintillation cocktail into the scintillation bottle containing the sample and shake well. Prepare background sample by pipetting 1.5 mL of 1M HCl and 6 mL of Ultima Gold uLLT into a LS bottle. Shake well.
5. Wait 18 days until ^{90}Sr and ^{90}Y are in equilibrium. Store samples in dark and cool place. Check and ensure that phases have not been separated in LS bottle before counting the samples.
6. Before placing the scintillation bottles LS counter (Quantulus) wash the closed LS bottles in ultrasound washing system for 3 min. in distilled water and then 3 min. in alcohol.
7. Start measurement next day after samples has been placed in Quantulus (constant temperature achieved).

(2) Procedures for $^{238, 239, 240, 241}\text{Pu}$ and ^{241}Am analysis from environmental samples

Pu is routinely analyzed in STUK from seawater, surface water, soil, sediment, vegetation and urine. Samples are first digested using microwave digestion (MARS5, CEM) or wet ashing.

Pu is separated from the digested sample with anion exchange (Dowex 1x4 resin). Pu sources are prepared through electrodeposition or co-precipitation. ^{238}Pu and $^{239+240}\text{Pu}$ are determined with Alpha Analyst alpha spectrometer (Canberra) and analyzed with Canberra Genie2000 based software. Chemical yield of Pu is determined by ^{242}Pu tracer. ^{241}Pu (if wanted) is determined by liquid scintillation counting with beta and alpha/beta -separation procedures.

Typical sample size for Pu analysis from soil is 15 g and the associated minimum detectable activity (MDA) is 0.01 - 0.02 Bq/kg. Pu analysis is typically carried out in 2-3 weeks. Detailed description of $^{239, 240}\text{Pu}$ analysis from soil, vegetation and sediment is given below.

Example II: $^{238, 239, 240}\text{Pu}$ and ^{241}Am analysis from soil, vegetation and sediment

Samples are first digested using microwave digestion or wet ashing. Pu is separated with anion exchange. Am is separated with oxalate precipitation, iron hydroxide precipitation, extraction, cation exchange and anion exchange. Pu and Am sources are prepared through electro-deposition or co-precipitation.

Digestion of the samples

1. Sample size 10 - 60 g
2. Weigh dried and homogenized sample into a digestion flask
3. Add ^{242}Pu and ^{243}Am tracers into the digestion flask
4. Samples are digested using microwave digestion (MARS5) or wet ashing with 65% HNO_3 , 37% HCl and 30% H_2O_2 (Tecator)
5. If using wet ashing (Tecator), filter the digested sample through a GF-filter using Bühner-funnel with suction. Rinse the flask and the precipitate with 8 M HNO_3 few times. Transfer the solutions into a 400-mL beaker and evaporate until salts appear.
6. If using microwave digestion (MARS5), transfer the digested sample from the digestion flask into a Teflon beaker and evaporate to dryness (*Teflon beaker can be used max. 200-250°C*).

Pu separation by anion exchange

1. Dissolve the residual into 100 mL of 8 M HNO_3 . Heat and add 1 mL of 30% H_2O_2 . Cover the beaker with a watch glass and heat at 90 °C for 1 hour. Add approx. 2 g (1 teaspoon) NaNO_2 to the hot solution. Let cool for 1 h. (Pu^{3+} is oxidized to Pu^{4+} . Reaction is vigorous so add NaNO_2 in bit by bit)
2. Prepare an anion exchange column (*Figure. 11*): place approx. 12.5 g anion exchange resin Dowex 1 x 4 (50 - 100 mesh) in nitrate form into an anion exchange column (\varnothing 1 cm) using 8 M HNO_3 . (*Resin is brought in nitrate form by treating it with 50 mL of conc. HNO_3 and 2 x 50 mL of 8 M HNO_3*)
3. Place glass wool on bottom of the column. Load the sample solution into the anion exchange column (15 cm resin in the column). Wash the resin with 150 mL of 8 M HNO_3 . Collect the load and wash solutions for Am analysis. (*8 M HNO_3 solution contains: Am^{3+} , Cm^{3+} , lanthanides, Sr^{2+} , Pb^{2+} , Ra^{2+} , Fe^{3+} , U^{6+} , Po*)
4. Wash the resin with 150 - 200 mL 37% HCl . Discard the wash solution. (*Wash solution contains Th^{4+}*)
5. Elute Pu with freshly made 60 mL of 37% HCl + 5 mL of 1 M NH_4I solution. (Pu^{4+} is reduced to Pu^{3+} . 1 M NH_4I can be preserved for one month when covered from light)

- Evaporate Pu eluate to dryness. Add few milliliters of 65% HNO_3 and 37% HCl and evaporate. Repeat this 2 - 3 times. Evaporate and add small amounts of 65% HNO_3 (< 1 ml) until no residual remains in the beaker.



Figure. 11. Anion exchange columns

Source preparation

Pu sources are prepared by either electro-deposition or co-precipitation

Electro-deposition

- Add 25 drops of 2 M HNO_3 into the beaker by washing the walls of the beaker at the same time. Heat and let cool. Pour the solution into an electrolysis vessel. Wash the beaker with small amount of distilled water and add wash solution into the electrolysis vessel, repeat. Volume of the solution should not exceed 4 - 5 ml.
- Add 3 - 4 drops of methylred. Add 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ dropwise until colour changes from red to yellow. Add 2 M HNO_3 dropwise until the solution turns red (solution now acid). Add 4 drops more 2 M HNO_3 .
- Carry out the electrolysis for 45 - 90 min using 1.7 - 1.9 A (current) and 6 - 9 V (voltage) in ice water bath with Pt-spiral as an anode and steel plate as cathode. (45 min is enough for Pu but Am requires 1.5 h.) Stop the electrolysis by adding 2 mL of 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ into the vessel, wait 1 min before taking the vessel out.
- Wash the steel plate with distilled H_2O and ethanol. Anneal with Bunsen burner, upper part of the flame, until tinged with red. Let cool.
- Measure Pu with α -spectrometry

Co-precipitation

Dissolve the residual into 2-5 mL of 1 M HNO_3 . Transfer into plastic test tube and wash the beaker twice with few milliliters of 1M HNO_3 . Add wash solutions into the test tube. Add 0.5

mL of Ce-carrier (Ce 100 µg/mL) into the test tube and mix with Vortex mixer. Co-precipitate Pu with CeF by adding 1.5 mL of 40 % HF acid. Mix the sample with Vortex and place the test tube in ice bath for 45 min. Filter the precipitate. Measure ^{238}Pu and $^{239+240}\text{Pu}$ with α -spectrometry

2.3.2 Performance evaluation of the analytical methods

Current Sr and Pu methods used in STUK are very robust and have been successfully used in several international inter-comparisons exercises. Within last three years, STUK has participated in 8 inter-comparison related $^{89, 90}\text{Sr}$ analysis and 6 related to $^{239, 240}\text{Pu}$. Environmental Radiation Surveillance (VALO) at STUK is a testing laboratory accredited by FINAS Finnish Accreditation Service under the registration number T167. The laboratory meets the requirements laid down in standard EN ISO/IEC 17025:2005.

2.3.3. Emergency preparedness methods

Even though the regular analytical methods used for ^{90}Sr and Pu isotopes are very robust, they are time consuming. Therefore the methods have been modified for emergency purpose so that results will be obtained faster.

(1) Emergency preparedness methods for $^{89, 90}\text{Sr}$

Emergency preparedness method for $^{89, 90}\text{Sr}$ in water and air filter has been tested and can be carried out within a day.

Analysis of Sr from water/deposition

1. Add Sr carrier (30 mg) and Cs carrier (30 mg) into a 500 mL water sample. Acidify with HNO_3 and stir for 10 min.
2. Add NaOH until pH 8-9 and heat the sample. Precipitate Sr by adding 10 g of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ (20 g/L) and stir for 15 min.
3. Centrifuge, discard solution and dissolve precipitate into 8 M HNO_3 (20 mL).
4. Carry out Sr extraction chromatography : load sample to Sr columns, wash twice with 20 mL of 8 M HNO_3 and once with 3 M HNO_3 (20 mL), note time of last wash, elute Sr with 60 mL of 0.05 M HNO_3 .
5. Precipitate Sr from alkaline solution (pH 8-9) by adding 3 - 4 g of $\text{NH}_4\text{CO}_2\text{NH}_2$ and heat. Filter the Sr precipitate onto pre-weighed filter paper and determine the Sr yield by weighing.
6. Activity measurements: sample is divided into two parts: Cerenkov counting with liquid scintillation (^{89}Sr) and measurement with proportional counter ($^{89+90}\text{Sr}$). If there is more time, then only liquid scintillation is used by first measuring the sample by Cerenkov and then after adding cocktail measuring it again with liquid scintillation counting (^{89}Sr , ^{90}Sr , ^{90}Y). If only ^{90}Sr is present in the sample, liquid scintillation counting is used.

Analysis of Sr from glass fiber filter

1. Weigh and transfer the sample into a Ni-crucible, add about 100 g $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (note exact mass) and mix.

2. Add NaOH granules (6 x sample mass) and 2 tsp Na_2CO_3 (anhydrous) and heat with Bunsen burner.
3. Add ~3 tsp of NaNO_3 until all carbon is burned and the sample turns greenish.
4. Dissolve the fused sample with 100 mL of distilled water while heating. Centrifuge the sample solution while hot and discard the solution. Wash the residual with 30 mL of boiling water. Dissolve the precipitate with small amount of 8 M HNO_3 and dilute with water to 30 mL.
5. Carry out carbonate precipitation by adding 25% $\text{NH}_3\cdot\text{H}_2\text{O}$ until pH 8 - 9. Add 2 g of $\text{NH}_4\text{CO}_2\text{NH}_2$, heat, cool and centrifuge. Discard the solution. Dissolve the residual into 30 mL of 8 HNO_3
6. Carry out extraction chromatography with Sr resin as mentioned before, followed by carbonate precipitation and $^{89,90}\text{Sr}$ measurement.

(2) Emergency preparedness methods for Pu isotopes

1. Liquid sample is acidified, tracers are added and Pu precipitated as $\text{Fe}(\text{OH})_3$ by adding Fe-carrier (50 mg) and $\text{NH}_3\cdot\text{H}_2\text{O}$ until pH is 9. Precipitation is separated through centrifugation.
2. Solid sample is combusted with microwave using $\text{HNO}_3+\text{HCl}+\text{H}_2\text{O}_2$
3. Pu is separated with anion exchange: Dowex 1x4, 50-100 mesh. Anion exchange is carried out with faster speed (25 drops/min) than in regular Pu analysis
 - a. Load sample solution (40 mL of 8 M HNO_3 + 2 g NaNO_2)
 - b. Wash with 50 mL of 8 M HNO_3 and with 50 mL of 37% HCl
 - c. Elute Pu with 30 mL of 37% HCl+3 mL of 1M NH_4I
 - d. Evaporate and treat with acids
 - e. Pu is co-precipitated by dissolving the sample with few milliliters of 1 M HNO_3 , adding Ce carrier (50 μg), 1.5 mL of HF and letting to precipitate for 45 minutes. The sample is filtered with 0.1 μm membrane.
4. The precipitate is counted with alpha detector (^{238}Pu and $^{239+240}\text{Pu}$)
5. If ^{241}Pu is needed the sample is divided before co-precipitation and liquid scintillation is used to measure ^{241}Pu .

2.3.4 Potential improvements

(1) Co-precipitation vs. electrodeposition in Pu method

Radiochemical separation method used traditionally in STUK for Pu and Am has included a step where Pu/Am is deposited on a steel plate using electrodeposition prior to alpha counting. Electrodeposition that has been traditionally used is a suitable method for source preparation but it is sensitive to impurities that might exist in the sample and it is also more sensitive to malfunction in equipment as well as dependent on the operator. Co-precipitation of Pu/Am as cerium fluoride into a membrane is an alternative technique for electrodeposition. Co-precipitation technique is known to be less sensitive for impurities and it also works as an additional source purification step, since only trivalent and tetravalent elements can be precipitated. Co-precipitation is also simpler to carry out and requires less time.

To validate co-precipitation technique, samples have been analyzed in STUK using both electrodeposition and co-precipitation. Both chemical recovery and the Full width at half

maximum (FWHM) has been recorded. The results will be reported in the final report of this project.

(2) Analysis of Pu from air filters in emergency conditions

The emergency preparedness method for Pu has not been tested recently for air filters in STUK. However, the air filters are one of the most important matrices needed to be analyzed in emergency conditions and there is need to test and improve the method for different type of filters. Glass fiber filters are commonly used in STUK and especially the sample dissolution technique for glass fiber filter has to be tested and improved: fusion vs. acid leach. It is also important to determine how long time it takes to carry out the appropriate method.

2.4 Analysis of Sr, Th, U, Pu and Am at IFE

The methods used for the analysis of Sr, Th, U, Pu and Am at IFE are developed to fit our main purpose, which is the analysis of internal samples and of samples collected in connection with the environmental surveillance programme. The procedures are of sequential manner, in that the same sample can be used to analyze several radionuclides. All the procedures are described in our quality assurance book and are tested in relevant inter-comparison exercises. The procedures are also adapted to analyze other kind of samples.

2.4.1 Treatment of various samples

(1) Discharge water from IFE

A representative sample is acidified, tracers added and the solution is dried and ashed at 450 °C. The salts are then treated with 65% HNO₃ before they are dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(2) Water from Nitelva river

Pre-concentrated sample (by evaporation) is added 65% HNO₃ and tracers and evaporated to dryness. The salts are then treated with 65% HNO₃ before they are dissolved with 20-30 mL 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(3) Water from manholes in connection with the discharge pipeline

The water sample is added 65% HNO₃ and tracers and evaporated to dryness. The salts are then treated with 65% HNO₃ before they are dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(4) Precipitation

Pre-concentrated sample (by evaporation) is added 65% HNO₃ and tracers and evaporated to dryness. The salts are then treated with 65% HNO₃ before they are dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(5) Urine

The sample is added 50 mL of 65% HNO₃ pr. liter sample, appropriate tracers, 2 mg Sr- and 100 mg Ca-carrier. The sample is then heated at approx. 90 °C for 2 hours after the addition of a few drops of octanol. The heat is turned off and 1-2 mL conc. phosphoric acid is added and pH raised to 8-9 with NH₃·H₂O. The precipitate is allowed to settle and collected by centrifugation. The precipitate is then ashed at 450 °C, treated with 65% HNO₃ and dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(6) Sediment and soil samples

An ashed sample is treated with aqua regia for several hours and then filtered through glass fiber filter. The solution is evaporated to dryness and treated with 65% HNO₃ and the salts dissolved with 200 mL of 1 M HNO₃. 20 mL solution is added U-tracer and 3 mL 65% HNO₃ and used for U-analysis with UTEVA. The rest of the solution is added Pu- and Sr-tracers and 1.0 g of NH₂OH·HCl and 100 mg of Ca-carrier. The solution is heated and added oxalic acid and the pH adjusted to 5-6 by carefully adding NH₃·H₂O. After cooling, the solution is filtered through paper filter and the precipitate is ashed at 600 °C. The salts are then treated with 65% HNO₃ and dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

(7) Biota

Ashed sample is added tracers and treated with aqua regia for several hours. After cooling the solution is filtered through glass fiber filter and evaporated to dryness. The salts are then treated with 65% HNO₃ and dissolved with 20-30 mL of 3 M HNO₃ - 0.1 M sulphamic acid - 0.1 M ascorbic acid - 0.3 M Al(NO₃)₃. The solution is then filtered through membrane filter.

2.4.2 Separation of Sr, Th, U, Pu and Am

UTEVA-TRU-Sr columns are connected together (UTEVA on top) and conditioned with 5-10 mL of 3 M HNO₃. The solution from the different treatment steps of the various matrixes is then loaded. The columns are then rinsed with 10 mL of 3 M HNO₃ and disconnected.

(1) Sr-Resin

The column is rinsed with 10 mL of 8 M HNO₃ followed by 5 mL of 3 M HNO₃ - 0.05 oxalic acid and 5 mL of 3 M HNO₃ and Sr is eluted with 0.05 M HNO₃. The solution is then set aside for the ingrowth of ⁹⁰Y. Y is separated from Sr using oxalate and hydroxide precipitation and finally counted using beta counter (Risø).

(2) UTEVA-Resin

The column is rinsed with 10 mL of 3 M HNO₃ followed by 5 mL of 9 M HCl. Th is then eluted with 15 mL of 4 M HCl. For samples containing high levels of Po (soil samples etc) the column is rinsed with 50 mL of 4 M HCl - 0.05 M oxalic acid and U eluted with 15 mL of 0.01 M HCl.

(3) TRU-Resin

The column is rinsed with 10 mL of 3 M HNO₃ - 0.1 M NaNO₂ followed by 2 mL of 9 M HCl. Am and Cm are eluted with 10 mL of 4 M HCl and the column rinsed with 10 mL of 4 M HCl before Pu is eluted with 10 mL of 4 M HCl added 200 µL of 15% TiCl₃.

Source preparation of the actinides is done by micro co-precipitation of fluorides and collection on membrane filters. Activity determination is done by alpha spectrometry.

2.4.3 Discussion and perceptiveness

IFE is mostly very satisfied with the current procedures, and inter-comparison exercises show that the methods give correct answers. Since IFE does not use HF for the digestion of

sediment samples in the surveillance work, inter-comparison exercises have shown that the results for U are lower than the true value when HF is not used. The procedures are modified when analyzing other matrixes, but in overall the pattern remains the same. When analyzing samples that may contain high levels of Ca, larger Sr-columns are used. If needed, HF digestion of samples is also used. In samples that contain large amounts of lanthanides, Am is normally purified by using TEVA column.

3. Method improvement by applying rapid analytical techniques

Experiments were performed in each institute to improve analytical efficiency during 2014: 1) DTU Nutech (Denmark) has improved the current Pu-Np seawater analytical procedure by using NaOH treatment to enhance the decontamination factor of U. A vacuum box system has been built up and will be used for the inter-comparison exercises in 2015. Analytical procedure for Sr in seawater has been updated based on an internal evaluation and amendment, further experimental tests to replace the use of $(\text{NH}_4)_2\text{CO}_3$ and fuming nitric acid are on-going. A CaC_2O_4 co-precipitation method has been developed to improve method applicability for different matrix content in Pu determination and experiments for processing real-samples is in progress.

2) STUK (Finland) has tested the performance of co-precipitation v.s. electro-deposition for Pu/Am source preparation. It was found that both electro-deposition and co-precipitation are well suited for Pu and Am as source preparing. Comparatively, co-precipitation is simple, rapid and less sensitive to operator. STUK (Finland) has also developed a rapid method for Pu air filters analysis in emergency conditions. Two different dissolution techniques (fusion with NaOH/ Na_2CO_3 and acid leach with HF, HNO_3 , HCl) have been tested followed by anion exchange and co-precipitation for source preparation. Acid leach with HF was found to be more suitable than fusion because multiple samples could be analyzed at the same time

3) FOI (Sweden) has improved the stability and chemical yields of Pu in their current Pu analytical method for soil and sediment. In their previous experiments, Pu was identified in the U- and Am-fractions and a low recovery of Pu was noticed. After series improvement in the valence adjustment step for Pu, it was observed that with careful control of the temperature, the valence of Pu(IV) can be well stabilized and no loss of Pu was found in the other fractions (U and Am). To further improve the chemical yield of Pu, column separation was optimized and it was found that, with increase the volume of elution solution from 5 mL to 10 mL, Pu chemical yield can be improved from 40-50% to 90-100%.

4) IFE (Norway) has partly tested the application of Sr resin in ^{210}Pb analysis for water samples. MnO_2 co-precipitation has been investigated for Ac, Th and Ra determination in Urine, the results were not satisfactory and further improvement is on-going. IFE also is improving ^{90}Sr seawater method to reduce the amount of fuming nitric acid by applying the current analytical method used in DTU Nutech.

3.1 Methodology improvement in Sr and Pu environmental analysis in DTU Nutech

3.2.1 Improvement for the determination of ^{90}Sr in Seawater and lake water

On the currently used procedures, methodology improvement was carried out in DTU Nutech during 2014 to enhance the chemical yield for determination of ^{90}Sr in seawater and lake water samples based. Results presented here cover the selection of optimal pH value in the steps of carbonate precipitation by theoretical calculation and the experimental investigation of the effect of elevated temperature on the Ca decontamination.

Materials and methods

A ^{85}Sr standard solution purchased from Isotope Products Laboratories (3017 N San Fernando Blvd, Burbank, CA 91504) and diluted to 2100 Bq/mL in 1 M HCl were used as a chemical

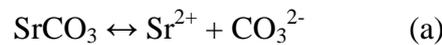
yield for Sr. All reagents used in the experiment were of analytical reagent grade and prepared using ultra-pure water (18 MΩ·cm). Seawater samples were collected around Danish and Greenland coast during 2011-2014 and lake water samples were collected at different location in Denmark

The analytical processes applied in this work for ^{90}Sr seawater or lake water analysis basically follow the steps described in *Figure. 2*. The effect of different experimental operation and conditions on the chemical yield of Sr and the efficiency of Ca decontamination were investigated herein and the details are summarized below.

Results and Discussion

(1) Theoretical calculation during carbonate precipitation for Sr pre-concentration

For pre-concentration, carbonate is used to scavenge most Sr into the residue as strontium carbonate. The chemical reaction between Sr and carbonate during the pre-concentration process is:



For which the solubility product, K_{sp} is:

$$K_{\text{sp}} = [\text{Sr}^{2+}] [\text{CO}_3^{2-}] \quad [1]$$

Assuming the solubility of strontium carbonate is S , its unit is M . All weak acids, denoted H_2CO_3 , react with water by donating a proton to H_2O . Dissociation of weak acid:



Wherein, the acid dissociation constant is $K_{\text{a}1}$.



Wherein, the acid dissociation constant is $K_{\text{a}2}$.

When the (a), (b), (c) reactions are in equilibrium,

$$[\text{Sr}^{2+}] = S \quad [2]$$

$$[\text{CO}_3^{2-}] = C \cdot \delta \quad [3]$$

In which, C is concentration of added CO_3^{2-} , usually add 1L of 1M $(\text{NH}_4)_2\text{CO}_3$ into 45L seawater, so $C=0.044 M$; δ is the distribution coefficient of CO_3^{2-} .

$$\delta = \frac{K_{\text{a}1}K_{\text{a}2}}{([\text{H}^+] + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2})} \quad [4]$$

Put [2], [3], [4] into [1], thus

$$S \cdot C \cdot \frac{K_{\text{a}1}K_{\text{a}2}}{([\text{H}^+] + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2})} = K_{\text{sp}} \quad [5]$$

In which, $K_{a1}=4.46 \times 10^{-7}$, $K_{a2}=4.69 \times 10^{-11}$, $K_{sp}=9.3 \times 10^{-10}$, $C=0.044$. So Equation [5] can be changed to $S=f([H^+])$. And it can be seen from *Figure. 12* that, with the increase of pH from 7 to 11, the solubilities of $SrCO_3$ and $CaCO_3$ decrease simultaneously, but after the pH reaches to 11, the solubility of $SrCO_3$ will be constant regardless the increase of pH until 14. Therefore, pH=11 is can be theoretically selected as the optimal condition for carbonate precipitation and further experiments need to be carried out for its verification.

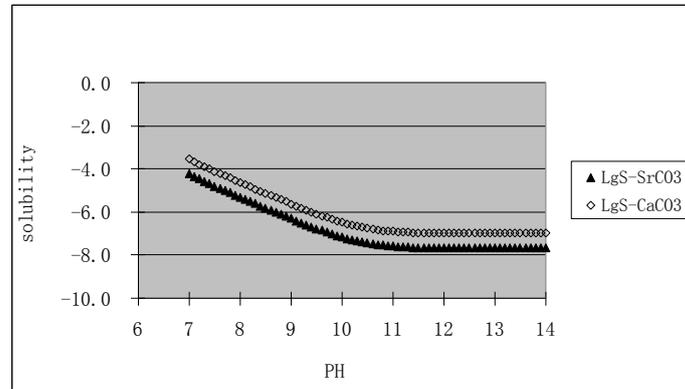


Figure. 12. The effect of pH on the solubilities of $SrCO_3$ and $CaCO_3$

(2) Decontamination of Ca

Following the carbonate precipitation, a hydroxide precipitation is performed in 0.2 M NaOH to remove large amount of Ca as well as other interfering radionuclide (actinides, Po and rare elements), whilst Sr remains in the supernatant. Afterwards, another carbonate precipitation is performed to concentrate Sr. The NaOH treatment offer advantages of low cost and better safety compared to the traditional methods using large amount of reported fuming nitric acid in literature. Therefore, the selection of optimal operational conditions for the NaOH treatment is crucial to ensure sufficient decontamination factor for Ca and other interferences.

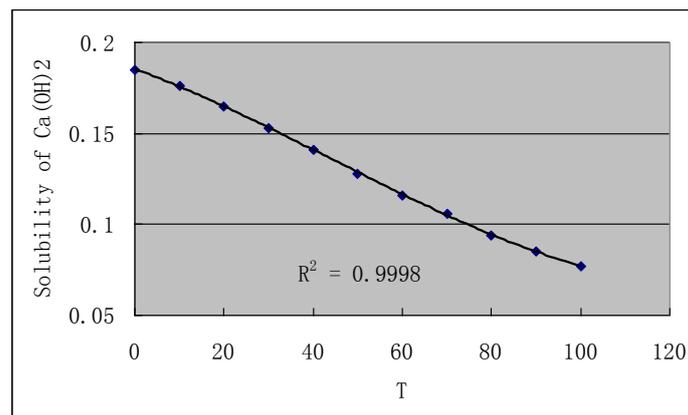


Figure. 13. The effect of temperature on the solubility of $Ca(OH)_2$.

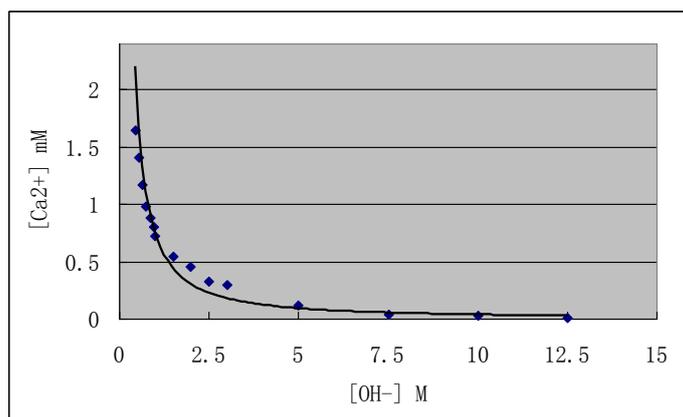


Figure. 14. The effect of $[\text{OH}^-]$ on the equilibrium concentration of Ca^{2+} ($[\text{Ca}^{2+}]$) in an aqueous solution saturated with solid $\text{Ca}(\text{OH})_2$, at $25.00 \pm 0.02^\circ\text{C}$

Theoretically, the solubility of $\text{Ca}(\text{OH})_2$ smoothly decreases with the increase of the temperature (*Figure. 13*). While under a constant temperature, the equilibrium concentration of Ca^{2+} ($[\text{Ca}^{2+}]$) decreases dramatically with the increase of $[\text{OH}^-]$ within 0 - 2.5 M in an aqueous solution saturated with solid $\text{Ca}(\text{OH})_2$ (see *Figure. 14*). In series experiment, it was observed that relatively higher temperature and higher concentration of $[\text{OH}^-]$ are favor for the decontamination of Ca. When the NaOH treatment was performed up 50°C , the Ca is better removed compared to the ones operated under room temperature. This is confirmed by the significant less amount of carbonate co-precipitate formed in the following step after the NaOH treatment as a consequence of less concomitant formation of CaCO_3 (see *Figure. 15*).



Figure. 15. Effect of temperature on the removal of Ca ($\text{Ca}(\text{OH})_2$ treatment process in 50°C water bath (left 1) and following SrCO_3 precipitation (left 2) vs. $\text{Ca}(\text{OH})_2$ treatment process under room temperature (left 3) and the following SrCO_3 precipitation (left 4)).

In the experiment, it was also observed that a floating layer was formed if the sample solution was exposed in air for a relatively longer time (e.g., overnight) in the step of NaOH treatment (see *Figure. 16*). After separating the layer from solution and checking the activity with gamma counter, it was found that 10-20% of Sr was lost in this portion. But by covering the sample with a Parafilm®, no white floating layer was observed. This phenomenon could possibly be a consequence of the reaction of Sr^{2+} with CO_2 in the air which forming saturated SrCO_3 as a floating layer.



Figure. 16. Effect of air exposure (left: exposed in the air overnight, and right: without air exposure)

With the use of improved NaOH treatment process (namely, relatively high temperature (50 °C) and avoid air exposure), the overall Sr chemical yields increased from ~ 70% to ~ 90 (see *Table. 1*), indicating temperature and air exposure are important parameters affecting the analytical performance for Sr determination.

Table. 1. The chemical yield of Sr for the entire analytical procedure

Before method improvement		After method improvement	
Sample ID	Chemical yield (%)	Sample ID	Chemical yield (%)
2011-0486	67.30	2014-2051	91.91
2012-2052	74.93	2014-2052	89.58
2012-2053	74.29	2014-2053	88.24
2012-2055	82.53	Average	89.91
2013-0463	36.90		
2013-0537	52.65		
2013-0538	60.87		
2013-2052	81.40		
2013-2053	87.39		
2013-2054	76.26		
2014-0484	54.32		
Average	68.08		

Conclusions

Based on the theoretical calculation, pH=11 is can be regarded as a starting point for the further experimental test to select the optimal carbonate precipitation condition for the pre-concentration of Sr. Applying relatively high temperature (50 °C) and avoid the exposure of air during the NaOH treatment, the chemical yields of Sr were improved from ~ 70% to ~90%.

3.2.2 Improvement in method applicability for Pu soil/sediment analysis

In DTU Nutech, rapid Pu analytical methods based on sequential injection extraction chromatography (TEVA) and ICP-MS detection has been developed and applied in different radioecology studies. Even though the previous method is simple and rapid due to the automated chromatographic operation, we experiences difficulties and challenges in application of these methods to certain type of environmental samples containing high

proportion of transit metal elements such as Fe, Mn, Ni. For these samples, whenever $\text{Fe}(\text{OH})_3$ co-precipitation is employed for the pre-concentration, a large amount of transit metal (Fe, Mn, Ni) is always present in the Pu fraction and make the sample volume before chromatographic separation very large (e.g., typically 50-100 mL for 10 g soil or sediment) and complicated (*see Figure. 17 (left)*). As a consequence, the performance of column separation is normally deteriorated resulting in low and variable chemical yields for Pu, since TEVA is sensitive to matrix content in the sample solution. In the worst case, a column breakthrough is encountered when a relatively small column (e.g., 2-mL TEVA) is used, therefore Pu is totally lost during the column separation. We have improved the method by using a large anion exchange column (10-20 mL) as a guard to avoid the breakthrough of the TEVA column. But in this case, the two times column separation is needed, which make the analytical procedure tedious and lab intensive.

To overcome the high susceptibility of TEVA to matrix content, development of an alternative co-precipitation technique using CaC_2O_4 could be possible to eliminate the scavenge of most metal elements contained in the samples (Fe, Mn, Ni, Co), since the co-precipitation is normally operated in low pH (1-2). As a consequence, one TEVA column separation might be sufficient for the further purification of Pu. Thus the analytical time will be reduced comparing to the one using an extra anion exchange column.

Besides, our previous method used for Pu solid analysis is not suitable for sample containing refractory Pu oxides, since acid leaching is not able to extract Pu from refractory oxides. In this case, alkaline fusion is needed for the pre-treatment of samples and boric fusion have been tested in DTU Nutech in 2014. In this report, preliminary results on the method improvement for Pu soil/sediment analysis are presented.

Materials and methods

(1) Standards, reagents and samples

A ^{242}Pu standard solution (0.1037 Bq/g in 2 mol/L HNO_3) diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL) was used as a chemical yield tracer for both plutonium and neptunium. Standard solutions of uranium (1.000 g/L in 2 mol/L HNO_3) were purchased from NIST (Gaithersburg, MD). All reagents used in the experiment were of analytical reagent grade and prepared using ultra-pure water (18 M Ω ·cm). 2-mL Econo-Columns (0.5 cm i. d. \times 10 cm length, BioRad Laboratories Inc., Hercules, CA) was utilized for chromatographic separation. TEVA (100-150 μm particle size) extraction chromatographic resin was purchased from TRISKEM International (Bruz, France).

For the method development, two soil samples collected at Poyang Lake (S4 (102.92 °E, 25.03 °N) and L9 (102.92 °E, 25.02 °N)) in China during 2013 were used throughout the work.

(2) Alkaline fusion vs. acid dissolution

An alkaline fusion procedure was investigated in order to extend the Pu method applicability to soil or sediment which contains refractory Pu oxides. Lithium metaborate was used as a fusion flux and mixed with the soil sample in a ratio of 5: 2 (weight) in a graphite crucible. The graphite crucible was placed in an oven for about two hours at 650°C for pre-oxidization and thereafter the sample was heated for 20 minutes at 1200°C.

The crucible was allowed to cool to room temperature and thereafter the melt was transferred to a beaker and dissolved with 1.4 M HNO₃. In order to prevent precipitation of silicic acids during the following separation procedure, 2 mM PEG2000 was added to flocculate the dissolved Si. The precipitate was removed by filtering.

To compare the efficiency of alkaline fusion pre-treatment, a total dissolution of the sample soil sample was also performed with consecutive attack with 65% HNO₃ + 40% HF + 60% HClO₄ on a hotplate (200-250 °C). Sample solutions obtained from both pre-treatment were diluted to suitable times by 0.5 M HNO₃ and delivered for ICP-OES measurement for the matrix elements.

(3) CaC₂O₄ co-precipitation

To develop the CaC₂O₄ co-precipitation, 10 g of dried soil sample was used and after ashing the sample at 450 °C overnight, 5-10 mBq ²⁴²Pu was spiked as a chemical yield tracer. The sample was then digested with *Aqua regia* on a hotplate at 150°C for 30 min and then 200 °C for 2 h. The beaker was covered with a glass-watch to prevent significant evaporation of the acid solution. After cooling, water was added and the sample was filtered through a GF/A filter (glass microfiber filters, 125 mm ø, Whatman International Ltd, Maidstone, England) and the filtrate was directly collected into a centrifuge tube. The beaker and the filter were gently washed with 30 mL of 0.2 mol/L HCl.

To select the optimal condition of CaC₂O₄ co-precipitation, the effect of pH, amount of Ca and oxalate added were investigated. Therefore, 1-3 g of CaCl₂·2H₂O (see details Table 1) was added to the filtrate and the sample pH was adjusted to 1- 4 (see details in Table 2) with conc. NH₃·H₂O. Weigh 3-66 g H₂C₂O₄·2H₂O to a beaker and dissolve with HCl solution with corresponding pH (1-4) which is the same as the sample solution. Add the dissolved oxalate acid solution to the sample, and then decant the supernatant after centrifugation (3000 rpm for 10 minutes). For the decomposition of CaC₂O₄, the precipitate was ashed in a muffle oven at 450 °C overnight after dried at 100°C. The residue was dissolved with 5-10 mL of conc. HCl and then diluted to ca. 40 mL with water. 10 mg of Fe³⁺ was added to the solution and NH₃·H₂O was slowly added to concentrate Pu in Fe(OH)₃ precipitate. After centrifugation, the precipitate was dissolved with 1 mL of conc. HNO₃ and then a 100-µL aliquot was taken and diluted for 10-100 times with 0.5 M HNO₃ for Pu quantification with ICP-MS.

(4) Automated FI chromatographic separation scheme

A multi-sample processing flow injection (FI) system was used for the chromatographic purification of Pu, wherein for four samples can be handled simultaneously. As indicated in *Figure. 4*, the FI system consists of a four-channel peristaltic pump (Watson-Marlow Inc. Wilmington, MA), a 10-port multi-position selection valve (MSV, Valco Instruments, Houston, TX) and 8 solenoid valves (SV1-8). All outlets of MSV were connected through PEEK ferrules and fittings with rigid PTFE tubing of 2.4 mm i.d./3.2 mm o.d., while all outlets SV1-8 were connected with PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d). Four Econo-Columns (Bio-Rad Laboratories Inc., Hercules, CA) packed with TEVA, UTEVA or AGMP-1M resin were integrated in the flow system through PEEK ferrules and fittings, whereupon the chemical purification of analytes were controlled automatically via the aid of the user-friendly FIALab software (FIALab Instruments, Bellevue, WA).

The extraction chromatographic procedure was performed according to the following five steps: I. precondition the TEVA with 20 mL 3 mol/L HNO₃ at a flow rate of 2.0 mL/min; II. Load sample solution (ca. 15-25 mL) onto the TEVA column at 1.0 mL/min; III. Rinse the TEVA column with 60 mL of 1 mol/L HNO₃ to remove most matrix elements and U at 1.0 mL/min IV. Rinse the TEVA column with 40 mL of 6 mol/L HCl to remove thorium at 2.0 mL/min; V. Elute Pu 20 mL of 0.5 mol/L HCl at 1.0 mL/min.

Each eluate was evaporated to dryness on a hot-plate to eliminate hydrochloric acid. The residue was reconstituted in 5 mL of 0.5 mol/L HNO₃ for ICP-MS measurement.

(5) Detection with ICP-MS and ICP-OES

ICP-MS measurement

The detection of ²³⁸U, ²³⁹Pu, ²⁴⁰Pu and ²⁴²Pu was performed with ICP-MS instrument (X Series^{II}, Thermo Fisher Scientific, Waltham, MA) equipped with an Xt-skimmer cone and an ultrasonic nebulizer (U5000AT⁺, CETAC, USA) under hot plasma conditions. ²³⁸U concentrations in different fractions were determined after appropriate dilution with 0.5 mol/L HNO₃. ¹¹⁵In (as InCl₃) was exploited as an internal standard and prepared to a concentration of 1 µg/L in each sample. A 0.5 mol/L HNO₃ solution was used as washing solution among consecutive assays. Prior to each measurement, the ICP-MS instrument was tuned to maximum transmission of target analytes. Typical sensitivities of U and Pu ranged from 1×10⁶ to 5 ×10⁶ cps per µg/L.

ICP-OES measurement

ICP-OES measurement performed on a Varian VISA AX CCD simultaneous spectrometer (Palo Alto, CA) was used for the determination of concentrations of the matrix elements in the samples after total dissolution or alkaline fusion. An aliquot of 0.5 mL was taken from each sample solution and diluted to certain times (depending on the detection limit of ICP-OES for certain elements) with 0.5 mol/L HNO₃. The samples were measured using axial mode to assure that the instrument would be able to measure to the highest sensitivity for the elements of interest. All samples were blank-corrected.

Results and Discussion

Alkaline fusion vs. acid dissolution

Table. 2. Results of matrix elements concentration in soil S4 by ICP-OES measurement

Experimental condition	Sample size, g	Operational time, h	Concentration of element, mg/g							
			Al	Ba	Ca	Cu	Fe	Mg	Mn	Ni
Acid dissolution	2	48	67.559	0.262	5.062	0.192	99.426	7.077	1.048	0.053
Alkaline fusion	2	3	84.102	0.273	5.572	0.154	103.337	9.414	1.067	0.000

Table. 2 summarizes the matrix elements concentrations in soil S4 pre-treated by either acid dilution or alkaline fusion. It can be seen that the concentrations for most elements obtain via the two different methods are comparable, which indicating the reliability of both pretreatment. However, considering the analytical time used in each method, alkaline fusion is much more effective using only few hours in contrast to acid total dissolution taking about 2 days.

Optimization of CaC_2O_4 co-precipitation

Effect of pH

The selections of optimal pH for the CaC_2O_4 is crucial because it will directly determine the effectiveness of Pu scavenge as well as the removal of matrix elements including Fe, Mn, Al etc. Too low pH will cause the dissolution of Pu but under too high pH most metal elements will form precipitate and thus entry into the Pu fraction.

In this work, several pH ranging from 0-4 have been tested and the results are summarized in *Table. 3*. When pH is lower than 1, it is very difficult to form CaC_2O_4 precipitate due to the relatively high solubility of CaC_2O_4 in acidic condition. While when pH increased to above 2.16, the color of the sample solution turns to be brownish, and Fe hydroxide precipitate start to form. Within the range of pH=1 - 2 the formation of CaC_2O_4 is generally quantitative, but at pH=1, it requires more $\text{H}_2\text{O}_2\text{O}_4$ to form CaC_2O_4 precipitate (see L9-3 & L9-4 in *Table. 3*). Thus pH=2 could be regarded as the best condition to both quantitatively form CaC_2O_4 precipitate and removal of Fe. From *Figure. 17* it also can be seen that, with the use of CaC_2O_4 co-precipitation, the amount of precipitate obtained after centrifugation is significantly reduced compared to the one obtained from $\text{Fe}(\text{OH})_3$ co-precipitation, which should possibly reduce the analytical burden in the following chemical purification and improve the chemical yield of Pu.

Table 3 Effect of pH on the co-precipitation efficiency of CaC_2O_4 for 10 g of Chinese soil

Sample ID	pH	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ added or experimental phenomena, g	Precipitate amount after ashing (mainly CaCO_3), g*	Removal of Fe, %
L9-3'	< 0.5	No precipitate	-	
L9-3	1.0	66*	1.73	75.3
L9-4	1.0	36	0.36	93.6
S4-3	1.5	18	1.5	88.7
S4-4	2.0	18	1.94	99.6%
S4-4'	>2.16	Fe starts to precipitate	-	

* 0.8 g of Ca^{2+} (as CaCl_2) was added in each sample, and if Ca^{2+} could precipitated quantitatively with $\text{C}_2\text{O}_4^{2-}$, then the CaCO_3 obtained after ashing under 450 °C overnight should be ca. 2 g.



Figure. 17. $\text{Fe}(\text{OH})_3$ precipitate (left) vs. CaC_2O_4 precipitate (right) obtained after pre-concentration of 10 g Chinese soil

Effect of calcium and oxalic acid amount

In general, soil samples contain certain level of Ca. but due to the different type of samples, the content of Ca may vary from sample to samples. Extra addition of Ca maybe necessary to ensure the quantities absorption of Pu, the formation of CaC_2O_4 should be sufficient. On the hand, excessive amount of Ca may cause problems for the further chemical purification and deteriorate the column separation performance. Except to form CaC_2O_4 precipitation with Ca^{2+} , the oxalic acid added into the sample could complex with Al, Fe, Mn, Ni and other metal elements under relatively lower pH, as a consequence of the readily complexation properties of $\text{C}_2\text{O}_4^{2-}$ with metal cations. Thus, the addition of oxalic acid should consider both the content of Ca^{2+} and the existence of other complexing metal elements. Moreover, too much sulphurs addition of oxalic acid could possibly also form complexes with Pu ions, thus the chemical yields of Pu will be deteriorated. Therefore, selection of appropriate addition of oxalic acid is also very crucial to ensure the quantities scavenge of Pu.

It can be seen from *Table. 4* that, the precipitate obtained after ashing the CaC_2O_4 increases with the addition of Ca^{2+} , when the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ addition is less than 1 g, the dissolution of CaC_2O_4 is relatively significant ($> 30\%$) due to the low $[\text{Ca}^{2+}]$ and $[\text{C}_2\text{O}_4^{2-}]$, e.g., for OX-10 in Table 4, dissolution of $\text{CaC}_2\text{O}_4 = (0.68-0.47)/0.68 * 100\% = 30.9\%$. Therefore, the preliminary results could possibly suggest that minimum existence of 2 g of Ca should be needed in the sample solution. In the case for samples contain low level of Ca, external Ca addition is necessary to form quantitative precipitation of CaC_2O_4 .

Table 4. Effect of Ca amount on the co-precipitation efficiency of CaC_2O_4

Sample ID	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added, g	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ added, g	Amount of precipitate after ashing (mainly CaCO_3), g*
OX-9	0.5	0.5	0.15 (0.34)
OX-10	1	1	0.47 (0.68)
OX-11	2	2	1.22 (1.35)
OX-12	5	5	3.33 (3.38)

*The values in the brackets are the expected CaCO_3 amount after quantitative co-precipitation with $\text{C}_2\text{O}_4^{2-}$ and ashing under $450\text{ }^\circ\text{C}$.

The results in *Table. 5* confirm the complexation of with Fe^{3+} and when extra addition of $\text{C}_2\text{O}_4^{2-}$ is three times of Fe^{3+} , CaC_2O_4 precipitation could be formed relatively quantitatively. Therefore, it was presumably regarded that the complex ratio is around $\text{Fe}^{3+}:\text{C}_2\text{O}_4^{2-}$ (mole ratio) = 1: 3. Therefore, the optimal addition of oxalic acid should be related to the content of complexion elements, mainly Al, Fe, Mn, Ni, Mg, in which case a matrix screening by ICP-OES for each soil/sediment sample may be favourable before the chemical analysis of Pu.

Table 5. Effect of Fe on the CaC_2O_4 co-precipitation efficiency

Sample ID	Fe^{3+} , g	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added, g	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ added, g	Amount of precipitate after ashing (mainly CaCO_3), g*
OX-5	0.2	3.0	3.0	0.61
OX-6	1	3.0	9.8	1.48
OX-7	5	3.0	42.4	1.66
OX-8	10	3.0	70.5	0.95

* 0.8 g of Ca^{2+} (as CaCl_2) was added and the CaC_2O_4 co-precipitation was carried at pH=1.5 in each sample

Conclusions

An alkaline fusion method was developed for sample pre-treatment in DTU Nutech, which showed high effectiveness (taking few hours) compared to the ones using acid total dissolution taking about 2 days. This method can be used for future matrix elements determination by ICP-OES as well as the determination of Pu and other actinides in samples containing refractory oxides, thus exploring the applicability of our current analytical method for Pu and other actinides.

A CaC_2O_4 co-precipitation was tested preliminarily for the pre-concentration of Pu in soil/sediment samples. The results indicate the selection of optimal of pH, addition of Ca and oxalic acid during the co-precipitation process are important parameters affecting the analytical performance. Experiment will be done in the near future for further optimization the performance in combining the chemical yields of Pu and decontamination of U.

3.2 Measurement of Pu and major elements in soil and sediment using ICP-OES and ICP-SFMS in FOI

At FOI CBRN Defence and Security, ^{239}Pu and ^{240}Pu are measured in different sample matrices using both alpha spectrometry and inductively coupled plasma sector field mass spectrometry (ICP-SFMS). The sample dissolution technique used is chosen depending on the sample matrix and after dissolution, solid phase extraction (SPE) is performed to separate the measurand from concomitants. After the whole sample preparation procedure is done, nuclide specific measurement is performed with techniques suitable for the nuclide of interest.

In this report, FOI's nuclear emergency preparedness method for ^{239}Pu and ^{240}Pu has been put to test on a low Pu-level Chinese soil sample and a reference material, NIST SRM 4357, and the plutonium measurements were performed on an ICP-SFMS. Major elements have also been measured using ICP-OES. Possible improvements as well as limitations of this nuclear emergency preparedness method are discussed.

3.2.1 Materials and methods

(1) Materials

A standard solution containing ^{242}Pu (NIST SRM 4334G; National Institute of Standards and Technology, Gaithersburg, MD, US) was used to spike the samples for yield determinations. For calibrating the ICP-SFMS regarding mass bias and uranium hydride formation, IRMM-073/1 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium) was used. IRMM-184 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium) was used as a control for the correction factors established with IRMM-073/1 and to establish knowledge of the tailing on nearby masses from m/z 238. The certified sediment reference material used for this study was NIST SRM 4357 (National Institute for Standards and Technology, Gaithersburg, Maryland, US).

The reagents used were HNO_3 (p.a., Merck Millipore, Darmstadt, Germany), HCl (37%, Scharlau, Sentmenat, Spain), NaNO_2 (Merck Millipore, Darmstadt, Germany), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (Merck Millipore, Darmstadt, Germany), lithium metaborate flux (LiBO_2 , Puratronic 99,997%, Alfa Aesar), polyethylene glycol (PEG 2000, Merck Millipore, Darmstadt, Germany) and hydroxyethylidene diphosphonic acid (HEDPA, purum <97%, Sigma Aldrich Chemie GmbH)

Extraction chromatographic material, TEVA, (100-150 μm , Triskem International, Bruz, France) was used for the separation of plutonium. The separations were performed in disposable 10 ml plastic columns (Poly-prep, BioRad). Graphite crucibles (27 ml, Gammadata Instrument AB, Sweden) were used for the fusion of samples and filters (Munktell OOH, Grycksbo Pappersbruk AB, Grycksbo, Sweden) were used for the separation of flocculated Si.

(2) Sample preparation procedure

1 g of soil or sediment was placed in a graphite crucible and mixed with 3 g of lithium metaborate and thereafter spiked with ^{242}Pu for chemical yield determination. The graphite crucible was placed in an oven for about two hours at 650°C for pre-oxidization and thereafter the sample was heated for 10-15 minutes at 1050°C .

The crucible was allowed to cool to room temperature and the melt (which formed a glass bead which was easily picked up with tweezers from the crucible) was thereafter transferred to a beaker and dissolved with 1.4 M HNO₃. In order to prevent precipitation of silicic acids during the following separation procedure, 2 mM PEG2000 was added to flocculate the dissolved Si. The precipitate was removed by filtering and the resulting filtrate, after evaporation to half the volume, was suitable for the following solid phase extraction procedure, see *Figure. 18*.

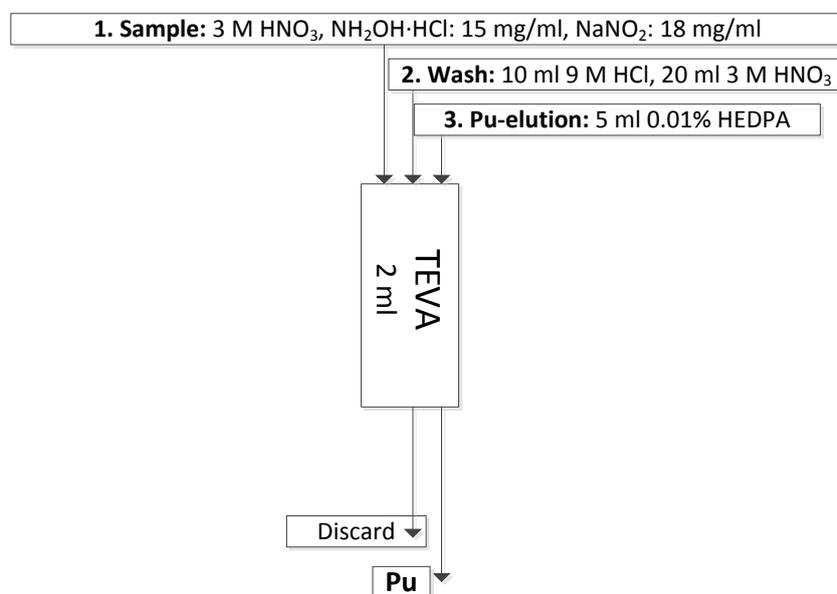


Figure. 18. Schematic outline of the SPE procedure

Before the separation using solid-phase extraction of plutonium from concomitant elements, a redox procedure was used to adjust Pu to Pu(IV) while keeping Am as trivalent. First, Pu is reduced to the trivalent state by adding NH₂OH·HCl (375 mg ml⁻¹) and heating at 90°C for 5 minutes. After cooling to approximately 40°C, NaNO₂ (450 mg ml⁻¹) is added to oxidise Pu(III) to Pu(IV). The TEVA-containing column was conditioned with 3 M HNO₃ and thereafter the sample was loaded. Under these conditions, Pu(IV) is retained on the TEVA resin and U and Am will pass through the column. The TEVA column was thereafter rinsed with 9 M HCl to remove thorium, followed by 3 M HNO₃ to remove uranium. Plutonium was then eluted using 0.01% HEDPA and the sample was ready for measurement on ICP-MS.

3.2.2 Instrumentation

(1) ICP-OES

An iCap7400 ICP-OES Duo (Thermo Scientific, Bremen, Germany) was used for the determination of concentrations of the major elements in the samples before TEVA separation described above. In order to measure the elemental concentration 0.5 mL of each sample was taken out for analysis using ICP-OES. The samples were then spiked with 0.2 mL of indium (9925 µg/mL) as internal standard, 0.2 mL concentrated HNO₃ and MQ was added so that the samples were diluted to a volume of 10 mL 2% HNO₃. The samples were measured using axial mode to assure that the instrument would be able to measure to the highest sensitivity for the elements of interest. All samples were blank-corrected.

Table. 6 Operating parameters and data acquisition parameters for the Element XR

Isotope	Sample time	Samples/peak	Mass window	Detection mode
²³² Th	0.003	100	5	both
²³³ U	0.010	100	5	both
²³⁴ U	0.010	100	5	both
²³⁵ U	0.010	100	5	both
²³⁶ U	0.010	100	5	both
²³⁷ Np	0.010	100	5	both
²³⁸ U	0.003	100	5	both
²³⁹ Pu	0.010	100	5	both
²⁴⁰ Pu	0.010	100	5	both
²⁴¹ Pu	0.010	100	5	both
²⁴² Pu	0.010	100	5	both
²⁴³ Am	0.010	100	5	both
²⁴⁴ Pu	0.010	100	5	both
Total time	00:04:57			
Resolution, $m/\Delta m$	300			
Runs/passes	20·25			
Scan type	E-scan			
Magnet mass	232.038 u			
Dead time correction	Active, $\tau = 33$ ns			

(2) ICP-SFMS

An Element XR double focusing sector field ICP-MS (Thermo Scientific, Bremen, Germany) equipped with a Jet interface was used for the determination of plutonium in soil and sediment. The instrument was equipped with a Micromist nebuliser (GE) and a Cyclonic spray chamber (GE, dead volume 20 mL). The measurements were performed in self-aspiration mode, resulting in a sample flow rate of approximately 0.1 mL/ min. Operating parameters and measurement acquisition parameters can be seen in [Table. 6](#).

The concentrations of the measurands are evaluated relative to the signal of the spike nuclide, *i.e.* ²⁴²Pu. The intensities are corrected for blank levels and the ratio of analyte to spike is corrected for mass bias, using the exponential relationship, and also hydride formation where necessary.

3.2.2 Results and discussion

(1) ICP-OES

The results from the ICP-OES measurement show that the predominant elements in the soil sample are aluminium (Al), iron (Fe), magnesium (Mg), nickel (Ni) and uranium (U). One replicate each for the sample and the reference material is presented in [Table. 7](#) but during this work three replicates for the Chinese soil sample and two for the reference material were measured and all showed agreeable results for each major element.

Table. 7 Measured concentrations of major elements ($\mu\text{g/mL}$) in the Chinese soil-191 sample and in the sediment reference material NIST SRM 4357.

	Al	Ba	Ca	Cr	Cu	Fe	La	Mg	Mn	Ni	Pb	Sr	U	V	Y	Zn	Zr
Soil-191	85000	60	2900	130	18	57000	31	2800	360	8600	<9	24	10000	350	26	<19	190
4357	13000	110	5800	26	<0.5	6400	3	1700	85	1600	<9	52	720	14	7	<19	70
4357 ^a	24700	143	6267	27	82	10700	25	3930	-	97	12	64	-	21	12	45	540

^a Informational values for the reference material NIST SRM 4357

^b Element concentrations reported as less-than values are below detection limit for the instrument. Measurement uncertainties are 10% of the concentrations.

According to [Table 7](#), the information values and the measured values are generally not in agreement with each other, the ones that are in agreement have been marked in bold. The control sample used during the measurement contained $1 \mu\text{g/mL}$ of the elements reported in [Table 7](#). The results for the quality control sample were accurate for all elements but zinc (Zn) and nickel (Ni). The reason for these deviations may be that the spectral lines used had interference from another elements spectral line. There were no other suitable spectral lines available for either Zn or Ni, and to overcome the problem with spectral interferences there is a need for mathematical corrections to be added in the software. Seeing as this measurement method still needs to be validated with reference materials the results should be viewed as guidelines rather than perfect concentrations.

(2) ICP-SFMS

The correction factors needed for isotope dilution mass spectrometry of Pu (mass bias and hydride formation correction factors) were determined using the reference material IRMM-073/1. As a control sample, the reference material IRMM-184 was used and the resulting ratios for $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{235}\text{U})/n(^{238}\text{U})$ can be seen in [Figure 19](#). The results are in agreement with the certified values for the mentioned isotope amount ratios.

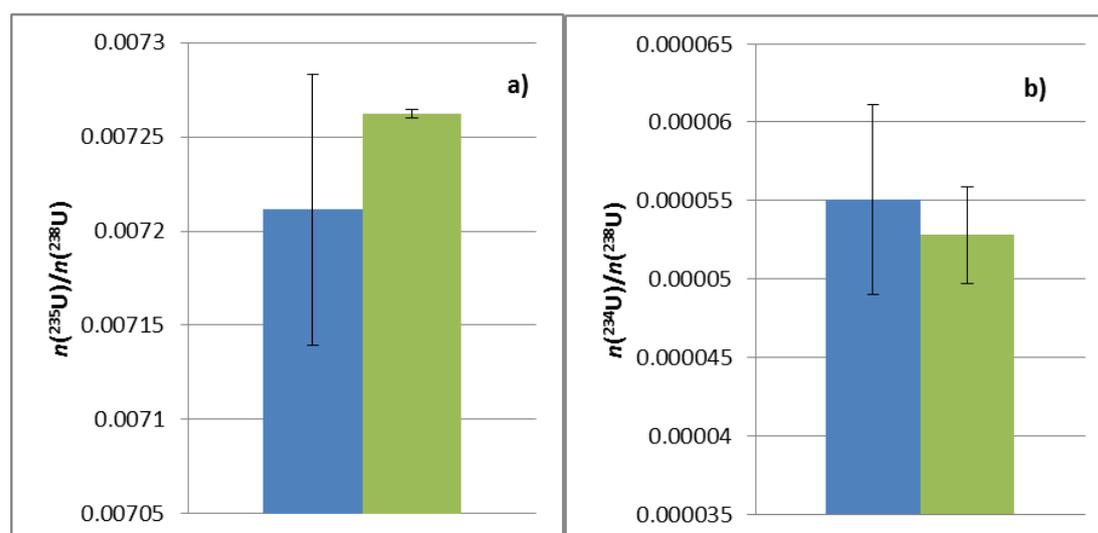


Figure. 19. Isotope amount ratios for a) $^{235}\text{U}/^{238}\text{U}$ and b) $^{234}\text{U}/^{238}\text{U}$. The blue bars represent the results from this study and the green bars show the certified values for the reference material IRMM-184. The error bars correspond to the expanded measurement uncertainty ($k=2$).

The abundance sensitivity, that is the tailing on nearby masses have also been controlled, using IRMM-184. The results for the reference material NIST SRM 4357 and the Chinese soil 191 samples are presented in *Table 8*, both as corrected and uncorrected for abundance sensitivity.

The reason for presenting two sets of results was to show the importance of establishing correction factors for certain spectral interferences such as mass bias, hydride formation and abundance sensitivity. For the results corrected for mass bias and hydride formation, it can be seen that the expanded measurement uncertainties for both the $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ ratio and the specific activity for ^{239}Pu are relatively high and the $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ ratio is only reported as an information value. The expanded measurement uncertainties are large, the measurement uncertainty ($k=1$) is up to 40%, indicating that the results are close to or at the detection limit for these type of measurements.

Studying the results where all three correction factors have been applied, it can be seen that ^{239}Pu and ^{240}Pu as well as the $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ ratio fall below the detection limit.

The largest sources of uncertainty for the determination of ^{239}Pu and ^{240}Pu were the determination of the hydride formation correction factor to correct the m/z 239 signal for contribution from ^{238}UH and the measurement uncertainty of the signal on m/z 239. The relatively small signal on m/z 239 (about 10 cps) and the large measurement uncertainty on the hydride formation correction factor cause the detection limit for ^{239}Pu to be high. Another important uncertainty contribution is the correction for abundance sensitivity on nearby masses.

The low level soil sample (approximately 0.2 Bq/kg $^{239+240}\text{Pu}$) contained high iron concentration (see Table 2) and this may have caused a vast amount of the redox chemicals to be used up by the redox reaction for iron instead of for plutonium. If the redox reaction for plutonium was incomplete this in turn would have caused the recovery, during the separation on TEVA, to be considerably reduced compared to a sample with lower iron concentration. The low recovery for plutonium during the separation meant that a smaller amount of plutonium was available for the ICP-SFMS measurement. This led to a low signal for both ^{239}Pu and ^{240}Pu . As the contribution from the corrections for mass bias, hydride formation and abundance sensitivity dominated the total signal measured, for both the plutonium isotopes, this led to non-detectable amounts of plutonium.

The results for the reference material NIST SRM 4357 are within the range of results that are normally achieved in this laboratory for this reference material. The reference material had lower concentrations of iron and uranium in the sample and the specific activities of plutonium are higher than that of the Chinese sample, thereby the two sets of results are similar as the spectral interference corrections are not the major contributor to the measured signal at m/z 239 and 240.

For this work, the detection limits for ^{239}Pu and ^{240}Pu are 0.7Bq/kg and 2.5 Bq/kg, respectively, for 1 g of soil/sediment. The analytical turnover time for plutonium is one day for soil/sediment, including the time that the samples are left for flocculation of silicon (12 hours).

Table. 8 Specific activity (Bq/kg) and $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ in soil and sediment samples.

	$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	S ^{239}Pu (Bq/kg)	S ^{240}Pu (Bq/kg)
Soil	0.19(15)*	2.4(1.6)*	1.66(30)
NIST SRM 4357	0.153(10)	14.25(39)	8.05(50)

^a The measurement uncertainties given in bracket are expanded with a coverage factor, k , 2. Results marked with * are only reported as informational values as the expanded measurement uncertainties are large, the measurement uncertainty ($k=1$) is up to 40%, indicating that the results are close to or at the detection limit for these type of measurements.

3.2.3 Conclusions

The results in this work show that the nuclear emergency preparedness method including lithium metaborate fusion and separation procedure using TEVA is robust for specific activity levels of plutonium above 0.7 and 2.5 Bq/kg for ^{239}Pu and ^{240}Pu , respectively, but for low activity samples and for samples containing high concentrations of uranium and iron the method needs to be altered.

The correction of spectral interferences on m/z 239 and m/z 240 caused a major contribution to, and increase of, the combined measurement uncertainty. Therefore we see isotope amount ratios and specific activities close to the detection limit for this work. A continuation of this work may consist of increasing the sample amount in order to achieve higher signal intensities on m/z 239 and m/z 240, as well as improving the determination of the spectral interference correction factors. This would lead to decreased expanded measurement uncertainties and hence a lower detection limit may be achieved. By increasing the sample amount three times the sample volume that need to be processed would be increased and therefore the time for the separation procedure would get longer. However, a three times as large sample volume would not make a drastic change the total turnover time for the method - it would still be one day. This is because the major part of the turnover time is due to the time that the samples are allowed to stand to flocculate silicates prior to separation.

Determination of major constituents in samples, in which certain radionuclides need to be determined, can give good information on the sample preparation procedures suitability. For the determination of plutonium it can be a major concern to know the concentrations of iron and uranium due to the large influence that both these elements have on the sample preparation and the ICP-SFMS measurement. By having knowledge of major constituents in a sample, the sample preparation procedure can be altered. For example, by increasing the amount of redox chemicals would ensure that that the redox process for plutonium is complete before the plutonium separation despite the high concentration of iron in the sample. By separating uranium from the sample before the plutonium separation, the concentration of uranium in the sample to be measured would be reduced and therefore the tailing from ^{238}U on both ^{239}Pu and ^{240}Pu will have less importance.

In this work the determinations of major elements in soil and sediment have been included even though these kinds of measurements are still in its early stages at FOI. To improve the measurements of the major elemental concentrations, in soil and sediment using ICP-OES, potential spectral interferences need to be mathematically corrected for. There is also a need to validate the method using a certified reference material.

3.3 Improvement in source preparation and Pu air filter analysis in STUK

Pu and Am analysis from environmental samples are very time consuming. The aim of this work was to a) test if co-precipitation could be used instead electrodeposition methods as source preparing step in the Pu/Am methods to decrease time spent in analysis and b) test and develop Pu method for air filters in emergency situations that is faster than the normal method used in STUK.

3.3.1. Comparing co-precipitation vs electrodeposition as a source preparing technique for Pu and Am

Radiochemical separation method used traditionally in STUK for Pu and Am analysis has included a step where Pu/Am are deposited on a steel plate using electrodeposition prior to alpha counting.

Co-precipitation of Pu/Am as cerium fluoride into a membrane is an alternative technique for electrodeposition. The aim of this work was to test if the co-precipitation would be suitable alternative for electrodeposition in STUK. Electrodeposition that has been traditionally used is also a well suitable method for source preparation but it is sensitive to impurities that might exist in the sample and it is also more sensitive to malfunction in equipment. Additionally the technique is dependent on the operator. Co-precipitation technique is known to be less sensitive for impurities than electrodeposition. It also works as an additional purification step as only elements with valence states 3 and 4 will precipitate. Co-precipitation is also simpler to carry out and requires less time than electrodeposition.

To validate cop-precipitation technique replicate samples were analyzed both using electrodeposition and co-precipitation. Both chemical recovery and the **full width at half maximum** (FWHM) were recorded.

Materials and Methods

Samples were prepared by adding a known value of tracers (^{242}Pu or ^{243}Am) into 1 M HNO_3 solution.

(1) Electro-deposition

Platinum spiral is placed into the sample vessel and electricity is turned on. Pt spiral works as an anode and stainless steel as cathode. As a result metal present in the solution is reduced and is precipitated on stainless steel (Letho and Hou, 2011).

Preparation of samples and pretreatment of steel plates

Stainless steel plates (\varnothing 17.5 mm) were cleaned with water, ethanol and heated with Bunsen burner. 30 mL Nalgene® bottles were used as electrodeposition vessels. The stainless steel plate was placed into the Nalgene bottle and the bottle was attached into the apparatus (*Figure. 20*).

3 ml of tracer solution (0.1 Bq/sample) and 400 μl MilliQ-water was added to the sample bottle. 3 – 4 drops of methyl indicator solution was added and the sample was stirred. Conc. NH_3 was added dropwise until color was changed from red into yellow. The sample was

acidified by adding 2 M HNO₃ dropwise until the colour turned red and four additional drops of 2 M HNO₃ was then added.

Electrolysis

Current used was 1.7 - 1.9 A. Pu samples were electrodeposited for 1 hour and americium samples for 1.5 hours. Electrolysis was finished by adding 2 ml concentrated NH₃ into the sample solution. The steel plates were rinsed with water, ethanol and heated with Bunsen burner for 15 seconds. Heating was used to ensure that Pu is properly attached on the plate. The diameter of the average precipitation area was 15.5 mm.



Figure. 20. Electrodeposition apparatus.

(2) Co-precipitation

Small amount of Ce (or Nd) is added into the sample solution and precipitated as CeF₃ by adding HF into the sample solution. Actinides co-precipitate in oxidation states +III/+IV. The precipitation is filtered on a membrane filter and the membrane filter is attached on a suitable base.

Precipitation procedure

3 ml of ²⁴²Pu/²⁴³Am –tracer solution (0.1 Bq/sample) was added into plastic centrifuge tubes. 0.5 ml cerium –carrier (Ce 100 µg/mL) and 1.5 ml of 40 % hydrofluoric acid (HF) were added to the sample solution. Solution was mixed thoroughly with Vortex® and placed into an ice bath for 45 minutes while shaking now and then.

Sample filtering

The sample solution was filtered on Metricell® polypropylene membrane (0.1 µm, ø 25 mm). Filtering apparatus is shown in *Figure. 21*. After placing the filter membrane on the filtering apparatus, 5 mL ethanol was filtered followed by the sample solution. Sample container was rinsed twice with 5 mL of HF -solution (50 drops of 40 % HF/250 mL water) that was also filtered. Finally 5 mL ethanol was filtered through and the membrane was removed and air dried. The dried membrane was glued on a stainless steel plate. The diameter of the average area with precipitation on it was about 23.5 mm.



Figure. 21. Filtering apparatus for co-precipitated samples.

(3) Measurement of alpha sources

Electro-precipitated and co-precipitated sources were measured by alpha spectrometry (Canberra, Alpha Analyst) with PIPS-detector. Detectors with surface area of 300 mm² were used for electrodeposited sources and those of 450 mm² for co-precipitated samples. Samples were counted for 22-31 hours.

Results and Discussion

Table. 9. Full with half maximum (FWHM) and chemical yields for Pu samples.

Electro-deposition			Co-precipitation		
Sample	FWHM (keV)	Yields, %	Sample	FWHM (keV)	Yield, %
1	60.1	79.6	1	46.8	87.1
2	61.3	85.2	2	64.5	89.4
3	48.8	86.1	3	42.5	89.1
4	62.2	87.8	4	61.2	85.4
5	57.5	92.6	5	31.2	106.0
6	77.6	93.2	6	34.3	110.4
7	58.7	82.4	7	36.7	104.4
8	24.3	73.9	8	34.0	92.5
9	63.1	93.1	9	36.3	104.9
10	61.6	84.8	10	37.7	95.4
11	68.0	89.9	11	33.0	91.9
12	58.6	90.4	12	30.3	97.6
13	49.8	92.2	13	36.8	93.5
14	66.0	89.4	Average	40	96
15	63.3	91.3	Standard deviation	11	8.1
16	54.7	89.3	Std dev (%)	27	8.4
Average	59	88			
Standard deviation	11	5.4			
Std dev (%)	20	6.1			

Average chemical yield for Pu in co-precipitated samples was 96 % and that from electrodeposited samples was 88 % (*Table. 9*). Full with half maximum (FWHM) that describes energy resolution was 40 keV for co-precipitated samples and 59 keV for electrodeposited samples. Average chemical yields and FWHM-values were similar when taking consideration standard deviation of results.

Average chemical yield for Am from co-precipitated samples was 96 % and that from electrodeposited samples was 92 % (*Table. 10*). Full with half maximum (FWHM) that describes energy resolution was 32 keV for co-precipitated samples and 52 keV for electrodeposited samples (table 2). Average chemical yields were similar when taking consideration standard deviation of results. However, average FWHM-values and associated standard deviation were somewhat larger for electrodeposited samples than for co-precipitated samples.

Table. 10. Full with half maximum (FWHM) and chemical yields for Am samples.

Electro-deposition			Co-precipitation		
FWHM (keV)	Yields, %	FWHM (keV)	Yields, %	FWHM (keV)	Yields, %
1	45.6	90.2	1	32.3	93.9
2	42.3	98.4	2	30.1	95.4
3	33.6	84.3	3	27.7	96.4
4	41.4	92.5	4	31.0	95.2
5	62.1	86.4	5	29.9	95.9
6	54.7	97.1	6	33.8	96.9
7	47.9	103.5	7	34.2	96.6
8	63.6	94.0	8	31.2	96.1
9	64.6	83.1	9	32.4	96.4
10	39.2	96.1	10	33.1	95.7
11	74.4	91.4	11	31.0	94.0
Average	52	92	12	31.0	99.2
Standard deviation	13	6.3	13	34.4	94.4
Std dev (%)	25	6.8	14	32.7	93.2
			15	32.7	98.4
			Average	32	96
			Standard deviation	1.8	1.6
			Std dev (%)	5.7	1.7

Electro-deposition is more time consuming than co-precipitation. Electro-deposition is also more sensitive to impurities. The advantage of the electrodeposition is that the radionuclide can be deposited into a very thin layer that is needed for good resolution in alpha spectrum. Electro-deposited samples need to be heated with Bunsen burner to assure that Pu and Am are well attached on plate. Estimating how long the plate need to be heated is challenging and requires experience. If the sample is heated too long part of Pu may evaporate. On the other hand if the sample is heated too short, impurities may be left on the sample plate.

Pretreatment of the sample and preparing the equipment takes more time in electro-deposition than in co-precipitation. The equipment needs oversights when running as the voltage may

change during the electro-deposition. Current may have to be adjusted during the electrodeposition due to changes in voltage. Sample container is hold in ice bath to avoid sample evaporation and additional ice has to be added several times during the electrodeposition.

Co-precipitation was simpler technique than the electrodeposition previously used in STUK. Co-precipitation was not so sensitive to the operator than electrodeposition. Co-precipitation was also not so sensitive to impurities of the sample. Disadvantage in co-precipitation is that other elements in valence states 3 and 4 may also precipitate.

Conclusions

Based on the results it was found that both electrodeposition and co-precipitation are well suited for Pu and Am source preparing. The advantage of co-precipitation is simplicity and rapidity of the method that together decreases the time needed to prepare Pu/Am source. Additionally it was found that co-precipitation technique is less sensitive to operator.

3.3.2 Analysis of Pu from air filters in emergency conditions

The Pu method that is used in STUK for regular samples takes several days to carry out. In emergency situation results are needed faster, preferably within a day. Air filters are one of the most important matrices needed to be analyzed in emergency conditions, especially in the early phase of the emergency. The aim of this work was to test and improve the method for determination of Pu from glass fiber air filters in emergency conditions. The goal was that the Pu analysis could be carried within one working day. To dissolve the glass fiber filters two different techniques, NaOH-Na₂CO₃ fusion and HF acid leach, were tested.

Materials and Methods

Samples used in the experiments were air samples collected on glass-fiber filters 12.8.2014. The size of one individual glass fiber filter is about 8.7 cm x 8.2 cm and the diameter of the area where the air sample is collected is about 7.8 cm. Samples were dissolved either with a) NaOH-Na₂CO₃ fusion or b) with HF acid leach (mixture of HF, HNO₃, HCl). Four samples were analyzed: 2 samples with fusion and 2 with acid leach. Dissolved samples were then purified by anion exchange followed by co-precipitation and alpha counting. NaOH-Na₂CO₃ fusion was chosen to be tested as one dissolution technique because it is regularly used in STUK in Sr determination. When developing the methods for emergency situation the aim was that the methods would be rather similar to the regular methods used in STUK so that the laboratory personnel is familiar with them. However for the emergency purpose the methods need to be modified in a manner that they can be carried out faster than during normal operation.

(1) Dissolution of glass fiber filter with fusion

The glass fiber air filter (8.7 cm x 8.2 cm, ~ 0.57 g) was weighed and cut into small pieces with scissors into a Ni crucible. 1 mL of ²⁴²Pu tracer (A=0.0289 Bq/ml, ref date 7.6.1994) was added to the sample. About 100 g SrCl₂·6H₂O was added to the sample. NaOH granules (6 x sample mass) and 2 tea spoon of Na₂CO₃ (anhydrous) were added to the sample and it was heated with a Bunsen burner. About three teaspoons of NaNO₃ were added until all carbon was burned. The fused sample was dissolved with 100 mL of distilled water while heating.

The sample solution was centrifuged while hot and the solution discarded. The residual was washed with 30 mL of boiling water and the solution was discarded. The precipitate was dissolved with ~30 mL of 8 M HNO₃.

(2) Dissolution of glass fiber filter with acid leach

The glass fiber filter (8.7 cm x 8.2 cm) was split into two parts and one half was used for an analysis. Each sample filter half was weighed and transferred into a 250 mL Teflon beakers and 1 mL of ²⁴²Pu tracer (A=0.0289 Bq/mL, ref date 7.6.1994) was added to the sample. 10 mL of HF, 10 mL of HNO₃ and 10 mL of HCl were added to the sample. The Teflon beaker was heated at the hotplate until sample solution was evaporated to dryness. Then 0.5 g of boric acid and 5 mL of HNO₃ were added to the beaker and the sample solution was evaporated to dryness. Sample residual was dissolved into 30 mL of 8 M HNO₃.

(3) Anion exchange chromatography

Prior to anion exchange the cooled sample was filtrated (GF/A) to remove the small amount of residual present. The sample was heated, 1 mL of hydrogen peroxide was added and the sample was heated for 15 minutes. Then 2 g of NaNO₂ was added to the hot sample that was then let cool for 30 minutes.

The Dowex 1 x 4, (50-100 mesh) anion exchange column was prepared in a glass column (ø 1 cm, 7.5 mL resin). Glass wool was placed on bottom of the column and on top of the resin. Resin was brought in nitrate form by treating it with 25 mL of 65% HNO₃ and 50 mL of 8 M HNO₃. The sample solution was loaded into the anion exchange column (speed was ~ a drop in 2 s, faster than in STUK regular analysis). The resin was washed with 50 mL of 8 M HNO₃ and with 50 mL of 37% HCl. Pu was eluted with freshly made 30 mL of 37% HCl + 3 mL of 1 M NH₄I solution. Pu eluate was evaporated to dryness. Few mL of 65% HNO₃ and 37% HCl were added and evaporated. This was repeated and residual dissolved into 2-5 mL 1 M HNO₃.

Above mentioned procedure was modified from the normal procedure used in STUK by using a smaller column (7.5 mL instead of 15 mL) and consequently smaller amounts of washing solution. This allowed faster separations. As the amount of matrix in air filter sample is not too large this was not expected to have significant effect on yields or purity of the alpha spectrum. Secondly the solutions were stripped faster through the columns than in normal procedure also saving significant amount of time. This could result slightly lower yields that are, however, acceptable in emergency situations.

(4) Co-precipitation and alpha counting

The sample solution was transferred into a plastic centrifuge tube. 0.5 mL cerium-carrier (Ce 100 µg/mL) and 1.5 mL 40 % hydrofluoric acid (HF) were added to the sample solution. Solution was mixed thoroughly with Vortex® and placed into an ice bath for 30 minutes while shaking now and then. The sample solution was filtered on Metricell® polypropylene membrane (0.1 µm, ø 25 mm) as described in chapter 2.1.2. Samples were then measured with alpha spectrometry (Canberra, Alpha Analyst) PIPS-detector (450 mm²) for 6000 minutes. Shorter measurement time would be used in emergency conditions (probably overnight) but for these test better statistics were needed.

Results and discussion

(1) Chemical yields and FWHM

Chemical yields were relatively low (28-40%) for the samples that were digested with NaOH-Na₂CO₃ fusion as shown in Table 3. This is because prior to anion exchange when H₂O₂ were added to sample solution, silicates precipitated in the sample. Sample was filtrated and the residual containing silicates were discarded. Obviously some Pu was also carried away with silicates. If fusion is to be used silicates should be removed prior to anion exchange and an additional step would be required. Silicates could be removed by using HF acid and evaporating the sample or by carrying out an additional precipitation step. Additional precipitation step with iron could be used to precipitate Pu and further remove impurities from the sample solution prior to anion exchange. This would however require more time. Full width half maximum (FWHM) that describe energy resolution was also larger in samples where fusion was used (38-90) suggesting that purification was not satisfactory.

Samples that were digested with HF had no problems with silica interfering as the silicates were removed while heated with HF. Chemical yield and FWHM-values were good for samples leached with HF (*Table. 11*). Chemical yields varied from 78 to 96 %. As one of the membrane filters (sample 1) was glued to the steel plate prior to counting, it became a little wrinkled (due to the lack of practice of the operator) causing the yield to be somewhat lower (78%) than in the other sample that was properly prepared (yield was 96%). FWHM-values for samples leached with HF varied from 30 to 32 KeV suggesting good purification from impurities.

Table. 11. Full with half maximum (FWHM), chemical yields and ^{239,240}Pu activity in air filter samples using the procedure for emergency conditions.

Dissolution technique	Sample number	Chemical yield (%)	FWHM (Pu-242 peak)	^{239,240} Pu, Bq/sample	Unc. (2 sigma)
NaOH-Na ₂ CO ₃ Fusion	1	28	38	<3 x10 ⁻⁴	
NaOH-Na ₂ CO ₃ Fusion	2	40	90	2.3 x10 ⁻³	30 %
HF acid leach	3	78	30	3.3 x10 ⁻⁴	50 %
HF acid leach	4	96	32	<2 x10 ⁻⁴	

(2) Time required for the analysis

Time scheme for the analysis is shown in *Figure. 22*. Two samples were prepared simultaneously. It took 6 hours and 30 min. to carry out NaOH-Na₂CO₃ fusion and radiochemical purification of Pu and 5 hours and 40 min. to conduct HF digestion followed by anion exchange and co-precipitation. Alpha counting was not included in the time scheme. It should be noted that if a batch of four samples were to be analyzed it would take an additional 30 min. if fusion was to be used to digest samples. However if a batch of four samples were to be analyzed using HF acid digestion the analysis time would not increase from 5 h 40 min. Therefore HF acid leach is faster to carry out than NaOH-Na₂CO₃ fusion for glass fiber filters especially if multiple samples are to be analyzed simultaneously. Additionally, if NaOH-Na₂CO₃ fusion would be used, an additional step to remove the silicates that interfere the analysis should be added that would increase the time.

Conclusions

It was found feasible to digest and radiochemically separate Pu from glass fiber filters within one working day using either NaOH-Na₂CO₃ fusion or HF acid leach to dissolve the glass fiber filter material. However, if fusion were to be used that would require an additional step to remove silicates that otherwise will decrease chemical yields and interfere in the alpha spectrum.

Leaching with HF acid resulted satisfactory yields and was faster to carry out than fusion especially if multiple samples are to be analyzed together. Therefore leaching with HF acid is suggested to be used for glass fiber filters in emergency (see *Table. 12*) However if there are refractory particles present in air that do not dissolve easily into HF acid, fusion might be required to dissolve the particles.

Table. 12. Suggested Pu analysis from glass fiber filter in emergency conditions

<p>Digestion (1 h 20 min)</p> <ul style="list-style-type: none"> • Weigh the filter into a 250 mL Teflon beaker • Add ^{242}Pu tracer into the Teflon beaker • Add 10 mL HF, 10 mL HNO_3 and 10 mL HCl to Teflon beaker and evaporate to dryness at a hot plate (<i>these amounts are used for an glass fiber filter with an area of 36 cm^2 and weigh 0.29 g, adjust accordingly</i>) • Add 0.5 g boric acid and 5 mL HNO_3 and evaporate to dryness • Dissolve the residual into 30 mL 8 M HNO_3 • Filter cooled sample if needed (GF/A)
<p>Anion exchange (3 h 20 min)</p> <ul style="list-style-type: none"> • Heat and add 1 mL H_2O_2. Cover the beaker with a watch glass and heat at 90°C for 15 minutes. Add approx. 2 g (1 teaspoon) NaNO_2 to the hot solution. Let cool for 1 h. • Prepare an anion exchange column: place glass wool on bottom of the column and approx. 7.5 mL anion exchange resin Dowex 1 x 4 (50 – 100 mesh) in nitrate form into an anion exchange column (ϕ 1 cm) using 8 M HNO_3. (<i>Resins is brought to nitrate form by treating it with 25 ml conc. HNO_3 and 50 mL 8 M HNO_3</i>) Place glass wool on top of the column • Load the sample solution into the anion exchange column and wash the resin with 50 mL 8 M HNO_3 (speed ~ drop in 2-3 s). Discard the load and wash solutions unless Am is to be determined • Wash the resin with 50 mL 37% HCl. Discard the wash solution. • Elute Pu with freshly made 30 mL 37% HCl + 3 mL 1 M NH_4I solution.
<p>Co-precipitation (2 hours)</p> <ul style="list-style-type: none"> • Evaporate Pu eluate to dryness. Add few ml conc. HNO_3 and HCl and evaporate. Repeat this 2 times. • Dissolve the residual into few mL 1 M HNO_3. Transfer into plastic test tube where 0.5 mL Ce-carrier (Ce 100 $\mu\text{g}/\text{mL}$) has been added. Wash the beaker twice with few mL 1M HNO_3. Add wash solutions into the test tube. • Co-Precipitate Pu with CeF by adding 1.5 mL 40 % HF acid. Mix the sample with Vortex and place the test tube in ice bath for 30 min. • Filter the precipitate on Metricell® polypropylene membrane (0.1 μm, ϕ 25 mm) • Measure Pu with α-spectrometry

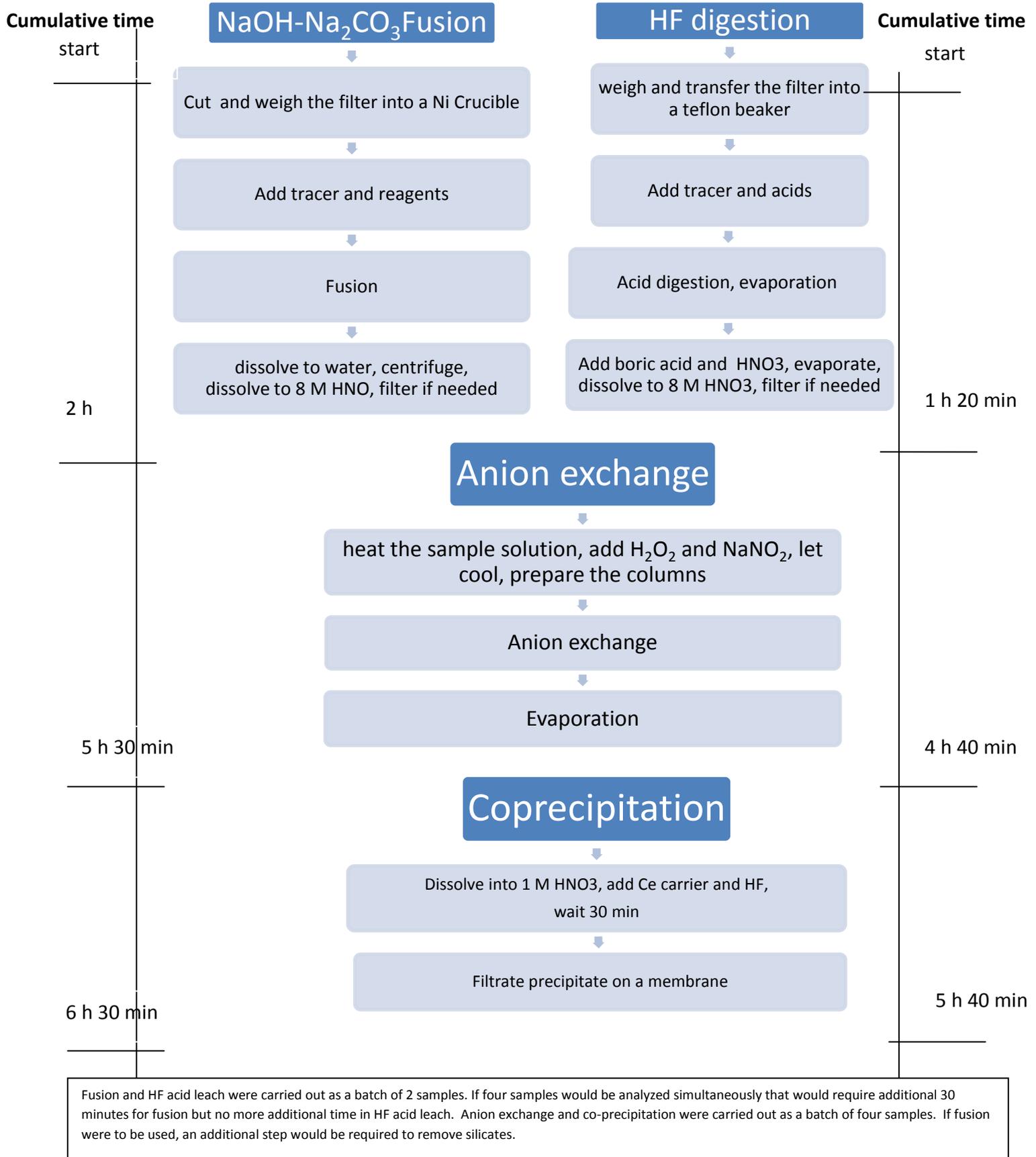


Figure. 22. Time scheme for analysis of Pu from glass fiber filters in emergency conditions

4. Conclusions

In 2014, Rapid-Tech project gathered scientists working in radiochemistry among Nordic countries and oversaw the problems and needs in developing effective radiochemical methods. Based on screening the current analytical methods for common radionuclides (e.g., Sr, actinides) assays in individual institute, challenges and future development needs were identified by each institute and presented in this report. Experiments in applying distinct novel techniques in each institute were also performed and the preliminary results obtained in each institute are assessed and summarized in this report.

In the planned continuing phase of the activity, NKS-B Rapid-Tech project aims to explore practical evaluation and experience exchange for the application of effective and automated sample processing techniques. Analytical benefits can be gained by using these novel techniques, leading to easier method optimization for distinct purposes and improvement of current radio-analytical methods.

To fulfil these objectives, an inter-comparison exercise (e.g., for determination of ^{90}Sr , actinides) will be run within the collaborative institutes to compare the analytical performance of different novel techniques (e.g., vacuum box, flow injection (FI) /sequential injection (SI), HPLC-ICP-MS). An inter-exchange program can also be planned with authorized permission for project participants, regarding specific novel techniques of interest that are applied in other partner institutes.

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Abstract max. 2000 characters	<p>NKS Rapid-Tech project 2014 aims to explore the application of different rapid techniques in determination of radionuclides, thus to improve the analytical efficiency and capacity of present radioanalytical methodologies used for different purposes in the areas of E, W and R. Specific tasks are described as follows:</p> <ul style="list-style-type: none"> • Identification of current needs and problems in methodology development for rapid determination of radionuclides (e.g., ⁹⁰Sr, actinides). • Identification of individual processes/operations wherein rapid techniques can be potentially applied to improve the analytical efficiency. • Establishment of practical solutions/suggestions in the application of rapid techniques in radiochemical procedures. • Development and optimization of rapid methods for determination of radionuclides (e.g., ⁹⁰Sr, actinides) in environmental samples using automation and effective sample treatment techniques. • Assessment of analytical performance and summarization of successes/failures, challenges and future attempts. <p>In 2014, Rapid-Tech project gathered scientists working in</p>

radiochemistry among Nordic countries and oversaw the problems and needs in developing effective radiochemical methods. Based on screening the current analytical methods for common radionuclides (e.g., Sr, actinides) assays in individual institute, challenges and future development needs were identified by each institute and presented in this report.

Experiments in applying distinct novel techniques in each institute were also performed: 1) DTU Nutech (Denmark) improved method applicability for different matrix content in Pu determination by exploring oxalate co-precipitation, and improved Sr seawater procedure; 2) STUK (Finland) improved Pu/Am source preparation technique and Pu procedure in air filter analysis for emergency preparedness; 3) IFE (Norway) improved ^{90}Sr seawater method in terms of reducing the use of fuming nitric acid and testing the application of Sr resin to ^{210}Pb analysis in water samples; 4) FOI (Sweden) tested new redox reagents for improving the stability of Pu analytical method and investigated the matrix effect on TEVA resin to improve the chemical yield of Pu. The preliminary results obtained in each institute are assessed and summarized in this report.

Key words

Rapid determination, Pu, Sr, Tc, environment analysis, emergency preparedness