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Standardization of Radioanalytical Methods for Determination of ^{63}Ni and ^{55}Fe in Waste and Environmental Samples

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Abstract

This report presents the progress on the NKS-B STANDMETHOD project which was conducted in 2014-2015, aiming to establish a Nordic standard methods for the determination of ^{63}Ni and ^{55}Fe in nuclear reactor processing water samples as well as other waste and environmental samples. Two inter-comparison exercises for determination of ^{63}Ni and ^{55}Fe in waste samples have been organized in 2014 and 2015, an evaluation of the results is given in this report. Based on the the results from this project in 2014-2015, Nordic standard methods for determination ^{63}Ni in nuclear reactor processing water and for simultaneous determination of ^{55}Fe and ^{63}Ni in other types of waste and environmental samples respectively are proposed. Meanwhile an analytical method for determination of ^{55}Fe in reactor water samples is also recommended. In addition, some procedures for sequential separation of actinides are presented for the simultaneous determinaiton of isotopes of actinides in waste samples are presented.

Key words

Radioanalysis; ^{63}Ni ; ^{55}Fe ; standard method; reactor water

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—NKS-B StandMethod project report 2015

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Abstract

This report presents the progress on the NKS-B STANDMETHOD project which was conducted in 2014-2015, aiming to establish Nordic standard method for the determination of ^{63}Ni and ^{55}Fe in nuclear reactor processing water samples and effluent from nuclear power plants which was required by European Commission, as well as other waste and environmental samples, which are important for the characterisation of decommissioning waste, repository of nuclear waste and evaluation of the environmental impact of the human nuclear activities. Based on the review of the radioanalytical methods for determination of ^{55}Fe and ^{63}Ni used in Nordic labs as well as other labs all over the world, an inter-comparison exercise for determination of ^{63}Ni and ^{55}Fe in water samples have been organized in 2014, and the evaluation report on the performance of different methods has been published as NKS report (NKS-327). Based on the evaluation, the improved methods were proposed and a new intercomparison on determination of ^{63}Ni and ^{55}Fe was implemented in 2015. Seven labs participated in the intercomparison, and an evaluation of the results is given in this report. Based on the the results from this project in 2014-2015, Two nordic standard methods for the determination of ^{63}Ni in nuclear reactor processing waters and for simultaneous determination of ^{55}Fe and ^{63}Ni in all types of nuclear waste and environmental samples respectively are proposed. In addition, radioanalytical methods for determination of actinides in waste and environmental samples were reviewed, and some procedures for sequential separation of actinides are presented for the simultaneous determination of isotopes of actinides in waste samples. A review article on the topic of radiochemical analyses in Nordic laboratories has been prepared and submitted to a peer reviewed journal for publication.

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5. Conclusion and perspectives

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1. Introduction

The NKS STANDMETHOD project was initiated in 2014, aiming to establish a close collaboration between research institutions, radiation protection authorities and nuclear industries in Nordic countries; to validate the presently applied radioanalytical methods through inter-comparison exercises; to standardize the analytical methods for the important radionuclides in the laboratories of the nuclear industry/research institutes/authorities; and to identify the new needs of the nuclear industry. The project was proposed to be implemented in two stages in 2014 and 2015, respectively. In the first stage of this project in 2014, the present status of the radioanalyses in the Nordic laboratories was reviewed by a close collaboration of 7 project partners. A Nordic inter-comparison exercise has been organized to analyse 3 samples (one spiked water and two real water samples from Forsmark nuclear power plant) for ^{63}Ni , and 7 Nordic laboratories analyzed these samples using their methods. The analytical results showed that the measured ^{63}Ni values in the spiked sample agree relatively well for all laboratories. However, the measured values in the two real nuclear reactor processing water sample are significantly scattered by a factor of more than 10 (Hou et al. 2015). This big variation is mainly attributed to the analytical method used in some laboratories, which could not effectively remove the interfering radionuclides. Based on this achievement and the proposed final goal of the project, the second stage of the project focused on: (1) to organize the second inter-comparison exercise for determination of ^{63}Ni in real samples using improved methods; (2) to validate and test the performance of the standard method; (3) to extend the inter-comparison exercise to include the determination of ^{55}Fe ; (4) to review and propose procedures for simultaneous determination of important radionuclides (uranium, plutonium, curium and americium) in nuclear process and waste samples and environmental samples to meet the requirement of the Nordic as well as EU authorities; (5) and finally to establish Nordic standard analytical methods for determination of ^{63}Ni , and to recommend methods for simultaneous determination of ^{55}Fe ; and ^{63}Ni .

The major achievements in this stage of the project are presented in this report.

2. Intercomparison exercise on determination of ^{63}Ni and ^{55}Fe in water samples

2.1 *Intercomparison samples*

Two water samples were prepared: (1) DTU-1: Spiked water samples was prepared by Technical University of Denmark by spiking ^{63}Ni , ^{55}Fe , ^{60}Co , ^{152}Eu and ^{137}Cs in 1.0 liter of tap water which was acidified to pH 1 using HNO_3 ; (2) Forsmark-1 reactor coolant water collected at Forsmark NPP unit 1,

2.0 liter samples were acidified with HNO₃, this sample contains various activation product radionuclides, mainly ³H, ⁵¹Cr, ⁵⁴Mn, ⁵⁸Co, ⁶⁰Co, ⁶⁵Zn, ^{110m}Ag and ¹²⁴Sb; This nuclear reactor processing water sample was prepared by the partner at Forsmark NPP. Table 1 summarizes the features of the two intercomparison samples.

Table 1 Composition of the intercomparison samples

Code	Sample	Matrix	Major radionuclides contained
DTU-1	Spiked tap water	1.0 L in HNO ₃	⁶³ Ni, ⁵⁵ Fe, ⁶⁰ Co, ¹³⁷ Cs
Forsmark-1	Reactor coolant water from Forsmark NPP	2.0 L water with HNO ₃	⁶³ Ni, ⁵⁵ Fe, ³ H, ⁵¹ Cr, ⁵⁴ Mn, ⁵⁸ Co, ⁶⁰ Co, ⁶⁵ Zn, ^{110m} Ag, ¹²⁴ Sb

2.2 Analytical methods used in Nordic labs for determination of ⁶³Ni and ⁵⁵Fe

Two methods were used in Nordic labs for the separation of ⁶³Ni from water samples. The first method is based on extraction chromatography using two sequential Ni columns (Fig. 1), while the second method is a combination of ion exchange chromatography (for separation of Fe also) and extraction chromatography using Ni resin (Fig. 2).

Based on the last inter-comparison results in 2014, the first method including two sequential Ni columns obtained a better separation and purification of ⁶³Ni from radioactive cobalt (⁶⁰Co and ⁵⁸Co). In this method, the water sample is first spiked with stable Ni, and then evaporated to dryness. The residue is then dissolved in 8 M HNO₃ solution. A AgI precipitation step might be carried out after addition a few milligrams of Ag⁺ carrier and HCl to remove possible ^{110m}Ag. After removed AgI precipitation using filtration or centrifuge, the filtrate or supernatant is loaded to a 2 ml TRU column (Triskem standard 2 ml column), followed by rinsing with 8M HNO₃. The influent and the rinse are combined and evaporated to near dryness. The residue is dissolved in 1 M HCl solution, ammonium citrate is added to complex most of transit element to prevent from formation of hydroxides. Ammonium solution is added to adjust pH to about 9, the solution is then loaded to the Ni column (Triskem, standard 2 ml column), and rinsing with a 0.2 M ammonium citrate-ammonium solution (pH 9) to remove matrix elements and interfering radionuclides. ⁶³Ni remained on the column as a complex of Ni-DMG (dimethylglyoxime) is eluted using 2-3M HNO₃, which can remove the DMG and the DMG-Ni complex from the resin, the eluate is evaporated to near dryness. The evaporated eluate is prepared in ammonium citrate solution again and Ni is separated again using another Ni column by the

same procedure as the first Ni column (Fig.1). Finally the eluate is used for measurement of ^{63}Ni using liquid scintillation counting after addition of scintillation cocktail.

For the determination of ^{55}Fe , there are also two methods, extraction chromatography and ion exchange chromatography as shown in Fig. 1 and 2. In the first method (Fig. 1), the solution is evaporated to dryness after the addition of stable iron as carrier and yield tracer, the residue is then dissolved with 8M HNO_3 . The prepared solution is loaded to a TRU extraction chromatographic column (Triskem, 2 ml standard column). After rinsing with 8M HNO_3 , iron on the column is finally eluted using 2M HNO_3 solution. This method can be also combined with the first method for simultaneous determination of ^{63}Ni , where the influent and rinsing solution are combined for separation of ^{63}Ni .

The second method (Fig. 2) is a combined method for simultaneous determination of ^{55}Fe and ^{63}Ni . In this method, stable Fe and Ni are added as carriers and chemical yield tracers. Eu, Co, Mn, and Cr are also added as hold-back carriers in order to improve the decontamination of the corresponding interfering radioactive isotopes of these elements which exist in the samples in a low mass concentration. Fe and Ni in the solution are first separated from the solution by hydroxide precipitation (as $\text{Fe}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$). In this case, other transit metals and actinides are also precipitated with iron. The hydroxides precipitate is dissolved using concentrated HCl, and the concentration of HCl is adjusted to 9M, the prepared solution is loaded on a strong base anion exchange chromatographic column, the column is rinsed with 9M HCl. All elements which do not form anions with Cl^- such as alkali and earth alkaline metals, rare earth elements, Ni^{2+} , Cr^{3+} , etc. will pass through the column. The influent and rinsing solution are collected for further purification of Ni. The column is further rinsed using 4M HCl to remove the most of interfering radionuclides, metals such as $^{60}\text{Co}^{2+}$, Cu^{2+} , etc. which form weak anion complex in high concentration of Cl^- but not in low concentration of Cl^- solution will be removed. Iron on the column is finally eluted using 0.5 M HCl solution, while the strong binding elements such as all anion (I^- , Br^- , etc.) and metals forming strong anion complex with Cl^- at low HCl concentration solution such as Zn^{2+} , will remain on the column. The separated iron in the eluate is finally evaporated to dryness and dissolved in H_3PO_4 solution to obtain a colorless iron solution based on the formation of colorless complex of Fe^{3+} with H_3PO_4 . The solution is used for measurement of ^{55}Fe using liquid scintillation counter by counting the Auger electrons of ^{55}Fe decay. The Ni fraction of influent and rinsing solution is evaporated to dryness, and dissolved with 1M HCl, 1M ammonium citrate is added, and the solution is adjusted to pH 9, the solution is then loaded to the Ni column (Triskem, standard 2 ml column), and rinsed with a 0.2 M ammonium citrate-ammonium solution (pH 9). ^{63}Ni remaining on the column is eluted using 3M HNO_3 , the eluate is finally evaporated to 0.2-0.5 ml and transferred to LSC vial. After addition of scintillation cocktail, ^{63}Ni is measured using LSC.

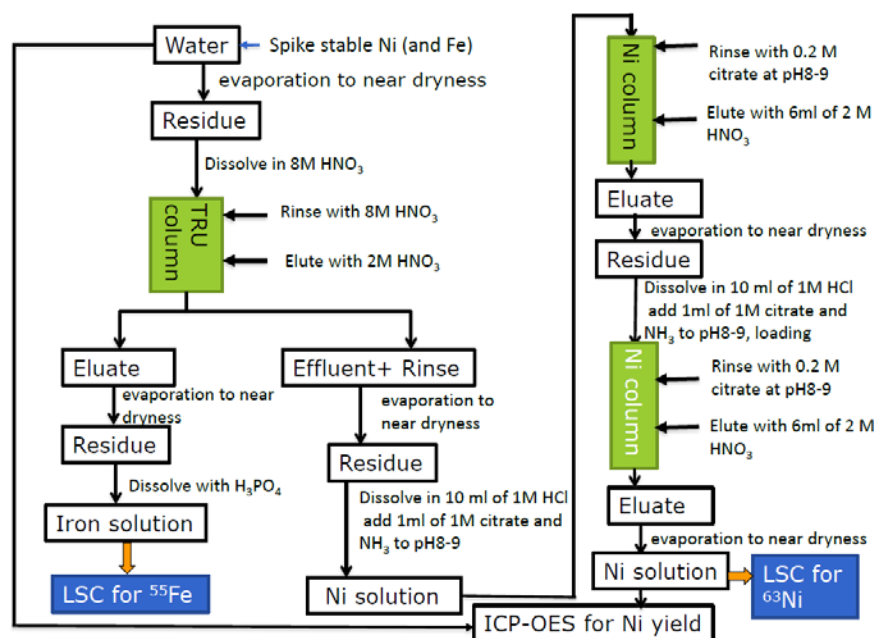


Fig. 1 Analytical procedure for determination of ^{63}Ni and ^{55}Fe in water samples using extraction chromatography (modified from Eriksson et al. 2013)

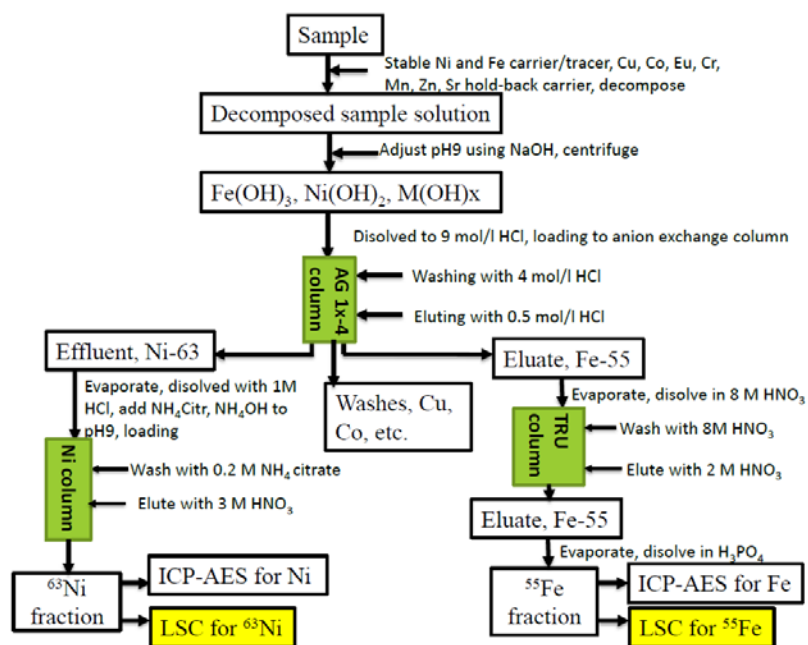


Fig. 2 Analytical procedure for determination of ^{63}Ni and ^{55}Fe using combined techniques of precipitation, ion exchange chromatography and extraction chromatography (Hou, et al. 2005)

2.3 Results of the intercomparison

Seven partner labs participated in the analysis of the two inter-comparison water samples, six laboratories reported their analytical results for ^{63}Ni , and three labs reported ^{55}Fe results. Fig. 3-4 show the analytical results of ^{63}Ni and Table 2 presents the analytical results of ^{55}Fe .

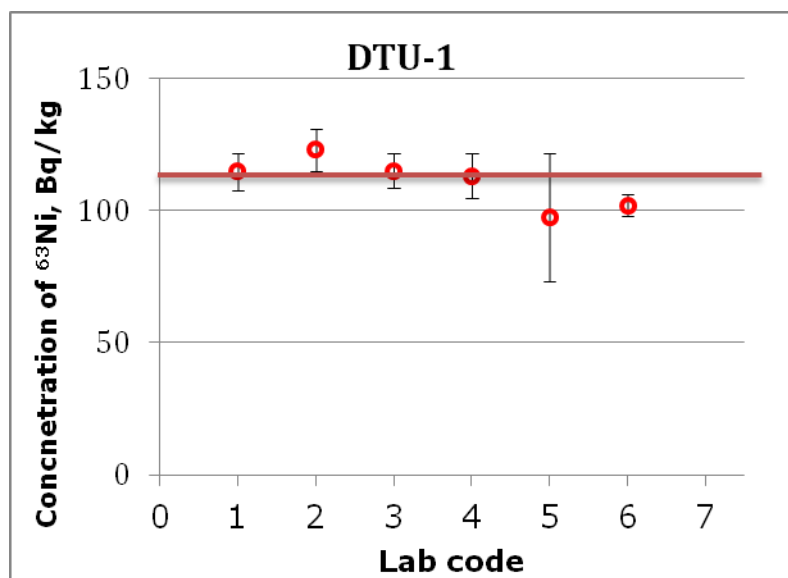


Fig. 2 Results of the inter-comparison analysis of spiked water samples for ^{63}Ni

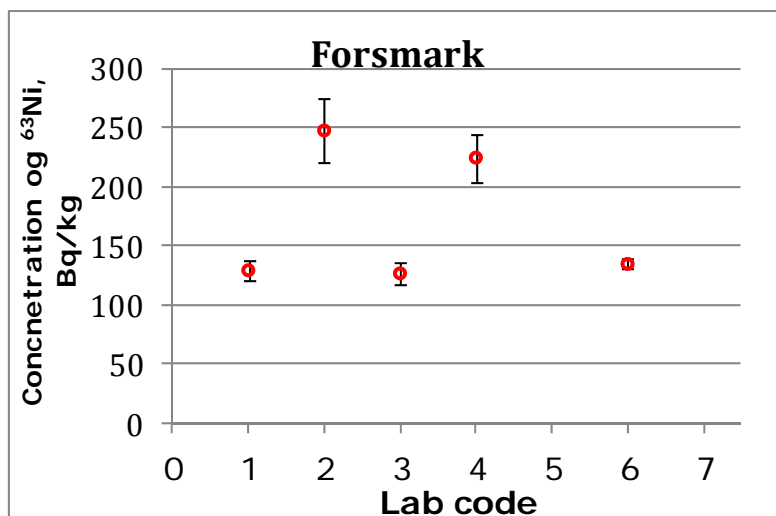


Fig. 3 Results of the inter-comparison analysis of nuclear coolant water samples for ^{63}Ni

Table 2 Results of the inter-comparison analysis of two water samples for ^{55}Fe

Lab Code	^{55}Fe concentration, Bq/kg (decay corrected to 1 May 2015)			
	DTU-1 (Spiked solution)		Forsmark-1 (coolant)	
	Value	Unc. (k=1)	Value	Unc. (k=1)
1	238.9	6.9	14.6	7.3
2	277.0	8.9	15.0	0.7
4	341.0	25.6	21.1	1.6
Spiked value	238.0	5.6		

For the spiked sample (DTU-1), the analytical results of ^{63}Ni from all 6 laboratories vary from 97.3 Bq/kg to 123.0 Bq/kg with an average 110.8 ± 9.4 Bq/kg. This is in very good agreement with the spiked concentration of ^{63}Ni of 114.3 ± 3.2 Bq/kg in this sample. This showed better results compared to the inter-comparison carried out in 2014, indicating an improvement in the analyses. This year, all laboratories that applied the first method and used only one Ni-column in the last inter-comparison have adapted the improved method by using two sequential Ni columns for Ni separation and purification. This result also indicates that all labs reported the results can perform a reliable analysis of the spiked samples for ^{63}Ni .

For the real reactor water samples (Forsmark-1 nuclear reactor coolant water), the ^{63}Ni analytical results show a relatively large variation (Fig. 4) from 127.0 Bq/kg to 248.0 Bq/kg, and one lab only reported a detection limit of 219 Bq/kg. The reported data can be classified into two groups; one group with two labs reported a value about 2 times higher than another group with 3 labs. The reactor water samples were measured by gamma spectrometry, showing high concentrations of ^{60}Co (18000 Bq/kg) and ^{58}Co (22500 Bq/kg). Meanwhile, it also contains other activated corrosion products such as ^{51}Cr , ^{54}Mn , ^{65}Zn and ^{124}Sb . The higher value reported in the two labs might be attributed to insufficient decontamination of radiocobalt and no correction for the interference of ^{58}Co . Gamma measurement of the separated Ni fraction using the first method has showed signals of ^{58}Co and ^{60}Co . Application of two Ni columns can remove most of the radiocobalt, but the decontamination factor was still not sufficiently high in one laboratory and the remained ^{58}Co and ^{60}Co was still relative higher compared to the level of ^{63}Ni . A correction for the interference of ^{60}Co has been proposed and

applied by some labs, while the interferences from ^{58}Co was not well corrected. For the reactor water sample that is analyzed shortly after collection (“fresh sample”), the ^{58}Co concentration is relative high; the unsatisfied decontamination of radiocobalt and unsuitable correction for both ^{60}Co and ^{58}Co might cause an overestimation of the ^{63}Ni concentration in the samples. However, it should be mentioned that the first method by using two Ni columns under well controlled separation procedure and with suitable correction of ^{60}Co and ^{58}Co , can produce a reliable result of ^{63}Ni in nuclear reactor processing water samples. The second method using a combined procedure of anion exchange chromatography and Ni column has reported good results for both water samples, indicating its reliability and suitability for this analysis.

Only 3 labs reported the analytical results of ^{55}Fe in two water samples. The reported ^{55}Fe concentrations in the spiked water (DTU-1) vary from 238.9 Bq/kg to 341.0 Bq/kg. The values measured by the second method (238.9 Bq/kg) is in very good agreement with the spiked value of 238.0 ± 5.6 Bq/kg, indicating a high reliability. While the other two values measured by the first method using only TRU column showed a slightly higher value (277-341 Bq/kg) compared to the spiked value (238.0 ± 5.6 Bq/kg). The reported ^{55}Fe concentrations in the reactor coolant water show a good agreement varying from 14.6 Bq/kg to 21.1 Bq/kg, considering the relatively low concentration of ^{55}Fe in this sample, the analytical results are relatively good. This might demonstrate that the labs that reported the results can perform analyses of ^{55}Fe in reactor water samples. Among these three labs, both methods were used for analysis. This also indicates that both methods can provide a reliable measurement of ^{55}Fe in nuclear reactor processing water. The slight variation of the reported results of ^{55}Fe from the three labs might be attributed to the insufficient removal of interfering radionuclides from ^{55}Fe . The beta spectra of ^{55}Fe fraction separated from reactor coolant water samples by both anion exchange chromatography and TRU extraction chromatography (Fig. 4) show the presence of other radionuclides with higher energies than ^{55}Fe . The gamma spectrometry measurement of long time (15h) confirms the presence of ^{60}Co and ^{58}Co in the separated ^{55}Fe sample (Fig. 5). This might be attributed to the more than three orders of magnitude higher ^{58}Co and ^{60}Co concentrations (30-50 kBq/L) in the reactor coolant water sample compared to ^{55}Fe . This also indicates that an improved procedure using two TRU column or anion exchange combined with TRU column might be needed for obtaining a sufficiently high decontamination of ^{60}Co and ^{58}Co for low level ^{55}Fe measurements.

It was reported by partner labs which used TRU and two Ni columns for separation of ^{63}Ni or/and ^{55}Fe that precipitate or residue in DTU sample occurred during column separation, which blocked the TRU column or significantly reduced the flow rate through the TRU column after loading the dissolved residue of evaporated water (DTU-1), and making the separation difficult. The DTU sample was prepared by spiking ^{63}Ni , ^{55}Fe and other radionuclides into tap water collected at Risø, Denmark. The

problem of residue or precipitate occurred in the experiment should be attributed to the matrix of this sample. In the tap water from Risø, Denmark, the dissolved salt content, especially calcium concentration is relative high. When the water was evaporated to dryness for pre-concentration, Ca will be converted to insoluble precipitate/residue which is not easily dissolved. If the solution with this precipitate is loaded to the TRU column or Ni-column, the column will be blocked or the flow rate will become very low. This indicates that the procedure using evaporation followed by TRU and Ni columns is only suitable for analysis of relative pure water samples with low content of dissolved salt such as coolant water of boiling water reactor and spent fuel pool water, and not suitable for other type of water including environmental water samples which might contain high dissolved salt and residues. It was noted that the laboratories which used a relatively large amount (>200 mL) of sample in the analysis, enhanced the amount of formed precipitate, and met the problem of column blockage or very low flow rate. The labs using a smaller amount (e.g. 50 mL) did not meet the problem. However, this will cause a higher detection limit and is not suitable for analysis of low level samples. In addition, one lab could not report the analytical results for ^{63}Ni in the reactor coolant water samples instead of just giving a detection limit of their method. This is because of a big variation in the results among the same samples, due to the very small difference of the analytical results of samples with the blank samples, and the variation of results in the blank samples. This is attributed to the small sample size of only 1 ml that was used for the analysis, causing the problem that no reliable ^{63}Ni could be measured. It is suggested that a bigger amount (50-200 ml) of sample should be used for the analysis.

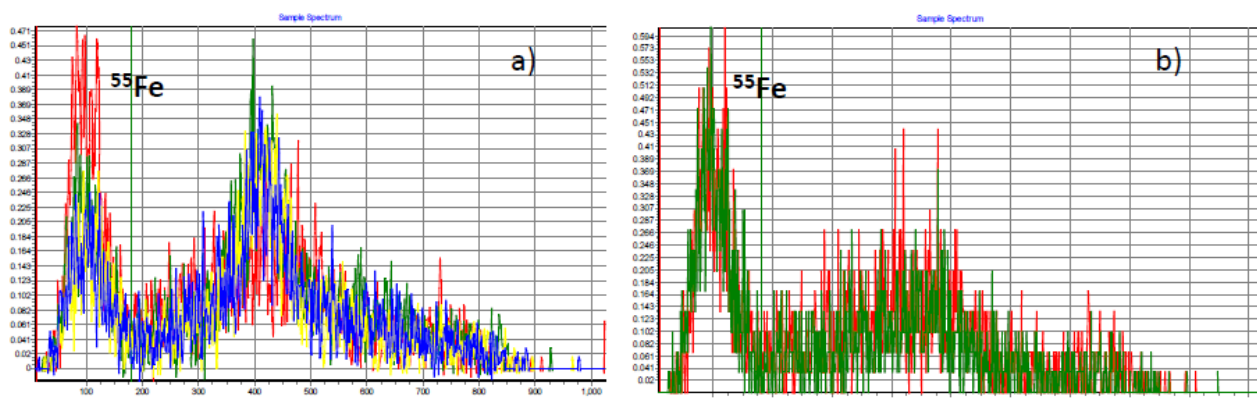


Fig. 4 LSC spectra of ^{55}Fe separated using anion exchange chromatography (a), and TRU extraction chromatography (b)

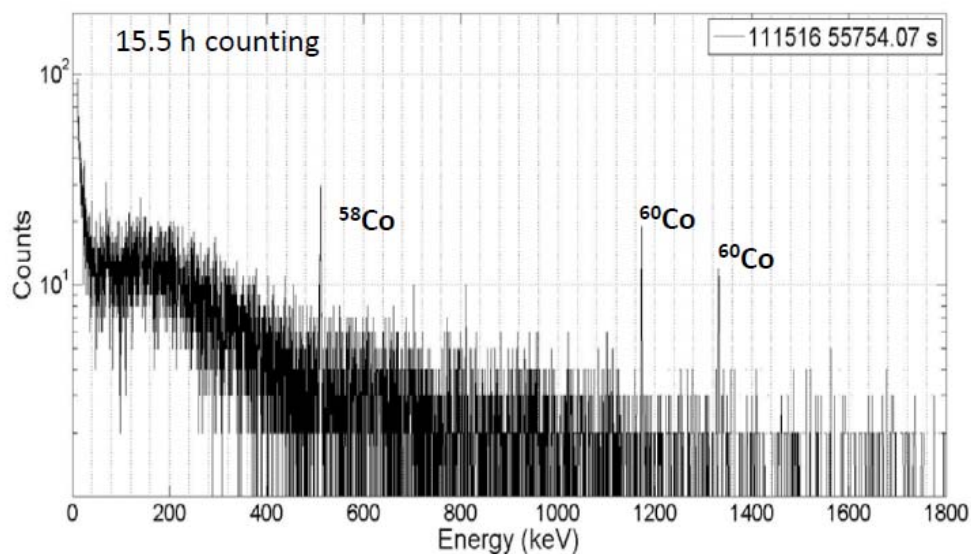


Fig. 5 Gamma spectrum of ^{55}Fe fraction separated by chromatography using anion exchange or TRU extraction chromatography for 15h, showing the presence of small amount of ^{58}Co and ^{60}Co

In the determination of ^{63}Ni using both methods, it was observed that the LSC spectrum of the separated ^{63}Ni is not very clean in the higher energy part beyond the spectrum of ^{63}Ni (Fig. 6). The gamma spectrometry measurement of the separated ^{63}Ni fraction for a long time (24.6 h) (Fig.7) indicates the presence of small amount of $^{110\text{m}}\text{Ag}$. This result suggests that a step for removal radioactive silver might be necessary for the ^{63}Ni determination, especially for low level samples.

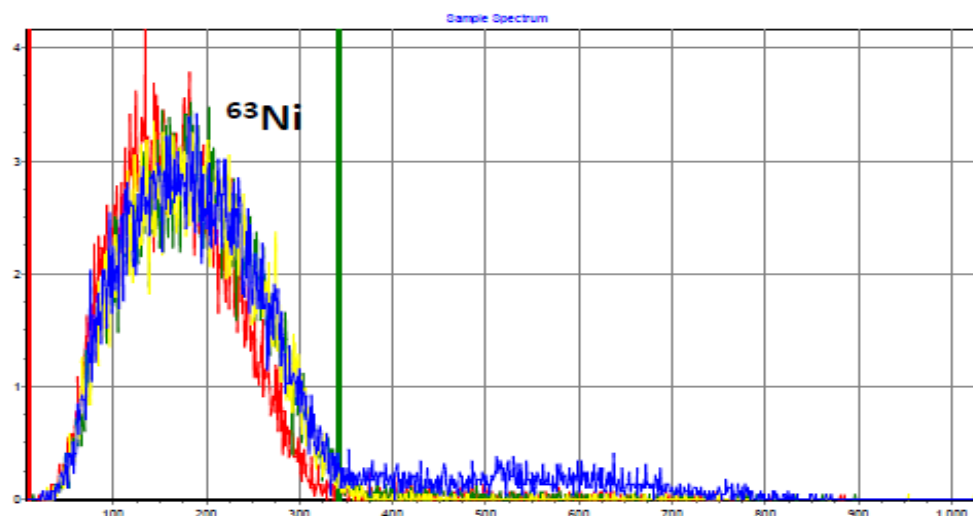


Fig. 6 LSC spectrum of ^{63}Ni separated using anion exchange and/or Ni extraction chromatography

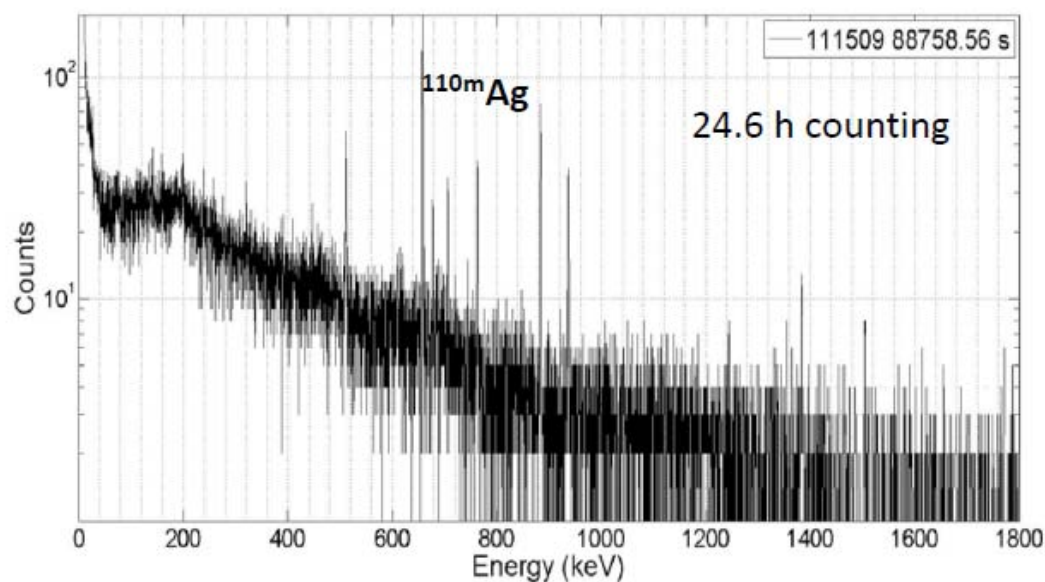


Fig. 7 Gamma spectrum of ^{63}Ni fraction separated by anion exchange and/or Ni columns

In the separation of ^{55}Fe using TRU column (Triskem standard 2 ml column), iron is often added as a carrier and chemical yield tracer. However, it was observed that the capacity of TRU resin for iron is relative small. When 2 mg of Fe^{3+} was added as carrier, the TRU column separation (Fig. 8) showed that the front band of Fe^{3+} already reaches to the bottom of the column, indicating a maximum capacity of the 2 ml TRU resin is 2 mg. This suggests that when using TRU for the separation of ^{55}Fe , the carrier added should be less than 2.0 mg. Meanwhile, it also indicates the TRU column is not suitable for the separation of ^{55}Fe from sample with high iron content, such as soil and metals.

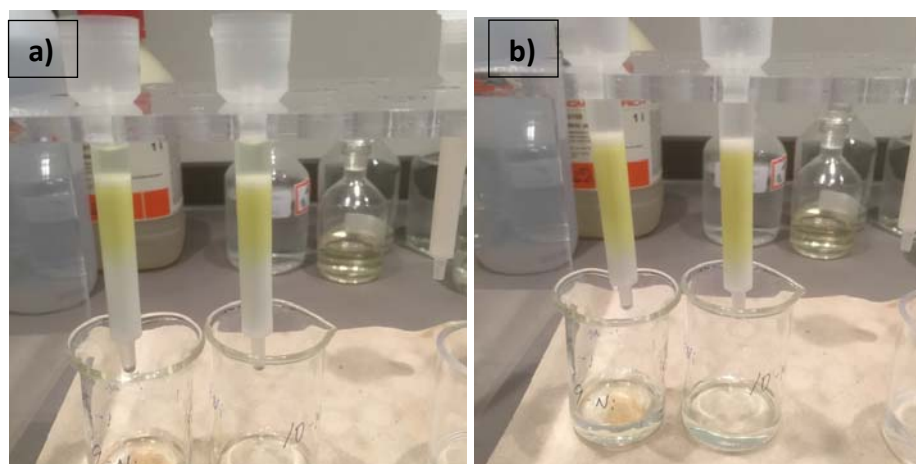


Fig. 8 Loading of solution with 2.0 mg Fe^{3+} in 8M HNO_3 (a), and rinsing with 8M HNO_3 (b)

3. Nordic standard and recommended methods for ^{63}Ni and ^{55}Fe

Based on the inter-comparisons exercises organized in 2014 and 2015 in this NKS project, two methods are proposed as Nordic standard methods for the determination of ^{63}Ni , one for nuclear reactor processing water (e.g. reactor coolant, spent fuel pool water, resin and evaporation waste) which contain less matrix elements, and another for all types of samples including environmental and waste samples (e.g. all types of water, metals, graphite, concrete, soil, sediment, etc.). The method for nuclear reactor processing water is based on evaporation, followed by a TRU column and two Ni columns separation. Measurement of radiocobalt in the separated Ni fraction has to be carried out by gamma spectrometry and a correction of the contribution of ^{60}Co (and ^{58}Co in the case of “fresh sample”) to ^{63}Ni has to be implemented. A schematic diagram of the procedure is shown in Fig. 9. A detailed procedure is presented below.

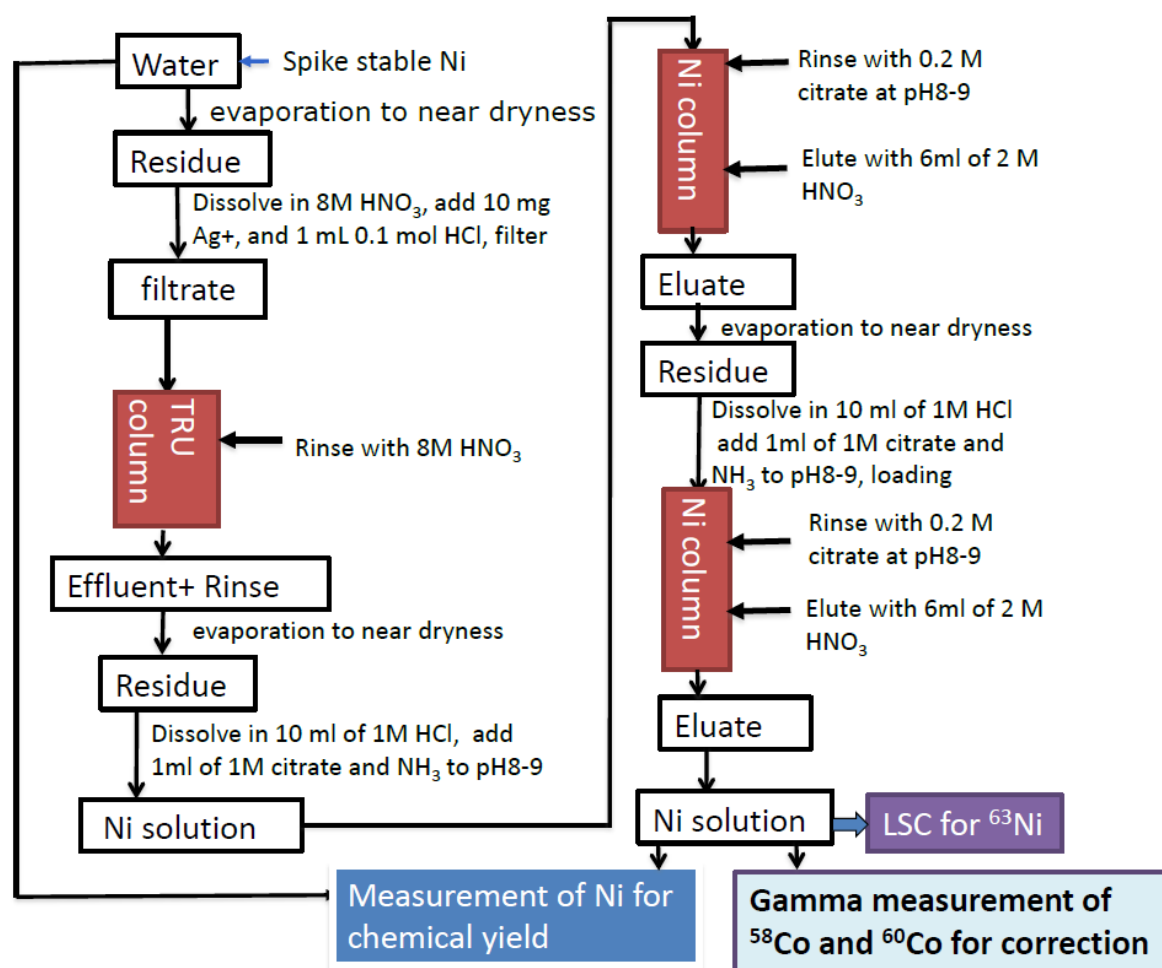


Fig. 9 Schematic diagram of Nordic standard method for determination of ^{63}Ni in reactor processing water

Nordic standard method for chemical separation and LSC measurement of ^{63}Ni from nuclear reactor processing water

- 1) Water sample (50-1000 mL, depending on the estimated concentration of ^{63}Ni) is taken to a beaker, 0.05-2.0 mg Ni^{2+} carrier is added. The sample is evaporated to dryness on a hotplate.
- 2) Dissolve the residue using 5-15 ml of 8 M HNO_3 , add 10 mg Ag^+ to the solution and mixed.
- 3) Add 1 ml of 0.1 M of HCl to the solution. After well mixed, pass the slurry/solution through a filter paper to separate the form precipitate (AgI), collect the filtrate.
- 4) Load the filtrate to a 2 mL TRU column (Triskem standard 2 mL column) which has been conditioned using 10 ml of 8M HNO_3 . After all solution passed through the column, rinse the column using 5-15 mL of 8M HNO_3 . The influent and rinse solution are collected in a beaker.
- 5) Evaporate the collected solution to near dryness (0.2-1.0 mL). Be careful, not evaporate to dryness.
- 6) Add 5-10 ml of 1M HCl to the beaker to dissolve the residue. Add 1.0 mL of 1M ammonium citrate to the solution. Add NH_3 solution to adjust pH8-9 (the colour of the solution changes from light blue to dark blue if more than 1 mg Ni carrier was added).
- 7) Load the solution to a 2 mL Ni column (Triskem, 2mL standard column) which has been conditioned using 10 mL of 0.2 M ammonium citrate solution (which was adjusted to pH8-9 using NH_3). Rinse the column using 20 mL of 0.2 M ammonium citrate solution (pH8-9), discard the influent and rinsing solution.
- 8) Elute ^{63}Ni on the Ni column using 10 mL of 2-3 M HNO_3 .
- 9) Evaporate the eluate to near dryness (0.2-1.0 mL), Be careful, not evaporate to dryness.
- 10) Add 5-10 ml of 1M HCl to the beaker to dissolve the residue. Add 1.0 mL of 1M ammonium citrate to the solution. Add NH_3 solution to adjust pH8-9 (the colour of the solution changes from light green to blue if more than 1 mg Ni carrier was added).
- 11) Load the solution to a 2 mL Ni column (Triskem, 2mL standard column) which has been conditioned using 10 mL of 0.2 M ammonium citrate solution (which was adjusted to pH8-9 using NH_3). Rinse the column using 20 mL of 0.2 M ammonium citrate solution (pH8-9), discard the influent and rinsing solution.
- 12) Elute ^{63}Ni on the Ni column using 10 mL of 2-3 M HNO_3 . Measure the total weight of the eluate, take 0.1-0.5 mL of eluate (depending on the amount of Ni carrier added) for measurement of stable Ni in the eluate and calculation of the chemical yield of Ni during separation.
- 13) Transfer the remained eluate to a LSC vial, measure ^{60}Co and ^{58}Co in the remained eluate using gamma spectrometry.
- 14) Add scintillation cocktail to the vial, measure ^{63}Ni using LSC.

- 15) Correct the ^{63}Ni activity for quench effect using a quench curve. Correct the ^{63}Ni activity for chemical yield during chemical separation; correct for a fraction of the final sample solution used for measurement of Fe.
- 16) Correct the contribution of ^{60}Co and ^{58}Co to the ^{63}Ni in the separated samples using the measured ^{58}Co and ^{60}Co by gamma spectrometry and the correction factor at different quench level for ^{58}Co and ^{60}Co respectively.

Another Nordic standard method was proposed for simultaneous determination of ^{63}Ni and ^{55}Fe in nuclear processing and waste samples and environmental samples (Hou et al. 2005). This method is based on the separation of Fe and Ni from each other and from other radionuclides using anion exchange chromatography, and purification of ^{63}Ni using Ni column. Meanwhile a pre-concentration and separation of ^{63}Ni and ^{55}Fe from sample matrix is implemented by hydroxide co-precipitation. Fig. 10 shows the schematic diagram of this procedure. The detailed method is presented below.

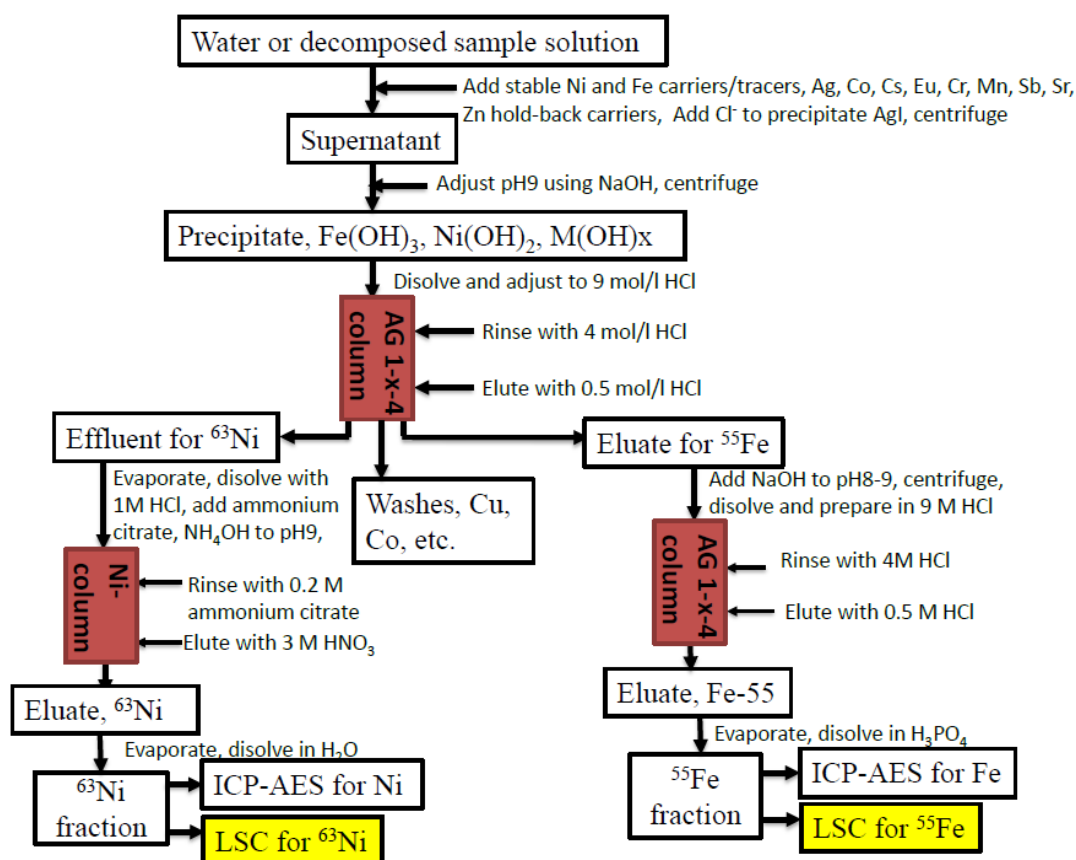


Fig. 10 Schematic diagram of standard method for simultaneous determination of ^{63}Ni and ^{55}Fe in waste and environmental samples

Nordic standard method for simultaneous determination of ^{63}Ni and ^{55}Fe in all types of samples

- 1) The solid samples are first decomposed and dissolved in acid to transfer Fe and Ni into solution; the water samples are first acidified using HNO_3 and filtered to remove suspending material, and the filtrate is collected for analysis.
- 2) To the sample solution/filtrate, 1-2 mg Ni and 2-4 mg of Fe as carriers/tracers for ^{63}Ni and ^{55}Fe and Ag, Co, Cs, Eu, Cr, Mn, Sb, Sr, Zn as hold-back carriers are added. Take 0.5-1.0 ml solution to measure the concentration of Ni and Fe for yield monitoring.
- 3) Add 0.1-1.0 M NaOH solution to the solution/filtrate to adjust pH8-9 to precipitate metals as hydroxides, centrifuge to separate precipitate. To be noticed that >0.5 M NaOH should be added when $\text{pH}>3$ to prevent from precipitation of Ca and Mg.
- 4) Dissolve the precipitate using small amount of 12M HCl, measure the volume of the solution, add 12M to adjust the final HCl concentration of 9 M.
- 5) Load the solution to a strong base anion exchange chromatographic column (e.g. AG1- \times 4 resin, Cl^- form, 1.0 cm in diameter and 25 height) which has been conditioned with 30-40 ml of 9M HCl, rinse the column with 20 ml of 9M HCl, collect the influent and 9M HCl rinse solution for ^{63}Ni determination (^{63}Ni fraction). To be noticed, a long column (35-40 cm in height) should be used for samples containing more than 100 mg of iron, such as steel or iron sample.
- 6) Rinse the column using 40-50 ml of 4M HCl, discard the rinsing solution.
- 7) Elute Fe on the column using 30 ml of 0.5 M HCl solution, transfer to a centrifuge tube.
- 8) Add 1.0 M NaOH to the eluate to adjust pH8-9, centrifuge. Dissolve the residue using 12 M HCl, measure the volume of the solution, add 12M HCl to final HCl concentration of 9M.
- 9) Load the solution to a new anion exchange chromatographic column (e.g. AG1- \times 4 resin, Cl^- form, 1.0 cm in diameter and 25 height) which has been conditioned with 30-40 ml of 9M HCl, rinse the column with 20 ml of 9M HCl and 40-50 ml of 4M HCl, discard the influent and rinsing solution.
- 10) Elute Fe on the column using 30 ml of 0.5 M HCl solution.
- 11) Evaporate the eluate to dryness, dissolve the residue with 1-2 mL of 1.0 M H_3PO_4 solution.
- 12) Transfer the solution to a LSC vial, wash the beaker 3 times using 0.5 ml of 1.0M H_3PO_4 solution each time. Combine the washing solution to the LSC vial.
- 13) Take 0.10 ml of solution for measurement of Fe (e.g. by ICP-OES, AAS), calculate the recovery of Fe during separation by comparing the amount of Fe in the final solution with the amount in the start solution.
- 14) Add scintillation cocktail to the LSC vial with sample and measure ^{55}Fe using LSC.

- 15) Correct the ^{55}Fe activity for quench effect using quench curve or standard additional method; Correct the ^{55}Fe activity for chemical yield during chemical separation; correct for a fraction of the final sample solution used for measurement of Fe and a small fraction of the start solution used for measurement of Fe.
- 16) The ^{63}Ni fraction collected from the anion exchange chromatographic separation is evaporated to dryness on a hot plate, dissolve the residue using 2 ml of 1M HCl. Add 1.0 mL of 1M ammonium citrate to the solution, then adjust pH8-9 using 1M NH_3 solution (the colour of the solution changes from light green to blue).
- 17) Load the solution to a 2 mL Ni column (Triskem, 2mL standard column) which has been conditioned using 10 mL of 0.2 M ammonium citrate solution (which was adjusted to pH8-9 using NH_3). Rinse the column using 20 mL of 0.2 M ammonium citrate solution (pH8-9), discard the influent and rinsing solution.
- 18) Elute ^{63}Ni on the Ni column using 10 mL of 3 M HNO_3 .
- 19) Evaporate the eluate to near dryness (0.2-0.5 mL), Be careful not to evaporate to dryness.
- 20) Transfer the remained solution to a LSC vial, wash the beaker 3 times using 0.5 ml H_2O of each, combine the washes to LSC vial.
- 21) Measure the total mass of the solution. Take 0.10 mL solution to a tube and measure the mass.
- 22) Determine Ni concentration in the solution, calculate the chemical yield of Ni during separation by comparing the amount of Ni in the final solution with that in the start solution/filtrate.
- 23) Add 10 ml of scintillation cocktail to the remaining Ni solution in LSC vail, measure ^{63}Ni using LSC.
- 24) Correct the ^{63}Ni activity for quench effect using quench curve or standard additional method; correct the ^{63}Ni activity for chemical yield during chemical separation; correct for fraction of the final sample solution used for measurement of Ni and a small fraction of the start solution used for measurement of Ni.

The methods for decomposition of solid samples such as graphite, steel, aluminium, lead and concrete have been reported in order to determine ^{55}Fe and ^{63}Ni by Hou et al. (2005). For soil and sediment samples, an acid leaching can be applied because ^{55}Fe and ^{63}Ni in the environmental sample is mainly released from nuclear facilities, which should present on the surface of the soil and sediment samples and can be quantitatively leached out using acid (or aqua regia). The biological samples such as vegetation and animal can be first ashed at 450-500 $^{\circ}\text{C}$, then dissolved in HNO_3 or aqua regia. High temperature ($>600^{\circ}\text{C}$) ashing should be avoided to prevent the formation of refractory compound of Fe and Ni.

A Nordic method for determination of ^{55}Fe in nuclear reactor processing water is recommended. This method is based on the separation of Fe using TRU extraction chromatography. Fig. 11 shows the schematic diagram of the analytical procedure. The detailed analytical method is presented below.

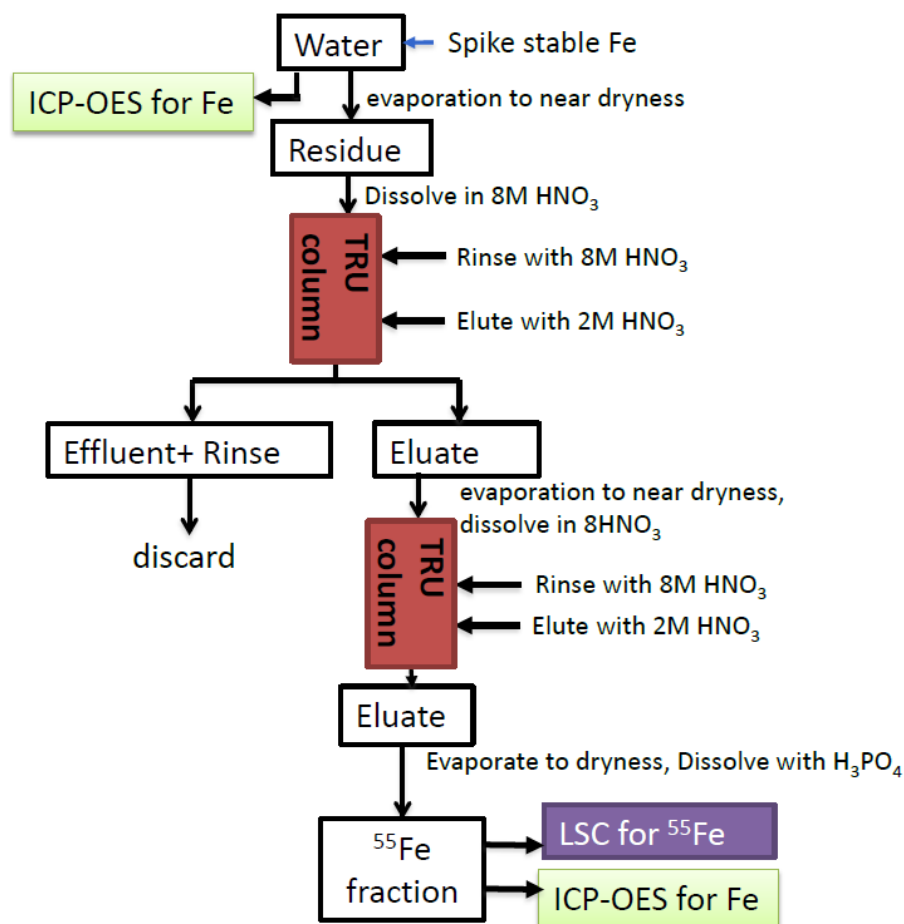


Fig. 11 Schematic diagram of recommended method for determination of ^{55}Fe in reactor processing water

Nordic recommended method for determination of ^{55}Fe in nuclear reactor processing water

- 1) Water sample (50-500 mL, depending on the estimated concentration of ^{55}Fe) is taken to a beaker, add 0.5-1.0 mg Fe^{3+} carrier. 1-2 g sample is taken for measurement of stable iron concentration. The sample is evaporated to dryness on a hotplate.

- 2) Dissolve the residue using 5-15 ml of 8 M HNO_3 , add 10 mg Ag^+ to the solution and mixed.
- 3) Add 1 ml of 0.1 M of HCl to the solution. After well mixed, pass the slurry/solution through a filter paper to separate the form precipitate (AgI), collect the filtrate.
- 4) Load the filtrate to a 2 mL TRU column (Triskem standard 2 mL column) which has been conditioned using 10 ml of 8M HNO_3 . Rinse the column using 5-15 mL of 8M HNO_3 .
- 5) Elute Fe on the column using 10 mL of 2.0 M HNO_3 . Evaporate the eluate to dryness.
- 6) Dissolve the residue using 5 mL of 8 M HNO_3 .
- 7) Load the solution to a new 2 mL TRU column (Triskem standard 2 mL column) which has been conditioned using 10 ml of 8M HNO_3 . Rinse the column using 5-15 mL of 8M HNO_3 .
- 8) Elute Fe on the column using 10 mL of 2.0 M HNO_3 . Evaporate the eluate to dryness.
- 9) Dissolve the residue using 2-5 mL of 1M H_3PO_4 solution. Transfer the solution to a LSC vial. Wash the beaker 3 times using 0.5 ml of 1.0M H_3PO_4 solution each time. Combine the washing solution to the LSC vial.
- 10) Take 0.10 ml of solution for measurement of Fe (e.g. by ICP-OES, AAS), calculate the recovery of Fe during separation by comparing with the Fe added to sample.
- 11) Add scintillation cocktail to the LSC vial with sample and measure ^{55}Fe using LSC.
- 12) Correct the ^{55}Fe activity for quench effect using quench curve or standard additional method; Correct the ^{55}Fe activity for chemical yield during chemical separation; correct for a fraction of the final sample solution used for measurement of Fe and a small fraction of the start solution used for measurement of Fe.

The analytical method for ^{55}Fe can be also combined with the method for ^{63}Ni to simultaneous determination of ^{55}Fe and ^{63}Ni in nuclear reactor processing water. In this case, both Fe and Ni carriers should be added to the sample before chemical treatment. The nuclear reactor processing water in this report refers to reactor coolant water, spent fuel pool water, and evaporated waste waters. The major feature of this sample is its relative high purity in view of dissolved metals and other salts. Fig. 12 shows the combined procedure for simultaneous determination of ^{55}Fe and ^{63}Ni .

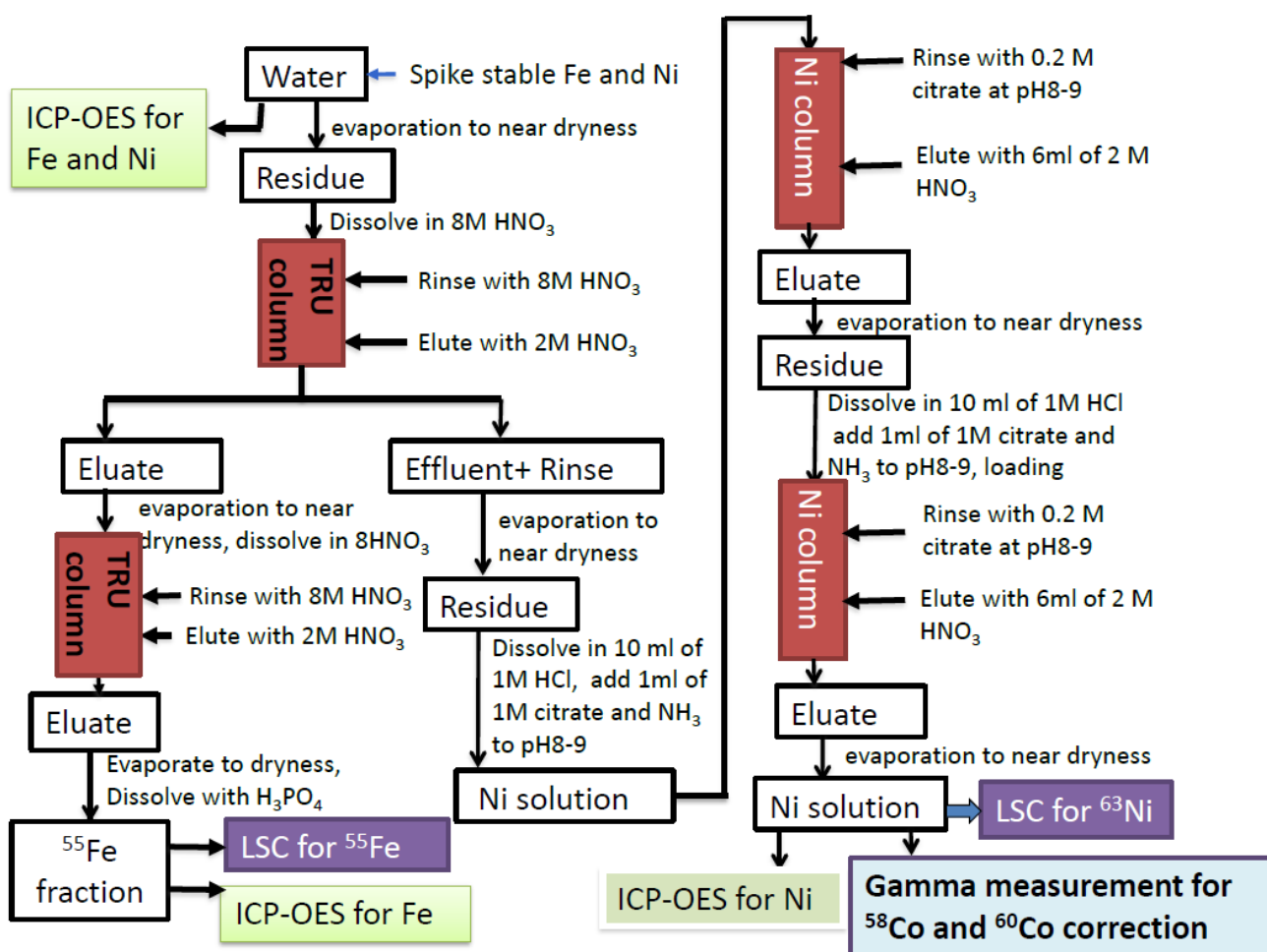


Fig. 12 A combined method for simultaneous determination of ^{63}Ni and ^{55}Fe in nuclear reactor processing water sample

4. Procedures for simultaneous determination of isotopes of actinides

Actinides, as a group of radioactive elements, are often required to be determined for monitoring of radioactive level in reactor processing water, characterization of nuclear waste, as well as environmental radioactivity and environmental tracer studies using radionuclides. These radionuclides normally include isotopes of uranium ($^{234}, ^{235}, ^{236}, ^{238}\text{U}$), plutonium ($^{238}, ^{239}, ^{240}, ^{241}\text{Pu}$) and curium ($^{242}, ^{233}, ^{234}\text{Cm}$), ^{237}Np and ^{241}Am . Among these radionuclides, ^{241}Pu is a pure beta emitter, it needs to be measured by beta counting, mass spectrometry or indirectly measured by alpha spectrometry using the decay daughter of ^{241}Am . ^{241}Am emits measurable gamma ray during its alpha decay, therefore can be measured using gamma spectrometry when the concentration is sufficiently high, but often measured

by alpha spectrometry in low level. All others are pure alpha emitting radionuclides, therefore measured by alpha spectrometry and mass spectrometry.

Many methods have been reported for the determination of isotopes of different actinides using various chemical separation procedures. To improve the analytical efficiency and rapid analysis of all interesting actinides for purposes of monitoring of reactor processing water and emergency analysis, procedures for simultaneous determination of isotopes of multi-actinides are required. Numerous combined procedures for simultaneous determination of actinides have been reported (Ramebäck & Skålberg 1999; Salminen et al. 2004; Nygren et al. 2007; Maxwell 2008; Qiao, et al. 2013, 2015; Dai, et al. 2014). Based on a review of the published methods, three procedures for simultaneous determination of actinides are presented below (Fig. 13, 14, 15), which might be considered in development of Nordic recommended methods for simultaneous determination of actinides in reactor processing water, waste sample and environmental samples.

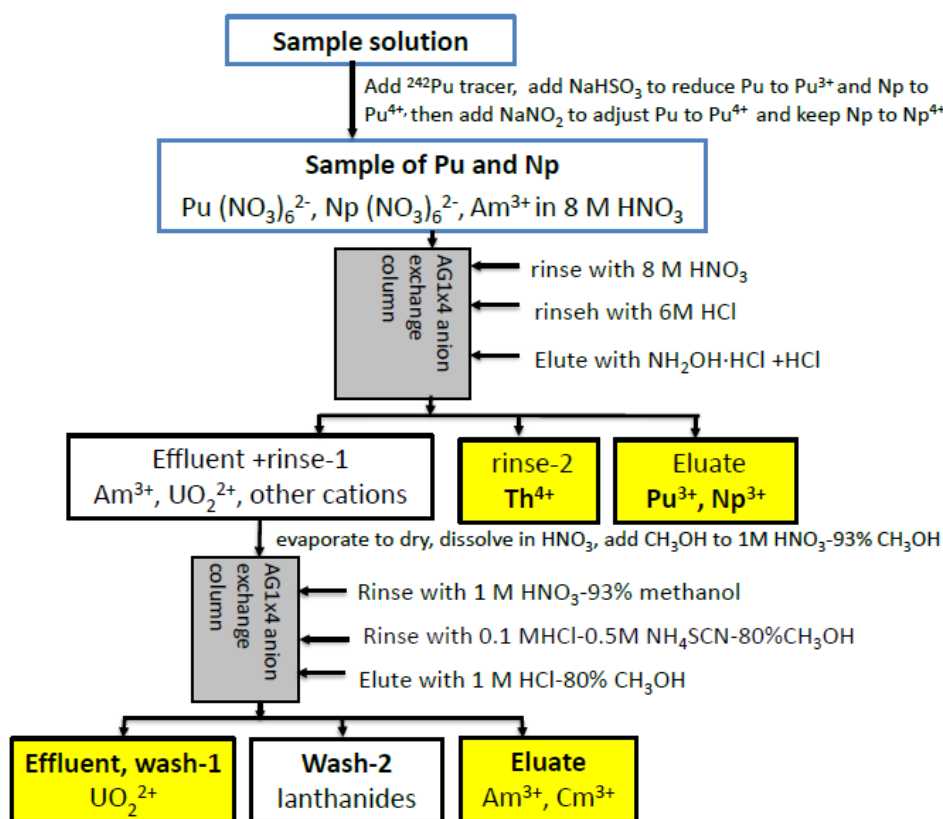


Fig. 13 A combined procedure for simultaneous determination of isotopes of Th, U, Pu, Np, Am and Cm based on anion exchange chromatography

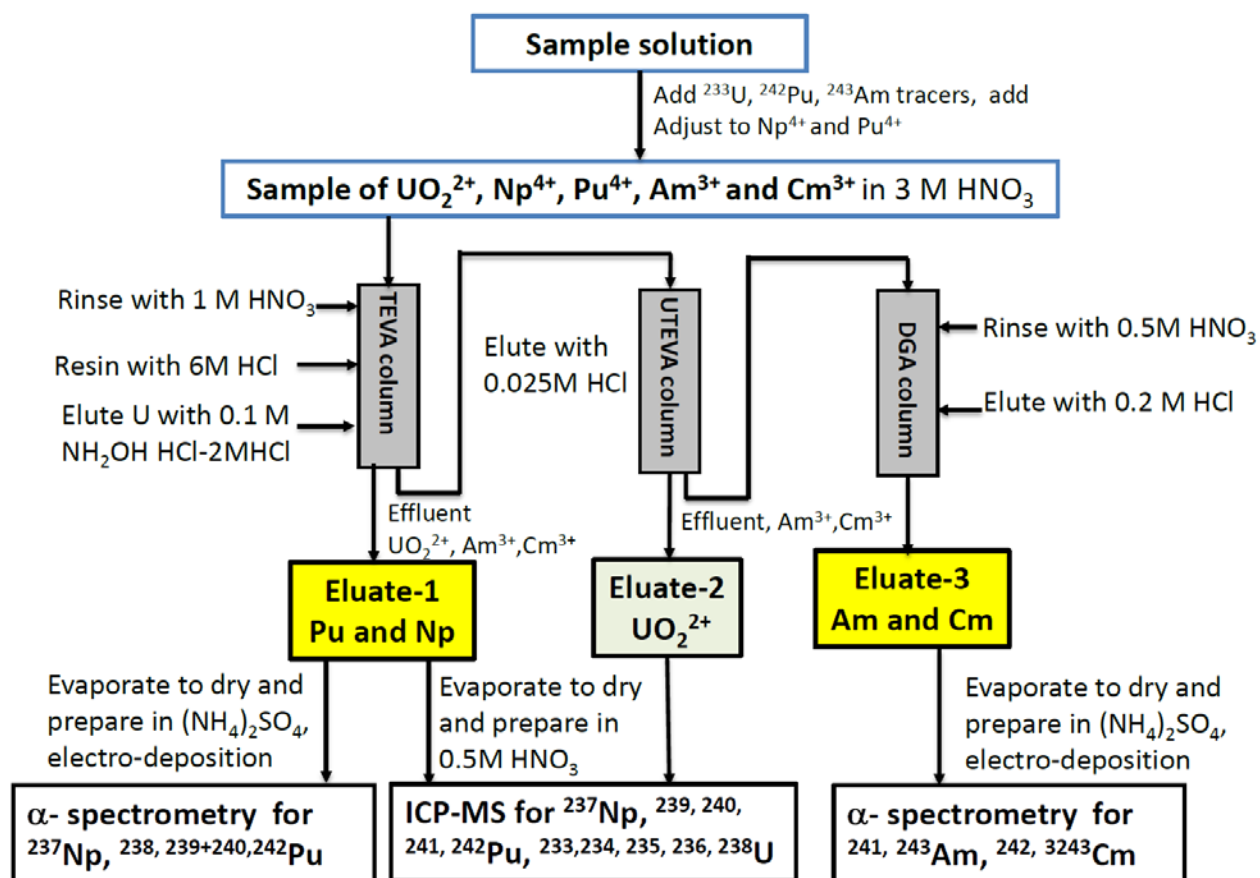


Fig. 14 A combined procedure for simultaneous determination of isotopes of U, Np, Pu, Am and Cm using sequential extraction chromatography separation and measurements using alpha spectrometry and ICP-MS.

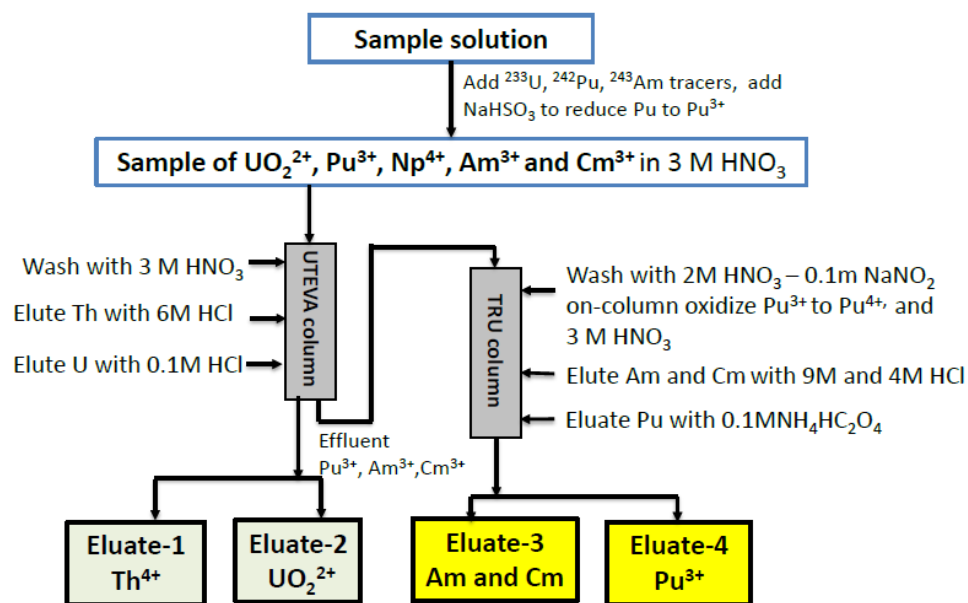


Fig. 15 A combined procedure for simultaneous determination of actinides using UTEVA and TRU columns.

5. Review article

A review article entitled on "Progress and perspective on radiochemical analysis of radionuclides in Nordic countries" has been prepared under a close collaboration with all partners of NKS STANDMETHOD project. The manuscript of the review article has been submitted to J. Radioanal. Nucl. Chem. for publication. The content of this review article is listed below:

- 1) Introduction
- 2) Requirements of radiochemical analysis in Nordic countries
- 3) Present status of radioanalytical chemistry for determination of important radionuclides of difficult to measure
 - 3.1) Major fission products (^{90}Sr , ^{99}Tc , ^{129}I)
 - 3.2) Major activation products (^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{63}Ni , ^{89}Sr)
 - 3.3) Actinides (isotopes of Th, U and Pu, Np, Am and Cm)
- 4) Recent progress on radiochemical analysis of radionuclides
 - 4.1) Measurement techniques
 - 4.2) Radiochemical separation techniques
 - 4.3) Speciation analysis of radionuclides

4.4) Rapid, automated and multi-radionuclides simultaneous determination

Tritium and ^{14}C

- ^{36}Cl and ^{129}I
- ^{55}Fe , ^{63}Ni and ^{59}Ni
- ^{41}Ca and ^{90}Sr
- Actinides (U, Np, Pu, Am and Cm)

5) Summary and perspectives

6. Summary and Remarks

Throughout this project, the collaboration in radioanalyses among Nordic labs, especially laboratories from Nordic nuclear power plants and other nuclear industry has been strengthened. Under a close cooperation, a review article on the present status of radioanalytical chemistry in the Nordic laboratories and perspective of the radiochemical analysis of radionuclides has been prepared. The analytical methods for determination of ^{55}Fe and ^{63}Ni in reactor processing water and other types of waste and environmental samples has been critical reviewed. Two inter-comparison exercises for the determination of ^{63}Ni and ^{55}Fe in water samples have been organized in 2014 and 2015. The problems in the first run of intercomparison in 2014 have been solved in the second run of the intercomparison, and the performance of analysis in the partner labs have been significantly improved through the intercomparison exercises. Based on the results, two Nordic standard methods are proposed, one method is for the determination of ^{63}Ni in nuclear reactor processing waters, and another method is for simultaneous determination of ^{55}Fe and ^{63}Ni in other types of waste and environmental samples. Meanwhile a Nordic method for determination of ^{55}Fe in nuclear reactor processing water is recommended.

Besides ^{55}Fe and ^{63}Ni , other radionuclides are also determined in Nordic labs. Among them isotopes of actinides are important ones not only in waste treatment, decommissioning, environmental radioactivity studies and emergency analysis, but also in the monitoring of the process in the nuclear power plants. Based on a review of the present methods for the determination of actinides, a few procedures for the simultaneous determination of isotopes of actinides are proposed. A further development and confirmation of these methods is expected in order to promote the rapid and accurate analysis of these radionuclides in Nordic laboratories.

References

- Dai X.X., Kramer-Tremblay S. Five-column chromatography separation for simultaneous determination of hard-to-detect radionuclides in water and swipe samples, *Anal. Chem.* 2014, 86:5441-5447.
- Eriksson S., Vesterlund A., Olsson M., Rameback H. Reducing measurement uncertainty in Ni-63 measurements in reactor coolant water with high ^{60}Co activity, *J. Radioanal. Nucl. Chemistry*, 2013, 296(2): 775-779.
- Hou X.L., Frøsig Østergaard L., Nielsen S.P. (2005). Determination of ^{63}Ni and ^{55}Fe in nuclear waste samples using radiochemical separation and liquid scintillation counting. *Anal. Chim. Acta*, 2005, 535 : 297-307.
- Maxwell S.L. Rapid method for determination of Pu, Am and Am in large soil samples. *J. Radioanal. Nucl. Chem.* 2008, 275(2):395-402.
- Nygren U., Ramebäck H., Nilsson C. Age determination of plutonium using ICP-MS, *J. Radioanal. Nucl Chem.*, 2007, 272: 45-51
- Qiao J.X., Hou X.L., Steier P., Golser R., Sequential injection method for rapid and simultaneous determination of ^{236}U , ^{237}Np , and Pu isotopes in seawater, *Anal. Chem.*, 2013, 85(22): 11026-11033.
- Qiao J.X., Shi K.L., Hou X.L., Nielsen S.P., Roos P., Rapid multi-sample analysis for simultaneous determination of anthropogenic radionuclides in marine environment, *Environment. Sci. Technol.* 2014, 48:3935-3942.
- Ramebäck H., Skålberg M. A sequential procedure for the analysis of ^{90}Sr , ^{154}Eu , and the actinides ^{237}Np , ^{239}Pu , ^{241}Am and ^{244}Cm . *J. Radioanal. Nucl. Chem.*, 1999, 240(2): 661-663.
- Salminen S.; Outola I.; Pulli S.; Jaakkola T., Pulli S.; Zillacus R.; Lehto J., Method for determining plutonium in air filters in detection of nuclear activities, *Radiochimica Acta*, 2004, 92(8): 467-473.

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Abstract max. 2000 characters	This report presents the progress on the NKS-B STANDMETHOD project which was conducted in 2014-2015, aiming to establish a Nordic standard methods for the determination of ^{63}Ni and ^{55}Fe in nuclear reactor processing water samples as well as other waste and environmental samples. Two inter-comparison exercises for determination of ^{63}Ni and ^{55}Fe in waste samples have been organized in 2014 and 2015, an evaluation of the results is given in this report. Based on the the results from this project in 2014-2015, Nordic standard methods for determination ^{63}Ni in nuclear reactor processing water and for simultaneous determination of ^{55}Fe and ^{63}Ni in other types of waste and environmental samples respectively are proposed. Meanwhile an analytical method for determination of ^{55}Fe in reactor water samples is also recommended. In addition, some procedures for sequential separation of actinides are presented for the simultaneous determinaiton of isotopes of actinides in waste samples are presented.
Key words	Radioanalysis; ^{63}Ni ; ^{55}Fe ; standard method; reactor water