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Progress on Radiochemical Analysis for  
Nuclear Waste Management in  
Decommissioning

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## **Abstract**

This report summarized the progress in the development and improvement of radioanalytical methods for decommissioning and waste management completed in the NKS-B RadWaste 2011 project. Based on the overview information of the analytical methods in Nordic laboratories and requirement from the nuclear industry provided in the first phase of the RadWaste project (2010), some methods were improved and developed. A method for efficiently separation of Nb from nuclear waste especially metals for measurement of long-lived  $^{94}\text{Nb}$  by gamma spectrometry was developed. By systematic investigation of behaviours of technetium in sample treatment and chromatographic separation process, an effective method was developed for the determination of low level  $^{99}\text{Tc}$  in waste samples. An AMS approachment was investigated to measure ultra low level  $^{237}\text{Np}$  using  $^{242}\text{Pu}$  for AMS normalization, the preliminary results show a high potential of this method. Some progress on characterization of waste for decommissioning of Danish DR3 is also presented.

## **Key words**

Radioanalysis, radionuclides, decommissioning, radioactive waste

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# Progress on Radiochemical Analysis for Nuclear Waste Management in Decommissioning

—NKS-B RadWaste project report 2011

Edited by *Xiaolin Hou*

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## 1. Introduction

With the increased numbers of nuclear facilities have been closed and are being or are going to be decommissioned, it is required to characterise the produced nuclear waste for its treatment by identification of the radionuclides and qualitatively determine them. Of the radionuclides related to these activities, the pure beta and alpha emitters have to be chemical separated from the matrix and other radionuclides before measurement. Although much effort has been carried out, the accurate determination of them is still a major challenge because of the complex matrix and high requirement in radiochemical separation of radionuclides.

In order to improve and maintain the Nordic competence in analysis of radionuclides in waste samples, a NKS B project on this topic was launched in 2009. During the first phase of the NKS-B RadWaste project (2009-2010), a good achievement has been reached on establishment of collaboration, identifying the requirements from the Nordic nuclear industries and optimizing and development of some analytical methods (Hou et al. NKS-222, 2010). In the year 2011, this project (NKS-B RadWaste2011) continued. The major achievements of this project in 2011 include: (1) development of a method for determination of long-lived  $^{94}\text{Nb}$  in the nuclear waste; (2) development of a sensitive method for measurement of  $^{237}\text{Np}$  using AMS; (3) improvement of analytical method for determination of  $^{99}\text{Tc}$  using ICP-MS; (4) improvement of method for  $^{14}\text{C}$  measurement using LSC; and (5) Characterization of steel samples from Danish research reactor DK-3 for decommissioning. These progresses are summarized below.

## 2. Development of analytical method for measurement of $^{94}\text{Nb}$

$^{94}\text{Nb}$  is one of the important radionuclides in the waste depository due to its long half-life ( $2 \times 10^4$  y), and relative high inventory in the nuclear waste, specially the construction materials such as stainless steel dismantled from nuclear reactor.

Niobium has only one stable isotope,  $^{93}\text{Nb}$ , and more than 30 radioisotopes. Beside  $^{94}\text{Nb}$ ,  $^{93\text{m}}\text{Nb}$  (16.1 y) is another important radioisotope of Nb.  $^{94}\text{Nb}$  and  $^{93\text{m}}\text{Nb}$  are both fission products of uranium and plutonium, but the fission yield of  $^{94}\text{Nb}$  is very low, only one millionth of a percent.  $^{94}\text{Nb}$  and  $^{93\text{m}}\text{Nb}$  in are also produced by neutron activation reactions of stable niobium, via  $^{93}\text{Nb}(n,\gamma)^{94}\text{Nb}$  and  $^{93}\text{Nb}(n,$

n)  $^{93m}\text{Nb}$ , which is the major route of their production in the nuclear waste, because stable niobium ( $^{93}\text{Nb}$ ) exists as a component or impurity in the structural materials, nuclear reactor pressure vessels and cladding of nuclear fuel. Due to relative short half life (16.1 year), most of  $^{93m}\text{Nb}$  produced from  $^{93}\text{Nb}$  and fission of uranium quickly decay within 100 years. However,  $^{93m}\text{Nb}$  is a also decay daughter of long-lived  $^{93}\text{Zr}$  (1.53 Ma) and  $^{93}\text{Mo}$  (4 ka), therefore it will be one of the major radionuclides of Nb in the waste.  $^{93m}\text{Nb}$  decays by isomeric transition with emission of 30 keV gamma ray of very low intensity, therefore difficult to be measured. However, the amount of  $^{93m}\text{Nb}$  can be easily estimated from the concentration of  $^{93}\text{Mo}$  and  $^{93}\text{Zr}$  in the aged nuclear waste. This work does not focus on its determination.

$^{94}\text{Nb}$  decays to excited state of  $^{94g}\text{Mo}$  (5.0 ps) by emission of beta particles with a maximum energy of 471 keV. This excited state in turn decays to stable  $^{94}\text{Mo}$  by emission of gamma rays of 702.6 keV (97.9%) and 871.1 keV (100%) (Fig. 1). It therefore can be easily measured by gamma spectrometry. However, the concentration of  $^{94}\text{Nb}$  in the nuclear waste is normally some orders of magnitude lower compared with other radionuclides such as  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ , therefore completely overlapped by Compton background of  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  in the gamma spectra. As a consequence chemical separation is necessary to be able to measure its activity.

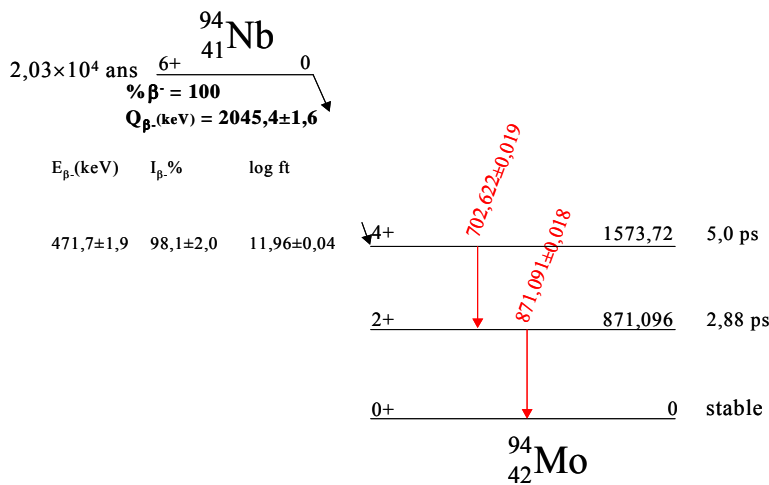


Fig. 1. Decay scheme of  $^{94}\text{Nb}$

The work aims to establish a fast and reliable method for the separation of niobium from sample matrix and most of interfering radionuclides, such as  $^{60}\text{Co}$ ,  $^{58}\text{Co}$ ,  $^{54}\text{Mn}$ ,  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ , and  $^{65}\text{Zn}$ . Since the high concentration of stable Nb in construction materials of nuclear reactor, especially stainless less with Nb

as a component, and the high neutron exposure of the construction materials, the metals (stainless steel) samples collected from a decommissioned nuclear reactor are used for this study.

Niobium belongs to 5<sup>th</sup> group elements in the periodic table, existing in four valence state from +2 to +5, but absolutely the most common oxidation state is +5. The most stable oxide of niobium is pentoxide, Nb<sub>2</sub>O<sub>5</sub>, it is very insoluble in water and normal acid, but dissolves in HF. It can be also dissolved by alkali fusion. Due to its high oxidation state Nb(V) does not form simple cation (M<sup>5+</sup>) in aqueous solutions, and exists only in complex ion forms. In acid solutions niobium exists as a niobyl oxocation NbO<sup>3+</sup> and forms complexes with the anions of the acid, such NbOF<sub>5</sub><sup>2-</sup> in hydrofluoric acid. Only in concentrated hydrofluoric acid niobium forms complex in nonoxic forms MF<sub>6</sub><sup>-</sup> and NbF<sub>7</sub><sup>2-</sup>. Niobium is readily hydrolyzable forming insoluble hydrous oxide with a nonstoichiometric composition. The soluble hydrolysis product in slightly acidic to neutral pH is niobic acid HNbO<sub>3</sub> (or Nb(OH)<sub>5</sub>), which turns into niobate NbO<sub>3</sub><sup>-</sup> (or Nb(OH)<sub>6</sub><sup>-</sup>) in the pH above 7. Since the solubility of niobium is very low these species exist in solutions in only very low concentrations. Nb has a strong tendency to form colloids in solutions. To ensure a true solution, strong complexing agents, such as F<sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, are added to the solution. Trace amounts of niobium are unstable in acid solution without complex forming anions and tends to adsorb on glassware, and on many precipitates, such as sulfides, hydroxides and zirconium phosphate and silica gel. Based on the insolubility of Nb<sub>2</sub>O<sub>5</sub> in most acids, niobium can be separated by successive precipitations as Nb<sub>2</sub>O<sub>5</sub> (Espartero *et al.* 1998). Relying on the formation of stable anion complex of Nb in HF acid, anion exchange (Osvath *et al.* 2008) can be used for its separation. Solvent extraction has also been used for the separation of Nb (Bombard, 2005). In addition, it has been reported that Nb can be sufficiently adsorbed on silica gel (Lin & Ting, 1976), this property can be also used for rapid separation of Nb from interferences. Based on the chemical properties of Nb, two chemical separation procedures, anion exchange chromatography and silica gel adsorption, were investigated for its separation.

## **2.1 Experimental**

### *(1) Sample and Nb carrier*

Four stainless steel samples, which has been exposed to a neutron irradiation in a research reactor, were used in this work, the gamma measurement showed the dominated radioactivity of <sup>60</sup>Co (0.4-0.7

MBq/g) in these samples, as well as visible gamma rays of  $^{152}\text{Eu}$ . The radiochemical analysis with chemical separation and LSC measurement showed a relative high  $^{55}\text{Fe}$  (100-1000 Bq/g) and  $^{63}\text{Ni}$  (100-500 Bq/g). The stainless steel samples were dissolved using mixtures of concentrated HCl,  $\text{HNO}_3$  and HF at  $200^\circ\text{C}$ . The solution was used for the method development in this work.

A carrier solution of niobium was prepared using niobium pentoxide.  $\text{Nb}_2\text{O}_5$  (>99.9%) powder was weighed in a Teflon beaker, concentrated HF (22 M) was added to dissolve the oxide by heating on a hot plate. The solution was evaporated to about 1 ml, 2 ml of 1 M  $\text{H}_2\text{C}_2\text{O}_4$  solution is added to condition the solution. Finally the carrier solution was transferred to a bottle with 0.1 M HF solution. The concentration of Nb in the solution was obtained by the weight of the  $\text{Nb}_2\text{O}_5$  and the volume of the final solution.

#### *(2) Radioisotope tracers*

Due to the difficulties in obtaining a  $^{95}\text{Nb}$  (or  $^{95}\text{Zr}$ - $^{94}\text{Nb}$ ) tracer solution in 2011, stable Nb is used to measure the chemical recovery of  $^{94}\text{Nb}$  during chemical separation.

$^{60}\text{Co}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$  and  $^{152}\text{Eu}$  solutions of activity 200-500 Bq/ml in  $\text{HNO}_3$  media were supplied by Risø National Laboratory and used for investigation of the decontamination of these radionuclides in the chemical separation.

#### *(3) Measurement of stable Nb by ICP-MS*

Stable Nb ( $^{93}\text{Nb}$ ) in the separated solution was measured by ICP-MS (Thermo Scientific) using Xs cone in hot plasma condition, the detection limit for Nb is 0.3 ng/L. Indium ( $\text{InCl}_3$ ) was used as international standard for instrument calibration for sample introduction and ionization efficiency. The Nb standard was prepared using Nb carrier solution by dilution with  $\text{HNO}_3$ + $\text{H}_2\text{C}_2\text{O}_4$  solution.

#### *(4) Measurement of $\gamma$ spectrometry*

The gamma emitters including  $^{94}\text{Nb}$ ,  $^{85}\text{Sr}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$  and  $^{152}\text{Eu}$  are measured using a gamma spectrometer equipped with an HPGe detector and Canberra Genie 2000 software. The spectrometry shows a resolution of 1.92 keV for 1332 keV  $\gamma$  peak, and 42% relative counting efficiency.

#### *(5) Separation of Nb using column chromatography filled with silica gel*



Silica gel (Aldrich, Davisil grade 645, 60-100 mesh, >99% purity) was taken to a beaker, 4 M HCl was added to the beaker, and the sample in the beaker was heated at 90°C for overnight under reflux in order to activate the silica gel. The prepared silica gel was transferred to a plastic column (0.9 cm in diameter and 2.5 cm in height (total 1.6 mL), the column was washed with deionized water and conditioned with 4M HCl before using.

3 mL sample solutions or 1M HCl acid was taken to a Teflon beaker, 5.0 µg of niobium carrier, tracer solutions of  $^{60}\text{Co}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ , and  $^{152}\text{Eu}$  were added and the solution was evaporated to dryness. 5 mL of concentrated HCl was added to the beaker, and the solution was evaporated to 0.3-0.4 mL. 0.1M HCl is added to the solution to obtain a final solution of 0.5 M HCl. The sample solution was loaded to the column, followed by washing with 10 mL of 0.50 M HCl and 20 mL of 5.5M HCl. Nb retained on the column was then eluted using a solution contained 12M HCl and 2 M HF. The eluate was evaporated to about 1.5 ml and transferred to plastic vial with 0.1M HCl for  $\gamma$ -measurement. A solution containing the sample and radioisotope tracer was prepared in the same geometry as samples and measured by  $\gamma$  spectrometry to comparing with samples in order to calculate the decontamination factor. After  $\gamma$  measurement, the solution was transferred to a beaker, and then evaporated to dryness. 20 mL solution contained 5%  $\text{HNO}_3$  and 0.05M oxalic acid was added to dissolve the residue, and the solution is transferred to a vial. 0.20 mL solution was taken and diluted with 5%  $\text{HNO}_3$  and 0.05M oxalic acid (and In-internal standard) solution for the ICP-MS measurement.

#### *(6) Separation of Nb using anion exchange chromatography*

3mL sample solution or 1M HCl was taken to a Teflon beaker, 5.0 mg of niobium carrier and tracer solutions of  $^{60}\text{Co}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ , and  $^{152}\text{Eu}$  were added, the solution was then evaporated to dryness. 20 mL of 4M HCl was added and the solution was heated to dissolve the residue. The solution was transferred to a centrifuge tube with 4 M HCl, and centrifuged for 5 min at 3000rpm. The supernatant was discarded and the precipitate was transferred to a Teflon beaker with 5 mL concentrated HF. The solution was heated until the residue was completely dissolved, then evaporated to dryness. 3 mL of 4M HCl was added and the solution was evaporated to dryness. 20 mL of 4M HCl was added to the residue and heated, then the solution was transferred to a centrifuge tube, and centrifuged 5 min at 3000rpm. The supernatant was discarded and the residue was washed with 10 mL of 4M HCl.

The precipitate was transferred to a Teflon beaker with concentrated HF, and dissolved by heating on a hot plate. The solution was loaded to an anion exchange column in diameter of 0.9 cm and 10 cm height (AG 1- $\times$ 8, chloride form, 100-200 mesh), which had been conditioned with 6mL of 11M HF. The column was then washed sequentially with 20mL solution of 4M HF and 3M HCl and 20mL solution of 1M HF and 0.1M HNO<sub>3</sub>. The Nb retained on the column as anion fluoride complex was finally eluted with 10 mL solution of 0.2M HF and 4 M HNO<sub>3</sub>. The eluate was collected in a vial and measured by  $\gamma$  spectrometry. A solution containing the sample and radioisotope tracer was prepared in the same geometry as samples and measured by  $\gamma$  spectrometry to comparing with samples in order to calculate the decontamination factor.

After  $\gamma$  measurement, 0.2 mL of eluate was taken to a Teflon beaker, the solution was evaporated to dryness. A solution of 5% HNO<sub>3</sub> and 0.05M oxalic acid was added to the beaker and heated to completely dissolve the residue. The solution was transferred to a bottle and weighted. 0.20 mL solution was taken and diluted to 20mL solution of 5% HNO<sub>3</sub> and 0.05 M oxalic acid. 40 $\mu$ l of the diluted solution was taken to a plastic tube, InCl<sub>3</sub> solution was added as internal standard, then the solution was diluted to 10 mL with solution of 5% HNO<sub>3</sub> and 0.05M oxalic acid for ICP-MS measurement. An Nb standard solution was prepared with Nb carrier solution in the silimar method as samples.

## ***2.2 Results and discussion***

The recovery of Nb and the decontamination factor the major interfering radionuclides in the separation procedure using silica gel method are shown in Table 1. A quantitative recovery of Nb was observed in the HCl solution without sample, meanwhile a high recovery of Nb was also obtained for sample-4 when only 5  $\mu$ g Nb was added, confirming the procedure is effective for Nb separation. However, a excessive high recovery of Nb was observed for sample-1 when only 5  $\mu$ g Nb was added. This might be attributed to the high Nb concentration in the matrices of sample-1. In sample stainless steel, Nb is added as a component with a concentration of a few percent. An ICP-MS measurement of the original solution of sample-1 confirmed this assumption. When 5 mg of Nb is added to the samples, low recovery of Nb was observed for all samples, this might attributed to the low capacity of silica gel to adsorption of Nb, as well as other metals. It is therefore this method is only applicable when no Nb carrier was added to the solution, and the concentration of stable Nb in the samples is not very high.

The decontamination factors for four representative radionuclides are higher than 1000 when steel samples were analyzed, indicate a good removal of interfering radionuclides. Actually there is no remarkable  $\gamma$ -ray peaks of  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$  and  $^{152}\text{Eu}$  can be measured, and the  $\gamma$ -ray peaks of  $^{60}\text{Co}$  was also slightly higher than the background, meanwhile the Compton background of the  $\gamma$  spectra for the separated samples is similar as the background sample, confirming a very sufficiently removal of all interferences for gamma measurement including pure beta emitters. Relative lower decontamination factors of 4 radionuclides was observed for blank sample (HCl) compared with samples, this might be attributed to the small amount of tracers added to the blank. Since relative high amount of  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  exist in the steel samples, and some more tracers were added to the samples, this cause a higher decontamination factor in the samples. Actually due to the very small peaks of tracer radionuclides in the spectra of separated samples, the decontamination factors presented in the Tables are under estimated. Even higher decontamination factors are expected if sufficiently high amount of tracer were added to the samples solution.

Table 1 Separation efficiency of Nb using silica gel method

Sample	Recovery of Nb, %	Decontamination factor			
		$^{60}\text{Co}$	$^{85}\text{Sr}$	$^{137}\text{Cs}$	$^{152}\text{Eu}$
HCl+5 $\mu\text{g}$ Nb	106.5 $\pm$ 8.4	375 $\pm$ 23	250 $\pm$ 16	594 $\pm$ 35	268 $\pm$ 11
Steel-1+5 $\mu\text{g}$ Nb	155.2 $\pm$ 3.2	3217 $\pm$ 38	1028 $\pm$ 184	1108 $\pm$ 19	1479 $\pm$ 11
Steel-4+5 $\mu\text{g}$ Nb	103.2 $\pm$ 4.2	6540 $\pm$ 150	1268 $\pm$ 16	1073 $\pm$ 19	309 $\pm$ 11
Steel-1+5 mg Nb	10.0 $\pm$ 3.5				
Steel-2+5 mgNb	9.7 $\pm$ 1.5				
Steel-3+5mg Nb	7.6 $\pm$ 2.1	7432 $\pm$ 274	1156 $\pm$ 15	980 $\pm$ 19	1794 $\pm$ 70
Steel-4+5mg Nb	9.6 $\pm$ 1.2				

Table 2 shows the separation efficiency of Nb using anion exchange chromatography, a high recovery of Nb was observed for the blank samples (HCl), while the recoveries of Nb in the samples are relatively low, only about 50%. For all samples and blank, high decontamination factors for four

radionuclides were obtained. In the gamma spectra of the separated samples, no remarkable  $\gamma$ -ray peaks of the tracer radionuclides were observed. In this method, 5 mg Nb carrier was added to the solution, and repeated precipitation of  $\text{Nb}_2\text{O}_5$  was carried out to separate Nb from matrices and interferences. The results indicate anion exchange method is effective for the separation of Nb from the sample matrices and the interfering radionuclides. Especially for samples with high Nb concentration or Nb carrier is added to the samples. However, the recovery of Nb in this procedure is not satisfactorily high, and some more work might need to improve the recovery of Nb in this procedure. In addition the anion exchange separation took considerably longer time than the silica gel method.

In all samples, except one samples with visible  $\gamma$ -ray peaks in the  $\gamma$  spectra of separated solution,  $^{94}\text{Nb}$  could not be detected in all other samples (Sample-1), indicating the low production rate of  $^{94}\text{Nb}$  in the waste during its irradiation by neutrons from the reactor compared with  $^{60}\text{Co}$ ,  $^{152}\text{Eu}$  and other radionuclides. To be able to measure  $^{94}\text{Nb}$  in these samples, a larger sample might be needed.

Table 2 Separation efficiency of Nb using anion exchange chromatography

Sample	Recovery of Nb, %	Decontamination factor			
		$^{60}\text{Co}$	$^{85}\text{Sr}$	$^{137}\text{Cs}$	$^{152}\text{Eu}$
HCl +5 mg Nb	95.5±4.4				
Steel-1+5 mg Nb	52.8.0±4.1	8756±79	2234±99	3479±123	4563±134
Steel-2+5 mgNb	47.3±1.2				
Steel-4+5mg Nb	50.2±3.3	9794±56	3002±19	4278±34	3194±70

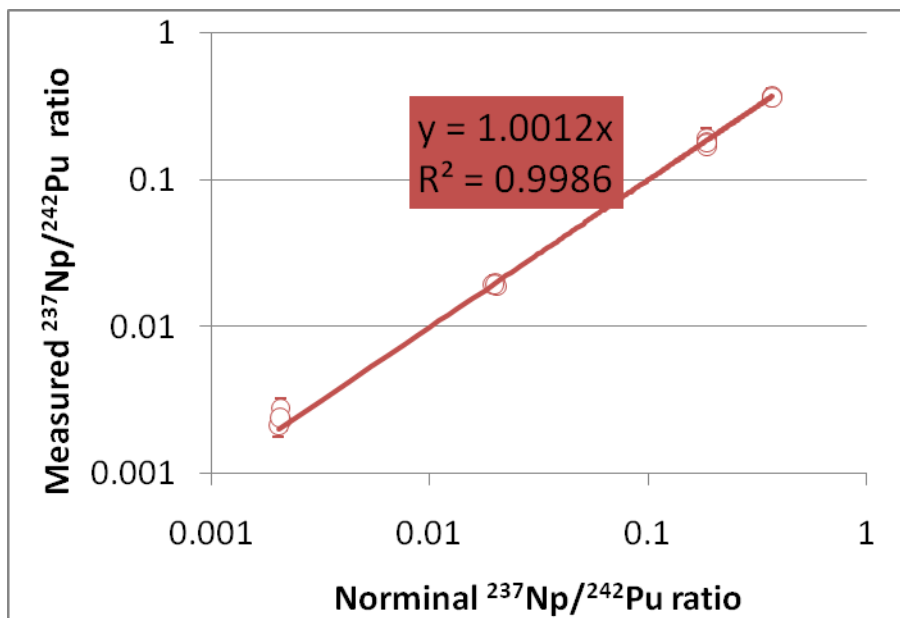
The results show that both methods are efficient for separation of Nb from sample matrices with high chemical yield, and sufficiently high decontamination factor for concerning interfering radionuclides. Comparing these two methods, silica gel adsorption is simple and rapid, but could not treat a big sample solution and samples with high Nb content. While anion exchange method takes slightly longer time for separation, but could deal with large sample solution and sample with high Nb concentration.

### 3. Development of a sensitive method for measurement of $^{237}\text{Np}$ using AMS

$^{237}\text{Np}$  is a long-lived alpha emitter with half life of  $2.14 \times 10^6$  years, it is one of most important radionuclides in the waste depository due to its long half-life and high mobility in environment.  $^{237}\text{Np}$  can be measured by alpha spectrometry and ICP-MS, but the sensitivity is not very good, especially for the analysis of small samples such as hot particles and less active waste. A new measurement method was developed using AMS combined with chemical separation. The major challenge in the determination of  $^{237}\text{Np}$  is the chemical tracer,  $^{236}\text{Np}$  ( $1.55 \times 10^5$  years) is the most suitable tracer, but not available with a sufficient purity, although some effort has been given in the community. Short lived  $^{239}\text{Np}$  (2.36 d) can be used for the purpose of yield tracer, but need a nuclear reactor, or a production line using cyclotron. When AMS is used for measurement of  $^{237}\text{Np}$ , other isotope has to be used for normalization of the instrument, the lack of suitable isotope of neptunium make it a big challenge. A method development work has been carried out to utilize  $^{242}\text{Pu}$  as chemical yield tracer and isotope for AMS normalization at Center for Nuclear Technologies, DTU with collaboration with Ion Beam Physics ETH Zurich (Lachner et al. 2011). With an effective control the separation procedure,  $^{237}\text{Np}$  follows the  $^{242}\text{Pu}$  to be separated from samples, which is then prepared by co-precipitation with  $\text{Fe}(\text{OH})_3$ , and converted to oxides by calcination at high temperature. The prepared sample is mixed with niobium powder and pressed in a sample holder for AMS measurement.

A series of standards with different amount of  $^{237}\text{Np}$  using  $^{242}\text{Pu}$  were prepared, the first AMS measurement was implemented in TANDY AMS system (ETH Zürich) in order to search for possible background interfering with the sensitive determination of low-level  $^{237}\text{Np}$  concentrations and to determine the stability of the measurement of  $^{237}\text{Np}$  relative to  $^{242}\text{Pu}$ . The normalization of the signal of an isotope using an isotope of another element requires obtain a stable signal ratio of these two isotopes of different element, ideally the same sensitivity. The measurement results of a series of standards (containing 0-180fg  $^{237}\text{Np}$  and 500fg  $^{242}\text{Pu}$ ) show equal efficiencies of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  (Fig.2). In addition, a good linear correlation between the  $^{242}\text{Pu}$  signal and  $^{237}\text{Np}$  in different level is obtained (Fig. 2), indicating the feasibility to use  $^{242}\text{Pu}$  to normalize the instrument for qualitative

measurement of  $^{237}\text{Np}$ . The detection limit of AMS for  $^{237}\text{Np}$  can reach to 0.1 fg or 3 nBq, which is more than one order of magnitude lower than that of ICP-MS.



**Fig. 2** Comparison of nominal and measured  $^{237}\text{Np}/^{242}\text{Pu}$  ratios in samples of standards

#### 4. Improvement of analytical method for determinaiton of $^{99}\text{Tc}$ using ICP-MS

Technetium-99 ( $^{99}\text{Tc}$ ) is one of the few most important radionuclides in waste depository due to its long half-life ( $2.13 \times 10^5$  y) and high mobility (weak sorption of  $\text{TcO}_4^-$  to geological media). Several methods have been reported for  $^{99}\text{Tc}$  determination; these methods generally include sample pretreatment, pre-concentration, purification and measurement of  $^{99}\text{Tc}$ . The stability of  $^{99}\text{Tc}$  in sample solution during evaporation step is very critical, and might cause a significant loss of  $^{99}\text{Tc}$ . As a pure  $\beta$ -emitter with maximum energy of 0.292 MeV,  $^{99}\text{Tc}$  is conventionally measured by  $\beta$  counting using gas flow Geiger-Müller (GM) counter or liquid scintillation counting (LSC). However, the relatively high detection limit or long counting time restricts application of these techniques, especially for analysis of large number of samples in decommissioning and for emergency analysis. Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) is a better choice for this purpose. In ICP-MS

measurement of  $^{99}\text{Tc}$ , stable  $^{99}\text{Ru}$  and molecular ion  $^{98}\text{Mo}^1\text{H}$  are two main isobaric interferences,  $^{99}\text{Mo}$  also affect the measurement of  $^{99}\text{Tc}$  due to tailing of  $^{98}\text{Mo}$  to the mass of 99. These seriously worsen detection limit for  $^{99}\text{Tc}$  and hinder its accurate determination. In Center for Nuclear Technologies, DTU, we systematically investigate stability of technetium in evaporation procedures in order to develop reliable methods for sample pretreatment and technetium separation, and to explore behaviors of technetium, ruthenium and molybdenum on TEVA resin to find an efficient approach for sufficient removal of ruthenium and molybdenum for measurement of  $^{99}\text{Tc}$  in low level environmental samples using ICP-MS.

#### ***4.1 Loss of technetium during evaporation of sample solution.***

The stability of technetium in different evaporation conditions was investigated. The results (Table 3) show that temperature and solution composition are key parameters determining the stability of technetium during evaporation. No significant loss of technetium was observed when evaporation was carried out at temperature lower than 100 °C in  $\text{HNO}_3$  media, even in a  $\text{HNO}_3$  solution up to 8 mol/L. While technetium becomes unstable when the temperature is increased. At 150 °C, an increased loss of technetium was observed with increasing  $\text{HNO}_3$  concentration from less than 5% in 0.001 mol/L  $\text{HNO}_3$  to more than 20% in 8 mol/L  $\text{HNO}_3$ . In addition, the same stability of technetium in 25%  $\text{NH}_3\cdot\text{H}_2\text{O}$  as that in diluted  $\text{HNO}_3$  solution (0.001 mol/L) was observed during evaporation process. The addition of salt in solution can significantly reduce the loss of technetium in evaporation process. In 8 mol/L  $\text{HNO}_3$  media with 25 g/L KCl, no significant loss of technetium was observed when the solution was evaporated to dryness at 150 °C, compared with more than 20% loss of technetium when no KCl was added. Technetium is highly unstable in HCl media during evaporation, even at 100 °C and in 0.001 mol/L HCl solution. The loss of technetium significantly increases with the increased concentration of HCl, more than 98% of technetium was lost when evaporation was carried out in 6 mol/L HCl at 100 °C. Based on this finding, it is recommended that technetium solution should be evaporated in  $\text{HNO}_3$  or alkali media at lower temperature (< 150 °C), and the solution should not be evaporated to complete dryness if the temperature is more than 100 °C.

**Table 3. Stability of technetium in evaporation of sample solution at different conditions <sup>a</sup>**

Solution media	Yield of Tc in different temperature on hot plate			Status after evaporation
	(%)			
	100 ± 2 °C	150 ± 2 °C	200 ± 2 °C	
25% NH <sub>3</sub> .H <sub>2</sub> O	97.0 ± 2.1	94.6 ± 1.9	71.1 ± 2.6	dryness
0.001 mol/L HNO <sub>3</sub>	95.8 ± 1.4	94.3 ± 1.8	–	dryness
0.001 mol/L HNO <sub>3</sub> with salt	98.7 ± 2.1	99.4 ± 2.5	–	dryness
0.1 mol/L HNO <sub>3</sub>	99.1 ± 2.4	86.4 ± 2.3	–	dryness
0.1 mol/L HNO <sub>3</sub> with salt	98.2 ± 2.3	95.4 ± 2.1	–	dryness
8 mol/L HNO <sub>3</sub>	98.5 ± 1.9	79.4 ± 2.7	59.5 ± 3.9	dryness
8 mol/L HNO <sub>3</sub> with salt	100.5 ± 2.3	96.3 ± 3.0	70.6 ± 3.3	dryness
0.001 mol/L HCl	90.2 ± 2.1	65.1 ± 3.7	–	dryness
0.001 mol/L HCl with salt	98.4 ± 1.9	103.2 ± 4.6	–	dryness
0.1 mol/L HCl	79.2 ± 2.0	53.1 ± 1.9	–	dryness
0.1 mol/L HCl with salt	94.1 ± 2.1	72.7 ± 1.1	–	dryness
3 mol/L HCl	32.2 ± 2.3	10.7 ± 4.1	–	dryness
3 mol/L HCl with salt	84.1 ± 1.9	53.9 ± 3.6	–	dryness
6 mol/L HCl	1.3 ± 0.3	1.8 ± 0.2	1.5 ± 0.4	dryness
3 mol/L HCl with H <sub>2</sub> O <sub>2</sub>	37.2 ± 1.8	13.2 ± 3.2	–	dryness
3 mol/L HCl with salt	99.1 ± 2.3	88.8 ± 1.5	–	0.5 mL solution left
3 mol/L HCl with H <sub>2</sub> O <sub>2</sub>	97.4 ± 2.6	72.9 ± 3.1	65.2 ± 3.4	0.5 mL solution left
8 mol/L HNO <sub>3</sub>	98.5 ± 1.7	97.1 ± 2.6	–	0.5 mL solution left

<sup>a</sup>The yields are presented as the average and 2SD of three replicates

#### 4.2 Removal of molybdenum and ruthenium using extraction chromatography

The distribution factors of TcO<sub>4</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup> and RuO<sub>4</sub><sup>-</sup> on TEVA resin as a function of HNO<sub>3</sub> concentration are shown in Fig. 3. Compared with MoO<sub>4</sub><sup>2-</sup> and RuO<sub>4</sub><sup>-</sup>, a high sorption of TcO<sub>4</sub><sup>-</sup> on TEVA resin was observed in low concentration of HNO<sub>3</sub>, the  $K_d$  of TcO<sub>4</sub><sup>-</sup> on the TEVA resin decreases rapidly with increased HNO<sub>3</sub> concentration. When HNO<sub>3</sub> concentration is higher than 4 mol/L, the  $K_d$  of TcO<sub>4</sub><sup>-</sup> is lower than that of MoO<sub>4</sub><sup>2-</sup> and RuO<sub>4</sub><sup>-</sup> (Fig.3). MoO<sub>4</sub><sup>2-</sup> also shows a decreased  $K_d$  with increased HNO<sub>3</sub> concentration, while the  $K_{d,Mo}$  are still high in low concentration of HNO<sub>3</sub>. In order to remove molybdenum but keep technetium on the column, loading solution in 0.1 mol/L HNO<sub>3</sub> and



washing solution of 1 mol/L HNO<sub>3</sub> were selected. Although a relatively low  $K_d$  ( $< 10$ ) of RuO<sub>4</sub><sup>-</sup> on TEVA resin was observed, it does not obviously vary with HNO<sub>3</sub> concentration. This means that the adsorbed RuO<sub>4</sub><sup>-</sup> is not easily removed from the TEVA column by washing with HNO<sub>3</sub> in a higher concentration.

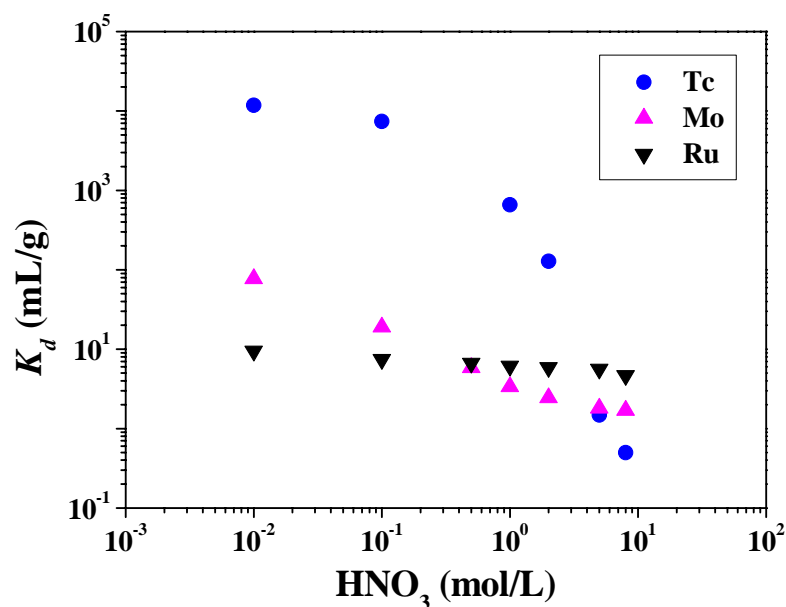


Figure 3. Distribution coefficients of TcO<sub>4</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup> and RuO<sub>4</sub><sup>-</sup> on TEVA resin as a function of HNO<sub>3</sub> concentration obtained at room temperature and an equilibrium time of 6 h.

Although RuO<sub>4</sub><sup>-</sup> has a low  $K_d$  value ( $< 10$ ) in low HNO<sub>3</sub> concentration, the  $K_{d,Ru}$  does not vary with HNO<sub>3</sub> concentration, consequently the absorbed ruthenium cannot be easily removed from the TEVA column. A few methods have been reported to removal ruthenium from technetium, based on the high volatility of RuO<sub>4</sub>, ruthenium is removed from sample solution by oxidizing with strong oxidant and heating at high temperature in H<sub>2</sub>SO<sub>4</sub> media. This method is simple but quite time consuming and risk to loss <sup>99</sup>Tc at high temperature. An experiment was carried out to investigate the effect of treatment of loading solution with 30% H<sub>2</sub>O<sub>2</sub> in different media on the removal of ruthenium using TEVA column.

The results (Table 4) show that the treatment of the loading solution with H<sub>2</sub>O<sub>2</sub> in 1 mol/L NaOH media can significantly reduce the adsorption of ruthenium on the TEVA column, and more than 98% of ruthenium in the loading solution is removed to the effluent and 1 mol/L HNO<sub>3</sub> washes. As comparison, the treatment with H<sub>2</sub>O<sub>2</sub> in neutral media (in H<sub>2</sub>O) and no treatment result in a removal of ruthenium only 79% and 49%, indicating that ruthenium might be effectively reduced to low oxidation state by H<sub>2</sub>O<sub>2</sub> in alkaline media and therefore significantly reduced the absorption of ruthenium on the TEVA column. By this approach, the decontamination factor of more than 1×10<sup>5</sup> for ruthenium is achieved.

Table 4. Effect of pretreatment of sample solution with 30% H<sub>2</sub>O<sub>2</sub> in different media on the removal of ruthenium by extraction chromatography using 1.5 mL TEVA column <sup>a</sup>

chromatographic step	volume of effluent/washes (mL)	concentration of Ru in the effluent or washes with different pretreatment of the loading solution (μg/L)		
		pretreatment with H <sub>2</sub> O <sub>2</sub>		untreatment
		1 mol/L NaOH	H <sub>2</sub> O	
effluent (in 0.1 mol/L HNO <sub>3</sub> )	0-4	0.131	0.102	0.070
	4-8	0.197	0.150	0.091
	8-12	0.197	0.159	0.089
	12-16	0.196	0.154	0.092
	16-20	0.195	0.154	0.089
washing (1 mol/L HNO <sub>3</sub> )	0-4	0.067	0.054	0.045
	4-8	< 0.001	0.004	0.003
	8-12	< 0.001	0.004	0.002
	12-16	< 0.001	0.005	0.002
	16-20	< 0.001	0.005	0.003
relative amount of Ru in both effluent and washes compared with the original amount of Ru in the loading solution		98%	79%	49%

<sup>a</sup> After pretreated using 30% H<sub>2</sub>O<sub>2</sub> in 1 mol/L NaOH and H<sub>2</sub>O, the solution was acidified to pH 1 with HNO<sub>3</sub> before loading; as comparison, the results for Ru in 0.1 mol/L HNO<sub>3</sub> (without treatment using 30% H<sub>2</sub>O<sub>2</sub>) are also listed.

Based on these results, a rapid and efficient method for the determination of <sup>99</sup>Tc in environmental solid samples was developed using chromatographic separation combined with ICP-MS measurement.

A novel approach was developed to improve the removal of molybdenum and ruthenium in chromatographic separation using 30% H<sub>2</sub>O<sub>2</sub> pretreatment of loading solution and extraction chromatographic separation using two serial small TEVA columns. The decontamination factors of more than  $4 \times 10^4$  and  $1 \times 10^5$  are achieved for molybdenum and ruthenium, respectively. Chemical yields of technetium in entire procedure range from 60% to 95% depending on the type and amount of samples, and the detection limit of 0.15 mBq/g for <sup>99</sup>Tc was obtained. The method has been successfully applied for the determination of <sup>99</sup>Tc in environmental solid samples (Shi et al. 2012).

## 5. Measurement of <sup>14</sup>C in different form using LSC

<sup>14</sup>C is one of the most important radionuclides in the decommissioning of nuclear facilities, because it exists in almost all materials from the nuclear reactor due to high mobility of <sup>14</sup>C as CO<sub>2</sub> produced as an activation product in nuclear reactors. <sup>14</sup>C in the samples is normally separated by oxidation combustion, and the released CO<sub>2</sub> is trapped in alkali solution. When using NaOH as trap solution, <sup>14</sup>C will form Na<sub>2</sub>CO<sub>3</sub> in the solution. A commercial trap solution “Carbo Sorb E”, an organic amine (2-methoxy ethylamine), is available from Perkin Elmer for this purpose. <sup>14</sup>C in the trap solution is often measured using LSC after mixed with scintillation cocktail, such as Permafluor R E+ for Carbo Sorb, and Ultima Gold LLT for normal aqueous solution.

In DTU, a standard solution of <sup>14</sup>C in Na<sub>2</sub>CO<sub>3</sub> form was obtained from AEA Technology (Braunschweig, Germany) in 2003, which was transferred to a glass flask and diluted with deionized water. In 2010, some solution was taken and mixed with scintillation cocktail and measured using LSC against a <sup>14</sup>C standard (in <sup>14</sup>C-stearic acid form) from PerkinElmer. It was observed that an extremely low <sup>14</sup>C activity has been measured compared with the expected value. A test was carried out to check the stability of <sup>14</sup>C in Na<sub>2</sub>CO<sub>3</sub> form. It was found that the carrier free Na<sub>2</sub>CO<sub>3</sub> is easily adsorbed on the wall of the flask, shaking bottle and addition of Na<sub>2</sub>CO<sub>3</sub> solution can partly remove the adsorbed <sup>14</sup>C from the surface of the flask. In addition, it was observed that the loss of <sup>14</sup>C in the Na<sub>2</sub>CO<sub>3</sub> solution increases with the time, after 10 days, more than half of <sup>14</sup>C was lost from the solution. Addition of Na<sub>2</sub>CO<sub>3</sub> carrier to the solution can reduce the adsorption of <sup>14</sup>C and therefore the loss of <sup>14</sup>C from the solution.

An experiment was also carried out to investigate the stability of  $^{14}\text{C}$  in  $\text{Na}_2\text{CO}_3$  and  $^{14}\text{C}$ -stearic acid form during the LSC measurement.  $^{14}\text{C}$ - $\text{Na}_2\text{CO}_3$  and  $^{14}\text{C}$ -stearic acid were taken to LSC vials, two types of scintillation cocktails, Ultima Gold LLT and Permafluor R were added. After mixed, the solution was repeat measured in 4 days using LSC, the results are show in Fig. 4 and Fig. 5.

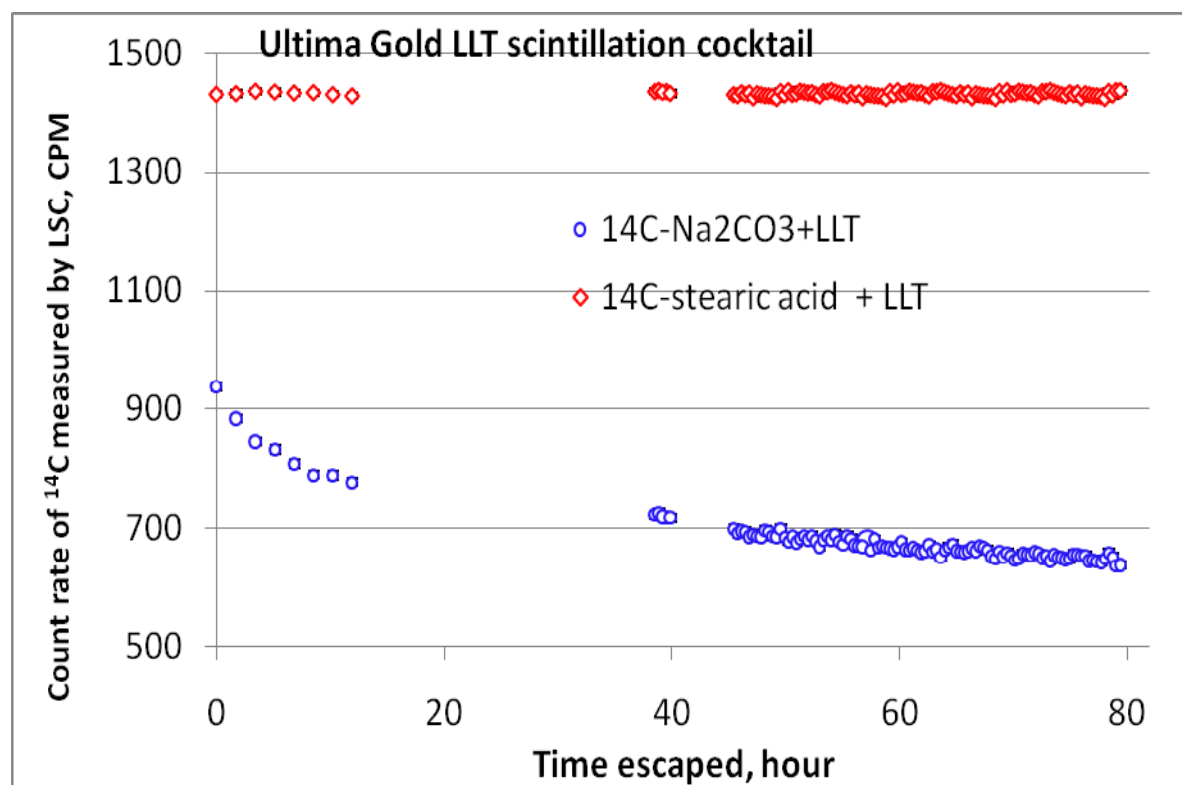


Fig. 4 Variation of count rate of  $^{14}\text{C}$  in  $\text{Na}_2\text{CO}_3$  and stearic acid forms mixed with Ultima Gold LLT scintillation cocktail and measured by LSC

It was observed that  $^{14}\text{C}$ - $\text{Na}_2\text{CO}_3$  mixed with Ultima Gold LLT is unstable even during the LSC measurement, a gradually decreased  $^{14}\text{C}$  count rate was measured for the same samples by repeat measurement, and 30% reduction of  $^{14}\text{C}$  activity was measured in the same solution after 3 days (Fig. 4). While the  $^{14}\text{C}$  activity in stearic acid form keeps the same in 4 days measurement in the same scintillation cocktail, indicating the carrier free  $\text{Na}_2\text{CO}_3$  is high unstable, even after mixed with Ultima

Gold LLT scintillation cocktail. This might attribute to the significant adsorption of  $\text{Na}_2\text{CO}_3$  on the wall of plastic vial.

However, when mixed with small amount of Carbo Sorb and Permafluor R scintillation cocktail, the  $^{14}\text{C}$  activity keeps the same during 4 days measurement for both  $\text{Na}_2\text{CO}_3$  and in stearic acid form, indicating  $^{14}\text{C}$  in all these forms are stabilized by Carbo Sorb and Permafluor R (Fig. 5).

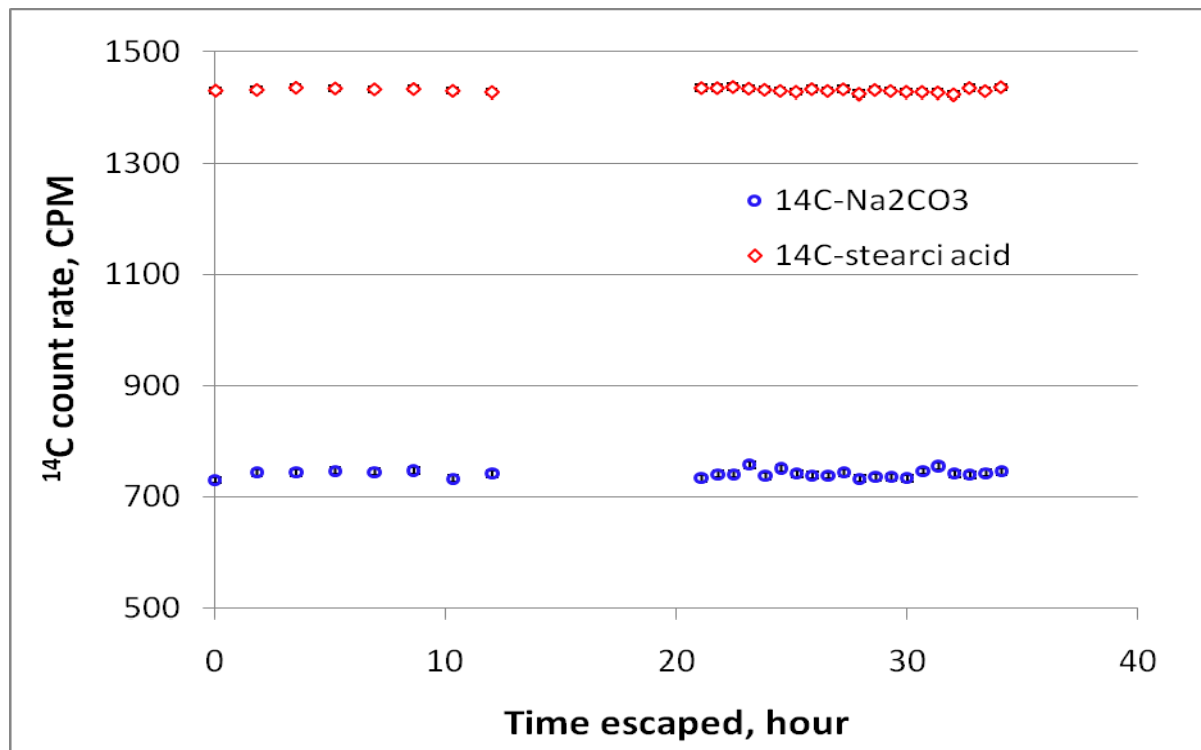


Fig. 4 Variation of count rate of  $^{14}\text{C}$  in  $\text{Na}_2\text{CO}_3$  and stearic acid forms mixed with Carbo Sorb and Permafluor R scintillation cocktail measured by LSC

This experiment indicates that  $^{14}\text{C}$  in carbonate form might adsorb on the surface of the vials, even after mixed with scintillation cocktail. To overcome the problem of stability of  $^{14}\text{C}$  in carbonate form, the  $^{14}\text{C}$ - $\text{Na}_2\text{CO}_3$  solution should be stabilized in Carbo Sorb and mixed with Permafluor scintillation cocktail before measurement. In this case, the  $^{14}\text{C}$  is stable, no significant change of count rate was observed in the experimental time of 2 months.

## **6. Characterization of steel samples from Danish research reactor DK-3 for decommissioning.**

### ***6.1 Description of Danish Reactor 3 (DR3)***

Danish research reactor DR3 was operated from January 1960 to March 2000 with a thermal power of 10 MW, which gives in total energy output of 108,000 MWD. The reactor used 19.75% enriched uranium in the fuel elements, and was moderated and cooled with heavy water. The reactor core consists of 26 fuel elements, which together contained approx. 3.3 kg of U-235, on average during routine operation at 10 MW. These elements were arranged in a square grid on the bottom of a D<sub>2</sub>O-filled aluminium tank. Surrounding the aluminium tank is a graphite reflector of approx. 30 cm thick. All these compartments are in a steel tank, which is clad with Boral and lead, to reduce the thermal neutron and gamma radiation from the core. Outside is a biological shield of barytes concrete (Fig. 6). A total of 18 experimental tubes for neutron irradiation are located around the reactor core, four of these are horizontal tangential tubes with a diameter of 7 inch, and the remaining 14 facilities are all vertical tubes, of which 4 × 7 inch tubes and 4 × 4 inch tubes were immersed in the heavy water in the aluminium tank, while the remaining 6 tubes are 4 inch tubes in the graphite reflector. It was also possible to place experimental materials in the 2 inch tubes located in the middle of the fuel elements. At 10 MW, the maximum thermal and fast flux is approx.  $1.5 \times 10^{14}$  n/cm<sup>2</sup>s and approx.  $4.5 \times 10^{13}$  n/cm<sup>2</sup>s respectively (Lauridsen, 2011). The reactor itself appears as a square, iron-clad concrete block with sides measuring 6.1 m in length and a height of 10.53 m (Fig. 6)

### ***6.2 Characterization of steel sample from the bottom of TSR in DR-3 reactor***

In 2009, a sampling plan from the bottom plate of the Top Shield Ring was initiated. Since the 4VGR holes penetrate the Top Shield Plug (TSR), it is attempted to collect a sample from the TSR bottom plate through one of the 4VGR holes. Of these 4VGR3 and 4VGR6 holes are selected. The hole was first investigated by use of a handheld RIDGID™ inspection camera, in particular the region between the bottom of the TSR and the top of the graphite reflector. The pictures revealed that the bottom plate of the TSR was quite rusty with visible flakes of rust. The reason for the rust is presumably that the surface of the TSR is covered by a mild steel layer, not stainless steel, and that the air of the reactor cavity has had significant moisture content after the heavy water leak of the reactor tank developed.

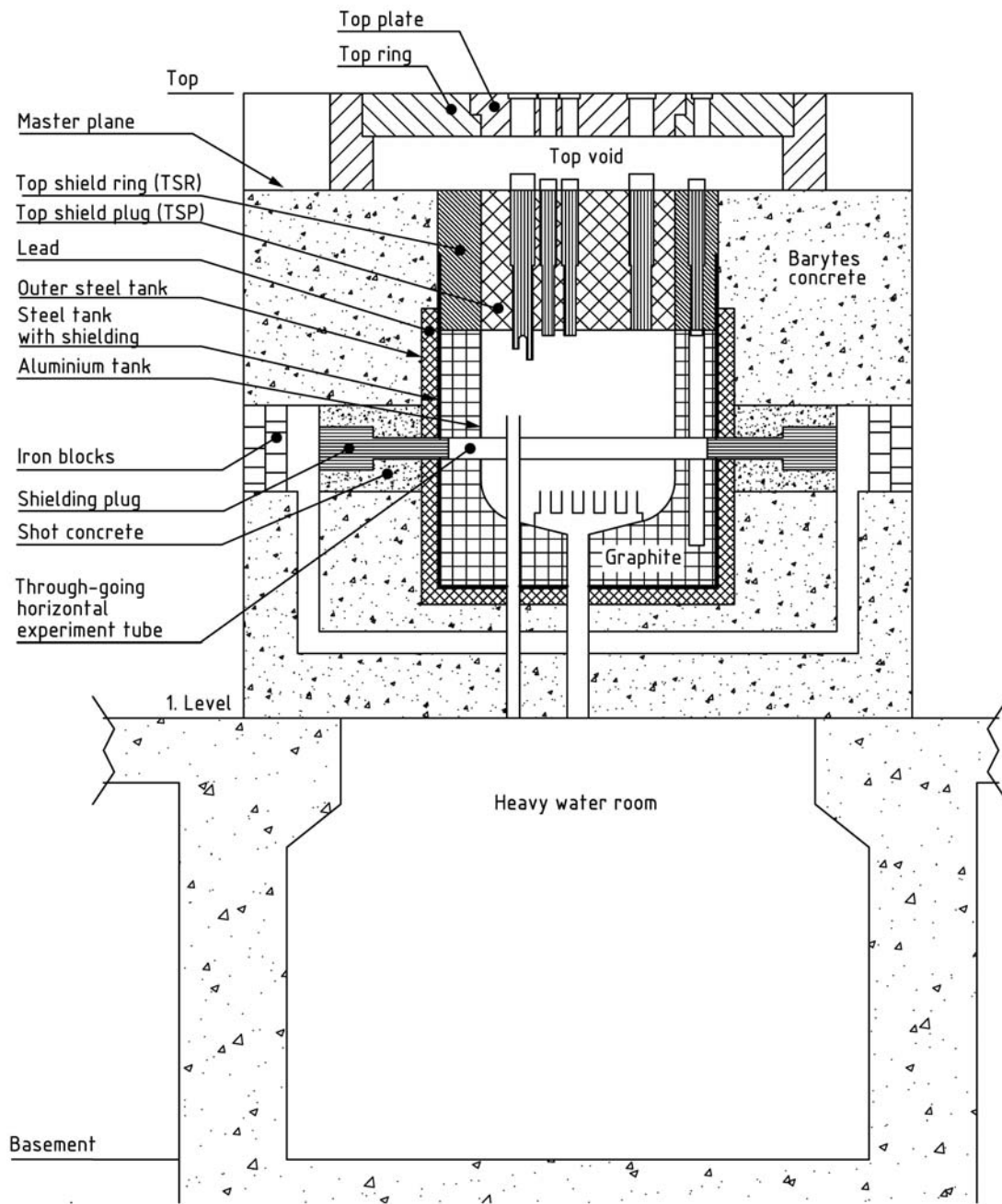


Fig. 6 Sketch diagram of Danish reactor DR 3

Based on the pictures of the inspection camera, it seems that samples of rust could be scraped from the surface of the bottom plate of the TSR. Because this rust originates from the bottom plate, the activity of such bottom samples, corrected for their content of oxygen, should be a reasonable measure of the activity of the TSR bottom plate. An aluminum rod of about 4 meters length was used to scrap the samples from the surface of TSR bottom plate. At its bottom end it was provided with a circular plate, protruding from the rod at an angle of 90° to the axis of the rod. The plate was provided with an edge with a height of about 5 mm.

A tool was lowered down into the 4VGR6 hole with the outer end of the plate in contact with the wall of the hole. When reached to the hole bottom, the tool was lowered a small distance further down. The plate was then moved in under the bottom of the TSR, lifted up to contact with the TSR bottom plate, and the scraping with the tool against the bottom plate was performed. The tool was moved out into the hole, lifted up, and the rust, a fine, orange powder, was poured down into a fairly large plastic bag in order to ease the transfer of the sample from the tool plate to the plastic bag. Four scraping samples were obtained. The maximum dose rates on the surface of the plastic bags were 25-330 μSv/h (Table 5). All samples were first measured using a γ-spectrometry; it is observed that the activity of all samples was dominated by that of <sup>60</sup>Co. The results of these measurements are shown in Table 5.

Table 5 Radionuclides in Iron Oxide Samples

Sample (rusty)	No. 1	No. 2	No. 3	No. 4
<sup>60</sup> Co, Bq/g	$(6.06 \pm 0.62) \times 10^5$	$(6.68 \pm 0.69) \times 10^5$	$(7.67 \pm 0.77) \times 10^4$	$(5.86 \pm 0.59) \times 10^5$
Radiation dose rate, μSv/h	42	25	330	166

Table 6. <sup>60</sup>Co activity at the Bottom Plate of the TSR

Fe-sample	No. 1	No. 2	No. 3	No. 4
<sup>60</sup> Co, Bq/g	$8.36 \times 10^5$	$9.22 \times 10^5$	$1.058 \times 10^6$	$8.09 \times 10^5$



According to the Force Institute rust scraped off the bottom of the TSR is  $\text{Fe}_3\text{O}_4$ . Since oxygen does not contribute to the activity, the data in Table 3 has to be multiplied by a factor of 1.38 to give the activity of the iron in the TSR (Table 6).

The neutron flux varied across the 4VGR6 hole. Thus the direction as compared to the core center was also noticed. Sample No. 3 was obtained in the direction of the core center, sample No. 4 was taken in a direction  $90^\circ$  to that of the direction of the core center and No. 1 and 2 were taken in the direction toward the elevator of the DR3, i.e. roughly  $45^\circ$  to the direction to the center of the core. Thus, it was to be expected that sample No. 3 would have the highest specific activity, sample No. 4 the lowest while remaining two samples would have activities in between. As seen from Table 1, this was found to be the case, but the variation of the specific activities is quite modest.

Of particular interest is the activity of the TSR bottom plate at its inner edge, close to the bottom plate of the TSP. Based on the activities of the steel plates on top of the lead layer of the TSP and TSR it is estimated that the activity of the inner edge is about a factor of 3 higher than at the 4VGR6. Thus the activity at the edge is about  $2 \cdot 10^6$  Bq/g, a significant activity, but still a factor of 10 lower than that of bottom plate of the TSP. At the outer edge of the bottom plate of the TSR the activity will of course be lower than at the inner edge, perhaps a factor 5.

## **7. Conclusion and perspectives**

With the establishment of a Nordic network on radioanalysis of waste samples from decommissioning and waste management through this project, the exchange of experiences and information on the requirement for analytical methods were implemented. Among project partners, some development and optimization of radioanalytical methods for decommissioning waste have been carried out, the progress in this issue are presented in this report.

It has been proposed to organize an inter-comparison exercise on determination of 2 radionuclides of difficult to measure such as  $^{14}\text{C}$  and  $^{63}\text{Ni}$  in 1-2 waste samples; this was also discussed in detailed during the project meeting. However, it seems impossible to get more than 2 analyses for each sample by the partners' lab due to the limited numbers of laboratories could do the radioanalysis in Nordic countries, revealing lack of the sufficient radiochemical laboratories for characterization of nuclear waste in Nordic, probably over Europe. Therefore the inter-comparison excises has to be cancelled in

this year, but it is proposed to investigate the possibility to do it in the future by involving laboratories outside Nordic countries to be able to obtain enough analytical data for statistical analysis.

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Abstract	<p>This report summarized the progress in the development and improvement of radioanalytical methods for decommissioning and waste management completed in the NKS-B RadWaste 2011 project. Based on the overview information of the analytical methods in Nordic laboratories and requirement from the nuclear industry provided in the first phase of the RadWaste project (2010), some methods were improved and developed. A method for efficiently separation of Nb from nuclear waste especially metals for measurement of long-lived <math>^{94}\text{Nb}</math> by gamma spectrometry was developed. By systematic investigation of behaviours of technetium in sample treatment and chromatographic separation process, an effective method was developed for the determination of low level <math>^{99}\text{Tc}</math> in waste samples. An AMS approachment was investigated to measure ultra low level <math>^{237}\text{Np}</math> using <math>^{242}\text{Pu}</math> for AMS normalization, the preliminary results show a high potential of this method. Some progress on characterization of waste for decommissioning of Danish DR3 is also presented.</p>

Key words                      Radioanalysis, radionuclides, decommissioning, radioactive waste