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Radioanalytical procedures

**used to study the release of
radionuclides from spent nuclear
fuel and the diffusion into
bentonite clay**

Henrik Ramebäck, Yngve Albinsson, Mats Skålberg
Department of Nuclear Chemistry,
Chalmers University of Technology, Göteborg, Sweden

Ulla-Britt Eklund
Studsvik Nuclear AB,
Hot Cell Laboratory, Nyköping, Sweden

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Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19



Abstract

This report presents radio-analytical procedures for the assay of ^{90}Sr , ^{99}Tc , ^{237}Np , ^{239}Pu , ^{241}Am and ^{244}Cm . These analytical procedures were used in a project studying the release and diffusion of radionuclides from spent nuclear fuel into bentonite clay.

The main task was to use methods giving a high specificity in the detection combined with a low detection limit. A high specificity will eliminate errors caused by interferences, yielding errors in the analysis. A low detection limit was necessary since the release was often very low.

Solvent extraction was used in order to remove interferences. The detection methods, radiometric or mass spectrometric, were chosen to give the lowest detection limit.

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1 Introduction

Within the SKB spent nuclear fuel programme, a project was initiated in 1985 with the purpose to study the release and diffusion of radionuclides present in spent nuclear fuel into a compacted bentonite clay/synthetic groundwater system. Because of the decay properties of some radionuclides, this called for reliable analytical methods. The main task was therefore to develop analytical procedures with both high specificity and low detection limits.

Traditionally, radionuclide measurements are made through detection of the emitted particle involved in the radioactive decay. Radionuclides emitting γ -rays in their decay are often readily detected using high purity germanium (HPGe) detectors, which do not usually require any chemical separation. However, analysis of α - and pure β^- -emitting radionuclides almost always require chemical separation. Since the β^- -spectrum is continuous, ranging from zero to a maximum energy of the β^- -particle, β^- -counting often suffers from being non-specific. Although the energy of the α -particle is monoenergetic, overlaps from different isotopes often occur in an α -spectrum. One example is ^{241}Am and ^{238}Pu , which both emit α -particles with almost identical energies, that can not be resolved from one another.

During the last decade, ICP-MS detection of radionuclides has become an alternative to radiometric detection, especially for those that are long-lived and/or emit radiation not suitable for radiometric detection. However, interferences also occur in ICP-MS analysis. Isobaric interferences are species having the same mass to charge ratio (m/z) as the analyte, e.g. ^{99}Ru and ^{98}MoH in ^{99}Tc analysis. Polyatomic species, e.g. ^{238}UH , will give a signal at the same m/z ratio as ^{239}Pu and will therefore interfere in ^{239}Pu detection.

One aim of chemical separation is to remove the interfering species, after which a specific analytical signal can be registered. Chemical separations, such as solvent extraction, extraction chromatography and precipitation techniques, can all remove interferences. The separation methods utilized can either be a batch- or on-line method. For radionuclide assays, both methods have their advantages and their disadvantages.

The methods presented in this report were applied to bentonite samples originating from an experiment which purpose was to study the release and diffusion of radionuclides from spent nuclear fuel into bentonite clay /Skålberg et al, 1988/. The results from these experiments have been reported in different publications /Skålberg et al, 1988; Albinsson et al, 1991; Ramebäck et al, 1994; Ramebäck et al, 1998a; Ramebäck et al, 1998b/.

2 Analysis of ^{90}Sr

Figure 2-1 presents the general analytical scheme for the assay of ^{90}Sr in bentonite clay /Ramebäck, 1994/. It is a modification of the procedure presented by Liljenzin and Johnsson /1985/.

Sample pretreatment comprised acid leaching with 3 mL 4 M nitric acid for 5 h. After centrifugation (centrifugation was applied in order to remove the solid phase), 1 mL of the leaching solution was diluted to 1 M nitric acid, thereafter ^{90}Y was extracted into 4 mL 1 M HDEHP in Solvent 70 (an aliphatic kerosene). The aqueous solution was stored for some days to let ^{90}Y grow in. After a certain time, t_i , a new ^{90}Y separation was done. 1 mL of this solution was transferred to a glass vial for Cherenkov measurement. Half-life measurement verified the radiochemical purity of ^{90}Y .

The efficiency of the Cherenkov counting was measured by analysing a standard solution containing ^{90}Y in equilibrium with ^{90}Sr . In the geometry used, 1 mL of the organic phase in a 20 mL scintillation glass vial, the counting efficiency was determined to be $65\pm 2\%$. Separate tracer experiments were carried out to estimate the chemical recovery in the leaching procedure. The average leaching yield was $100\pm 2\%$. The yield in the extraction was higher than 99.5%.

According to Currie /1968/, the instrumental detection limit for a 1000-minute counting time was 15 mBq.

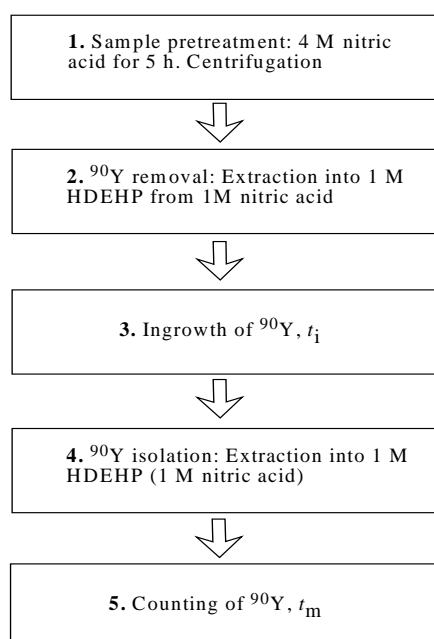


Figure 2-1. Analytical procedure for ^{90}Sr .

This analytical procedure was compared with ICP-MS analysis of ^{90}Sr . The samples used were dissolved spent UO_2 fuel specimens and samples from fuel leaching experiments. Good agreement between the methods was achieved. The ICP-MS analysis was done at the Studsvik Hot Cell Laboratory /Eklund, 1998/.

3 Analysis of ^{99}Tc

This procedure for the separation of technetium for ICP-MS analysis was described earlier /Ramebäck et al, 1998c/. Figure 3-1 gives the schematic outline of the analytical procedure. The acid leaching procedure was the same as used by Skålberg /1991/.

Technetium was leached from the bentonite clay (around 0.1 g) with a mixture of 2 M sulfuric acid and 10 mM sodium bromate at 60°C for at least 10 h. After centrifugation to remove the solid phase, technetium (as pertechnetate) was extracted into 2 mL 50 mM Alamine-336 (sulfate form) in chloroform. The extraction was done twice. Technetium was back-extracted in a new separation funnel three times, with 2 mL 1 M nitric acid.

The ICP-MS was optimised for technetium analysis by introducing a ^{99}Tc solution. The instrumental response was maximised by changing the position of the torch box, the nebuliser gas flow and the potentials to the ion lens system. ^{115}In was used as an internal standard at a concentration of 1 ng/ml in each sample.

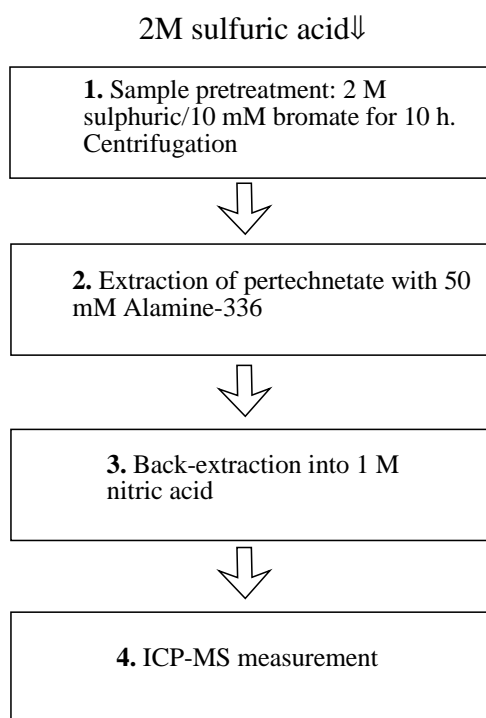


Figure 3-1. Analytical procedure for ^{99}Tc .

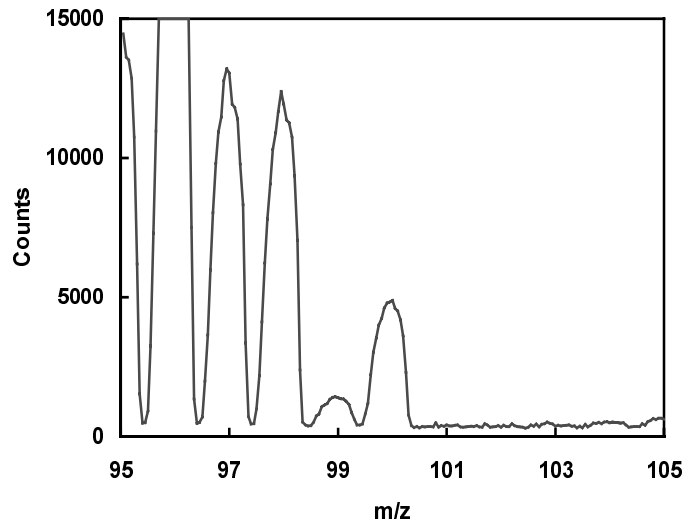


Figure 3-2. ICP-MS spectrum of an analysed sample. The absence of a peak at m/z ratio of 101 shows that no ruthenium is present in the sample.

Figure 3-2 shows a mass spectrum of one sample from the combined fuel leaching and radionuclide diffusion experiment containing 0.16 ng ^{99}Tc (0.10 Bq). The absence of a peak at the mass to charge ratio of 101 proves that no ruthenium is present in the sample.

In experiments to evaluate the chemical recovery, the leaching and separation yields were found to be $99\pm 2\%$ and $98\pm 2\%$, respectively.

The detection limit was calculated according to Currie /1968/. For a 10 minute measurement requiring an 8-mL sample, the instrumental detection limit was 0.45 pg/mL (0.28 mBq/mL), which for a sample is equivalent to 6.7 pg (4.2 mBq) ^{99}Tc . The main advantages of applying ICP-MS detection for the assay of ^{99}Tc are twosome: i) a specific analytical signal is provided if interferences could be handled; and ii) a far more rapid detection is possible. Radiometric detection often takes hours, and even several days is not uncommon.

The results from the ICP-MS analytical procedure of ^{99}Tc were compared with a radiometric procedure /Albinsson et al, 1990/ utilizing the separation method presented by Skålberg /1991/, see Figure 3-3.

The discrepancy between the two methods was later shown to be caused by radioactive impurities (mainly ^{60}Co) in the radiometric method and resulted in an overestimation of the amount of ^{99}Tc .

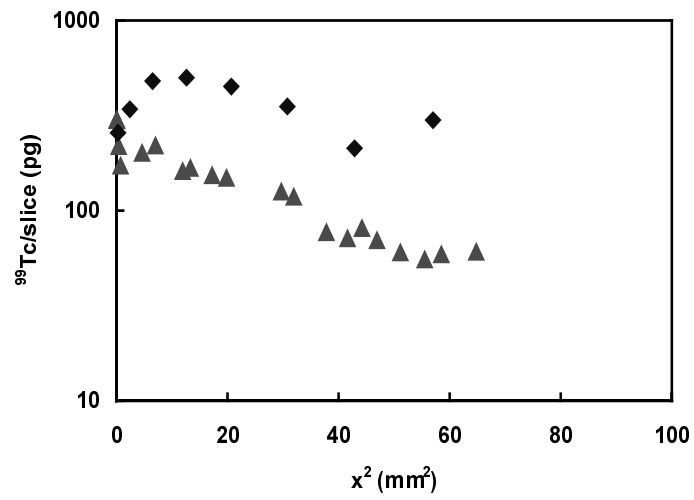


Figure 3-3. Diffusion profiles of ⁹⁹Tc. Diamonds: Radiometric method, Triangles: ICP-MS method.

4 Analysis of actinides

This analytical procedure was presented by Ramebäck and Skålberg /1998/. Sample pretreatment of the bentonite samples involved acid leaching with 3 mL 1 M nitric acid, containing 20 mM sodium bromate, at 65°C for 12 hours. After centrifugation (to remove the solid phase), 2.5 mL of the solution was diluted to 0.1 M nitric acid. Thereafter, uranium, neptunium, plutonium, americium and curium were extracted three times with 2 mL 1 M HDEHP in Solvent 70. Americium and curium were back-extracted three times with 1 mL 5 M nitric acid each time.

Neptunium was back-extracted with 3 mL 1 M nitric acid containing 0.2 M hydroxyl amine hydro nitrate. The contact time in the neptunium back-extraction was six hours. The organic phase was then washed two times with 1 mL 1 M hydrochloric acid to remove residues of nitric acid. Finally, plutonium was back-extracted with 3 M hydrochloric acid containing 60 mM TiCl₃. The contact time here was ten minutes. The solution containing the plutonium fraction was converted to nitric acid by evaporation of the hydrochloric acid and dissolving in nitric acid containing a small aliquot of hydrofluoric acid. The separation procedure is presented in Figure 4-1.

Both radiometric and ICP-MS detection was used in the analysis of the actinides. The short-lived radionuclides ²⁴¹Am and ²⁴⁴Cm were detected using α -spectroscopy. γ -spectroscopy was also used for ²⁴¹Am detection. ²³⁷Np and ²³⁹Pu detection was done by means of ICP-MS measurements. In the detection of ²³⁷Np, a desolvating nebuliser was used (Mistral, VG Elemental, England).

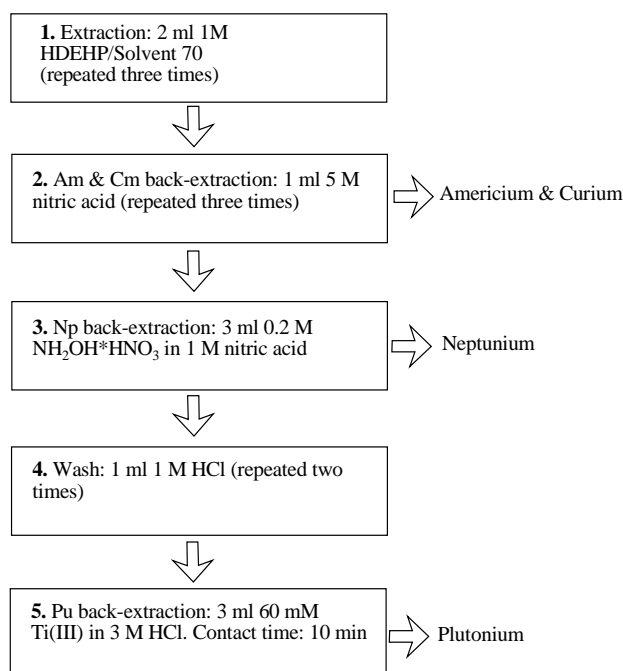


Figure 4-1. Analytical procedure actinide analysis.

^{239}Np was used as yield tracer in the analysis of ^{237}Np . It was produced by irradiating depleted ^{238}U , thereafter ^{239}Np was separated from the uranium solution according to a method described by Stary /1964/. The purity of this solution was checked by ICP-MS before use. In the ^{239}Pu determination, ^{244}Pu was used as yield tracer for isotope dilution analysis. The ^{244}Pu tracer consisted of a mixture of $^{240-244}\text{Pu}$, with no ^{239}Pu , and was purified from small contents of ^{241}Am . The purity of this yield tracer was measured with ICP-MS and γ -spectrometry (^{241}Am , 59.5 keV) prior to use.

The yield in the ^{241}Am determination was determined by the following procedure: before the start of the analytical procedure, ^{241}Am was measured using a lithium drifted silicon detector, Si(Li). This detector has a low counting efficiency for high energy γ -rays, and the high activity of ^{137}Cs and ^{60}Co will thus not disturb the measurement. After separation, the americium fraction was measured using an HPGe detector, at which the yield could be determined. Both the Si(Li) and the HPGe detectors were calibrated with ^{241}Am standards (Amersham plc., England). In the ^{237}Np and the ^{239}Pu determinations the yield tracers were added at the start of the analytical procedure. ^{239}Np was then measured using γ -spectrometry. ^{244}Pu was measured by ICP-MS in the plutonium fraction. In the ICP-MS detection of ^{237}Np , ^{233}U was used as an internal standard.

^{239}Pu was evaluated from the known amount of ^{244}Pu added at the start of the procedure, assuming that no significant mass discrimination occurred in the mass range used in the analysis. Mass discrimination certainly occurs, however, within all experimental and analytical errors the contribution from mass discrimination was proven to be insignificant.

Figure 4-2 shows an example of an unseparated sample. It can be seen that uranium interferes severely on the m/z peak of 237, i.e. the peak for ^{237}Np identification.

Figures 4-3 – 4-5 show spectra of the americium/curium, neptunium and plutonium fractions after the separation. The absence of plutonium in the americium/curium fraction is evident, since ^{239}Pu would otherwise appear at the energy of 5.15 MeV, see Figure 4-3.

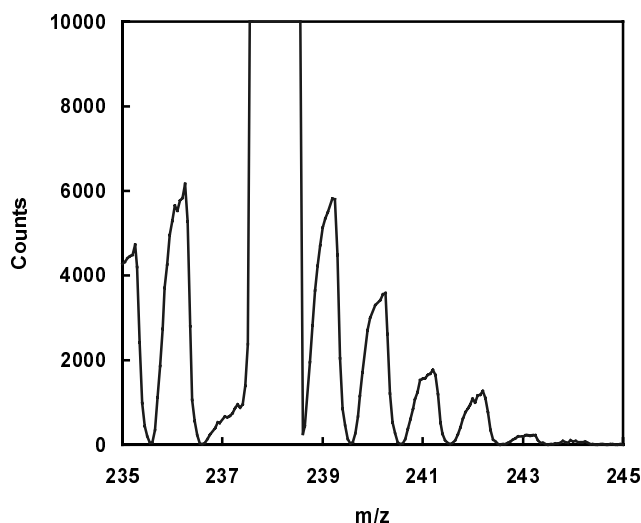


Figure 4-2. ICP-MS spectrum of an unseparated sample.

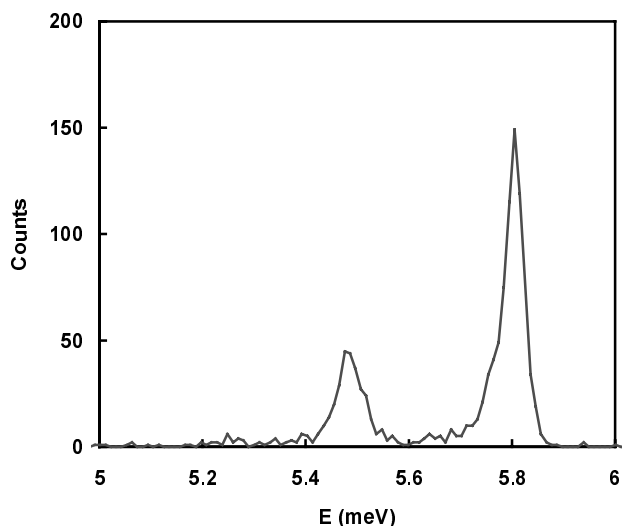


Figure 4-3. α -spectrum of one americium/curium-fraction.

Figure 4-4 shows the lowering of uranium, resulting in resolved peaks of neptunium and uranium. The uranium decontamination factor in the neptunium back-extraction was about 2000.

Figure 4-5 shows one plutonium fraction where the uranium content is lowered (decontamination factor: ~ 200) and the formation of UH^+ could therefore be neglected. The ratio between UH^+ and uranium was found to be about 10^{-5} . A small peak at the m/z ratio of 244 is observed in the neptunium fraction, Figure 4-6 no. 3, which is caused by the $\sim 5\%$ of the plutonium that ended up in the neptunium fraction.

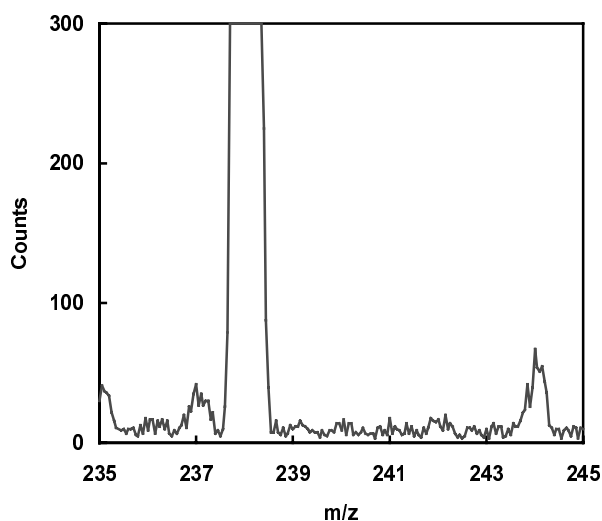


Figure 4-4. ICP-MS spectrum of one neptunium sample. The spectrum shows that the amount of uranium is lowered, resulting in resolved peaks of uranium and neptunium.

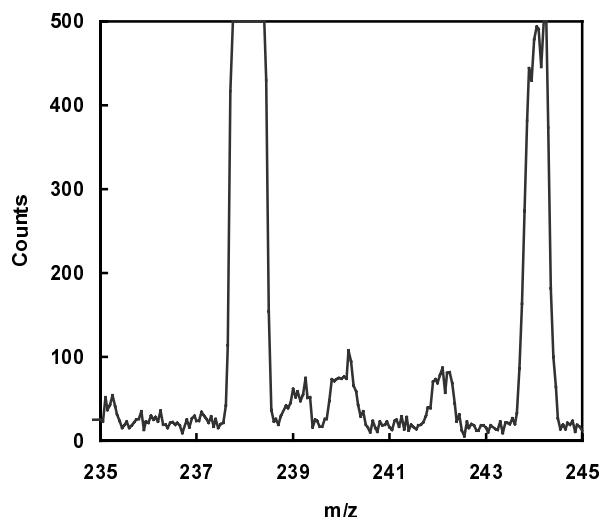


Figure 4-5. ICP-MS spectrum of one plutonium fraction.

The isotope ratios deviating from the expected isotopic ratios of plutonium in spent UO_2 fuel shown in Figure 4-5 result from the addition of the ^{244}Pu standard. As mentioned before, this tracer consisted of a mixture of $^{240-244}\text{Pu}$, but no ^{239}Pu .

The chemical yields in the separation were evaluated in separate tracer experiments, see Table 4-1.

Table 4-1. Chemical yields in the actinide analytical procedure.

Isotope	Recovery (%)
^{237}Np	82 ± 3
^{238}Pu	91 ± 1
^{241}Am and ^{244}Cm	97 ± 2

The detection limits for the different actinides are presented in Table 4-2.

Table 4-2. Detection limits in the actinide analytical procedure.

Isotope	Detection method	Instrumental detection limit [Cur 68]	L_D per sample (yield included)
^{237}Np	ICP-MS ^I	0.06 pg/mL (2 $\mu\text{Bq/mL}$)	0.3 pg (10 μBq)
^{239}Pu	ICP-MS ^{II}	0.6 pg/mL (1 mBq/mL)	4.5 pg (11 mBq)
^{241}Am	α -spectrometry	0.4 mBq (3 fg)	0.4 mBq (3 fg)
^{244}Cm	α -spectrometry	0.4 mBq (0.1 fg)	0.4 mBq (0.1 fg)

^I Internal standard: ^{233}U

^{II} Internal standard: ^{244}Pu

The differences in the detection limit of ^{237}Np and ^{239}Pu with ICP-MS analysis result from the use of the desolvating nebuliser in the ^{237}Np detection. This module increases the sample fraction to the plasma, resulting in more efficient detection. A quantitative solid sample preparation was assumed for the calculation of the detection limit for ^{241}Am and ^{244}Cm , although the total sample was not used in the measurement.

The results obtained using the analytical procedure presented were compared with ICP-MS data from the same fuel. In some samples, small fuel fragments were assumed to be present due to the high actinide concentration and a significantly higher dose rate from these samples. From the analytical results of those samples it was therefore possible to calculate the inventory of the different actinides. The inventory was calculated as the specific amount (μg or GBq) per g uranium in the sample. The results are presented in Table 4-3, together with the inventory analysis using only ICP-MS /Eklund, 1998/ and corrections due to interferences /Forsyth, 1992/.

According to Table 4-3 there are a few minor differences between the two methods. However, these may be the result of differences in burnup for the different fuel specimens, since the same fuel specimens were not used in the diffusion experiment as in the analysis of the inventory.

Table 4-3.

Sample	^{239}Pu ($\mu\text{g/g U}$)	^{237}Np ($\mu\text{g/g U}$)	^{241}Am (GBq/g U)
1	7.8	0.63	0.12
2	7.9	0.77	0.13
3	6.2	0.57	0.12
Eklund, 1998	5	0.5	0.09

4.1 Integration of actinide and ^{90}Sr analysis

Since the same separation agent (HDEHP) was used in both the analysis of ^{90}Sr and the analysis of actinides, these two methods could be integrated into one procedure /Ramebäck and Skålberg, 1998/. The result is a method which makes it possible to analyse several radionuclides of interest in research and environmental monitoring with only one procedure.

After the actinide separation, the remaining aqueous phase was adjusted to 1 M nitric acid, thereafter the samples (six bentonite clay samples after actinide analysis were used in this experiment) were set aside for some days to let ^{90}Y grow in (^{90}Y was first removed at the actinide group separation). ^{90}Y was thereafter extracted once more into 1 M HDEHP in Solvent 70. The extraction was done twice with 10 mL organic phase each time. The organic phase was measured by means of Cherenkov counting using a liquid scintillation counter (LKB Wallac 1219 Rackbeta, Finland).

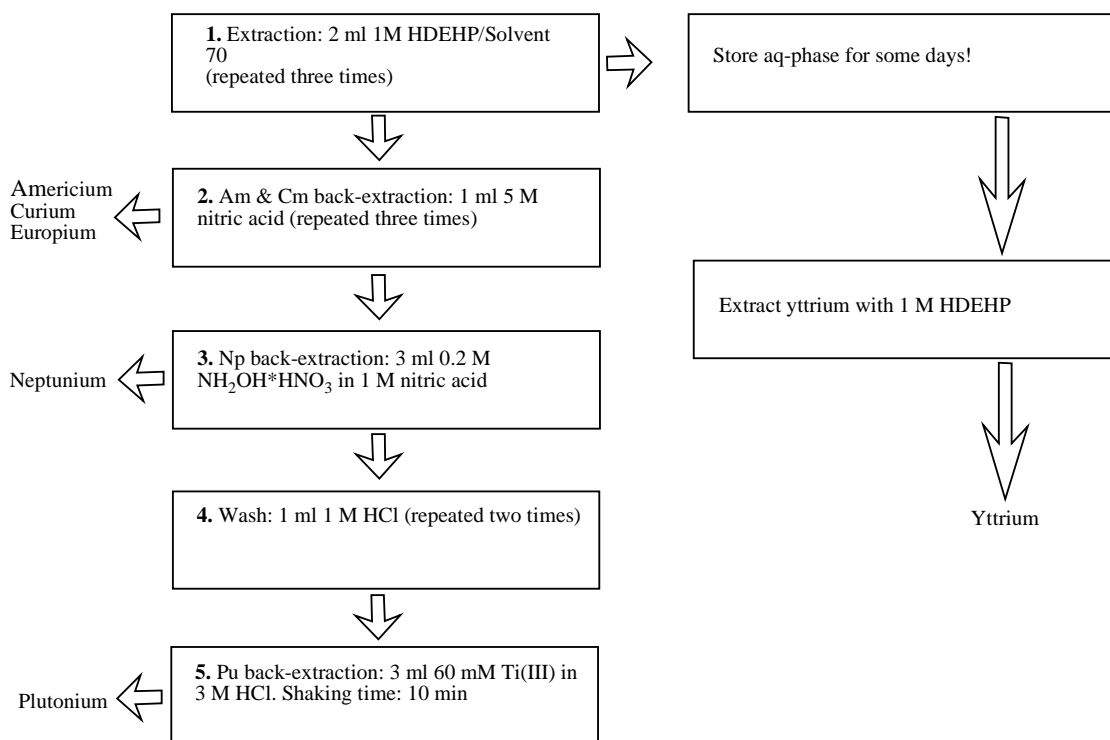


Figure 4-6. Analytical procedure for ^{90}Sr and actinide analysis.

The counting efficiency for a 10-mL sample was $75\pm 1\%$, to be compared with $65\pm 2\%$ when measuring only 1 mL. The increase in counting efficiency is due to an improved counting geometry. The complete procedure for the assay of ^{90}Sr , neptunium, americium, curium and plutonium is presented in Figure 4-6.

5 Uranium analysis

The clay samples were treated with a 10-mL solution containing 1 M nitric acid at 65°C for 12 hours. After centrifugation, 8 mL was used for analysis with ICP-MS. All measurements involved ^{233}U as the internal standard, assuming that the response at the m/z ratio of 236 was the same as for the m/z ratio of 233. This was later verified by comparing standard solutions containing ^{233}U and ^{238}U . In Figure 4-2, a peak at the m/z ratio of 236 is present, originating from the ^{236}U content in the sample.

Since the natural uranium content of the bentonite clay is high, analysis of uranium by means of ^{235}U or ^{238}U was impossible. It is therefore not possible to distinguish between the uranium present in the bentonite clay and the uranium originating from the spent UO_2 fuel. Uranium was therefore analysed by means of ^{236}U , which is not naturally present in bentonite clay but is formed by (n, γ)-reactions in ^{235}U and by the decay of ^{240}Pu .

Both different bromate and different nitric acid concentration were used to study the influence on the leaching yield. Leaching in two sequences with 10 mL each time was also used. None of these methods gave different yield than using 10 mL 1 M nitric acid.

6 Conclusions

Three analytical procedures for assay of the radionuclides ^{90}Sr , ^{99}Tc and actinides present in bentonite clay have been presented. The method for ^{90}Sr was an existing analytical procedure that was modified to handle the sample matrix (bentonite clay) originating from the experiment. The other methods were designed and developed for this project. These procedures may, of course, after some modifications depending e.g. on the sample matrix, be applied to other sample types.

All methods are specific, i.e. after chemical separation the analytical signals from the different detection methods are free from interference. No corrections are therefore needed. The detection methods used (radiometric or ICP-MS) were chosen to give the lowest possible detection limit for each radionuclide.

7 References

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