Extraction Chromatographic Separation of Sr, Pu and Am in Environmental Samples

By

Rajdeep Sidhu

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Abstract

An accurate determination of radionuclides from various sources in the environment is essential for assessment of the potential hazards and suitable countermeasures both in case of an authorised release, accidents and routine surveillance. Due to the short range of alpha and beta radiation, the accurate determination of pure alpha and beta emitters must always include radiochemical separations to separate the analytes from the matrix and from other interfering stable and radioactive nuclides. Hence, the procedures used for their determination are usually tedious and involve several pre-concentration and separation steps.

This work deals with the determination of $^{90}$Sr, $^{241}$Am, $^{238}$Pu, $^{239,240}$Pu and $^{244}$Cm, which are some of the most important artificial radionuclides. Due to either absence or low yield of gamma radiation, a secure determination of low concentrations of all these nuclides requires a dedicated chemistry.

Selective extraction chromatographic resins (TRU- and Sr-Resin) have been utilised to develop new procedures for the analyses of Pu, Am and Cm isotopes in seawater and both these and $^{90}$Sr in soil, sediment, urine and low-level liquid radioactive effluents. The proposed method for the analyses of Pu and Am in seawater offers a quick and secure mode for the determination of these radionuclides in marine waters. Combined pre-concentration of actinides and strontium (oxalate or phosphate precipitation) followed by dual column separation on TRU- and Sr-Resin significantly reduces the throughput time and costs compared to traditional ion exchange and precipitation methods. The greatest gain in productivity and environmental friendliness is achieved in Sr separations using Sr-Resin instead of precipitations involving fuming nitric acid and oxalate, hydroxide, chromate and carbonate precipitations.
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Rajdeep Sidhu
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# 2. Abbreviations

<table>
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<th>Abbreviation</th>
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<tr>
<td>AMS</td>
<td>Accelerator Mass Spectrometry</td>
</tr>
<tr>
<td>CMPO</td>
<td>octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide</td>
</tr>
<tr>
<td>DAAP</td>
<td>diamyl amylphosphonate</td>
</tr>
<tr>
<td>DDCP</td>
<td>dibutyl-N,N-diethylcarbamoyl phosphonate</td>
</tr>
<tr>
<td>DMG</td>
<td>dimethylglyoxime</td>
</tr>
<tr>
<td>DTBCH18C6</td>
<td>4,4'(5')-di-t-butylcyclohexano 18-crown-6</td>
</tr>
<tr>
<td>DTPA</td>
<td>diethylenetriaminepentaacetic acid</td>
</tr>
<tr>
<td>FCV</td>
<td>Free column volume</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HDEHP</td>
<td>bis(2-ethylhexyl) phosphoric acid</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma - Mass Spectrometry</td>
</tr>
<tr>
<td>PMBP</td>
<td>1-phenyl-3-methyl-4-benzoyl-5-pyrazolone</td>
</tr>
<tr>
<td>PUREX</td>
<td>Plutonium and Uranium Recovery by Extraction (Process)</td>
</tr>
<tr>
<td>TALSPEAK</td>
<td>Trivalent Actinide/Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Complexes</td>
</tr>
<tr>
<td>TBP</td>
<td>tri-n-butylphosphate</td>
</tr>
<tr>
<td>TIMS</td>
<td>Thermal Ionization Mass Spectrometry</td>
</tr>
<tr>
<td>TIOA</td>
<td>tri-isooctylamine</td>
</tr>
<tr>
<td>TNOA</td>
<td>tri-n-octylamine</td>
</tr>
<tr>
<td>TOPO</td>
<td>tri-n-octylphosphine oxide</td>
</tr>
<tr>
<td>TRU</td>
<td>Transuranium</td>
</tr>
<tr>
<td>TRUEX</td>
<td>Transuranium Extraction (Process)</td>
</tr>
<tr>
<td>TTA</td>
<td>thenoyltrifluoroacetone</td>
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3. Introduction

3.1. Background

The utilisation of nuclear weapons and nuclear power has led to environmental distribution of artificial radionuclides. Although the concentration and therefore the radiological significance of artificial radionuclides in our surroundings is much lower than primordial radionuclides, it is essential to carefully monitor their inventories since many of them have long half lives and are potentially hazardous and highly radiotoxic. These types of studies offer valuable information on the chemistry of these elements, and provide us with general scientific information and a wider understanding of environmental, ecological and biogeochemical phenomena.

The most important global source of actinides and fission products in the environment are the about 500 atmospheric weapon tests performed during 1945 – 1980 [1]. Prior to 1952 the explosions had a low yield and the detonations were carried out in the troposphere. After 1952 the detonations were carried out in the stratosphere, which lead to a more global dispersion of the radionuclides. Since most of the detonations were carried out in the northern hemisphere, about 2/3 of the activity released is found there [2]. Accidents such as the Chernobyl accident and SNAP-9A satellite accident have also contributed to the global dispersion of radionuclides. In contrast, the two B-52 accidents in Palomares, Spain, and Thule, Greenland, and authorised and accidental non-explosive releases from nuclear installations (i.e. power plants, fuel fabrication plants and reprocessing plants) have mainly led to localised contamination of the environment.

An accurate determination of radionuclides from various sources in the environment is essential for assessment of the potential hazards and suitable countermeasures both in case of an authorised release, accidents and routine surveillance. The determination of gamma emitters is normally quite straightforward and can be accomplished through gamma spectrometry on untreated samples for the determination of several radionuclides simultaneously. Chemistry is only involved when the amount of
analytes is so low that they have to be pre-concentrated or when the sample contains gamma emitters with gamma lines that cannot be distinguished. Care must also be taken to compensate appropriately for self-absorption in the sample for gamma emitters with low energy gamma rays (e.g. \(^{210}\)Pb, \(^{226}\)Ra, \(^{241}\)Am).

Due to the short range of alpha and beta radiation, the accurate determination of pure alpha and beta emitters must always include radiochemical separations to separate the analytes from the matrix and from other interfering stable and radioactive nuclides. Hence, the procedures used for their determination are usually much more tedious and involve several pre-concentration and separation steps.

This work deals with the determination of \(^{90}\)Sr, \(^{241}\)Am, \(^{238}\)Pu, \(^{239,240}\)Pu and \(^{244}\)Cm, which are some of the most important artificial radionuclides. Due to either absence or low yield of gamma radiation, a secure determination of low concentrations of all these nuclides requires a dedicated chemistry.

### 3.2. Objective and outline

The major objective of this work has been to explore the use of selective extraction chromatographic resins to simplify the determination of \(^{90}\)Sr, \(^{238}\)Pu, \(^{239,240}\)Pu and \(^{241}\)Am in environmental (seawater, soil, sediment) and bioassay samples (urine) as well as low-level liquid effluents from a small nuclear research reactor. Emphasis is given to the use of commercially available selective extraction chromatographic resins. Simpler and faster pre-concentration, pre-treatment and separation techniques are explored.

Chapter 4 provides a basic introduction to extraction chromatography and resins used for actinide and Sr separation, with an emphasis on the commercially available TRU- and Sr-Resin.

Chapter 5 describes the principles of Sr and actinide analysis and presents this work in a broader context.
Chapter 6 presents the procedures that have been developed during this study.

Chapter 7 summarises the findings.
4. Extraction chromatography

4.1. General principles

Two methods widely used in radiochemical separations are solvent extraction and ion exchange. Solvent extraction offers the great advantage of choosing between numerous extractants that can be made highly selective. It is generally too labour consuming for routine analysis, because several extractions must take place to completely separate the analytes from the bulk of the solution. Furthermore, difficulties in phase separation and the mutual solubility of the two phases can produce a significant loss of the analyte. In contrast, ion exchange chromatography is simple, has high capacity, does not require supervision, but offers limited selectivity. Therefore, ion exchange chromatography is often followed by solvent extraction to achieve high yields and chemical purity.

Extraction chromatography, also referred to as reversed-phase partition chromatography, is a process combining the diversity and selectivity of solvent extraction with the ease of use and multistage nature of ion exchange chromatography. The term Extraction chromatography was suggested by E. K. Hulet in 1963 [3]. In this technique the stationary phase consists of one or more extractants sorbed on a porous support material. The inert support is normally composed of porous silica or organic polymers with particle sizes typically between 50 and 150 µm. Diluents are sometimes added to dissolve the extractant and to increase the hydrophobicity of the stationary phase. The aqueous solution is normally acidic and can be added complexing agents to further increase the selectivity.

The pioneering work on extraction chromatography was done during the late 50’s and early 60’s and the technique was first proposed by Siekierski in 1959 [4]. Since then many different resins have been prepared and evaluated. It is a well-established technique and has been used widely for the separation of inorganic analytes. A comprehensive survey of this technique is given in the treatise by Braun and Ghersini [5] and Cortina and Warshawsky [6].
Many well known extractants as bis(2-ethylhexyl) phosphoric acid (HDEHP), tri-n-butylphosphate (TBP), tri-n-octylphosphine oxide (TOPO), octylphenyl-N,N-di-isobutyl carbamoylphosphate oxide (CMPO), thenoyltrifluoroacetone (TTA), tri-n-octylamine (TNOA), tri-n-octylmethylammonium chloride (Aliquate-336) etc. have all been used in extraction chromatographic separation of especially actinides.

The use of extraction chromatography in radionuclide separations found a wider application in the 1990’s when a series of new resins became commercially available. Horwitz and co-workers have developed several such extraction chromatography resins containing well-known extractants. A description of these can be seen in Table 4.1.

**Table 4.1** Resins commercially available from Eichrom Industries [7].

<table>
<thead>
<tr>
<th>Resin</th>
<th>Active extractant</th>
<th>Application</th>
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<tbody>
<tr>
<td>Sr-Resin</td>
<td>bis-4,4’(5’)-tertbutylecyclohexano-18-crown-6</td>
<td>Sr, Pb, Po</td>
</tr>
<tr>
<td>TRU-Resin</td>
<td>octylphenyl-N,N-di-isobutyl carbamoylphosphate oxide (CMPO)</td>
<td>Th, U, Pu, Am, Cm, Fe</td>
</tr>
<tr>
<td>RE-Resin</td>
<td>octylphenyl-N,N-di-isobutyl carbamoylphosphate oxide (CMPO)</td>
<td>Rare earth elements</td>
</tr>
<tr>
<td>UTEVA-Resin</td>
<td>diaminyl amylyphosphonate (DAAP)</td>
<td>U, Th, Np, Pu</td>
</tr>
<tr>
<td>TEVA-Resin</td>
<td>Tri-n-octylmethylammonium chloride (Aliquat 336)</td>
<td>Th, Np, Pu, Tc, Am/Ln separation</td>
</tr>
<tr>
<td>Ni-Resin</td>
<td>dimethylglyoxime (DMG)</td>
<td>Ni</td>
</tr>
<tr>
<td>Actinide-Resin</td>
<td>P-P’-di(2ethylhexyl)-methaenediphosphonic acid</td>
<td>Am, Pu, Th, U</td>
</tr>
<tr>
<td>Pb-Resin</td>
<td>bis-4,4’(5’)-tertbutylecyclohexano-18-crown-6</td>
<td>Pb</td>
</tr>
<tr>
<td>Ln-Resin</td>
<td>bis(2-ethylhexyl) phosphoric acid (HDEHP)</td>
<td>Lanthanides, Pa, Ra</td>
</tr>
</tbody>
</table>
All the resins are available from Eichrom Ind. (Darien, I.L., USA) in particle sizes ranging from 20 - 150 \( \mu \)m, either in prepacked columns or cartridges with 0.7 gram material or as bulk resins. A major advantage of some of these resins is that they can be coupled together to facilitate sequential analysis of several radionuclides in the same sample. A procedure using the coupling of TRU-Resin on top of Sr-Resin is utilised in Paper V for the separation and isolation of Sr, Pu and Am from urine, soil and sediment samples.

### 4.2. TRU-Resin

In this resin the inert backbone, Amberchrom TM CG-71, is coated with 13 wt. % CMPO dissolved in 27 wt. % tri-n-butylphosphate, TBP [8, 9]. The resin has a working capacity, 20% of maximum loading, of 2 mg Am per ml resin. The chemical structures of CMPO and TBP are shown in Figure 4.1 and Figure 4.2, respectively. The material is based on the TRUEX-process [10-12], where the combination of CMPO/TBP in a suitable organic diluent is used to extract tri-, tetra-, and hexavalent actinides during reprocessing of used reactor fuel. The extractant was specifically designed to extract Am(III) from nitric acid solutions, a task which is not accomplished with TBP in the PUREX process.

![Structure of octyl(phenyl)-N,N-diisobutyl-carbamoylmethyl-phosphine oxide, CMPO](image)

**Figure 4.1.** Structure of octyl(phenyl)-N,N-diisobutyl-carbamoylmethyl-phosphine oxide, CMPO
The pioneering work done by Siddall [13, 14] on the evaluation of bidentate organophosphorus compounds as extractants has lead to the preparation and evaluation of various bidentate extractants. One of the best reagents for the extraction of trivalent actinides and lanthanides from nitric acid solutions is CMPO. The extractant CMPO contains multidentate oxygen donors (P=O, C=O), which can be effectively packed around the f-element, in a manner that gives maximum number of ligand donor-metal interactions with a minimum of steric hindrance [15]. While substituents on nitrogen primarily influence the extractants solubility, the substituents on phosphorous also influence the extraction capacity. The extraction of metals is significantly increased, and the solubility in water decreased, when alkyl groups on phosphorous are replaced by more electronegative aryl substituents [16, 17]. The close approximation of the less basic carbonyl group gives the extractant chelating properties, which influence the selectivity of the extractant. The bridge between the functional groups influences both the solubility and the extraction properties. Short and linear bridges give the highest extraction, as the gap between the chelating groups is minimised and steric hindrance avoided.

In nitric acid solutions Am(NO₃)₃ is complexed by three CMPO molecules and Pu(NO₃)₄ and UO₂(NO₃)₂ by two CMPO molecules and thereby removed from the aqueous solution. As CMPO does not extract trivalent actinides from hydrochloric acid, extracted Am(III) and Pu(III) can be easily eluted by shifting the aqueous medium to hydrochloric acid. Tetra and hexavalent actinides are strongly complexed, even in hydrochloric acid medium, and must either be reduced to their trivalent state and/or complexed by aqueous complexing agents to facilitate an elution.
Figure 4.3 and Figure 4.4 show the uptake of several actinides from HNO₃ and HCl media, respectively. The Y-axis shows the number of free column volumes (FCV) to peak maximum, k’. One FCV is approximately 65% of the bed volume of a column. k’ equals volume distribution ratio (D) times the ratio of the stationary phase volume (vₛ) by mobile phase volume (vₘ) on a column, \( k' = D \cdot \frac{v_s}{v_m} \). Values higher than 100 indicate strong retention, values between 1 and 50 indicate weak retention, and values below 1 indicate no retention on a column. As seen in Figure 4.3 tri-, tetra-, and hexavalent actinides are strongly extracted by the resin from HNO₃ solutions.

While Fe(II) does not show any negative effect on the uptake of the actinides, Fe(III) is extracted by CMPO and thereby suppresses the extraction of actinides. In this work Fe(III) is reduced to Fe(II) by the addition of ascorbic and sulfamic acid (Paper III and V). Ascorbic acid reduces Fe(III) quickly but is unstable in nitric acid solutions due to the presence of nitrite. Sulfamic acid is therefore added to remove nitrite.

**Figure 4.3** Uptake of metal ions by TRU-Resin from HNO₃ [9].

**Figure 4.4** Uptake of metal ions by TRU-Resin from HCl [9].
The addition of Al(NO$_3$)$_3$ (Paper III and V) has a positive effect on the retention of Am(III). In this manner the nitrate concentration can be increased without increasing the acidity. As aluminium is hydrated in aqueous solutions it further increases the nitrate activity and promotes the formation of extractable Am(NO$_3$)$_3$ complexes. In addition Al(III) forms strong complexes with potentially interfering fluoride and phosphate ions and thereby reduces their negative impact on the retention of the actinides.

The oxalate ion, due to the formation of strong oxalate complexes, has a negative effect on the retention of actinides. Thus oxalate solutions can be used to elute actinides from the column. If Ca-oxalate precipitation is used to pre-concentrate Pu or Am, Paper V, oxalate must be completely destroyed before TRU-Resin separation.

The strong retention of Pu(IV) allows the use of small amount of resin for the concentration of Pu(IV) from large volume solutions. The uptake of Pu(IV) from 1 litre 2 M HNO$_3$ – 0.05 M NaNO$_2$ on varying amount of resin can be seen in Figure 4.5.

![Figure 4.5 Pu(IV) uptake from 1 litre 2 M HNO$_3$ – 0.05 M NaNO$_2$ with varying amount of TRU-Resin on a column with an internal diameter of 5 mm and a flow of 4 ml/min [18].](image-url)
Eichrom pre-packed columns have an internal diameter of 7 mm to allow a reasonable flow without any vacuum source. Columns with an internal diameter of 5 mm in connection with a vacuum source were used throughout this study to improve the chromatographic parameters by minimizing the diameter.

Due to the fast extraction kinetics large flow rates can be utilized. The influence of flow rate on the uptake of Pu was studied and the results are shown in Figure 4.6. The results show that even at a flow rate of 7 ml/min, 300 mg TRU-Resin is capable of extracting about 75% of Pu(IV) from 1 litre 2 M HNO₃ – 0.05 M NaNO₂ solution.

TRU-Resin has been used for the analysis of actinides from various materials as soil, sediment, bioassay samples, water, air filters, milk, algae, lobster, crab, fish, mussel, waste solutions, seawater [8, 19-37].

\[ \text{Figure 4.6 Pu(IV) uptake from 1 litre 2 M HNO}_3 - 0.05 \text{ M NaNO}_2 \text{ on a 5 mm internal diameter column containing 300 mg TRU-Resin with varying flow rate [18].} \]
4.3. Sr-Resin

The extractant in Sr-Resin consists of the crown ether 4,4'(5')-di-t-butylecyclohexano 18-crown-6, abbreviated DTBCH18C6 (Figure 4.7), dissolved in 1-octanol [38-40].

![Figure 4.7 Structure of 4,4'(5')-di-t-butylecyclohexano 18-crown-6](image)

Crown ethers were accidentally discovered by Pedersen in 1967 [41]. These macro cyclic polyethers contain ethylene bridges separated by donor oxygen atoms. The cavity, which is ringed with electronegative oxygen atoms, gives the interior of the crown a hydrophilic character whilst the surrounding ethylene groups, forming the cyclic framework, give the exterior of the crown a hydrophobic character. This leads to a great flexibility as the crown can either expose hydrophilic ether oxygen atoms or lipophilic ethylene groups to the surrounding medium. This feature also leads to rapid, and reversible ion binding characteristics [42].

A major aspect of crown ether chemistry is the “size fit” of the metal with respect to the crown ether cavity. When the ionic diameter of a metal ion fits with the size of the cavity, the metal ion can get incorporated inside the cavity. The cavity size of 18 membered rings is about 2.6 – 3.2 Å [42], which means that Sr (2.4 Å), Pb (2.4 Å), K (2.7 Å), Ba (2.7 Å) and Ra (3.0 Å) (ionic diameter) [43] all can get incorporated inside the cavity.
Substituents on the benzo groups also play an important role. The bulky t-butyl groups in the DTBCH18C6 minimize aggregation of the crown at higher concentration and therefore lead to a higher extraction of Sr than the unsubstituted crown. The counter anion and diluent are of prime importance in the extraction. Since hard anions such as nitrate are hydrated in aqueous solutions they cannot be transferred to nonpolar solvents without removal of the hydration sphere. In Sr-Resin octanol is used as diluent. The hydrogen-bonding nature of octanol allows the extraction of nitrate in its hydrated state by increasing the H$_2$O concentration in the organic phase [44]. The Sr-extraction efficiency with a crown ether from acidic nitrate media into a given solvent is in fact directly proportional to the solvents ability to dissolve water [45].

Figure 4.8 shows the Sr-Resin uptake of alkaline earth elements from nitric acid solutions. Sr has the highest extraction efficiency of all the elements. As most environmental samples contain large amounts of potassium, and the resin also retains small amounts of potassium, a good separation from $^{40}$K is normally achieved before Sr-Resin separation by performing an oxalate precipitation of Sr (Paper V). Large amounts of Ca in the sample also lead to low recoveries of Sr. When using a 2 ml Sr-Resin column Sr recoveries start to drop when Ca amount exceeds about 0.3 gram and almost no Sr is retained when Ca amount exceeds about 1.3 gram.

As seen in Figure 4.8 Ba is also extracted by the resin. A good separation from Ba can be achieved by loading or washing the column with concentrated nitric acid, e.g. 8 M HNO$_3$. 

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Figure 4.8 Sr-Resin uptake of alkaline earth elements from HNO₃ [40].

Figure 4.9 shows the uptake of actinides with Sr-Resin. Tetravalent actinides are extracted very strongly by the resin and Pu(IV) retention is even higher than Sr(II) retention for nitric acid concentrations above about 1 M. Actinides can although be stripped very easily from the column, without stripping Sr, by washing the column with nitric acid containing oxalic acid. In this manner the resin can also be used to perform Pu separations.

A major advantage of crown ethers lies in the reversibility of the extraction. High nitrate concentration promotes the extraction of Sr while contact with water reverses the reaction thereby stripping the Sr. In this manner Sr can easily be stripped without use of any complexing agents. When extracting Sr from 3 M HNO₃, less than 0.5% of the Sr introduced is eluted with the first 30 FCV’s (free column volume) while about 98% is eluted with the first 2.5 FCVs when the medium is shifted to water [38]. When using liquid scintillation for Sr-activity determination this is an advantage as quenching is minimized.
A drawback is though the low Sr-capacity of the resin. Sr amounts exceeding about 10 mg lead to a sharp decrease in Sr-recovery on a 2 ml resin. Thus “normal” Sr-Resin columns containing 0.7 gram resin cannot be used for the analysis of $^{90}$Sr in seawater as seawater contains about 8 mg/litre of inactive Sr.

Figure 4.9 Sr-Resin uptake of actinides and Sr from HNO$_3$ [40].

Sr-Resin extracts Sr very efficiently at the same nitric acid concentrations as TRU-Resin extracts Pu. Hence, these resins can easily be coupled together to achieve a sequential analysis of both Pu and Sr in the same sample solution. This is utilized in Paper V where TRU-Resin is coupled on top of Sr-Resin for the separation and analysis of Pu, Am and Sr in soil, sediment and urine samples.

The use of Sr-Resin for Sr analysis is getting increasingly popular due to the simplicity. The resin has been used for the analysis of Sr in grass, soil, sediment, milk, urine, nuclear waste, production of Y-90 for medical applications, etc. [23, 38-40, 45-60].
5. Radiochemical analysis of Pu, Am and Sr

The method of choice depends on several factors. The most important are the actinide content and the physical composition of the sample, as well as the concentration of other elements and compounds in the sample. The procedure used will also be influenced by the goal of the investigation; total radionuclide content, chemical speciation distribution, information about one or several radionuclides etc.

In general a radiochemical procedure consists of the following main steps:

- Pre-treatment
- Pre-concentration
- Dissolution
- Chemical separation
- Radioactivity determination

5.1. Pre-treatment

In order to obtain information about “dissolved” and/or suspended particulate fractions, the water sample is filtered through appropriate filters before acidification to pH 1-2. For the determination of “total dissolved analyte” the cut-off limit is by definition set at 0.45 μm particle size. Acidification at an early stage is extremely important to avoid the formation of hydrolysed actinide species with great affinity towards exposed surfaces. Lovett et al. [61] studied the adsorption of $^{241}$Am from unacidified and acidified (pH11) filtered seawater onto the walls of a 25-litre polyethylene container. Their results show that approximately 50% of the Am is lost from the solution in two weeks if the water is not acidified. Acidification also helps in leaching of radionuclides from colloidal and particulate matter.
Tracers should be added after acidification as hydrolysis of the tracer can lead to an uneven distribution. In the analysis of elements that can co-exist in several oxidation states with different chemical behaviour, e.g. Pu, it is important to ensure that the chemical procedure employed does not discriminate between the different oxidation states. Ensuring that Pu only exists in one oxidation state, normally Pu(III), by performing a unequivocal redox cycle, or that Pu exits in oxidation states with minimal difference in chemical behaviour can minimize the discrimination. A discussion on Pu chemistry is given in Paper I.

The pre-treatment of solid samples usually requires drying (105 °C) and dry ashing (450 °C). If only part of the sample is to be analysed, samples should be sieved to achieve an accurate determination of dry and ash weight and to homogenise the sample.

5.2. Pre-concentration of water samples

Due to the low concentration of artificial radionuclides in environmental waters (90Sr: 0.5 - 10 mBq/l; 239,240Pu: 0.5 - 10 μBq/l. The Irish Sea contains larger amounts), large water samples must be analysed to achieve a secure determination of the analytes. Pu and Am determination in most environmental waters requires the analysis of about 200 litre water samples while 90Sr-analysis requires about 50 litres. The analytes must therefore be concentrated to a smaller volume before further chemical separations can take place.

The method of choice is usually co-precipitation. Many different precipitating agents have been employed.

CaCO3
Calcium in seawater can be precipitated as CaCO3 by increasing the pH of the water to about 10. Mixed CaCO3 and Mg(OH)2 precipitation has earlier been used for the co-precipitation of Pu [62, 63]. It is in limited use today as tests have shown that not all oxidation states of Pu are effectively precipitated [64-66]. Nevertheless, carbonate
precipitation is an effective way of concentrating Sr from seawater. The succeeding separation schemes must be able to separate Sr from large amounts of Ca (400 mg/l).

\textbf{NdF}_3 / \text{LaF}_3 / \text{CeF}_3

Rare earth fluorides are very effective scavengers of actinides in oxidation state III and IV, while they do not co-precipitate actinides in oxidation state V and VI. This fact has been employed in several separation schemes. A procedure has been developed for the determination of reduced (Pu(III) & Pu(IV)) and oxidized (Pu(V) & Pu(VI)) fractions of Pu in water samples [67, 68]. After acidification the water sample is added a soluble chromate salt which oxidises Pu(III) to Pu(IV) and Pu(V) to Pu(VI). Chromate simultaneously prevents the reduction of Pu when HF is added to co-precipitate reduced Pu with NdF$_3$. The precipitate is then separated and oxidised Pu in the supernatant is reduced and precipitated with the addition of Nd. Cross contamination between the different fractions, monitored with the addition of $^{242}$Pu(IV) and $^{236}$Pu(VI), is less than 2%.

Several other separations between actinides are possible: Chemically stable Th(IV) can be separated from oxidised actinides (U(VI), Np(V), Pu(V) and Pu(VI)). Pu can be reduced to Pu(III) or Pu(IV) and separated from U(VI) or Pu can be oxidised and separated from Am(III) [69]. CeF$_3$ micro co-precipitation followed by collection of the fluorides on a 0.1 µm membrane filter is used as a source preparation step in \textit{Paper II – Paper V}.

\textbf{Fe(OH)$_2$ and Fe(OH)$_3$}

Ferric and ferrous hydroxide co-precipitation of actinides is extensively used to preconcentrate actinides from large water volumes [[61, 70-73]. The method became an early standard after its introduction in 1971 [74]. While reduced actinides (oxidation states III and IV) co-precipitate with small quantities of Fe(OH)$_3$, the quantitative co-precipitation of oxidized actinides requires at least 10 mg/l Fe$^{3+}$ [61]. The iron hydroxide slurry is subsequently collected and brought to solution by treatment with mineral acids. Quite often a second Fe(OH)$_3$ co-precipitation step is carried out to further concentrate the actinides, before a preliminary separation from Fe can be achieved with e.g. Ca-oxalate co-precipitation. The oxalates are then destroyed by either dry or wet ashing and the salts picked up with mineral acids. After
treatment with redox agents the actinides are separated from each other and from other interfering elements with the use of solvent extraction, ion exchange and/or extraction chromatographic techniques.

**MnO$_2$**

MnO$_2$ has long been known to scavenge actinides. A method for the co-precipitation of Pu with MnO$_2$ was proposed in 1978 by Wong et al. [75]. They added KMnO$_4$ to the acidified water and reduced it to MnO$_2$ for the co-precipitation of Pu after adjustment of pH to about 9. Although they achieved high Pu yields, 80-90% when analysing 400 litre water samples, and MnO$_2$ is mentioned as an effective scavenger of Pu in several publications [76-78], this scavenger has been given very little attention. Recently La Rosa et al. utilised MnO$_2$ to preconcentrate Pu and Am from 500 litre seawater [79].

Due to its many advantages, MnO$_2$ precipitation was chosen in this work (**Paper II** and **Paper III**) to pre-concentrate Pu and Am from 200 litre water samples. When KMnO$_4$ is added to the acidified water the MnO$_4^-$ ion helps in leaching Pu and Am by oxidising colloidal organic matter present in the water. Secondly the MnO$_4^-$ ion oxidises Pu(III) to Pu(IV) and Pu(V) to Pu(VI) and thereby increases the particle affinity of Pu. MnO$_2$ also forms larger aggregates that precipitate fast and are easily collected by filtration. In this work MnO$_2$ is collected both by filtration through a glass wool column (**Paper II**) and by settling (**Paper III**). MnO$_2$ is then dissolved using mineral acids and H$_2$O$_2$ and subjected to chemical treatment for separation of Am and Pu.

When combined with TRU-Resin this gives an additional advantage as Mn is poorly extracted by CMPO and the large amounts of Mn do not influence the uptake of Pu(IV). In contrast, large amounts of Mn lead to a sharp decrease in Am(III) uptake by CMPO. Mn must therefore be removed before Am can be separated using TRU-Resin (**Paper III**). In this work this is achieved by performing a second small-scale precipitation of Fe(OH)$_3$ at pH 5.5. At this pH manganese stays in the solution while Fe(OH)$_3$ carries the actinides.
MnO$_2$-impregnated cartridges have also been used to collect actinides from very large volumes (4000 litre) [75, 80-83]. The method has shown to be effective for Th and Am but gives varying results for Pu [82]. In experiments by Mann et al. the Pu recovery varied between 16-100% [80]. Wong et al. achieved good correlation with Fe(OH)$_3$ scavenging for lagoon and open ocean water (but not for shallow and ground water [83]). It seems as if Pu in different oxidation states is discriminated due to kinetic effects.

**Ca-oxalate and Ca-phosphate**

Ca-oxalate precipitation is frequently used to pre-concentrate Sr from large seawater samples [84]. Both oxalate and phosphate precipitations are very effective, especially when sequential analyses are desired, as they co-precipitate both Sr and the actinides. With the addition of approximately 100 mg Ca$^{2+}$ and 5 ml conc. H$_3$PO$_4$, Sr and the actinides can be recovered almost quantitatively from a 24-hour urine sample when the pH is raised above about 8 (Paper V). Oxalate precipitation is frequently used in the preconcentration of actinides and Sr$^{2+}$ (and Y$^{3+}$), and to remove interfering elements as K$^+$ and Fe$^{3+}$ as they are left in the solution. This is utilized in Paper V for the sequential analysis of Sr and Pu in soil and sediment, to avoid the interference of K in Sr separation, and Fe in Pu separation.

**5.3. Sample dissolution**

The analytes must be brought into solution before further chemical separations. The ash from pre-treatment of solid samples is therefore subjected to treatment with hot hydrochloric and nitric acid. Leaching of the ash with mineral acids does not necessarily leach out all of the analyte, but the amount not leached is generally low. Radionuclides bound to or incorporated into refractory oxides are much more difficult to leach.

Total dissolution of the matrix using either hydrofluoric acid in combination with mineral acids or by fusion with various fluxes (e.g. Na$_2$CO$_3$ and alkali borates) is also used. While total dissolution ensures availability of the analyte and a complete
exchange between the added tracer and the analyte, it is a laborious procedure complicating the analysis due to the large amount of other elements present in the solution.

Since the amount leached depends on the chemical species of the analyte, matrix and the chemical and physical parameters of the leaching procedure, the leaching is usually conducted at elevated temperature by treating the ash for several hours, even overnight, with large amounts of acid.

The use of microwave ovens can considerably simplify the leaching process. As microwaves act on the molecular level they increase the vibration of the molecules and thereby increase the kinetics of the various reactions taking place. Closed microwave systems, requiring the use of pressure vessels, or so-called “bombs”, are very effective. These vessels hold strong mineral acids or alkalis at temperatures well above normal boiling points, thereby allowing complete digestion or dissolution of samples that would react slowly or incompletely at atmospheric pressure. The drawback is the inability to handle large amount of material, typically only 0.1 - 1.0 gram.

In recent years, open focused microwave ovens have also been introduced. Since the reactions take place in an open vessel there is no pressure build up. Hence, larger amounts of material can be handled and reagents can be added during the digestion. Since the energy is directed only at the portion of the vessel in the path of the focused microwaves, the neck of the vessel and the refluxer remain cool and ensure refluxing.

The usefulness of an open focused microwave oven for the analysis of Sr and Pu in soil and sediment samples is tested in Paper V. The results so far are very encouraging as they show that the same amount of Pu and Sr can be leached out using small amount of acids on an open focused microwave oven in a shorter time, compared to traditional hot plate digestion procedures.
5.4. Radiochemical analysis of Pu and Am

5.4.1 Ion exchange chromatography

Ion exchange chromatography is one of the most popular techniques for radiochemical separations of actinides and several excellent monographs have been published on this technique [85-88].

Both cation exchange and anion exchange from HCl and HNO₃ media has been used for the separation and isolation of Pu. Due to the pronounced ability of the higher valence state actinides to form anionic complexes, anion exchange chromatography from is the most selective, and this is the only method discussed here.

Elements forming anionic nitrate complexes and consequently are retained on anion exchangers from strong nitric acid solutions include; Th(IV), Pa(V), Np(IV), Pu(IV), Pd(II), Au(III), Re(VII) and Tc(VII). These metals are easily separated from elements which are not sorbed, including Al(III), Fe(II&III), alkali metals, alkaline earth metals, rare earth metals (Pr to Lu), trivalent actinides, Be, Cd, Co, Ni, Cr(III), Ga, Zn, Ti, V(V). U(VI) is only weakly absorbed from strong nitric acid solutions [86]. Since Pu(IV) also forms anionic chloride complexes in strong hydrochloric acid it can be separated from Th(IV), which does not form anionic chloride complexes, by shifting the medium to hydrochloric acid. Usually the column is loaded and washed with 8 M HNO₃ before Th is eliminated by wash with 10 - 12 M HCl. Pu is reductively eluted with HCl containing a reducing agent (HI, NH₄I, N₂O₅-HCl) [72, 74, 89-96]. Since neither Sr nor Y is retained on the anion exchange column, the HNO₃ effluent from the column can be used for the isolation of these elements, thereby facilitating a sequential analysis of several radionuclides from the same sample.

Am(III) and lanthanides are very weakly retained on anion exchange columns from pure nitric acid solutions unless some of the acid is substituted with an alcohol [73, 97]. Both Am(III) and light lanthanides are retained on an anion exchanger from 1 M HNO₃ - 93% methanol [98]. Since actinides form stronger complexes with soft donor atoms (S, N) than lanthanides, separation between Am(III) and lanthanides is
sub sequentially achieved using NH₄SCN. As Am(III) forms anionic Am(SCN)₄⁻ complexes with SCN⁻ and lanthanides do not, Am remains retained and the lanthanides are washed out when the media is shifted to e.g. 0.1 M HCl – 0.5 M NH₄SCN – 80% methanol. Am can then be eluted using hydrochloric or nitric acid - methanol solution with a higher content of water [71, 90, 91, 94, 96, 97, 99-101].

Several variations of these facts have been used to separate and purify Pu and Am. When analyzing complex samples ion exchange separation is either repeated or combined with other separation techniques.

5.4.2 Solvent extraction

Being the principle technique of choice in the reprocessing of spent fuel and treatment of radioactive waste, several reviews and monographs have been published on solvent extraction techniques and reagents [86, 102-104].

**HDEHP (bis(2-ethylhexyl) phosphoric acid)**

HDEHP is a cationic extractant capable of extracting trivalent actinides and lanthanides quantitatively from HCl or HNO₃ solutions with pH higher than about 2.5. They are not extracted below pH about 1.3 [105]. Simultaneous extraction of Fe(III) and the formation of precipitants at pH 2-3 can cause problems [98, 101]. Combination of lactic acid and DTPA (diethylenetriaminepentaacetic acid) solution at pH 2.5-3.0 can be used to separate between trivalent actinides and lanthanides. In the TALSPEAK process the lanthanides are extracted with HDEHP from aqueous solutions of DTPA and lactic acid, and in the reversed TALSPEAK process [106] the actinides are stripped from HDEHP using DTPA and lactic acid. Extraction with HDEHP can be used to separate trivalent actinides and lanthanides from tetravalent actinides either by extracting tetravalent actinides from strong nitric acid solution (e.g. 4 M HNO₃) or by extracting both trivalent and tetravalent actinides from a solution with pH higher than about 2.5 and then scrubbing the HDEHP for trivalent actinides by washing with a strong nitric acid solution [107]. Pu in the organic phase can be separated from other tetravalent actinides by reductively stripping it as Pu(III) [108].
As HDEHP also extracts Y(III), this extractant can be used to perform sequential
determination of several actinides and $^{90}$Sr in the same sample [109].

**TBP (tri-n-butylphosphate)**

TBP is frequently used to separate tri-, tetra- and hexavalent actinides from each
other. While TBP extracts tetra and hexavalent actinides, tri- and pentavalent
actinides and fission products are left in the solution. Reducible tetravalent actinides,
e.g. Pu(IV) can then be separated from U(VI) by reductive elution from the TBP
phase. Uranium can subsequently be eluted with dilute nitric acid. In the PUREX
process TBP is used to separate Pu and U from trivalent actinides (Am, Cm) and
fission products.

**TTA (thenoyltrifluoroacetone)**

TTA has also been used to separate actinides in different oxidation states. Extraction
of all other oxidation states except tetravalent is negligible at pH 1, while tri-, tetra-
and hexavalent can be extracted quantitatively at pH about 4-5, the extraction of
heptavalent actinides being negligible [110, 111]. TTA extraction has also been used
to separate Pu from Fe. Pu and Fe are extracted with 0.5 M TTA from 1 M HNO$_3$.
When Pu(IV) is stripped with 10 M HNO$_3$, Fe(III) stays in the organic phase [112,
113].

**Other extractants**

Sekine et al. used TNOA (tri-n-octylamine) to extract Pu(IV) from 4 M HNO$_3$ after
treatment of 50 grams of soil. Pu was then reductively stripped with HCl containing
NH$_4$I [99]. TIOA (tri-isooctylamine) has also been used to separate U, Np and Pu by
extracting them all with TIOA from 8 M HCl. Pu is reductively eluted with 8 M HCl
– NH$_4$I, Np with 4 M HCl – 0.02 M HF and U with 0.1 M HCl [114]. DDCP (dibutyl-
N,N-diethylcarbamoyl phosphonate) is a good extractant for the extraction of trivalent
actinides and lanthanides from concentrated (12 M) HNO$_3$ [32, 90, 101].
5.4.3 Extraction chromatography

Extraction of actinides with TRU-Resin is described in Chapter 4.2. Eichrom UTEVA-Resin containing the extractant diamyl amylphosphonate is a good extractant for tetra- and hexavalent actinides from concentrated (> 5 M) nitric acid solutions [115]. As trivalent actinides are not extracted, Pu(IV) can be reductively eluted. Th(IV) and U(VI) can be eluted with 4 M HCl and 1 M HCl, respectively [7]. The resin has been used to extract U(VI) and Th(IV), prior to Pu(IV) and Am(III) extraction on TRU-Resin [116]. Morgenstern et al. used UTEVA to perform a single-column separation of U(VI), Pu(IV), Np(VI) and Am(III) [117].

Beside the commercial Eichrom products, Testa has for many years, since his article in 1961 on TNOA impregnated paper for the chromatographic separation of metal ions [118], worked with extraction chromatographic separations [119-131]. For Pu separations his group has used TOPO and TNOA columns. Yttrium, for the determination of $^{90}$Sr, and americium separation was utilized using HDEHP columns.

5.5. Radiochemical analysis of Sr

There are two different ways to determine $^{90}$Sr ($E_{\beta_{\text{max}}} = 0.55$ MeV; $t_{1/2} = 29.1$ y):

Either through the direct isolation of $^{90}$Sr or via its daughter nuclide $^{90}$Y ($E_{\beta_{\text{max}}} = 2.3$ MeV; $t_{1/2} = 64.1$ h).

The classic way of analysing $^{90}$Sr, “fuming nitric-acid method”, makes use of the low solubility of Sr(NO$_3$)$_2$ in fuming nitric acid solutions [84, 132]. In this procedure Sr is precipitated as nitrate several times to achieve a good separation from most elements, especially Ca. Then a series of chromate precipitations are performed to eliminate Ba, Ra and Pb, followed by hydroxide precipitations to eliminate traces of Y. Sr-recovery is determined gravimetrically or by checking the gamma activity of the added $^{85}$Sr tracer and the solution is left for 2 weeks for the ingrowth of $^{90}$Y. Y is then separated from Sr with a series of hydroxide precipitations and finally precipitated and collected as oxalate. After $^{90}$Y activity determination, Y-recovery is calculated gravimetrically...
or by complexiometric titration. Although this procedure - which is used in various modifications - is reliable, it is very time-consuming (2-3 weeks) and hazardous due to the use of fuming nitric acid.

Sr-Resin has considerably eased the isolation of Sr. As explained in Chapter 3 the resin extracts Sr from concentrated nitric acid solutions while Sr can be eluted using dilute nitric acid or water. Using water or dilute nitric acid to elute Sr also minimizes quenching effects if Sr is to be detected by liquid scintillation. Interfering K can be removed by oxalate precipitation of Ca and Sr. Interfering Ca can be removed by Ca(OH)₂ precipitation, leaving Sr in the solution. Either loading in 8 M HNO₃ or washing the column with 8 M HNO₃ can eliminate Ba interferences. Actinides on the column can be eluted with 3 M HNO₃ – oxalic acid.

When ⁹⁰Sr is in equilibrium with its daughter ⁹⁰Y many alternative methods utilise the more favourable separation chemistry of Y to extract and isolate Y with e.g. TBP or HDEHP [119, 133-135]. Using TBP, Y(III) is extracted from concentrated nitric acid and eluted using H₂O. This allows the measurement of ⁹⁰Sr activity via ⁹⁰Y without need for any in growth period. TBP extraction of Y after Pu, Am and Cm separation using TRU-Resin is in this work used for the sequential analysis of Pu, Am, Cm and Sr in low-level liquid radioactive effluents (Paper IV).

5.6. Combined sequential analysis of ⁹⁰Sr and actinides

The preparation and pre-treatment of samples is often the most time consuming and tedious step in a radiochemical analysis. The use of combined procedures where several analytes can be determined in the same sample offers great timesaving, better economy and higher throughput. In addition, such procedures permit a more reliable determination of activity ratios, and yield lower analysis costs and reduced waste production. Lower activities can be determined by analysing the whole sample, rather than dividing it into small sub samples for each individual analysis.
Although Am, when desired, is almost always separated and analysed in connection with Pu analysis, very few actually use the “waste fractions” from Pu separation for Sr analysis. On TRU-Resin Pu and Am are retained while Sr and Y are found in the nitric acid effluents. This has been used to simplify the analysis of Sr in Paper IV and Paper V.

In Paper IV the analysis of Pu, Am and Sr in low-level effluents is described. Here Pu and Am are first retained and separated on TRU-Resin while the effluents are subjected to $^{90}$Y analysis using TBP extraction. TRU-Resin removes tri-, tetra- and hexavalent actinides and TBP separates Y from Sr.

In Paper V the analysis of Pu, Am and Sr in soil, sediment and urine samples is described. Here TRU-Resin is coupled on top of Sr-Resin. When loading in 3 M HNO$_3$, TRU-Resin retains Pu and Am while Sr passes right through and is retained by Sr-Resin. Since Fe(III) interferes with Pu separation on TRU-Resin and K interferes with Sr separation on Sr-Resin, these interferences in soil and sediment samples are removed by co-precipitation of Pu and Sr with Ca-oxalate prior to the double column separation.

La Rosa et al. separated plutonium using anion exchange, precipitated the Sr in the effluents as oxalate to remove iron, and extracted the ingrown Y with TBP [89]. Sanchez and Singleton used the same procedure, extracting Y with HDEHP [136]. Figueira et al. and Rosner et al. used “fuming nitric acid method” for the isolation of Sr after the anion exchange isolation of Pu [95, 137].

Bakhtiar et al. isolated Th, Pu, U and Am using anion exchange chromatography followed by Sr isolation using “fuming nitric acid method” [138].

Jia et al. describes a procedure using TNOA column to extract Pu from 4-6 M HNO$_3$, followed by two HDEHP columns to extract Y and Am. Am was further purified by PMBP – TOPO extraction. The procedure was used on 30 grams of soil giving good recoveries and low detection limits [119].
Jiang et al. used sequential extractions with TBP, TIOA, TTA and HDEHP to analyse Pu, Am and Cm in environmental samples [139].

Moreno et al. used TRU-Resin for the isolation of Pu, anion exchange chromatography in methanol media for the purification of Am and Sr-Resin for the isolation of Sr [140, 141]. Ware et al. reversed the isolation, using first Sr-Resin for Sr isolation and followed by anion exchange chromatography for Pu isolation and TRU-Resin for Am and Cm isolation [142].

Lee et al. precipitated Sr in bioassay samples as carbonate and used the solution for the determination of Pu by anion exchange chromatography, while Sr was separated using the “fuming nitric acid method” [143].

Maxwell and Fauth coupled TEVA-Resin on top of TRU-Resin for the isolation of Pu(IV) and Np(IV) on TEVA-Resin and U(VI) and Am(III) on TRU-Resin. Sr in the effluents was purified using Sr-Resin [144]. Moody also used TRU-Resin and TEVA-Resin for the separation of Th, U, Pu and Am in human soft tissue [145].

Spry et al. isolated Pu and Am using TRU-Resin, evaporated the effluents to dryness, dissolved them in 8 M HNO₃ and isolated Sr using Sr-Resin [146]. In Paper V, TRU-Resin is coupled directly on top of Sr-Resin, avoiding loading the column twice, for the sequential determination of Pu, Am and Sr.

Testa et al. isolated Pu using a TOPO column followed by an isolation of Y using HDEHP column [129].

Mellado et al. separated Th and U using UTEVA-Resin followed by the isolation of Pu and Am using TRU-Resin and Sr using Sr-Resin [147]. Vajda et al. isolated Th, U and Pu with UTEVA and used TRU-Resin and TEVA-Resin for the isolation of Am and Cm [148].
5.7. Activity determination of Pu and Am

5.7.1 Alpha-spectrometry

The detection method of choice is usually alpha spectrometry after source preparation by either electro deposition or micro co-precipitation with rare earth fluoride. Alpha spectrometry is an elegant technique for the qualitative and quantitative determination of alpha emitters. At ideal conditions low detection limits, $1 \cdot 10^{-5} - 3 \cdot 10^{-4}$ Bq [149], and easily interpreted spectra are obtained. Since a large detecting area leads to broader alpha peaks, detectors with an active area of $\leq 450$ mm$^2$ are normally used. This leads to low counting efficiency and therefore requires long counting times and a stable system with low background. Due to the small difference in $^{239}$Pu and $^{240}$Pu alpha particle energies, it is not possible to distinguish between these two Pu isotopes using alpha spectrometry and the results are therefore presented as combined $^{239,240}$Pu activities.

Electrodeposition

Electrolysing a solution reduces the proton concentration near the cathode, which in turn leads to the formation of hydrolysed actinide species with low solubility and strong affinity towards the cathode surface [150]. The deposition is usually done from a solution with a pH of about 1-4. A high pH can lead to hydrolysis and sorption of the actinides to the deposition cell, and a low pH demands longer deposition times. As the deposition time varies with the start pH, careful pH adjustment is required. Organic and inorganic impurities in the deposition solution can also lead to low deposition yield, thick source and consequentially indistinguishable alpha peaks. Actinides are most often deposited for 2-4 hours from sulphate media [151]. Despite the care that must be taken in both the separation and the deposition scheme, electrodeposition is a widely used technique as it produces thin sources with good spectral resolution.

Micro co-precipitation

Micro co-precipitation of actinides is usually performed using rare earth fluorides [152-156]. A quantitative co-precipitation of actinides in tri- and tetra-valent state can
be achieved by adding 50-100 μg Ce/Nd/La³⁺ and HF to a 20 - 30 ml solution. The fluorides are collected on a membrane filter after about 30 minutes and are then ready for activity determination. U(VI), Ra, Fe etc. do not precipitate. Uranium precipitation requires a reduction to U(IV) by e.g. TiCl₃. The use of micro co-precipitation gives a higher flexibility on the choice of eluents. Solutions containing e.g. TiCl₃ simply cannot be electrodeposited due to the formation of colloidal TiO₂.

Since micro co-precipitation is much simpler, more robust and less sensitive to impurities than electrodeposition, micro co-precipitation was chosen for the source preparation in this work (Paper II-V). Using micro co-precipitation also allowed the use of hydroquinone and TiCl₃ as Pu reducers in the eluent. Using 50 μg Ce(III) to precipitate Pu, Am and Cm as fluorides gave an alpha-peak FWHM (full width at half maximum) of about 35 keV on a 450 mm² detector when counting the sample (diameter = 2 cm) at a detector distance of 1 cm.

5.7.2 Liquid scintillation
Liquid scintillation has two main advantages compared to alpha-spectroscopy; counting efficiency and source preparation. 100% counting efficiency can be gained due to the 4π geometry. Source preparation also is simplified as eluents can be counted directly with the addition of an appropriate cocktail and no thin sources are needed. Liquid scintillation spectrometers as Quantulus give a alpha-peak FWHM of 280 ± 10 keV, which allows the determination of ²³⁹Pu and ²³⁶Pu as long as there are low amounts of other alpha emitters. Background in the energy area of Pu (0.035 CPM) gives a theoretical MDA of about 2.5 mBq ²³⁹Pu for a 1000 minutes counting and 100% counting efficiency and chemical yield [157]. As beta emitters also can be analyzed with liquid scintillation this also allows the secure determination of ²⁴¹Pu. Source preparation by micro co-precipitation may offer an advantage as the source first can be analyzed for alpha emitters using PIPS detectors and then analyzed for beta emitters with liquid scintillation [141].
5.7.3 Mass spectrometry

Radiometric detection methods as alpha spectrometry require long counting times when low activities are to be determined. Mass spectrometric techniques as ICP-MS (Inductively Coupled Plasma - Mass Spectrometry), TIMS (Thermal Ionization Mass Spectrometry) and AMS (Accelerator Mass Spectrometry) have several advantages. Due to the low specific activity of long lived radionuclides, many of these are more conveniently detected using mass spectrometric techniques. Mass spectrometric techniques also enable the individual determination of $^{239}$Pu and $^{240}$Pu, a task that is difficult using alpha spectrometry. In addition, techniques as AMS have very low detection limit. But, as these instruments are very sensitive they also require a greater effort on the separation chemistry. A poor separation from e.g. $^{238}$U will complicate the determination of $^{238}$Pu and $^{239}$Pu due to isobaric interferences ($^{238}$U) and adduct formation ($^{238}$UH). Another disadvantage is the cost of purchase and maintenance.

5.8. Activity determination of $^{90}$Sr

$^{90}$Sr has been counted directly using liquid scintillation [50, 56, 58, 79, 147, 158] or precipitated as carbonate and counted by proportional counters [138, 143, 159]. When Y is isolated from the sample, $^{90}$Y activity has been determined using either gas proportional counters [47, 119, 133, 134, 137, 160], or cherenkov counting [84, 135]. In this work $^{90}$Y activity is determined using anticoincidence gas flow GM counters (Riso) (Paper IV and Paper V).

Yield determination

Sr yield can be determined either through the addition of stable Sr or by using the gamma emitter $^{85}$Sr as spike, while Y yield determination is always achieved using stable Y. The mode of yield determination significantly determines the choice of chemical separation procedure that can be used. If $^{85}$Sr is used as the Sr yield determinant, $^{90}$Sr activity is almost always determined by the subsequent isolation and activity determination of $^{90}$Y. This is done since $^{85}$Sr can interfere in the direct activity determination of $^{90}$Sr. When $^{90}$Sr is measured directly, the Sr yield is most
often determined using Sr carrier. In this case a prior knowledge of stable Sr content in the sample is required.

Hence, the procedure most often used to overcome these obstacles is:

1. Isolation of Sr and yield determination through $^{85}$Sr
2. Addition of a known amount of Y carrier and ingrowth of $^{90}$Y
3. Separation of Y from Sr
4. $^{90}$Y activity determination
5. Y yield determination

This approach was chosen for the analysis of $^{90}$Sr in soil and sediment samples (Paper V), as the stable Sr content in soil is approximately 0.5 mg/gram and Sr amounts exceeding about 10 mg lead to a sharp decrease in Sr recovery on a 2 ml Sr-Resin.
6. Results and discussion

The procedures developed during this study are thoroughly discussed in Paper II – Paper V and in the previous chapters. This chapter presents an overall discussion and a schematic overview of the various procedures.

Preconcentration from large volumes
Hydrated manganese dioxide co-precipitation of Pu and Am is an effective way of concentrating plutonium and americium from natural waters. From 200 litre seawater the recoveries of Pu and Am are typically above 80%. MnO$_4^-$ and MnO$_2$ ensure oxidation of organic matter and adjustment of Pu oxidation states. MnO$_2$ can subsequently be collected by either settling and decantation, or by filtration through glass wool cartridge. In field analysis this simplifies the transport of the concentrate. When only Pu is analysed Mn does not need to be separated from the solution prior to Pu isolation on TRU-Resin. When Am analysis is also of interest Mn has to be separated from the solution - a task that can be done by precipitating the actinides on Fe(OH)$_3$ at low pH, where Mn stays in solution.

Open focused microwave digestion of soil and sediment samples
This is an effective way of leaching the analytes from the matrix. Only small amounts of mineral acids are consumed and the technique is much quicker than conventional “hot-plate” digestion. However the amount of sample that can be treated this way is small (typically below 10 grams).

TRU-Resin separation of Pu and Am
The resin selectively extracts Pu and Am, leaving most other matrix elements in the solution. The presence of Fe(III) has a dramatic effect on the extraction of the actinides. Fe(III) should therefore be reduced to Fe(II) by the addition of e.g. ascorbic and sulfamic acid. While Am(III) simply can be eluted using 4 M HCl, Pu(IV) needs to be reduced to it trivalent state before elution. TiCl$_3$ in HCl is a better reductant than hydroquinone. No spill over of other alpha emitting radionuclides in the Pu or Am (Cm) fraction is observed in this study. In contrast to ion exchange chromatography,
TRU-Resin allows the concentration and purification of both Pu and Am from complex solutions, using only one column. In addition the analytes can be eluted using small amount of eluent, facilitating direct source preparation without evaporation. The extraction kinetics of TRU-Resin are also faster than ion exchange kinetics of ion exchange resins, allowing faster flow volumes.

**Sr-Resin separation of Sr**
The resin selectively extracts Sr from concentrated nitric acid solutions. Thereafter Sr can easily be eluted using small amount of H₂O. This is advantageous as $^{90}\text{Sr}$ levels can be determined directly using liquid scintillation. The water eluant also minimizes quenching effects. When analysing samples containing large amounts of potassium, an oxalate precipitation should be undertaken prior to Sr-Resin separation to avoid interferences. When samples containing large amount of calcium are to be analysed, calcium/strontium separation is required prior to Sr-Resin separation.

**Coupling of TRU-Resin and Sr-Resin**
As both resins extract the analytes from fairly concentrated nitric acid solutions, these resins can easily be coupled together to facilitate sequential analysis. When oxalate precipitation is used to concentrate the analytes, the oxalates must be completely destroyed prior to column loading, as oxalate complexation has a negative effect on the retention of actinides on TRU-Resin.

**Source preparation**
Micro co-precipitation of Pu and Am with CeF₃ is a simple and fast way of preparing alpha sources suitable for alpha spectrometric analysis. About 50 μg Ce(III) is capable of quantitatively co-precipitating Pu and Am from about 10 ml solution. The technique is advantageous if the beta emitter $^{241}\text{Pu}$ is also to be determined. The filter can first be counted for alpha emitters using e.g. PIPS detector and then analysed for $^{241}\text{Pu}$ using liquid scintillation.

The procedures developed during this study are schematically presented in Figure 6.1 – Figure 6.5.
Figure 6.1 Schematic presentation of the proposed procedure for the analysis of plutonium in large water samples.
200 L water sample

- pH = 1
- 10 g KMnO₄
- 50 mg Fe(III)
- pH 8-9
- Na₂SO₃ \( \Rightarrow \) MnO₂

Precipitate

- Dissolve with HCl and Na₂SO₃
- NaOH (pH 0-1) \( \Rightarrow \) Fe(II) (clear solution)
- NaNO₂ \( \Rightarrow \) Fe(III) (yellow solution)
- pH 8-9 \( \Rightarrow \) Fe(OH)₃ + Mn(OH)₂
- pH 5-6 \( \Rightarrow \) Fe(OH)₃ + Mn²⁺

Supernatant

- Dissolve with 8 M HNO₃, evaporate
- Dissolve with 3 M HNO₃ – 0.5 Al(NO₃)₃
  - 0.2 M sulfamic acid – 0.2 M ascorbic acid

TRU-Resin

- Wash with 15 ml 2 M HNO₃
- Wash with 5 ml 2 M HNO₃ – 0.2 M NaNO₂
- Wash with 2 ml 9 M HCl
- Am: 10 ml 4 M HCl
- Wash with 10 ml 4 M HCl
- Pu: 10 ml 4 M HCl – 0.02 M TiCl₃

CeF₃ micro co-precipitation followed by α-spectrometry

Figure 6.2 Schematic presentation of the proposed procedure for the analysis of plutonium and americium in large water samples.
Effluent water

- pH 1 + tracers
- Evaporate and wet ash with HNO₃
- 3 M HNO₃ + 0.2 M Na₂SO₃ $\Rightarrow$ Pu(III)
- 0.2 M NaNO₂ $\Rightarrow$ Pu(IV)

0.5 g TRU-Resin

- Wash with 20 ml 2 M HNO₃ – 0.1 M NaNO₂ (save effluents for ⁹⁰Y determination)
- Wash with 2 ml 9 M HCl
- Am and Cm: 10 ml 4 M HCl
- Wash with 10 ml 4 M HCl
- Pu: 10 ml 4 M HCl – 0.02 M TiCl₃

HNO₃ effluents from TRU-Resin

- Evaporate and wet ash with HNO₃
- 14 M HNO₃ and Y extraction with TBP

Y strip with H₂O

- Oxalate precipitation and beta counting

- Dry ashing and Y-yield determination using complexiometric EDTA titration

CeF₃ micro co-precipitation followed by α-spectrometry

Figure 6.3 Schematic presentation of the proposed method for the analysis of Sr, Pu, Am and Cm in low-level liquid radioactive effluents.
Figure 6.4 Schematic presentation of the proposed method for the analysis Sr and Pu in soil and sediment samples.
Figure 6.5 Schematic presentation of the proposed method for the analysis Sr, Pu and Am(Cm) in urine samples.
7. Conclusion

The wide variety of selective extraction chromatographic resins available has increased the flexibility in radiochemical separations. These resins can either be used as stand alone, coupled together with each other or combined with other separation techniques. The proposed method for the analyses of Pu and Am in seawater offers a quick and secure mode for the determination of these radionuclides in marine waters. Combined pre-concentration of actinides and strontium (oxalate or phosphate precipitation) followed by dual column separation on TRU- and Sr-Resin significantly reduces the through put time and costs compared to traditional ion exchange and precipitation methods. The greatest gain in productivity and environmental friendliness is achieved in Sr separations using Sr-Resin instead of precipitations involving fuming nitric acid and oxalate, hydroxide, chromate and carbonate precipitations.

8. Future work

As mentioned earlier, Sr-Resin is also a good extractant for Pu(IV) – the extraction of Pu(IV) being even higher than Sr(II) at acidities above approximately 2 M HNO₃. The possibility to use this resin for the simultaneous separation of Pu and Sr in environmental samples should be explored.

The Ln-Resin containing the extractant HDEHP should be explored to achieve a simple determination of Sr-90 (via Y-90) in seawater. After insurance of equilibrium between Y-90 and Sr-90, yttrium can be enriched using hydroxide precipitation and Ln-Resin can possibly be used to separate yttrium from impurities.

The commercial Eichrom resins are costly. Detailed studies on their reuse and memory effects should be performed.
9. References


[70] Livingston, H.D., Mann, D.R., and Bowen, V.T., 1975, "Double-tracer studies to optimize conditions for the radiochemical separation of plutonium from large seawater samples." in Reference methods for marine radioactivity studies II., IAEA: Vienna. p. 69-76.


Environmental chemistry of plutonium

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1. Introduction

Artificial plutonium, as $^{238}$PuO$_2$, was first produced in December 1940 by G. T. Seaborg, A. C. Wahl and J. W. Kennedy by irradiating $^{238}$UO$_2$ with deuterons from a cyclotron. In August 1942 pure $^{238}$PuO$_2$ was isolated. This was then believed to be the first visual observation of a synthetic element. In 1948 G. T. Seaborg and M. L. Perlman isolated traces of $^{239}$Pu from a 400 gram sample of pitchblende concentrate and demonstrated that plutonium is a natural, not an artificial element. Mass spectrometric studies have also revealed traces of $^{244}$Pu in the earth's crust, indicating that vast amounts, $\sim 10^{13}$ - $\sim 10^{15}$ kg, of $^{244}$Pu must have been formed during the formation of the earth [1]. Today Pu can be considered as an artificial element as the amount of man made Pu far exceeds natural Pu.

2. Physical Properties

Plutonium has atomic number 94 and is one of the actinides. Actinides are formed by filling of 5f electron shells and have many similarities with lanthanides, which are formed by filling of the 4f orbitals. 5f electrons are more protected from the nucleus than 4f electrons and the energy difference between 5f, 6d and 7s electrons in actinides is therefore lower than 4f, 5d and 6s electrons in lanthanides. This results in that while oxidation state III is the most stable for the lanthanides, higher and more oxidation states are possible for actinides.

Metallic plutonium is like other actinides shiny and very reactive. In air the metal is quickly covered by oxide film and reaction with hydrogen leads to the formation of pyrophoric plutoniumhydride. At normal pressure Pu can exist in six different allotropes and Pu is also
one the few metals which floats on its own melt at melting point. Pu can be characterized as a “poor” metal as its thermal conductivity is ~1/10 that of silver and ~10 times greater than that of fire clay [2].

Up to now 17 Pu-isotopes have been produced and characterized. All Pu-isotopes, except $^{241}$Pu, are 100% alpha-emitters. $^{241}$Pu disintegrates to $^{241}$Am with the emission of a beta-particle. The nuclear properties of the most important Pu-isotopes are shown in Table 1.

**Table 1.** Nuclear properties of some Pu-isotopes.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half life (y)</th>
<th>Decay mode</th>
<th>Decay Energy (MeV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{236}$Pu</td>
<td>2,858</td>
<td>$\alpha$</td>
<td>5,768</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>87,74</td>
<td>$\alpha$</td>
<td>5,499</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>$2,411 \times 10^4$</td>
<td>$\alpha$</td>
<td>5,157</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>$6,563 \times 10^3$</td>
<td>$\alpha$</td>
<td>5,168</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>14,35</td>
<td>$\beta$</td>
<td>0,02</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>$3,750 \times 10^5$</td>
<td>$\alpha$</td>
<td>4,901</td>
</tr>
</tbody>
</table>

* $\alpha$: Most abundant, $\beta$: Maximum energy.

3. Aquatic chemistry of plutonium

3.1. Red-ox chemistry

The most important aspect of the aquatic chemistry of plutonium is plutonium’s ability to exist in several oxidation states. This is important as the chemistry, due to the large difference in complex formation, varies significantly for the different oxidation states.

In solution plutonium ions can exist in oxidation states III – VII. While oxidation states III-VI occur commonly in aqueous solutions, Pu(VII) is only stable in the presence of powerful oxidizing reagents in strong alkaline solutions [2]. Reduced plutonium, Pu(III) and Pu(IV), exist as simple ions while oxidized plutonium, Pu(V) and Pu(VI), exist as binary dioxocations, $\text{PuO}_2^+$ and $\text{PuO}_2^{2+}$ respectively.
As a general rule for all polyvalent cations, the lower oxidation states are stabilized in acidic solutions, and the higher oxidation states become more stable as the acidity is reduced [3]. Redox potentials of Pu in both acidic and alkaline environment are quite similar. Disproportion and electron transfer reactions due to this, can lead to the simultaneous existence of the oxidation states III-VI.

Disproportion: 
- \( 2\text{Pu(IV)} \leftrightarrow \text{Pu(III)} + \text{Pu(V)} \)
- \( 2\text{Pu(V)} \leftrightarrow \text{Pu(IV)} + \text{Pu(VI)} \)
- \( 3\text{Pu(IV)} \leftrightarrow 2\text{Pu(III)} + \text{Pu(VI)} \)
- \( 3\text{Pu(V)} \leftrightarrow \text{Pu(III)} + 2\text{Pu(VI)} \)

Electron transfer: \( \text{Pu(IV)} + \text{Pu(V)} \leftrightarrow \text{Pu(III)} + \text{Pu(VI)} \)

The simultaneous existence of the four oxidation states reflects a meta stability and not a thermodynamic equilibrium [4]. This enriches the chemistry of plutonium and complicates our understanding of it, as it is difficult to study the chemistry of the different oxidation states, separately.

Since the redox-reactions between oxidation states III & IV and oxidation states V & VI only require an electron transfer, these conversions are independent of pH and easily obtainable. Transfer between the reduced (III & IV) and oxidized (V & VI) states is more difficult as oxygen bridges must be built or broken down before an electron transfer can take place. Formation and decomposition of the plutonyl ion is pH-dependent according to:

\[ \text{Pu}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{PuO}_2^{+} + 4\text{H}^{+} + e^{-} \] [4]. Thus reduction of \( \text{PuO}_2^{+} \) and \( \text{PuO}_2^{2+} \) increases with reducing pH and the formation of oxo bridges increases with increasing pH. This leads to that disproportion of e.g. \( \text{PuO}_2^{+} \) is fast at pH < 1.7 and pH > 7, but slow at pH 3.5 [5].

The ability of Pu to exist in four relatively easily accessible oxidation states is a great advantage in Pu-separations as manipulation of these can be used to separate Pu from other actinides.
3.2 Complex formation

Actinide cations are hard acids and react with anionic species through ionic bonds. As hard acids actinides prefer to react with hard bases as oxygen or fluoride atoms in preference to soft bases as nitrogen, sulphur or phosphor donors [6]. In general the weaker the acid is, Pu forms stronger complexes with the conjugated anion. The most common Pu complexes are those of oxygen, oxygen-containing anions (OH\(^-,\) CO\(_3^{2-}\) > HPO\(_4^{2-}\), SO\(_4^{2-}\), NO\(_3^-\)) and the halides (F>Cl>Br>I) [4, 7].

Due to the ionic nature of Pu\(^{n+} \cdots \cdots X^{m-}\) interactions the complex strength should normally increase with increasing n for same m. This is not the case for Pu as the most observed complexation sequence is: Pu\(^{4+}\) > PuO\(_2^{2+}\) > Pu\(^{3+}\) > PuO\(_2^+\) [2, 3]. This is due to the fact that the central Pu-atom in the linear dioxocations [O-Pu-O]\(^{2+}\) and [O-Pu-O]\(^+\) has an effective charge of 3.3 and 2.3 respectively [3].

Due to its large metallic and ionic radius Pu has relatively high coordination numbers. For Pu(II/IV) and Pu(V/VI) coordination numbers of respectively 6-12 and 2-8 have been observed. The number of ligands and there geometric coordination around the metal is primarily governed by steric and electrostatic factors. Complex formation is initiated by the formation of outer-sphere complexes where Pu and the ligand are separated by at least one water molecule. If the ligand is strong enough to push out the water molecule, inner-sphere complexes are formed, which normally are thought to be stronger. In general the complex has a outer-sphere nature if the ligand pKa < ~2 for Pu\(^{3+}\), pKa < ~1 for Pu\(^{4+}\) and pKa < ~1.7 for PuO\(_2^{2+}\). This implies that Cl\(^-\) forms outer-sphere complexes, while SO\(_4^{2-}\), HCO\(_3^-\), CO\(_3^{2-}\) and most organic acids as fulvic and humic acids form inner-sphere complexes [6].

3.3 Hydrolysis and polymerisation

The water molecule is a very important ligand in plutonium chemistry. Pu-ions in all oxidation states form strong ion-dipol bonds with water and are strongly hydrated in water solutions. The hydrated Pu-ions act as Brønsted acids where the acidity increases with the effective charge (charge/radius) of the central atom. Pu(IV) and Pu(VI) have higher effective charge and are therefore stronger acids than Pu(III) and Pu(V) [7]. The hydrolysis of Pu(IV)
and Pu(VI) therefore starts at lower pH than hydrolysis of Pu(III) and Pu(V) and the hydrolysis increases with pH.

\[
\begin{align*}
\text{pH where the hydrolysis becomes significant [3]:} & \quad \text{Pu(IV): } 0-1 \\
& \quad \text{Pu(VI): } 4-5 \\
& \quad \text{Pu(III): } 6-8 \\
& \quad \text{Pu(V): } 9-10 
\end{align*}
\]

The hydrolysed species have strong affinity for exposed surfaces and particulate matter and a very low solubility \((K_{sp} \text{Pu(OH)}_4 \sim 10^{-54})\) ([2]).

At sufficiently high hydrolysis and Pu concentration the hydrolysed monomers can combine via Pu-O bonds to form oligomers and polymers. For Pu(III) and Pu(V) the hydrolysis is normally too weak for this to appear. Fresh polymers can easily be decomposed by simple acidification, but the older the polymers get, specially Pu(IV) polymers, the more resistant they get to reversion to monomers. This is presumably due to the conversion from hydroxide bridges to oxo-bridges. Generally polymer formation requires a Pu-concentration of greater than \(10^{-6} \text{ M} (> 550 \text{ Bq/ml } ^{239}\text{Pu})\) [3], but dilution will not destroy the polymers formed due to irreversibility. Ligands that can effectively complex Pu or terminate hydroxide bridges, greatly reduce the polymer formation.

4. Plutonium in the environment

4.1. Sources

The largest source of Pu in the environment are the many atmospheric detonations carried out since 1945. Most of the detonations were carried out in the period 1952 – 1958 and 1961 – 1963. The total number of atmospheric detonations are assumed to be approximately 500. The detonations have contaminated the earths environment with 0,3 PBq (0,5kg) \(^{238}\text{Pu}\), 9 PBq (3900 kg) \(^{239}\text{Pu}\), 6 PBq (700 kg) \(^{240}\text{Pu}\), 170 PBq (45 kg) \(^{241}\text{Pu}\) and 0,02 PBq (0,5 kg) \(^{242}\text{Pu}\). About 80% of Pu is spread globally and 20% near the detonation areas [6, 8]. Approximately 2/3 of Pu in the explosions is thought to be formed via \(^{238}\text{U} (n,\gamma)\) reactions with accompanying \(\beta^-\)-desintegration, and the rest is due to unfissiioned weapon grade Pu [9]. Due to the fact that
that most of the detonations were performed on the northern hemisphere, $\frac{3}{4}$ of the Pu is found here and the highest Pu concentrations on both hemispheres are found at mid latitudes [1, 10].

Pu has also found its way to nature due to accidents. In April 1964 the satellite SNAP-9A, with $\sim 0.6$ PBq $^{238}$Pu ($\sim 1$ kg) as energy source, burned up above the Indian Ocean due to problems with launching. $\frac{3}{4}$ of Pu from the satellite deposited on the southern hemisphere and lead to a tripling of this Pu-isotope in nature [11]. Another accident occurred in January 1966 above Palomares, Spain. An explosion during the fuel filling of a B-52 aeroplane lead to a local spread of Pu and the $^{239,240}$Pu activity after clearing and decontamination is estimated to $\sim 0.1$ TBq [12]. In January 1968 another B-52 crashed near Thule, Greenland, which resulted in a spread of $\sim 1$ kg PuO$_2$. About 90% of Pu was removed, and the remaining ($\sim 1$ TBq $^{239,240}$Pu) is now distributed on an area of 1000 km$^2$ [12]. The Chernobyl accident in 1986 resulted in a spread of 37 TBq $^{239,240}$Pu [13]. Most of the Pu is deposited locally [14].

Significant amounts of plutonium have also been released to the environment through controlled discharge of low-level radioactive liquid waste from reprocessing plants. The reprocessing plant at Sellafield in Cumbria has discharged approximately 730 TBq Pu $\alpha$-emitters ($590$ TBq $^{239,240}$Pu) into the Irish Sea since 1952. This amounts to about 50% of the total release of $^{239,240}$Pu from atmospheric detonations to The North Atlantic Ocean [15, 16]. The discharge of Pu $\alpha$-emitters peaked at 66 TBq/year in 1973 and have since then steadily declined due to the operation of several waste treatment plants [17]. Most of the Pu is bound to sediments close to the discharge point and the remaining is transported both southwards and north around the Scottish coast to the North Sea and to the Norwegian Coast. A study of $^{238}$Pu/$^{239,240}$Pu ratios in water from Norwegian and Greenland Sea also seem to suggest that Pu bound to sediments in the Irish Sea to some extent also is being remobilised from the sediments [18]. The reprocessing plant at La Hague in France has also discharged Pu, but the levels are very small ($\sim 0.4\%$) compared to Sellafield [16].

**Source identification**

The ratio between the different Pu-isotopes in a given sample is often used to identify the source of the radioactive contamination. The $^{238}$Pu/$^{239,240}$Pu-ratio in weapon grade Pu, on the northern hemisphere due to global fallout, discharge from Sellafield and Chernobyl accident release is 0.016, 0.04, 0.25, 0.47 respectively [14, 19].
4.2 Environmental chemistry of plutonium

Our understanding of the chemistry of plutonium in natural systems is complicated due to the low Pu concentrations encountered and the existence of Pu in several oxidation states simultaneously. Wrong interpretations of the results are often encountered since Pu obviously changes its chemical form during the pre-treatment and pre-concentration steps. The most important factor governing plutonium’s environmental chemistry is its oxidation state since hydrolysis, complexation, sorption, colloid formation and solubility differ significantly from one oxidation state to another [20].

Many models describing thermodynamic stable Pu complexes at different redox conditions, pH and ion strength have been developed. Most of these models are based on data collected from analysis of macro concentrations of Pu and many of the dissociation and complexation constants are unreliable due to analytical uncertainties [8]. Many natural reactions can also be irreversible and/or kinetic dependent and not only dependent on the thermodynamics of the reaction products [21, 22].

Depending on the Pu-source, recipient redox conditions, pH, ion strength, kind and concentration of organic and inorganic ligands and the reaction kinetics and thermodynamics, plutonium can exist as simple hydrated ions, complex molecules, hydrolysis products, polymers, colloids, suspended particles or sediment bound [23].

4.2.1. Natural inorganic ligands

As mentioned the water molecule is an important ligand in determining the fate of Pu as it will compete with other ligands and lead do the formation of hydrolysis products with great affinity for suspended matter. The Pu-complexation sequence for commonly encountered anions in many natural waters is: OH\(^-\), CO\(_3\)^{2-} > F\(^-\), HPO\(_4\)^{2-}, SO\(_4\)^{2-} > Cl\(^-\), NO\(_3\)\(^-\) [4]. Plutonium forms sparingly soluble complexes with all these except Cl\(^-\) and NO\(_3\)\(^-\), and due to the comparatively large concentrations and complex formation ability, hydrolysis and carbonate complexation are the dominating reactions for plutonium [9].
4.2.2. Natural organic ligands

Natural waters, especially fresh water, contain many organic molecules as proteins, lipids, carbohydrates, amino acids, fatty acids and humic substances that effectively can complex Pu. Humic substances are the most important as they due to the presence of carboxylic, hydroxylic and fenolic groups can form very strong complexes with many metals [24]. Reducing fenolic groups can also reduce Pu(V&VI) to Pu(III&IV) [25]. Humic substances are commonly divided into three groups depending on their solubility:

- Humin: insoluble at all pH
- Humic acid: soluble at pH above 3
- Fulvic acid: soluble at all pH

Humic substances in natural waters can either be dissolved, colloidal or sorbed on the surface of inorganic colloids [20]. A large part of Pu in the environment is bound to humic substances. In general an increasing concentration of dissolved organic carbon (DOC) in a water reservoir will lead to an increase in Pu concentration in the water, but large aggregates of colloidal size can also precipitate as the salt concentration in the water increases [9, 26, 27].

4.2.3. Particle affinity

The interaction of trace elements in aqueous solutions with solid matter can be described by three idealized sorption mechanisms [9]:

- Physical adsorption: Non-specific attraction forces. The process is fast, reversible, concentration dependent, non selective and only slightly dependent of the ion exchange capacity of the solid matter.

- Electrostatic adsorption: Ion exchange. The process is fast, reversible and dependent on the concentration of the metal, the ion exchange properties of the solid matter and the existence of other competing ions.
Chemisorption: Specific adsorption due to chemical attraction between dissolved and solid matter. Solid matter where e.g. OH\textsuperscript{-}, F\textsuperscript{-}, PO\textsubscript{4}\textsuperscript{3-} can function as chemisorbing molecules. The process is slow, slightly irreversible and selective and dependent on the concentration and the composition of the solid matter.

Physical adsorption is the dominating sorption mechanism for Pu(III) and Pu(IV) which are easily hydrolysed at the prevailing conditions in natural waters. Ion exchange is less significant [28].

5. Fate of environmental plutonium

The fate of environmental plutonium is dependent on the environment Pu is exposed to and on the source of the contamination. Plutonium oxides formed during nuclear explosions are sparingly soluble and are relatively quickly incorporated into soil and sediments. Plutonium in low-level effluents from reprocessing facilities and other nuclear installations generally reaches equilibrium with its surroundings much quicker.

In the terrestrial environment, Pu from atmospheric nuclear detonations is concentrated in the upper soil layers penetrating downwards a few cm. The vertical transport is very slow and the transfer to plants is very small [29]. The upper layer generally contains large amounts of organic matter from the degradation of vegetation. Microbial and enzymatic degradation leads to the formation of many complexing ligands as humic and fulvic acids, citric acid, bicarbonate and carbonate ions. Most of the plutonium in soil and sediment is either directly bound to inorganic components (oxides, hydroxides, carbonates, sulphates, phosphates, clay minerals etc.) or organic components as humus substances which cover the surface of the inorganic particles. Pu in such an environment is very little mobile.

In most natural waters Pu(VI) is quickly reduced to the less reactive Pu(V) [30]. Pu(V) acts in a conservative manner as long as its not exposed to suspended particles, but is relatively quickly reduced in contact with humic substances and mineral surfaces as FeOOH [22, 31]. MnO\textsubscript{2} can also oxidize Pu(V) to Pu(VI) [32]. Experiments indicate that most of the “dissolved Pu” in natural waters exists in an oxidized form (Pu(V) or Pu(VI)) [33], with Pu(V) being the most
probable oxidation state [30]. In the Baltic Sea 99% of the Pu is associated with the sediments [14].

The large particle affinity of Pu has resulted in that above 95% of Pu from global atmospheric detonations now is bound to either soil or sediments. In general the Pu-activity in natural waters and sediments (soil) is in the range mBq/m³ and mBq/g, respectively, but waters where most of the Pu still is dissolved do exist. Most of the “dissolved Pu” in these waters is bound to suspended particles and large organic molecules. The activity of $^{238}\text{Pu}$ and $^{239,240}\text{Pu}$ in unfiltered surface water from different waters in the north is shown in Table 2. In comparison the $^{239,240}\text{Pu}$ concentration in filtered (0.45 μm) water in the Irish Sea in the period 1988-1993 was in the range 100 – 5000 mBq/m³ [33].

### Table 2. Activity (mBq/m³) of $^{238}\text{Pu}$ and $^{239,240}\text{Pu}$ in unfiltered surface water [34].

<table>
<thead>
<tr>
<th>Hav</th>
<th>$^{238}\text{Pu}$</th>
<th>$^{239,240}\text{Pu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Sea (west)</td>
<td>12 ± 11</td>
<td>42 ± 17</td>
</tr>
<tr>
<td>North Sea (east)</td>
<td>3 ± 3</td>
<td>6 ± 3</td>
</tr>
<tr>
<td>Norwegian Sea</td>
<td>1.4 ± 0.7</td>
<td>9 ± 4</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>1.1 ± 0.2</td>
<td>7.7 ± 0.6</td>
</tr>
<tr>
<td>Barents Sea</td>
<td>0.7 ± 0.4</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>Greenland Sea</td>
<td>0.6 ± 0.3</td>
<td>5 ± 1</td>
</tr>
</tbody>
</table>

The Framvaren Fjord in Vest Agder in south Norway is a particularly interesting basin as it is permanently anoxic below 18 m depth due to limited water exchange. The Pu-concentration in the surface water is comparable with that found in the North Sea and Norwegian Sea, but increases drastically with depth. The total (dissolved + particulate) $^{239,240}\text{Pu}$ concentration at 1 m and 175 m depth is approximately 7 and 410 mBq/m³ [35]. Above 99% of the total Pu inventory of the fjord exists in the permanent anoxic zone and approximately 75% of Pu from global discharges still exists in the water column [36]. The increased solubility of Pu in this fjord is probably due to reduction and dissolution of Fe/Mn oxides in the sulphur rich water and complexation of Pu with dissolved organic matter [37].
References


Rapid Determination of Environmental Plutonium in Large Water Samples by Means of Manganese Dioxide Co-Precipitation and Extraction Chromatographic Separation

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Plutonium / Seawater / MnO₂ / Extraction chromatography / TRU-Resin / Micro-Coprecipitation

Summary

Plutonium activity determinations in environmental water samples are routinely performed in many laboratories. Due to the low plutonium concentrations and the complexity of the plutonium aqueous chemistry, these analysis involve cumbersome preconcentration and separation procedures and long measurement times. We describe a procedure where MnO₂(s) is used as scavenger to preconcentrate Pu prior to separation by the transuranium specific extraction chromatographic resin TRU-Resin. The ability of MnO₂/MnO₂(s) to destroy organic matter and oxidise plutonium is combined with the specific behaviour of the TRU-Resin for transuranium elements. The method facilitates a rapid preconcentration and separation of plutonium. With the use of this procedure, the laboratory work on one sample can be performed in one day with minimum attention. The overall yields from a 200 litre fresh- or seawater sample to a measurable Pu source are between 70–85%.

1. Introduction

At present about 1300–1400 tons of plutonium have so far been produced (and mainly stored) throughout the world. The main source of environmental plutonium contamination are the atmospheric weapons tests performed in the period 1945–1963. The estimated total fallout amounts to ~4.6 tons or ~3 PBq of the main α-emitters ²³⁹,²⁴⁰Pu in addition to small amounts of ²³⁸Pu (0.3 PBq) and ²⁴¹Pu (0.02 PBq). Furthermore, ~45 kg or 170 PBq of the soft β-emitter ²⁴¹Pu (T₁/₂ = 14.4 y) are released, which decays to the α-emitter ²⁴¹Am [1]. These nuclear explosions imposed a relatively uniform and global distribution of Pu. Other releases, e.g., discharges from fuel reprocessing plants and the small number of reactor accidents have given rise to enhanced local or regional concentrations.

The concentration of Pu in natural waters is negligible compared to primordial radioelements, e.g., uranium, thorium, actinium and radium. In surface seawater the ²³⁹,²⁴⁰Pu concentration is typically in the range of a few mBq/m³. Therefore, Pu must be preconcentrated and isolated chemically from large water samples before an accurate measurement of the activity can be made. A widely accepted and often applied procedure for this involves the co-precipitation of Pu with Fe(OH)₃ from a large volume of seawater (≥ 200 litres). Many metals, e.g., Ca, Mg and α-emitters like U, Th and Ra also co-precipitate at these conditions. The precipitate must therefore be treated further to separate plutonium from interfering species, normally by means of anion exchange. These operations are highly cost ineffective because of long turn-over times (~4–7 days/water sample), and the yields (50–60%) are not quite satisfactory. However, the results are reliable and reproducible.

Both direct precipitation of MnO₂(s) in a bulk sample [2, 3] and in situ adsorption of Pu on MnO₂(s) impregnated filter cartridges [2, 4–6] have been used to concentrate Pu from large water samples. Although the in situ procedures seem to discriminate between reduced (Pu(III) and Pu(IV)) and oxidised (Pu(V) and Pu(VI)) plutonium [7, 8], no such effects have been encountered in batch experiments. The drawback of these methods has been the time consuming ashing of the cartridge and use of unselective ion exchange resins for the further separation and purification of Pu. Hence, Wong et al. [3] recommend the use of two anion exchange columns to eliminate the interferences from naturally occurring radioelements, e.g., Ra and Th.

The chemical analysis of radioelements in environmental samples has been substantially made easier by the recent development of a series of extraction chromatographic materials for the selective sorption of several radioelements. One of these resins, TRU-Resin (Eichrom Ind., Darien, IL, USA), is a transuranium specific resin comprising 13 wt-% of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in 27 wt-% tributyl phosphate (TBP) (0.75 M CMPO in TBP) supported on the inert polymeric substrate Amberchrom TM CG-71 [9, 10]. The resin is based on the well known TRUEX-process [11–14], where a combination of CMPO/TBP in a suitable solvent is used to extract tri-, tetra-, and hexavalent actinides during reprocessing of nuclear fuel. TRU-Resin was originally meant to be used for the decontamination of highly radioactive acid-effluents,
but its selectivity for transuranium elements has promoted a wider use, in analysis of soil [15–18], urine [14, 19, 20] and faeces [21]. However, despite the high extraction capacity and selectivity for transuranium elements, the use of TRU-Spec in the analysis of Pu in natural waters has so far not been reported in literature.

In the present paper, we describe a simple, safe, fast and cost-effective procedure for Pu preconcentration and separation from large water samples. The method is based on the co-precipitation of Pu on MnO$_2$(s) from a MnO$_2$ solution, followed by chemical isolation of Pu on TRU-Resin columns.

2. Experimental

Reagents and materials

A $^{242}$Pu standard was obtained from The Norwegian Radiation Protection Agency and used as a tracer for the analysis of the samples. The tracer solution consisted of 0.1 Bq/ml of $^{242}$Pu in 2 M HN$_2$O$_4$. Unfiltered surface coastal seawater collected at Bygdøy (Oslo, Norway) in September 1997 and ordinary tap water were used in the experiments. The extraction chromatographic resin used for the separation of plutonium was TRU-Resin SPS (50–100 μm) (Eichrom Ind., Darien, IL, USA). The filters used for the alpha spectrometric source preparation were Sartorius Cellulose Nitrate 0.1 μm filters. NaOH was of technical grade and the other reagents were of normal analytical grade.

Apparatus

A glass column of dimensions 6 × 40 cm, tightly packed with about 200 grams of quartz or glass wool was used to collect MnO$_2$(s). This cartridge was connected to the sample container in one end and a vacuum source (water pump) in the other (see Fig. 1). In this way the filtered water followed the tap water out through the normal water channels. An i.d. 5 mm glass column with a glass wool fitting at bottom and top was used to make an extraction chromatographic column of 0.50 gram TRU-Resin.

Measurement

A 50 ml polysulfone filter funnel (Gelman Sciences) was used to mount the filters when preparing the α-source. The activities of $^{242}$Pu and $^{239,240}$Pu were measured with a PIPS detector with an active surface of 450 mm$^2$ and 100 μm thickness (Canberra) placed in a vacuum chamber and connected to a multichannel analyser. The distance between the source and the detector was kept at 1 cm, giving a counting efficiency of 14 ± 1%.

3. Procedure for the determination of plutonium in 200 litres of fresh- or seawater

Preconcentration

— Collect 200 litres of filtered (0.45 μm) sample water in a polyethylene container, acidify to pH 1 with conc. HNO$_3$ and add $^{242}$Pu tracer while stirring. If pressurised air is available in the lab, this can be used to provide a continuous stirring. (According to literature procedures, the water should be left to stand overnight after the addition of the acid, to ensure the leaching of Pu from particulate matter and the well mixing of the tracer.)

— Add 10 grams of KMnO$_4$ dissolved in a small amount of water and leave the solution for about 30 min. This will oxidise Pu(III) to Pu(IV) and Pu(V) to Pu(VI).

— Raise pH to 8–9 with concentrated NaOH solution.

— Still keeping pH at 8–9, reduce MnO$_2$ to MnO$_2$(s) with NaHSO$_3$ dissolved in water, and let the water rest until most of the MnO$_2$(s) has settled (~1 hour).

— Either discard the supernatant or, if the MnO$_2$(s) has not settled sufficiently, filter it through a 6 × 40 cm glass column tightly packed with 200 grams of glass wool. (Applying vacuum with a water pump gives a flow of about 3 litres/min.) The bottom slurry should be filtered under observation to ensure maximum recovery of MnO$_2$(s) or avoid plugging of the cartridge.

— Dissolve the MnO$_2$(s), the one collected on the column directly in about 0.5–1 litre of 1 M HCl + 0.5% H$_2$O$_2$ and wash the glass wool with 0.5 litre of 1 M HCl.

— Evaporate the solution to dryness on a rotavapor.

Separation

— Dissolve the resulting saltcake in ~70 ml of 3 M HNO$_3$ and filter through Whatman GF/C filter. Wash the filter with small amounts of 3 M HNO$_3$. 

![Fig. 1. MnO$_2$ collecting apparatus. The arrows show the water flow.](image-url)
Rapid Determination of Environmental Plutonium in Large Water Samples

250 - 3150 - 100

Fig. 2. Alpha-spectrum of the plutonium fraction from a 200 L seawater sample.

90 - 120

Fig. 3. Alpha-spectrum of the plutonium fraction from a 200 L tapwater sample.

- Reduce Pu (IV, V and VI) to Pu(III) with 0.2 M Na2SO3 for 30 min [22].
- Oxidise Pu(III) to Pu(IV) with 0.2 M NaN02 for 20 min.
- Inject the solution on an i.d. 5 mm column containing 0.50 g TRU-Resin preconditioned with 3 M HNO3. A flow of about 1-2 ml/min is obtained with a water pump.
- Wash the column with 15 ml of 2 M HNO3, 2 ml of 9 M HCl and 10 ml of 4 M HCl [10].
- Elute Pu with 15 ml of an aqueous solution of 4 M HCl + 0.1 M hydroquinone, directly into a 20 ml polyethylene scintillation vial [10].

Source preparation for alpha-spectrometry [23]

- Add 100 μg of Ce3+ (Ce(NO3)3 dissolved in water) and 1 ml of conc. HF to the Pu fraction and leave the solution for at least 30 min for the co-precipitation of Pu with CeF3.
- Mount a 0.1 μm membrane filter with the glassy side down in the filtration rack and precondition it with 4 ml of 80% ethanol followed by 3 ml of H2O.
- Filter the Pu fraction and wash the sample container with 5 ml of H2O followed by 4 ml of 96% ethanol.
- Glue the filter on a 25 mm steel planchet with double sided tape and allow it to dry. The source is then ready for alpha-spectrometry.

4. Results and discussion

The 242Pu-yields in Table 1 are calculated by assuming that the 242Pu alpha-peaks (Figs. 2 and 3) are “clean” and do not contain strong contributions from other alpha-emitting nuclides. Since the width at the base of the peak is about 300 keV, a strong influence from
Table 1. $^{242}$Pu-yield, FWHM of the $^{242}$Pu α-peak and the $^{239,240}$Pu content in the analysed water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{242}$Pu-yield (±σ) (%)</th>
<th>FWHM (keV)</th>
<th>$^{239,240}$Pu-content (±σ) (mBq/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 L Tapwater</td>
<td>72 ± 5%</td>
<td>67</td>
<td>9 ± 4</td>
</tr>
<tr>
<td>200 L Tapwater</td>
<td>80 ± 6%</td>
<td>76</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>200 L Tapwater</td>
<td>74 ± 6%</td>
<td>71</td>
<td>13 ± 4</td>
</tr>
<tr>
<td>200 L Seawater</td>
<td>85 ± 6%</td>
<td>70</td>
<td>34 ± 7</td>
</tr>
<tr>
<td>200 L Seawater</td>
<td>77 ± 6%</td>
<td>74</td>
<td>29 ± 6</td>
</tr>
<tr>
<td>200 L Seawater</td>
<td>89 ± 7%</td>
<td>75</td>
<td>24 ± 4</td>
</tr>
</tbody>
</table>

The uncertainties include all counting uncertainties and are mostly due to different count rates observed for the many $^{242}$Pu standards that were detected.

$^{231}$Pa (5.01 MeV), $^{229}$Th (4.85 MeV), $^{234}$U (4.78 MeV) and $^{237}$Np (4.79 MeV) can interfere in the determination of the $^{242}$Pu activity. It is therefore crucial to eliminate the interference from these nuclides. To verify this, a blank 200 litre seawater sample, i.e., without $^{242}$Pu tracer, was treated with the same procedure. The spectrum in Fig. 4 shows that there is no significant contribution from any other alpha-emitters in the $^{242}$Pu region. The $^{242}$Pu peaks are therefore free from interference from other nuclides and the calculated yields are only due to $^{242}$Pu.

The peak resolutions (FWHM) are not as good as those obtained with electrodeposition under ideal conditions (~30 keV), but are sufficient for the determination of $^{239,240}$Pu in natural low level waters. If the $^{239,240}$Pu activity in the sample water is too large, the tailing from the $^{239,240}$Pu α-peak can interfere in the accurate determination of $^{242}$Pu, used as a tracer. This problem can be overcome by using $^{236}$Pu ($E_α = 5.768$ MeV) as a tracer. If Pu is to be electrodeposited, the hydroquinone must be eliminated before electrolysis to avoid the formation of sparingly soluble hydroquinone/quinone complexes.

The high yields, the clean Pu-fractions and the short throughput time indicate that this is a very cost-effective procedure. From the addition of KMnO₄ until the source preparation, the whole procedure can be undertaken in one day and with minimal supervision.

Fe(III) is a problem ion in actinide analysis since it has similar effective ionic radius as tetra-valent actinides. A high content of Fe(III) in the sample solution, which is unavoidable with Fe(OH)₃ as scavenger, thus normally results in low Pu recovery because of the competition. In the present work this is avoided by using Mn⁷⁺, which is not extracted by TRU-Resin [10]. An important feature is also that the dissolved KMnO₄ helps in establishing equilibrium between natural and added Pu tracer, by decomposing organic matter which can be present in significant amounts in fresh waters. It has been argued that practically all inorganic particles formed in natural waters are rapidly covered with a layer of organic coating [24]. MnO₄⁻ will efficiently destroy this film and enhance the leaching of Pu. In addition both MnO₄⁻ and MnO₂(s) are capable of oxidising the less reactive Pu(III) and Pu(V) to Pu(IV) and Pu(VI) respectively. Furthermore, MnO₂(s) has better scavenging and filter abilities than Fe(OH)₂(s).

The method has as yet only been optimised for Pu analysis, but co-precipitation of other radio-elements with MnO₂(s) can possibly be used in combination with a sequential elution on TRU-Resin (with or without combination with other resins) to determine the content of other α-emitters of interest in the same sample.

5. Conclusion

Plutonium preconcentration with MnO₂(s) co-precipitation seems to be a more suitable procedure than Fe(OH)₂-co-precipitation. The strongly oxidising conditions imposed by adding KMnO₄ to the acidic

![Fig. 4. Alpha-spectrum of the plutonium fraction from a 200 L blank seawater sample.](image-url)
sample water increases plutonium’s particle affinity by oxidising the less reactive Pu(III) to Pu(IV) and Pu(V) to Pu(VI). The permanganate ion also helps to decompose the organic matter, thereby releasing organically bound plutonium. The use of MnO2(s) instead of Fe(OH)2(s) further simplifies the following procedure, as MnO2 precipitates more easily and has better filtering abilities than Fe(OH)2(s). The high manganese content in the samples does not hamper plutonium extraction or separation by TRU-Resin, as manganese is not extracted by this resin. The combination of plutonium preconcentration by MnO2(s) co-precipitation, separation by TRU-Resin and source preparation by micro-coprecipitation seems to be a very reliable and cost-efficient procedure for the determination of plutonium in large water samples. The active laboratory work is estimated to roughly 2–3 hours per sample, which is more efficient than any other routine procedure for preconcentration and separation of Pu so far used.

References
A robust procedure for the determination of plutonium and americium in seawater

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A new procedure for the analysis of Pu and Am in large water samples is presented. In this procedure, the actinides are first preconcentrated from 200 liter water samples with combined MnO₂ and Fe(OH)₃ co-precipitation. Pu and Am are then separated from the large amount of Mn by performing a second precipitation of Fe(OH)₃ at pH 6. The final separation of Pu and Am from interfering elements and from each other is achieved with the use of a single extraction chromatographic column of TRU-Resin™. The α-activities are then determined using α-spectrometry after source preparation by CeF₃ micro co-precipitation. The procedure described is faster, simpler, more robust and gives higher chemical yields than procedures normally used for routine analysis of Pu and Am. The chemical yields of Pu and Am, when analyzing 200 liter sea water samples, are between 80–85%.

Introduction

Numerous procedures are available for the analysis of alpha-emitters, but very few of these are suitable for low-activity analysis which require large amounts of sample material. Time consuming and laborious procedures must normally be employed to achieve satisfactory separation from naturally occurring stable and radioactive elements.

In routine analysis of large water samples, Pu and Am are preconcentrated by iron hydroxide precipitation, followed by separation from other elements using a series of co-precipitation, ion exchange and/or extraction procedures, before the activity is determined using alpha-spectrometry. Such procedures are very time consuming and often also give low chemical yields because of the use of conventional ion exchange resins, which require many separation steps. The IAEA recommended procedure for seawater for example involves the use of two Fe(OH)₃ precipitation steps, one anion exchange step for the separation of plutonium, two Ca-oxalate precipitation steps, two ion exchange steps and one extraction step for the separation of Am.¹

In the recent years, the commercial availability of actinide selective extraction chromatographic resins has led to the development of many new procedures for the determination of actinides in environmental samples.²⁻¹⁰ In a previous publication the use of one such resin (TRU-Resin™, Eichrom Ind.) for the analysis of Pu in large water samples was demonstrated.¹¹ In this work the same procedure is modified to also incorporate the analysis of Am. Since Cm(III) behaves like Am(III), the procedure described can also be used for the analysis of Cm isotopes, provided that they are present in detectable amounts.

Experimental

Reagents

Filtered (0.45 μm) surface coastal seawater collected at Bygdøy (Oslo, Norway) in September and October 2000 was used throughout this study. The ²⁴²Pu and ²⁴³Am standards consisted of 0.1630 Bq/ml ²⁴²Pu and 0.0891 Bq/ml ²⁴³Am in 2M HNO₃. The extraction chromatographic resin used for the separation of Pu and Am was TRU-Resin™ SPS (50–100 μm) (Eichrom Ind., Darien, IL, USA). NaOH was of technical grade and the other reagents were of normal analytical grade.

Apparatus

An internal diameter (i.d.) 5 mm glass column with a glass wool fitting at bottom and top was used to make an extraction chromatographic column of 0.70 g TRU-Resin™. 0.1 μm polypropylene membrane filters (i.d. 25 mm) fitted in a 50 ml polysulfone filter funnel (Gelman Sciences) was used collect the fluorides when preparing the α-sources.

Activity determination

The α-activities were measured with 450 mm² PIPS detectors placed in multichamber racks (Canberra). The vacuum in the chambers was kept under 10 torr and the distance between the source and the detector at 1 cm, giving a counting efficiency of 17±1%. Data treatment was done with the Canberra Alpha Analyst software.

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Preconcentration of Pu and Am

200 liter seawater sample was acidified to pH 1 with conc. HNO₃ and 24²Pu (30 mBq) and 24³Am (20 mBq) tracers and FeCl₃, corresponding to 50 mg Fe, added. After establishment of equilibrium for 24 hours, 10 g KMnO₄ dissolved in water was added and the solution left for 30 minutes before the pH was adjusted to 9 with conc. NaOH solution. MnO₄⁻ was then reduced to MnO₂ with the careful addition of a Na₂S₀₃ solution. The hydrated MnO₂ was then allowed to settle over night before the supernatant was drained off. MnO₂ slurry was then transferred to a large beaker and HCl added to approximately 0.5M. MnO₂ was subsequently dissolved with the addition of solid Na₂SO₃.

Separation from Mn

The solution was then heated for 10-15 minutes before the pH was raised to approximately 1 with the addition of conc. NH₃. At this point the solution turns from yellow to colourless due to the reduction of Fe(III) to Fe(II). Approximately 2 g of solid NaNO₂ was subsequently added and left for 10 minutes for the oxidation of Fe(II). The pH was then raised to 8-9 with the addition of conc. NH₃. This leads to the formation of both Fe(OH)₃ and Mn(OH)₂. Mn was then brought into solution by careful addition of 4M HCl to pH 5–6. Fe(OH)₃ was agitated for about 20 minutes and the solution cooled in a water bath. The supernatant was then decanted off, and Fe(OH)₃ collected by centrifugation. Fe(OH)₃ was then dissolved with 8M HNO₃ and the solution evaporated to dryness on a hot plate. The salts were then dissolved with 30-40 ml 3M HNO₃-0.5M Al(NO₃)₃-0.2M sulfamic acid – 0.2M ascorbic acid and the solution filtered through Whatman GF/C filter.

Separation of Pu and Am

An i.d. 5 mm column was packed with 0.7 g pre-equilibrated (with 3M HNO₃) TRU-Resin™ and the analyte solution passed through using a flow of 1-2 ml/min. The resin was then washed with 15 ml 2M HNO₃, followed by 5 ml 2M HNO₃-0.2M NaNO₂ and 2 ml 9M HCl. Am was then eluted with 10 ml 4M HCl, the column was washed with 10 ml 4M HCl and Pu stripped with 10 ml 4M HCl-0.02M TiCl₃. The Am and Pu fractions were collected in two separate 20 ml scintillation vials.

Source preparation for alpha-spectrometry

To the Am and Pu fractions were added 50 µg Ce(III), 1 ml 40% HF and the fluorides allowed to develop for at least 30 minutes. The fluorides were then collected by filtration through 0.1 µm membrane filter pre-treated with 80% ethanol and the vials and filter were washed with 5 ml H₂O followed by 5 ml 96% ethanol. The filters were then mounted on steel planchets with double-sided tape, dried at 60 °C, and the alpha-activity determined using PIPS detectors.

Results and discussion

MnO₂ is known to scavenge many metals and its use to preconcentrate Pu before a separation on TRU-Resin™ is demonstrated earlier. WONG et al. have also demonstrated the usefulness of MnO₂ in preconcentrating Am from large water volumes.

The active extractant in TRU-Resin™, octyphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO), is an actinide selective molecule and does not extract manganese to any significant extent. In the previously mentioned work it was shown that the presence of Mn, even in concentrations as high as 0.6M, does not depress the extraction of Pu(IV). The situation becomes quite different when determining Am(III). Preliminary experiments in using MnO₂ to preconcentrate Am showed that large amounts of Mn have an depressing effect on the extraction of Am with TRU-Resin™. When 100 ml 2M HNO₃-0.6M Mn(NO₃)₃ (10 g KMnO₄ corresponds to an Mn concentration of 0.6M in a 100 ml solution) is loaded on 0.5 g TRU-Resin™, only about 15% of Am is extracted by CMPO. Without Mn, more than 80% of Am is extracted. Therefore, Mn has to be eliminated before Am can be separated using TRU-Resin™. This can be done by adding iron to the solution and utilising the differences in the solubilities of Mn(OH)₂ and Fe(OH)₃. First both Mn(OH)₂ and Fe(OH)₃ are formed at pH 8–9, and when the pH is subsequently reduced to 6, manganese is brought into solution while the insoluble Fe(OH)₃ carries Pu and Am.

Since CMPO is also a good extractant for the ferric ion, Fe(III) must be reduced to Fe(II) before a separation of Pu and Am is performed with TRU-Resin™. This is done with the addition of ascorbic acid and sulfamic acid. Ascorbic acid alone is unstable in nitric acid, but the sulphamate ion scavenges nitrite and enables a fast reduction of Fe(III). Under these conditions Pu is also reduced to Pu(III). It is important to oxidize Pu(III) to Pu(IV), before Am(III) is eluted, to avoid the elution of Pu(III) together with Am(III). This is accomplished with an on-column oxidation of Pu(III) with NaNO₂, before Am(III) is eluted with 4M HCl.

Plutonium can then be eluted by simply reducing it back to Pu(III). In the previously mentioned work this reduction was utilised with hydroquinone, but detailed work by the author and others has revealed that hydroquinone, in the presence of nitrite compounds, has rather slow kinetics for the reduction of Pu(IV).
R. S. SEDRU: A ROBUST PROCEDURE FOR THE DETERMINATION OF PLUTONIUM AND AMERICIUM IN SEAWATER

Table 1. Chemical yields of $^{242}$Pu and $^{243}$Am, and the content of $^{238}$Pu, $^{239,240}$Pu and $^{241}$Am in 200 liter seawater samples

<table>
<thead>
<tr>
<th>Water sample (200 l)</th>
<th>$^{242}$Pu-recovery, %</th>
<th>$^{238}$Pu, mBq/m³</th>
<th>$^{239,240}$Pu, mBq/m³</th>
<th>$^{242}$Am-recovery, %</th>
<th>$^{241}$Am, mBq/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water ($n=5$)</td>
<td>78 ± 9</td>
<td>2 ± 1</td>
<td>13 ± 4</td>
<td>85 ± 9</td>
<td>2 ± 1</td>
</tr>
</tbody>
</table>

The elution profile when using 7 portions of 3 ml 4M HCl–0.1M hydroquinone to elute Pu from a 0.7 g TRU-Resin™ column can be seen in Fig. 1. As it can be seen the elution is rather slow (a broad elution peak) and only about 70–80% of the extracted Pu is eluted with 21 ml 4M HCl–0.1M hydroquinone. As Grate et al. indicate this is presumably due to the presence of nitrite compounds, probably N$_2$O$_3$, on the column as Pu is more effectively eluted (reduced) when nitrite is not present. In this work TiCl$_3$ was chosen as the Pu(IV) reductant, and the elution profile of 7 portions of 3 ml 4M HCl–0.02M TiCl$_3$ can be seen in Fig. 2. Pu elution is here complete, and over 90% of the Pu is eluted with the first 6 ml of the eluent.

The chemical yields for both $^{242}$Pu and $^{243}$Am are approximately 80–85% (Table 1) indicating that the procedure used is effective in concentrating these elements from large water samples. The alpha-spectrum of the Pu and Am fraction for a typical seawater sample are shown in Figs 3 and 4, respectively. The three peaks in the Pu fraction correspond to $^{242}$Pu, $^{239,240}$Pu and $^{238}$Pu, the peaks in the Am fraction to $^{243}$Am and $^{241}$Am. This clearly shows that TRU-Resin™ effectively separates the analytes from other interfering radionuclides.

Source preparation with CeF$_3$ micro-precipitation gives a peak resolution, FWHM, of approximately 35 keV, which is generally good enough for the secure determination of the analytes. In the proposed procedure no separation is achieved between Am and the lanthanides, but this does not cause any problems in the quantification of $^{241}$Am as the levels of lanthanides in seawater are in the range of 2–5 µg/200 liter. If such separation is desired the Am fraction can be evaporated to dryness and dissolved with 2M NH$_4$SCN–0.1M formic acid. When loaded on an extraction chromatographic resin containing Aliquat 336, TEVA-Resin™, the lanthanides pass right through while Am(IH) is extracted. Traces of the lanthanides can then be washed out with 1M NH$_4$SCN–0.1M formic acid and Am eluted with 2M HCl. Cm(III) follows Am(III) throughout the whole procedure and if enough $^{243}$Cm or $^{244}$Cm are present, the procedure can also be used for the determination of these radionuclides.

Micro co-precipitation of Pu and Am with CeF$_3$, is a simple and fast method for preparing counting sources for α-spectrometry. In addition, this procedure offers a
simple mode for the determination of the low energy (21 keV) β-emitter $^{241}$Pu ($T_{1/2} = 14.4$ y). Following the activity determination of Pu α-emitters the membrane filter can be detached from the double sided tape and transferred to a 20 ml liquid scintillation vial. The filter is then treated with a mixture containing H$_3$BO$_3$, HNO$_3$ and ethanol to dissolve the fluorides, a scintillation cocktail is added and the β-activity is determined using liquid scintillation counting.$^{21}$ This is an important feature, as $^{241}$Pu often comprises the largest fraction of the total transuranium activity in low-level radioactive waste from nuclear power plants.

Many laboratories prefer electrodeposition instead of micro co-precipitation as the alpha-source preparing step. Electrodeposition leads to narrower alpha-peaks and thus more secure results. While the Am fraction can simply be evaporated to near dryness and dissolved with a suitable electrodeposition solution after treatment with conc. HNO$_3$, this is not feasible with the Pu fraction because of the presence of Ti. When evaporated to dryness, colloidal TiO$_2$ is formed which complicates further treatment. This can be avoided with the use of an other reductant for Pu(IV) or by the coupling of Eichrom's UTEVA-column on top of the TRU-column. UTEVA-Resin$^\text{Tm}$ contains the extractant diamyl amylphosphonate which only extracts tetra- and hexavalent actinides. While U(VI) and Th(IV) are extracted by UTEVA-Resin$^\text{Tm}$, Pu(III) and Am(III) pass right through and are extracted by the TRU-Resin$^\text{Tm}$. After washing both columns with 2M HNO$_3$, the columns are decoupled and the TRU-column is washed with 2M HNO$_3$ containing NaNO$_2$. Am is then eluted with 4M HCl, after treatment with 9M HCl, and Pu can then be eluted with 0.1M NH$_4$H$_2$C$_2$O$_4$. Pu can then simply be electrodeposited after the addition of NH$_4$Cl.$^{13}$

Conclusions

An effective procedure for the determination of Pu and Am in large water samples is presented. The procedure offers quick and environmentally friendly means of analysing Pu and Am in marine waters.

The financial support of the Norwegian Research Council is highly acknowledged.

References

Sequential analysis of Sr, Pu, Am and Cm: Low-level liquid radioactive effluents

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Abstract. A new sequential procedure for the analysis of Pu, Am, Cm and Sr in low-level liquid radioactive effluents is presented. The proposed method utilises an actinide specific extraction chromatographic resin (TRU-Resin) for the isolation and separation of the actinides. \(^{90}\)Sr determination is accomplished via analysis of its progeny \(^{90}\)Y, which is purified with TBP extraction. The proposed method is simpler, faster and more robust than traditional ion exchange, extraction and precipitation methods used in routine analysis of actinides and \(^{90}\)Sr. The chemical yield of all analytes, when analysing 200 ml low-level effluent, is between 80-95%.

1. INTRODUCTION

The operation of nuclear power plants undesirably leads to the formation of liquid and solid radioactive waste containing activation and fission products. While the solid waste is suitably stored in repositories, the low-level liquid waste is normally discharged to appropriate surroundings, after decay of the shortest living radionuclides. Before such an operation can be undertaken the radionuclide content of the liquid must be examined. The Environmental Monitoring Section (EMS) of The Institute for Energy Technology (IFE), performs surveillance of discharges originating from IFE's nuclear activities to ensure that the discharge limits given by the Norwegian Radiation Protection Authority are not exceeded. The liquid effluents are analysed for gamma emitters (including \(^{241}\)Am), \(^{3}\)H, \(^{35}\)S, uranium, \(^{90}\)Sr, \(^{238}\)Pu and \(^{239,240}\)Pu. The gamma analysis is performed directly on the liquid samples using HPGe detectors with low-energy windows. Analysis of \(^{90}\)Sr, \(^{238}\)Pu and \(^{239,240}\)Pu is performed using standard separation procedures.

The low-level liquid waste at IFE originates from the operation of a small (thermal output 2 MW) research reactor and the production of radiopharmaceuticals. The waste from different locations at IFE is collected in large drums to allow the decay of the shortest living radionuclides before an evaluation on the discharge of the liquid is undertaken. Representative samples from the drums are then analysed for \(\alpha\)-, \(\beta\)- and \(\gamma\)-emitters. The composition of the liquid and the radionuclide content varies with the activities at the specific time. The general level of some radionuclides in the liquid is shown in Table 1.

Table 1: Activities of some radionuclides in the low-level waste from IFE.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>(^{60})Co</th>
<th>(^{90})Sr</th>
<th>(^{134})Cs</th>
<th>(^{137})Cs</th>
<th>(^{239,240})Pu</th>
<th>(^{241})Am</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity (Bq/l)</td>
<td>1-230</td>
<td>0-150</td>
<td>0.5-10</td>
<td>1-150</td>
<td>0-240</td>
<td>0-5</td>
</tr>
</tbody>
</table>

In our lab \(^{90}\)Sr is analysed using the traditional "fumic nitric acid method" [1,2]. Several nitrate, chromate, hydroxide and carbonate precipitations are used to pre-concentrate Sr and to eliminate interfering elements as Fe, Y, actinides, Ba, Ca and K. Sr-recovery is then determined by gamma analysis of the \(^{85}\)Sr-spike and the solution is set aside for the ingrowth of \(^{90}\)Y. Y is then precipitated several times as Y(OH), before a final precipitation as Y-oxalate. The oxalate is collected by filtration and the \(^{90}\)Y-activity determined using a low-level beta GM multicounter (Risø GM-25-5). Y-recovery is
then determined using EDTA titration. $^{239,240}$Pu analysis is done on a separate sample using traditional anion exchange procedure before the activity on electroplated discs is determined using PIPS detectors.

In an effort to optimise these analyses the use of extraction chromatography coupled with liquid-liquid extraction to develop a sequential procedure for the analysis of $^{90}$Sr and $\alpha$-emitters was studied. Since the gamma detection limit of $^{241}$Am is quiet high, an alpha analysis of $^{241}$Am was also desired. The wastewater is normally stored for at least a month before radiochemical separations are undertaken. $^{90}$Sr activity in the water therefore equals the activity of its progeny $^{90}$Y. In the proposed procedure the more favourable separation chemistry of Y(III) is utilized to determine the activity of $^{90}$Sr via $^{90}$Y. An additional advantage in analysing $^{90}$Y is it’s short half-life ($t_{1/2} = 64.1$ hours), which enables a simple check of chemical purity of the final source by just following it’s decay.

2. EXPERIMENTAL

2.1 Reagents and apparatus

Seven different low-level liquid waste solutions were analysed for Sr, Pu, Am and Cm. $^{242}$Pu (0.163 Bq/ml) and $^{243}$Am (0.086 Bq/ml) were used as tracers for Pu and Am (Cm) yield determination, respectively. Y-carrier (10 mg/ml) was prepared from pa grade $Y_2$($NO_3$)$_3$·6 $H_2$O purified by TBP-extraction [1]. The extraction chromatographic resin used for the separation of Pu, Am and Cm was TRU-Resin SPS (50-100 µm) (Eichrom Ind.). All chemicals were of analytical reagent grade.

An i.d. 5 mm glass column with a glass wool fitting at bottom and top was used to make an extraction chromatographic column of 0.50 gram TRU-Resin. 0.1 µm polypropylene membran filters (25 mm) fitted in a 50 ml polysulfone filter funnel (Gelman Sciences) were used to collect the fluorides when preparing the $\alpha$-sources.

$^{90}$Y-beta activity was determined using a low level beta GM multicounter (Riso GM-25-5). The alpha-activities were measured with 450 mm$^2$ PIPS detectors placed in multichamber racks (Canberra). The vacuum in the chambers was kept under 10 torr and the distance between the source and the detector at 1 cm, giving a counting efficiency of 17±1 %. Data treatment was done with the Canberra Alpha Analyst software.

2.2 Procedures

200 ml effluent water was acidified with 10 ml 65% $HNO_3$ and 0.2 ml each of $^{243}$Am- and $^{242}$Pu-traser and 1 ml of Y-carrier solution added before the sample was evaporated to dryness. The salts were then treated twice with 10 ml 65% $HNO_3$.

The salts were dissolved with 15 ml 3 M $HNO_3$ and $Na_2$SO$_3$ added to 0.2 M. The solution was left for 20 minutes for the complete reduction of Pu to Pu(III). $NaNO_2$ was added to 0.2 M and the solution left for 20 min for the oxidation of Pu(III) to Pu(IV). The solution was then loaded on a TRU-Resin column pre-treated with 3 M $HNO_3$ and the column washed with 10 ml 2 M $HNO_3$ and 10 ml 2 M $HNO_3$-0.1 M $NaNO_2$ (Flow: 1-2 ml/min). All effluents were kept for Y-analysis. After washing the column with 2 ml 9 M HCl, Am was eluted with 10 ml 4 M HCl and Pu with 10 ml 4 M HCl-0.02 M TiCl$_3$ directly into two different 20 ml scintillation vials. The Am and Pu-fractions were added 50 µg Ce and 1 ml 40% HF and the fluorides allowed to develop for at least 30 min. The fluorides were then collected by filtration through 0.1 µm membrane filter pre-treated with 80% ethanol and the vials and filter washed with 5 ml H$_2$O followed by 5 ml 96% ethanol. The filters were then attached to planchets with double sided tape, dried at 60 °C, and the alpha-activity determined using PIPS detectors.

The Y-fraction from TRU-Resin was evaporated to dryness, treated once with 5 ml 65% $HNO_3$ and the salts picked up with 30 ml 14 M $HNO_3$. Y was then extracted twice with 30 ml TBP preconditioned with 14 M $HNO_3$ and the separation time between Sr and Y noted. The TBP phases were combined, washed with 30 ml 14 M $HNO_3$, and Y stripped twice with 30 ml H$_2$O. NH$_3$ was then added to pH 2-3 and Y-oxalate precipitated with the addition of saturated oxalic acid solution. The solution was heated for approximately 1 hour at 90 °C, cooled, and the oxalate collected on a 25 mm Whatman 42 ash less
filter paper. $^{90}$Y-activity was then determined using a GM-counter. After β-counting the Y-oxalate was ashed at 900 °C for 90 minutes and the $\text{Y}_2\text{O}_3$ picked up with 3 ml 65% HNO$_3$. The solution was evaporated to dryness and the salts dissolved with 20 ml acetate buffer at pH 4.4. 1 drop of 0.5% xylene orange indicator was then added and Y titrated with 0.01 M EDTA until a color change from red to yellow was observed. Y-recovery was then determined by comparing the EDTA consumption of the analyte solution versus that of a reference solution containing 10 mg Y [4].

3. RESULTS AND DISCUSSION

In normal routine operations where the analysis of Sr and actinides is desired for a sample the analyses are performed on different sample aliquots. One aliquot is analysed for Sr and another for Pu and Am. This requires the pre-treatment of two different sub samples. Since the pre-treatment step for many matrices is the most time consuming step a considerable gain in throughput can be achieved by using the same sample for both Sr and actinide analysis. In a two-step sequential procedure the time used for the analysis of the second analyte can additionally be reduced as many interfering elements are eliminated in the first step.

In the proposed procedure tri-, tetra- and hexa-valent actinides are extracted by TRU-Resin while most other elements pass right through. Some Y(III) is also extracted, but this is washed out of the column with 2 M HNO$_3$ [3]. When the column is washed with HNO$_3$ containing NaNO$_2$ any remaining traces of Pu(III) are oxidised to Pu(IV). Since trivalent actinides are not extracted by CMPO (the active extractant in TRU-Resin) from HCl solutions, 4 M HCl is used to elute Am and Cm. As Cm(III) resembles Am(III) the recovery of $^{243}$Am equals the recovery of Cm. The activity of other Cm isotopes can also be calculated. After the removal of trivalent actinides plutonium can be reductively eluted with 4 M HCl - 0.02 M TiCl$_3$. The α-sources are then made by micro co-precipitation with CeF$_3$.

TBP extraction is here used to extract Y and separate it from Sr and other mono and divalent cations. Only those elements that are not extracted by CMPO from 2-3 M HNO$_3$ but extracted by TBP from 14 M HNO$_3$ and form sparingly soluble oxalates at pH 2-3 can interfere in the determination of $^{90}$Y. The possible co-precipitation of radionuclides interfering in the determination of $^{90}$Y can easily be checked by following the decay of the Y-source. In none of the seven samples analysed did the decay deviate from that of $^{90}$Y. The chemical yield of Y is traditionally checked by gravimetric methods. This however can give a too high yield estimate as other elements also can precipitate together with Y-oxalate. In our lab we have found pH-controlled EDTA titration to be more reliable than gravimetric methods for the determination of Y-recovery [4]. The chemical yield of Pu, Am, Y and Sr for the proposed and traditional methods is shown in Table 2.
Table 2: Chemical yields of Pu, Am, Y and Sr using the proposed and the traditional methods.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pu</th>
<th>Am</th>
<th>Y</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (Proposed method)</td>
<td>94 ± 9%</td>
<td>87 ± 12%</td>
<td>79 ± 7%</td>
<td>n.d.</td>
</tr>
<tr>
<td>Yield (Traditional methods)</td>
<td>24 ± 12%</td>
<td>n.d.</td>
<td>80 ± 12%</td>
<td>67 ± 27%</td>
</tr>
</tbody>
</table>

While the recoveries of both Sr and Y are high using the tradition method, the recovery of Pu is very low. Using the proposed method the recoveries of all analytes are very high. In addition the new method allows a simple α-analysis of Am and Cm. The traditional method requires the use of about one week for Pu analysis and 3 weeks for Sr-analysis. The proposed method offers significant time reduction as separation and source preparation of Pu, Am and Y can be achieved in one day.

4. CONCLUSION

A simple, rapid and reliable method for the analysis of Pu, Am, Cm and Sr in low-level liquid effluents is proposed which offers higher chemical yields, is less time consuming and more environmentally friendly than traditional methods.

References


Sequential extraction chromatographic separation of Pu, Am, Cm and Sr in soil, sediment and urine samples.

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Abstract
A method for the sequential determination of Pu, Am, Cm and Sr in bioassay and environmental matrices is described. After pre-treatment of the samples, including microwave assisted leaching of the radionuclides, the analytes are separated from interfering elements using actinide and strontium specific extraction chromatographic columns coupled together.

Introduction
Traditional methods for the separation and isolation of transuranium elements include the use of precipitation, ion exchange and solvent extraction, while the isolation of strontium is traditionally achieved using the “fuming nitric acid procedure” in combination with chromate, oxalate, hydroxide and carbonate precipitations. Although experience has shown that the methods employed yield clean analyte fractions, the procedures used, especially in the isolation of strontium, are very elaborate.

During the last ten years the availability of selective extraction chromatographic resins have considerably eased the separation and analysis of e.g. transuranics and strontium in environmental samples. The commercially available UTEVA-, TEVA-, TRU- and Sr-Resin have been used for the separation of actinides and strontium in a variety of samples. As these resins extract the analytes from moderate to high nitric acid concentrations, some of them have also been coupled together to facilitate a sequential isolation and separation of several radionuclides in the same sample.
Maxwell and Fauth coupled TEVA-Resin on top of TRU-Resin for the isolation of Pu(IV) and Np(IV) on TEVA-Resin and U(VI) and Am(III) on TRU-Resin. Sr in the TRU-Resin effluents was purified using Sr-Resin [1]. Moody et al. coupled TRU-Resin and TEVA-Resin for the separation of Th, U, Pu and Am in human soft tissue [2]. Spry et al. isolated Pu and Am using TRU-Resin, evaporated the effluents to dryness, dissolved them in 8 M HNO₃ and isolated Sr using Sr-Resin [3]. Mellado et al. separated Th and U using UTEVA-Resin followed by the isolation of Pu and Am using TRU-Resin and Sr using Sr-Resin [4]. Vajda et al. isolated Th, U and Pu with UTEVA and used TRU-Resin and TEVA-Resin for the isolation of Am and Cm [5].

To the authors knowledge no one has so far coupled TRU-Resin and Sr-Resin together to achieve a simple way of separating actinides and strontium from each other and from other interfering elements. In this work TRU-Resin is coupled on top of Sr-Resin to facilitate an isolation and separation of actinides and strontium in soil, sediment and urine samples. The use of open focused microwave oven to facilitate an easy leaching of the radionuclides in soil and sediment samples is also studied.

**Experimental**

**Reagents and apparatus**
The microwave oven used for the leaching of radionuclides was CEM Star System 2. The ²⁴²Pu and ²⁴³Am standards were supplied by Risø National Laboratory, Denmark. ⁸⁵Sr-tracer was purchased from Amersham. Y-carrier (10 mg/ml) was prepared from pa grade Y₂(NO₃)₃·6 H₂O purified by TBP-extraction. Pre-packed 2ml TRU- and Sr-Resin (particle size: 100 – 150 μm) columns were used for the isolation of actinides and Sr, respectively. 0.1 μm polypropylene membran filters (25 mm) fitted in a 50 ml polysulfone filter funnel (Gelman Sciences) were used to collect the fluorides when preparing the α-sources.

⁵⁰Y-beta activity was determined using a low level beta GM multicounter (Risø GM-25-5). The alpha-activities were measured with 450 mm² PIPS detectors. The vacuum in the chambers was kept under 1 torr and the distance between the source and the detector at 0.5 cm, giving a counting efficiency of 25±1 %.
**Treatment of soil and sediment samples**

Soil and sediment samples were dried at 105 °C to constant weight and dry ashed at 450 °C. A 5-gram aliquot of each matrix was then transferred to a microwave oven sample container and 242Pu-, 243Am- and 85Sr-tracers added. The samples were then treated according to the procedure described in Table 1.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Chemical addition</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 ml conc. HCl</td>
<td>90 °C</td>
<td>20 min</td>
</tr>
<tr>
<td>2</td>
<td>30 ml conc. HNO3</td>
<td>100 °C</td>
<td>20 min</td>
</tr>
<tr>
<td>3</td>
<td>20 ml conc. HCl</td>
<td>110 °C</td>
<td>25 min</td>
</tr>
</tbody>
</table>

The resulting solution was then filtered through glass fiber filters (GF/C), evaporated to dryness and dissolved with 200 ml 1 M HNO3. Pu was then reduced to Pu(III) with the addition of 1 gram NH2OH • HCl. The solution was then heated, 5 grams oxalic acid added and the pH raised to 5-6 with the addition of NH3. The solution was then cooled after 10 minutes and the oxalates collected on an ash less paper filter. The filter and the oxalates were then dry ashed at 450 °C.

**Treatment of urine samples**

24 hour urine samples were added 3-4 drops of 1-octanol, 100 ml conc. HNO3, 100 mg Ca, and 242Pu-, 243Am- and 85Sr-tracers. The solution was then heated for 3 hours at 90 °C before 5 ml conc. phosphoric acid was added. The pH was then raised to 8-9 with the addition of conc. NH3. The solution was sub sequentially cooled in water bath and the phosphates collected by decantation and centrifugation. The phosphates were then destroyed by dry ashing at 450 °C.

**Chemical separation and activity determination**

The ash from the treatment of the oxalates and phosphates was dissolved with 10 ml conc. HNO3 and evaporated to dryness and the salts dissolved with 20 ml 3 M HNO3 – 0.1 M sulfamic acid – 0.1 M ascorbic acid – 0.5 M Al(NO3)3. The solution was then loaded on pre-treated (3 M HNO3) TRU-Resin connected on top of Sr-Resin. A flow of approximately 2 ml/min was achieved using water pump. The columns were then washed with 10 ml 3 M HNO3 and disconnected.
**Strontium**

Sr-Resin was further washed with 10 ml 8 M HNO₃ followed by 5 ml 3 M HNO₃ - 0.05 M oxalic acid to elute traces of actinides. Sr was finally eluted using 10 ml H₂O and the time between $^{90}$Sr and $^{90}$Y separation noted. $^{85}$Sr chemical recovery was then determined using NaI detector. The solution was then added 10 mg Y and set aside for about 2 weeks for $^{90}$Y ingrowth. Yttrium was then separated from strontium by performing hydroxide precipitations using NH₃ to adjust the pH to 8. Finally yttrium was precipitated as oxalate with the addition of 1 ml hot saturated oxalic acid solution and adjustment of pH between 2-3. The oxalates were sub sequentially collected by filtration through ashless paper filter and mounted in a suitable dish for beta activity determination using GM counter. After activity determination the Y-source was set aside for another 3 weeks and recounted to check background. The oxalates were then destructed by dry ashing and the salts treated with cone. HNO₃ before they were dissolved with 20 ml acetate buffer at pH 4.4. After addition of one drop of xylene orange, Y content was determined by performing a complexiometric titration with 0.01 M EDTA solution. Sr content in the sample was determined using a spreadsheet that takes into account the Sr-yield, Y-yield, $^{90}$Y background and $^{90}$Y ingrowth time.

**Plutonium and Americium**

TRU-Resin was washed with 10 ml 3 M HNO₃ - 0.1 M NaNO₂ followed by 2 ml 9 M HCl. Am was then eluted using 10 ml 4 M HCl and the column washed with 10 ml 4 M HCl before Pu was eluted using 10 ml 4 M HCl - 0.02 M TiCl₃. The Am and Pu fractions were collected in two separate 20 ml scintillation vials. The Am and Pu fractions were added 50 µg Ce(III), 1 ml 40 % HF and the fluorides allowed to develop for at least 30 min. The fluorides were then collected by filtration through 0.1 µm polypropylene filter pre-treated with 80% ethanol and the vials and filter washed with 5 ml H₂O followed by 5 ml 96% ethanol. The filters were then mounted on steel planchets with double-sided tape, dried at 60 °C, and the alpha-activity determined using PIPS detectors.

**Results and discussion**

Open focused microwave oven assisted leaching of plutonium from sediment samples was compared with acid leaching on hot plate. Four different surface sediment samples were gathered from a river (Nitelva river) flowing close to Institute for Energy Technology. The samples were dried at 105 °C to constant weight. 10 grams of each of the samples were then subjected to different leaching procedures:
Traditional method: The samples were added $^{242}$Pu tracer and dry ashed at 450 °C and treated with 200 ml aqua regia for 6 hours.

Microwave oven: The samples were added $^{242}$Pu tracer and treated with 20 ml conc. HCl for 30 minutes in an ultrasonic bath. The samples were then transferred to microwave oven sample holder and treated according to the procedure described in Table 1.

Plutonium in each of the samples was then pre-concentrated using Fe(OH)$_3$ co-precipitation and separated from interfering radionuclides using 10% TIOA in xylene extraction followed by anion exchange separation. Pu was finally electrodeposited and the alpha activities determined using PIPS detectors. The $^{239,240}$Pu content found in the samples using these leaching methods is shown Table 2.

Table 2. $^{239,240}$Pu content (Bq/kg d.w. ± 2σ) in four sediment samples acid leached in two different ways.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Aqua regia treatment on hot plate</th>
<th>Open focused microwave oven treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,16 ± 0,10</td>
<td>1,12 ± 0,10</td>
</tr>
<tr>
<td>2</td>
<td>0,70 ± 0,08</td>
<td>0,71 ± 0,06</td>
</tr>
<tr>
<td>3</td>
<td>0,50 ± 0,06</td>
<td>0,47 ± 0,10</td>
</tr>
<tr>
<td>4</td>
<td>0,75 ± 0,08</td>
<td>0,76 ± 0,10</td>
</tr>
</tbody>
</table>

The results show that there is no significant difference in plutonium leaching ability between these two methods for these particular sediment samples. To completely verify the effectiveness of the microwave assisted leaching procedure, more samples, in particular certified reference materials, should be analyzed.

The procedure for the analyses of Pu, Am and Sr in urine samples was tested in PROCORAD intercomparison test. In this study three 1000 ml urine samples were received for actinide determination and three 500 ml urine samples for Sr determination. One sample in each batch was a blank sample.
The samples were split into two: One fraction was analyzed using traditional methods (ion exchange separation of Pu and “fuming nitric acid” separation of strontium) and the other fraction was analyzed using TRU-Resin for Pu, Am and Cm and Sr-Resin for Sr determination. The results are shown in Table 3 – Table 5.

Table 3. $^{238}$Pu results achieved in PROCORAD urine intercomparison using anion exchange and TRU-Resin separation of Pu

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Ion exchange $^{238}$Pu (Bq/sample ± 2σ)</th>
<th>TRU-Resin $^{238}$Pu (Bq/sample ± 2σ)</th>
<th>Reference value $^{238}$Pu (Bq/sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(7.14 ± 0.64) • 10^{-3}</td>
<td>(7.00 ± 0.36) • 10^{-3}</td>
<td>6.52 • 10^{-3}</td>
</tr>
<tr>
<td>B</td>
<td>(8.78 ± 1.34) • 10^{-4}</td>
<td>(11.3 ± 1.24) • 10^{-4}</td>
<td>9.50 • 10^{-4}</td>
</tr>
</tbody>
</table>

Table 4. $^{241}$Am and $^{243,244}$Cm results achieved in PROCORAD urine intercomparison using TRU-Resin separation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TRU-Resin $^{241}$Am (Bq/sample ± 2σ)</th>
<th>Reference value $^{241}$Am (Bq/sample)</th>
<th>TRU-Resin $^{243,244}$Cm (Bq/sample ± 2σ)</th>
<th>Reference value $^{244}$Cm (Bq/sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(6.92 ± 0.39) • 10^{-3}</td>
<td>7.19 • 10^{-3}</td>
<td>(1.48 ± 0.15) • 10^{-3}</td>
<td>1.85 • 10^{-3}</td>
</tr>
<tr>
<td>B</td>
<td>(9.77 ± 1.15) • 10^{-4}</td>
<td>1.05 • 10^{-3}</td>
<td>(1.79 ± 0.16) • 10^{-3}</td>
<td>1.85 • 10^{-3}</td>
</tr>
</tbody>
</table>

Table 5. Comparison of $^{90}$Sr results achieved in PROCORAD urine intercomparison using traditional “fuming nitric acid” and Sr-Resin separation of Sr.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>“Traditional method” $^{90}$Sr (Bq/l ± 2σ)</th>
<th>Sr-Resin $^{90}$Sr (Bq/l ± 2σ)</th>
<th>Reference value $^{90}$Sr (Bq/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4.69 ± 0.56</td>
<td>4.61 ± 0.54</td>
<td>4.65</td>
</tr>
<tr>
<td>C</td>
<td>3.00 ± 0.36</td>
<td>2.84 ± 0.34</td>
<td>3.08</td>
</tr>
</tbody>
</table>

The PROCORAD intercomparison results indicate that extraction chromatographic separation of Pu, Am, Cm and Sr in urine samples gives results similar to traditional separation procedures and very close to reference values.
The Pu, Am and Sr yields achieved using TRU-Resin and Sr-Resin in the PROCORAD exercise was for all of the radionuclides above 80%.

Four 24-hour urine samples (1.8 – 2.9 liter) gathered from IFE workers were subjected to the sequential procedure described earlier. On average the chemical recoveries of $^{85}\text{Sr}$ and $^{243}\text{Am}$ were 60%, and those of $^{242}\text{Pu}$ were 90%.

The Pu and Am fractions did not show any existence of interfering radionuclides. No attempt is here made to separate Am and Cm from rare earth elements. When analyzing urine samples, this does not cause a problem due to the low content of rare earth elements in urine. But, when soil and sediment samples are to be analyzed, Am and Cm must be separated from rare earth elements. This can either be achieved using NH$_4$SCN and formic acid mixture on TEVA-Resin or 0.1 M HCl – 0.5 M NH$_4$SCN – 80% methanol mixture on an anion exchange resin.

The Y-90 source, prepared by milking the Sr-90 fraction, showed the presence of a short-lived radionuclide (Figure 1). Most probably this is Ac-228 ($t_{1/2} = 6.15$ h), a daughter of Ra-228.

![Figure 1](image.png)

**Figure 1.** Background subtracted measured counts (open dots) and theoretical decay of Y-90 (closed dots) for a urine sample that contained approx. 10 mBq/l Sr-90. The dotted line shows the instrument background.
Traces of Ac-228 are often observed in the Y-90 fraction, even when traditional precipitation procedures (nitrate-, hydroxide-, chromate, oxalate precipitations) are used for Sr-90 isolation. Work is under progress to see if radium co-precipitation with barium chromate, prior to yttrium isolation by hydroxide and oxalate precipitation, can eliminate the Ac-228 contamination.

Conclusion

A sequential procedure for the analyses of Pu, Am, Cm and Sr in soil, sediment and urine samples is described. The soil and sediment procedure utilizes open focused microwave oven assisted leaching and oxalate precipitation pre-concentration of the analytes. In analyses of urine samples the analytes are pre-concentrated using calcium phosphate co-precipitation. The analytes are then separated from interfering elements and from each other using a dual column of TRU-Resin coupled on top of Sr-Resin.

References


