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RADCHEM
Radiochemical procedures for the determination of Sr, U, Pu, Am and Cm

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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 accidents, authorised release and routine surveillance. Reliable radiochemical separation and detection techniques are needed for accurate determination of alpha and beta emitters. Rapid analytical methods are needed in case of an accident for early decision-making. The objective of this project has been to compare and evaluate radiochemical procedures used at Nordic laboratories for the determination of strontium, uranium, plutonium, americium and curium.

To gather detailed information on the procedures in use, a questionnaire regarding various aspects of radionuclide determination was developed and distributed to all (sixteen) relevant laboratories in the Nordic countries. The response and the procedures used by each laboratory were then discussed between those who answered the questionnaire. This report summaries the findings and gives recommendation on suitable practice.

Key words

Radiochemistry, radioecology, strontium, uranium, plutonium, americium, curium

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Contents

1. Background and introduction

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 accidents, authorised release and routine surveillance. Reliable radiochemical separation and detection techniques are needed for accurate determination of alpha and beta emitters. Rapid analytical methods are needed in the case of an accident for early decision-making.

The objective of this project has been to compare and evaluate radiochemical procedures used at Nordic laboratories for the determination of strontium, uranium, plutonium, americium and curium.

A similar task was undertaken in 1985 in the framework of NKS (NKA): "The Sampling and Analysing Methods of Radionuclides used in The Nordic Countries for Environmental Samples", Edited by Tarja K. Taipale [1]. Since then new separation methods and instrumentation has been introduced and is in use in most laboratories.

To gather detailed information on the procedures in use, a questionnaire regarding various aspects of radionuclide determination was developed and distributed to all (sixteen) relevant laboratories in the Nordic countries. The questionnaire can be found on page 5. Nine laboratories answered the questioannaire, while four laboratories responded that they did not perform the specified analysis. The response and the procedures used by each laboratory were then discussed between those who answered the questionnaire. This report summaries the findings and gives recommendation on suitable practice. This report is not to be seen as describing the full Nordic scenario as two laboratories that also perform the specified analysis did not respond to the questionnaire. Never the less, this report covers the procedures most often used in the Nordic countries.

Radionuclide: Specify only those radionuclides you analyse in a similar manner (e.g. ^{238}Pu and ^{239,240}Pu). The rest of the form should refer to this/these radionuclides. Use different forms for different radionuclides.
Matrix: What matrices do you analyse with respect to the specified radionuclide?
Sampling: Sampling methodology, design, use of special equipment, representativeness etc.
Pre-treatment and enrichment Storage, preservation, cleaning (e.g. remove stones from soil, soil from grass, particles from water, flesh from bones etc.), drying and dry ashing temperatures, when do you add the tracer/spike (before or after drying/ashing), preconcentration of analyte from liquids etc.
Dissolution/Leaching Do you mostly use leaching methods or total dissolution of the sample? How do you leach the analyte from various samples? Which method do you use to ensure total dissolution of various samples?
Separation Amount of sample you subject to a specific separation procedure (specify if its fresh/dry or ashed). Separation procedure in detail, e.g.: Chromatography (ion-exchange or extraction): Resin type, column dimensions, flow, load and wash solutions and volumes, eluent volume. Do you reuse columns? Any memory effects? Extraction: Extractant, solvent, aqueous solution etc. Precipitations: describe the system Typical recoveries, any impurities?
Source preparation Electrodeposition: solution, pH, current, time, disc, distance, peak resolution etc. Micro co-precipitation: reagents, solution volume, filter type and pore diameter, peak resolution etc. Precipitation: reagents
Activity determination Detectors for alpha spectrometry, beta counting, mass spectrometry etc. and their specifications. How do you determine the chemical yield?
Rapid procedure Do you have any rapid procedures? Please describe these. Have you checked these against routine procedures or reference materials etc.?
Quality assurance Do you have a quality assurance protocol? How do you ensure good quality? Do you analyse reference materials, do you participate in intercomparison and proficiency tests, how do you otherwise check your procedures? How do you prevent and account for contamination of samples? Do you screen your samples prior to analysis? How? Blank analysis (do you keep track of the blank values, do you subtract the blank value from the sample value, how often do you analyse blanks etc.). Uncertainty: Does your result indicate uncertainties? What uncertainties do you account for? Do you have different laboratories to handle different levels of analyte concentration? How are these laboratories divided/defined (ultra low-level, low-level and higher level)? Do you have written guidelines on the permitted activity levels that can be handled in each laboratory? MDA: How do you calculate MDA?
Comments Do you have any problems with the procedures you utilise (insufficient separation from interferences, low chemical yield, bad peak resolution etc.)? Are you satisfied with the procedures you are using? Would you like to eliminate the use of certain chemicals etc.?

2. Sampling

Sampling is probably the most critical step in the entire analytical process. First of all one should have a clear understanding of the goal of the investigation. The nature of both the analyte and the matrix must be clearly defined. Next, the isolated sample must as closely as possible represent the matrix sampled. Cross contamination of the samples should be avoided and it must be kept in mind that gathering, treatment and storage of the sample can greatly alter the chemical speciation of the analyte, and the composition of the sample. Sampling and sampling procedures are major topics, which deserve special attention. These topics will be discussed in future NKS-projects (FOREST and SAMPSTRAT).

The participating laboratories indicate that samples are gathered according to their quality manuals or received from contractors or research institutes. For information on how the samples are gathered, please refer to the previous NKS-report on radiochemistry [1].

Table 1. Matrix and sampling procedures

Matrix	Type and sampling procedure
Water/Precipitation	Effluent water, lake water, seawater collected by e.g. pumping in appropriate containers. Mostly filtered after collection. Precipitation samples continuously collected with deposition samplers with different areas.
Soil	Grab or corer: slicing or division into e.g. litter, organic and mineral fraction.
Sediment	Grab or corer (slicing)
Biota	Grass, peat: collection from restricted area (0.25-0.5 m^2), agricultural products and fish etc.
Filter/Swipe	Organic filters or swipes.
Milk	Collection from farms.
Urine	24 hour sample

3. Pre-treatment

In this context pre-treatment is defined as the treatment of the samples after collection, but prior to e.g. enrichment or ashing. This treatment step should "define the sample" and ensure that the defined sample is not altered during storage. Liquid samples are often made acidic and biological samples are often stored in freezers or added preservation chemicals. Please refer to IAEA Technical Report Series No. 295 for further information [2].

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, especially for actinide determination, as hydrolysed actinide species have great affinity towards exposed surfaces. Lovett et al. [3] studied the adsorption of ^{241}Am from unacidified and acidified (pH1) filtered seawater onto the walls of a 25-litre polyethene 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. It must be kept in mind that addition of acids and other chemicals can alter the speciation of the analyte.

Depending on the purpose of the study, large objects as stones are normally removed from soil and sediment samples. Solid samples are dried between 60-105 ^{o}C. One lab also uses freeze-drying for this purpose. After drying, biota is normally grinded. Soil, sediment and biota samples are then normally sieved through 2 mm sieve before further treatment.

It is a general agreement that the carrier or tracer should be added to the sample as soon as possible after the sample has been defined. How soon is this? For deposition samples, some add carriers to the sampling vessel prior to sampling. One lab adds tracer prior to drying of solid samples, while most labs add it after dry ashing. There is no simple answer to this. As long as we are reasonably sure that no, or only an insignificant amount of analyte is lost during drying and ashing, the tracer can be added after ashing.

Table 2. Pre-treatment of different matrices

Matrix	Pre-treatment
Water/Precipitation	Filtration, acidification (pH1-2), tracer/carrier addition, redox treatment. Precipitation: Carriers prior to sampling, acidification, drying, ashing.
Soil	Removal of stones, drying (60-105 ^{o}C) or freeze-drying, sieving (2mm), tracer addition
Sediment	Removal of stones, drying (60-105 ^{o}C) or freeze-drying, sieving (2mm), tracer addition
Biota	Carrier/tracer addition, drying (60-105 ^{o}C), preservation with $Na_2S_2O_5$, grinding, sieving (2mm)
Filter/Swipe	Tracer/carrier addition
Milk	Tracer/carrier addition
Urine	Acidification, tracer addition, heating

4. Enrichment from liquid samples

Pu and Am determination in most environmental waters requires the analysis of about 100-200 litre water samples while ^{90}Sr-analysis requires about 25-50 litres. Significantly less amount of water is needed from more contaminated areas. The analytes must therefore be concentrated to a smaller volume before further chemical separations can take place. Evaporation is normally only used for pre-concentration purposes when the samples involved have a fairly low volume or low salt content. Precipitation samples are almost always evaporated to desired volume or dryness. The method of choice for large samples is usually co-precipitation. Many different precipitating agents have been employed.

$CaCO_3$
Calcium in seawater can be precipitated as $CaCO_3$ by increasing the pH of the water to about 10. Mixed $CaCO_3$ and $Mg(OH)_2$ precipitation has earlier been used for the co-precipitation of Pu [4, 5]. It is in limited use today as tests have shown that not all oxidation states of Pu are effectively precipitated [6-8]. Nevertheless, carbonate precipitation is an effective way of concentrating Sr from seawater. The succeeding separation schemes must be able to handle large amount of Sr and Ca, as seawater (35 ‰) contains about 8 mg/l Sr and 400 mg/l Ca.

NdF_3 / LaF_3 / 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 [9, 10]. After acidification a soluble chromate salt is added to the water sample to oxidise 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) [11].

$Fe(OH)_2$ and $Fe(OH)_3$
Ferric and ferrous hydroxide co-precipitation of actinides is extensively used to preconcentrate actinides from large water volumes [3, 12-15]. The method became an early standard after its introduction in 1971 [16]. 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+} [3]. 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.

MnO_2
MnO_2 has long been known to scavenge actinides and a method for the co-precipitation of Pu with MnO_2 was proposed in 1978 by Wong et al.[17]. Recently a few new methods using MnO_2 for the pre-concentration of actinides from large water volumes have been published [18, 19]. MnO_2-impregnated cartridges have also been used to collect actinides from very large volumes (4000 litre) [17, 20-22] . The method has shown to be effective for Th and Am but gives varying results for Pu [22]. In experiments by Mann et al. [20] the Pu recovery varied between 16-100%. Wong et al. achieved good correlation with $Fe(OH)_3$ scavenging for lagoon and open ocean water (but not for shallow and ground water [17]). 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 [23]. Both oxalate and phosphate precipitations are very effective, especially when sequential analyses are desired, as they can co-precipitate both Sr and the actinides. With the addition of approximately 100 mg Ca^{2+} and 5 ml conc. H_3PO_4, Sr and the actinides can be recovered almost quantitatively from a 24-hour urine sample when the pH is raised above about 8. 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.

Most laboratories use $Fe(OH)_3$ co-precipitation for actinide enrichment from liquid samples. One laboratory uses NdF_3 co-precipitation to enrich uranium from small water samples, while another lab uses MnO_2 to enrich actinides from large water samples and phosphate precipitation to enrich strontium and actinides from urine samples. One lab performs sequential enrichment of actinides and strontium from large water samples. Actinides are first precipitated with $Fe(OH)_3$, then strontium in the supernatant is precipitated as carbonate or oxalate.

Table 3. Enrichment of radionuclides from liquid samples

Matrix	Enrichment procedure
Water	Small low salt content waters: Evaporation Actinides: $Fe(OH)_3$ or MnO_2 precipitation, NdF_3 precipitation of uranium in small water samples Sr: carbonate or oxalate precipitation (from supernatant of actinide precipitation)
Milk	Evaporation
Urine	Actinides and Sr: phosphate precipitation Actinides: $Fe(OH)_3$ precipitation

5. Destruction of organic matter

Organic matter is normally destructed using dry ashing in muffle furnaces (400-700 ^oC, depending on the analyte). While some laboratories cover their samples during ashing, others do not. Covering the samples avoids cross contamination and loss, but reduces oxygen flow to the sample, thereby yielding poorly ashed samples. As a loss would be more dramatic for small samples, these should preferentially be covered during ashing. Large samples can be ashed uncovered, but care should be shown to not ash these together with samples with very different activity levels. The area exposed to air should be kept as large as possible. Ashing aids as oxalic acid can also be added to aid the ashing of covered samples. The interior of the muffle furnace should be cleaned periodically to avoid contamination.

Wet ashing on hotplate or in a microwave oven is occasionally used for ashing purposes, but mostly acid treatment is used for leaching the analyte from the sample. One lab only wet ash their samples prior to determination of transuranium elements and sometimes also prior to strontium determination.

6. Dissolution and leaching

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 mineral acids. Leaching of the ash with mineral acids does not necessarily leach out all of the analyte, but the amount not leached is generally low. Uranium, which can be part of the interior of the matrix, and radionuclides bound to or incorporated into refractory oxides are 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_2CO_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. Normally fusion is performed on small samples.

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 alkalies 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 to a few grams.

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 (10 grams) 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.

Only a few laboratories use fusion and total dissolution techniques. There is a need for a comparison between the different leaching techniques. Such a study is underway at Helsinki University and Institute of Energy Technology. In emergency situations where only a small amount of sample is desired, fusion is recommended.

7. 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 [24-27].

Both cation exchange and anion exchange from HCl and HNO_3 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 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 [25]. 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 HNO_3 before Th is eliminated by wash with 10 - 12 M HCl. Pu is reductively eluted with HCl containing a reducing agent (HI, NH_4I, $NH_2OH{\cdot}HCl$) [14, 16, 28-35]. Since neither Sr nor Y is retained on the anion exchange column, the HNO_3 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 [15, 36]. Both Am(III) and light lanthanides are retained on an anion exchanger from 1 M HNO_3 - 93% methanol [37]. Since actinides form stronger complexes with soft donor atoms (S, N) than lanthanides, separation between Am(III) and lanthanides is sub sequentially achieved using NH_4SCN. 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 NH_4SCN – 80% methanol. Am can then be eluted using hydrochloric or nitric acid - methanol solution with a higher content of water [13, 29, 30, 33, 35, 36, 38-40].

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

8. 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 [25, 41-43].

HDEHP (bis(2-ethylhexyl) phosphoric acid)
HDEHP is a cationic extractant capable of extracting trivalent actinides and lanthanides quantitatively from HCl or HNO_3 solutions with pH higher than about 2.5. They are not extracted below pH about 1.3 [44]. Simultaneous extraction of Fe(III) and the formation of precipitants at pH 2-3 can cause problems [37, 40]. 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 [45] 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 HNO_3) 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 [46]. Pu in the organic phase can be separated from other tetravalent actinides by reductively stripping it as Pu(III) [47]. 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 [48].

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 [49, 50]. 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 [51, 52].

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_4I [38]. 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_4I, Np with 4 M HCl – 0.02 M HF and U with 0.1 M HCl [53]. DDCP (dibutyl-N,N-diethylcarbamoyl phosphonate) is a good extractant for the extraction of trivalent actinides and lanthanides from concentrated (12 M) HNO_3 [29, 40, 54].

9. Extraction chromatography

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. 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 [55]. 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 [56] and Cortina and Warshawsky [57].

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 carbamoylphosphine 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.

Table 4. Resins commercially available from Eichrom Industries.

Resin	**Active extractant**	**Application**
Sr-Resin	bis-4,4'(5')-tertbutylcyclohexano-18-crown-6	Sr, Pb, Po
TRU-Resin	octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)	Th, U, Pu, Am, Cm, Fe
RE-Resin	octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)	Rare earth elements
UTEVA-Resin	diamyl amylphosphonate (DAAP)	U, Th, Np, Pu
TEVA-Resin	Tri-n-octylmethylammonium chloride (Aliquat 336)	Th, Np, Pu, Tc, Am/Ln separation
Ni-Resin	dimethylglyoxime (DMG)	Ni
Actinide-Resin	P-P'-di(2ethylhexyl)-methaenediphosphonic acid	Am, Pu, Th, U
Pb-Resin	bis-4,4'(5')-tertbutylcyclohexano-18-crown-6	Pb
Ln-Resin	bis(2-ethylhexyl) phosphoric acid (HDEHP)	Lanthanides, Pa, Ra

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 [58], worked with extraction chromatographic separations [59-71]. 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.

10. Strontium determination

10.1 Strontium separation

Three different methods are used for Sr-separation: Nitrate precipitations, solvent extraction (TBP) and extraction chromatography (Sr-Resin).

Fuming nitric acid procedure: This classic way of analysing ^{90}Sr makes use of the low solubility of $Sr(NO_3)_2$ in fuming nitric acid solutions [23, 72]. The procedure is used in two laboratories. 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. The use of fuming nitric acid can be avoided using the procedure proposed by Bojanowski (J. Radioanal. and Nucl. Chem., Vol. 138, No 2 (1990) 207-218). One lab achieves low Sr yields when using the tradition fuming nitric acid procedure for the determination of Sr in seaweed and seawater samples.

- Nitrate precipitation (Sr sep. from Ca)
- Hydroxide precipitation (Sr sep. from actinides and yttrium)
- Chromate precipitation (Sr separation from Ba, Ra and Pb)
- Carbonate precipitation

TBP-extraction: Advantageous if the Sr-90 activity is determined through Y-90, as TBP extracts Y from conc. HNO_3, and Y can be stripped using H_2O. Care should although be shown as some other elements as U(VI) and trivalent actinides and lanthanides (especially when the nitrate concentration is high) can follow Y. One other aspect is also the amount of H_2O used to elute Y. As TBP also extracts HNO_3, washing TBP with H_2O, reduces the HNO_3 concentration in TBP. If too much H_2O is used this lowers the HNO_3 conc. so much that other elements (e.g. Th) also follow Y. One laboratory uses this procedure for the determination of ^{90}Sr in milk.

- Extraction of Y-90 with TBP from 14 M HNO_3
- Elution of Y-90 with H_2O

Sr-Resin: The extractant in Sr-Resin consists of the crown ether 4,4'(5')-di-t-butylcyclohexano 18-crown-6, abbreviated DTBCH18C6, dissolved in 1-octanol. High nitrate concentration promotes the extraction of strontium, while contact with water reverses the reaction thereby stripping Sr. In this manner Sr can easily be stripped without use of any complexing agents. When extracting Sr from 3 M HNO_3, less than 0.5% of Sr introduced is

eluted with the first 30 FCV's (free column volume) while about 98% is eluted with the first 2.5 FCV's when the medium is shifted to water [73].

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. If the final Sr or Y source is made by oxalate precipitation, this separation can also be achieved in the source preparation step. 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. 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. 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. 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 standard 2 ml column (0.75 gram resin). One lab uses 3 gram columns to avoid this. They also reuse the columns several times (5-10) after appropriate washing with H_2O and HCl.

The procedure is advantageous for samples not containing too high amounts of Sr or Ca. In emergency situations Sr-Resin separation is recommended due to both its simplicity and since this procedure, contrary to TBP-extraction, also allows the determination of Sr-89. Sr-Resin extracts Sr at the same nitric acid concentration as TRU-Resin extracts Pu and Am. Hence, these resins can also be coupled together to achieve a sequential determination of Sr, Pu and Am. Procedure for the sequential determination of Sr, Pu and Am in various matrices has been developed and is now undergoing verification and testing.

Two labs only use Sr-Resin for Sr-separations (one of the labs uses large Sr-columns when determining Sr in samples containing too much Ca og Sr), while one lab uses both the traditional method and Sr-Resin. The traditional method is very laborious while the Sr-Resin procedure occasionally shows poorer decontamination.

- Sr-Resin (0.7 grams, 3.0 grams)
- Load: 8 M HNO_3 or
  3 M HNO_3 – 0.1 M sulphamic acid – 0.1 M ascorbic acid – 0.3 M $Al(NO_3)_3$
  (sequential analysis using TRU- and Sr-Resin)
- Wash: 8 M HNO_3
- Wash: 3 M HNO_3
- Wash: 3 M HNO_3 – 0.05 M oxalic acid
- Sr elution: 0.05 M HNO_3 or H_2O

10.2 Strontium source preparation and activity determination

^{90}Sr has been counted directly using liquid scintillation or precipitated as carbonate and counted by proportional counters. When Y is isolated from the sample, ^{90}Y activity has been determined using either gas proportional counters, or Cerenkov counting.

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 determinated 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.

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 (hydroxide precipitation)
4. Y source preparation (oxalate precipitation)
5. ^{90}Y activity determination
6. Y yield determination

In principle 2 methods can be distinguished for the source preparation. After ingrowth of ^{90}Y, Y is precipitated as oxalate before beta measurement. If both ^{90}Sr and ^{89}Sr are analysed, Sr is first precipitated as carbonate with ammoniumcarbamate. Then the sample is dissolved. After 2-3 weeks ingrown ^{90}Y is precipitated as hydroxide and then oxalate.

Two laboratories have the possibility to analyse Sr directly using LSC. These labs use Sr-Resin and Atomic Absorption Spectroscopy for Sr-yield determination. Two labs count the ^{90}Y source after ingrowth. These labs use ^{85}Sr as yield determinant. One lab determines the Y-yield gravimetrically, while the others use EDTA titration for this purpose. EDTA titration has proven to be more accurate, and is recommended for this purpose. Very often (at least in one lab) the final Y-oxalate source contains ^{228}Ac. The reason for this is unclear.

11. Uranium determination

11.1 Uranium separation

Three different methods are used for uranium-separation: Anion exchange chromatography, solvent extraction (TBP) and extraction chromatography (UTEVA-Resin).

Anion exchange from HCl:
Resin: Dowex 1x4 or 1x8
Column dimension: 1x12 cm
Flow: Approx. 1 ml/min
Load: 9-12 M HCl
Th removal: 9-12 M HCl
Elute U: 0.1 M HCl

No separation is here achieved between U(VI) and Pu(IV) and Fe(III). Interference from Fe(III) and Pu(IV) can be avoided by loading under reducing conditions (Fe(II) and Pu(III)). Interference from Fe(III) can also be avoided by washing the column with 8M HNO_3 prior to uranium elution.

Anion exchange from HNO_3: Resin: BIORAD AG-1x4 or Dowex 1x4
Column dimension: 1x12 cm
Flow: Approx. 1 ml/min
Load: 8 M HNO_3
Wash: 8 M HNO_3
Elute U: 0.1 M HCl

No separation is achieved between U(IV) and Th(IV) and Pu(IV). Pu(IV) interference can be eliminated by loading under reducing conditions and Th(IV) can be stripped with 9 M HCl, prior to U(VI) elution.

Solvent extraction: Water phase: 8 M HNO_3
Organic phase: 100% TBP
Wash: 8 MHNO_3 (repeated)
Dilute org. phase with xylene
Wash with 1.5 M HCl (Th) (repeated)
Elute U with H_2O (repeated)

Three labs use TBP extraction for uranium separation. This is a simple and effective procedure.

Extraction chromatography: Column: UTEVA-Resin (0.7 gram)
Load: 3 M HNO_3 – 1 M $Al(NO_3)_3$
Wash: 9 M HCl
Wash: 5 M HCl – 0.05 M oxalic acid
U elution: 0.01 M HCl

Three labs use this procedure. In one lab the procedure is combined with TRU-Resin for Pu-determination, and in an other it is combined with both Sr-, TRU- and TEVA-Resin. This is a simple and effective procedure.

11.2 Source preparation of actinides

Source preparation is one of the most important steps in the radiochemical analysis. Poor sample preparation cannot be replaced by better spectrometric equipment or software programs for peak evaluation.

Generally sources for alpha spectrometric measurement of environmental samples are prepared by electrodeposition. Platinum is used as anode and the cathode is a disc of electro-polished stainless steel (Ø= about 20 mm). It is also possible to use graphite as anode and other metals, copper, zinc, silver, platinum etc. as anode material. The electrolyte is for example sodium sulphate solution (6 ml in a liquid scintillation vial), prepared by adding some sodium sulphate to the sample, thereafter pH is adjusted to about 2 with ammonia. The electrolysis time is 1-5 hours at 0.6-1 A and an anode–cathode distance of a few mm. This method was described by Hallstadius in 1984 [74]. The paper is only on 2 pages and 3 references but has now been cited over 100 times.

There are also other electrolytes such as oxalate medium, nitric acid pH adjusted with ammonia and nitric acid-methanol mixture. Interestingly also Radium deposits from this latter method and the deposition time is only about 20 minutes with a current of 100 mA. Further more it seems possible to use aluminium as cathode material, while the aluminium is dissolved by the sodium sulphate method.

A competing method, especially if a rapid method is desired, is fluoride precipitation. The oxidation state of the actinide must be +3 or +4. A rare earth element such as Ce or Nd (50 μg) in solution is added to the sample and HF is added until precipitation occurs (normally less than 1 ml 40% HF). The sample is filtered through a 0.1 μm membrane filter (polypropylene). The efficiency is high and the only drawback is that the resolution is not as good as for electrodeposition. It is recommended that those who use this procedure also try direct precipitation and collection: Precipitation of the analyte with e.g. CeF_3 directly from the eluted solution (without evaporation and further treatment) and collection on untreated membrane filters. One lab uses this procedure and is satisfied with the results. Using smaller planchets and filters can increase the counting efficiency of alpha-detectors. This should be tested.

If the actinides are measured by mass spectrometric techniques the final solution is in weak HNO_3. If liquid scintillation is applied the appropriate scintillation cocktail is prepared.

Electrodeposiiton: Catode: polised stainless steel (diameter 20 mm)
Anode: platinum
Distance: 5-10 mm
Solution: 8-15 ml 2 M $(NH_4)_2SO_4$ or Na_2SO_4 plus H_2SO_4 ($NaHSO_4$), pH = 2-3
0.8-2 ampere for 1-4 hours

5 labs use only electrodeposition, while one lab uses both electrodeposition and micro co-precipitation.

Micro co-precipitation: Solution: 10 ml 4 M HCl or 4 ml 1 M HCl
50 μg Ce (Nd)
$TiCl_3$ (for U reduction)
1-2 ml 40% HF
Filtration through 0.1 μm polypropylene filter (pre-treated with CeF_3 or NdF_3 substrate solution)

One lab uses only micro co-precipitation while another lab uses both this and electrodeposition.

11.3 Activity determination of uranium

Alpha-spectrometry using PIPS detectors (450 mm^2) is the preferred method in most laboratories. One laboratory uses ICP-MS, while another determines the total amount of uranium using fluorescence analysis after fusion with NaF. Direct determination of uranium in leached solution using ICP-MS offers a great time saving.

12. Plutonium determination

12.1 Plutonium separation

Three different methods are used for plutonium-separation: Anion exchange chromatography, solvent extraction (TIOA, TBP) and extraction chromatography (TRU-Resin).

Anion exchange: Resin: BIORAD AG-1x4, 1x8 or Dowex 1x4
Column dimension: 1x12 cm, two labs use 1x3-5 cm columns
Flow: Approx. 1-2 ml/min
Load: 8 M HNO_3 added $NaNO_2$ (save for Am and Cm analysis)
Wash: 8 M HNO_3 (save for Am and Cm analysis)
Elute Th: 9-12 M HCl
Pu: 9 M HCl – NH_4I or 1.2 M HCl + H_2O_2 (two labs)

This method is used in 7 out of 8 labs that perform Pu-analysis. For determination of Pu in large samples, anion exchange is either repeated (one lab then uses anion exchange from HCl media for complete separation from Th) and/or combined with solvent extraction with TBP, TIOA or TTA, prior or after anion exchange. Most labs have good Pu-recoveries using anion exchange. There apparently does not seem to be any difference in the results achieved by the use of either Dowex or the more expensive BIORAD resin. Two labs are also using small columns and still achieving good results. These features should be tested also by other labs. While most labs elute Pu with conc. HCl containing NH_4I, two labs use diluted HCl containing H_2O_2. Why is H_2O_2 added? Is uranium contamination a problem using dilute HCl? (uranium is also poorly retained from dilute HCl).

Solvent extraction: Liquid phase: 1.4 M HNO_3 added $NaNO_2$
Organic phase: 10% TIOA or 20% TBP in xylene
Pu elution: 1.2 M HCl containing 30% H_2O_2

Liquid phase: 1 M HNO_3
Organic phase: 0.5 M TTA (xylene or freon)
Pu elution: 8 M HNO_3

One lab has poor Pu-recoveries (less than 50%) when using TTA extraction. This is an effective and rapid procedure, especially when small samples are handled.

Extraction Chrom.: TRU-Resin (0.7 gram)
Column dimension: 8 mm diameter
Flow: 1-2 ml/min
Load: 2 – 3 M HNO_3 added $Al(NO_3)_3$, sulphamic and ascorbic acid
Wash: 2 M HNO_3 added $NaNO_2$
Wash: 0.5 M HNO_3 (one lab does this)
Wash: 9 M HCl
Am: 4 M HCl
Wash: 4 M HCl + 0.1 M HF (one lab does this)
Pu: 4 M HCl added $TiCl_3$ or 0.1 M ammonium oxalate

The resin is used in 4 of 6 labs that perform Pu-analysis and is also combined with either UTEVA or Sr-Resin for uranium and Sr determinations, respectively. Fe(III) causes serious reduction in Pu(IV) retention. It has to be reduced to Fe(II). There is no need to add additional iron to the sample in the form of ferrous sulphamate to reduce Fe(III) and Fe(II), sulphamic acid can do the job. One lab washes the resin with 4 M HCl – 0.1 M HF, prior to Pu elution. This step removes Th from the column before Pu is eluted. This rinse is probably not necessary when Pu is eluted with e.g. $TiCl_3$. When $TiCl_3$ is used to elute Pu, plutonium can not be electrodeposited due to the formation of colloidal TiO_2. Can other reducing agents be used? Hot solution of 4 M HCl containing NH_4I? Ammonium oxalate is also used to elute Pu from TRU-Resin. It must be kept in mind that this eluent also elutes uranium and thorium if they are present on the column.

Anion exchange procedure works satisfactorily in most labs. In case of emergency, the faster TTA extraction or one step anion exchange is to be recommended. TRU-Resin offers an advantage especially if subsequent Am determination is desired, as the Am fraction from TRU-Resin only will contain trivalent actinides and lanthanides.

12.2 Source preparation of plutonium

As for uranium.

12.3 Activity determination of plutonium

The alpha emitters are determined using either alpha spectrometry or ICP-MS. Beta emitting ^{241}Pu is determined in three different ways: If the source is made by micro co-precipitation, the membrane filter can be counted for ^{241}Pu using LSC, after alpha determination using alpha spectrometry. One lab simply divides the Pu fraction in two – one part is used for the determination of alpha emitters using alpha spectrometry and the other is counted for ^{241}Pu with LSC. The third method utilizes the ingrowth of the alpha emitting ^{241}Am. After a suitable ingrowth period, Am is separated from Pu and counted using alpha spectrometry.

13. Americium and curium determination

13.1 Americium and curium separation

Two different procedures are used for Am separation; anion exchange and extraction chromatography.

Anion exchange (after Pu-separation using anion exchange)

Oxalate precipitation (pH 1-1.5, 4), dry ashing (450-600 ^{o}C), followed by $Fe(OH)_3$ precip. and/or anion exchange and/or liquid liquid extraction (TIOA) to remove traces of interfering actinides before final separation. One lab purifies the Am fraction further using HDEHP-TBP extraction followed by mixed cation-anion exchange before final purification.

Final purification:

Resin: BIORAD AG-1x4 or Dowex 1x4
Column dimension: 1x12 cm, one lab uses 1x3 cm column
Flow: Approx. 1 ml/min
Load: 1 M HNO_3 – 86% (93%) CH_3OH
Wash: 1 M HNO_3 – 86% (93%) CH_3OH
Lanthanide removal: 0.1 M HCl - 80% (75%) CH_3OH - 0.5M (1M) NH_4SCN
Elute Am/Cm: 1.5 M HCl – 86%CH_3OH

This procedure is used by three labs. One lab uses a procedure that is considerably simpler than others, and still scores well in intercomparison exercises: Oxalate precipitation of the effluents from Pu-separation followed by anion exchange from 8M HNO_3 to remove traces of interfering elements before a final separation between actinides and lanthanides using anion exchange from thiocyanate media. One lab has tested this procedure and their results indicate that the simple procedure is suitable for samples not containing too large amount of interfering elements (lanthanides etc), but fails otherwise.

Extraction chromatography

If the sample does not contain interfering amounts of lanthanides, the Am fraction from TRU-Resin is pure enough for Am-determination. The interfering amount depends on following source preparation and activity determination procedure.

Three labs uses TRU-Resin followed by TEVA-Resin for the separation of Am and Cm from effluents from Pu-separation using anion exchange, or U-separation using UTEVA-Resin :

- Oxalate precipitation (pH 1.5)
- Ash at 600 ^oC
- 3M HNO_3 – 1M $Al(NO_3)_3$ – Fe-sulphamate – ascorbic acid
- TRU-Resin
    - Wash with 2 M HNO_3
    - Wash with 2 M HNO_3 – 0.1 M $NaNO_2$
    - Wash with 0.5 M HNO_3
    - Am and Cm elution with 4 M HCl
- Evaporate and dissolve in 2 M NH_2SCN – 0.1 M formic acid
- TEVA-Resin
    - Wash with 1 M NH_2SCN – 0.1 M formic acid
    - Am and Cm elution with 2 M HCl

One lab combines this procedure with UTEVA- and Sr-Resin for the sequential determination of Sr, U, Pu, Am and Cm in precipitation and filter samples. When TRU-Resin has been used for Pu separation, this resin offers a simple separation of actinides from lanthanides. The low Am-yields experienced by a couple of labs when using TRU- and TEVA-Resin for Am separation can be due to high concentration of lanthanides in the sample. In some publications it is stated that ^{243}Am cannot be used as a tracer for Cm, as Cm and Am behave differently on this resin [75, 76]. Tests are now being performed to check this.

Comparing the methods used twenty years ago [1] to those being used today results in two main conclusions:

- The number on laboratories carrying out Am analyses has increased considerably. In 1985 only three out of eleven laboratories reported Am analysis. Now in 2004 six laboratories out of seven have the capability to do analysis.

- In 1985 two laboratories used a long analysis procedure based on oxalate and ferric hydroxide precipitations, HDEHP extractions and ion exchange step. One lab used a procedure based on cation and anion exchange. Now three out of six laboratories use extraction chromatographic methods and one additional laboratory is developing methods based on extraction chromatography.

Four laboratories do the Am analysis after Pu separation by anion exchange. Thus the starting solution in Am analysis is 8M HNO_3. Laboratories 3 and 4 use extraction chromatography both in their Am and Pu analysis. Laboratory 2 is utilising extraction chromatography in Am analysis and laboratory 5 is developing extraction chromatography based Am analysis as well.

Laboratories 5 and 7 use classical methods in which there are first Ca oxalate and $Fe(OH)_3$ co-precipitation steps for the enrichment of Am and removal of interfering elements. Thereafter the main separation/purification steps are based on ion exchange and solvent extraction. In the solvent extraction step Laboratory 5 uses HDEHP to remove lanthanides and Th and Laboratory 7 uses TIOA/Xylene to remove Po, U and Fe. Laboratory 5 removes iron prior to solvent extraction by anion exchange. After solvent extraction an ion exchange step is in both Laboratories' procedure: Laboratory 5 uses mixed cation/anion resin bed to remove Th, Fe, Po and U and Laboratory 7 uses anion exchange to remove Th. At the end of the separation both Laboratories have an anion exchange step in methanol to remove lanthanides with ammonium thiocyanide. Am(Cm) is electrodeposited for the activity measurement with alpha spectrometry.

Compared to the Laboratories 5 and 7 the method reported by the Laboratory 1 is also based on classical methods but it much shorter: it consists only of Ca oxalate co-precipitation whereafter two anion exchange steps are used, the latter one being done in methanol medium to remove lanthanides with ammonium thiocyanide.

Laboratory 4 reports that they are using only extraction chromatographic methods and Eichrom standard procedures. They don't use ion exchange resins at all. This is also the case in Laboratory 3's Am separation. In their Am analysis they first enrich Am by $Fe(OH)_3$ and MnO_2 in case of sea water and with calcium oxalate in case of urine. Thereafter they separate both Pu and Am with TRU resin. They also report that this method is not capable of separating lanthanides from the Am fraction.

The method used in the Laboratory 2 is mainly based on extraction chromatography. After Pu separation by anion exchange iron is removed by Ca oxalate co-precipitation. Thereafter there are two extraction chromatography steps: first with TRU resin and then with TEVA-resin. The method being developed by the Laboratory 5 is based on the same procedure.

13.2 Source preparation of americium and curium

As for uranium.

13.3 Activity determination of americium and curium

As for Pu alpha emitters.

14. Rapid procedures

Americium: Addition of ^{243}Am followed by hydroxide, oxalate, fluoride etc. precipitation and activity determination using gamma spectrometry.

Pu-isotopes: TTA extraction of Pu from 1 M HNO_3 or 1 M HCl, elution with 8 M HNO_3. (small samples). Quick anion exchange.

Uranium: ICP-MS determination without separation using ^{233}U as tracer.

Sr-isotopes: LSC counting (Cerenkov and LSC). Combination of proportional counter and LSC.

Sequential analysis: Using combinations of separation schemes. One lab has a sequential procedure for the determination of Sr, U, Pu, Am and Cm in "low interference" samples.

Activity determination: LSC or ICP-MS

15. Quality assurance

Quality assurance has become increasingly important during the last twenty years. Quality management systems, permanent QA procedures and total uncertainty calculations have become more necessary. One lab is accredited and all labs have their own in-house quality management procedures. Good quality is ensured by: quality assurance protocol, intercomparison exercises, analysis of reference materials, cross check using independent procedure, blank determination, labs to handle different activity levels, detector calibration and background determination, uncertainty determination (counting and tracer activity), internal auditing etc.

16. Comments

Most labs are satisfied with the procedures they use.

- Developing individual matrix-dependant separation procedures can speed up the analytical methods, but this requires a more stringent supervision.

- Smaller ion exchange columns and reduced “washing and elution volumes” for the separation of actinides can be used to speed up the analysis without negative effects.
- Do not throw away Pu-sources as they can be used to get valuable information on ^{241}Pu content.
- Problems with low Am-yields and poor Am-separation when using TRU- and TEVA-Resin.
- HCl-$TiCl_3$ elution of Pu from TRU-Resin eliminates Po-interference caused when Pu is eluted with ammonium oxalate.
- Not always necessary to separate trivalent actinides from lanthanides.
- One lab has occasional problem with poor separation of Pu from uranium when using TIOA extraction and anion exchange (2x) for Pu-separation (drainage water).
- Low Pu-recoveries when using TTA extraction.
- Several labs are working with the development of sequential procedures.
- Occasional high background when Sr-Resin is used for Sr separation (effluent water).
- Observe ^{228}Ac in the ^{90}Y fraction.
- Low yields when using the “fuming nitric acid” procedure for the determination of ^{90}Sr in seawater and seaweed.
- Indirect determination of ^{90}Sr in seawater using ^{90}Y separation and determination should be tested.
- Avoid the use of fuming nitric acid.

17. Conclusion

The detailed information provided by the labs on their practise regarding the specified analysis, is very valuable. The benefits are obvious as radiochemical analysis now can be studied and compared in detail. It is now 20 years ago such a study was last undertaken in the Nordic countries. Although, most of the techniques in use are still the same, some deviations can be seen: Besides Pu separation using anion ex. chrom., there is not a single procedure that is used in all labs. More labs are doing americium determination. Due to the commercial availability of extraction chromatographic resins, more labs are now using this technique. A comparison of the results provided by different labs in the NKS-B LABINCO excersise, will also provide a direct comparison of the different procedures in use.

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Questionnaire response from Lab 1

Radionuclide: ^{235}U, ^{234}U, ^{238}U
Matrix: Air, Water, soil, sediment, biota, reactor fuel, nuclear waste
Sampling. Air. Air filtration microsorban filter, *Water*: Pumping or large volume sampler. *Sediment*: Kayak corer-slicing in ½-1 cm. *Grass, moss, lichen* from a 1/4 m^2 frame, *Macroalgae*-random sampling about 1 kg. *Soil:* corer and slicing
Pre-treatment and enrichment: *Water*: adding of tracer, acidification PH = 2, reducing with $Na_2S_2O_5$, precipitation with NaOH, dissolve with HCl, reprecipitate with NH_3, *Sediment*: removal of stones, drying at 60 ^oC, ashing at 550 ^oC, *Biota*, direct drying or preservation with $Na_2S_2O_5$, grinding, ashing at 550 ^oC, *Soil:* as for sediment, tracer added before ashing for soil, sediment and biota.
Dissolution/Leaching. *Water precipitate*: dissolved in 8M HNO_3. *Soil, sediment and biota:* leaching with *aqua regia*. In some cases H_2O_2 is added. The sample is dissolved in HCL and hydroxides precipitated with ammonia at pH 9-10. The precipitate is centrifuged and dried at 80 ^oC.
Separation: *Amount:* 10-50 g dry weight. Dissolve in 20-100 ml 8 M HNO_3. Add 10 ml TBP and shake for 2 minutes. Discard the aqueous phase. Wash with 2x10 ml of 8 M NO_3. Discard the aqueous layer. Add 20 ml Xylol + 15 ml 1.5 m HCL. Wash with 2x 15 ml 1.5 M HCL (The HCL phase contains Th). Backextract U with 2x 15 ml water. Evaporate and continue with electrolysis.
Source preparation: Electro deposition onto stainless polished steel discs. Φ= 20 mm. Solution: 2 M $(NH_4)_2SO_4$, 8ml, 1 A, 2 h, pH = 2. Platinum anode, distance cathode-anode 5 mm.
Rapid procedure.
Quality assurance. Participation in IAEA intercalibration exercises and also EML exercises. Using previous IAEA intecalibration sample for continuous check. Trying to avoid cross contamination by not analyzing very different levels at the same time. Special lab. utensils for hot samples. At present one time use of resins and columns. Blank not done as often as I wish. Uncertainty. Propagated error in counting statistics of a quota Total error is the sum of the square roots of this counting statistics error in square + the square of a 5 % systematic error. MDA well I would say 100 uBq for a 10^6 s counting time. General formula does not work very well with the very low background on alfa detectors.
Comments: We are quite satisfied. Methods could be speeded up by having more individual treatment for different matrixes-but then it must be supervised not only by technicians. I also see that acid volumes can be reduced. We are using smaller and smaller columns and have not reduced the other volumes (washing and elution) in proportion. This would also speed up the procedure.

Radionuclide: ^{238}Pu and $^{239+240}Pu$
Matrix: Air, Water, soil, sediment, biota, reactor fuel, nuclear waste
Sampling. Air. Air filtration microsorban filter, *Water*: Pumping or large volume sampler. *Sediment*: Kayak corer-slicing in ½-1 cm. *Grass, moss, lichen* from a 1/4 m^2 frame, *Macroalgae*-random sampling about 1 kg. *Soil:* corer and slicing
Pre-treatment and enrichment: *Water*: adding of tracer, acidification PH = 2, reducing with $Na_2S_2O_5$, precipitation with NaOH, dissolve with HCl, reprecipitate with NH_3, *Sediment*: removal of stones, drying at 60 ^oC, ashing at 550 ^oC, *Biota*, direct drying or preservation with $Na_2S_2O_5$, grinding, ashing at 550 ^oC, *Soil:* as for sediment, tracer added before ashing for soil, sediment and biota.
Dissolution/Leaching. *Water precipitate*: dissolved in 8M HNO_3. *Soil, sediment and biota:* leaching with *aqua regia*. In some cases H_2O_2 is added. The sample is dissolved in HCL and hydroxides precipitated with ammonia at pH 9-10. The precipitate is centrifuged and dried at 80 ^oC.
Separation: *Amount:* 10-50 g dry weight. Dissolved in 20-100 ml 8 M HNO_3 + small amount of Na NO_2. *Ion exchange*, BIORAD AG-1x4, 100-200 mesh. Column dimension 10 x 30 mm. Regenerate with 20 ml 8 M HNO_3. Sample load 1 ml min^{-1}. Wash with 20 ml 8 M HNO_3. Elute Th with 40 ml 9M HCl all 1 ml min^{-1}. Elute Pu with fresh =.1 M NH_4I-9 M HCl. Add small amount of HNO_3 and evaporate to almost dryness. If large samples and large amounts of Fe. Start the procedure by extracting Pu in 8M HNO_3 with TBP (10 ml). Wash with 20 ml 8M HNO_3. Add 30 ml xylene. Extract Th with 1.5 M HCl 2x30 ml). Back extract Pu with 9M HCl-0.1M NH_4I. (2x30 ml). If high purification from U is necessary end the procedure by extracting Pu from 1M HNO_3+ small amount of $NaNO_2$ into 5 ml 5% TTA dissolved in xylene. Wash with 10 ml 1M HNO_3. Back extract Pu with 2x 10 ml 8 M HNO_3.
Source preparation: Electro deposition onto stainless polished steel discs. Φ= 20 mm. Solution: 2 M $(NH_4)_2SO_4$, 8ml, 1 A, 2 h, pH = 2. Platinum anode, distance cathode-anode 5 mm.
Rapid procedure. The TTA extraction works alone on small samples which can be dissolved in 1 M HNO_3 or HCL
Quality assurance. Participation in IAEA intercalibration exercises and also EML exercises. Using previous IAEA intecalibration sample for continuous check. Trying to avoid cross contamination by not analyzing very different levels at the same time. Special lab. utensils for hot samples. At present one time use of resins and columns. Blank not done as often as I wish. Uncertainty. Propagated error in counting statistics of a quota Total error is the sum of the square roots of this counting statistics error in square + the square of a 5 % systematic error. MDA well I would say 100 μBq for a 10^6 s counting time. General formula does not work very well with the very low background on alfa detectors.
Comments: We are quite satisfied. Methods could be speeded up by having more individual treatment for different matrixes-but then it must be supervised not only by technicians. I also see that acid volumes can be reduced. We are using smaller and smaller columns and have not reduced the other volumes (washing and elution) in proportion. This would also speed up the procedure.

Radionuclide: ^{241}Pu
Matrix: Air, Water, soil, sediment, biota, reactor fuel, nuclear waste
Sampling. Air. Air filtration microsorban filter, *Water*: Pumping or large volume sampler. *Sediment*: Kayak corer-slicing in ½-1 cm. *Grass, moss, lichen* from a 1/4 m^2 frame, *Macroalgae*-random sampling about 1 kg. *Soil:* corer and slicing
Pre-treatment and enrichment: Our method is based on build up of ^{241}Am from stored Pu-discs or solutions.
Dissolution/Leaching. The stored discs are leached in conc. HNO_3 + 1-2 drops of HCL on the disc. ^{243}Am is added as yield determinant.The disc is picked up-washed and the sample is evaporated to dryness.
Separation: The sample is dissolved in 1M HNO_3-93% CH_3OH. Americium is sorbed on an anion-exchange column (see procedure for Am, Cm). The column is washed with 30 ml of the feed solution. The effluents and washings containing Fe and Ni are discarded. ^{241}Am is eluted with 30 ml of 9 M HCl. Pu can be recovered from the column. Several discs from same specie/area etc. can be pooled. On basis of the rate of build-up of ^{241}Am the concentration of ^{241}Pu can be calculated.
Source preparation: Electro deposition onto stainless polished steel discs. Φ= 20 mm. Solution: 2 M $(NH_4)_2SO_4$, 8ml, 1 A, 2 h, pH = 2. Platinum anode, distance cathode-anode 5 mm.
Rapid procedure. This is not a rapid procedure but once when you have waited for build-up it is a rapid separation method.
Quality assurance. There have been very few if any intercalibration exercises for ^{241}Pu. Participation in IAEA intercalibration exercises and also EML exercises. Using previous IAEA intecalibration sample for continuous check. Trying to avoid cross contamination by not analyzing very different levels at the same time. Special lab. utensils for hot samples. At present one time use of resins and columns. Blank not done as often as I wish. Uncertainty. Propagated error in counting statistics of a quota. Total error is the sum of the square roots of this counting statistics error in square + the square of a 5 % systematic error. MDA depend on time for build up and the ^{241}Pu concentration.
Comments: Keep your old Pu.discs!

Radionuclide: ^{241}Am, ^{242}Cm, $^{243+244}Cm$
Matrix: Air, Water, soil, sediment, biota, reactor fuel, nuclear waste
Sampling. *Air.* Air filtration microsorban filter, *Water*: Pumping or large volume sampler. *Sediment*: Kayak corer-slicing in ½-1 cm. *Grass, moss, lichen* from a 1/4 m^2 frame, *Macroalgae*-random sampling about 1 kg. *Soil:* corer and slicing
Pre-treatment and enrichment: *Water*: adding of tracer, acidification PH = 2, reducing with $Na_2S_2O_5$, precipitation with NaOH, dissolve with HCl, reprecipitate with NH_3, *Sediment*: removal of stones, drying at 60 ^oC, ashing at 550 ^oC, *Biota*, direct drying or preservation with $Na_2S_2O_5$, grinding, ashing at 550 ^oC, *Soil:* as for sediment, tracer added before ashing for soil, sediment and biota.
Dissolution/Leaching. *Water precipitate*: dissolved in 8M HNO_3. *Soil, sediment and biota:* leaching with *aqua regia*. In some cases H_2O_2 is added. Hydroxides are precipitated with NH_3 at pH 9-10. The precipitate is centrifuged and dried at 80 ^oC.
Separation: This separation is generally done in sequence with Pu separation. The HNO_3 eflluent and washings from the Pu separation are evaporated to dryness. The sample is dissolved in HCl and diluted to 300 ml with water. 200 mg $CaCl_2$ + 20 g oxalic acid are added and the sample heated. Oxalates are precipitated at pH 4 with NH_3. The calcium oxalate is collected on a filter and incinerated at 550 ^oC. To ensure separation from interfering element the sample is dissolved in 8M HNO_3 and a small amount of anion exchange resin is added. The sample is then passed through an anion exchange resin. Effluent and washings are collected and evaporated. The sample is then dissolved in 1M HNO_3-86% CH_3OH. Anion exchange is performed on an identical column as for plutonium but generated with 20 ml The sample is loaded with about 1 ml min^{-1}. The column is washed with 30 ml of the feed solution. Lanthanides are removed by 25 ml of 0.1 M HCL-80% CH_3OH-0.5 M NH_4SCN. Am and Cm are eluted with 40 ml of 1.5 M HCL-86% CH_3OH. The sample is evaporated and thiocyanates destroyed by HNO_3. If Cm-isotopes are of interest, ^{227}Th daughter product of ^{227}Ac in the ^{235}U series might interfere in the spectra-especially if the samples are not counted immediately. Ac is absorbed on a cation exchage resin, Dowex AG 50x8 from 3 M HNO_3 solution. From a column 1x 3 cm Cm (and Am) are in the first 25 ml of effluent and washings and Ac remains on the column.
Source preparation: Electro deposition onto stainless polished steel discs. Φ= 20 mm. Solution: 2 M $(NH_4)_2SO_4$, 8ml, 1 A, 2 h, pH = 2. Platinum anode, distance cathode-anode 5 mm.
Rapid procedure. If levels are high enough a hydroxide precipitation is performed followed by oxalate and/or fluoride precipitation. ^{241}Am can then be measured by gamma spectrometry. ^{243}Am is also a gamma emitter and can be used as yield determinant.
Quality assurance. Participation in IAEA intercalibration exercises and also EML exercises. Using previous IAEA intecalibration sample for continuous check. Trying to avoid cross contamination by not analyzing very different levels at the same time. Special lab. utensils for hot samples. At present one time use of resins and columns. Blank not done as often as I wish. Uncertainty. Propagated error in counting statistics of a quota Total error is the sum of the square roots of this counting statistics error in square + the square of a 5 % systematic error. MDA well I would say 100 uBq for a 10^6 s counting time. General formula does not work very well with the very low background on alfa detectors.
Comments: We are quite satisfied. Methods could be speeded up by having more individual treatment for different matrixes-but then it must be supervised not only by technicians. For example the amount of lanthanides are quite different in different matrixes and different washing volumes are required. I also see that acid volumes can be reduced. We are using smaller and smaller columns and have not reduced the other volumes (washing and elution) in proportion. This would also speed up the procedure.

Questionnaire response from Lab 2

RADCHEM Project: Routine and emergency practice regarding radiochemical analysis

Contribution from: University of Helsinki
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The Laboratory of Radiochemistry at the University of Helsinki is a teaching and research organisation and therefore most analyses are performed as part of different research projects. Method development is an important part of the work done in the laboratory. No routine surveillance is carried out and therefore no rapid procedures have been developed.

The Laboratory of Radiochemistry has no formal quality assurance system. The importance of high quality and continuous improvement has been recognized and action has been taken to introduce quality assurance and quality control procedures in the laboratory. These include the analysis of the present situation, documentation and implementation of quality assurance protocols and improvement of good laboratory practices. Reference materials are presently used occasionally. Relevant intercomparison exercises or proficiency tests have not been available lately.

The laboratory has dedicated areas for handling different activity levels in the samples. Environmental samples are handled in the low level laboratory. Extraction chromatography and ion exchange resins are not reused to avoid cross contamination of samples.

A method for the determination of combined uncertainties for all procedures is not well implemented. MDA is determined using the formula published by L. Currie in 1968.[1]

The methods included in this survey have been limited to those that were not published in the NKA report 'The Sampling and Analysing Methods of Radionuclides used in the Nordic Countries for Environmental Samples' from 1985.

[1] Currie, L. A. Anal. Chem., Vol. 40, No. 3 (1968), 586 – 593

^{234}U AND ^{238}U IN NATURAL WATERS

Radionuclides

^{234}U and ^{238}U

Matrix

Natural waters

Sampling

Pumps are used to collect and filter the water samples.

Pre-treatment and enrichment

The water sample is filtered through a 0.45 µm membrane filter. The sample is acidified with HCl (5 ml of 37% HCl/1 L). An aliquot (100 – 1000 ml) is taken for the analysis.

Uranium-232 tracer is added to the aliquot and the sample is let to equilibrate for a minimum time of 30 min. Uranium is coprecipitated with NdF_3 as follows:

> Nd-carrier is added (100 mg of Nd/1 L). U is reduced to U(IV) with 0.5-1 ml of 15% $TiCl_3$ in HCl. 40% HF is added to precipitate NdF_3. The sample is filtered though a 0.45 µm membrane filter.

For samples with high Ca concentration $Fe(OH)_3$ coprecipitation is carried out instead of the NdF_3 coprecipitation:

> 10 mg Fe is added and $Fe(OH)_3$ is precipitated with 25% NH_3 at pH 7. The sample is filtered though a 0.45 µm membrane filter.

Dissolution/Leaching

The precipitate and the filter are digested by boiling in a mixture of 16 M HNO_3 and 12 M HCl. The sample is then dissolved in 10-20 ml of 12 M HCl.

Separation

The purification of U is done by anion exchange (Dowex 1x4, 50-100 mesh) as follows:

> The resin is treated with 30 ml of 12 M HCl before loading the sample. Th is removed by washing the column with 40 ml of 12 M HCl and U is eluted with 40 ml of 0.1 M HCl.

The sample is evaporated to dryness before the source preparation.

If $Fe(OH)_3$ coprecipitation is used or if the sample contains high concentrations of Fe, the Fe is removed using anion exchange (Dowex 1x4, 50-100 mesh) as follows:

> The resin is treated with 20 ml 16 M HNO_3 and 30 ml of 8 M HNO_3. Sample is loaded in 5 ml of 8 M HNO_3, the column is washed with 5 ml of 8 M HNO_3 and U is eluted with 25 ml of 0.1 M HCl.

The sample is evaporated to dryness before the source preparation.

Source preparation

The alpha source is prepared using CeF_3 coprecipitation method:

The sample is dissolved in 4 ml of 1 M HCl. Then 0.5 ml of Ce-carrier (100 µg of Ce/ml of 1 M HCl) and 2-4 drops of 15% $TiCl_3$ solution in HCl are added. CeF_3 is precipitated with 0.6 ml of 40% HF. The precipitation is let to settle for a minimum time of 30 min.

The sample is filtered through a 0.1 µm membrane filter. The filter is treated with 10 ml of Ce-substrate solution (4.3 mg $CeCl_3$ + 454 ml 1 M HCl + 48 ml 40 % HF) before the filtration.

Activity determination

The activity is determined using alpha spectrometry. PIPS detectors with 450 mm^2 surface area are used. The chemical yield is determined from the tracer activity. Recoveries are typically above 80%.

Quality assurance

Blank analyses are carried out with each batch of samples to check for possible cross contamination. Alpha spectrometers are calibrated regularly.

Two parallel aliquots are analysed for each sample and the weighted mean is reported.

Comments

The same method is used to analyse ^{234}U and ^{238}U concentrations in the particulate fraction (particle size > 0.45 µm). The particulates and the filter are digested by boiling in a mixture of 16 M HNO_3 and 12 M HCl before the first coprecipitation step.

^{234}U AND ^{238}U IN ROCKS AND SEDIMENTS

Radionuclides

^{234}U and ^{238}U

Matrix

Rocks and sediments

Sampling

Drill and sediment corers

Pre-treatment and enrichment

The samples are dried, ground and homogenized.

Dissolution/Leaching

Complete dissolution of mineral matrices (mainly silicates) is achieved with HNO_3, HCl and HF. Partial dissolution for speciation studies is carried out using dilute mineral acids, mixtures of organic acids and chelates. Sample sizes vary from 10 mg to several grams.

After dissolution the sample is dissolved in 30 ml of 9 M HCl and ^{232}U tracer is added to the sample.

Separation

The purification of U is done by anion exchange (Dowex 1x4, 50-100 mesh) as follows:

> The resin is treated with 50 ml of 9 M HCl before loading the sample. U (and Po) is strongly adsorbed whereas Th and Ra run through the column. The column is washed with 30 ml of 9 M HCl and uranium is eluted with 30 ml of 0.1 M HCl Po being still adsorbed. The eluate is evaporated to dryness and dissolved into 1M HCl.

Source preparation

The alpha source is prepared using CeF_3 coprecipitation method:

> The sample is dissolved in 4 ml of 1 M HCl. Then 0.5 ml of Ce-carrier (100 µg of Ce/ml of 1 M HCl) and 2-4 drops of 15% $TiCl_3$ solution in HCl are added. CeF_3 is precipitated with 0.6 ml of 40% HF. The precipitation is let to settle for a minimum time of 30 min.

The sample is filtered through a 0.1 µm membrane filter. The filter is treated with 10 ml of Ce-substrate solution (4.3 mg $CeCl_3$ + 454 ml 1 M HCl + 48 ml 40 % HF) before the filtration.

Activity determination

The activity is determined using alpha spectrometry. PIPS detectors with 450 mm^2 surface area are used. The chemical yield is determined from the tracer activity. Recoveries are typically above 80%.

Quality assurance

Background checks are performed every two months, longer background measurements are done once or twice a year. Blank analysed are carried out once a month.

Pu, Am AND Cm IN ENVIRONMENTAL SAMPLES

Radionuclides

^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm and ^{244}Cm

Matrix

Soil, vegetation, peat

Sampling

Soil profiles are taken using a corer (inner diameter 10.4 cm, length of 22 cm). Soil is divided into five horizons: litter, organic, and three mineral layers. Vegetation is collected by cutting them above ground level. For peat analyses a surface layer of 3-5 cm was collected from a 0.5 m^2 area.

Pre-treatment and enrichment

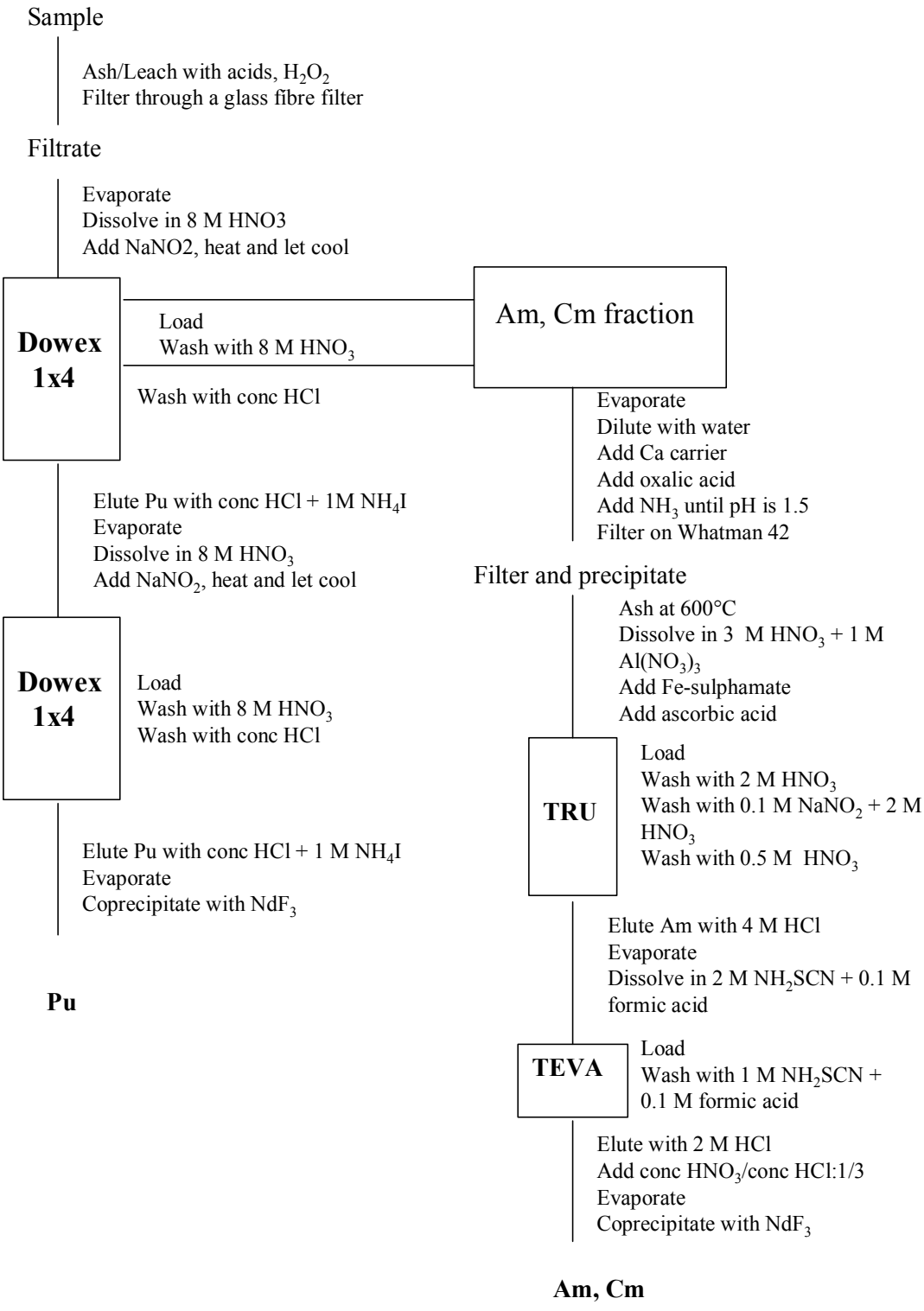
Samples are dried at 105 °C and then ashed in 400 – 600°C.The dried soil is sieved with a mesh size of 2 mm. All samples are homogenised. ^{242}Pu and ^{243}Am tracers are added before the digestion procedure. The sample sizes analysed for dried soil, vegetation and peat are 15-40 g, 15-100 g and 100 g, respectively.

Dissolution/Leaching

The samples are wet-ashed with 16 M HNO_3 and 12 M HCl. Total dissolution is not used. The residue is filtered through a glass fiber filter and the filter is discarded. The solution is evaporated to dryness and dissolved in 8 M HNO_3.

Separation

The oxidation state of Pu is adjusted to Pu(IV) by adding $NaNO_2$. The separation scheme for the determination of Pu and Am/Cm activities is shown in the figure below. Pu is separated using anion exchange (Dowex 1x4, 50−100 mesh). TRU Resin and TEVA Resin obtained from Eichrom Industries are used for the purification of the Am/Cm-fraction. The particle size of both resins is 100−150 μm.


Sample
Ash/Leach with acids, H_2O_2
Filter through a glass fibre filter
Filtrate
Evaporate
Dissolve in 8 M HNO3
Add NaNO2, heat and let cool
Dowex 1x4
Load
Wash with 8 M HNO_3
Wash with conc HCl
Am, Cm fraction
Evaporate
Dilute with water
Add Ca carrier
Add oxalic acid
Add NH_3 until pH is 1.5
Filter on Whatman 42
Filter and precipitate
Elute Pu with conc HCl + 1M NH_4I
Evaporate
Dissolve in 8 M HNO_3
Add $NaNO_2$, heat and let cool
Dowex 1x4
Load
Wash with 8 M HNO_3
Wash with conc HCl
Elute Pu with conc HCl + 1 M NH_4I
Evaporate
Coprecipitate with NdF_3
Pu
Ash at 600°C
Dissolve in 3 M HNO_3 + 1 M $Al(NO_3)_3$
Add Fe-sulphamate
Add ascorbic acid
TRU
Load
Wash with 2 M HNO_3
Wash with 0.1 M $NaNO_2$ + 2 M HNO_3
Wash with 0.5 M HNO_3
Elute Am with 4 M HCl
Evaporate
Dissolve in 2 M NH_2SCN + 0.1 M formic acid
TEVA
Load
Wash with 1 M NH_2SCN + 0.1 M formic acid
Elute with 2 M HCl
Add conc HNO_3/conc HCl:1/3
Evaporate
Coprecipitate with NdF_3
Am, Cm

Source preparation

The alpha sources are prepared using NdF_3 coprecipitation method:

> The sample is dissolved in 4 ml of 1 M HNO_3. Then 0.5 ml of Nd-carrier (100 µg of Nd/ml of 1 M HNO_3). NdF_3 is precipitated with 0.6 ml of 40% HF. The precipitation is let to settle for a minimum time of 30 min.

The sample is filtered through a 0.1 µm membrane filter. The filter is treated with 10 ml of Nd-substrate solution (3.9 mg Nd_2O_3 + 454 ml 1 M HNO_3 + 48 ml 40 % HF) before the filtration.

Activity determination

The activity is determined using alpha spectrometry. PIPS detectors with 450 mm^2 surface area are used. The chemical yield is determined from the tracer activity. ^{243}Am tracer is used for both americium and curium. Pu recoveries have typically been above 80%.

Quality assurance

Blank analyses are performed regularly. Background measurements are done every three months and background checks approximately once a month.

Comments

The recoveries for Am and Cm have been variable. Some spectra have also indicated that the purification for Am/Cm has not been complete and that the samples contain impurities. Further studies are needed to investigate these problems in detail.

Pu and U IN AIR FILTERS AND SWIPES

Radionuclides

^{238}Pu, $^{239, 240}Pu$, ^{241}Pu, ^{235}U, ^{238}U

Matrix

Organic air filters, organic swipes

Sampling

Samples were received from the IAEA with no information on the sampling.

Pre-treatment and enrichment

The samples were ashed in 400 °C over night.

Dissolution/Leaching

^{242}Pu and ^{236}U tracers were added to the sample before leaching. The samples were leached with 16 M HNO_3 for 6 hours.

Separation

After leaching the filtered and evaporated sample is dissolved in 10 ml of 3 M HNO_3 + 1 M $Al(NO_3)_3$. 2 ml of 0.6 M ferrous sulphamate and 200 mg of ascorbic acid are added. 2 ml of resin is loaded into a polypropylene column (8 mm x 40 mm). The UTEVA Resin column is preconditioned with 5 ml of 3 M HNO_3 and the TRU Resin column with 5 ml of 2 M HNO_3. Sample solution is loaded into a UTEVA Resin column and the eluate and 2 x 5 ml of 3 M HNO_3 of the washing solution are collected for Pu separation. The column is further washed with 4 ml of 9 M HCl and 20 ml of 5 M HCl+0.05 M oxalic acid. Uranium is eluted with 15 ml of 0.01 M HCl.

Pu solution is loaded into a TRU Resin column and the beaker is washed with 5 ml of 2 M HNO_3 and 5 ml of 2 M HNO_3 + 0.1 M $NaNO_2$. The column is washed with 5 ml of 0.5 M HNO_3, 3 ml of 9 M HCl, 20 ml of 4 M HCl and 25 ml of 4 M HCl + 0.1 M HF. Pu is eluted with 10 ml of 4 M HCl + 0.02 M $TiCl_3$.

Source preparation

The alpha sources are prepared using NdF_3 coprecipitation method:

> The sample is dissolved in 4 ml of 1 M HNO_3. Then 0.5 ml of Nd-carrier (100 µg of Nd/ml of 1 M HNO_3). NdF_3 is precipitated with 0.6 ml of 40% HF. The precipitation is let to settle of a minimum time of 30 min.

The sample is filtered through a 0.1 µm membrane filter. The filter is treated with 10 ml of Nd-substrate solution (3.9 mg Nd_2O_3 + 454 ml 1 M HNO_3 + 48 ml 40 % HF) before the filtration.

Activity determination

The activity is determined using alpha spectrometry. PIPS detectors with 450 mm^2 surface area are used. The chemical yield is determined from the tracer activity.

After the alpha measurement the membrane filters are wetted with 0.6 M $H_3(BO_3)_4$, liquid scintillation cocktail is added and samples are measured with Quantulus 1220 low level liquid scintillation counter for the determination of ^{241}Pu. The chemical yield is determined by recovery of ^{242}Pu tracer. Pu recoveries vary from 40% to 100%, median value is 74%. U recoveries are between 46% and 100% with the median value of 78%.

The concentrations of the uranium isotopes are determined by ICP-MS at the Technical Research Centre of Finland.

Quality assurance

Energy calibrations are performed regularly. Background measurements are done 3-4 times a year. Background checks are carried out approximately once a month. Blank analyses are performed after each set of samples.

Comments

When Pu was eluted from the TRU Resin column with $NH_4HC_2O_4$ solution, ^{210}Po was present as an impurity in many samples. After changing the elution solution to 4 M HCl + 0.02 M $TiCl_3$ no Po was detected.

Questionnaire response from Lab 3

Radionuclide: Sr-90

Matrix: Soil, sediment, precipitation, fresh water, seawater, biological samples, effluent water, filters, milk

Sampling: Most of the samples are gathered in connection with our main work, recipient control around the institute. Low-level liquid radioactive effluents (1 litre gathered prior to discharge). Water (filtered through 0.45 µm as quickly as possible), fish, water plants, sediment (core) etc are collected in the Nitelva River that receives the discharges from the institute. In addition: Soil (grab or core), precipitation (collection in appropriate jars and removal of foreign objects by filtration), grass (all grass within 0.25 m^2 area down to ground), agriculture products (gathered at nearby farms) are collected both within the institute and the surrounding area. In addition samples are appropriately gathered in connection with ongoing research activities.

Pre-treatment and pre-concentration

Soil, sediment and biological samples: Drying (105 ^oC), sieving and ashing (450 ^oC). Tracer (Sr-85) added after ashing.
Milk: Sr-carrier and tracer (Sr-85) are added before drying (125 ^oC) and ashing (500 ^oC)
Water: filtration, acidification, addition of tracer (Sr-85) and Sr-carrier before preconcentration either by evaporation or carbonate precipitation (sea water).
Urine: acidification, heating and phosphate precipitation (in combination with Pu and Am analysis)

Dissolution/Leaching

Soil, sediment, biological samples and filters: leaching with concentrated HCl and HNO_3. Sr in the leached solution is co-precipitated with ca-oxalate when Sr-Resin is used for Sr-separation.
Milk: Dissolution of ash with 14 M HNO_3
Urine: Phosphate destruction using dry/wet ashing (HNO_3/H_2O_2)
Tracer is always added before dissolution/leaching

Separation (The traditional separation schemes are adopted from HASL)

Soil (up to 50 g dry/ash), sediment (up to 50 g dry/ash), seawater (50 L), biological samples (up to 10 g ash) and precipitation: Separation from Ca and other elements by nitrate precipitation from fuming nitric acid, hydroxide precipitation to get rid of insoluble hydroxides, chromate precipitations to remove Ba, Ra and Pb and carbonate precipitations. Occasionally Sr-Resin separation is used.
Milk (1 L): TBP-extraction of Y from conc. HNO_3 and elution with H_2O.
Urine and effluent water: Sr-Resin separation done in connection with Pu and Am analysis using TRU-Resin coupled on top of Sr-Resin. Sr-Resin separation: 2 ml prepacked (100 – 150 µm) columns. Precondition: 3 M HNO_3. Load: 3 M HNO_3 – sulfamic acid – ascorbic acid – $Al(NO_3)_3$. Flow 1-2 ml/min. Wash 1: 10 ml 3 M HNO_3. Wash 2: 10 ml 8 M HNO_3. Wash 3: 5 ml 3 M HNO_3 – 0.05 M oxalic acid. Sr elution: 10 ml 0.05 M HNO_3.
After separation, 10 mg Y is added and the solution is set aside for Y-90 ingrowth.

Source preparation

After ingrowth of Y-90, Y is precipitated as oxalate, and collected on ash less paper filter (blue ribbon).

Activity determination

Measurement of beta activity (Y-90) using GM counter
Determination of chemical yields: Sr: Gamma analysis (NaI) of added Sr-85 against a Sr-85 standard solution. Y: EDTA titration (0,01 M EDTA) against a standard.

Quality assurance

Every step in each of the procedures used (sampling to result validation) is defined in our internal quality assurance protocol. The methods are regularly controlled by participation in intercomparison exercises and proficiency tests. Reference materials are occasionally used to control performance for routine analysis using established methods. New methods are checked against established and well-controlled procedures and/or reference materials.
Contamination, control and measures: Three different levels of laboratories to handle different levels of analyte concentration. Written guidelines on permitted activity levels that can be handled in each laboratory have just recently been established. So far guidelines for which laboratory to choose have concerned the origin/history of the sample rather than activity levels. Screening with handheld instruments is recommended. Written guidelines for storing (covered or in closed container) and handling (preferable in a fume hood) of samples, cleaning of equipment (equipment that has been in contact with the sample is cleaned with decontaminants (eg RBS))
Blank values are kept track of by analysing blank samples (distilled water) every two months. If the blank value suddenly increases significantly, decision is made on how to handle the situation (reject the last sample results, decontaminate the lab and perform the analysis once again after the blank value is under control etc). Blank values are usually not subtracted.
Measurement uncertainties includes counting uncertainties, uncertainty in detector efficiency, tracer activity uncertainties (given by supplier), uncertainties in volume/mass determination (sample, tracer, EDTA)
MDA is calculated according to Currie.

Comments

We occasionally have problems with high background in the Y-90 fraction. Especially when effluent water is analysed using Sr-Resin. When low activity samples are analysed, we observe traces of Ac-228 in the Y-90 fraction. We often have low Sr-yields when analysing seaweed and seawater. We would like to simplify the determination of Sr-90 in seawater, a task that probably can be accomplished via the indirect determination of Sr-90 through Y-90 analysis. We want to find alternatives so that we don't have to use fuming HNO_3, and we have ongoing work to validate the use of Sr-resin for different sample types. We also have ongoing work to simplify the treatment of solid samples using open focused microwave oven. Attempts are also made to simplify the separation procedures with the use of extraction chromatographic resins, with an aim of developing sequential analysis of several radionuclides in the same sample.

Radionuclide: U

Matrix: Sediment, soil, drainage water (only sediments are analysed on a regularly basis)

Sampling: Sediments are regularly gathered in connection with our main work, recipient control around the institute.

Pre-treatment and pre-concentration

Sediments: Samples are dried (105 ^{o}C) and sieved (2 mm).

Dissolution/Leaching

Sediments (10 gram dry): Leaching with HNO_3

Separation

N.A.

Source preparation

Fusion with NaF

Activity determination

Fluorescence analysis (Jarwell Ash instrument). Samples are analysed together with standards and blanks. Background (blank result) is subtracted. Results are determined by comparing with standard curves drawn from measurement of the standards.

Quality assurance

The procedure is defined in our internal quality assurance protocol.
At least two parallels of each sample are analysed
The method will be compared with mass spectrometry analyses.
We have not participated in intercomparison or proficiency tests with this method.
Uncertainties include uncertainty in standard concentration, accuracy of current reading (samples, standards and blanks), uncertainty in volume of samples and standards (pipetting) and curve fitting. Measurement uncertainties are currently not being reported in connection with recipient control.
MDA: 0.1 – 1 μg/g

Comments

Because quite few samples are analysed each year, and the instrument is rather old, we might send the samples away for mass spectrometric analyses in the future.

Radionuclide: Pu

Matrix: Soil, sediment, precipitation, fresh water, seawater, biological samples, effluent water, filters

Sampling: Most of the samples are gathered in connection with our main work, recipient control around the institute. Low-level liquid radioactive effluents (1 litre gathered prior to discharge). Water (filtered through 0.45 μm as quickly as possible), fish, water plants, sediment (core) etc are collected in the Nitelva River that receives the discharges from the institute. In addition: Soil (grab or core), precipitation (collection in appropriate jars and removal of foreign objects by filtration), grass (all grass within 0.25 m^2 area down to ground), agriculture products (gathered at nearby farms) are collected both within the institute and the surrounding area. In addition samples are appropriately gathered in connection with ongoing research activities.

Pre-treatment and pre-concentration

Soil, sediment and biological samples: Drying (105 ^oC), sieving and ashing (450 ^oC)
Water: filtration, acidification and preconcentration by either evaporation or $Fe(OH)_3$ / MnO_2 co-precipitation.
Urine: acidification, addition of ^{242}Pu, heating and phosphate precipitation (in combination with Am and Sr analysis)

Dissolution/Leaching

Soil and sediment: max. 20 g ash, biological samples (5 g ash), seawater: 200 l
Soil, sediment, biological samples and filters: addition of tracer (^{242}Pu) followed by aqua regia + H_2O_2 treatment on hot plate, samples below 10 g are sometimes treated with aqua regia in open focused microwave.
Urine: Phosphate destruction using dry/wet ashing (HNO_3, H_2O_2)

Separation

Soil, sediment, seawater, biological samples and precipitation: 10% TIOA/xylene extraction from 8 M HCl, reductive elution of Pu (with NH_4I) followed by anion exchange Large soil and sediment samples (20 g ash) are ion exchanged twice. Occasionally TRU-Resin separation is used: If the sample contains large amounts of iron an oxalate precipitation is performed to get rid of it.
Small water samples and filters: Anion exchange or TRU-Resin.
Urine: TRU-Resin separation (in combination with Am and Sr determination using TRU-Resin coupled ontop of Sr-Resin)

Anion exchange sep.: AG1-X4 (1.4 x 13 cm column). Precondition: 8 M HNO_3. Load: 8 M HNO_3.
Flow: 1 ml/ min. Wash 1: 150 ml 8 M HNO_3 + $NaNO_2$. Wash 2: 115 ml conc. HCl. Pu elution: 80 ml 2 M HCl – 2 g $NH_2OH{\cdot}HCl$.

TRU-Resin separation: 2 ml prepacked (100 – 150 μm) columns. Precondition: 3 M HNO_3. Load: 3 M HNO_3 – sulfamic acid – ascorbic acid – $Al(NO_3)_3$. Flow 1-2 ml/min. Wash 1: 10 ml 3 M HNO_3.
Wash 2: 10 ml 3 M HNO_3 – $NaNO_2$. Wash 3: 2 ml 9 M HCl. Am elution: 10 ml 4 M HCl (this fraction also contains lanthanides if they are in the sample). Wash 4: 10 ml 4 M HCl. Pu elution: 10 ml 4 M HCl – $TiCl_3$. Occasionally Sr-Resin in coupled together with TRU-Resin to facilitate a sequential analysis.

Source preparation

Electrodeposition: Deposition from sulphate solution at pH 2.5 for 3-4 hours on stainless steel planchets (diameter = 2 cm) at 0.6 A/cm^2. Distance between electrodes = 1 cm.
Micro co-precipitation: 10 ml solution is added 50 µg Ce(III) and 2 ml 40% HF. The fluorides are then collected after 30 min on 0.1µm membrane (polypropylene) filter.

Activity determination

Alpha spectrometry using PIPS (450 mm^2) detectors.

Quality assurance

Every step in each of the procedures used (sampling to result validation) is defined in our internal quality assurance protocol. The methods are regularly controlled by participation in intercomparison exercises and proficiency tests. Reference materials are occasionally used to control performance for routine analysis using established methods. New methods are checked against established and well-controlled procedures and/or reference materials.
Contamination, control and measures: Three different levels of laboratories to handle different levels of analyte concentration. Written guidelines on permitted activity levels that can be handled in each laboratory have just recently been established. So far guidelines for which laboratory to choose have concerned the origin/history of the sample rather than activity levels. Screening with handheld instruments is recommended. Written guidelines for storing (covered or in closed container) and handling (preferable in a fume hood) of samples, cleaning of equipment (equipment that has been in contact with the sample is cleaned with decontaminants (e.g. RBS))
Blank values are kept track of by analysing blank samples (distilled water) every two months. If the blank value suddenly increases significantly, decision is made on how to handle the situation (reject the last sample results, decontaminate the lab and perform the analysis once again after the blank value is under control etc). Blank values are usually not subtracted.
Measurement uncertainties includes counting uncertainties, uncertainty in detector efficiency, tracer activity uncertainties (given by supplier), uncertainties in volume/mass determination (sample, tracer)
MDA is calculated according to Currie.

Comments

When using anion exchange we occasionally have problems with insufficient separation from natural alpha emitters. It would be interesting to perform systematic analyses on the use of ion exchange resins: how small amount of resin can be used for different matrices and can the wash/elution solution volumes be reduced appropriately. Rapid analysis of Pu is most often done using microwave oven destruction, TRU-Resin separation and source preparation by micro co-precipitation. We have on going work to simplify the treatment of solid samples using open focused microwave oven. Attempts are also made to simplify the separation procedures with the use of extraction chromatographic resins, with an aim of developing sequential analysis of several radionuclides in the same sample.

Radionuclide: Am and Cm

Matrix: Effluent water and urine (occasionally other matrix is gathered in connection with ongoing research activities)

Sampling: Low-level liquid radioactive effluents (1 litre gathered prior to discharge). 24-hour urine samples gathered periodically.

Pre-treatment and pre-concentration: Effluent water: acidification, addition of ^{243}Am, evaporation and dry-ashing. Urine: acidification, addition of ^{243}Am heating and phosphate precipitation.

Dissolution/Leaching: Effluent water: Treatment with conc. HNO_3. Urine: Phosphate destruction using dry/wet ashing (HNO_3, H_2O_2).

Separation

Effluent water and urine: TRU-Resin separation (in combination with Pu and Sr determination using TRU-Resin coupled on top of Sr-Resin)
When determining Am or Cm in samples that contain interfering amounts of lanthanides, a lanthanide/actinide separation is performed using anion exchange in methanol, nitric acid and thiocyanate medium.

TRU-Resin separation: 2 ml prepacked (100 – 150 µm) columns. Precondition: 3 M HNO_3.
Load: 3 M HNO_3 – sulfamic acid – ascorbic acid – $Al(NO_3)_3$. Flow 1-2 ml/min.
Wash 1: 10 ml 3 M HNO_3. Wash 2: 10 ml 3 M HNO_3 – $NaNO_2$. Wash 3: 2 ml 9 M HCl. Am elution: 10 ml 4 M HCl (this fraction also contains lanthanides if they are in the sample).
Wash 4: 10 ml 4 M HCl. Pu elution: 10 ml 4 M HCl – $TiCl_3$.

Source preparation

Micro co-precipitation: 10 ml solution is added 50 µg Ce(III) and 2 ml 40% HF. The fluorides are then collected after 30 min on 0.1µm membrane (polypropylene) filter.

Activity determination

Alpha spectrometry using PIPS (450 mm^2) detectors.

Quality assurance

Every step in each of the procedures used (sampling to result validation) is defined in our internal quality assurance protocol. The TRU-Resin separation of Am in urine has been checked in an intercomparison exercise. A background urine sample is analysed together with the samples. Written guidelines for storing (covered or in closed container) and handling (preferable in a fume hood) of samples, cleaning of equipment (equipment that has been in contact with the sample is cleaned with decontaminants (e.g. RBS))
Blank values are kept track of by analysing blank samples (distilled water) every two months. If the blank value suddenly increases significantly, decision is made on how to handle the situation (reject the last sample results, decontaminate the lab and perform the analysis once again after the blank value is under control etc). Blank values are usually not subtracted.
Measurement uncertainties includes counting uncertainties, tracer activity uncertainties (given by supplier), uncertainties in volume/mass determination (sample, tracer)
MDA is calculated according to Currie.

Comments

TRU-resin separation of Am and Cm does not separate these from trivalent lanthanides, therefore the indicated procedures can only be used for matrices that contain small amount of lanthanides.

Questionnaire response from Lab 4

Answers to questionnaire on routine and emergency practice regarding radiochemical analysis

(NKS-B project RADCHEM)

The answers refer to documented in house procedures. These are today in principle Eichrom procedures but we have started to develop new rapid procedures mostly for preparedness.

The laboratory is today not focused on routine analysis but on rapid procedures for preparedness. However, we may in a near future be more focused on routine work to some extent.

1. Radionuclides:

^{90}Sr

^{241}Am

^{238}Pu, $^{239+240}Pu$

2. Matrices

soil, vegetation, air filter, water, ^{90}Sr in milk

3. Sampling

Basically no sampling activities but strategies for sampling is under development.

4. Pre-treatment and enrichment

Storage: Freezer if needed

Spike: Added before pre-treatment

5. Dissolution/leaching

Soil: Lithium borate fusion

Vegetation: Wet ashing (nitric acid/hydrogen peroxide)

Water: no pretreatment

Air filters: as for soil

i.e. ”total” dissolution

Comment: We have recently purchased a microwave oven and we will evaluate this for rapid analysis

6. Separation

Amount of sample: 3 g soil, 20 g vegetation and 100 ml water

Separations: Eichrom resins and procedures

Reuse: We do not reuse resins

Recoveries: Soil: about 60% for Pu, LOW! 20% for Am, about 65% for Sr; Vegetation: Between 60-70% for all analytes; air filters: around 60% for all analytes; Water: Between 60-80% for all analytes

7. Source prep.

Electrodep.: $Na_2SO_4/NaHSO_4$, 90 min @ 0.75 A

8. Activity determ.

α-spec: 6 PIPS detecors

LSC: one Quantulus and one Packard

MS: one Finnigan Element 2 (double focusing sector ICP-MS)

Chemical yield: Yield tracers (α-spec: IDAS using ^{243}Am, ^{242}Pu, stable Sr with AAS)

9. Rapid proc.

The difficulty is how to define a rapid method! We have today one method (in press) that we would define as a truly rapid analytical protocol for Pu, Am and Cm. Morover, one rapid method for ^{90}Sr in preparedness situations is/will be under evaluation.

10. QA

QA: Participation in EML QAP. (This will stop after this spring so we have to look for another QAP.)

Contamination: Proc. blanks

Uncertainty: GUM approach

2 labs: Isotope lab for high activities and one lab for ”environmental” samples

Guidelines on permitted activity levels: Yes! (SSI regulations)

MDA: Currie approach

11. Comment

Low yield for Am in soil

Questionnaire response from Lab 5

STUK- Helsinki- TK Ikäheimonen

Procedure I

Radionuclide: ^{89}Sr and ^{90}Sr

Matrix: Environmental and biological samples

Sampling: All sampling is done according to our laboratory quality manual (tens of methods depending on matrix)

Pre-treatment and enrichment: Fresh milk is vaporized and ashed at 450^{o}C. Vegetation samples are dried at 105^{o}C and ashed at 450^{o}C. Soil and sediment samples are dried or freezedried. Sea water water samples are vaporized to about 0,5 litres. Fresh water samples are vaporized to dryness and ashed at 450^{o}C. Fishes are dried at 105^{o}C and ashed at 450^{o}C. Deposition samples are dried and ashed at 450^{o}C. Filter samples are treated with fusion.

Dissolution/Leaching: Ashed samples are leached with nitric or hydrochloric acid. Soil and sediment samples are leached with hydrochloric acid and water . Sea water samples are diluted to about 4 litres and some contaminants are removed with ferric hydroxide leaching. Fused air filter samples are dissolved in deionized water. In the end a strontium carbonate precipitation is made, which is then dissolved in 20 ml of 8 M HNO_3.

Separation: Extraction chromatography with 3 grams of Eichroms Sr-resin, 100-150 μm. Column diameter about 8 mm. Load solution of 8 M HNO_3, wash solutions with 8 M HNO_3 and with 3 M HNO_3, elution with 0,05 M HNO_3. Columns are reused for five times (at least). Before reuse the column is washed with 6 M HCl to remove the possible daughters from radioactive lead.

Source preparation: Strontium is precipitated as carbonate with ammoniumcarbamate ($NH_4CO_2NH_2$).

Activity determination: First the sample is counted with low-background proportional counter (^{89}Sr, ^{90}Sr and ingrowing ^{90}Y) and then the strontium carbonate precipitate is dissolved with HCl and left to waite about 18 days for ingrowth of ^{90}Y. Then the ^{90}Y is separated with carbonate-free ammonia as a hydroxide and the solution is used for Sr yield determination with atomic absorption spectrometer. Yttriumhydroxide is dissolved in nitric acid and yttrium is precipitated as an oxalate with oxalic acid. The ^{90}Y -preparate is counted at least twice to ensure the purity of the preparate. Yttrium yield is determined with EDTA-titration.

Rapid procedure: All the counting is done from the first strontium carbonate preparate. The preparate is dissolved in 1,6 ml of 1 M HCl and an aliquot of 0,1 ml is taken for yield determination. First the sample is counted with Cerenkov counting with low-background liquid scintillation counter and after adding of scintillation cocktail again for few times.

Quality assurance: Reference and blank samples are analysed at least once a year. Uncertainty estimation includes uncertainties from counting, pipetting, weighing, yield determinations and repeatability. MDAs are calculated as follows

$$MDA = \left(3 * \sqrt{B}\right) / \left(e * \sqrt{t}\right)$$

where B is background, e is efficiency and t is counting time.

Comments:

STUK- Helsinki - Pia Vesterbacka

Procedure V

Radionuclide: U-234, U-235 and U-238

Matrix: Ground water

Sampling: Ground water samples are collected into polyethylene bottles either directly from well or from tap. Water samples are not filtrated before analysing them so no special equipments are needed in sampling.

Pre-treatment and enrichment: Samples are stored in cold before acidifying them. Uranium is concentrated from water by applying iron scavenging using NH_3.

Dissolution/Leaching: The iron precipitate is separated from solution by centrifuge and precipitate is dissolved in concentrated HCl.

Separation: Uranium isotopes are separated from other radionuclides by ion exchange method using Dowex 1x8, 50/100 mesh ion exchange resin. 12 ml of ion exchange resin is used in each column, which have high of 17 cm and diameter of 1 cm. Columns are conditioned using 30 ml of concentrated HCl. Columns are reused ten times. During the usage columns are washed using 40 ml of 0.1M HCl, 40 ml of 6M $NaHSO_4$, 40 ml of 6M HCl and 40 ml of H_2O (Ultra pure). The flow rate is 12 drops per minute. Uranium is eluted from the column by 40ml of 0.1M HCl. Typical recover is 80% - 90%.

Source preparation: Before source preparation uranium is reduced from oxidation state +6 to oxidation state +4 using strong oxidation agents $TiCl_4$. For the measurement preparation uranium is co-precipitating with CeF_3 to the membrane, which has a pore size of 0.1 μm.

Activity determinations: The samples are counted with AlfaAnalyst (Canberra) alpha spectrometer. Chemical yield is calculated from U-232 tracer, which is added into analysis at the beginning of the procedure.

Quality assurance: Before usage the alpha spectrometer is calibrated. Energy calibration is done using standard mixed alpha preparation and efficiency calibration is done using standard Am-241 preparation. The quality assurance of alpha spectrometer is ensured regularly by pulse check and background measurements. In addition, blank and reference samples are analysed regularly. Inter-comparisons are participated if suitable materials are available.

Overall uncertainty covers uncertainty from measurement with its 95% confidential level (2σ) and from activity of tracer. Uncertainty due to weighting the sample is insignificant compared to uncertainty due to measurement and activity of tracer used in yield determination.

Contamination in laboratory is avoided using separate glass for different radionuclides. Also purity of glass is ensured by analysing blank samples regularly. If activity in blank samples increases, they are no longer used in low level determinations.

MDA is calculated according to Currie definition.

STUK- Helsinki - TK Ikäheimonen

Procedure II

Radionuclide: ^{238}Pu, ^{239,240}Pu and ^{241}Pu ANION EXCHANGE METHOD

Matrix: Environmental, foodstuffs and biological samples

Sampling: According to laboratory quality manual (tens of methods depending on matrix)

Pre-treatment and enrichment: Pu in water samples is co-precipitated as $Fe(OH)_3$ and the prcipitate is dissolved in 8 M HNO_3 and oxidized with H_2O_2 and $NaNO_2$. Solid samples are wet ashed with concentrated HNO_3 and HCl (and HF is necessary). Evarorated and dissolved in 8 M HNO_3.

Separation: Dowex 1x4, 50-100 mesh, in NO_3^- -form is added to the 8 M HNO_3 solution and mixed with magnetc stirrer about 1 h. The resin is transferred to ion chromatography column and the solution is collected to 400 ml decanter glass. The column is washed with 8 M HNO_3 and the washing solution is combined with earlier solution, this solution is preserved for Am separation. Column is washed with concentrated HCl and the washing solutions are discarded. Pu is eluated with conc. HCl + 1 M NH_4I solution. The eluate is evaporated to dryness on a hot plate Vaporization to dryness is continued with small amounts of conc. HNO_3, until no colour is noticed.

Source preparation: Sample is dissolved in dilute HNO_3 and divided to half. Other half is electrodeposited after its vaporized to dryness and dissolved in 2 M HNO_3 and small amount of water. Electrodeposition is done from slightly acidic solution, time 45 to 90 minutes, current 1,7-1,9 A and voltage 6 to 9 V with Pt-spiral as an anode and stainless steel disc as a cathode. Other half is prepared for liquid scintillation counting: sample is vaporized to dryness and dissolved in 1 M HCl and transferred to liquid scintillation vial, Optiphase Hisafe 2 cocktail is added.

Activity determination: ^{238}Pu and ^{239,240}Pu are determined with alphaspectrometer. Chemical yield is determined with ^{242}Pu tracer. ^{241}Pu is determined by liquid scintillation counting the sample with beta and alpha/beta -separation procedures.

Rapid procedure: The overall procedure is carried out about 3 times quicker. Or a evaporation sample is prepared and measured. Or an total actinide separation with ion exchange is performed and measured.

Quality assurance: Before usage the alpha spectrometer is calibrated. Energy calibration is done using standard mixed alpha preparation and efficiency calibration is done using standard Am-241 preparation. The quality assurance of alpha spectrometer is ensured regularly by pulse check and background measurements. In addition, blank and reference samples are analysed regularly. Inter-comparisons are participated if suitable materials are available.

Overall uncertainty covers uncertainty from measurement with its 95% confidential level (2σ) and from activity of tracer (incl. pipetting) and repeatability ot the method. Uncertainty due to

weighting the sample is insignificant compared to uncertainty due to measurement and activity of tracer used in yield determination.

Contamination in laboratory is avoided using separate glass for different radionuclides. Also purity of glass is ensured by analysing blank samples regularly. If activity in blank samples increases, they are no longer used in low level determinations.

MDA is calculated according to Currie definition.

STUK- Helsinki- TK Ikäheimonen

Procedure III

Radionuclide: ^{241}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm

Matrix, Sampling, Pre-treatment and enrichment: See Pu -procedure II

Separation: Solution from Pu analysis (see Pu determination) is vaporized to dryness and the residue dissolved in water and conc. HCl. The solution is diluted with water and Am is precipitated with oxalic acid, the precipitate ashed in 450 °C. Am and Cm are co-precipitated with $Fe(OH)_3$. The precipitate is dissolved in HCl and introduced to ion exchange column, Dowex 1x4 (50-100 mesh), ,the solution is gathered, the column is washed with HCl and the washing solution combined with sample solution.
Solution is vaporized to dryness and dissolved in water, pH is adjusted accurately to 2-3 and a liquid extraction with HDEHP-TBP-toluene -solution is performed. The organic phase is washed with 0,075 M HCl and Am(Cm) is backextrected with 4 M HNO_3.
The solution is brought to dryness and dissolved in HCl and introduced to double layer ion exchange column. The column has in the bottom layer of Dowex 1x4 (100-200 mesh) anion exchange resin and in the upper layer of Dowex 50Wx8 (100-200 mesh) cation exchange resin. Solution is poured to the column and gathered. Column is washed with HCl and the washing solution gathered to the same beaker.
The eluate is brought to dryness, the residue is dissolved in 1 M HNO_3 - 93% CH_3OH -solution. Ion exchange column of Dowex 1x4 (100-200 mesh) is prepared . The column is pre-conditioned with 1 M HNO_3 and with 1 M HNO_3 - 93% CH_3OH. The sample solution is transferred to the column and the column is washed with 1 M HNO_3 - 93% CH_3OH and of 0,1 M HCl-75 % CH_3OH-1 M NH_4SCN -solution. Am(Cm) is eluted with 1,5 M HCl - 86% CH_3OH -solution. The eluate is evaporated to dryness on a hot plate.

Source preparation: Sample is dissolved in 2 M HNO_3 and small amount of water. Electrodeposition is done from slightly acidic solution, time 90 minutes, current 1,7-1,9 A and voltage 6 to 9 V with Pt-spiral as an anode and stainless steel disc as a cathode.

Activity determination: ^{241}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm are measured with alphaspectrometer and the chemical yield determined with ^{243}Am -tracer.

Quality assurance: Before usage the alpha spectrometer is calibrated. Energy calibration is done using standard mixed alpha preparation and efficiency calibration is done using standard Am-241 preparation. The quality assurance of alpha spectrometer is ensured regularly by pulse check and background measurements. In addition, blank and reference samples are analysed regularly. Inter-comparisons are participated if suitable materials are available.

Overall uncertainty covers uncertainty from measurement with its 95% confidential level (2σ) and from activity of tracer. Uncertainty due to weighting the sample is insignificant compared to uncertainty due to measurement and activity of tracer used in yield determination.

Contamination in laboratory is avoided using separate glass for different radionuclides. Also purity of glass is ensured by analysing blank samples regularly. If activity in blank samples increases, they are no longer used in low level determinations.
MDA is calculated according to Currie definition.

STUK- Helsinki- TK Ikäheimonen

Procedure VI

Radionuclide: Sr, U, Pu, Am and Cm from the same sample EXTRACTION CHROMATOGRAPHIC METHOD

Matrix: Fallout, rainwater, air filters,(availability for other env. samples is on process)

Sampling: According to laboratory quality manual

Pre-treatment and enrichment: Adding of tracers (Pu-242, Am-243, U-232) and Sr-carrier. Fe-hydroxide precipitation for waters, Sr analysis continuing from liquid fraction, others from OH-precipitation. Oxalate precipitation for Sr. Dissolving of hydroxide in dil.HNO_3. For solid samples micro wave digestion before hydroxide precipitation.

Separation: Sr: : Extraction chromatography with 3 grams of Eichroms Sr-resin, 100-150 µm. Column diameter about 8 mm. Load solution of 8 M HNO_3, wash solutions with 8 M HNO_3 and with 3 M HNO_3, elution with 0,05 M HNO_3. Columns are reused for five times (at least). Before reuse the column is washed with 6 M HCl to remove the possible daughters from radioactive lead.

U and transuranics: 2 methods:

1) Separation of U with UTEVA (Eichrom)resin in 3M HNO_3-0.5 M $Al(NO_3)_3$, Extraction of TRUs with HNO_3, eluation of U with dil. HCl. Separation of Pu and Am(Cm) with TRU (Eichrom)resin, purification Am-fraction with TEVA (Eichrom)resin.

2) Separation of Pu and U with anion exchange (Dowex 1x4, nitrate form), Am(Cm) not adsorped. Eluation of Pu with HCl-NH_4I and U with dil. HCl. Am(Cm) fraction is purified with TRU and TEVA resins like in method 1).

Source preparation: Sr like in Sr-method I, Pu,U,Am(Cm) like in Pu-method (II) with electrodeposition.

Activity determination: Sr like in Sr-method (I). Others with alphaspectrometer and liquid scintillator (Pu-241) (II).

Rapid procedure: This is rapid procedure.

Quality assurance: Like Sr and Pu methods (I and II)

Questionnaire response from Lab 6

Procedure IV

Radionuclide: ^{90}Sr
Matrix: Environmental samples from artic and sub-arctic region, for example: water (rain water, lake water), milk, plant, soil, bone and fish.
Sampling: Tens of methods depending on matrix
Pre-treatment and enrichment: The water samples are acidified by nitric acid to pH 1 and dried under infrared lamps in large porcelain crucibles. Sr, Cs, Ba and Ce carriers are added to water samples before drying. After drying the samples are ashed at 450 ºC. Sr- and Cs carriers are added to the soil and sediment samples together with ^{85}Sr tracer. After drying the samples are homogenized and ashed at 450 ºC.
Dissolution/Leaching: Sample amount is usually 10-15 g of ash.
Separation: Two methods are used for the separation, the traditional fuming HNO_3 method and Eichrom extraction chromatography method according the standard procedures. In the fuming nitric acid method Sr is purified by fuming nitric acid treatment, barium chromate precipitation, and iron hydroxide scavenging of Y. In order to determine the chemical yield, ^{85}Sr-tracer is added to the samples. The chemical recovery of Sr is measured by γ- spectrometry evaluating the 514 keV γ-line of ^{85}Sr. After separation of strontium, Y-carrier is added to the samples and ^{90}Y is let to grow in the samples. After the equilibrium is reached ^{90}Y is precipitated as Y-oxalate and counted on a low-background beta counter. The chemical yield of Y is determined by EDTA-$ZnSO_4$ titration after counting. The total recovery is usually 60-80%.
Source preparation: ^{90}Y is precipitated as Y-oxalate and the filtered precipitate is mounted on a disc, cover with Mylar, and the assembly is fastened with a ring.
Activity determination: Low-level beta GM Multicounter System, Risø GM-25-5, Risø National Laboratory
Rapid procedure:
QA: QA is maintained during the research by a regular systematic assurance programme • qualified personnel • certified standards for checking up the stability of the β-counter • internal tracer (^{85}Sr) • analysis of certified reference material • reagent blanks • regular background measurements • intercomparisons with other laboratories • uncertainty estimations • internal auditing
Comments:

Questionnaire response from Lab 7

Radionuclide	$^{238,239,240}Pu$
Matrix	Soil, sediment, water, biota
Pre-treatment and enrichment	Water: Store in cubitainers until analysis. Acidify 200 litres unfiltered (HCl), add Pu-tracer, add $K_2S_2O_5$, precipitate Fe-Ca-$Mg(OH)_2$ with NaOH. Reprecipitate with ammonia, reprecipitate with NaOH to remove amphoteric elements. Sediment/soil: 10g. Sieving 2mm. Ash 550 C, add tracer afterwards. Biota: Ashing 550C.
Dissolution/Leaching	Mostly leaching in aqua regia. Hot particles with HF.
Separation	Pre-cleaning by extraction from 6M HCl in 10% TIOA/Xylene to remove U, Po and Fe. Pu^{3+} not extracted. Then ion-exchange in 8M HNO_3 (1cm x 12cm Bio-Rad 1x4 100-200 mesh), gravity flow. 100ml wash 8M HNO_3, 50 ml 9M HCl. Elute with 2M HCl+2g NH_2OH-HCl. Repeat column.
Source preparation	Electrodeposition from Na_2SO_4 at pH2 for 4-5h at 1Ampere. Electrode distance about 5mm. Peak resolution always detector limited.
Activity determination	Alpha spectrometry (semiconductor)/mass-spectrometry.
Rapid procedure	No standard procedure.
Quality assurance	Intercalibration excercises. Separate semi-hot lab. Clean room. Blank samples occasionally. Only counting uncertainty and tracer calibration included in total uncertainty. MDA usually as 2 sigma.
Comments	Only routine samples described. Highly individual treatment in any step for other sample volumes (eg soil 1kg or interstitial sediment water). Normally high yields (>90%) and very few signs of interfering elements.

Radionuclide	^{241}Am
Matrix	Soil, sediment, water, biota
Pre-treatment and enrichment	Water: Store in cubitainers until analysis. Acidify 200 litres unfiltered (HCl), add Am-tracer, precipitate Fe-Ca-$Mg(OH)_2$ with NaOH. Reprecipitate with ammonia, reprecipitate with NaOH to remove amphoteric elements. Sediment/soil: 10g. Sieving 2mm. Ash 550 C, add tracer afterwards. Biota: Ashing 550C (seaweed 700 C)
Dissolution/Leaching	Mostly leaching in aqua regia. Hot particles with HF.
Separation	Ca-Oxalate precipitate at pH 1-1.5 from the evaporated 8M HNO_3 fraction during Pu-analysis. Wet ash/ash precipitate and precipitate $Fe(OH)_3$ at pH 6.5. Extraction from 6M HCl in 10% TIOA/Xylene to remove U, Po and Fe (discard organic phase). Evaporate water phase, dissolve in 8M HNO3 and pass through 1cm x 12cm Bio-Rad 1x4 100-200 mesh, gravity flow to remove Th. Evaporate and re-dissolve in 1M HNO_3 – 93% MeOH and pass through 1cm x 12cm Bio-Rad 1x4 100-200 mesh, gravity flow. Wash with 20 ml 1M HNO_3 – 93% MeOH, 100 ml 0.1M HCl – 0.5M NH_4SCN – 80% MeOH, 50 ml 1M HNO_3 – 93% MeOH. Elute Am with 1.5M HCl – 86% MeOH.
Source preparation	Electrodeposition from Na_2SO_4 at pH2 for 4-5h at 1Ampere. Electrode distance about 5mm. Peak resolution mostly detector limited unless large soil/sediment samples with insufficient REE removal.
Activity determination	Alpha spectrometry (semiconductor).
Rapid procedure	No standard procedure.
Quality assurance	Intercalibration excercises. Separate semi-hot lab. Clean room. Blank samples occasionally. Only counting uncertainty and tracer calibration included in total uncertainty. MDA usually as 2 sigma.
Comments	Only routine samples described. Highly individual treatment in any step for other sample volumes (eg soil 100g). Normally high yields (>90%) and very few signs of interfering elements.

Radionuclide	^{238}U, ^{235}U, ^{234}U (^{236}U)
Matrix	Soil, sediment, water, biota, urine
Pre-treatment and enrichment	Water: Store in cubitainers until analysis. Acidify 0.1-100 litres unfiltered (HCl), add ^{232}U-tracer, precipitate Fe-Ca-$Mg(OH)_2$ with NaOH. Reprecipitate with ammonia, reprecipitate with NaOH to remove amphoteric elements. Sediment/soil: 1-5g. Sieving 2mm. Ash 550 C, add tracer afterwards. Biota: Ashing 550C (seaweed 700 C)
Dissolution/Leaching	Always HF or melt (Lithium metaborate).
Separation	8M HNO_3 extraction TBP. Back extract Th with 1.5M HCl (dilute TBP with xylene) and backextract U with water.
Source preparation	Electrodeposition from Na_2SO_4 at pH2 for 4-5h at 1Ampere. Electrode distance about 5mm. Peak resolution mostly detector limited unless large soil/sediment samples with insufficient REE removal.
Activity determination	Alpha spectrometry (semiconductor) /Mass-spectrometry
Rapid procedure	No standard procedure.
Quality assurance	Intercalibration excercises. Separate semi-hot lab. Clean room. Blank samples occasionally. Only counting uncertainty and tracer calibration included in total uncertainty. MDA usually as 2 sigma.
Comments	Only routine samples described. Highly individual treatment in any step for other samples. Uranium usually determined without separation when ICP-MS is used (^{233}U used as tracer).

Questionnaire response from Lab 8

Reply to NKS Questionnaire on routine and emergency practice regarding radionuclide analysis, 2004

Avd för Radiofysik, Linköping, HBL Pettersson

Radionuclide

Uranium isotopes (^{238}U, ^{235}U, ^{234}U)

Matrix

Freshwater, seawater, seabed sediments (normally only by gamma spectrometry but on occasion by radiochemistry/alpha spec.)

Sampling

Freshwater: simple sampling of 1-5 litre in plastic bottles from drinking water taps and hydrofores, normally no replicates

Seawater: subsampling in plastic bottles from Niskin bottles from General Oceanics Model 1010 samplers, replicate samples occasionally

Seabed sediments: core samples from Gemini type sampler, core sub-sampling from small box core sampler, replicate samples occasionally

Pre-treatment and enrichment

Freshwater: immediate acidification by conc HCl, storage in refrigerator, on analysis transfer to glass beakers (about 0.5-1 litre of water), sample weight determination gravimetrically, addition of tracer (^{232}U), equilibrate the sample for min 1 h, pre-concentration by MnO_2 ppt, separation of ppt by filtration.

Seawater: immediate acidification by conc HCl, storage in refrigerator in home lab. On analysis transfer to glass beakers (about 1 litre of water), sample weight determination, addition of tracer (^{232}U), equilibrate the sample for min 1 h, pre-concentration by MnO_2 ppt, separation of ppt by filtration

Seabed sediments: core slicing onboard (1-2 cm slices), transfer of slices to plastic leak proof bottles, storage in room temp onboard, storage in deep freezer in home lab. On analysis determination of fresh weight, freeze drying about 48 hrs, removal of stones, Mn-nodules etc., determination of dry weight, (analysis by gamma spectrometry).

Dissolution/Leaching

Freshwater/Seawater: dissolve MnO_2-ppt by HCl and H_2O_2, hot plate digestion to dryness in HCl, hot plate digestion in 8 M HNO_3, final preparation in 20 ml 8 M HNO_3

Seabed sediments: transfer of dry sample (up to 3 g dry matter) to μ-wave containers, addition of tracer ^{232}U, addition of conc HNO_3 and ca 1 ml conc HF, equilibrate the sample for min 1 h. Digestion (5 min ramp, 60 min digestion, 160-200 ^{o}C). If necessary digestion by aqua regia. Total dissolution desired but not always obtained. Hot plate evaporation of acids (repeated), final preparation in 20 ml 8 M HNO_3 and boric acid and filtration of any remaining solids.

Separation

Freshwater/Seawater/Seabed sediments: Separation of actinides by liquid-liquid extraction in TBP from 8 M HNO_3 in 50 ml separatory funnels Repeated washing of TBP by 8 M HNO_3. Separation (repeated) of e.g. Th in 1.5 M HCl from TBP diluted in xylene. Extraction (repeated) of uranium in demin water.

Source preparation

Hot plate evaporation to near dryness, addition of 1 ml 0.3 M Na_2SO_4, evaporation to dryness, addition of 300 μl konc H_2SO_4, dissolve by gentle heating, add 4 ml demin water and 2 drops of thymol blue, adjust pH to about 2, transfer solution to deposition cell and rinse beaker (Packard LSC 20 ml flasks), adjust pH between 2.1-2.4, electrodeposit (Pt-wire) at

about 5-7 mm distance at 1.2 A during 1 hour, add conc NH_3, rinse stainless steel disc (20 mm diameter) with 1% NH_3 and then aceton, dry the disc.

Activity determination
Alpha spectrometry; PIPS 450 mm^2, Ortec Octête plus system, Ortec MAESTRO-32 MCA. Peak resolution (single peaks) about 20-30 keV. Counting time; 0.5-3 days. Peak/activity determinations made manually from pre-determined ROI's. Chemical yield determined from measured ^{232}U activity on the disc (detector counting efficiency not very precisely determined).
Chemical yields typically >60%

Rapid procedure
Not available here (ICP-MS analysis performed at Örebro Univ)

Quality assurance
The basis of our quality assurance is participation in intercomparisons (IAEA, NKS etc.). Since the radiochemical work involves traceable radiotracers, the quality assurance in terms of quantification is not a critical issue, assuming the tracer quality is good. Normally no reference material is analysed alongside sample analysis, only when new series of samples are going to be analysed. For water analysis cross-check has been made with ICP-MS analysis.
Blank samples are not standard procedure but introduced occasionally, thus contamination control is not done on regular basis. Blank values/activities, when detectable, are subtracted from the gross sample activities. In general, with these kind of analysis, contamination is not a major problem. With good GLP including good quality reagents, contamination risks can easily be handled.
Screening of samples is not standard procedure, but often (sediments) gamma spectrometry analyses have been made prior to radiochemistry work. Only one laboratory in place for all analysis. In principle only low (trace level) activities are handled.

MDA is calculated based on the s.d. of the detector background, σ, from counting of discs with ^{232}U tracer electro-deposited. MDA is calculated for 95% CI (4.66 σ)

Comments
The method is well established and works for most matrices. However, it can not be regarded as a fast method. If analysis of U isotopic ratios is not needed, the ICP-MS technique is both more elegant, faster and show lower MDA.

Reply to NKS Questionnaire on routine and emergency practice regarding radionuclide analysis, 2004

Avd för Radiofysik, Linköping, HBL Pettersson

Radionuclide
Plutonium isotopes (^{238}Pu, ^{239,240}Pu)

Matrix
Seabed sediments

Sampling
Core samples from Gemini type sampler, core sub sampling from small box core sampler, replicate samples occasionally

Pre-treatment and enrichment
Core slicing onboard (1-2 cm slices), transfer of slices to plastic leak proof bottles, storage in room temp onboard, storage in deep freezer in home lab. On analysis determination of fresh weight, freeze drying about 48 hrs, removal of stones, Mn-nodules etc., determination of dry weight, (analysis by gamma spectrometry).

Dissolution/Leaching
μ-wave leaching procedure: Transfer of dry sample (up to 3 g dry matter) to μ-wave containers, addition of tracer ^{242}Pu, addition of conc HNO_3. Equilibrate the sample for min 1 h. Digestion (5 min ramp, 60 min digestion, 160-200 ^{o}C). If necessary digestion by aqua regia (total dissolution normally not required when only anthropogenic input is assessed). Hot plate evaporation of acids, dilution with demin water, adjust pH to about 7, ppt of hydroxides, centrifuge, add 100 mg Fe^{3+} and repeat ppt, centrifuge and combine ppt, dry over night (105^{o}C), dissolve in 8 M HNO_3 + drops of H_2O_2. Proceed with ion-exchange.

Hot plate leaching procedure: Transfer of dry sample (up to ca 50 g dry matter) to porcelain crucible, add 5 g oxalic acid, dry ash at 550^{o}C over night, addition of ^{242}Pu tracer and 8 M HNO_3 + drops of H_2O_2, equilibrate the sample for min 1 h. Leaching during heating (hot plate) for about 6 h, cool and centrifuge, repeated leaching on solids, centrifuge and combine supernates, adjust pH to about 7, ppt of hydroxides, centrifuge, add 100 mg Fe^{3+} to supernate and repeat ppt, centrifuge and combine ppt, dry over night (105^{o}C), dissolve in 150 ml 8 M HNO_3 + drops of H_2O_2. Proceed with ion-exchange

Separation
Add 100 mg of $NaNO_2$ to the supernate, heat a few min to dissolve, cool. Pass the solution through the ion exchange resin at 1 ml/min (anion AG1X8, 100-200 mesh, height 10 cm, column 0.8 cm diameter). Wash column with 10 CV of 8 M HNO_3. Eventually collect effluents for further Am/Cm analysis. Elute Th with 10CV 10 M HCl. Elute Pu with 80 ml 1.2 M HCl + 1 ml H_2O_2 at 1-2 ml/min. Evaporate effluents to dryness, dissolve in 10 M HCl. Pass solution through 2nd column at 1 ml/min (anion AG1X8, 100-200 mesh, height 5 cm) to elute remaining Th. Elute Pu with 40 ml 10 M HCl + 0.6 g NH_4I, evaporate to near dryness, add conc HNO_3 + 1 ml H_2O_2 (gently) to expel I_2. Proceed with electrodeposition.

Source preparation
Hot plate evaporation to near dryness, addition of 1 ml 0.3 M Na_2SO_4, evaporation to dryness, addition of 300 μl konc H_2SO_4, dissolve by gentle heating, add 4 ml demin water and 2 drops of thymol blue, adjust pH to about 2, transfer solution to deposition cell and rinse beaker (Packard LSC 20 ml flasks), adjust pH between 2.1-2.4, electrodeposit (Pt-wire) at

about 5-7 mm distance at 1.2 A during 1 hour, add conc NH_3, rinse stainless steel disc (20 mm diameter) with 1% NH_3 and then aceton, dry the disc.

Activity determination
Alpha spectrometry; PIPS 450 mm^2, Ortec Octête plus system, Ortec MAESTRO-32 MCA. Peak resolution about 20-30 keV (single peaks). Counting time; several days. Peak/activity determinations made manually from pre-determined ROI's. Chemical yield determined from measured ^{242}Pu activity on the disc (detector counting efficiency not very precisely determined).
Chemical yields typically >50%

Rapid procedure
Not available (sample analysis also performed by ICP-MS at Örebro Univ)

Quality assurance
The basis of our quality assurance is participation in intercomparisons (IAEA, NKS etc.). Since the radiochemical work involves traceable radiotracers, the quality assurance in terms of quantification is not a critical issue, assuming the tracer quality is good. Normally no reference material is analysed alongside sample analysis, only when new series of samples are going to be analysed. For sediment analysis cross-check has been made with ICP-MS analysis of ^{239}Pu, ^{240}Pu.
Blank samples are not standard procedure but introduced occasionally, thus contamination control is not done on regular basis. Blank values/activities, when detectable, are subtracted from the gross sample activities. In general, with these kind of analysis, contamination is not a major problem. With good GLP including good quality reagents, contamination risks can easily be handled.
Screening of samples is not standard procedure. Only one laboratory in place for all analysis. In principle only low (trace level) activities are handled.

MDA is calculated based on the s.d. of the detector background, σ, from counting of discs with ^{242}Pu tracer electro-deposited. MDA is calculated for 95% CI (4.66 σ)

Comments
The method is well established and works for most matrices. Need for a fast method (see development at Örebro Univ.)

Questionnaire response from Lab 9

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Questionnaire on routine and emergency practice regarding radiochemical analysis

Radionuclide: $^{239, 240}Pu$

Matrix: Sediment, soil/geological matrices.

Sampling: See Håkan Pettersson, Linköping.

Pre-treatment and enrichment
See Håkan Pettersson, Linköping.
Tracer added after drying.

Dissolution/Leaching
Leaching on hot-plate or microwave digestion in concentrated HNO_3 or *Aqua Regia*.

Separation
Hot-plate leaching: 1-50 grams of dry sediment.
Microwave digestion (CEM MARS 5): 0.5 grams of dry sediment.

Ion-exchange: AG1-X4, 100-200 mesh.
Column dimensions: diameter 10mm, height 300 mm, resin height 50mm.
Flow rate 1-2 ml per minute.
Before starting the ion-exchange procedure plutonium is converted to the tetravalent state with 0.7 g $NaNO_2$ per ml solution.
Conditioning of the resin with 40 ml of 8 M HNO_3, wash1 50 ml 8 M of HNO_3, wash2 30 ml of 10 M HCl, wash3 40 ml of 1.2 M HCl containing 1 ml 30% H_2O_2.
Typical recoveries: 80-95%
Impurities: Some ^{238}U remains in the sample solution together with the Pu-fraction after separation. For samples from Wightown Merse Calibration Site, Scotland the concentration of ^{238}U after separation was 10-30 times higher than the concentration of ^{239}Pu. It caused no interference from $^{238}UH^+$ since the desolvator eliminated H_2O enough.

Liquid-liquid-extraction:
Before extraction plutonium is converted to the tetravalent state with 0.7 g $NaNO_2$ per ml solution.
Extraction from 1.4M HNO_3 into 10% TOA in xylen or 20% TBP in xylen. Back-extraction with 1.2 M HCl containing 30% H_2O_2.
Extraction from 1 M HNO_3 into 0.5 M TTA in xylene or freon. Back-extraction with 8 M HNO_3.
Typical recoveries:
TOA 80-110%, TBP 50-100%, TTA less than 50%

Source preparation
Samples were dissolved in 2% HNO_3.

Activity determination
Quadrupole ICP-MS (Agilent 4500) equipped with an ultrasonic nebulizer (CETAC 6000AT+). Operating parameters: plasma power 850 W, nebulizer flow 0.85 l/min, sample flow 1.5-2.0 ml/min. Chemical yields are determined from the added tracer ^{242}Pu (4334G, National Institute of Standards and Technology, USA)

Rapid procedure
A batch of 14 samples can be analysed in 12 hours, including atom ratio $^{240}Pu/^{239}Pu$ (microwave digestion, ion exchange, quadrupole ICP-MS). Plutonium concentrations obtained by quadrupole ICP-MS are in fair agreement with determination by alpha-spectrometry in Linköping.

Quality assurance
Blank samples are analysed by routine in each batch of analysed samples.

Comments
Liquid-liquid-extraction with TTA gives low recoveries and problems using the USN due to organic substances appearing in the aqueous solution after back extraction.

Instability of the ion throughput to the MS.

Bibliographic Data Sheet **NKS-124**

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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 accidents, authorised release and routine surveillance. Reliable radiochemical separation and detection techniques are needed for accurate determination of alpha and beta emitters. Rapid analytical methods are needed in case of an accident for early decision-making. The objective of this project has been to compare and evaluate radiochemical procedures used at Nordic laboratories for the determination of strontium, uranium, plutonium, americium and curium.

To gather detailed information on the procedures in use, a questionnaire regarding various aspects of radionuclide determination was developed and distributed to all (sixteen) relevant laboratories in the Nordic countries. The response and the procedures used by each laboratory were then discussed between those who answered the questionnaire. This report summaries the findings and gives recommendation on suitable practice.

Key words Radiochemistry, radioecology, strontium, uranium, plutonium, americium, curium

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