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Separation of actinides from a bone ash matrix with extraction chromatography

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Abstract

A method based on extraction chromatography for the separation of actinides from bone ash has been developed and tested. Group separation of Th, U, Pu and Am from the sample matrix, and, e.g. Sr, was done with a TRU Resin® column. The sequential separation of the actinides was performed with UTEVA Resin® and TRU Resin® columns. The mean recoveries for the bone ash analyses were 78±2, 86±5, 81±5 and 76±4% (1 s) for Th, U, Pu and Am, respectively. The activity levels were 1 mBq g^{-1} of sample for Th, U and Pu and 10 mBq g^{-1} of sample for Am. The different actinide fractions were pure and the peak resolution in the α spectra was sufficient. Sample sizes ranged from 3 to 5 g. The problems caused by the loss of the organic extractant from the columns during the elution of Th and Am with 4–9 M HCl was eliminated completely by decomposition of the organic residues using strong mineral acids, HNO_3, HCl, HF and/or $HClO_4$, before the sample preparation. The separation method is simple and faster than traditional methods based on anion exchange and liquid–liquid extraction. Less strong acid and organic wastes are produced. Strontium-90 concentrations can be analysed from the same sample as the actinides, which saves time and lowers the detection limits when the quantity of sample material is limited. © 1998 Elsevier Science S.A.

Keywords: Separation; Actinides; Extraction chromatography; Bone

1. Introduction

The wide use of nuclear power and nuclear waste disposal plans have made the public increasingly concerned about health hazards of radionuclide pollutants in nature. Actinides are considered the most toxic radionuclides in the environment, as most of them are α active and have long half-lives. These elements are enriched through numerous food chains to humans and, even in small amounts, can cause health hazards [1]. Accurate, precise, reliable and rapid analytical methods with low detection limits are therefore needed to determine the concentrations of actinides in environmental samples.

Since the Manhattan project in the United States during the Second World War many methods for the determination and separation of actinides have been developed. Most of them are highly time consuming and produce variable but usually large amounts of organic solvent and strong acid wastes. The activity levels of radionuclides in environmental radiochemistry are often very low resulting in the need for large sample sizes. In many cases the sample matrices are complicated, and long separation procedures are needed before the samples are ready for activity measurements.

The aim of this work was to develop a rapid and simple method for actinide analysis in different environmental samples with low amounts of problematic wastes. Sequential separation of actinides using extraction chromatography was tested and modified for the modern analytical needs of advanced radiochemical laboratories. The method was used for Th, U, Pu and Am analysis from a future bone ash reference material prepared by the National Institute of Standards and Technology (NIST).

2. Method development

Extraction chromatography is a combination of liquid–liquid extraction and chromatographic technique. Highly specific resins have added interest in extraction chromatography as a separation method for actinides in environmental samples. Horwitz and co-workers have developed special extraction chromatographic resins for the separation of radionuclides from different sample materials. These resins comprise different organic stationary phases

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sorbed on inert polymeric supports [2–4]. They have already been successfully used in many laboratories for the separation of radionuclides from different sample matrices [5–8]. The extraction chromatographic resins used in this work were UTEVA Resin® and TRU Resin®, commercially available from Eichrom Industries, Inc., USA.

2.1. Separation procedure

Tracer experiments with ^{229}Th, ^{238}U, ^{239}Pu, ^{241}Am and ^{244}Cm were performed to optimise the separation procedure for these nuclides and check the recoveries and purity of each actinide fraction. The method used is based on the procedures published by Eichrom Industries for customer use [9,10]. These experiments resulted in the separation procedure shown in Fig. 1.

UTEVA Resin® was used to separate Pu, Am, and Cm from Th and U. The separation of Pu from Am and Cm was performed using TRU Resin®. The activities were measured with α-spectrometry. Americium-241 and ^{244}Cm were measured together due to the sufficiently different α energies of these nuclides, 5.49 and 5.81 MeV, respectively. Neodymium fluoride coprecipitation [11] and electrodeposition from ammonium sulfate media [12] were used for sample preparation.

The tracers were added to a sample of 5 ml of 3 M HNO_3–0.5 M $Al(NO_3)_3$. Aluminium nitrate is used for enhancing the separation procedure. Some anions such as

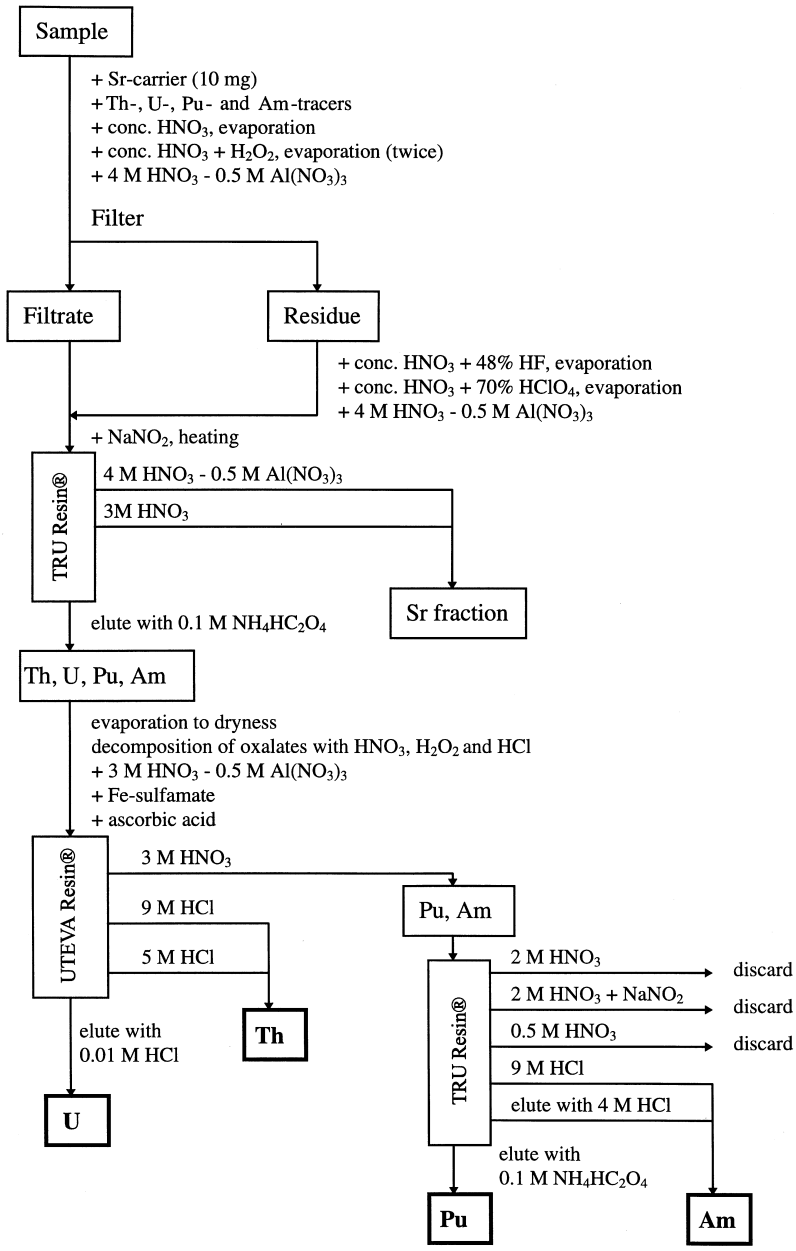

Fig. 1. The scheme for the separation of Th, U, Pu and Am from a bone ash matrix.

PO_4^{3-}, SO_4^{2-} and $C_2O_4^{2-}$ have strong effects on actinide retention on the resins. Aluminium(III) will complex the anions present which will decrease their interfering effect on the separation. Raising the acid concentration will have the same effect because protonation also decreases the anion concentration in the sample [2,8]. Ferrous sulfamate was used to reduce plutonium to Pu(III) and ascorbic acid to keep Fe in the +2 state. The sample was then loaded onto a UTEVA Resin® column preconditioned with 5 ml of 3 M HNO_3. The trivalent nuclides, Pu, Am and Cm, run through the column in 3 M HNO_3. After converting the column to chloride system by adding 4 ml of 9 M HCl, Th was eluted with 20 ml of 5 M HCl. Some Th might elute with 9 M HCl, and consequently the two HCl fractions were combined for Th analysis. U was eluted with 15 ml of 0.01 M HCl. Gravity flow rates of maximum 0.5 ml min^{-1} were used in all experiments.

The Pu/Am/Cm fraction was loaded onto a TRU Resin® column, which had been preconditioned with 5 ml of 2 M HNO_3. Then 5 ml of 2 M HNO_3–0.1 M $NaNO_2$ was passed through the column to oxidise Pu(III) to Pu(IV). Subsequently, 5 ml of 0.5 M HNO_3 and 3 ml of 9 M HCl were used to convert the column to chloride system, after which Am and Cm were eluted with 20 ml of 4 M HCl and Pu with 10 ml of 0.1 M $NH_4HC_2O_4$. As with Th analysis, the two HCl fractions were combined for Am and Cm measurements.

2.2. Results and discussion

The mean recoveries for the separation procedure for the actinides concerned are presented in Table 1. Results from both sample preparation methods for counting are included. These mean values cover four to 17 replicate analyses for each nuclide. The recoveries for Th, Am and Cm when electrodeposition was used for sample preparation varied in the ranges 58–107, 51–100 and 40–84%, respectively. For U and Pu the variation was noticeably lower. For comparison, some U samples were also measured with ICP-AES where no sample preparation for counting was needed. The mean value for these eight experiments was 76±4% (1 s).

Coprecipitation was chosen for Th, Am and Cm as a sample preparation method for the final procedure. In those experiments where electrodeposition was used for Am and Cm, the recoveries were variable while the coprecipitation method gave higher recoveries with less variation. This was due to the loss of organic extractant from the column during the elution which lowered the electrodeposition recoveries. When electrodeposition was used to prepare the Th samples for α-spectrometry 4–6% of the U added to the sample was found in the Th fraction. Pure Th fractions were achieved using the coprecipitation method. Some organic extractant was also lost during Th elution but the effect was worse with the TRU Resin® than with the UTEVA Resin®. Decomposition of the organic residues with 1–2 ml of 65% HNO_3, 36% HCl and 70% $HClO_4$ before the coprecipitation eliminated this problem completely. Electrodeposition was chosen for U and Pu due to higher recoveries and slightly better resolutions. No crossing over of nuclides other than U to the Th fraction was observed.

When determination of Th and Cm concentrations from the same sample is needed some problems can be anticipated. Thorium-229, used as a tracer here, decays to ^{225}Ac with a half-life of 7340 a. Ac follows Am and Cm in the separation procedure used. As the α energies of ^{244}Cm and ^{225}Ac are almost identical, 5.81 and 5.83 MeV, respectively, their peaks overlap in the α spectrum. A second measurement of the Am and Cm samples 2–4 months after the separation gave pure peaks also for ^{244}Cm because of the short half-life of ^{225}Ac (10 days).

Americium and Cm have similar chemical behaviour and a common tracer is often used in the separation procedures for these nuclides [13–15]. The Cm recoveries in all these experiments were, however, about 10% lower than the Am recoveries. This phenomenon was also reported by Ham who found that Cm recoveries were only 80% of the Am recoveries [16]. This might be explained by stronger effects of small chemical differences of these two nuclides on highly selective extraction chromatographic resins than on resins and reagents used in traditional actinide separation methods, e.g. ion exchange.

Table 1
Mean values for separation recoveries of Th, U, Pu, Am and Cm using extraction chromatography and coprecipitation and electrodeposition as the sample preparation methods

Nuclide	Coprecipitation recovery (%)	Electrodeposition recovery (%)
^{229}Th	81±3	88±23
^{238}U	67±7	78±4
^{239}Pu	70±6	94±8
^{241}Am	85±6	78±20
^{244}Cm	73±6	66±19

The uncertainties correspond to the standard deviation of the means of the individual analysis at the 1-s level.

3. Bone ash analysis

The separation procedure was successfully applied for bone matrix. NIST had prepared bone ash samples to be used as standard reference materials after certification of some radionuclide concentrations. The nuclides of interest were ^{90}Sr, ^{210}Pb, ^{210}Po, ^{226}Ra and actinides. The material consisted of 4.3% actinide-contaminated human bone ash and 95.7% diluent bovine bone ash. The activity levels were 1 mBq g^{-1} of sample for Th, U and Pu and 10 mBq g^{-1} of sample for Am. The material was carefully ashed and homogenised, and five 15-g samples were delivered to each participating laboratory [17].

3.1. Separation procedure

Some improvements and modifications were done to the separation procedure described earlier. Due to the limited quantity of sample material, the actinides and Sr were analysed from the same sample. A 3–5-g sample from each bottle was analysed for ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{238}U, ^{238}Pu, ^{239,240}Pu and ^{241}Am using α-spectrometry, and ^{90}Sr using liquid scintillation counting. The scheme for actinide separation from bone ash is presented in Fig. 1. The separation procedure for Sr is described elsewhere [18].

The bone ash was dissolved nearly completely by repeated digestions and evaporations with boiling 65% HNO_3 (5–10 ml) together with 30% H_2O_2 (1 ml) additions. After the last digestion, the evaporated sample was dissolved in 10 ml of boiling 4 M HNO_3–0.5 M $Al(NO_3)_3$. A small insoluble residue was filtered off and digested with 1–2 ml of boiling 65% HNO_3, 48% HF and 70% $HClO_4$ to solubilize any actinides and Sr present. After evaporation, this sample was dissolved in 1–2 ml of boiling 4 M HNO_3–0.5 M $Al(NO_3)_3$, a possible insoluble residue was again filtered, and the two filtrates were combined. With this solution the separation of actinides from Sr was performed using a preconditioned TRU Resin®. The oxidation state of Pu was adjusted to +4 by adding 100 mg of $NaNO_2$ and heating. Strontium and Ca passed through the column in 4 M HNO_3, while the actinides were retained and eluted afterwards as a group with 20 ml of 0.1 M $NH_4HC_2O_4$. The oxalates were decomposed by boiling the sample with 1 ml of 65% HNO_3 and five drops of 30% H_2O_2, and then 1–2 ml of 65% HNO_3 and 36% HCl before loading the sample into a UTEVA Resin® column. The sequential separation of the actinides was performed as described above (see Fig. 1).

Table 2
The recoveries of five replicate analysis of Th, U, Pu and Am from the future bone ash reference material

Sample	^{229}Th (%)	^{232}U (%)	^{242}Pu (%)	^{243}Am (%)
1	81±3	89±3	85±3	71±1
2	74±3	85±3	73±3	78±1
3	78±3	89±3	86±3	75±1
4	80±3	88±3	79±3	80±1
5	78±3	78±3	81±3	77±1
Mean	78±2	86±5	81±5	76±4

The uncertainties presented for samples 1–5 are the total uncertainties of individual analysis at the 1-s level. The uncertainties for the mean values are the standard deviations of the five values at the 1-s level.

3.2. Results and discussion

Pure α spectra were achieved for all the nuclides concerned, as shown in Fig. 2. The average resolution was about 50 keV. The detection limit determined as presented by Currie [19] for 5 g of bone ash, with a count time of 4 days, was 0.1 mBq.

Leaching of the organic phase from the column with 4–9 M HCl caused some problems in the sample preparation of Th and Am, even when NdF_3 coprecipitation was used. This was overcome by decomposition of the residues using strong mineral acids, HNO_3, HCl, HF and $HClO_4$, before the precipitation. The recoveries of five replicate analysis of Th, U, Pu and Am from the future bone ash reference material are presented in Table 2.

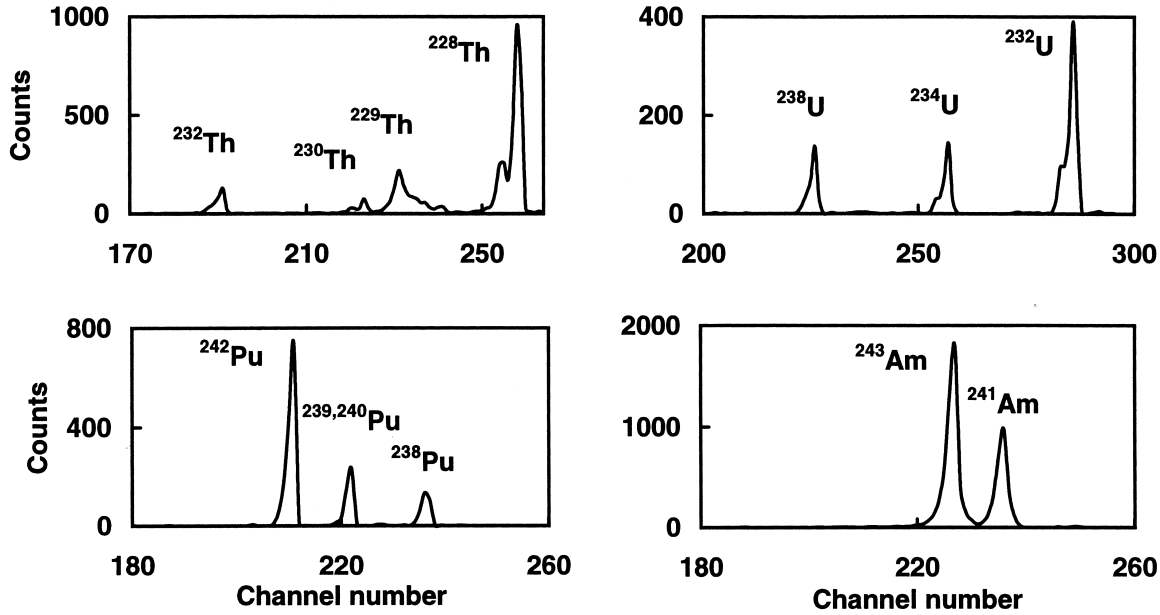

Fig. 2. Alpha spectra for Th, U, Pu and Am separated from a bone ash sample. Count time was 4 days.

4. Conclusions

Separation of actinides from environmental samples, especially in the trivalent state has been a complicated and time-consuming task. The chromatographic resins for extraction have given an opportunity to develop fast and simple separation methods for many radionuclides. The dissolution of the sample, and the separation of Th, U, Pu and Am from a bone ash matrix, could be performed in 1.5 working days with the method presented here. According to Cadieux and Reboul, flow rates of 2–4 ml min^{-1} could be used by using vacuum systems on the bottom of the columns without degrading the separation [5]. This would make the separation procedure even faster.

Lower detection limits are reached by analysing actinides and Sr from a single large sample when the quantity of sample material is limited. This also decreases the required time for sample dissolutions.

HCl (4–9 M) was used for the elution of the Am/Cm and Th fractions. Some bleeding of the organic extractant from the columns was observed during these separation steps. These organic residues could be destroyed by hot digestion with 1–2 ml of 65% HNO_3, 36% HCl, 48% HF and/or 70% $HClO_4$, thereby eliminating the interferences in the sample preparation by the coprecipitation method.

This method can be easily modified for actinide analysis of different low activity level sample matrices.

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