

Actinide separations using extraction chromatography

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Introduction

Radiochemistry has always been and still is a crucial tool in the field of radionuclide determination; this holds particularly in the case of alpha and beta emitters. In environmental samples the concentrations of actinides are very low. Therefore special chemical procedures are needed for preconcentration and separation of these nuclides from different matrices and from each other.

Separation methods based on extraction chromatography have become increasingly popular in radiochemical analysis. This is due to their simplicity, rapidity and the savings in reagent and waste disposal costs compared to the traditional separation methods based on, e.g., anion exchange and liquid-liquid extraction.

In solvent extraction, an ion is transferred from the aqueous phase to the organic phase. Extraction chromatography is a combination of liquid/liquid extraction and the chromatographic technique. The mobile phase is an aqueous solution and the stationary phase is an organic solution loaded onto an inert support. In the majority of cases the compounds to be analysed, flowing through the column with the eluent, form an extractable species at the boundary of the aqueous and organic phases. The transfer of the species between the phases happens simultaneously with the complex formation or association processes (Siekirsky *et al.*, 1975).

Philip Horwitz and co-workers have developed special extraction chromatographic resins for the separation of actinides from different sample matrices. They are commercially available from Eichrom Industries, Inc., U.S.A. These resins are comprised of different organic stationary phases sorbed onto inert polymeric supports.

The resins used in this work were UTEVA Resin, TRU Resin and TEVA Resin. The UTEVA Resin was developed for the separation of uranium and tetravalent actinides from different matrices. It consists of diamyl amyolphosphonate sorbed onto an inert polymeric support called Amberlite XAD-7 (Horwitz *et al.*, 1992).

The TRU Resin is used for separation of transuranic elements. It consists of octyl(phenyl)-*N,N*-diisobutylcarbamoymethylphosphine oxide (CMPO) dissolved in tributyl phosphate (TBP) supported on an inert substrate Amberlite XAD-7. In addition to sequential separation of actinides the TRU Resin can be used for group separation of actinides from large amounts of impurities and other radio-isotopes, e.g. Sr (Horwitz *et al.*, 1990).

The TEVA Resin will strongly adsorb all tetravalent actinides. This resin is comprised of an aliphatic quarternary ammonium salt called Aliquat 336N supported on Amberlite XAD-7 (Horwitz *et al.*, 1993).

A method has been developed for the separation of Th, U, Pu, and Am, all from a single sample (Pilviö *et al.*, 1998; 1999). However, in environmental samples the natural radionuclides of Th and U are often present in far greater quantities than Pu, and Am, which are of artificial origin. An average concentration of natural U in seawater is 3.3 ppb, corresponding to 41 mBq.l⁻¹ (Ivanovich *et al.*, 1982), while Pu and Am concentrations in most seas are orders of magnitude less. (Sholokovitz *et al.*, 1983; 1989). Th and U are also enriched in certain minerals, compared to Pu and Am which originate only from man-made sources. (Hardy *et al.*, 1982; Eisenbud, 1987). Therefore two separate methods are also presented: first for the determination of Pu and Am and the second for Th (and U). These methods were adapted and optimised from previously published methods (Pilviö *et al.*, 1998; 1999; Maxwell, 1997) and applied to (i) the determination of Pu and Am in diluted MOX material and (ii) the analyses of ²³⁰Th from soil. The activities of the samples were determined using alpha spectrometry.

I Analytical methods

Separation of Th, U, Pu and Am from bone ash

Bone is a critical organ for accumulation of many radionuclides including ^{90}Sr and actinides. The National Institute of Standards and Technology (NIST) prepared bone ash samples in view of producing a standard reference material. The determination of the actinide concentration in this material was performed using TRU Resin for the group separation of actinides from Sr and other major impurities, e.g. Ca and phosphates. After this UTEVA and TRU resins were used for the sequential separation of Th, U, Pu and Am. The source preparation for alpha spectrometry was done by electrodeposition (Talvitie, 1972) (U and Pu) and NdF_3 coprecipitation (Hindman, 1983) (Th and Am). The separation scheme for the method used is presented in Figure 1. The details are presented elsewhere. (Pilviö *et al.*, 1998-1999).

Separation of Pu and Am from MOX

The separation of Pu and Am from a diluted MOX material was performed using TEVA and TRU Resins, according to a procedure published earlier. (Maxwell, 1997; Pilviö *et al.*, 2000). The source preparation for alpha spectrometry was performed by NdF_3 coprecipitation. (Hindman, 1983). The scheme for the separation of Pu and Am is presented in Figure 2.

Separation of Th from soil

Thorium-230 concentrations in soil samples were analysed using a procedure shown in Figure 3. Th was coprecipitated with $\text{Fe}(\text{OH})_3$ and the sample loaded into an anion exchange column in 8 M HNO_3 . Th was eluted from the column with 37% HCl. The chemical separation of Th from the impurities and other radionuclides still present in the sample was performed using UTEVA Resin columns.

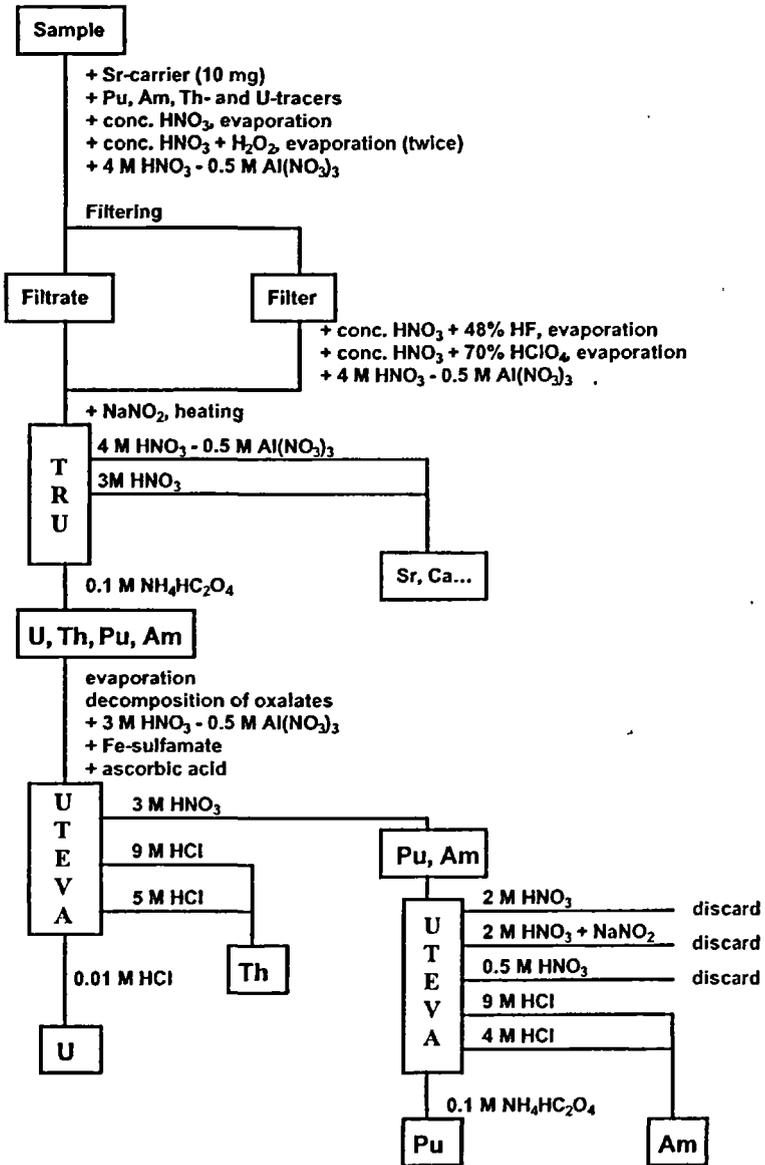


Figure 1
Scheme for the separation of Th, U, Pu and Am from bone ash.

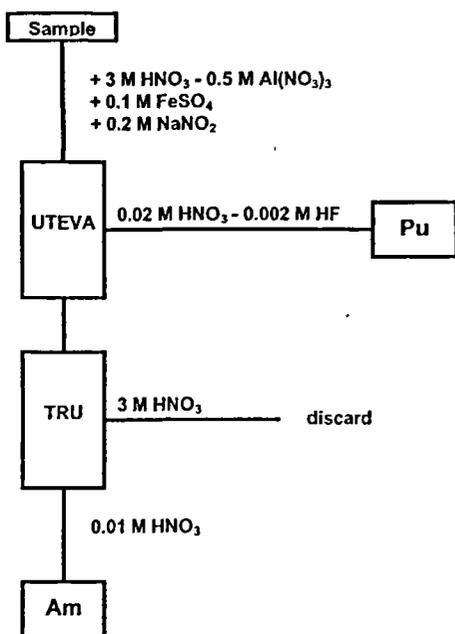


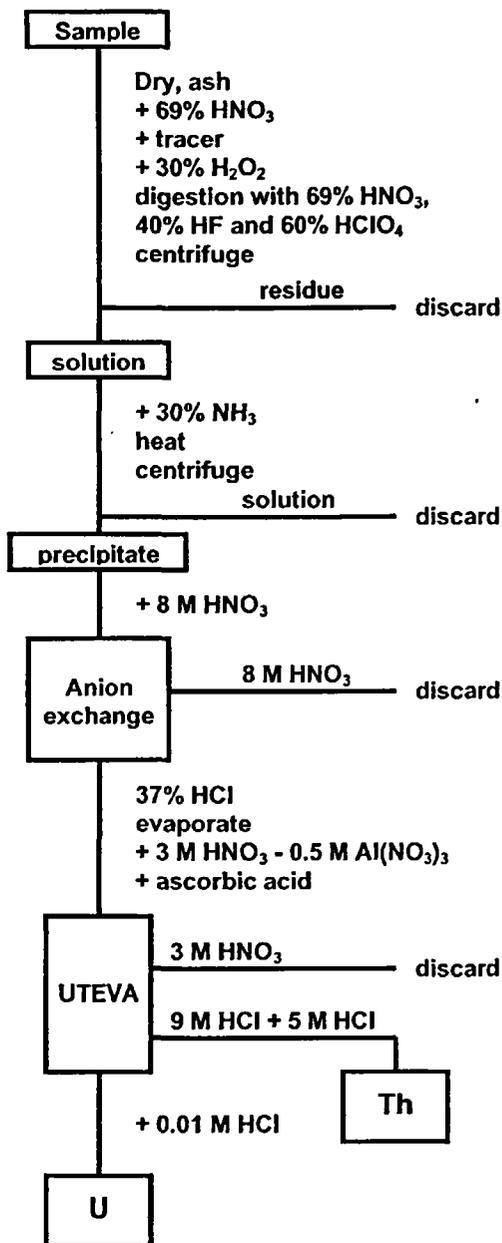
Figure 2
Scheme for the
separation of Pu
and Am from MOX
material.

If requested U concentrations can also be determined using this method. The source preparation for alpha spectrometry was performed by NdF₃ coprecipitation. (Hindman, 1983).

Results and discussion

Pure alpha spectra were achieved for all the nuclides concerned. The summary of the recoveries for the actinides determined in bone ash, MOX material and soil are presented in Table 1. The recoveries were all high. The variations in the Th results were due to large differences in the composition of the 19 soil samples analysed. The measured actinide concentrations in bone ash agreed well with the NIST certified values, as shown in Figure 4.

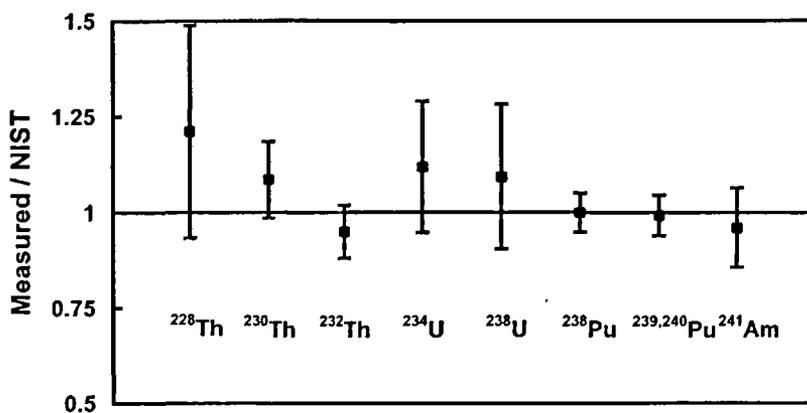
Figure 3
Scheme for
the separation
of Th from soil.



Sample	Th	U	Pu	Am
Bone ash	89 ± 3	86 ± 5	81 ± 5	87 ± 4
Soil	75 ± 20			
MOX material			94 ± 4	100 ± 2

■ Table 1

A summary of the recoveries for the determinations of Th, U, Pu and Am in bone ash, Pu and Am in MOX material and Th in soil.



■ Figure 4

Ratios of the measured activity concentrations for Th, U, Pu and Am isotopes to the NIST certified values. The uncertainties are shown at the 1 s level.

Hydrochloric acid (4-9 M) was used for the elution of the Th and Am fractions in two of the methods. 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% HNO₃, 37% HCl, 48% HF and/or 70% HClO₄, thereby eliminating the interferences in the sample preparation by the coprecipitation method.

The separation of Pu and Am from MOX material was performed using TEVA and TRU Resins. Therefore the oxidation state of Pu

needs to be quantitatively adjusted to Pu(IV). For this purpose several redox reagents were tested. A commonly used agent is NaNO_2 together with heating. However, our experiments showed that an addition of 100 mg NaNO_2 to the sample and heating it up to boiling for 30 minutes left up to 10% of the Pu in the oxidation state Pu(III) and quantitative separation from Am(III) was not achieved. Increasing the amount of NaNO_2 only reduced the Am recovery.

H_2O_2 has also been used for the redox adjustment of Pu to Pu(IV) before separation of Pu from U with UTEVA Resin. (Apostolidis *et al.*, 1998). An addition of 350 ml of 30% H_2O_2 to a 5 ml sample, heating at 80°C for 25 minutes and cooling the sample for 10 minutes left up to 6% of the Pu to Pu(III).

A quantitative redox adjustment was achieved when Fe(II) was first used to reduce all the Pu present to Pu(III). After this NaNO_2 was added to oxidise Pu(III) to Pu(IV). (Maxwell, 1997). These reactions are rapid in room temperature and no heating or cooling is needed.

Th adsorbs very easily onto surfaces. There are many individual steps involved in the Th determination and strong adsorption onto e.g. the glass beaker walls may occur during the evaporation steps. To prevent this, 1 ml of NaHSO_4 solution ($50 \text{ mg}\cdot\text{ml}^{-1}$) was added to the sample before the last evaporation. In addition, all glassware used was cleaned by exposing it to 65% nitric acid fumes for a minimum time of 5 hours between analyses, to avoid cross contamination. (Holmes *et al.*, 2000).

Conclusions

The methods presented gave high recoveries and showed good reproducibility for Th, U, Pu and Am determinations. The method for the determination of Pu and Am has an advantage compared to previous extraction chromatography based methods, i.e. that no bleeding of organic residues from the column was observed because diluted acids were used for the elution of these radionuclides.

Quantitative redox adjustment of Pu to Pu(IV) was only achieved when Fe(II) was used to reduce Pu to Pu(III) and NaNO₂ to oxidise Pu(III) to Pu(IV). Both NaNO₂ and H₂O₂, together with heating, left part of the Pu to Pu(III).

These separation procedures can easily be adapted to different sample matrices by using modern or traditional digestion methods before loading the samples to the columns.

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