

One step ion exchange process for the radiochemical separation of americium, plutonium and neptunium in sediments

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A radiochemical separation is presented for americium, plutonium and neptunium from sediment samples by using an unique anionic exchange process. An oxidation-reduction step was introduced in the classical procedure of the radiochemical determination of transuranic elements in order to control the valence of the separated elements.

Introduction

The determination of low level radioactivity of α emitting transuranium elements is of great interest from both radiological and waste disposal viewpoints. The measurement of plutonium and americium activity concentrations by α -spectrometry after radiochemical separation is well described by other authors^{1–4} but methods which include the determination of neptunium are very sparse.^{5,6} However, neptunium 237 is present in the environment as a result of global (nuclear weapon tests) and local fallout (nuclear fuel reprocessing plants). Due to its long half-life ($2.14 \cdot 10^6$ y) this α emitter is one of the most important radionuclide remaining after long term storage of nuclear wastes. Moreover neptunium has a greater mobility in soils compared to plutonium and a greater uptake by vegetables compared to plutonium and americium, which implies a possible movement through the food chain.⁷

The aim of this study was to integrate the determination of neptunium into the sequential separation scheme allowing to measure other transuranium elements like plutonium, americium and curium. An oxidation-reduction process introduced before the elution on an anionic column allows the separation of the three phases: americium-curium, plutonium and neptunium by a one step ion exchange process.

This radiochemical separation was performed with a mixed solution of $^{243}\text{Am}+^{242}\text{Pu}+^{237}\text{Np}$. Radiochemical yields, for the three actinides, were higher than 65%.

In order to take into account the possible interferences of the other radionuclides present in the environment, experiments were also made with a sediment sample distributed by the International Atomic Energy Agency (IAEA) for an intercomparison exercise.

Experimental

All reagents used were of analytical grade and solutions were prepared with deionised water. Anionic

resins were: Bio Rad AGMP1 and Dowex 1 \times 4 100–200 mesh in chloride form and cationic resins: Aldrich Dowex 50W \times 8 100–200 mesh in chloride form.

Procedure

Classically the radiochemical separation involves a preconcentration step^{1,2} and two extraction procedures: the first one in order to separate the fraction containing both americium and curium, the second one in order to separate the plutonium before electrodeposition and counting by α -spectrometry. The modified procedure, proposed for the analysis of the three actinide elements in sediment samples, is presented below.

Organic matter is eliminated by calcination. After the addition of yield determinants: ^{242}Pu ($T_{1/2}=3.76 \cdot 10^5$ y) for plutonium isotopes, ^{243}Am ($T_{1/2}=7.38 \cdot 10^3$ y) for americium and curium isotopes and ^{235}Np ($T_{1/2}=1.085$ y) or ^{239}Np ($T_{1/2}=2.355$ d) for neptunium isotopes, the sediment is leached with 8M HNO_3 . Transuranium elements are then co-precipitated with ferric hydroxide in ammonia medium.

Before passing the sample through the anionic column in HNO_3 medium, we introduced an oxidation-reduction step (Fig. 1). The precipitate was dissolved in 1M HNO_3 + hydrazine sulphate (reduction step). This solution was then evaporated to near dryness and, after dissolution of the residue in 8M HNO_3 , $\text{NaNO}_2+\text{H}_2\text{O}_2$ were added (oxidation step). The sample was then passed through the column: americium and curium were in the effluent, plutonium and neptunium were retained. An elution with 10M HCl allowed the separation of interfering thorium. The elution of plutonium was then made with a mixture 10M $\text{HCl}+\text{NH}_4\text{I}$ (or HI) and neptunium was eluted with 4.5M $\text{HCl}+\text{HF}$ (Fig. 2).

After evaporation and oxidation of iodide by H_2O_2 in order to form easily eliminated iodine, plutonium isotopes were electrodeposited in sulphuric acid-ammonia media at pH 2.4, on a stainless-steel disk, with a current of 1 A applied for 1.5 hour. Neptunium was electrodeposited under the same conditions after evaporation.

The americium-curium fraction was extracted and electrodeposited as described in precedent papers.^{1,2,8}

IAEA intercomparison sample

This procedure was tested by analysing a marine sediment sample distributed by the Marine Environment Laboratory (MEL - IAEA) in Monaco for intercomparison purpose. The sediment, collected in July 1992 in the Bothnian sea (Baltic sea) and coded IAEA-300, was designed for measurements of artificial and natural radionuclides. Recommended values with confidence interval ($\alpha=0.05$) were given for ²³⁹⁺²⁴⁰Pu and ²⁴¹Am; only one information value was given for ²³⁸Pu.⁹

Alpha-spectrometry

Alpha spectra were measured with a dual alpha spectrometer EG & G Ortec 576A equipped with boron implanted silicon detectors of active area: 450 mm² and

alpha resolution (FWHM) 20 keV at 5.47 MeV. Pulses were analysed with a multichannel buffer analyser (Spectrum Master Ortec 919).

Results and discussion

The interest of this procedure was to extract and separate, using the same anionic column, the three transuranium elements: plutonium, americium and neptunium. In order to develop it, we have carried out the oxidation-reduction and the separation on column steps with a mixed solution of ²⁴³Am+²⁴²Pu+²³⁷Np.

The aim of the oxidation-reduction step is to have plutonium and neptunium in the Pu(IV) and Np(VI) oxidation state so that they be retained together on the column. The hydrazine sulphate in 1M HNO₃ reduces Pu(IV,V,VI) and Np(IV,V,VI) to oxidation states Pu(III) and Np(IV). Americium stays in Am(III) form. After evaporation, H₂O₂ and NaNO₂ in 8M HNO₃ media oxidise only the Pu in Pu(IV) form. So, at the end of this step, the researched transuranium elements are in the Am(III), Cm(III), Pu(IV) and Np(IV) oxidation states.

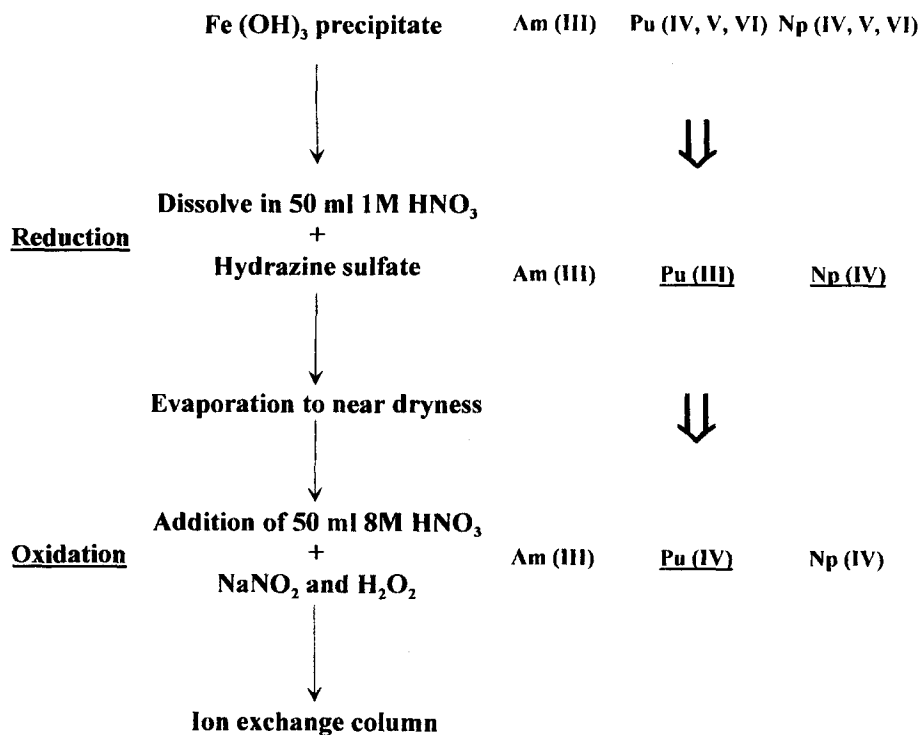


Fig. 1. New oxidation-reduction step introduced before the elution on anionic column in order to obtain the respective oxidation states Am(III), Pu(IV) and Np(IV)

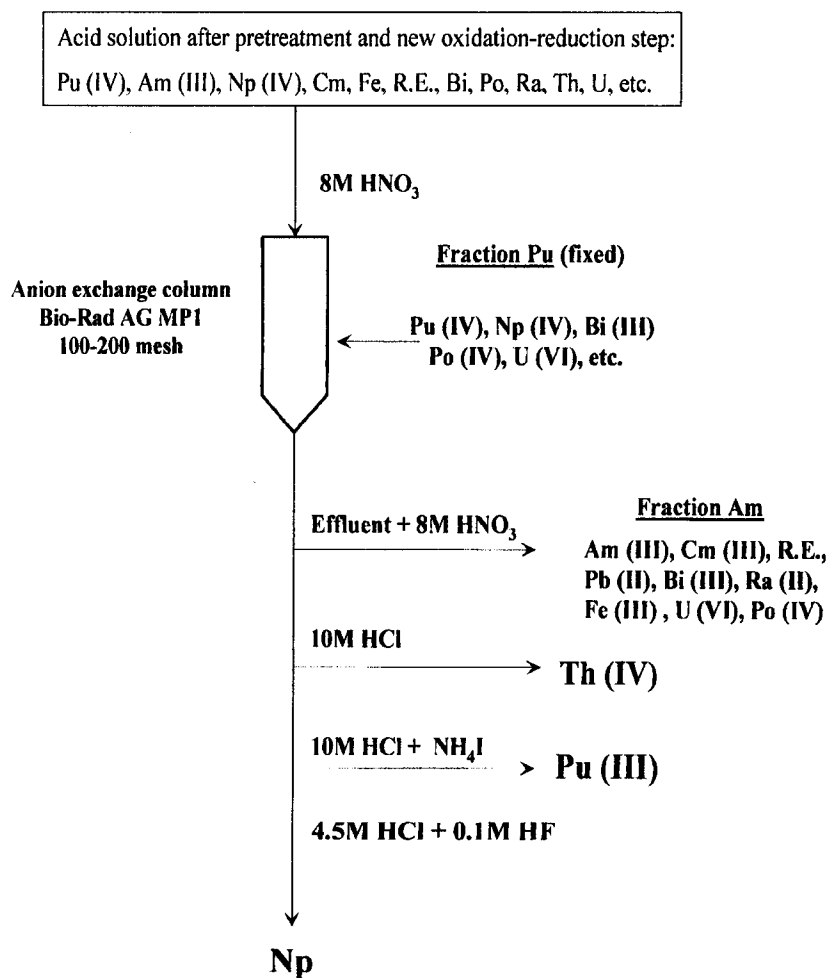


Fig. 2. Radiochemical separation of Am, Pu and Np

 Table 1. Chemical yields obtained with NaNO₂ added in 1M HNO₃, before the evaporation (1), with NaNO₂ added in 8M HNO₃ (2)

	Chemical yield (%)	
	¹ NaNO ₂ in 1M HNO ₃	² NaNO ₂ in 8M HNO ₃
²⁴² Pu	67±4	89±5
²⁴³ Am	69±7	83±9
²³⁷ Np	65±6	75±8

Table 2. Activity concentrations measured in the sediment sample IAEA 300. Comparison with the IAEA intercomparison exercise results

Nuclide	Activity, Bq/kg	
	Measured activity*	IAEA values ⁹
²³⁹⁻²⁴⁰ Pu	3.58±0.13	3.55 (3.44-3.65)
²³⁸ Pu	0.41±0.04	0.15 (0.1-0.6)
²⁴¹ Am	1.40±0.18	1.38 (1.2-1.5)

* Average activity of three analysed samples.

For the next step of the anion exchange process, the adsorption behaviour of two different commercial resins: AGMP1 (macroporous) and Dowex 1×8 (crosslinkage: 8%), has been studied. It became apparent that AGMP1 was superior to the other resin for this process. During elution with the sample in nitric solution through the anionic resin, Am(III) and Cm(III) pass through the column while Pu(IV) and Np(IV) are retained. Thorium is eliminated by elution with 10M HCl while Pu(IV) and Np(IV) form anionic complexes and remain consequently adsorbed on the anion-exchange resin. Pu(IV) is then reduced to Pu(III) with HI or NH₄I and, while the anionic chloride complex of Np(IV) is always adsorbed on the anion exchange resin, the Pu(III) passes through the column. Neptunium is then desorbed by elution with the 4.5M HCl+0.1M HF mixture.

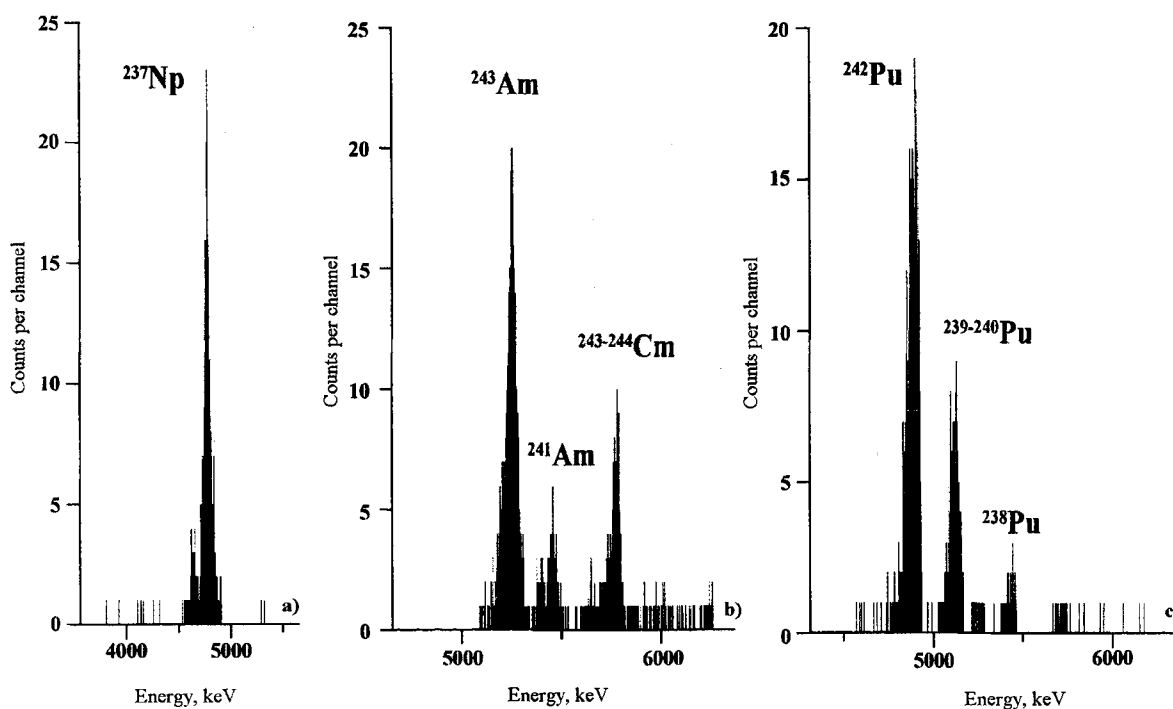


Fig. 3. Alpha-spectra of neptunium (a), americium (b) and plutonium (c) isotopes measured after the radiochemical separation from the IAEA 300 sediment sample

Results obtained for two different experiments are presented on Table 1. In experiment 1, for which the chemical yields are lower, sodium nitrite is added in 1M HNO₃ before evaporation while, in experiment 2, NaNO₂ is added in 8M HNO₃. Yields obtained with the second procedure are about twenty per cent better.

For each sample, 3 alpha-spectra were measured: one for counting the plutonium isotopes, the other by counting the isotopes of americium and curium and the third one for ²³⁷Np.

An intercomparison measurement was made by applying these modifications in the radiochemical analysis of the IAEA sample. The three spectra obtained after radiochemical separation for the IAEA 300 sample are presented in Fig. 3. These spectra present the characteristic peaks of the analysed elements without impurities. This shows that the oxidation-reduction step added to the classical procedure does not improve the selectivity of the method. Yields obtained are good. Results obtained for activity concentrations of ²³⁸Pu, ²³⁹⁺²⁴⁰Pu and ²⁴¹Am are presented in Table 2 and compared to those published after the IAEA intercomparison exercise. Results obtained are always in

the confidence interval defined by the IAEA. For neptunium 237, IAEA did not give any results, so we could only test our procedure and show that the modifying steps do not improve the procedure of radiochemical separation of americium and plutonium and that the chemical yield obtained for neptunium is good. In this experiment, it was 74%.

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