



# Sequential determination of Am, Cm, Pu, Np and U by extraction chromatography

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## ABSTRACT

Environmental contamination by artificial radionuclides and the evaluation of their sources require precise isotopic analysis and accurate determination of actinide elements above all plutonium and americium. These can be achieved by alpha spectrometry or by inductively coupled plasma mass spectrometry (ICP-MS) after chemical separation. In the present work, a simple, rapid method has been developed for the sequential separation of actinide elements from aqueous solutions and their determination by alpha spectrometry. Extraction chromatography was applied to the separation of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{239+240,238}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{238,235,234}\text{U}$  using microporous polyethylene supporting tri-*n*-octylamine as the stationary phase and hydrochloric acid with and without reducing agents as the mobile phase. Actinide in 9 M HCl solution is introduced into the anion exchange column; Pu (IV), Np (IV) and U(VI) are retained on the column while Am (III) and Cm passed through. Pu is eluted first, reductively, after which, Np and then U are eluted. The method can be applied to all aqueous solutions which do not contain strong complexing or precipitation agents for the elements considered.

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## 1. Introduction

A number of radionuclides have been released into the environment by nuclear weapon testing, nuclear facilities and nuclear accidents. Among these radionuclides, the actinides, particularly  $^{237}\text{Np}$  ( $T_{1/2} = 2.14 \cdot 10^6\text{y}$ ),  $^{239}\text{Pu}$  ( $T_{1/2} = 2.41 \cdot 10^4\text{y}$ ), and  $^{240}\text{Pu}$  ( $T_{1/2} = 6.56 \cdot 10^3\text{y}$ ), are important isotopes from the viewpoint of their extremely long half-lives and their radiological toxicities [1]. Determination of the concentration and isotope ratios of actinides is required in environmental monitoring, nuclear safeguards and nuclear forensic studies. For instance, plutonium is the most widespread element among the transuranium elements and it is represented in the irradiated nuclear fuel by five isotopes ( $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ , and  $^{242}\text{Pu}$ ). Knowledge of the isotopic composition of natural and artificial actinides is of great interest for evaluating their source (nuclear power plant accidents, nuclear weapons tests or weapons with depleted uranium) [2].

Radiometric approaches such as  $\alpha$ -spectrometry or liquid scintillation are well established for determination of most actinide isotopes especially those having half-life of less than 1000 years and are employed as routine techniques.

Liquid scintillation counting (LSC) coupled with selective solvent extraction is reasonably quick and gives reliable information on total uranium activity concentration and, to some extent, when  $^{235}\text{U}$  concentration is negligible, on  $^{234}\text{U}$  and  $^{238}\text{U}$  contents and ratios [3]. Beta emitting, as  $^{241}\text{Pu}$ , can be easily measured by LSC.

Alpha spectrometry is one of the oldest nuclear techniques that provide information about the composition of the alpha emitting radionuclides in various sample types. It can furnish complete isotopic information about  $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{234}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ , and radioactive tracers as  $^{242}\text{Pu}$ ,  $^{236}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{232}\text{U}$  and  $^{236}\text{U}$  but the beta emitting, as  $^{241}\text{Pu}$ , cannot be detected by this technique. Its major advantage is the relative low price of the equipment and the high sensitivity due to the low background and the high selectivity for alpha particles against other types of radiation. Very low detection limit can be achieved by alpha spectrometry. A limitation of this technique is that usually only the sum of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activity can be determined due to similar  $\alpha$  energies (5.24 MeV and 5.25 MeV, respectively). Implanted passivated junction silicon detectors and special spectra deconvolution software were proposed two decades ago to improve  $\alpha$  spectrometry resolution. However, this method did not find wide application for the measurement of  $^{239}\text{Pu}/^{240}\text{Pu}$  activity ratios because of its complexity [2].

When better resolution or higher sensitivity is required, mass spectrometry system offers a better choice [4]. Mass spectrometry (MS) is a highly sensitive and the newest developed non-radiometric technique. It is well-suited to measure the concentration of every actinide; however, due to the high costs required for instruments which measure the less abundant isotopes as  $^{234}\text{U}$  and  $^{235}\text{U}$  and for their maintenance, this method is not widely used for routine analysis [5].

Alpha spectrometry is, therefore, the most frequently used technique for routine actinide determination. Its major disadvantage originates from the necessity of the complete separation of alpha emitters from the sample components in order to obtain a very thin alpha source [6,7]. Radiochemical procedures, often fairly sophisticated ones, have to be applied to the samples to remove major and minor components.

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The aim of the present study is to develop a highly selective, simple and cheap radiochemical separation technique for the simultaneous measurement of the  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{239+240,238}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{238,235,234}\text{U}$  by alpha spectrometry.

The determination of these radionuclides by alpha spectrometry presents the following drawbacks [8,9]:

- The basic spectrometric interferences:  $^{237}\text{Np}$  and  $^{234}\text{U}$  have the same alpha energies (from 4.64 to 4.79 MeV);  $^{241}\text{Am}$  (5.44–5.49 MeV) completely overlapping with  $^{238}\text{Pu}$  (5.46–5.50 MeV).
- The necessity to add a radioactive yield tracer to calculate the final chemical yield sample by sample:  $^{242}\text{Pu}$  ( $T_{1/2}$ :  $3.8 \cdot 10^5\text{y}$ ) and  $^{238}\text{Pu}$  ( $T_{1/2}$ :  $8.2 \cdot 10^7\text{y}$ ) are suitable yield tracers for plutonium analysis;  $^{243}\text{Am}$  ( $T_{1/2}$ :  $7.4 \cdot 10^3\text{y}$ ) for americium and curium,  $^{232}\text{U}$  ( $T_{1/2}$ : 68.9y) or  $^{236}\text{U}$  ( $T_{1/2}$ :  $2.7 \cdot 10^7\text{y}$ ) for uranium isotopes, but there is not an available tracer for  $^{237}\text{Np}$  determination:  $^{239}\text{Np}$  could be used [10], but, presenting a very short half-life (2.4 d), it needs a regular weekly preparation and standardization which is time consuming and expensive.  $^{236}\text{Np}$  ( $T_{1/2}$ :  $1.2 \cdot 10^5\text{y}$ ) is not easy to prepare because it is produced by deuteron bombardment of  $^{235}\text{U}$ . Also  $^{235}\text{Np}$  could be used as a tracer [11], but it contains some  $^{237}\text{Np}$  impurities.
- $\text{Pu}$  and  $\text{Np}$  co-exist simultaneous in various oxidation states ( $\text{Pu}^{4+}$ ,  $\text{Pu}^{3+}$ ,  $\text{PuO}_2^+$ ,  $\text{PuO}_2^{2+}$ ,  $\text{Np}^{4+}$ ,  $\text{NpO}_2^+$  and  $\text{NpO}_2^{2+}$ ) or can be turned to a given state by slightly modifying the redox conditions in the solution.
- Because of the similar chemical behaviour of uranium, plutonium and neptunium, traces of these actinides can contaminate the source of uranium, plutonium and neptunium if chemical separations are not effective.

The separation method developed in this study is based on the reversed phase partition chromatography (exchange chromatography); this is a type of chromatography in which the stationary phase consists of a non-polar extractant adsorbed on an inert support (microporous polyethylene) while the mobile phase is a polar aqueous solution as the mobile phase.

In this study, the stationary phase is tri-*n*-octylamine (TNOA), a long-chain alkyl tertiary amine and the most frequently used liquid amine; TNOA reacts with acids to form an ion-association complex soluble in the organic phase; anions in the complex can be replaced by anionic actinide complexes in a manner analogous to anion exchange; hydrochloric acid with and without reducing agents is used as the mobile phase.

We decided to take into account, as stationary phase, TNOA prepared and used from the seventies from different authors [12] and not the latest TRU, TEVA and UTEVA columns (TRU: octyl(phenyl)-*N*, *N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) dissolved in tributyl phosphate (TBP) supported on an inert polymeric substrate called Amberlite XAD-7; TEVA: trialkylmethylammonium nitrate supported on Amberchrom CG-71 ms, and UTEVA: diamyl-amyolphosphonate supported on Amberlite XAD-7) developed from the nineties by Horwitz and colleagues at the Argonne National Laboratory (USA) because these materials present a higher cost and because of the need for many different materials [13,14].

## 2. Experimental

### 2.1. Apparatus

Alpha spectrometry chain (Canberra Industries, 800 Research Parkway, Meriden, CT 06450, USA) with a 450 mm<sup>2</sup> solid state alpha detector having a 28% counting efficiency, a background of  $<10^{-5}\text{s}^{-1}$  over the energy region of interest and a resolution (FWHM) of 15–25 keV ( $^{238}\text{U}$ ).

Electrodeposition apparatus (Carlo Erba, Italy) with perspex cells of 25 mm internal diameter, 20 mm diameter stainless-steel disks.

Chromatographic columns were 150 mm long and 9 mm wide.

### 2.2. Sample, standards and reagents

#### 2.2.1. Sample

Aqueous solution containing known activities (1–20 Bq kg<sup>-1</sup> per radionuclide) of nine alpha emitters ( $^{226}\text{Ra}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{239+240,238}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{238,235,234}\text{U}$ ) in dilute nitric acid was supplied by NPL (UK).

Table 1 shows the standard solution composition and the radionuclides concentration.

#### 2.2.2. Standards

$^{242}\text{Pu}$ ,  $^{243}\text{Am}$ , and  $^{236}\text{U}$  standard solutions was supplied by Amersham International (UK).

#### 2.2.3. Reagents

Low-density polyethylene powder (Icorene RT 70) was supplied by Verplast SRL (Bergamo, Italy). Tri-*n*-octylamine (TNOA) was supplied by Sigma-Aldrich (Milano, Italy). All the other reagents were analytical grade (Carlo Erba, Italy).

### 2.3. Chromatographic column preparation

The column consisted of microporous polyethylene powder supporting tri-*n*-octylamine (TNOA). 20 ml TNOA in toluene (20% v/v) were added to 16 g microporous polyethylene and the mixture was stirred for several minutes to furnish a homogeneous product which was then placed in an oven at 40–50 °C to evaporate the toluene and to get a porous powder. Every column containing 4.5 g microporous polyethylene–TNOA powder was preconditioned with 9 M HCl for actinides separation.

### 2.4. Recommended procedure

After several preliminary tests were carried out to find the better conditions of a complete separation, the following procedure is recommended.

0.5 ml of aqueous solution is taken to dryness. The residue is dissolved in 20 ml of 9 M HCl containing 0.05 M HNO<sub>3</sub>. After the addition of a known activity of  $^{243}\text{Am}$ ,  $^{242}\text{Pu}$ , and  $^{236}\text{U}$  as internal standards of yield, the sample solution is warmed at 80 °C for 10 min. The sample solution was then cooled and passed through a microporous-TNOA column preconditioned with 9 M HCl at a flow rate of 0.6 ml/min. The column is washed with 15 ml of 9 M HCl at the same flow rate. Plutonium is eluted from the column first with 50 ml of 9 M HCl containing 0.05 M KI at 0.6 ml/min; Np is eluted next with 20 ml of 1 M HCl containing 0.03 M oxalic acid 0.3 ml/min; finally U is eluted with 10 ml of water and 50 ml of 0.5 M HCl 0.1 ml/min. The Am, Pu, Np and U fractions are taken to dryness, the residues dissolved in conc. H<sub>2</sub>SO<sub>4</sub> and pH is adjusted to 4 with ammonia. The solutions are transferred to an electrolytic cell and electroplating is performed for 5 h at 600 mA on stainless-steel disk.

**Table 1**

Concentration of radionuclides indicated by NPL for the standard solution.

Radionuclide	Concentration
$^{226}\text{Ra}$	4.71
$^{237}\text{Np}$	9.38
$^{234}\text{U}$	14.60
$^{235}\text{U}$	0.680
$^{238}\text{U}$	14.76
$^{238}\text{Pu}$	11.86
$^{239}\text{Pu}$	10.13
$^{241}\text{Am}$	13.57
$^{244}\text{Cm}$	6.96

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