



# Chemically selective polymer substrate based direct isotope dilution alpha spectrometry of Pu



Sumana Paul <sup>a,\*</sup>, Ashok K. Pandey <sup>b</sup>, R.V. Shah <sup>a</sup>, S.K. Aggarwal <sup>a,\*</sup>

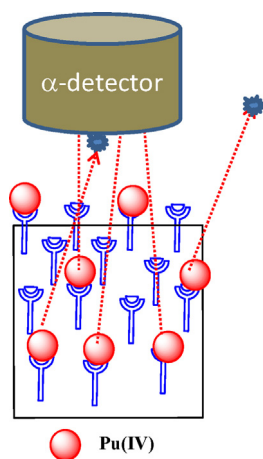
<sup>a</sup> Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

<sup>b</sup> Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

## HIGHLIGHTS

- Membrane based alpha spectrometry was developed for plutonium.
- A thin bifunctional layer was grafted on a porous membrane.
- UV method used for grafting is simple and highly reproducible.
- This method does not require pre-concentration and source preparation steps.
- Isotope dilution was used to enhance analytical performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Quantification of actinides in the complex environmental, biological, process and waste streams samples requires multiple steps like selective preconcentration and matrix elimination, solid source preparations generally by evaporation or electrodeposition, and finally alpha spectrometry. To minimize the sample manipulation steps, a membrane based isotope dilution alpha spectrometry method was developed for the determination of plutonium concentrations in the complex aqueous solutions. The advantages of this method are that it is Pu(IV) selective at 3 M HNO<sub>3</sub>, high preconcentration factor can be achieved, and obviates the need of solid source preparation. For this, a thin phosphate–sulfate bifunctional polymer layer was anchored on the surface of microporous poly(ethersulfone) membrane by UV induced surface grafting. The thickness of the bifunctional layer on one surface of the poly(ethersulfone) membrane was optimized. The thickness, physical and chemical structures of the bifunctional layer were studied by secondary ionization mass spectrometry (SIMS), scanning electron microscopy (SEM) and SEM–EDS (energy-dispersive spectroscopy). The optimized membrane was used for preconcentration of Pu(IV) from aqueous solutions having 3–4 M HNO<sub>3</sub>, followed by direct quantification of the preconcentrated Pu(IV) by isotope dilution alpha spectrometry using <sup>238</sup>Pu spike. The chemical recovery efficiency of Pu(IV) was found to be 86 ± 3% below Pu(IV) loading capacity (1.08 μg in 2 × 1 cm<sup>2</sup>) of the membrane sample. The experiments with single representative actinides indicated that Am(III) did not sorb to significant extent (7%) but U(VI) sorbed with 78 ± 3% efficiency from the solutions having 3 M HNO<sub>3</sub> concentration.

\* Corresponding authors. Tel.: +91 22 25593740; fax: +91 22 25505150/25505151.

E-mail addresses: [sumana@barc.gov.in](mailto:sumana@barc.gov.in) (S. Paul), [skaggr2002@gmail.com](mailto:skaggr2002@gmail.com) (S.K. Aggarwal).

However, Pu(IV) chemical recovery in the membrane remained unaffected from the solution containing 1:1000 wt. proportion of Pu(IV) to U(VI). Pu concentrations in the (U, Pu)C samples and in the irradiated fuel dissolver solutions were determined. The results thus obtained were found to be in good agreement with those obtained by conventional alpha spectrometry, biamprometry and thermal ionization mass spectrometry.

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## 1. Introduction

Several radiometric methods have been developed for quantifying actinides in the environmental, biological and nuclear samples. The simplest method of quantifying alpha emitting actinides is gross alpha counting by proportional or scintillation counters. However, Pu cannot be quantified by proportional or scintillation counter as it is always associated with other alpha emitting radionuclide like Am etc. The most commonly used method for the quantification of Pu is alpha spectrometry. Recently, Vajda and Kim have reviewed radiochemical procedures for the determination of Pu, Np, and Am in various matrices focusing on the environmental samples using alpha spectrometry [1]. The commonly used separation methods for alpha spectrometry are co-precipitation, solvent extraction, ion-exchange, and extraction chromatography using TEVA, TRU and/or UTEVA resins [1–6]. Chamizo et al. developed a method for isolation of Pu-isotopes from environmental samples using ion chromatography and their subsequent quantifications with accelerator mass spectrometry and alpha spectrometry [7]. A multi-dimensional (MD) separation based alpha spectrometry and ICP-MS methods were developed for the analysis of actinides in the environmental samples [8]. A new cloud point extraction procedure coupled to inductively coupled plasma mass spectrometry and alpha spectrometry has been found to be effective for the plutonium quantification [9]. In addition to separation/preconcentration methods, the improvements to data analyses in alpha-particle spectrometry have been also attempted [10].

The standard procedures for Pu analysis by alpha spectrometry are usually based on Pu separation using anion-exchange column, followed by alpha source preparation [1]. For obtaining high resolution alpha spectrum (full width at half maximum of at least 30–50 keV), it is essential to prepare a thin, flat, uniform source. The method of source preparation should also give high deposition of the radionuclide from the solution. Generally, three methods used for source preparation are evaporation, micro-precipitation and electrodeposition [1]. In evaporation method, 25–200  $\mu\text{L}$  volume of the sample solution is evaporated onto a stainless steel or platinum disk under IR heating, and ignited in hot flame to make sure that the radionuclides adhere tenaciously. However, uniformity and adherence remain the key issues in this method. Also, the presence of high salt content would create a deposit that would lead to loss of the energy of some alpha particles leading to a low energy tailing of the characteristic alpha energy peaks in the spectrum. Another method for alpha source preparation is microcoprecipitation of actinides with rare-earth fluoride like  $\text{NdF}_3$ , and filtration deposition on smooth surface membrane having 0.1–0.2  $\mu\text{m}$  pore size [1,11,12]. However, the most common method used for alpha spectrometry is the electrodeposition of actinides onto a polished metal (stainless-steel, silver, copper, nickel or platinum) cathode planchette/disc [13]. Ionic liquid has been used to improve electrodeposition of americium from the organic medium [14]. A standard protocol of electroplating of actinides for preparing alpha sources preparation was published in 2000 and reapproved in 2005 (ASTM C1284-00, 2000b) [1].

The multiple steps involved in alpha spectrometry lead to a high uncertainty in the results. The uncertainties at different steps can

be minimized using an isotope dilution or standard addition with appropriate radiotracer coupled with a suitable radiometric technique [15–19]. Though multistep hybrid methods are highly precise and accurate, the time required for obtaining results is a bottleneck particularly for emergency preparedness as well as for risk assessment of contaminated areas resulting from nuclear weapon tests, nuclear accidents, and the discharge of nuclear waste. One of the ways to overcome this problem is an automation using flow injection (FI) or sequential injection (SI) approach [20,21]. However, a solid thin source preparation is still required for alpha spectrometry. This can be avoided by using thin chemically selective sorbent that can be employed for direct alpha spectrometry [22–25]. The methods reported to date for chemically selective thin films for alpha spectrometry either involve sophisticated synthetic route [25] or reproducible self-supported thin film formation which are not amenable to routine uses [22–24].

The objective of the present work was to develop an alpha spectrometric method for the determination of Pu(IV) using a surface grafted membrane that combines source preparation, purification, and preconcentration of Pu(IV) in a single step. For this, a thin Pu(IV)-selective bifunctional polymer layer was anchored on the poly(ethersulfone) (PES) membrane by UV grafting for direct isotope dilution alpha spectrometry. The choice of phosphate–sulfate bifunctional polymer thin layer was based on previous work that indicated its high selectivity towards Pu(IV) ions in solutions containing 3 M  $\text{HNO}_3$  [26]. The porous substrate for anchoring bifunctional polymer layer was selected to obtain high accessibility of functional groups as the binding sites for Pu(IV) ions. The formation of a thin bifunctional layer on the PES membrane by UV grafted method has to be an easy, one step process, reusable and amenable for the routine applications for alpha spectrometric determination of Pu(IV) ions in the solutions having high  $\text{HNO}_3$  concentration. The fixed and reproducible alpha counting geometry is also necessary for obtaining a constant efficiency factor for Pu determinations by alpha spectrometry [26]. However, use of isotope dilution technique in the membrane based isotope dilution alpha spectrometry (Mem-IDAS) would account for the unforeseen errors during preconcentration and provide flexibility in mounting the membrane in the alpha counting chamber. The Mem-IDAS was employed for the determination of Pu concentration in the dissolver solution of irradiated fuel using enriched  $^{238}\text{Pu}$  spike.

## 2. Experimental

### 2.1. Reagents and apparatus

Suprapure grade acids, analytical reagent grade chemicals and de-ionized water ( $18\text{M}\Omega\text{cm}^{-1}$ ) were used throughout the study. Two different poly(ethersulphone) (PES) membranes of Pall Science make, having 0.1  $\mu\text{m}$  and 0.2  $\mu\text{m}$  pore sizes and 90  $\mu\text{m}$  thickness, were used in the present study. The functional monomers phosphoric acid 2-hydroxyethyl methacrylate ester (HEMP) (containing 700–1000 ppm monomethyl ether hydroquinone, purity 90%, 25% diester and rest in triester form) and 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS, 98%

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