



## Thin extractive membrane for monitoring actinides in aqueous streams

Vivek Chavan<sup>a</sup>, Sumana Paul<sup>b</sup>, Ashok K. Pandey<sup>a,\*</sup>, P.C. Kalsi<sup>a</sup>, A. Goswami<sup>a</sup>

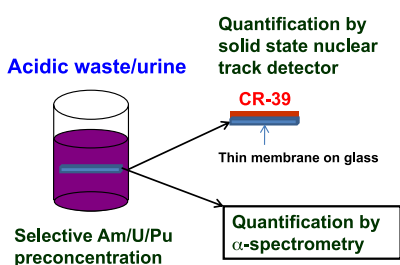
<sup>a</sup> Radiochemistry Division, Trombay, Mumbai 400 085, India

<sup>b</sup> Fuel Chemistry Division, Trombay, Mumbai 400 085, India

### HIGHLIGHTS

- Thin polymer inclusion membrane has been developed for selective actinide sorption.
- Actinide sorption in membrane is dependent on acidity and oxidation states.
- A scheme for selective preconcentration of target actinide has been developed.
- Quantification of actinide in membrane is possible by SSNTD or  $\alpha$ -spectrometry.
- This membrane was used for assay of Pu in acidic waste and urine

### GRAPHICAL ABSTRACT



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### ABSTRACT

Alpha spectrometry and solid state nuclear track detectors (SSNTDs) are used for monitoring ultra-trace amount of alpha emitting actinides in different aqueous streams. However, these techniques have limitations i.e. alpha spectrometry requires a preconcentration step and SSNTDs are not chemically selective. Therefore, a thin polymer inclusion membrane (PIM) supported on silanized glass was developed for preconcentration and determination of ultra-trace concentration of actinides by  $\alpha$ -spectrometry and SSNTDs. PIMs were formed by spin coating on hydrophobic glass slide or solvent casting to form thin and self-supported membranes, respectively. Sorption experiments indicated that uptakes of actinides in the PIM were highly dependent on acidity of solution i.e. Am(III) sorbed up to  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ , U(VI) up to  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  and Pu(IV) from  $\text{HNO}_3$  concentration as high as  $4 \text{ mol L}^{-1}$ . A scheme was developed for selective sorption of target actinide in the PIM by adjusting acidity and oxidation state of actinide. The actinides sorbed in PIMs were quantified by alpha spectrometry and SSNTDs. For SSNTDs, neutron induced fission-fragment tracks and  $\alpha$ -particle tracks were registered in Garware polyester and CR-39 for quantifications of natural uranium and  $\alpha$ -emitting actinides ( $^{241}\text{Am}/^{239}\text{Pu}/^{233}\text{U}$ ), respectively. Finally, the membranes were tested to quantify Pu in  $4 \text{ mol L}^{-1} \text{ HNO}_3$  solutions and synthetic urine samples.

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## 1. Introduction

Nuclear activity has generated strong need to monitor  $\alpha$ -emitting actinides within nuclear facility as well as in surrounding soil and other environmental media due to their high radio-toxicity [1,2]. Solid state nuclear track detectors (SSNTDs) are highly

\* Corresponding author. Tel.: +91 22 25594566; fax: +91 22 25505150/25505151.

E-mail addresses: [ashokk@barc.gov.in](mailto:ashokk@barc.gov.in), [memgreek@gmail.com](mailto:memgreek@gmail.com) (A.K. Pandey).

sensitive for studying rare events and quantifying ultra-trace concentrations of the fissile or alpha-emitting nuclides in the solids and liquids samples [3–9]. The applications of SSNTDs for ultra-trace detection and quantification of actinides is based on registering alpha or fission tracks in solution medium [10]. This is because of reproducibility in registration of the particles tracks from solution medium, which is essential for analytical applications. However, the loss of energy of a particle during its travel in solution to the surface of detector leads to significant decrease in the track registration efficiency [11]. The particle track registration from a thin electro-deposited source on suitable metallic substrate is a better approach but scanning of tracks on whole area of detector exposed to electro-deposited source is required to avoid errors originating from micro-inhomogeneity [12]. Another major problem associated with SSNTD technique is lack of chemical selectivity in registration of the particle tracks. To some extent, this can be overcome by achieving radiation selectivity using image analyses of the particle tracks [13]. However, the precise identifications of actinide isotopes are important for nuclear forensic and as well as for environmental monitoring of potential releases from nuclear installations. Combination of alpha-spectrometry and fission track analysis has been used for determination of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in human tissue [14].

Alpha spectrometry is less sensitive as compared to SSNTDs but radionuclide can be identified based on energy of alpha particles emitted. However, it is also chemically not selective and suffers from spectral interferences. For example,  $^{237}\text{Np}$  ( $E_{\alpha}=4.957\text{ MeV}$ ) and  $^{242}\text{Pu}$  ( $E_{\alpha}=4.983\text{ MeV}$ ) can not be distinguished by  $\alpha$ -spectrometry [15]. Also, a preconcentration step is needed to make alpha spectrometry applicable for quantification of ultra-trace amount of actinides in the aqueous samples. A preconcentration step is also needed in the coupled plasma-mass spectrometry methods that have greater sensitivity and efficiency and could replace many radiometric techniques [16]. The most commonly used separation/preconcentration methods for  $\alpha$ -spectrometry are co-precipitation, solvent extraction, ion-exchange, and extraction chromatography using TEVA, TRU and/or UTEVA resins [17–19]. The separation and  $\alpha$ -spectrometry has been combined by forming thin film of chemically selective polymer on the surface of passivated silicon diodes [20]. However, multiple measurements required replacement of previous film deposited on silicon diodes with fresh one as actinides forms irreversible complexes in the film.

The objective of present work is to develop the actinide selective thin polymer inclusion membrane (PIM) for alpha spectrometry and track registration in SSNTD. This thin PIM would not only enhance actinide detection limit due to high preconcentration factor but also provide chemical selectivity to alpha spectrometry and SSNTD. The thin PIM (2–3  $\mu\text{m}$ ) has been formed on hydrophobic glass support for preconcentration and determination of ultra-trace concentration of actinides by solid state nuclear track detector and  $\alpha$ -spectrometry. The PIM has been formed by spin coating of matrix forming polymer along with extractant bis(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in chloroform on silanized glass. Three different matrix polymers used for forming thin PIM are cellulose triacetate (CTA), poly(styrene) (PS) and poly(vinyl chloride) (PVC). For fission track analyses, self-supported PIM ( $\approx 40\ \mu\text{m}$ ) has also been prepared by solution casting method using CTA, plasticizer tri-(2-ethylhexyl)phosphate (TEHP) and HDEHP. The spin coated and self-supported PIMs have been studied for their efficiencies to take up representative actinides like Am, U and Pu. The direct quantifications of target actinide preconcentrated in the PIM has been carried out by alpha spectrometry as well as chemically-selective registration of  $\alpha$ -tracks using a scheme based on adjusting oxidation state of actinides and acidity of aqueous sample. The methodology developed in the

present work has been used to quantify Pu in acidic solutions and synthetic urine samples.

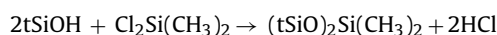
## 2. Experimental

### 2.1. Materials and apparatus

Analytical reagent grade  $\text{CHCl}_3$  (BDH), toluene (SISCO),  $\text{HNO}_3$  (Merck) and ultrapure water (18 M $\Omega$ /cm, gradient A-10 model, Milli-Q USA) were used throughout the work. Cellulose triacetate (CTA) (molecular weight 72000–74000, Fluka), poly(styrene) (PS) (Average  $M_w$  25,000, Acros Organics), poly(vinyl chloride) (PVC) (high molecular weight, Fluka), dimethyl dichloro silane (DMDCS) (Fluka), bis-(2-ethylhexyl)-phosphoric acid (HDEHP) (GPR, BDH) and tri-(2-ethylhexyl) phosphate (TEHP) (Koch Light) were used as obtained. The actinides isotopes used in the present work were available in Radiochemistry Division, BARC, Mumbai. pH meter [420 A, Thermo Orion, USA] was used after calibrating it with standard buffer solutions (Hamilton) having pH 4, pH 7 and pH 10. A digital micrometer (Mitutoyo, Japan) was used for determining thickness of the films with an accuracy of 1  $\mu\text{m}$ . The  $\gamma$ -activities of the radiotracers in the films and equilibrating solutions samples were monitored by using either a high purity germanium (HPGe) detector or a well-type NaI(Tl) detector based gamma ray spectrometer. All the samples and standard containing radioactivity were counted in identical sample-detector geometry. The samples were kept in 5 mL poly(propylene) tube having 5 cm height. The standard samples were made to check constant geometry. The  $\alpha$ -activity in aqueous sample was monitored by taking out 50  $\mu\text{L}$  sample, and adding it in a vial containing 5 mL of scintillation cocktail-O (Sisco Research Laboratory, India). The composition of cocktail-O was: 2,5-diphenyl oxazole = 10 g, 1,4-di-(5-phenyloxazolyl) benzene = 0.25 g, and naphthalene = 100 g in 1000 mL toluene, and 5 v/v % bis(2-ethylhexyl) phosphoric acid (HDEHP). The liquid scintillation counting was carried out in a home built liquid scintillation counter. Alpha spectra were taken using  $\alpha$ -spectrometer having passivated ion-implanted planar silicon (PIPS) detector with area 25 mm $^2$  and resolution of 15 KeV at 5.486 MeV of  $^{241}\text{Am}$ . For keeping fixed geometry in the alpha spectrometry, all membrane samples were mounted on Perpex plates and kept on a stage having fixed distance (2 cm) from detector. The track observations in solid state nuclear track detectors (CR-39 or Garware polyester) were carried using optical microscope (Zeiss or Olympus) under magnification of 400 $\times$ .

### 2.2. Preparation of polymer inclusion membranes

Two types of PIMs were synthesized. These were self-supported thick membrane (40  $\mu\text{m}$ ) and spin coated thin film (2–3  $\mu\text{m}$ ) on glass support. As surface of the glass is hydrophilic, the hydrophobic spin coated PIM film was detached from glass surface during equilibration in aqueous solution. To have good adherence between spin coated membrane and glass surface, the surface of glass substrate was made hydrophobic. First, glass surface was cleaned with ultrasonication in acetone, ethanol and then rinsed with de-ionized water. The dried glass slides were treated with Piranha solution containing conc.  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  in 3:1 volume proportion for 30 min. Treated glass slides were washed with water, air dried and immersed in 5% (v/v) solution of DMDCS in toluene for 3 h. The solution was then drained out and glass was air dried before spin coating. The bonded methyl groups impart hydrophobicity to surface of glass as shown below.



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