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Polymer based sorbent materials for thermal ionization mass spectrometric determination of uranium(vi) and plutonium(iv) ions

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Thermal ionization mass spectrometry (TIMS) is a widely used method for obtaining information about the isotopic composition of individual isotopes with high resolution and accurate quantification with considerably low detection limits. However, analyses by TIMS require an elaborate sample preparation step to eliminate the matrix and subsequent manual loading of small volumes of purified aqueous samples on a filament surface for thermal ionization. This is cumbersome, particularly for the handling of radioactive solutions. Therefore, in the present work, polymeric material based sorbents were explored for the single step matrix elimination and source preparation for the loading of U(vi) and Pu(iv) ions preconcentrated from a variety of environmental and nuclear fuel reprocessing samples. The solid phase loading offers a number of advantages for handling radioactive materials, and is amenable to matrix elimination and preconcentration of analytes that would further improve the detection limit of TIMS. The polymer based sorbents were prepared by anchoring neutral and acidic phosphate functional groups selective to actinide ions in porous poly(propylene) and poly(ethersulfone) matrices. One of the procedures used for the preparation of polymeric sorbents involved grafting of the monomers phosphoric acid 2-hydroxyethyl methacrylate ester and 2-ethylhexylmethacrylate (EHM) in 1:1 molar proportion by UV-initiator induced polymerization in the pores of the host matrix. In another route, the liquid extractants tris(2-ethylhexyl) phosphate (TEHP) along with bis(2-ethylhexyl) phosphoric acid (HDEHP), in different molar proportions, were physically immobilized by capillary force in the pores of poly(propylene) and poly(ethersulfone) membranes and beads. It was observed that the poly(propylene) pyrolyzed easily at a filament temperature close to that used for solution based sample loading, and thus was best suited for the analyses of U(vi) and Pu(iv) by TIMS. The composition of the polymer membrane supported liquid extractant based sorbents was optimized for the preconcentration of U(vi) from ground water and seawater, and also for the preconcentration of Pu(IV) from 3 mol L⁻¹ HNO₃, which is normally encountered in nuclear fuel reprocessing facilities. The parameters affecting the analytical performance of polymer sorbent based TIMS were evaluated, and tested for the guantification of U and Pu in the ppb concentration range in seawater and urine samples using the isotope dilution method.

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Introduction

Thermal ionization mass spectrometry (TIMS) is a versatile method for obtaining the isotopic composition and amount of actinides in nuclear materials, and environmental and biological samples.¹⁻⁷ However, TIMS involves a multistep sample manipulation to eliminate the undesirable matrix and loading of a small volume of solution on a filament for thermal ionization.¹⁻⁸ Multicollector inductively coupled plasma mass spectrometers (MC-ICP-MS) have also found wide applicability for the detection of ultratrace amounts of Pu in complex aqueous or solid matrices.⁹⁻¹² Zheng *et al.* have reviewed different atomic spectrometric techniques, including TIMS and ICP-MS, being used for the objective of radiation protection, and observed that TIMS has been gradually replaced by MC-ICP-MS in the fields of nuclear chemistry and geochemistry.¹³ Basically, ICP-MS combines an inductively coupled plasma source at normal pressure with a mass spectrometer, which is suitable for the analysis of liquid samples. TIMS is more amenable to a solid source. The comparison table given in the review of Zheng *et al.* seems to suggest that there is not much difference in both the techniques in terms of the limit of detection.¹³ Similar to TIMS, MC-ICP-MS also requires a chemical purification step to eliminate isobaric interferents like ²³⁸U in ²³⁸Pu determination or



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²⁴¹Am in ²⁴¹Pu determination, polyatomic interferents like
²³⁸UH in ²³⁹Pu determination, *etc.*

The most widely used purification methods for TIMS and MC-ICP-MS are based on anion-exchange column separation or chromatography using TEVA, UTEVA, TRU, DGA, DIPEX, DIPHONIX, *etc.*¹ However, these methods are cumbersome as elaborate precautions have to be taken during handling of radioactive materials. To overcome this problem, the automation of sample purification procedures has been developed by using on-line ion-exchange and/or extraction chromatography using flow injection/sequential injection and multi-dimensional approaches.¹⁴⁻¹⁸

A new emerging viable alternative to solution handling is solid phase extraction that offers a number of advantages such as a high preconcentration factor, minimization of liquid analytical waste, easy storage and the possibility of direct quantification of analytes pre-concentrated in the solid matrix.19 For the analyses of radioactive elements, single step solid phase extraction would also provide secure physical transportation reducing the possibility of contamination of the instrument, cross-contamination of samples, and minimizing the exposure to radiation by eliminating undesirable radioactivity. Single anion-exchange bead based TIMS methods have been developed for Pu(IV) and U(VI) ions.20-23 These beads are very small and difficult to mount on the filament. Recently, King et al. suggested a novel method for bead loading in TIMS using 1% glucose w/v solution as an adhesive for mounting the beads onto the rhenium filament that are dried under a heat lamp to set the glucose and fix the beads.20 Acoustic streaming has been used for a small volume of sample to improve the sorption kinetics of Pu(IV).24 It has been reported that filament carburization improves the analytical performance of TIMS for Pu determination.²⁵ Thus, the polymer beads used in TIMS for Pu sample loading would also act as a source for carbon. However, the beads in these methods have been used simply as the reservoir for Pu(IV) ions in the already purified aqueous sample, and no attempt has been made to use them for dual functions like elimination of the matrix as well as the selective preconcentration of analyte ions.

In the present work, a systematic study has been carried out to develop polymeric material based sorbents for loading of U(vI) and Pu(IV) ions in TIMS. The choice of TIMS over ICP-MS is based on the possibility of direct analysis of solid samples by TIMS, thereby reducing the chances of contamination and personnel exposure during the handling of radioactive samples. These polymeric sorbents have been developed using two routes. These are: (i) grafting of the phosphate bearing monomer in microporous poly(propylene) and poly(ethersulfone) membranes, and (ii) physical immobilization of liquid extractants in the same microporous membranes. The liquid extractant immobilized in the microporous membrane is also known as the supported liquid membrane in the field of separation science.26 This class of membranes has also been explored for analytical applications.27 The selection of phosphate functional group bearing extractants has been based on the fact that phosphate groups have strong affinity towards f-element ions. These polymeric sorbents have been studied for their efficacy to

selectively preconcentrate $U(v_l)$ and Pu(v) ions from a variety of environmental and nuclear fuel reprocessing samples, and subjected to the direct quantification of preconcentrated $U(v_l)$ and Pu(v) ions using the isotope dilution method.

Experimental

Reagents and apparatus

Analytical reagent grade chemicals, suprapure grade nitric acid (Merck, Mumbai, India) and deionized water (18 M Ω cm⁻¹) purified by Quantum[™] from Millipore (Mumbai, India), were used throughout the studies. Phosphoric acid 2-hydroxyethyl methacrylate ester (HEMP) (containing 25% diester, 90%), 2-ethylhexyl methacrylate (EHM) (98%, containing \sim 50 ppm monomethyl ether hydroquinone), and α, α' -dimethoxy- α -phenylacetophenone (DMPA) (99%) were obtained from Sigma-Aldrich (Steinem, Switzerland). Tris(2-ethylhexyl) phosphate (97%) (TEHP) and bis(2-ethylhexyl)phosphoric acid (96%) (HDEHP) were obtained from Koch Light Laboratories (Coinbrook Bucks, England) and BDH (England), respectively. Poly-(ethersulfone) (PES) was obtained from Goodfellow Cambridge Ltd. (England) and the PES membrane, having 0.2 µm pore size and 90 µm thickness, was obtained from Pall Science. The polypropylene (PP) membrane with 0.1 µm pore size was procured from Sterlitech Corporation, US. Polymerization of HEMP monomers within the pores of the PP membrane was carried out in a UV multilamp photoreactor procured from Heber Scientific, Chennai, India with $\lambda_{max} = 365$ nm. A microprocessor-based pH meter, model PHAN, from Lab India (Mumbai, India) was used for pH measurements. The images and elemental analyses of the HDEHP@PP membrane sample equilibrated with seawater and HNO3 were carried out using a MINI-SEM (SEC Global, Singapore) equipped with a Bruker EDX analyser.

The stock solutions of Pu, Am and U were obtained from Fuel Chemistry Division, BARC, Mumbai, India. The gross alpha activities of the actinides were measured with a home-built liquid scintillation counter equipped with a single channel analyser (SCA), using an Ultima Gold AB scintillation cocktail (Perkin Elmer). For the measurement of gamma activity, an HPGe detector (ORTEC, United States) with a resolution of 550 eV (FWHM) at 122 keV coupled to a PC-based MCA was used. Mass spectrometric analyses were carried out using an Isoprobe-T thermal ionization mass spectrometer equipped with multi-collector Faraday cups and a zone refined, high purity rhenium double filament assembly was used for the loading of the samples.

Preparation of pore-grafted sorbents

The details of the preparation of pore-grafted substrates are given in our earlier publications.^{28,29} Briefly, the monomers (HEMP and EHM) were dissolved in 1 : 1 molar proportion of ethanol and water. A photo-initiator (DMPA) (1 wt%) was added to it. This polymerizing solution was homogenized by ultrasonication for 5 min. The microporous substrates (PP and PES membranes) were immersed in the polymerizing solution for

pore-filling overnight. After overnight immersion, the pore-filled substrates were taken out and excess solution clinging on the surface was removed, and then irradiated in a UV reactor for 15 min. Thus grafted polymer sorbents were thoroughly washed with ethanol and water before use.

Preparation of extractant impregnated polymer sorbents

The method used in the preparation of extractant filled polymer substrates is similar to that reported for supported liquid membranes.^{26,27} Briefly, the mixtures of HDEHP and TEHP in 1:0, 3:1, 1:1, 1:5, 1:10 and 0:1 molar proportions were prepared. The PP membranes and PES beads, formed by the phase inversion method, were immersed in these solution mixtures overnight, and then taken out of the solutions. The excess of solution was dripped out and the extractant-filled membranes were gently washed with water.

Sorption of actinides

The methods used for studying the sorption of actinides are described in our previous publications.^{28,29} To study the sorption of actinides in the present work, about 100 mg of pore-filled PES beads or 2×1 cm² pieces of the extractant impregnated or poregrafted polymer sorbents were equilibrated with 5 mL of a wellstirred aqueous solution, spiked with ^{mix}Pu/²³³U/²⁴¹Am and having various concentrations of HNO3 for 2 h. The Pu solutions were treated with 30% H_2O_2 in 3 mol L^{-1} HNO₃ prior to sorption, to keep the Pu oxidation state at IV. The sorption efficiency (%) data of the polymer sorbent were obtained from the decrease in the alpha activities of ^{mix}Pu/²³³U, or gamma activities of ²⁴¹Am in the solution after the equilibration. To study the sorption of U(v1) from groundwater and seawater samples, 5 mL of groundwater/seawater was spiked with an appropriate amount of ²³³U and equilibrated with 2 \times 1 cm^2 pieces of the extractant impregnated polymer sorbents for 1 h with continuous stirring. The values of the distribution ratio (K_d) were determined by measuring the alpha activity of a solution containing $U(v_i)$ and $Pu(v_i)$ ions in 3 mol L^{-1} HNO₃ medium, before and after equilibration with the sorbent. The K_d values were obtained using the following equation:

$$K_{\mathrm{d}_{\mathrm{Pa}(\mathrm{IV})/\mathrm{U}(\mathrm{VI})}} = \frac{(A_0 - A_{\mathrm{e}})}{W} \times \frac{V}{A_{\mathrm{e}}} \tag{1}$$

where A_0 and A_e represent the alpha activities of ²³³U/Pu initially and after equilibration in the aqueous phase, *W* is the weight of the polymer sorbent sample, and *V* is the volume of the equilibrating aqueous phase. The time required to attain equilibrium sorption of Pu(v) and loading capacity of the polymeric sorbent was also determined in a similar manner except that the Pu(v) concentration was kept higher to saturate the binding sites of the polymeric sorbent. Briefly, \approx 100 mg of the polymer sorbent was equilibrated in 30 mL of aqueous solution containing Pu(v) with continuous stirring; 25 µL aliquot was taken out at regular intervals from the equilibrating solution to measure the Pu alpha activity.

Thermal ionization mass spectrometry

Polymeric sorbent based thermal ionization mass spectrometry (PolymSorb-TIMS) was studied employing the NIST SRM-947 Pu isotopic standard. This standard solution (2 mL) was treated with 30% H₂O₂ in 3 mol L⁻¹ HNO₃ to convert the oxidation state of Pu to Pu($_{IV}$), and then equilibrated with 0.5 \times 0.2 cm² pieces of the polymer sorbents for 1 h with continuous stirring. After equilibration, the polymer sorbent was collected from the solution using a pair of tweezers, washed with 3 mol L^{-1} HNO₃ to remove the surface adsorbed Pu(IV) ions, dried and directly loaded onto a high purity rhenium filament for TIMS analysis. The loading techniques for the various polymeric sorbents developed in the present study were: (i) the liquid extractant impregnated PES beads were wetted in 3 mol L^{-1} HNO₃ and placed at the centre of the Re filament and slowly heated to decompose the polymeric sorbent partially, (ii) $0.5 \times 0.2 \text{ cm}^2$ pieces of pore grafted PP and PES sorbents were wetted in 3 mol L^{-1} HNO₃ and placed along the length of the Re filament, and (iii) for loading the liquid extractant impregnated PP sorbent, a 0.5×0.2 cm² piece of the membrane was held vertically with a pair of tweezers in such a way that one end of the piece touches the centre of the Re filament; the filament was then slowly heated when the sorbent gradually melted and deposited at the centre of the filament.

All mass spectrometric analyses were performed in the static mode of data collection of the Isoprobe-T thermal ionization mass spectrometer equipped with multiple Faraday cups, using a double rhenium filament assembly. The polymer sorbent loaded filament served as the vaporization filament (VF) and the other filament served as the ionization filament (IF). The VF and IF temperature were slowly increased from 0 to 2 A and 0 to 5 A, respectively, in 600 s and degassing was carried out at these temperatures for 1800 s. Prior to the isotopic analysis, the temperature of the IF was increased to obtain an optimum $(\sim 200 \text{ mV})^{187} \text{Re}^+$ ion current. Then the VF temperature was then increased to obtain an optimum ²³⁹Pu⁺ ion current of 200 mV or more. To compare the results of isotopic analysis of the NIST SRM-947 standard by PolymSorb-TIMS with those of the conventional solution based TIMS method, the standard was treated with 30% H₂O₂, purified from ²⁴¹Am, using DOWEX 1X8 resin, and the purified Pu(v) was eluted using 0.3 mol L⁻¹ HNO₃. The purified Pu fraction was evaporated and then 10 µL of the concentrated solution was loaded on the Re filament for TIMS analysis.

The PolymSorb-TIMS method was employed for the determination of Pu(IV) ion concentration in the dissolver solution of irradiated UO2 fuel and also in other aqueous samples like seawater, synthetic urine samples spiked with known amounts of Pu(NO₃)₄. Pu concentrations in the samples were determined by using the isotope dilution (ID) technique as described elsewhere.29 For the determination of Pu concentration in the dissolver solution (U : Pu molar ratio \sim 1000 : 1), a 0.5 \times 0.2 cm² piece of liquid extractant impregnated polymer substrate (TEHP + HDEHP) was equilibrated with 3 mL of dissolver solution and its spiked mixture, separately, for 1 h with continuous stirring. After equilibration, the polymer sorbent was collected, washed and loaded onto the VF for isotopic composition (IC) analysis of Pu in the dissolver solution and its spiked mixture. A known Pu activity and its spiked mixture were added to 50 mL of seawater/synthetic urine separately, and equilibrated with a $0.5 \times 0.2 \text{ cm}^2$ piece of liquid extractant impregnated polymer sorbent (TEHP + HDEHP) for 24 h with continuous stirring. After preconcentration of Pu(IV) ions, the polymer sorbent pieces were loaded for TIMS analysis as described above, and Pu concentrations in various samples were calculated from the changes in isotope ratios in the spiked mixture with respect to that in the sample and the spike. For the determination of U(vi) concentration in groundwater and seawater samples, a known weight of natural uranium in the form of $UO_2(NO_3)_2$ was added to 50 mL of the aqueous samples. A known volume (100 μ L of 0.1 mol L⁻¹) of Na₂CO₃ was added to seawater/ground water to avoid hydrolysis of U(vi) ions. For isotope dilution, a known weight of the pre-calibrated ²³³U spike solution was added to the samples and the spiked samples were equilibrated with a 0.5×0.2 cm² piece of HDEHP impregnated polymer sorbent for 24 h with continuous stirring. After preconcentration of $U(v_1)$ ions, the polymer sorbent was subjected to U isotopic analysis by TIMS, and U concentrations in various samples were obtained from the change in 233 U/ 238 U ratios in the spiked mixture as described above for Pu analyses.

Results

Formation of polymeric sorbents

The polymeric sorbents were developed using two commercially available microporous PES and PP membranes. The extractants were anchored by UV-initiator induced graft polymerization in the pores of the host membranes and beads as described



Liquid Extractants



Polymer substrate



Fig. 1 Chemical structures of the components used for preparing the polymeric sorbents by grafting of the monomer and physical immobilization of the liquid lipophilic extractants in the microporous host membranes made up of PES and PP polymers.

elsewhere.^{28,29} The EHM was used as the spacer to reduce the degree of cross-linking caused by the triester and diester functionality present in the HEMP monomer having more than one polymerizing double bonds, as shown in Fig. 1.

It was observed that the Pu(Iv)-sorption efficiency of the polymer sorbent formed by grafting pure HEMP was quite low (20%) from 3 mol L⁻¹ HNO₃. However, the Pu(IV)-sorption efficiency increased to 80% under similar conditions when the spacer EHM was grafted along with HEMP in 1 : 1 molar proportion. This was attributed to the fact that heavy cross-linking would affect the accessibility of phosphate groups for binding with Pu(IV) ions. Thus, the spacer EHM provides flexibility to the grafted polymer chains which in turn increases the Pu(IV)-sorption efficiency. These polymeric sorbents grafted with 1 : 1 molar proportion of HEMP and EHM were termed as poly(HEMP-*co*-EHM)-PP and poly(HEMP-*co*-EHM)-PES sorbents.



Fig. 2 Representative SEM images of the (a) pristine PP membrane and (b) poly(HEMP-*co*-EHM) grafted PP membrane.



Fig. 3 Variations of sorption efficiency of the poly(HEMP-co-EHM)-PP sorbent towards Am(III) (\bigcirc), U(VI) (\triangle) and Pu(IV) (\square) ions as a function of HNO₃ concentration.



Fig. 4 The sorption profiles of Am(III) (a), Pu(IV) (b) and U(VI) (c) in the TEHP:HDEHP@PP having different molar proportions of the extractants as a function of HNO₃ concentration, and variation in the U(VI)-sorption efficiency from the ground water and seawater (d). The symbols ●, ▲, ■ and ▼ denote sorption efficiencies of the TEHP : HDEHP@PP having 3 : 1, 1 : 1, 1 : 0 (pure TEHP) and 0 : 1 (pure HDEHP) molar proportions of TEHP and HDEHP, respectively.

The comparison of the SEM images of the grafted membrane with those of the pristine membrane seems to suggest that the pores were partially filled, though the grafting yield was 70 wt%, see Fig. 2. Thus, the grafted sorbents were still porous that would be helpful in sorption kinetics. Another route used for the preparation of the polymeric sorbent was based on physical immobilization of the lipophilic liquid extractant in the pores of the host PP membrane and PES beads. The choice of the PP membrane or PES bead was based on the fact that these are hydrophobic and microporous materials that would be best suited for immobilizing the lipophilic liquid extractants and the pore size 0.1 μ m was optimum for providing capillary force with sufficient porosity to hold the liquid extractants.

The loading of liquid extractants HDEHP + TEHP (1:3 molar proportion) in the PP membrane was found to be 90-95 wt%. These classes of polymeric sorbents were termed as TEHP:H-DEHP@PP and TEHP:HDEHP@PES. The liquid extractants HDEHP and TEHP were selected to retain the same functional groups as used in the grafted sorbent. HDEHP and TEHP have similar chemical structures and phosphate functional groups to those of triester and diester components of HEMP, see Fig. 1. TEHP also acts as a diluent for HDEHP and, therefore, the different molar proportions of HDEHP and TEHP were used to optimize the sorption efficiency of the liquid extractant impregnated polymeric sorbents. The liquid extractants are held in the micropores of the PP membrane or PES beads by capillary force and require a considerable pressure to eject out of the pores.³⁰ Thus, the immobilized lipophilic liquid extractants have reasonably good stability in the host PP membrane or PES beads for one time use as a sorbent.

Actinide sorption studies

The sorption of actinides in the poly(HEMP-*co*-EHM)-PP sorbent was studied as a function of HNO₃ concentration using Am(III), U(vI) and Pu(IV) as the representative actinides. As can be seen from Fig. 3, the Pu(IV) and U(VI) sorption in the poly(HEMP-*co*-EHM)-PP sorbent increased with increasing HNO₃ concentration and attained constant sorption efficiencies of 70% and 85% for U(VI) and Pu(IV), respectively, above 2 mol L⁻¹ HNO₃. However, Am(III) sorption above 2 mol L⁻¹ HNO₃ was not significant (<5%). This is the typical behaviour of neutral phosphate based extractants.²⁶ It is clear from Fig. 3 that the poly(HEMP-*co*-EHM)-PP sorbent has good affinity towards Pu(IV) ions, and slightly lower affinity for the U(VI) ions.

The actinide sorption studies were also carried out in the polymer sorbent (TEHP:HDEHP@PP) using the same representative actinide ions as a function of HNO_3 concentration. The molar proportion of HDEHP and TEHP was varied as 1:0, 1:1, 1:3 and 0:1. The sorption profiles of Am(m), $U(v_1)$ and Pu(rv) are shown in Fig. 4. The measured $U(v_1)$ -sorption efficiencies of the TEHP:HDEHP@PP sorbent from ground water and seawater are given in Fig. 4d. It is seen from Fig. 4a that Am(m) sorption in the TEHP:HDEHP@PP and HDEHP@PP sorbents was not quantitative, and varied between 15% and 8% in the solutions having HNO_3 conc. more than 2 mol L⁻¹. However, Pu(rv) and $U(v_1)$ were sorbed with high efficiency in all

the TEHP:HDEHP@PP and HDEHP@PP sorbents, but not in the TEHP@PP sorbent. The Pu(IV)-sorption efficiency was optimum (95%) in the HDEHP@PP as shown in Fig. 4b.

The U(vi)-sorption efficiency of the TEHP:HDEHP@PP and HDEHP@PP sorbents was not affected by the acidity in the equilibrating solution or molar proportion of TEHP:HDEHP. In the case of seawater and ground water, the U(vi) sorption efficiency was optimum in TEHP: HDEHP@PP (1:10) and HDEHP@PP, see Fig. 4d. It is interesting to observe from the data given in Table 1 that the distribution ratios (K_d) of Pu($_{IV}$) and U(vi), when determined in the competing mode using a solution containing 1.35 μmol of Pu(IV) and 140.1 μmol of U(vi), were found to differ significantly depending on the composition of TEHP and DEHP in the TEHP:HDEHP@PP sorbents. The higher selectivity of the TEHP: HDEHP@PP (3 : 1) sorbent, as indicated by the $K_{\rm d_{Pu(w)}}/K_{\rm d_{U(w)}}$ ratio in Table 1, could be attributed to the fact that P=O has higher affinity towards Pu(v) as compared to that for U(v). As observed, the value of $K_{d_{Pn(n)}}$ is higher in the dynamic competition and increased more in the presence of neutral phosphate extractant TEHP in 3:1 molar proportion in the TEHP: HDEHP@PP sorbent.

The rates of Pu(IV) sorption from 3 mol L^{-1} HNO₃ by the poly(HEMP-co-EHM)-PP and TEHP: HDEHP@PP (3:1 molar proportion) as a function of time are shown in Fig. 5a. It is seen from Fig. 5a that the TEHP:HDEHP@PP sorbent attained optimum sorption equilibrium (92%) at 50 s. In the case of the poly(HEMP-co-EHM)-PP, the optimum sorption equilibrium (85%) was achieved at a longer period of time (100 s). This may be attributed to the fact that the functional groups are fixed in the poly(HEMP-co-EHM)-PP matrix leading to the diffusion of Pu(IV) ions by site jumping or direct interactions due to the porosity of the grafted matrix. In contrast, the carriers are mobile in the liquid fraction of the TEHP:HDEHP@PP sorbent. The variation of the Pu(IV)-sorption efficiency in the TEHP : H-DEHP@PP (3:1) sorbent as a function of volume of the equilibrating solution is shown in Fig. 5b. It is seen from this figure that the Pu(IV)-sorption efficiency remained unaffected (92 \pm 2%) up to 30 mL, and decreased thereafter. A longer equilibration time may be required to attain optimum sorption efficiency for a solution of volume higher than 30 mL.

Selection of sorbent for TIMS

One of the important requirements for selecting a sorbent for TIMS is vaporization filament (VF) temperature. Therefore, the

Table 1 Distribution coefficients of Pu(Iv) and U(vI) ions in the different compositions of TEHP : HDEHP@PP sorbents from the solution containing 1.35 μmol of Pu(Iv) and 140.1 μmol of U(vI) in 3 mol L^{-1} HNO₃

TEHP : HDEHP	$K_{\mathrm{d}_{\mathrm{Pu}(\mathrm{rv})}}\left(\mathrm{mL}\ \mathrm{g}^{-1}\right)$	$K_{d_{U(v)}}$ (mL g ⁻¹)	$K_{\mathrm{d}_{\mathrm{Pu(iv)}}}/K_{\mathrm{d}_{\mathrm{U(vi)}}}$
1:0	127 ± 9	16 ± 3	7.9
3:1	$\frac{127 \pm 3}{217 \pm 15}$	10 ± 0 19 ± 3	11.4
1:1	139 ± 10	26 ± 5	5.3
0:1	112 ± 8	29 ± 5	3.9



Sorption (%)

(a)



Fig. 5 (a) Variation of Pu(IV) sorption as a function of equilibration time in the poly(HEMP-*co*-EHM)-PP (\triangle) and TEHP : HDEHP@PP (3 : 1 molar proportion) (\Box) sorbents from 3 mol L⁻¹ HNO₃, and (b) variation of Pu(IV) sorption efficiency in TEHP : HDEHP@PP (3 : 1 molar proportion) as a function of volume of the solution.

variation of 239 Pu⁺ ion current, obtained by mounting the Pu(IV)loaded poly(HEMP-*co*-EHM)-PP/PES and TEHP : HDEHP@PP (3 : 1 molar proportion) sorbents on the Re filament in TIMS, was measured as a function of VF temperature.

As can be seen from Fig. 6, the VF temperature was dependent on the method as well as the base polymer used for preparing the sorbent, and also on the shape of the sorbent. It can be concluded from Fig. 6 that: (i) the flat sheet sorbent requires a lower VF temperature than the bead sorbent, (ii) PP is a better host matrix compared to PES for TIMS analysis at an optimum VF temperature, and (iii) liquid extractants physically immobilized in the TEHP:HDEHP@PP sorbents have a VF temperature profile comparable to that obtained from a solution based loading. The PP matrix loaded on the Re filament was found to decompose completely at the TIMS analysis temperature, but a residue was observed in the case of PES. This may be related to their chemical structures shown in Fig. 1. The PP membrane is made up of hydrocarbon that can be completely pyrolyzed. Also, the liquid fraction in the TEHP:H-DEHP@PP sorbent would be vaporized easily as compared to the poly(HEMP-co-EHM)-PP/PES sorbents where the extractants are covalently attached to the host matrices. Thus, the sorbent consisting of the liquid extractants physically immobilized in



Fig. 6 (a) Pu evaporation profiles obtained by using solution (\bullet) , TEHP : HDEHP@PP (3 : 1 molar proportion) (\blacksquare), and poly(HEMP-*co*-EHM)-PP (\blacktriangle) sorbents based loading on the Re filament in TIMS, and (b) poly(HEMP-*co*-EHM)-PES bead (\bullet) and membrane (\blacktriangle).

a flat sheet PP membrane is better suited for TIMS. To compare the reproducibility, isotope composition analyses of the NIST-SRM 947 Pu isotopic standard were carried out using TIMS using the solution, poly(HEMP-*co*-EHM)-PP and TEHP:H-DEHP@PP based loadings on the Re filament and the results thus obtained are given in Table 2.

It is seen from Fig. 7 that the precision is slightly poorer in the sorbent based Pu loading in TIMS as compared to that obtained by a solution based loading. Between the poly(HEMP-*co*-EHM)-PP and TEHP:HDEHP@PP, the precision was better in the TEHP:HDEHP@PP based loading in TIMS. The precision

Table 2Determination of the isotopic composition of Pu in the SRM-947 Pu standard by TIMS using polymeric sorbent based loading andsolution-based loading

Isotope	Certified value (atom%)	Solution loading (atom%)	Membrane loading (atom%)
²³⁹ D1	79.03 ± 0.02	78.96 ± 0.03	78.96 ± 0.04
²⁴⁰ Pu	19.02 ± 0.02 19.02 ± 0.02	18.99 ± 0.03	19.01 ± 0.03
²⁴¹ Pu	0.808 ± 0.006	0.723 ± 0.006	0.728 ± 0.007
²⁴² Pu	1.238 ± 0.004	1.225 ± 0.006	1.229 ± 0.008





Fig. 7 Relative standard deviation in the determination of the isotopic composition of the NIST-SRM 947 Pu isotopic standard using the solution (\Box), TEHP:HDEHP@PP (Δ), and poly(HEMP-*co*-EHM)-PP (\bigcirc) based loading on the Re filament in TIMS.

obtained for the ²⁴⁰Pu/²³⁹Pu atom ratio is better compared to those for ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu atom ratios, owing to the fact that ²⁴⁰Pu and ²³⁹Pu are the major isotopes present in the standard, whereas ²⁴¹Pu and ²⁴²Pu are the minor isotopes and also isotopic fractionation is lower due to less relative mass difference between ²³⁹Pu and ²⁴⁰Pu isotopes. Based on optimum VF temperature and lower uncertainty in the isotopic composition, the TEHP:HDEHP@PP sorbent was further tested for its analytical performance.

The isotope dilution method was used for the quantification of Pu(rv) and U(vr) because of the fact that it is not affected by experimental conditions including variation in the sorption efficiency of the sorbent. Basically, the isotope dilution method is based on the addition of a known weight $W_{\rm sp}$ of a pre-calibrated spike solution, having known concentration C_{sp} , to a known weight $W_{\rm sa}$ of the sample solution. Pu concentration $C_{\rm sa}$ in the sample can be correlated with a change in the isotopic ratio in the spiked mixture (R_m) with respect to that in the sample (R_{sa}) and the spike (R_{sp}) .²⁹ The average concentrations of Pu(IV) from 3-5 measurements determined by the isotope dilution method in the dissolver solution are given in Table 3. It is from this table we find that the obtained concentration of Pu(IV) by PolymSorb-TIMS was in reasonably good agreement with that obtained by a solution-TIMS within the uncertainty limit. Analysis of uranium isotopic standard ISU-09, having a certified $^{235}\text{U}/^{238}\text{U}$ ratio = 1.096 \times 10⁻², was also performed by PolymSorb-TIMS and the results were compared with those of

Table 3 Comparison of Pu(w) concentrations determined in the dissolver solution obtained by PolymSorb-TIMS using TEHP:H-DEHP@PP with that obtained by solution-TIMS

	Pu(IV) conc. (ppm)			
	PolymSorb-TIMS		Solution-TIMS	
Sample	Avg.	RSD (%)	Avg.	RSD (%)
Dissolver solution	12.90 ± 0.07	0.51	13.05 ± 0.04	0.30



Fig. 8 EDX analyses of the samples of the HDEHP@PP membrane equilibrated with seawater (a), washed with 3 mol L^{-1} HNO₃ after equilibration with seawater (b), and equilibrated with seawater spiked with 1.7 ppm U(vI) (c).

solution-TIMS. The 235 U/ 238 U ratio in the ISU-09 standard was found to be 1.0985 × 10⁻² and 1.0979 × 10⁻², respectively, by solution-TIMS and PolymSorb-TIMS. However, the 234 U/ 238 U ratio could not be measured since the Faraday cup detectors of the Isoprobe-T instrument are not capable of measuring such low intensity ion beams.

Matrix elimination by the sorbent for TIMS

It was observed from the energy dispersive X-ray spectrometer (EDX) attached to SEM that only U(v₁) ions were sorbed in the polymer sorbent from seawater when U(v₁) ions saturate the binding sites. However, other ions were sorbed when the binding sites in the polymer sorbent are not saturated with U(v₁) ions, see Fig. 8. In such conditions, the ions sorbed in the polymeric sorbent could be removed by equilibrating it with 3 mol L^{-1} HNO₃ as only U(v₁) and Pu(v₁) are sorbed at this acidity.

Application to natural water and biological samples

Finally, the PolymSorb-TIMS was applied to Pu(IV) and U(VI) quantifications in seawater, ground water and synthetic urine samples. The synthetic urine sample was prepared as described elsewhere.28 For Pu(IV) determination, the TEHP:HDEHP@PP sorbent was used for Pu(IV) preconcentration and subsequent loading for TIMS. The concentration of HNO₃ in sample solutions was adjusted to 3 mol L^{-1} HNO₃ as the Pu(IV)-sorption efficiency was maximum at this acidity. For U(vi) determination, the HDEHP@PP sorbent was used without adjusting the acidity of the sample as the U(vi)sorption efficiency of this sorbent is not affected by the acidity of the equilibrating sample, see Fig. 4. As shown in Table 4, the measured concentrations of Pu(IV) and U(VI) obtained using the isotope dilution based PolymSorb-TIMS are in reasonably good agreement with the expected concentrations. This clearly demonstrates the applicability of PolymSorb-TIMS developed in the present work to a wide variety of aqueous samples.

The dissolver solution contained several µg of Pu as shown in Table 3, but the aqueous samples listed in Table 4 had a few ng of Pu. The intensities of the ion beams, obtained during TIMS analysis, were much higher for the samples shown in Table 3 than in Table 4. Therefore, the uncertainties in the values obtained in Table 3 are lower than those in Table 4 because of differences in the Pu amounts available for TIMS analysis. Table 4 shows the comparison of U/Pu concentration, in nanogram per gram, determined in various aqueous samples by PolymSorb-TIMS with the respective expected values. The relative standard deviation (RSD%) values given in Table 4 were calculated from the triplicate TIMS analyses of each sample.

Table 4 Determination of $\mathsf{Pu}(\mathsf{iv})$ and $\mathsf{U}(\mathsf{vi})$ in the aqueous samples using isotope dilution based $\mathsf{PolymSorb}\text{-}\mathsf{TIMS}$

	•		Conc. (ppb)	
Sample (spiked)	Volume (mL)	Actinides	Expected	Measured
Synthetic urine	50	Pu(IV)	9.45	9.56 ± 0.21
Seawater	50	Pu(IV)	5.64	5.53 ± 0.11
Seawater (un-spiked)	50	U(vi)	3.31	3.62 ± 0.20
Ground water	50	U(vi)	3.12	2.83 ± 0.14

It can be seen from Table 4 that for Pu the values are 1.0116, 0.9805 with a mean of 0.99 \pm 1.6% and for U, 1.0936 and 0.9071 with a mean of 1.00 \pm 9.3%. Thus, the accuracy of about 2% and 10% was obtained for Pu and U(vi) determination, respectively, at the ng g⁻¹ concentration levels. The lower accuracy of U determination compared to that of Pu determination can be attributed to the poorer ionization efficiency of U, leading to lower ion currents available for the TIMS analysis of U(vi).

Conclusions

Polymeric material based sorbents for actinide loading in TIMS were developed in the present work using UV-initiator induced grafting and physical immobilization of lipophilic liquid extractants in microporous poly(propylene)/poly(ethersulfone) membranes and beads. It was observed that HDEHP and TEHP immobilized in the poly(propylene) membranes are the best suited for dual functions of the sorbent i.e. efficient preconcentration of Pu(IV) and U(VI) from a wide variety of aqueous matrices and TIMS analysis with low vaporization filament temperature. The HDEHP and TEHP immobilized in poly-(propylene) were applied successfully for the quantification of $U(v_1)$ and $Pu(v_2)$ in the synthetic urine sample, seawater and ground water using the isotope dilution method with reasonable accuracy and precision. U(vi) was preconcentrated in the sorbent without adjusting the acidity of the aqueous samples, but required adjustment to 3 mol L^{-1} HNO₃ for Pu(IV) preconcentration. The major advantage of the PolymSorb-TIMS developed in the present work is that it is a single step sample manipulation and loading process that would greatly reduce the analysis time and prolonged handling of radioactivity, eliminating the possibility of radioactive contamination and personnel exposure to radiation.

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