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## Superparamagnetic bi-functional composite bead for thermal ionization mass spectrometry of plutonium(IV) ions

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The single resin bead based thermal ionization mass spectrometry (TIMS) offers numerous advantages for Pu(IV) determinations in complex aqueous samples. These include the matrix and interfering ions removal by a one step process, selective preconcentration of Pu(IV) ions with a high chemical recovery, transportation without heavy shielding, avoiding the possibility of cross-contamination, and acts as a point source. The single bead TIMS method reported in literature is based on the anion-exchange resin that lacks the sorption-selectivity towards Pu(IV) ions, and also the beads are not easily retrievable from a large volume sample. Therefore, the silica coated superparamagnetic Fe<sub>3</sub>O<sub>4</sub> embedded functionalized porous poly(ethersulfone) (PES) beads were developed for the Pu(IV) preconcentration and analysis by TIMS. The beads were functionalized with a phosphate bearing monomer along with or without a quaternary ammonium bearing monomer by UV-induced surface grafting. Since the beads were used in highly acidic solution, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were protected with a silica coating formed by hydrolysis and condensation of tetraethoxysilane. The PES porous beads were prepared by a phase inversion method. The monomers used for UV-grafting were 2-hydroxyethyl methacrylate ester and (3-acrylamidopropyl)trimethyl ammonium chloride. The functionalized beads were characterized by scanning electron microscopy, energy dispersive analysis, and vibrating sample magnetometry. The sorption studies indicated that the bi-functionalized PES beads consisting of phosphate and quaternary ammonium groups not only have a higher distribution coefficient (K<sub>d</sub>) for Pu(IV) but also higher selectivity towards Pu(IV) ions in the presence of large excess of U(VI) ions (K<sub>d</sub>(Pu(VI))/K<sub>d</sub>(U(VI))=11.5). The phosphate functionalized PES bead showed comparable selectivity (K<sub>d</sub>(Pu(VI))/K<sub>d</sub>(U(VI))=9.1), but lower K<sub>d</sub> value for Pu(IV). The quaternary ammonium functionalized PES beads were found to have lower selectivity and K<sub>d</sub> values towards Pu(IV) ions. The analytical performance of single bifunctionalized bead based TIMS for the determination of Pu(IV) using isotope dilution was compared with the solution based TIMS, validated using the Pu isotopic standard reference material NIST-SRM-947, and applied to the real samples such as dissolver solutions and soil leach liquors.

### Introduction

The knowledge of Pu isotopic composition and its amount is important for the nuclear energy utilization, nuclear safeguards, nuclear forensics, and environmental contaminations. For nuclear forensics, the relative contents of Pu isotopes are useful as a finger print to identify the source of origin as the abundances of different isotopes of plutonium are highly dependent on the type of nuclear reactor, nuclear fuel burn-up etc. The various Pu measurement procedures have been developed using alpha spectrometry, mass spectrometry and other radiometric methods.<sup>1</sup> The three mass spectrometric methods being used for ultratrace

determinations of Pu concentrations in the complex aqueous samples are thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS).<sup>1-2</sup> Multiple collector mass spectrometers are capable of simultaneous determination of a number of isotopes. Sector-field multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS) are capable of analyzing less than 10 fg of Pu with a high precision (3% 2s).<sup>3</sup> However, a chemical purification step is required to eliminate the isobaric and polyatomic interferences such as <sup>238</sup>U interference in <sup>239</sup>Pu determination.<sup>4</sup> The chemical treatments using rapid column extraction with TEVA<sup>TM</sup> and TRU<sup>TM</sup> resin cartridges not only remove interferences but also make possible simultaneous analyses of the different actinides with ICP-MS.<sup>5</sup>

A combination of anion-exchange and extraction chromatography is better for achieving a higher Pu chemical recovery and U decontamination factor.<sup>6</sup> An automated sequential injection separation system in conjunction with MC-ICP-MS has been developed for simultaneous analysis of <sup>237</sup>Np and Pu isotopes in environmental samples.<sup>7</sup> The high chemical

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recovery (>90%) and low detection limits, 2.5, 2.1 and 0.42 fg mL<sup>-1</sup> obtained for <sup>237</sup>Np, <sup>239</sup>Pu and <sup>240</sup>Pu, respectively, reduces the soil and sediment samples requirement as low as 1 g.<sup>7</sup> The chemical purification along with isotope dilution technique makes MC-ICP-MS highly reliable for analyses of ultratrace concentration of Pu in the environmental sample.<sup>8</sup>

However, TIMS in conjunction with isotope dilution is also used commonly for the quantifications of Pu in the ng range in nuclear facilities.<sup>1-2</sup> TIMS analyses give a reproducibility of 0.1% (2s) for ≈1 ng Pu, 1.5% (2s) for 200–500 fg Pu, and 10% for <50 fg Pu.<sup>3b</sup> In general, the Pu analyses by TIMS require an appropriate sample preparation procedure involving dissolution/leaching to bring Pu into the solution, the matrix elimination and selective preconcentration of Pu, and finally manual deposition of small volume (≈ 10 μL) of solution onto a filament surface.<sup>9</sup> The general comparison of TIMS and ICP-MS based analytical methods is given in Table 1.

There is a possibility to use solid sample in TIMS instead of liquid sample. A single anion-exchange resin bead based TIMS method has been developed for the isotopic analysis of U and Pu in the safeguarded nuclear materials.<sup>10</sup> In this method, Pu(IV) ions are loaded in a bead either from the original sample or after purification using anion-exchange or extraction chromatography, and the Pu-loaded-bead is fixed on a Re filament and pyrolyzed during TIMS. Thus, the bead acts as the matrix for chemical separation, helps to secure physical transportation, hence reducing the possibility of contamination of instrument or cross contamination of the sample, and it is a point source for the thermal ionization. Sequential mass spectrometric analysis of uranium and plutonium has been carried out in our laboratory employing a single Dowex 1X8 resin bead loaded with about 10 ng of plutonium.<sup>10a</sup> To enhance the Pu(IV) sorption kinetics in a single bead for TIMS, the acoustic streaming has been used for the small sample volume.<sup>11</sup>

In the present work, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) embedded bi-functional poly(ethersulfone) (PES) beads have been developed for the single bead based TIMS analyses of Pu in the aqueous samples. The choice of quaternary ammonium and phosphate functional groups bearing monomers for UV-grafting on the PES beads has been based on a high affinity of phosphate group towards Pu(IV) ions,<sup>12</sup> and quaternary ammonium group would facilitate the sorption of hexanitrate anionic complex, Pu(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup>, existing in solution with a high concentration of 7-8 mol L<sup>-1</sup> HNO<sub>3</sub>. The PES polymer has been used as a base matrix due to its amenability for UV grafting,<sup>13</sup> and easy formation of the porous beads by phase inversion method. The superparamagnetic Fe<sub>3</sub>O<sub>4</sub> NPs have been immobilized in the bi-functional PES beads for their easy retrieval from a large volume sample using an external magnet. This concept is similar to magnetically assisted chemical separation for the remediation and analytical applications.<sup>14</sup> For single bead TIMS analyses of Pu, the isotope dilution method has been employed for the quantification to make the results independent of chemical recovery and unknown variations in the experimental parameters.<sup>15</sup>

## Experimental

### Reagents and apparatus

Analytical reagent grade solvents, suprapure grade nitric acid (Merck, Mumbai), and deionized water (18 MΩ cm<sup>-1</sup>) purified by Quantum from Millipore (Mumbai, India) were used. Hydroxylamine hydrochloride was obtained from SISCO Research laboratories Pvt. Ltd. (Mumbai). Hydrogen Peroxide (30%) was procured from Merck Specialties Pvt. Ltd. (Mumbai). The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained J.K. Impex, Mumbai, India. These particles were characterized by X-ray diffraction (XRD) and field emission gun scanning electron microscopy (FEG-SEM). The size distribution of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was ranging from 20-30 nm.

**Table 1.** Comparison of TIMS and ICP-MS based analytical methods.

Parameter	TIMS	ICP-MS
Ionization	Thermal ionization (produces ion beam with very high ionization yield and selectivity)	Inductively coupled plasma source at normal pressure
Sample	Amenable to solid sample (≈10 μL of aqueous sample solution is deposited on high purity Re filament surface or resin/bead mounted on Re filament)	More suited for liquid sample injection.
Interference	Formation of plutonium oxide that can be prevented by filament carburization	Isobaric (e.g. <sup>238</sup> U and <sup>238</sup> Pu, <sup>241</sup> Am and <sup>241</sup> Pu) and polyatomic (e.g. <sup>238</sup> UH and <sup>239</sup> Pu) interferences
Sample purification methods	Ion-exchange and extraction chromatography	Ion-exchange and extraction chromatography
Analytical Performance	<i>Advantage:</i> Excellent sensitivity Precise isotopic ratio determination. Small amount of analyte needed <i>Disadvantage:</i> Lacks multi-element capability, complicated sample preparation, restriction on elements with ionization potential <6 eV	<i>Advantage:</i> Excellent sensitivity, low detection limit, small amount of analyte, excellent simultaneous multielement analysis ability, on-line separation and analysis <i>Disadvantage:</i> Solid sample cannot be used, Matrix effect.
Major Applications	Isotopic composition determination of actinides	Quantification of isotopes in various environmental, biological and geological samples.

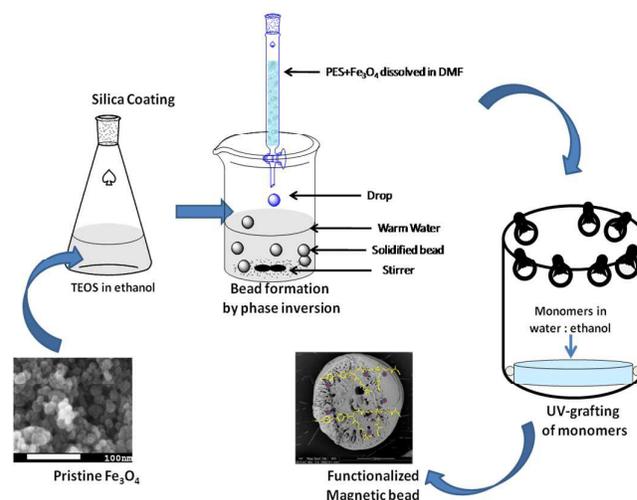
Poly(ethersulfone) was obtained from Goodfellow Cambridge Ltd. (England). Tetraethoxysilane, phosphoric acid 2-hydroxyethyl methacrylate ester (HEMP) containing 25% diester, 3-(acrylamido propyl) trimethylammonium chloride (APTAC) and *N-N'*-dimethylformamide (DMF) were obtained from Sigma-Aldrich (Steinem, Switzerland). The chemical structures of monomers are given in Scheme S1 (†ESI). The surface grafting of monomers on PES beads was carried out in a photo-reactor (Heber Scientific, Chennai, India) consisting of eight 8 Watt 365 nm UV lamps (Sankyo Denki, Japan) fitted in a circular geometry.

The purified stock solutions of <sup>mixed</sup>Pu, <sup>241</sup>Am and <sup>233</sup>U were obtained from Fuel Chemistry Division, B.A.R.C., Mumbai, India. The Pu was generated in an Indian Pressurised Heavy Water Reactor (PHWR) with an average burn-up of ~10,000 MegaWatt Day/Ton of U. The isotopic compositions of these tracers were determined by TIMS. The isotopic composition of Pu(IV) was <sup>238</sup>Pu (0.16%), <sup>239</sup>Pu (68.79%), <sup>240</sup>Pu (26.94%), <sup>241</sup>Pu (2.09%), <sup>242</sup>Pu (2.02%). The irradiated UO<sub>2</sub> fuel dissolver solution was obtained from Fuel Reprocessing Division, BARC, Mumbai, India, that contains the fission products, major actinides (U, Pu), minor actinides and activation products. The alpha activity of actinides in aqueous solution was measured by a home-built liquid scintillation counter, having a EMI 9514 photomultiplier tube and using Ultima Gold AB scintillation cocktail (Perkin Elmer). The gamma activity measurement was carried out using a well-type 3"x3" NaI(Tl) detector coupled to single channel analyzer (NUCLEONIX). The TIMS analyses were carried out using a model MAT-261 (Finnigan, Germany) equipped with 9 Faraday cups, each cup connected to a resistor of 10<sup>11</sup> ohm. The specifications of the TIMS instrument used in the present study are given in Table 2. The Pu<sup>+</sup> ion currents were measured under static mode of multi-collection and a double Re filament assembly was used for the sample loading.

### Synthesis of functionalized magnetic PES beads

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) were coated with tetraethoxysilane (TEOS) dissolved in ethanol constantly being shaken at room temperature for 12 h. The magnetic PES beads were synthesized by a phase inversion method.

Typically, PES granules were dissolved in the appropriate volume of DMF to get a saturated solution. To this, the TEOS coated Fe<sub>3</sub>O<sub>4</sub> NPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) were homogenously dispersed by sonication for 30 min. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> dispersed PES solution was added drop-wise to water with continuous stirring to produce nearly spherical magnetic PES beads having diameter ranging from 0.5-1 mm, as shown in Scheme 1. For grafting functional groups, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> loaded PES beads were equilibrated with an equimolar mixture of the two monomers HEMP and APTAC in solution consisting of 1:1 v/v water:ethanol. After equilibration, the polymerizing solution filled beads were irradiated for 15 min in a UV reactor ( $\lambda_{\text{max}} = 365 \text{ nm}$ ). During irradiation, the poly(ethersulfone) polymer chains undergo photolysis to generate free radicals,<sup>13</sup> which initiate graft polymerization of HEMP and/or APTAC monomers on the PES beads. The poly(HEMP), poly(APTAC) and poly(HEMP-co-APTAC) grafted magnetic PES beads obtained after irradiation were washed with ethanol to remove un-reacted monomers, air dried, and conditioned with 0.1 mol L<sup>-1</sup> NaCl before use. A detailed pictorial representation of the steps involved in formation of bi-functional magnetic PES bead is given in Scheme 1.



**Scheme 1.** Schematic representation of the synthesis of bifunctional magnetic PES beads by phase inversion method and UV-grafting.

**Table 2.** Specifications of Finnigan MAT-261 TIMS instrument used in the present study.

Parameter	MAT-261 TIMS instrument
Acceleration voltage	10 kV
Ion source & Filament	Thermal ionization with high purity rhenium double filament assembly
Analyser	Nine variable Faraday Cup detectors, designated as FAR2 to FAR10, each coupled to a 10 <sup>11</sup> ohms resistor
Isotopic mass assigned to Faraday Cup	<sup>239</sup> Pu to L1, <sup>240</sup> Pu to axial/centre cup, <sup>241</sup> Pu to H1 and <sup>242</sup> Pu to H2
Mass resolution ( $\Delta M/M$ ) at 10% valley	450
Abundance sensitivity	10 ppm (at $m/z=237/238$ )

### Sorption and desorption studies

The sorption and desorption studies of Pu(IV), Am(III) and U(VI) ions from the bi-functional super-paramagnetic PES beads were carried out using same procedure as described in our earlier work.<sup>12,15a</sup> Briefly, the sorption efficiencies of the actinide ions were measured by equilibrating 100 mg beads for 3-4 h with 5 mL of the well-stirred solutions containing 3 to 8 mol L<sup>-1</sup> HNO<sub>3</sub>, and spiked with fixed concentrations of <sup>mixed</sup>Pu/<sup>241</sup>Am/<sup>233</sup>U. The sorption efficiency of actinides ions in the beads were determined from the difference in  $\alpha$ -activity (<sup>mixed</sup>Pu and <sup>233</sup>U) or  $\gamma$ -activity (<sup>241</sup>Am) of the aliquots taken from the solution before and after equilibrations. For desorption, the beads were equilibrated with 3 mol L<sup>-1</sup> HNO<sub>3</sub>, 1

mol L<sup>-1</sup> NH<sub>2</sub>OH.HCl and 0.5 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> for Am(III), Pu(IV) and U(VI), respectively. The Pu(IV) sorption kinetics was studied by equilibrating 200 mg of PES beads with 30 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub> solution spiked with appropriate amount of Pu radiotracer, with continuous stirring. The uptake of Pu(IV) by the beads was monitored by taking 25 μL aliquots from this solution at regular intervals, and α-activities in these aliquots were measured as a function of equilibration time. For determination of the distribution coefficients (K<sub>d</sub>) of actinide ions, the PES beads were equilibrated with a mixture of <sup>233</sup>U and <sup>mixed</sup>Pu ions in 100:1 mol proportion, and the K<sub>d</sub> values for Pu(IV) and U(VI) ions were obtained using the following equation:

$$K_d = \frac{(A_0 - A_e) X}{W} \frac{V}{A_e} \quad (\text{mL g}^{-1}) \quad (1)$$

where A<sub>0</sub> and A<sub>e</sub> represent radioactivities of <sup>233</sup>U/<sup>mixed</sup>Pu before and after equilibration, respectively, W is weight of the PES beads and V is volume of the equilibrating solution.

### Thermal ionization mass spectrometry

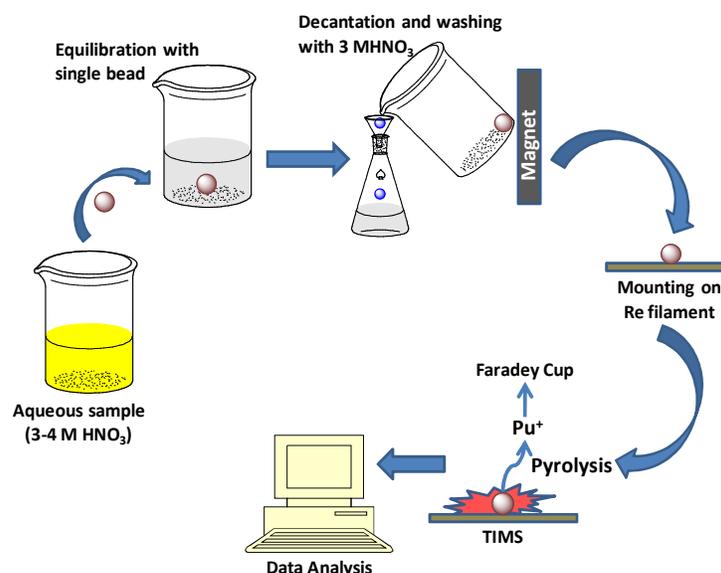
The analytical performance of the single bead based thermal ionization mass spectrometry (SB-TIMS) for Pu analysis was studied using a NIST SRM-947 Pu isotopic standard. The various steps involved in Pu analysis by SB-TIMS method are depicted in Scheme 2. The isotopic composition of Pu in the sample was determined by SB-TIMS by equilibrating a single magnetic bi-functional PES bead in 5 mL of the well-stirred 3 mol L<sup>-1</sup> HNO<sub>3</sub> solution, spiked with ~1 μg of Pu for 1 h. After equilibration, the bead was brought close to the solution surface using an external permanent magnetic bar and collected from the solution using tweezers. The collected bead was washed thoroughly with water and 3 mol L<sup>-1</sup> HNO<sub>3</sub>, air-dried and directly loaded onto a high purity rhenium filament for the TIMS analysis. Prior to the Pu analysis, the ionization filament

(IF) was heated to obtain ~200 mV equivalent of <sup>187</sup>Re<sup>+</sup> ion current. Thereafter, the vaporization filament (VF) was heated from 0 to 2A in 900 s and degassing was carried out at 2A for 1800 s. The degassing temperature (VF temp. 2 Amp) was sufficiently lower than the temperature required for the evaporation of Pu atoms loaded on the Re filament (VF temp 2.25 Amp). Therefore, practically no loss of Pu during the degassing period was observed. After degassing, VF heating was increased to obtain optimum Pu<sup>+</sup> ion current. During each determination of Pu, the blank beads were subjected to TIMS to observe significant Pu<sup>+</sup> ion current, if any. This ensured that there were no Pu contaminations in the beads.

The single bead based isotope dilution thermal ionization mass spectrometry (ID-SB-TIMS) technique was employed for the determination of Pu concentration in the dissolver solution of irradiated UO<sub>2</sub> fuel and in the soil leach liquor samples spiked with known amount of Pu(NO<sub>3</sub>)<sub>4</sub>. The Pu concentration was determined by isotope dilution (ID) technique, which involves addition of a known weight W<sub>sp</sub> of a pre-calibrated spike solution, having Pu concentration C<sub>sp</sub>, to a known weight W<sub>sa</sub> of the sample solution. Each sample and its spiked mixture were equilibrated with a bi-functional magnetic PES bead, and placed on Re filament for isotopic composition analysis by TIMS. The Pu concentration C<sub>sa</sub> in the sample can be correlated with the change in either <sup>240</sup>Pu/<sup>239</sup>Pu or <sup>242</sup>Pu/<sup>239</sup>Pu atom ratio in the spiked mixture (R<sub>m</sub>) with respect to that in the sample (R<sub>sa</sub>) and spike (R<sub>sp</sub>) by using the following equation:

$$C_{sa} = \frac{C_{sp} W_{sp}}{W_{sa}} \frac{(R_{sp} - R_m)}{R_{sp}(R_m - R_{sa})} \frac{AF_{sp}^{240/242} <At.Wt.>_{sa}}{AF_{sa}^{239} <At.Wt.>_{sp}} \quad (2)$$

For determination of the Pu concentration, the single bi-functional magnetic PES bead was equilibrated with 3 mL of the dissolver solution (U:Pu mole ratio ~1000:1) and its spiked mixture, separately, for 1 h and with continuous stirring.



**Scheme 2.** Depiction of different steps involved in the determination of Pu(IV) ions using single bead based isotope dilution thermal ionization mass spectrometry developed in the present work.

After equilibration, the single bead was washed and loaded onto Re filament for isotopic composition analysis of Pu in the dissolver solution and its spiked mixture. For quantification of Pu(IV) in a large volume sample, a known Pu concentration and its spiked mixture were added to 50 mL of the 3 mol L<sup>-1</sup> HNO<sub>3</sub> separately, and equilibrated with the single bi-functional magnetic PES bead for 24 h with continuous stirring. For determination of the Pu concentration in the soil samples, the solution containing a known Pu concentration was added to about 2 g of soil sample, collected from B.A.R.C. premises after digging one foot, homogenized manually, and dried under IR lamp for 2-3 h. The solution was sufficient to soak 2 g of soil. Then, the soil sample was treated with 50 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> containing 2-3 mL of 30% H<sub>2</sub>O<sub>2</sub>, and heating (65-70 °C) under IR lamp for 8 h. The obtained soil leach liquor was used for the Pu quantification.

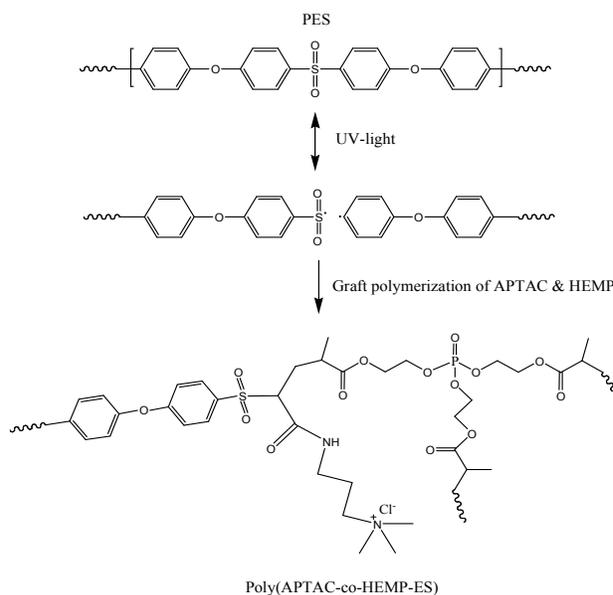
The same procedure was repeated for a spiked mixture of Pu. The leach liquor (50 mL) was equilibrated with a single bi-functional magnetic PES bead for 24 h with continuous stirring. After preconcentration of Pu(IV) ions, the beads were collected using a magnet, washed, dried and loaded onto Re filament for Pu isotopic composition analysis by TIMS. The Pu concentrations in various samples were calculated from the change in isotope ratios in the spiked mixture with respect to that in the sample and the spike.

## Results and discussion

### Characterization of functionalized magnetic beads

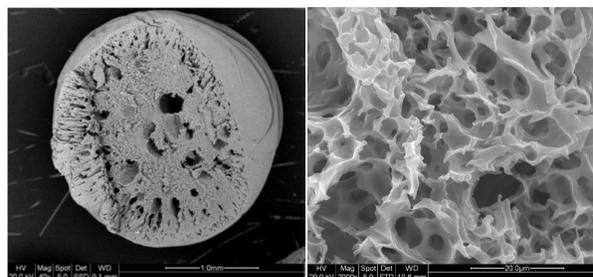
The functional monomers were anchored using the free radical formed during UV-light exposure of PES polymer chains.<sup>13</sup> The free radicals initiate graft polymerization of monomers. The monomers APTAC and HEMP used for the preparation of bi-functional PES beads are acrylate based and, therefore, are expected to graft-polymerize with comparable efficiencies as observed in our previous work.<sup>12</sup> The HEMP monomers have three or two double bonds that may lead to the formation of dense cross-linked grafted co-polymer on the surface layer of PES beads. The surface grafting of monomers on the PES was expected as 365 nm UV light would not penetrate deep into the interior of the matrix. The representative chemical changes involved in the grafting of monomers on the PES beads are shown in Scheme 3.

The physical and elemental characterization of the bi-functionalized superparamagnetic beads was carried out by scanning electron microscope (SEM) and energy dispersive spectrometer attached to it. As can be seen from the SEM images given in Fig.1, the PES beads prepared in the present work had a dense surface and highly porous interior. The physical structure of the beads did not change during grafting of the HEMP monomer with or without co-monomer APTAC. The silica coated Fe<sub>3</sub>O<sub>4</sub> NPs were not visible as these may be embedded in the PES matrix. The phosphorus elemental mappings at different locations across a bead showed that the grafting occurred uniformly.

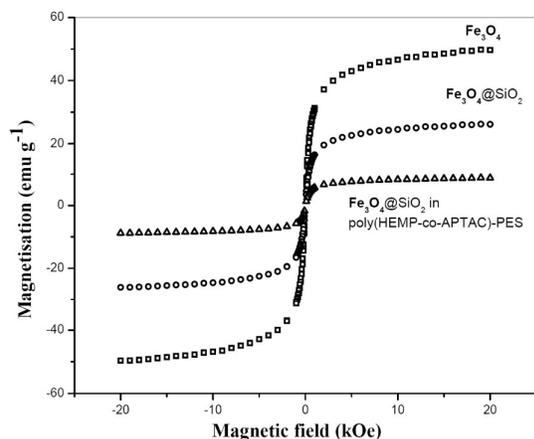


**Scheme 3.** The representative chemical modifications of PES beads during UV-grafting of phosphoric acid 2-hydroxyethyl methacrylate ester (HEMP) and 3-(acrylamido propyl) trimethylammonium chloride (APTAC).

The presence of elements such as S from the base PES matrix, Fe and Si from the silica coated Fe<sub>3</sub>O<sub>4</sub>, phosphorus and nitrogen from the grafted poly(HEMP-co-APTAC) were observed in the EDS spectra. As can be seen from Fig. S1 ((+ESI), the nitrogen (two N atoms in APTAC) and phosphorous (one P in HEMP) contents are comparable indicating that both monomers had polymerized with a same efficiency. As beads have to be equilibrated with the solution containing high concentration of HNO<sub>3</sub>, the beads were immersed in 3 and 8 mol L<sup>-1</sup> HNO<sub>3</sub>, separately, for 24 h and subjected to the elemental composition analyses. It is evident from Fig.1S ((+ESI) that the elemental composition of beads did not change during equilibration with a high concentration of acid. Thus, all the components including silica coated Fe<sub>3</sub>O<sub>4</sub> in the functionalized beads are highly stable against leaching in a solution having high concentrations of HNO<sub>3</sub>. The changes in the superparamagnetic properties of Fe<sub>3</sub>O<sub>4</sub> after coating silica and immobilizing in the bifunctional beads were studied by vibrating sample magnetometry (VSM).



**Fig. 1** SEM images of poly(HEMP-co-APTAC) grafted super-paramagnetic bead under different magnifications.



**Fig.2** VSM magnetization curves showing the superparamagnetic properties, and change in saturation magnetization of the bi-functionalized PES bead with respect to  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@SiO_2$  particles.

The comparison of magnetization curves is shown in Fig. 2. As can be seen from Fig. 2, the  $\text{Fe}_3\text{O}_4$  NPs retained their superparamagnetic properties except that the saturation magnetization decreased due to a magnetic shielding by the silica coating and PES matrix. For example, the saturation magnetization of  $\text{Fe}_3\text{O}_4$  particles decreased from  $50 \text{ emu g}^{-1}$  to  $26 \text{ emu g}^{-1}$  after the silica coating and further decreased to  $9 \text{ emu g}^{-1}$  after embedding them ( $\sim 2 \text{ wt.}\%$ ) in the matrix of bi-functionalized PES beads. However, the saturation magnetization of beads was found to be good enough for withdrawing the single bead from aqueous sample using an external permanent magnet kept outside.

#### Sorption properties of functionalized magnetic beads

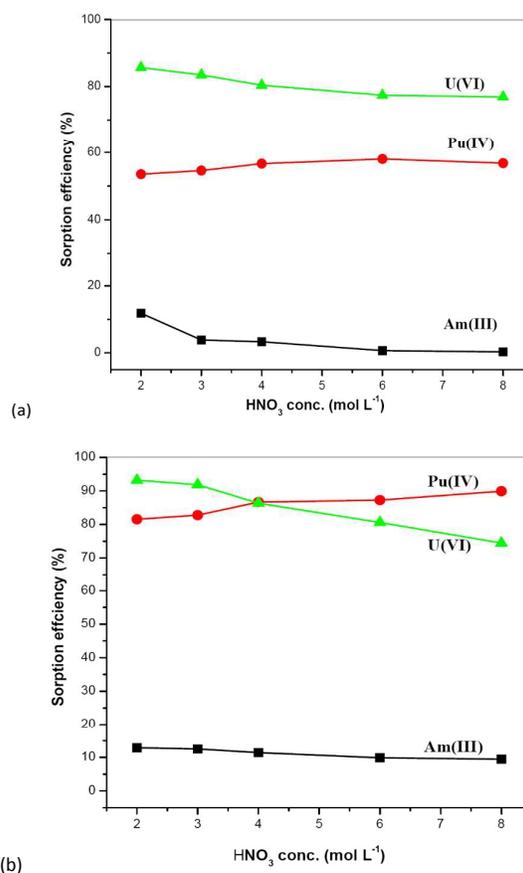
To understand the effect of bi-functionalization on the sorption of actinide ions, the uptake profiles of the representative actinides viz. Pu(IV), Am(III) and U(VI) were studied as a function of  $\text{HNO}_3$  concentration using the poly(HEMP) and poly(HEMP-co-APTAC) grafted magnetic PES beads. The Pu(IV), Am(III) and U(VI) uptake profiles given in Fig. 3 clearly show that Am(III), a representative of trivalent actinides, was not sorbed with any significant efficiencies in both mono/bi functionalized beads. Unlike Am(III), Pu(IV) and U(VI) ions were sorbed with a high efficiency. It is interesting to observe from Fig. 3 that the Pu(IV)-sorption efficiency did not change significantly in the  $\text{HNO}_3$  concentration range of 2 to  $8 \text{ mol L}^{-1}$  in both kinds of beads. However, the Pu(IV)-sorption efficiency of poly(HEMP-co-APTAC) grafted PES beads was considerably higher ( $\approx 90\%$ ) than that in the poly(HEMP) grafted PES beads ( $60\%$ ). This may be attributed to a fact that the anionic Pu(IV) complexes like  $[\text{Pu}(\text{NO}_3)_3]^-$  and  $[\text{Pu}(\text{NO}_3)_6]^{2-}$  exist in a higher  $\text{HNO}_3$  concentration and, therefore, the presence of quaternary ammonium groups improved the Pu(IV)-sorption efficiency.

In case of U(VI) ions, the sorption efficiency of poly(HEMP) and poly(HEMP-co-APTAC) grafted beads remained high (80-90%), and decreased slightly with an increase in  $\text{HNO}_3$  concentration.

**Table 3.** Distribution coefficient ( $K_d$  value) of Pu(IV) and U(VI) ions in the different sorbents from the solution containing  $4 \text{ mol L}^{-1} \text{ HNO}_3$  and 1:100 mole proportion of Pu(IV) to U(VI) ions.

Polymer sorbent	$K_d$ (Pu(IV)) ( $\text{mL g}^{-1}$ )	$K_d$ (U(VI)) ( $\text{mL g}^{-1}$ )	$K_d(\text{Pu(IV)})/$ $K_d(\text{U(VI)})$
Dowex 1X8	197	32	6.15
Poly(APTAC)-PES	98	46	2.13
Poly(HEMP)-PES	227	25	9.09
Poly(HEMP-co-APTAC)-PES	462	40	11.53

Thus, both kinds of beads would not differentiate between U(VI) and Pu(IV) ions present in the aqueous sample. The selectivity of polymer sorbents towards Pu(IV) and U(VI) ions was studied in a competitive mode by measuring their  $K_d$  values in the solutions containing a 100:1 mole ratio of U(VI) and Pu(IV) at  $4 \text{ mol L}^{-1} \text{ HNO}_3$ . It is seen from the data given in Table 3 that the  $K_d(\text{Pu(IV)})$  values are higher in all sorbents, including commercially available anion-exchange resin Dowex 1X8 and home-made poly(APTAC) PES beads. The data given in Table 3 suggest that the  $K_d$  value for Pu(IV) and ratio of  $K_d(\text{Pu(IV)})$  to  $K_d(\text{U(VI)})$  is highest in the bi-functional PES magnetic beads.



**Fig.3** The uptake profiles of actinides ions as a function of  $\text{HNO}_3$  concentration in the poly(HEMP) functionalized (a) and poly(HEMP-co-APTAC) grafted (b) magnetic PES beads.

The kinetics of Pu(IV) sorption by the bi-functional magnetic PES beads was studied to ensure optimum recovery of Pu(IV) from the sample during equilibration. The rate of Pu(IV) sorption by the beads from 3 M HNO<sub>3</sub> as a function of equilibration time is shown in Fig. S2 (†ESI). As shown in Fig. S2 (†ESI), the Pu(IV)-sorption equilibrium was attained within 80 min. The Pu(IV)-sorption rate followed a pseudo-second order equation (see †ESI).<sup>12</sup> The initial Pu(IV)-sorption rate was fast and reduced thereafter due to slow transfer of Pu(IV) ions from the surface to interior of the matrix. The sorption capacity of the bi-functional magnetic PES beads determined from the slope of plot of  $t/[Pu(IV)]$  vs.  $t/[Pu(IV)]_{eq}$  was found to be 93  $\mu\text{g of Pu g}^{-1}$ . This value is in a good agreement with the experimentally measured Pu loading capacity 92  $\mu\text{g of Pu g}^{-1}$ . The effect of volume of the equilibrating solution on the Pu(IV)-sorption efficiency of the bi-functional magnetic PES beads was also studied. The data presented in Fig. S3 (†ESI) indicate that the Pu(IV)-sorption efficiency was nearly constant up to 30 mL, but reduced thereafter because of the slower diffusion of Pu(IV) ions in a large volume of the equilibrating solution. Therefore, the preconcentration of Pu(IV) ions from a large volume sample, higher than 30 mL, would require a longer equilibration time (24 h for 50-100 mL) or better equilibration method like a flow cell.

#### Functionalized magnetic bead based thermal ionization mass spectrometry

For single bead thermal ionization mass spectrometry (SB-TIMS), the bead was fixed on a thin Re filament and subjected to high temperature for pyrolysis of bead, thermal desorption of the analyte, and subsequent ionization. The extent of ionization of the analyte is governed by Saha-Langmuir equation,<sup>16</sup> and the analyte should be in its chemically purest state in order to achieve the optimum ionization. The rate of evaporation of Pu atoms, which is proportional to the Pu<sup>+</sup> ion current, is important for the optimum analytical signal in TIMS. Therefore, the variations in <sup>239</sup>Pu<sup>+</sup> ion current as a function of vaporization filament temperature were studied in solution and single bead based TIMS. The plots of <sup>239</sup>Pu<sup>+</sup> ion current vs. vaporization filament temperature (VF) are shown in Fig. 4.

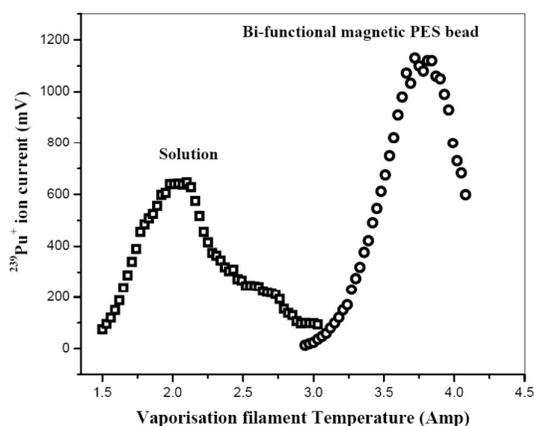


Fig.4 Variations of observed <sup>239</sup>Pu<sup>+</sup> ion current from the solution and bi-functionalized magnetic based Pu loadings as a function of vaporization filament temperature.

With increasing temperature of the VF, the Pu<sup>+</sup> ion current was found to increase according to Saha-Langmuir equation. In the present work, no PuO<sup>+</sup> ion current was observed during analysis due to the reducing atmosphere provided by the PES polymer present on the filament surface. The optimum VF heating current for the isotopic analysis of Pu was found to be about 4 Amp, at which about 1V signal corresponding to <sup>239</sup>Pu<sup>+</sup> ion current was obtained. The ionization efficiency of the SB-TIMS method was lower than the conventional solution based loading method, but the ion collection efficiency was comparable for both the techniques. The magnetic PES bead on the Re filament did not decompose completely. Therefore, it was important to carry out degassing of the bead loaded on filament prior to TIMS analysis to remove volatile impurities and obtain stable Pu<sup>+</sup> ion current. The effect of degassing on the precision of Pu isotopic atom ratio obtained from single magnetic PES bead fixed on Re filament was studied and compared with the precision obtained from the conventional TIMS method employing solution loading and 600 s degassing time.

As shown in Fig. S4 (†ESI), the best precision was obtained when degassing of the bead was carried out for a longer period of time. Therefore, the degassing was carried out for 1800 s prior to the analysis of each sample for obtaining a stable current. The comparison of Pu isotopic compositions in the standard NIST SRM-947 sample obtained by SB-TIMS and conventional TIMS is given in Table 4. The atom% of the two major isotopes, viz. <sup>239</sup>Pu and <sup>240</sup>Pu, determined by the two methods were found to agree within 0.2% whereas atom% of <sup>241</sup>Pu and <sup>242</sup>Pu, which were less abundant isotopes, were found to agree within 0.5%.

Table 4. Determinations of isotopic compositions of Pu in the SRM-947 Pu standard by TIMS using single bi-functionalized magnetic PES bead and solution based loadings.

Isotope	Certified value (atom %)	Bead loading (a) (atom %)	Solution loading (b) (atom %)
<sup>239</sup> Pu	79.03 ± 0.02	78.96 ± 0.04	78.96 ± 0.03
<sup>240</sup> Pu	19.02 ± 0.02	19.04 ± 0.012	18.99 ± 0.03
<sup>241</sup> Pu	0.808 ± 0.006	0.735 ± 0.006	0.723 ± 0.006
<sup>242</sup> Pu	1.238 ± 0.004	1.243 ± 0.008	1.225 ± 0.006

#### Analytical performance of SB-ID-TIMS

The quantitative determinations of concentrations in the level of several  $\mu\text{g L}^{-1}$  of Pu(IV) in the aqueous solution, irradiated fuel dissolver solution, and soil leach liquor samples were carried out by SB-ID-TIMS method. The isotopic compositions of Pu in the samples and spiked solutions used for the isotope dilution, determined by conventional TIMS, are listed in Table 5. Each aliquot of dissolver solution, generally in 3 to 4 mol L<sup>-1</sup> HNO<sub>3</sub> medium, was equilibrated with a single magnetic PES bead. The bead was directly analysed by TIMS after equilibration. For the dissolver solution, a PHWR grade Pu solution was chosen as a spike which contains about 27 atom% of <sup>240</sup>Pu and the change in <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio in the mixture with respect to that in the sample and the spike was monitored. The aqueous and soil leach liquor samples, 50-100

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mL of sample, were spiked with a known quantity of Pu, and equilibrated with a single magnetic bi-functional PES bead for 24 h.

**Table 5.** Isotopic compositions of Pu in the samples and spike solutions used in SB-ID-TIMS method.

Isotope	Dissolver solution (atom %)	<sup>240</sup> Pu Spike used for Dissolver solution (atom %)	(U, Pu)C (atom %)	<sup>242</sup> Pu Spike used for (U, Pu)C (atom %)
<sup>238</sup> Pu	0.022±0.001	0.192±0.005	0.150±0.005	0.02±0.001
<sup>239</sup> Pu	89.92±0.04	67.73±0.03	69.20±0.03	1.54±0.006
<sup>240</sup> Pu	9.119±0.009	27.35±0.03	26.23±0.03	2.97±0.005
<sup>241</sup> Pu	0.861±0.003	2.574±0.005	2.568±0.005	0.66±0.003
<sup>242</sup> Pu	0.070±0.001	2.15±0.006	1.846±0.006	94.81±0.04

The Pu spiked in aqueous samples and soil leach liquors contains ~26 atom% of <sup>240</sup>Pu, therefore a <sup>242</sup>Pu-enriched spike was used and the concentration was determined from the change in <sup>242</sup>Pu/<sup>239</sup>Pu atom ratio in the mixture with respect to that in the sample. The Pu concentrations in these samples determined by both the SB-ID-TIMS and conventional ID-TIMS methods are given in Table 6. It is observed from this table that the results agree within 1%. This indicates that SB-ID-TIMS has a reasonably good analytical performance.

**Table 6.** Determinations of Pu concentrations by SB-ID-TIMS method and by conventional ID-TIMS.

Sample	Pu concentration (µg g <sup>-1</sup> )	
	SB-ID-TIMS	ID-TIMS
Dissolver solution	11.8 ± 0.3	11.9 ± 0.2
4 mol L <sup>-1</sup> HNO <sub>3</sub>	3.37 ± 0.02	3.39 ± 0.02
Soil leach liquor	2.31 ± 0.02	2.32 ± 0.02

## Conclusions

A method was developed for simultaneous preconcentration of Pu using a superparamagnetic bifunctional PES bead grafted with poly(HEMP-co-APTAC), followed by determination of isotopic composition and concentration of Pu by SB-ID-TIMS method. This method provides a single step purification and preconcentration of Pu from 5 to 100 mL of solution. Thus, the sample manipulation steps, sample preparation time, exposure to radiations and secondary waste generation could be minimized. The PES bead based loading technique was found to provide comparable accuracy and precision with respect to the conventional solution loading technique. The presence of superparamagnetic Fe<sub>3</sub>O<sub>4</sub> NPs in the bi-functional PES beads allows easy retrieval of the bead from large volumes of aqueous solution. In addition to this, the higher loading efficiency ( $K_d(\text{Pu(IV)})$  value) and competitive-selectivity ( $K_d(\text{Pu(IV)})/K_d(\text{U(VI)})$ ) of the bi-functional magnetic PES beads towards Pu(IV) bead provide a possibility of using SB-ID-TIMS

analyses for Pu(IV) determination in the aqueous sample featuring a large excess of competing U(VI) ions.

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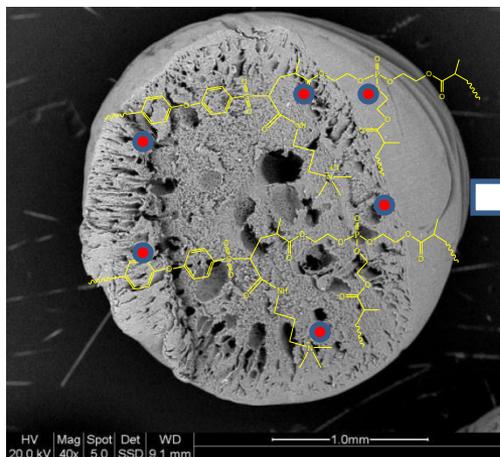
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## Graphical abstract



**Single Bead  
Thermal Ionization  
Mass Spectrometry**

● Pu(IV)