Electronic Supplementary Information

Phosphate bearing polymer grafted glass for plutonium(IV) ions selective alpha spectrometry

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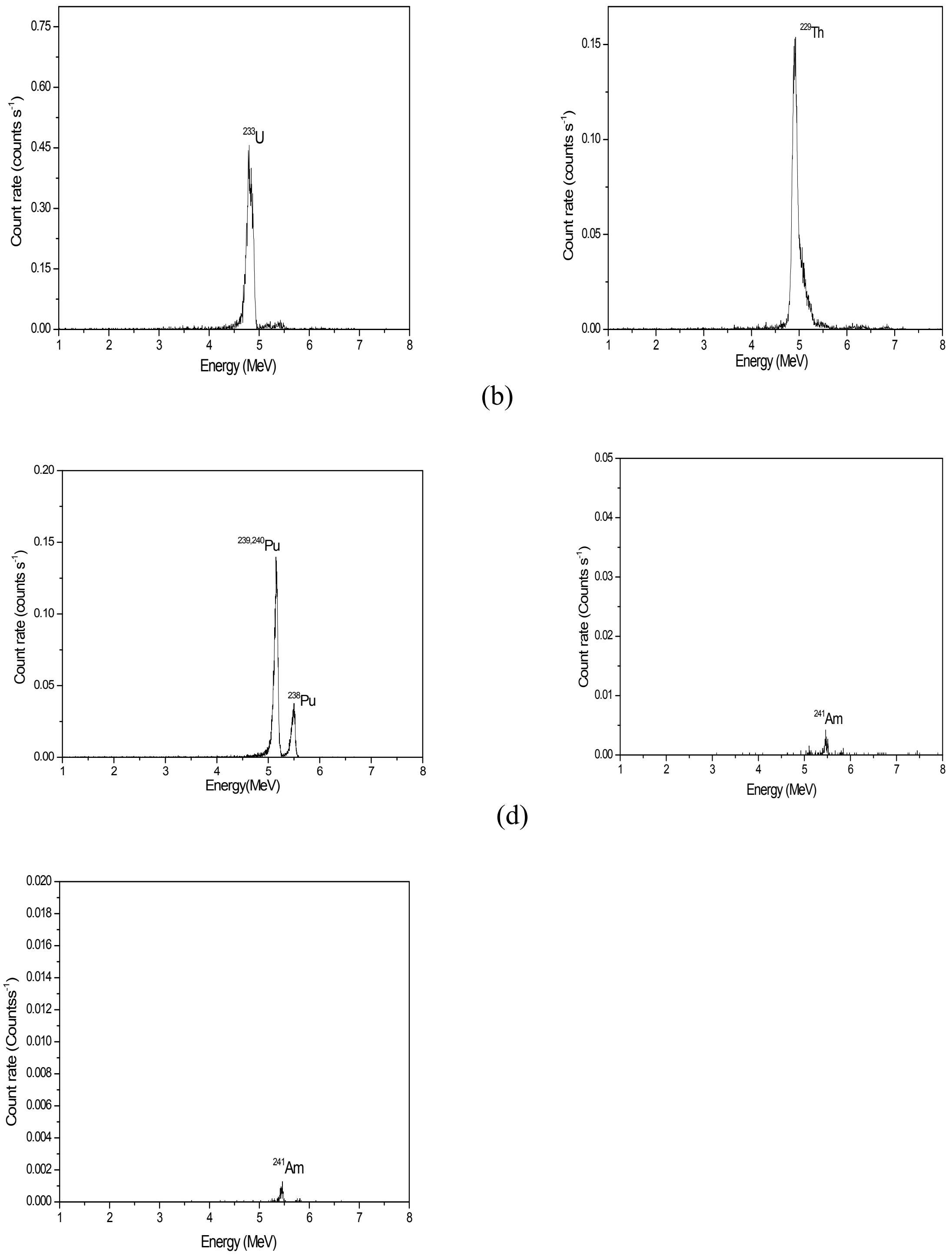
Fig. S1. The alpha spectra recorded from the glass@poly(BMEP) samples equilibrated with 3 mol L^{-1} HNO_3 containing UO_2^{2+} (a), Th^{4+} (b), Pu^{4+} (c) and Am^{3+} (d) ions, and solution having pH=2 and containing Am^{3+} ions (e).



(a)

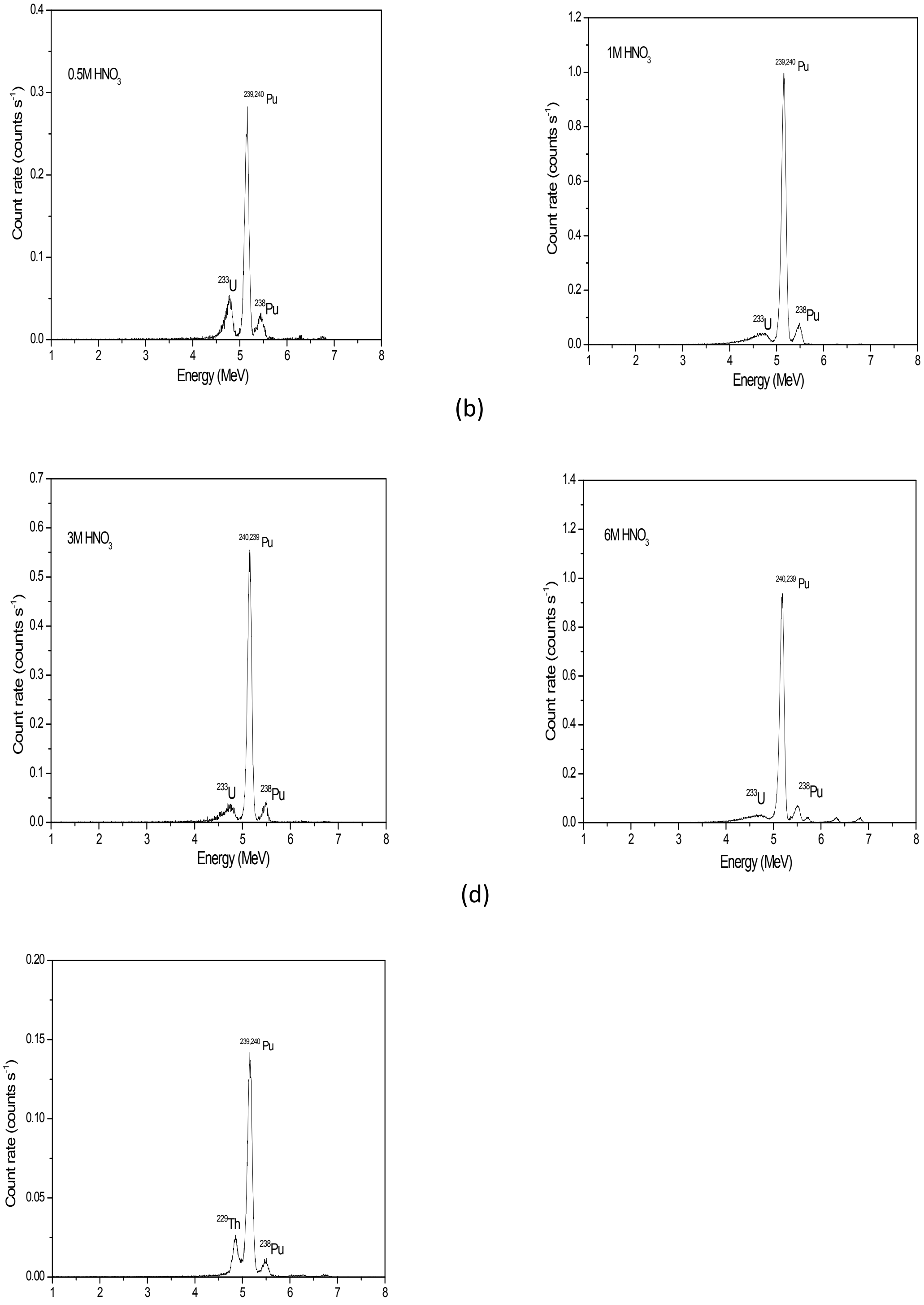
(b)

(c)

(d)

(e)

Fig. S2. Alpha spectra obtained from the glass@poly(BMEP) samples equilibrated with 0.5-6 mol L^{-1} HNO_3 containing $^{233}UO_2^{2+}$ and $^{mix}Pu^{4+}$ ions in 20:1 mol proportion (a-d), and 3 mol L^{-1} HNO_3 containing Th^{4+} and $^{mix}Pu^{4+}$ ions (e).



(a)

(b)

(c)

(d)

(e)

Fig. S3. Pu^{4+} ions fractional attainment of the optimum sorption in the glass@poly(BMEP) from 3 mol L^{-1} HNO_3.

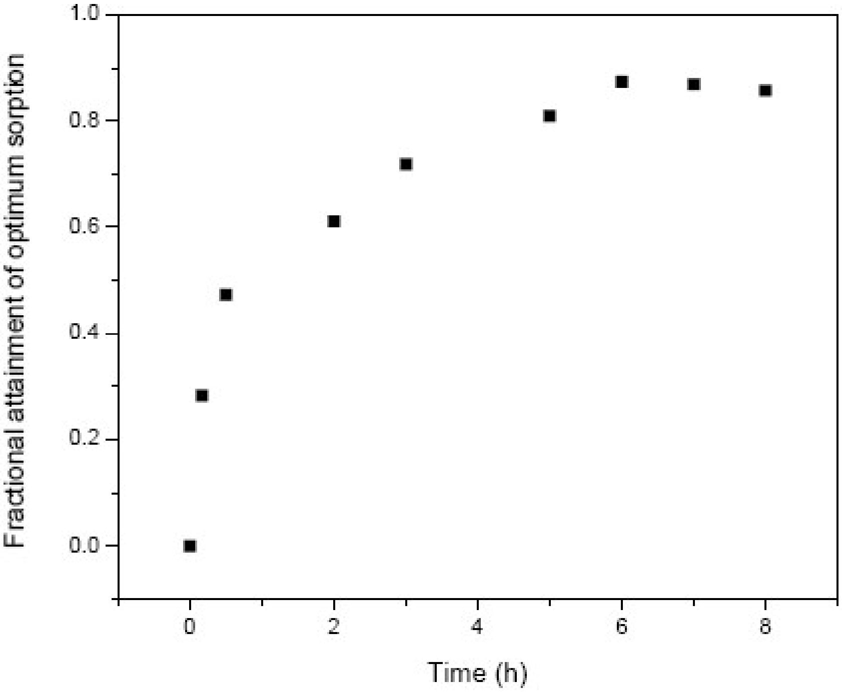


Fig. S4. Linear variation of alpha count rate obtained by alpha spectrometry of the glass@poly(BMEP) equilibrated with solution having 0.2 to 10 ppb Pu^{4+} in 3 mol L^{-1} HNO_3.

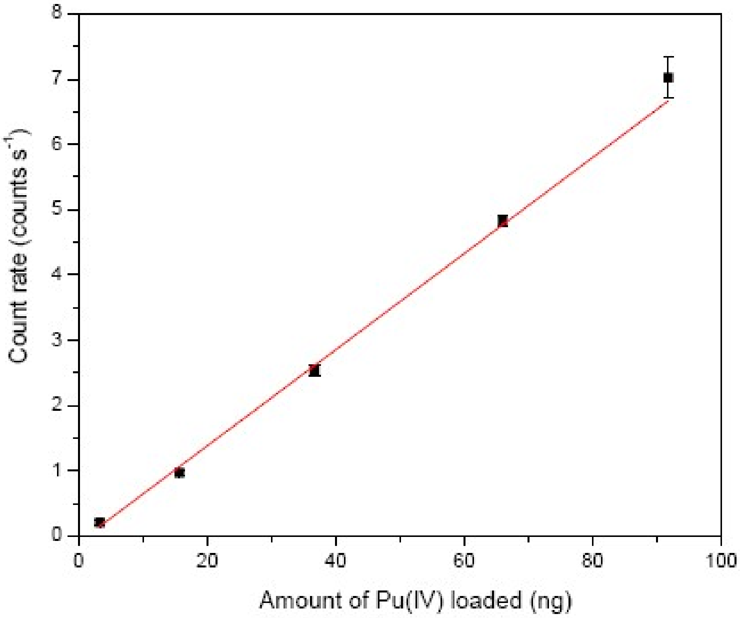


Fig. S5. (a) Alpha spectrum of Pu^{4+} loaded glass@poly(BMEP) (black line), and alpha spectra after equilibration in 0.2 mol L^{-1} hydrazine hydroxyl amine in 1 mol L^{-1} HNO_3 after 2h (red) and 5 h (green), (b) and reloaded with Pu^{4+} ions. The dotted line in Fig. S5 (b) correspond to the representative reloaded Pu^{4+} ions in the glass@poly (BMEP), indicating the reusability of the Pu^{4+}-deloaded glass@poly (BMEP) substrate.

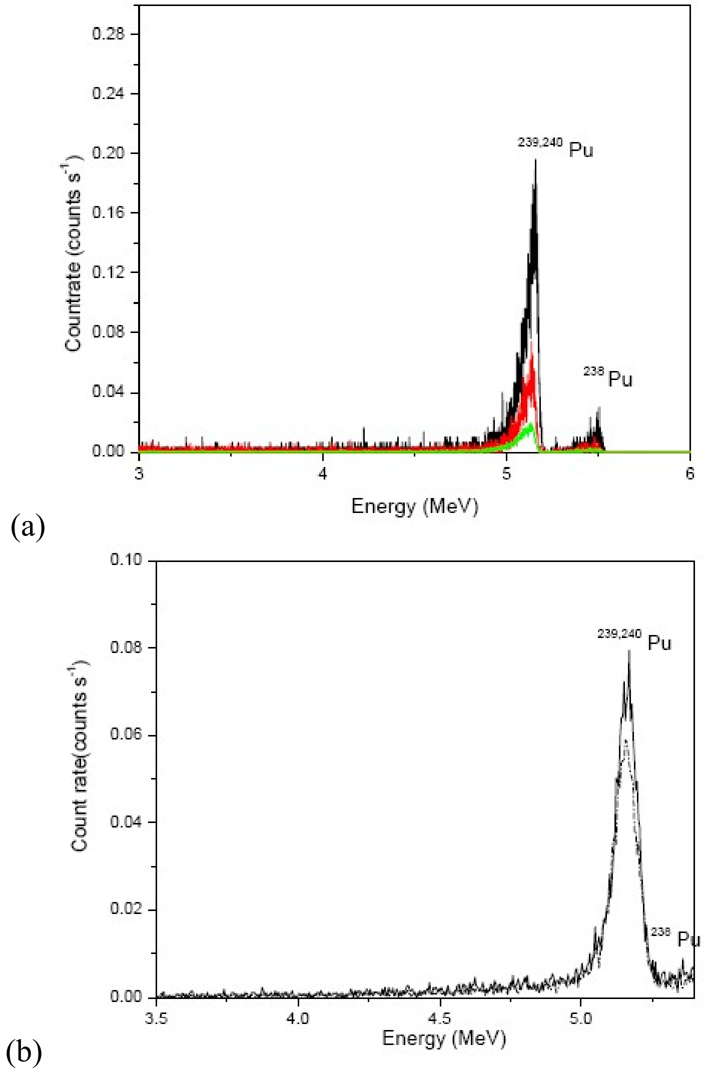


Table S1. Comparison of determinations of Pu contents in the spiked natural water samples using the glass@poly(BMEP) based isotope dilution alpha spectrometry with thermal ionization mass spectrometry. The acidity of sample was adjusted to 3 mol L^{-1} HNO_3 before equilibration with the glass@poly(BMEP). The statistical uncertainty on the measured concentration was obtained by triplicate experiments.

Sample	**Pu concentration (ppb)**	
	Alpha Spectrometry	**TIMS**
Seawater	15.14 ± 0.86	15.38 ± 0.62
Groundwater	16.65 ± 0.94	16.45 ± 0.66

Experimental Details

Reagents and apparatuses

The concavity micro glass slides used in present work were obtained from Polar industrial corporation (cavity diameter- 15mm, Depth of cavity- 0.5mm). The monomers bis[2-(methacryloyloxy)ethyl] phosphate (BMEP) from Sigma-Aldrich (Steinheim, Switzerland), Sodium hydroxide (AR grade) from S.D. Fine chem. limited, Mumbai, De-ionized water ($18 M\Omega cm^{-1}$) was used throughout the present work, *N,N'*-dimethtyl formamide obtained from Merk Life science Pvt. limited, Worli, Mumbai-400018(India), Hidrogen Peroxide (30%) obtained from Merk specialities Pvt limited,Worli Mumbai-400018(India), Sulphuric Acid (AR grade 98%) from Thomas Baker (chemicals)Pvt limited, Marine Drive,Mumbai-400002(India), Nitric Acid (AR grade 69-70%) from Thomas Baker (chemicals) Pvt limited, Marine Drive,Mumbai-400002(India), 3-(trimethoxysilyl)propyl acrylate (stabilised with BHT) obtained from Tokyo chemical industry Co. limited. 6-15-9 Toshima, KITA-KU, Tokayo, Japan. α,α'-dimethyl-α-phenylacetophenone (DMPA) obtained from FLUKA chemie GmbH, CH-9471, D-89502, Steinheim, Switzerland. Ethyl alcohol (99.9%) from Changshu Hongssheng fine chemical Co. Ltd., Sodium hydroxide, (AR grade) from S.D. Fine chem. limited. Hydroxyl Amine (50 wt % aqueous, Lancaster synthesis, Eastgate, More Cambe, England. Hydrazine Hydrate (99-100%), Merck specialities private limited, Worli, Mumbai-400018(India). The box type UV multilamp photoreactor used was procured from Heber Scientific, Chennai, India fitted with two 20 watt UV lamps (Sankyo Denki, Japan) having two types of phosphors with radiation peak at 352 nm and 368 nm, respectively. The SSNTD study for alpha radiography was carried out using CR-39 (allyl diglycol polycarbonate) plastics sheets having 500μm thickness obtained from Global Nanotech, Mumbai, India. The developed alpha tracks were observed under transmission optical microscope (Olympus fully motorized microscope model No. BX63, attached with QIMAGING QICAM CCD camera and cellSens Dimension Package for image analysis obtained from Olympus, Tokyo, Japan). The stock solution of Pu was obtained from the Radiochemistry Division, BARC, Mumbai, India having isotopic composition (at. %) as ^{238}Pu (0.16 ± 0.006), ^{239}Pu (68.79 ± 0.03), ^{240}Pu (26.94 ± 0.03), ^{241}Pu (2.09 ±0.005), and ^{242}Pu (2.02 ± 0.006). The stock solution was purified by the standard anion-exchange column method to remove ^{241}Am ions. Scintillation cocktail W (Sisco Research Laboratories Pvt. Limited, Mumbai). Tri Octyl phosphine Oxide (TOPO) obtained from S. D. Fine chem.. Ltd, Mumbai-400025. The α-activity was measured with a home-built liquid scintillation counter, and alpha spectrometer equipped with a passivated ion-implanted planar silicon (PIPS) detector (Canberra, PD-450-16-100AM) with an area of 450 mm^2 and a resolution of 16 keV (FWHM) at 5.486 MeV of ^{241}Am connected to a multi-channel analyzer.

Concavity micro slide used for surface grafting

Pu Uptake studies

The plutonium(IV) uptake study was carried out using grafted glass samples by equilibrating with 3M HNO_3 solution (10ml). The substrate was equilibrated with solution for 4 h. The amounts of Pu(IV) loaded in the glass substrate was quantified using liquid scintillation counting of aqueous samples (100 μL) taken from solution before and after equilibration of the glass substrates. The sorption efficiency (uptake) of actinide in the glass was obtained from following equation:

Uptake (%) = $[A_b - A_f] / [A_b] \times 100$

where A_b and A_f are radioactivity (scintillation count rate) of Pu(IV) in the solution before and after equilibration of grafted glass, respectively. The sorption experiments were carried out by stirring the solution for a fixed period of time, and the percentage uptake of Pu(IV) as a function of time was monitored.

The Pu loaded glass substrate then washed with 3M nitric acid to remove loosely bound activity on the glass surface and checked for loose contamination. The plutonium loaded thin film glass substrates were monitored at 2cm source to detector distance by alpha spectrometer equipped with a passivated ion-implanted planar silicon (PIPS) detector, having a resolution of 16 keV (FWHM) at 5.486 MeV, of ^{241}Am connected to a multi-channel analyzer. In order to confirm Pu preconcentration at cavity only, cavity was covered, then by recording the alpha spectrum of front and back surfaces.

U, Am uptake studies

The Uranium (VI) uptake study was carried out using grafted glass samples by equilibrating with 3M HNO_3 solution (10mL). The substrate was equilibrated with solution for 4 h. The amounts of U(VI) loaded in the glass substrate was quantified using liquid scintillation counting of aqueous samples (100 μL) taken from solution before and after equilibration of the glass substrates. Also the uptake of plutonium was studied in presence of uranium at 3M HNO_3. For this the uranium loaded glass was equilibrated with the plutonium solution.

Isotope dilution alpha spectrometry

Pu concentrations in seawater and groundwater samples were determined by isotope dilution alpha spectrometry (IDAS), using ^{238}Pu as a spike isotope. For IDAS, acidity of each sample was adjusted to 3M with HNO_3, then a weighed amount of pre-calibrated ^{238}Pu spike solution was added to a weighed amount of the sample. The mixture was treated with conc. HNO_3 for homogeneous mixing of the spike isotopes with the sample, followed by treatment with 3 M HNO_3 and 20% H_2O_2 to adjust Pu oxidation state to Pu(IV). After treatment, the samples were equilibrated with the ligand-anchored glass substrates for 1-2 hours with continuous stirring. After equilibration, the glass substrates were washed thoroughly with 3M HNO_3, dried and placed directly in front of a passivated ion-implanted planar silicon detector (PIPS Canberra, PD-450-17-100AM, 450 mm^2 surface area, 100 mm active thickness, 17 keV FWHM at 5.486 MeV), coupled to a PC-based 8K-MCA, to record the alpha spectra. The spectral analyses were carried out using PCA3 software. The Pu concentration in the natural water samples was determined from the change in ^{238}Pu/(^{239}Pu+^{240}Pu) alpha activity ratio in the mixture, w.r.t. that in the sample and the ^{238}Pu spike, using the following equation.

$$C_{sa} = \frac{C_{sp}W_{sp}\ \ (R_{sp} - R_m)\qquad\qquad (\lambda_{238}AF_{238})_{sp}\qquad\qquad < At.Wt. >_{sa}}{W_{sa}\ \ R_{sp}(R_m - R_{sa})(\lambda_{239}AF_{239})_{sa} + (\lambda_{240}AF_{240})_{sa} < At.Wt. >_{sp}}$$

where, C_{sa} and C_{sp} are the concentration and W_{sa} and W_{sp} are the weight of the sample and ^{238}Pu spike, respectively. R_{sa}, R_{sp} and R_m are ^{238}Pu/(^{239}Pu+^{240}Pu) alpha activity ratios in the sample, spike and spiked mixture, respectively. The Pu concentrations in the seawater and groundwater sample were found to be 15.14 ± 0.86 ppb and 16.65 ± 0.94 ppb, respectively.

Analysis of Minimum Detection Limit

The minimum detectable activity (MDA) for the radionuclide detection by instrumental method can be obtained by following equation:

$$MDA = \frac{L_d}{t \times \varepsilon}$$

Where is MDA is minimum detection limit (Bq) t is counting time (3646 s), ε is detector efficiency (2%), and Ld is the radioactivity measurement limit of detection in counts, which is determined at the 95% confidence level and obtained by Curie equation,[24] as given below:

$$L_d = 4.653\sqrt{C_b t} + 2.706$$

Where C_b is background count rate (0.572 cps). Using these equations the value of MDA was found to be 2.95 Bq. The minimum amount of Pu required in the glass@poly(BMEP) could be obtained as 1.25 ng using specific activity of Pu having isotopic composition used in the present work. Thus, 1.25 ng Pu has to be preconcentrated in the glass@poly(BMEP) from the appropriate volume of liquid samples.