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Solid phase extractive preconcentration of uranium(VI) using quinoline-8-ol anchored chloromethylated polymeric resin beads

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Abstract

A new chelating polymeric sorbent has been developed using Merrifield chloromethylated resin anchored with quinoline-8-ol (HQ). The modified polymeric resin was characterized by FT-IR spectroscopy and elemental analysis. The HQ anchored resin showed superior binding affinity for U(VI) over Th(IV) and La(III). The influence of various physicochemical parameters on the recovery of U(VI) were optimized by both static and dynamic methods. The phase exchange kinetic studies performed for U(VI) revealed that <5 min was sufficient for reaching equilibrium metal ion sorption. The maximum sorption capacity of HQ anchored resin for U(VI) was found to be 120.30 mg g^{-1} of resin which is higher than other solid phase extraction sorbents reported so far excepting *N*,*N*-dibutyl, *N*′-benzoyl thiourea sorbed Amberlite XAD-16. The developed HQ anchored polymeric resin is highly selective as none of the extraneous species were found to have any deleterious effect. Solid phase extraction (SPE) studies performed using HQ anchored polymeric resin offered enrichment factor of 100 and the lowest concentration below which recoveries become non-quantitative is 5 μg l^{-1}. The accuracy of the developed SPE method in conjunction with Arsenazo III procedure was tested by analyzing marine sediment (MESS-3) and soil (IAEA–Soil 7) reference materials. Furthermore, the above procedure has been successfully employed for the analysis of real soil and sediment samples.

Keywords: Quinoline-8-ol; Merrifield chloromethylated resin; Grafting; Preconcentrative separation; Uranium(VI); Soils and sediments

1. Introduction

Uranium and its compounds, like lead are highly toxic which cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death. The tolerable intake of uranium established by WHO based on Gilman's studies is 0.6 μg kg^{-1} of body weight per day [1–3]. The maximum permissible uranium concentration in drinking water as per WHO, Health Canada and Australian drinking water guidelines is 9, 20, and 20 μg l^{-1} [1,2]. Uranium concentrations in uncontaminated soils are usually very low and found to be higher in phosphate-rich soils. Thus, the measurement of uranium levels in soils and sediments is important: (i) in understanding its mobility from polluted soil, sludge or sediment arising from human additions through industrial activities; (ii) to understand the correlation between diseases of animals and aquatic organisms and soil chemistry; and (iii) to prepare soil maps.

Solid phase extraction (SPE) using a variety of sorbents has come to the forefront recently in view of the several advantages over other preconcentration techniques [4]. New polymeric sorbents have been synthesized either by direct polycondensation or polymerization of monomers containing chelating groups [5,6] or by chelate sorption or by chemical bonding chelate groups to polymeric crosslinked chains (preformed polymers) [7]. The most widely used polymeric sorbents are styrene-divinyl benzene copolymers with a hydrophobic surface [8,9]. Anchoring or grafting of chelates onto polymeric resins are preferred over nascent or chelate sorbed styrene-divinyl benzene polymers, as the latter two classes offer non-quantitative recoveries and unstable sorbents, respectively. Chelate anchored Merrifield

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chloromethylated styrene-divinyl benzene resin offer better retention capacities due to its small pore diameter and low bead surface area over Amberlite XAD resins [4]. Prabhakaran and Subramanian [10,11] have anchored thenoyltrifluoroacetone and di-bis(2-ethylhexyl)malonamide chelates onto above resin which has resulted in notable features like uranyl ion-selectivity, better metal sorption capacity, rapid attainment of phase equilibration and good enrichment factor values. However, these authors have neither tested the accuracy of the developed preconcentration procedures by analyzing certified reference materials nor applied to real samples. We now describe the synthesis of quinoline-8-ol anchored Merrifield chloromethylated styrene-divinyl benzene resin beads and its utility in analyzing certified reference materials, drinking water, soils and sediments for trace amounts of uranium(VI).

2. Experimental

2.1. Instrumentation

Absorbances were measured using Hitachi-220 microprocessor controlled double beam spectrophotometer (Hitachi, Japan). An LI-120 digital pH meter (ELICO, India) was used for pH measurements. IR spectra (4000–400 cm^{-1}) were taken by KBr pellet method using MAGNA IR-560 spectrometer (Nicolet, USA). Elemental analyses were carried out on a Perkin-Elmer elemental analyser (Rotkrewz, Switzerland).

2.2. Reagents

A stock solution of uranium(VI) (1000 $\mu\mathrm{g\,ml}^{-1}$)was prepared by dissolving 0.5047 g of $UO_2(NO_3)_2\cdot 6H_2O$ (Aldrich, USA) in 5 ml of conc. HNO_3 and diluted to 250 ml with deionized water. A 0.1% Arsenazo III (Aldrich, USA) solution was prepared by dissolving 0.1 g of the reagent in 100 ml of deionized water. Sodium acetate-acetic acid (pH 5.5) buffer (1.0 $\mathrm{mol\,l}^{-1}$) was used to maintain the pH of the aqueous phase. 5-Aminoquinoline-8-ol was obtained from Aldrich, USA. Triethylamine and tetrahydrofuran were obtained from E-Merck, India. All other chemicals including neutral electrolytes and other metal ions were of analytical reagent grade. The standard reference materials MESS-3 (marine sediment reference material supplied by National Research Council, Canada) and IAEA soil 7 (soil reference material supplied by International Atomic Energy Agency, Vienna) certified for trace metals were used for quality assurance. Merrifield chloromethylated styrene-divinylbenzene resin (capacity [Cl^-] ∼5.5 $\mathrm{mmol\,g}^{-1}$ resin, 16–50 mesh) obtained from Fluka chemicals was purified with methanol followed by successive water washings. The resin beads were filtered, dried and vacuumized prior to usage.

2.3. Synthesis of HQ anchored polymeric support

Five grams of dry chloromethylated resin matrix was functionalized with HQ by adding 5 g of 5-aminoquinoline-8-ol, 50 ml each of dry triethylamine and dry tetrahydrofuran and stirred for 2 h. The reaction mixture was refluxed at 60 °C for 12 h. The functionalized resin beads were purified from excess reactants by washing repeatedly with methanol, water and acetone. The resin beads were filtered and vacuum dried. The single-step synthesis leading to the formation of the desired chelating polymeric matrix is depicted in Fig. 1.

2.4. Recommended procedure for preconcentration and determination of uranium(VI)

Both column and batch methods were used to preconcentrate uranium(VI) from aqueous solutions.

2.4.1. Column “dynamic” method

The glass column (Vensil, size: 7.0 mm diameter and 10 cm length) was packed with 0.02 g of HQ anchored resin and washed three to four times with deionized water. A sample solution (100 ml) containing 5–200 μg of uranium(VI) was taken and the pH was adjusted to ∼5.5 after the addition of 1.0 $\mathrm{mol\,l}^{-1}$ of sodium acetate–acetic acid buffer and passed through the above column at a flow rate of 4.0 $\mathrm{ml\,min}^{-1}$. 100 μg of thorium(IV) or lanthanum(III) were also passed through the column under identical conditions mentioned for uranium(VI). The metal ions were eluted with 10 ml of 0.1 $\mathrm{mol\,l}^{-1}$ of Na_2CO_3 and determined spectrophotometrically (i) after the addition of 5 ml of conc. HCl 1.0 ml of 0.1% Arsenazo III and measuring at 656 and 660 nm (for

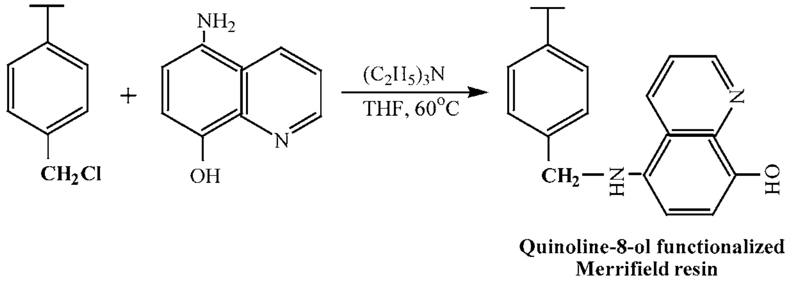

Fig. 1. Scheme for synthesis of quinoline-8-olanchored Merrifield chloromethylated styrene-divinyl benzene resin (HQ anchored resin) beads.

uranium(VI) and thorium(IV), respectively) and (ii) adjusting the pH to 7.2 ± 0.2 and adding 2.0 ml of 0.01%. Arsenazo I and measuring at 570 nm (for lanthanum(III)) [12].

The phase distribution ratios (*D*) were calculated using the following expression:

$$D = \frac{(A_o - A_t)V}{A_t W}$$

where A_o and A_t are the amount of metal ion in the aqueous phase before and after equilibration, *W* is the weight of the dry resin (g) and *V* is the volume of the aqueous phase (ml). The percent extraction was calculated using the following expression:

$$\%E = \frac{A_o - A_t}{A_o} \times 100$$

2.4.2. Batch "static" method

A sample solution containing 5–200 μg of uranium(VI) or 100 μg of thorium(IV) or lanthanum(III) in a volume of 10–1000 ml was taken and its pH was adjusted to ∼5.5 after the addition of 1.0 mol l^{-1} of sodium acetate–acetic acid buffer. HQ anchored resin (0.1 g) was added to the above solution and stirred for 10 min. The metal ion adsorbed chelating resin was filtered and eluted with 10.0 ml of 0.1 mol l^{-1} of Na_2CO_3 and subjected to spectrophotometric determination as mentioned in Section 2.4.1.

2.5. Procedure for the analysis of standard reference materials (MESS-3 and IAEA soil-7), soil and sediment samples

About 0.10–0.50 g of the sample was treated with 5.0 ml of HF and 1.0 ml of conc. H_2SO_4 at 150 °C on a hot plate. The process was repeated thrice. The residue was cooled and fused with 2.0 g of $KHSO_4$ at 800 °C in an electric bunsen for 45 min. The melt is then cooled, dissolved in 50 ml of deionized water. Preconcentration of uranium(VI) onto HQ anchored resin and determination by Arsenazo III procedure was carried out as described in Section 2.4.1.

2.6. Characterization studies

The Merrifield chloromethylated resin (I) and HQ anchored resin were subjected to IR and elemental analysis studies to prove the functionalization of I with HQ.

2.6.1. FT-IR spectral studies

Comparing the IR spectra of Merrifield chloromethylated resin and HQ anchored resin, the latter one show additional peaks at 1308 cm^{-1} and at 1580 cm^{-1} corresponding to –N–H bending indicating the formation of (–CH_2–NH–) between I and amino group of 5-aminoquinoline-8-ol. The absence of peak corresponding to –C–Cl bond peak in HQ anchored resin at 751 cm^{-1} is consistent with expectation of the formation of –CH_2–CH– bond. The occurrence of series of peaks in the frequency range 2919–2850 cm^{-1} indicates that aliphatic –CH_2 group of I is intact during anchoring.

2.6.2. Elemental analysis

The experimentally found values of elemental analysis studies of HQ anchored resin are (C = 78.0%, H = 6.62%, N = 3.68%) compared to calculated values (C = 78.2%, H = 5.80%, N = 10.10%) which indicates that the functionalization of Merrifield chloromethylated resin is only to an extent of ∼36%.

3. Results and discussion

The enrichment of uranyl ion from dilute aqueous solutions with HQ anchored resin by batch method was confirmed by FT-IR spectral and UV–vis spectral studies.

3.1. FT-IR spectral studies

Comparing the FT-IR spectra of uranium bonded modified Merrifield resin and HQ anchored resin, an additional peak at 903.87 cm^{-1} in former is due to UO_2^{2+} stretching mode [13]. Also an absorption peak in the far IR spectra appearing at about 426 cm^{-1} is similar to lanthanide –O complexes [14,15]. The above facts confirm that uranium is indeed bonded to modified Merrifield resin.

3.2. UV–vis spectral studies

The analysis of leachant obtained on equilibrating uranium bonded HQ anchored resin with 5.0 ml of 1.0 mol l^{-1} of HCl for uranium(VI) using Arsenazo III spectrophotometric method described in Section 2.4.1 confirms that uranium(VI) was indeed sorbed onto HQ anchored resin.

3.3. Batch "static" studies

3.3.1. Influence of solution pH on metal ion extraction

The resin's ability to extract analytes from weakly acidic solutions and at neutral condition was investigated within a wide range of solution pHs. Individual experiments were carried out with 0.1 g of resin beads equilibrated with metal ion solution (1000 ml, 0.1 μg ml^{-1}) for 10 min. From Fig. 2, it is evident that the system offers good extraction behaviour only for uranium(VI) over a pH range of 5.0–6.0. Under these conditions, the extraction of thorium(IV) and lanthanum(III) are very low.

3.3.2. Aqueous phase volume

The effect of aqueous phase volume was studied in the range 10–1000 ml on the individual extraction of 100 μg of uranium(VI), thorium(IV) and lanthanum(III) with 0.1 g of resin beads equilibrated for 10 min at pH values of 5.5 ± 0.5. The sorbed metal ions were eluted with 10 ml of 0.1 mol l^{-1}

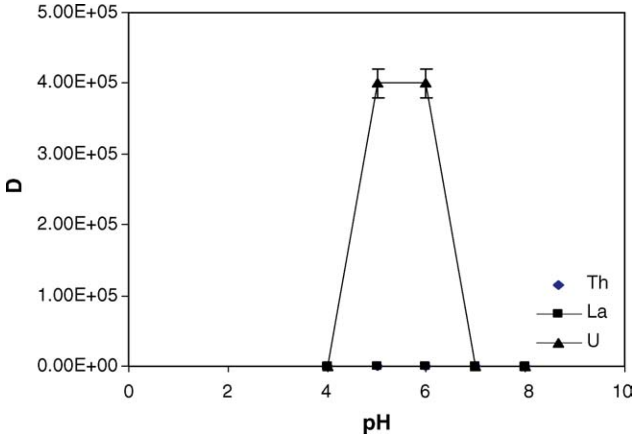

Fig. 2. Effect of pH on metal ion extraction (100 μg of U(VI)), Th(IV) or La(III), batch "static" method, aqueous phase volume, 1000 ml; 0.10 g of resin beads; preconcentration time, 10 min; eluent, 0.1 mol l^{-1} Na_2CO_3; eluent volume, 10 ml) (average of three determinations).

of Na_2CO_3. The sorption of uranium(VI) was found to be quantitative on changing the volume of the sample solution upto 1000 ml (see Table 1). The enrichment factor and the lowest concentration below which recoveries become non-quantitative are 100 and 5 μg l^{-1}, respectively.

3.3.3. Kinetics of U(VI), Th(IV) and La(III) extraction

Extraction rate studies were performed in pH 5.5 solutions using 0.1 g of the HQ anchored resin beads contacted with metal ion solution (100 ml, 1 μg ml^{-1}) for different time periods. The phase exchange kinetics were monitored in terms of fractional attainment of equilibrium [16] which is expressed as,

$$F = \frac{[M^R]_t}{[M^R]_{eq}}$$

where $[M^R]_t$ and $[M^R]_{eq}$ are the metal ion concentrations in the resin phase at time t and at equilibrium, respectively. From Fig. 3 it is evident that complete extraction of uranium(VI) was attained within 5 min with a half time ($t_{1/2}$) of <30 s (data obtained by plotting percent extraction as a function of time) owing to enhanced resin hydrophilicity.

3.3.4. Statistical and calibration parameters for batch method

Under the optimum conditions described above, the calibration curve was linear over the range 5–200 μg of U(VI) present in 1 l of solution (see Fig. 4). A sample of 50 μg of U(VI) present in 1 l gave a mean absorbance of 0.100 with a relative standard deviation of 3.96%. The detection limit corresponding to three times the standard deviation of the blank was found to be 5 μg l^{-1}. The linear equation with regression (R^2) is as follows.

$$A = 0.02C + 0.0003$$

$$R^2 = 0.99864$$

where A is the absorbance, C is the concentration in μg per litre and R^2 is the correlation coefficient. All the statistical calculations were based on the average of three determinations.

Table 1
Effect of aqueous phase volume on %E of U(VI), Th(IV) and La(III) (pH 5.5 ± 0.5, U(VI)/Th(IV)/La(III) = 100 μg)

Aqueous phase volume (ml)	50	100	500 (batch)	1000 (batch)
Percent extraction				
U	>99	>99	>99	>99
Th	15.8	15.8	15.8	15.0
La	10.4	10.3	10.4	10.3

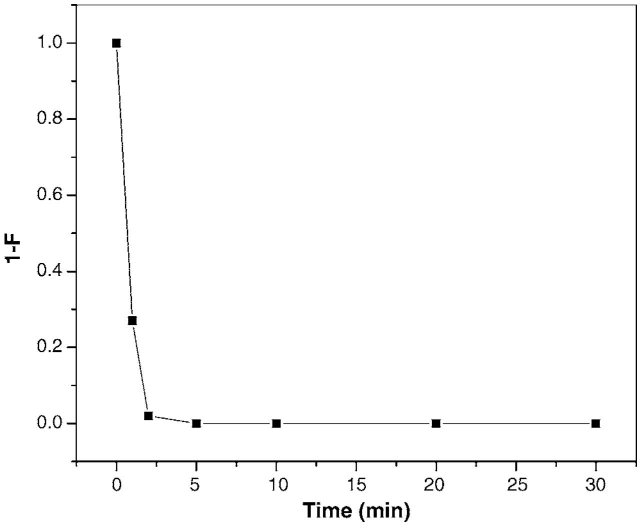

Fig. 3. Rate of metal ion phase equilibration.

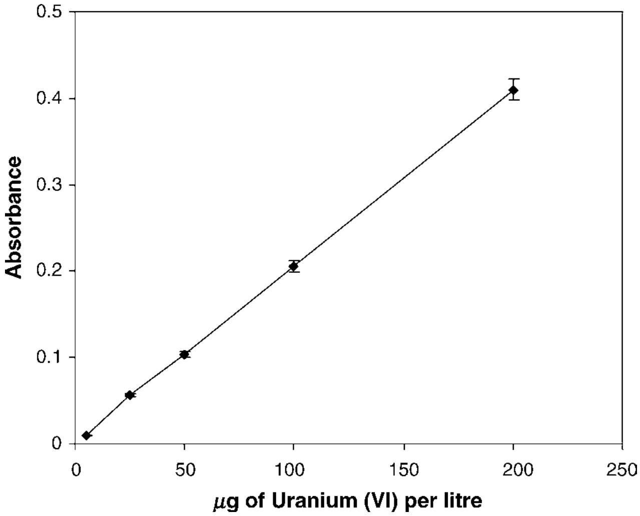

Fig. 4. Calibration graph with batch static studies (average of three determinations).

Table 2
Comparison of retention/sorption capacities of SPE materials prepared by using various sorbents for uranium(VI)

Serial no.	SPE material (chelate, sorbent)	Retention capacity (mg g^{-1} of SPE)	Reference
1	5,7-Dichloroquinoline-8-ol, naphthalene	1.88	[17]
2	1(2-Pyridylazo)-2-naphthol, benzophenone	2.34	[18]
3	Azooxine ion exchanger	7.14	[19]
4	Quinoline-8-ol, Amberlite XAD-4	2.74	[20]
5	*o*-Vaniline semicarbazone, Amberlite XAD-4	2.89	[21]
6	Succinic acid, Amberlite XAD-4	12.33	[22]
7	Octacarboxymethyl-c-methyl Calix[4] resorcinarene, Amberlite XAD-4	64.26	[23]
8	Bicine, Amberlite XAD-4	90.44	[24]
9	Pyrogallol, Amberlite XAD-2	6.71	[25]
10	*N*,*N*-Dibutyl-*N*′-benzoylthiourea, Amberlite XAD-16	214.20	[26]
11	[(2-Hydroxyarsinoylphenylamino) methyl] phosphonic acid, Amberlite XAD-16	59.50	[27]
12	37,38,39,40,41,42-Hexahydroxy 1,8,13,19,25,31-hexacarboxy Calix[8] arene, poly(styrene b-hydroxylamine)	97.82	[28]
13	Thenoyltrifluoroacetone Merrifield chloromethylate resin	33.32	[10]
14	Di-bis(2-ethylhexyl) malonamide, Merrified chloromethylated resin	62.50	[11]
15	Quinoline-8-ol, Merrifield chloromethylated resin	120.30	(Present method)

3.3.5. Retention or sorption capacity

The retention or sorption capacity was performed by taking a 100 ml solution containing varying amounts of U(VI) and 0.1 g of HQ anchored resin beads with 10 ml of 1.0 mol l^{-1} (pH 5.5) sodium acetate–acetic acid buffer and stirred for 2 h and filtered through filter paper. The amount of U(VI) adsorbed on HQ anchored resin beads was eluted with 10 ml of 0.1 mol l^{-1} Na$_2$CO$_3$ by stirring for 30 min and then determined by using Arsenazo III procedure. As seen from Fig. 5, the retention capacity increases with increase in initial U(VI) concentration and reaches a constant and maximum value of 120.30 mg of U(VI) per g of HQ anchored resin beads. Furthermore, a comparison of retention/sorption capacity obtained by the present method is higher when compared with reported retention–sorption capacities for different SPEs by various researchers (see Table 2) [17–28] excepting with *N*,*N*-dibutyl-*N*′-benzoylthiourea sorbed Amberlite XAD-16 [23]. However, the latter SPE materials [23] is physically sorbed and hence is unstable and less precise offering non-qunatitative recoveries, unlike the HQ anchored resin prepared by chemical immobilization.

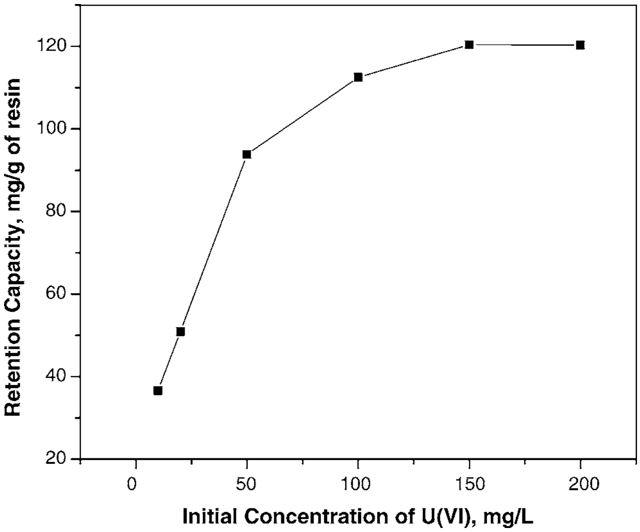

Fig. 5. Uranyl ion retention capacity of quinoline-8-ol functionalised Merrifield chloromethylated styrene-divinylbenzene resin, pH 5.5 ± 0.5. The data presented are average of three experiments.

3.4. Column "dynamic" studies

3.4.1. Sample and eluent flow rate studies

The rate at which quantitative extraction could be obtained was studied in terms of sample flow rates where the metal ion solution (100 ml, 100 μg) in pH 5.5 sodium acetate–acetic acid buffer solutions was passed through the resin bed. From Table 3 it is clear that the extraction of U(VI), Th(IV) or La(III) was unaffected when the flow rates are ≤3 ml min^{-1}. Similar study using 0.1 mol l^{-1} Na$_2$CO$_3$ as eluent shows that, the elution behaviour of U(VI), Th(IV) or La(III) is independent of the flow rates studied viz. 0.5–4 ml min^{-1}(see Table 3). Elution flow rates higher than 4.0 ml min^{-1} could not be attained under our experimental conditions.

Table 3
Effect of Preconcentration and elution flow rates on %*E* of U(VI), Th(IV) and La(III) (pH 5.5 ± 0.5, U(VI)/Th(IV)/La(III) = 100 μg)

Preconcentration flow rate (ml min^{-1})	1.0	2.0	3.0	4.0
Percent extraction				
U	>99	>99	>99	90.5
Th	15.8	15.8	15.9	1.6
La	10.3	10.4	10.3	10.5
Elution flow rate (ml min^{-1})	1.0	2.0	3.0	4.0
Percent extraction				
U	>99	>99	>99	>99
Th	15.8	15.8	15.9	1.6
La	10.3	10.4	10.3	10.3

Table 4
Choice of eluent[a]

Eluent (10 ml of 0.1 mol l^{-1})	Percent extraction of U(VI)
NH_3	13.30 ± 0.10
Sodium citrate	58.06 ± 0.20
Sodium acetate–acetic acid (pH 5.5)	67.74 ± 0.20
Monochloroacetic acid (pH 2.5)	61.29 ± 0.20
Sodium bicarbonate	53.57 ± 0.20
Sodium carbonate	>99

[a] Based on values obtained on triplicate analysis.

Table 5
Effect of eluent concentration and eluent volume on on %*E* of U(VI), Th(IV) and La(III) (pH 5.5 ± 0.5, U(VI)/Th(IV)/La(III) = 100 μg)

Eluent (Na_2CO_3) concentration (mol L^{-1})	0.1	0.5	1.0	2.0
Percent extraction				
U	>99	>99	>99	>99
Th	15.8	15.8	15.8	15.9
La	10.4	10.3	10.4	10.3
Eluent volume (ml)	5.0	10.0	20.0	
Percent extraction				
U	54.9	>99	>99	
Th	12.1	15.9	15.9	
La	10.9	10.4	10.3	

3.4.2. *Nature of eluent*

The results obtained on the nature of eluent on percent recovery of U(VI) was compiled in Table 4. As seen from Table 4, sodium carbonate alone elutes U(VI) quantitatively from the U(VI) sorbed HQ anchored resin beads.

3.4.3. *Eluent concentration and volume*

The eluent (i.e. Na_2CO_3) concentration and volume were varied in the range 0.1–2.0 mol l^{-1} and 5–20 ml, respectively. The results obtained from these studies are shown in Table 5 from which it is clear that as low as 0.1 mol l^{-1} Na_2CO_3 is enough and a minimum of 10 ml of eluent is required for quantitative desorption of enriched U(VI), Th(IV) or La(III).

3.4.4. *Column bed stability and reusability*

The uranium(VI) was sorbed and desorbed on 0.02 g of the HQ anchored resin bed several times. The reproducibility of recovery data of metal ions was less than 4.0% even after 30 cycles of operation (see Table 6 for actual data). This observation reflects the reusability of the HQ anchored polymeric resin.

Table 6
%*E* of U(VI) with number of adsorption–desorption cycles (pH 5.5 ± 0.5, U(VI) 100 μg, aqueous phase volume = 100 ml, eluent volume = 10 ml; eluent = 10 ml of 1.0 mol l^{-1} Na_2CO_3; preconcentration flow rate = 3 ml/min, elution flow rate = 4 ml/min)

No. of adsorption–desorption cycles	%*E* of U(VI)
5	>99
10	99
20	98.0
30	96.0

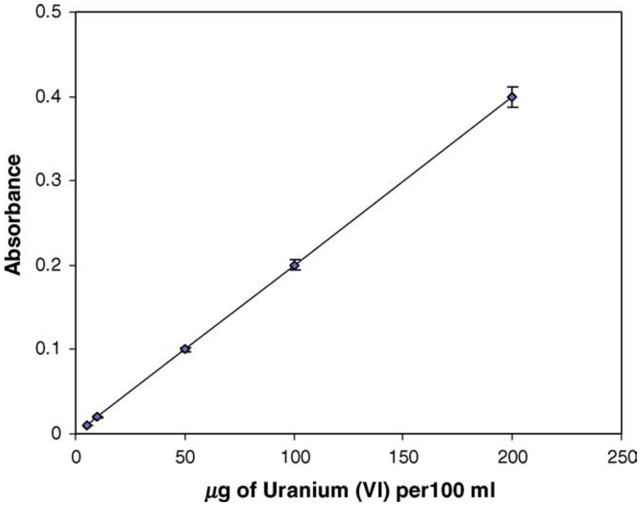

Fig. 6. Calibration graph with column dynamic studies (average of three determinations).

3.4.5. *Statistical and calibration parameters for column method*

Under the optimum conditions described above, the calibration curve was linear over the concentration range 5–200 μg of U(VI) present in 100 ml of solution (See Fig. 6). A sample of 50 μg of U(VI) in 100 ml gave a mean absorbance of 0.103 with a relative standard deviation of 2.50%. The detection limit corresponding to three times the standard deviation of the blank was found to be 5 μg per 100 ml. The linear equation with regression (R^2) is as follows:

$$A = 0.02C + 0.00035$$

$$R^2 = 0.9984$$

3.4.6. *Tolerance of neutral electrolytes and diverse ions*

The effect of various neutral electrolytes and diverse ions likely to be present in soil and sediment samples on the recovery of 10 μg of uranium(VI) present in 100 ml was studied. The results obtained are shown in Table 7 from which

Table 7
Effect of neutral electrolytes and diverse ions on the preconcentration of uranium(VI) in conjunction with Arsenazo III determination (10 μg of uranium(VI), pH 5.5)

Serial no.	Neutral electrolytes/diverse ions	Remarks
1	NaCl, $NaNO_3$, Na_2SO_4, NaSCN, $Na_2C_2O_4$, KCl, $KHPO_4$, KI, $MgCl_2$, $CaCl_2$, NH_4Cl, EDTA, sodium citrate and thiourea	No interference at 0.1 mol l^{-1} level
2	Li(I), Sr(II), Cu(II), Fe(II), Co(II), Ni(II), Mn(II), Hg(II), Zn(II), Cd(II), Pb(II), Al(III), Sb(III), As(V), V(V) and Mo(VI)	No interference at 1000 μg/100 ml level

Table 8
Analysis of water samples

Name of sample source of collection	Method adopted	Concentration of U(VI) ($\mu g\,l^{-1}$)	R.S.D. (%)[a]
Tap water, Trivandrum	Direct	2.85 ± 0.05	3.54
	SA	2.90 ± 0.05	3.22
Sea water, Arabian Sea, Trivandrum	Direct	4.21 ± 0.05	3.40
	SA	4.14 ± 0.05	3.25

[a] Based on values obtained on triplicate analysis.

it is clear that none of the neutral electrolytes and diverse ions tested were found to have deleterious effect on the determination of U(VI) using Arsenazo III spectrophotometric method.

3.4.7. Analysis of tap and sea water samples

The tap and sea water samples were subjected to uranium(VI) analysis by employing the developed preconcentration procedure in conjunction with the Arsenazo III spectrophotometric method. The results obtained based on direct and standard addition methods agree well (see Table 8). These results indicate the usefulness of the developed preconcentration procedure for monitoring U(VI) levels in drinking and sea water samples with a simple instrument like colorimeter/spectrophotometer.

3.4.8. Analysis of standard reference materials

The accuracy of the developed preconcentration procedure was tested by analyzing standard marine sediment (MESS-3) and soil (IAEA soil-7) reference materials. The samples were mineralized by using the dissolution procedure described in Section 2.5 and was subjected to preconcentration and determination by adopting the recommended procedure. The U(VI) contents established by the present procedure agree well with certified values (see Table 9).

Table 9
Analysis of marine sediment and soil reference materials

Sample	Uranium found, $\mu g\,g^{-1}$ of sample	
	Present method[a]	Certified value
Marine sediment (MESS-3)[c]	4.17 ± 0.03	4[b]
Soil (IAEA soil–7)[d]	2.72 ± 0.02	2.60 ± 0.01

[a] Average of three determinations.
[b] Information value.
[c] Supplied by National Research Council, Canada.
[d] Supplied by International Atomic Energy Agency, Vienna.

3.4.9. Analysis of soil and sediment samples

Soil sample collected from Trivandrum and sediment samples collected from Karamana river, Trivandrum and Arabian Sea, Trivandrum were subjected to dissolution, preconcentration and determination using the recommended procedure described in Section 2.5. The results obtained by the present method agree well with standard inductively coupled plasma-mass spectrometric (ICP-MS) values (See Table 10). Thus, the SPE preconcentration method developed in the present paper enables simple and low cost instrument like colorimeter to analyze soil and sediment samples containing trace and ultratrace amounts of U(VI).

4. Comparison with other methods

The HQ anchored resin exhibits the highest preconcentration factor for uranium (∼100) compared to Amberlite XAD-4-bicine (∼50) [24], Amberlite XAD-2-pyrogallol (∼70) [25] and Amberlite XAD-4-Quinoline-8-ol (∼40) [20]. Furthermore, the sorption capacity of HQ anchored resin is the highest compared to various chelate functionalized SPEs (See Table 2) excepting Amberlite XAD-16-*N*,*N*-dibutyl-*N*′-benzylthiourea. However, the latter procedure involves the functionalization of chelate onto Amberlite XAD-16 by adsorption and is beset with ligand leaching problems [26]. Two

Table 10
Analysis of real soil and sediment samples

Serial no.	Description of sample	Uranium(VI), $\mu g\,g^{-1}$ of sample			Recovery (%)
		Present method[a]		ICP-MS	
		Amountof U(VI) added	Amount of U(VI) determined		
1	Soil, Trivandrum	–	7.0 ± 0.2	6.96 ± 0.01	–
		7.0	14.0 ± 0.3		100
		14.0	21.1 ± 0.3		100.7
2	River sediment (Karamana River, Trivandrum)	–	8.1 ± 0.2		–
		8.0	16.1 ± 0.3	8.22 ± 0.01	101.3
		16.0	24.1 ± 0.4		100.6
3	Marine sediment (Arabian Sea, Trivandrum	–	4.8 ± 0.2		–
		5.0	9.8 ± 0.2		100
		10.0	14.9 ± 0.3		101

[a] Average of three determinations.

recent papers on enrichment of U(VI) with Amberlite XAD-4-octacarboxy-methyl-C-methyl Calix[4] resorcinarene [23] and poly(styrene) 8-hydroxyl-amine-37,38,39,40,41,42-hexahydroxy-1,8,13,19,25,31-hexacarboxy Calix[8] arene [28] involved tedious synthesis with high cost reagents unlike in the present procedure. Again, among the various chelate anchored Merrifield chloromethylated resins (See [10,11]), the HQ anchored resin gave higher retention capacity (See Table 2) and has been successfully employed for the analysis of certified and real samples of soils and sediments.

5. Conclusions

The SPE procedure developed in this paper using HQ anchored resin allows the determination of as low as 5 μg of uranium (VI) present in 1000 or 100 ml of solution by batch and column methods, respectively. Column method even though offers low detection limits but is more accurate (as R.S.D. value is low) and can be reused as the HQ anchored resin is unaffected even after 30 cycles due to high mechanical and chemical strength. The developed SPE method has good potential for its separation of U(VI) from host of coexisting alkali, alkaline earth, transition and heavy metal ions. The proposed method is simple and sorption capacity of the HQ anchored resin (120.30 mg g^{-1}) is much higher than other SPE materials reported in literature excepting *N*,*N*-dibutyl, *N*′-benzoyl thiourea sorbed Amberlite XAD-16 as seen from Table 2. Equilibration is fast as more than 90% of U(VI) is sorbed in less than 2 min of equilibration time making the analytical procedure reasonably fast. The accuracy of the developed method was tested by analyzing certified reference materials of marine sediment and soils for uranium(VI). Unlike thenoyl trifluoroacetone and di-bis(2-ethyl hexyl) malonamide anchored Merrifield chloromethylated resins, the HQ anchored resin offers reliable analysis of U(VI) in soil and sediment samples. Online flow injection analysis studies are in progress by packing the HQ anchored resin beads in home made microcolumns.

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