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Sequential Separation and Trace Enrichment of Thorium(IV) and Uranium(VI) on Chelating Resin Amberlite XAD-2-*ortho*-vanillinthiosemicarbazone (*o*-VTSC)

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ABSTRACT

Polystyrene–divinylbenzene-based Amberlite XAD-2 was functionalized with *ortho*-vanillinthiosemicarbazone and its analytical properties were investigated. The resin was used successfully for the separation and preconcentration of thorium(IV) and uranium(VI) ions prior to their determination by spectrophotometry and by ICAP-AES and GF-AAS, respectively. The influence of several ions as interferents is discussed. The resin exhibits good chemical stability, reuseability, and a faster rate of equilibration for their determination. The proposed method has been applied to sequential chromatographic separation of thorium(IV) and uranium(VI) on river water samples with good analytical reliability such as recovery of 97–98%, relative standard deviation of 2–3%, and a detection limit of 100 ng·mL^{-1}. The present method is also used for their determination in monazite sand and some standard geological materials.

Key Words. Chelating resin; ICAP-AES; GF-AAS; Preconcentration; Th(IV); U(VI)

INTRODUCTION

The selective and quantitative separation of metal ions from aqueous solutions have been extensively investigated by applying several techniques (1–3).

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Among them, approaches where specific sorbents are used have been considered as one of the most promising techniques (4–6) because they provide more flexible working conditions together with good stability, selectivity, high concentrating ability, and simple operation (7–9). Sorbents consist of a ligand (e.g., ion-exchange material or chelating agents), which interacts with the metal ions, and a carrier matrix, which may be an inorganic material (e.g., aluminum oxide, silica, etc.), or a polymer matrix, viz., poly(1-phenyl ethylene)–1,4-divinylbenzene (10–15), poly(1-pyridyl ethylene)–1,4-divinylbenzene (16), poly(1-cyano ethylene)–1,4-divinylbenzene (17), etc. Such chelating resins find application for preconcentration purposes in trace metal analysis, particularly for water systems and geological, biological, and industrial materials (18–20).

A number of chelating resins containing specific chelating agents, viz., amino carboxylic acid groups [e.g., ethylenediamine tetraacetic acid (21), iminodiacetic acid (22, 23), hydroxamic acid (24)], histidine (25), dithiosemicarbazone (26), bicine (27), etc. have been prepared and their analytical properties investigated for various transition metals, heavy metals, noble metals, etc. However, little work has been done for the separation and preconcentration of thorium(IV) and uranium(VI) on these polymeric resins. Recently Park and Suh (28) studied UO_2^{2+} ion adsorptivity on macroreticular chelating resin containing an amidoxime group.

In the present investigation, *ortho*-vanillinthiosemicarbazone has been covalently linked with commercially available polystyrene–divinylbenzene copolymer Amberlite XAD-2 through a —N=N— group (4, 8), having oxygen, nitrogen, and sulfur as binding sites, which is responsible for its wide analytical applicability. In an analytical application this polymeric resin was utilized for selective column concentration of Th(IV) and U(VI) from various standard samples. Their chromatographic separations from binary and ternary mixtures with interfering ions were also studied. In contrast to the solvent extraction procedure, the column concentration method eliminates the need for organic diluents, an attractive feature from an environmental aspect.

EXPERIMENTAL

Apparatus

A Hitachi 3210 UV/VIS spectrophotometer and 10 mm quartz cells were used for spectral measurements.

A Labtam Plasma Scan Model 710 sequential inductively coupled plasma atomic emission spectrometer (ICAP-AES) with a plasma scan multitasking computer and a peristaltic pump was used for thorium(IV) determination. Radiofrequency (rf), 27.12 MHz; incident power, 2000 W; Labtam GMK nebulizer; rf power, 5 W; observation height, 14 mm; argon coolant flow

rate, 10 $L \cdot min^{-1}$; argon carrier flow rate, 1 $L \cdot min^{-1}$; intergraph period, 10 seconds; resolution, 0.004 nm; peristaltic pump flow rate, 1 $mL \cdot min^{-1}$; wavelength, 283.73 nm.

AAS measurements were made in a Perkin-Elmer Model 420 with a pyrolytically coated HGA-76 graphite furnace (GF-AAS). A uranium hollow cathode lamp was used at 358.5 nm uranium wavelength with a spectral width of 0.2 nm. An atomization temperature of 2700°C and an argon gas purge were used.

The pH measurements were made on a Systronics digital pH meter model 335. The flow of liquid through the column was controlled by a Miclins Peristaltic pump PP-10.

Reagents

All chemicals used were of analytical grade from E. Merck or B.D.H., unless otherwise stated. Amberlite XAD-2, surface area 330 $m^2 \cdot g^{-1}$, pore diameter 90 Å, and bead size 20–50 mesh, was procured from Fluka. All aqueous solutions were prepared with Quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system.

Standard stock solutions (1000 ppm) of thorium(IV) and uranium(VI) were prepared by dissolving requisite amounts of thorium nitrate tetrahydrate and uranyl nitrate hexahydrate, respectively, in quartz-distilled deionized water containing small amounts of nitric acid. Their final concentrations were then determined spectrophotometrically (29, 30). pH adjustments were made with 0.1/0.01 M HCl or NaOH and/or acetate buffers. The glasswares used were soaked in 10% HNO_3 for 3 days before use and cleaned repeatedly with double distilled water. Water samples from the Sabarmati River were isokinetically collected in clean polyethylene bottles from locations near the Sabarmati thermal power station, Ahmedabad. The groundwater samples were collected from the Navrangpura region of Ahmedabad, India.

Synthesis of Amberlite XAD-2-*o*-VTSC Resin

A 5-g sample of Amberlite XAD-2 was treated with a nitrating mixture containing 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and stirred for 1 hour at 60°C on a water bath. The nitrated mixture was poured into ice-cold water. It was further filtered, washed repeatedly with distilled water until free from acid, and reduced with $SnCl_2$ (40 g), concentrated HCl (45 mL), ethanol (50 mL), and refluxed for 12 hours at 90°C. The amino polymer was filtered off and washed with distilled water and 2 N NaOH to obtain the free amino polymer.

The amino polymer was treated with 100 mL of 2 N HCl for 30 minutes, washed with distilled water to remove excess HCl, and suspended in 250 mL

of ice-cold water, then mixed with a diazotizing mixture of 1 N HCl and 1 N $NaNO_2$ in 1 mL aliquots, each time with constant stirring, until the reaction mixture showed a permanent blue color with starch-iodide paper. The diazotized resin was filtered, washed with ice-cold water and treated with *ortho*-vanillinthiosemicarbazone (2.5 g in 350 mL of glacial acetic acid and 150 mL DMF) at 0–3°C for 40 hours. The dark brown colored beads were filtered and washed. The schematic reaction sequence is given in Fig. 1.

Procedure for Column Concentration and Determination of Th(IV) and U(VI)

A glass column, 5 mm in diameter, was packed with 1 g of the functionalized resin. It was treated with 25 mL of 1 N HCl at the flow rate of 3 $mL \cdot min^{-1}$ and washed with double distilled water until the resin was free of acid. A 1-L solution of thorium(IV) or uranium(VI) in the 0.1–1 $\mu g \cdot mL^{-1}$ concentration range was passed through the column after adjusting to the appropriate pH with an optimum flow rate (Table 1). After this sorption step the column was washed with 100 mL of deionized water to remove any uncomplexed thorium or uranium from the resin bed. Stripping of the metals from the resin was carried out by suitable eluting agents like 0.1 N HNO_3 or 1 N HCl for thorium and 0.1 N HCl for uranium. The stripping solution was collected and analyzed spectrophotometrically using Arsenazo-I and III and by ICAP-AES and GF-AAS after appropriate dilution.

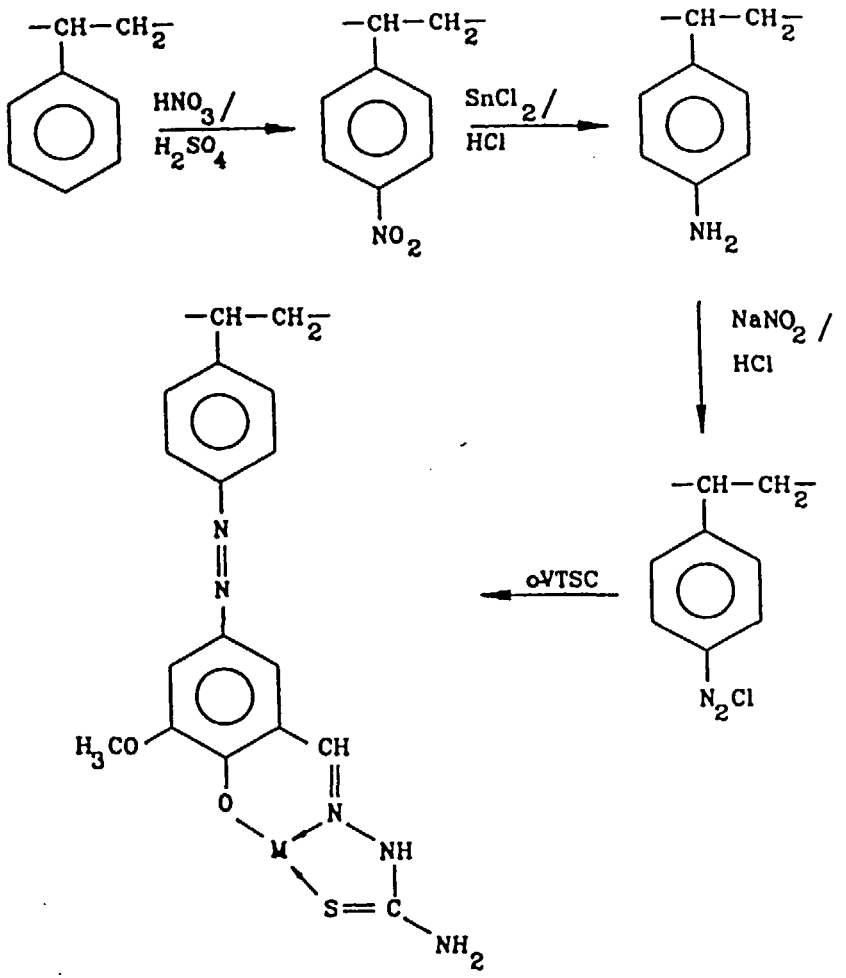
RESULTS AND DISCUSSION

pH Dependence of Metal Ion Uptake

The optimum pH of metal ion uptake was determined using the column procedure. The resin Amberlite XAD-2-*o*-VTSC (1.0 g) was packed in a 5-mm diameter column, and a suitable aliquot of metal ion solution [Th(IV) or U(VI)] was passed with an optimum flow rate at varying pH (Fig. 2). The degree or percentage of metal sorption was calculated by ICAP-AES and GF-AAS by measuring the metal content in the supernatant liquid and after desorbing the resin with a suitable eluant. The sorption experiments were duplicated for both metal ions.

Effect of Flow Rate

The degree of metal ion sorption on Amberlite XAD-2-*o*-VTSC was studied by varying the flow rate, and it was found that the optimum flow rate for both Th(IV) and U(VI) was 2.0 $mL \cdot min^{-1}$. However at flow rates greater than 2.5 there was a decrease in sorption efficiency (Fig. 3).



METAL-AMBERLITE XAD-2-o-VTSC

FIG. 1 Schematic representation of reaction sequence.

Sorption Capacity and Distribution Coefficient (K_D)

The sorption capacity of the resin was determined by a batch process by equilibrating 1.0 g of the resin sample with 100 mL of 50 $\mu g \cdot mL^{-1}$ thorium or uranium solution for 24 hours at their optimum pH at 30°C. The loading capacity for thorium and uranium on the resin was calculated from the differ-

TABLE 1
Parameters Optimized for Sorption and Desorption of Th(IV) and U(VI) on Amberlite-XAD-2-*o*-VTSC Resin

No.	Parameters	Metal ions	
		Thorium(IV)	Uranium(VI)
1	pH range	3.0–4.5	6.0–7.5
2	Flow rate ($mL \cdot min^{-1}$)	1.5–2.5	1.5–2.0
3	Concentration of acid for desorption	0.1 N HNO_3/1 N HCl	0.1 N HCl
4	Sorption capacity ($\mu g \cdot g^{-1}$ resin)	1600	1525
5	Preconcentration factor	105	100
6	Average recovery (%)	98	97–98
7	Relative standard deviation (%)[a]	2.2	2.6
8	Distribution coefficient (K_D)	3750	3684
9	$t_{1/2}$ for exchange (minutes)	7	10

[a] Five determinations of 1.5 $mg \cdot L^{-1}$ Th(IV) and U(VI).

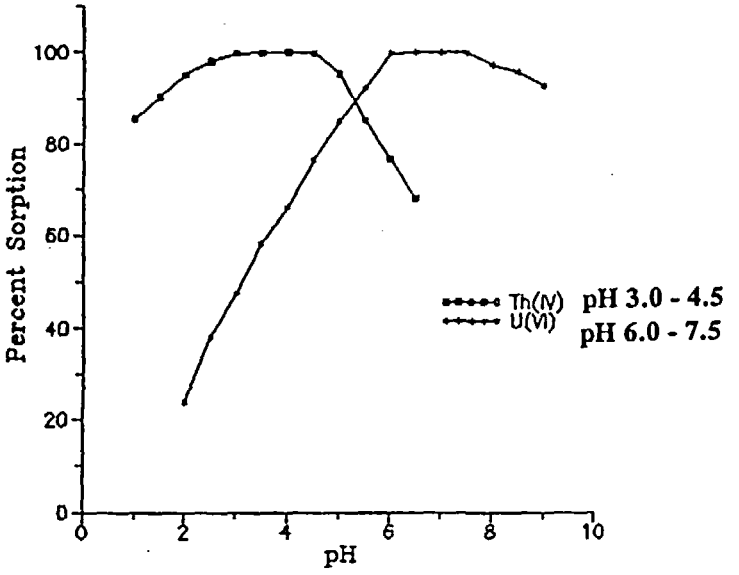


FIG. 2 Plot of percentage sorption of thorium and uranium against pH. Thorium: 3 $\mu g \cdot mL^{-1}$, 50 mL; eluant, 1 N HCl. Uranium: 3 $\mu g \cdot mL^{-1}$, 50 mL; eluant, 0.1 N HCl.

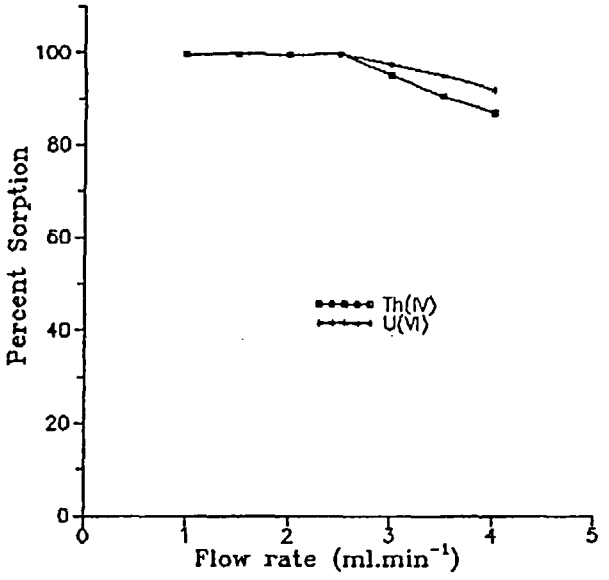


FIG. 3 Effect of flow rate on thorium and uranium sorption. Thorium: 3 μg·mL^{-1}, 50 mL, pH 3.5. Uranium: 3 μg·mL^{-1}, 50 mL, pH 6.5.

ence between the metal ion concentration before and after desorption. The values are given in Table 1.

The distribution coefficients (K_D) of the metal ions, defined by the equation

$$K_D = \frac{\text{amount of metal ion taken up by the resin}}{\text{amount of metal ion remaining in the solution}} \cdot \frac{\text{volume of the solution}}{\text{amount of resin taken}}$$

were determined by using the batch equilibration method. In the equilibration experiment, 25 mL of solution containing 300 μg of the metal ion in question at the optimum pH was treated with 0.2 g of fresh resin. The solution was stirred for 4 hours at room temperature (30°C), filtered to remove the resin, and the metal ion content of the filtrate was determined by ICAP-AES or GF-AAS. The results are given in Table 1.

Exchange Kinetics

To determine the rate of loading of thorium and uranium on the resin, batch experiments were carried out under the following conditions: 0.5 g of resin

beads was stirred with 250 mL of feed solution containing thorium or uranium at room temperature (30°C). Aliquots of 5 mL solution were taken out for analysis at predetermined intervals. The concentration of metal ion in the supernatant solution was determined and the amount of metal ion loaded on the resin phase was calculated by mass balance (in $\mu g \cdot g^{-1}$ resin). The loading half time $t_{1/2}$, defined as the time needed to reach 50% of the resin's total loading capacity, was estimated from the curves (Fig. 4). From the kinetics of thorium and uranium exchange, it was observed that an equilibrium time of about 2 hours was required for 99–100% sorption. However, the time required for 50% sorption of thorium and uranium was 7 and 10 minutes, respectively. The faster uptake of these metal ions on Amberlite XAD-2-*o*-VTSC reflects a better accessibility of the metal ions to the chelating sites in the resin.

Resin Stability Test

To test the resin's stability, it was subjected to several loading and elution batch operations. The conditions employed for the study were: 1 g of resin beads was stirred with a 20 $\mu g \cdot mL^{-1}$ 100 mL solution containing thorium

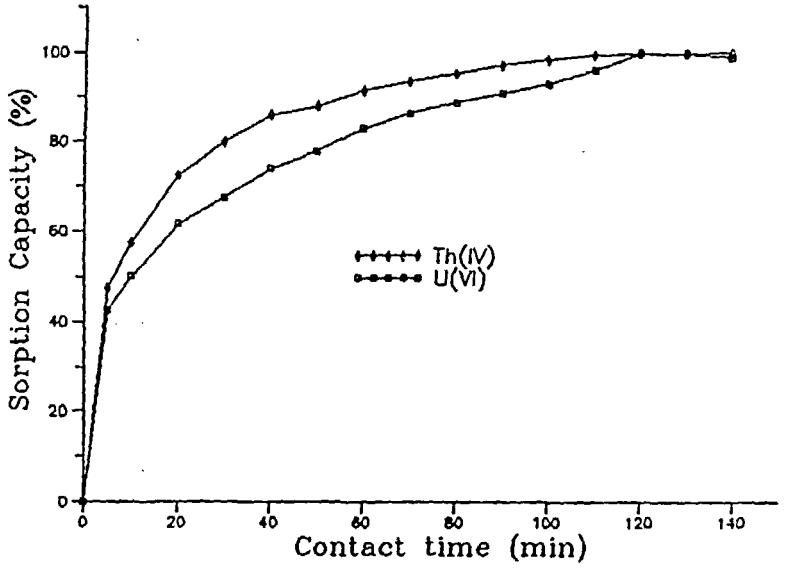


FIG. 4 Kinetics of thorium(IV) and uranium(VI) binding by Amberlite XAD-2-*o*-VTSC. Thorium: 10 $\mu g \cdot mL^{-1}$, 250 mL, pH 3.5. Uranium: 10 $\mu g \cdot mL^{-1}$, 250 mL, pH 6.5.

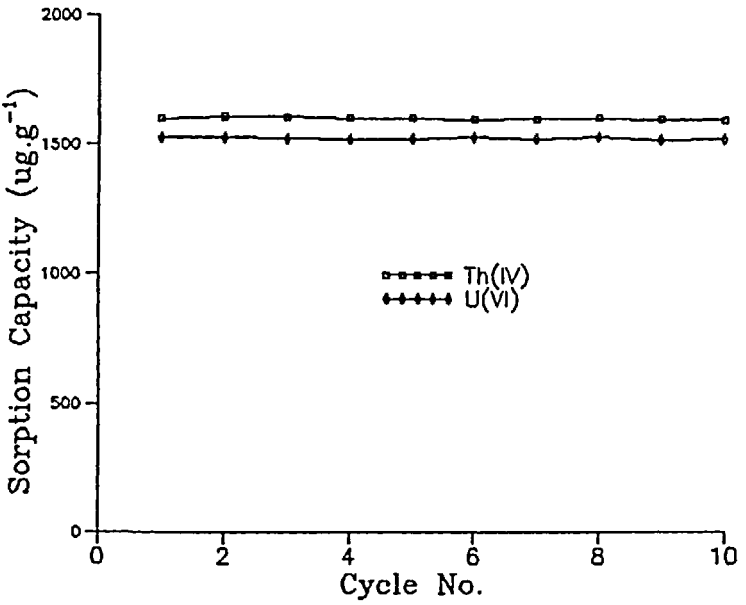


FIG. 5 Evaluation of the stability of the resin for thorium and uranium extraction. Elution Th(IV), 1 N HCl; U(VI), 0.1 N HCl.

and uranium for 24 hours at room temperature (30°C). The elution operations were carried out by shaking the resin with 50 mL of a suitable eluant for 4 hours to ensure complete equilibration. The operating capacity was calculated from the loading and elution tests. The results from both tests agreed within 2–3% error (Fig. 5).

Breakthrough Studies

The breakthrough capacities are more significant and useful than batch capacities in ion-exchange chromatographic applications. The breakthrough studies were carried out by taking 1 g of the resin in the column (5 mm diameter) and passing a 10 $\mu g \cdot mL^{-1}$ solution of thorium (pH 3) and uranium (pH 6) at a flow rate of 1 $mL \cdot min^{-1}$. Figure 6 shows that both curves are steep at the breakthrough points and reach their breakthrough points at different times, which suggests that the metals can be separated from their mixtures and preconcentrated from very dilute solutions.

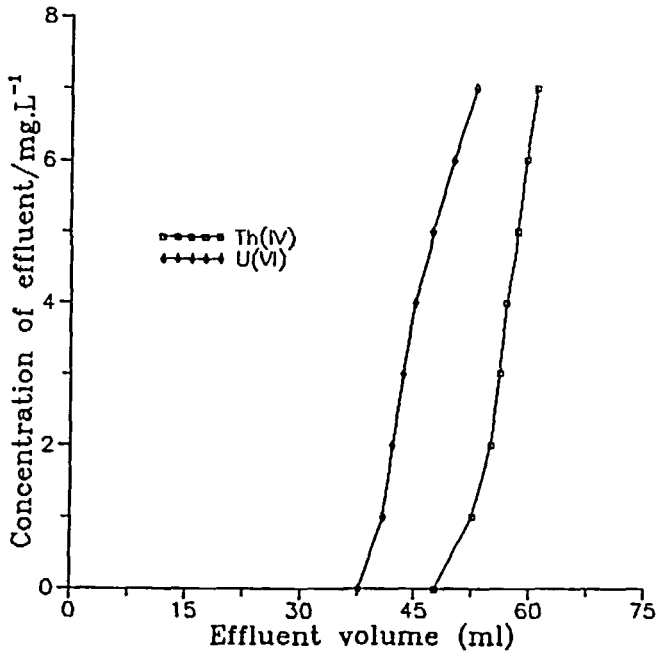


FIG. 6 Breakthrough curves for thorium and uranium on Amberlite XAD-2-*o*-VTSC. Thorium: 10 $\mu g \cdot mL^{-1}$, pH 3.5. Uranium: 10 $\mu g \cdot mL^{-1}$, pH 6.5. Flow rate: 1 $mL \cdot min^{-1}$.

Preconcentration of Thorium and Uranium on Amberlite XAD-2-*o*-VTSC

The performance of the resin in the column concentration of Th(IV) and U(VI) may be assessed from their elution profiles (Fig. 7). The column concentration behavior for both metal ions was evaluated in terms of the preconcentration factor (PF):

$$PF = \frac{\text{concentration of metal in the stripping solution}}{\text{initial concentration of metal in the feed solution}}$$

The profiles are constructed by plotting the preconcentration factor (PF) as a function of the volume of stripping solution.

Quantitative collection of thorium and uranium was possible from a solution concentration of the order of 100 $ng \cdot mL^{-1}$ with recovery up to 97–98%. The preconcentration factors for thorium and uranium were found to be 105 and 100, respectively. The results are given in Table 2.

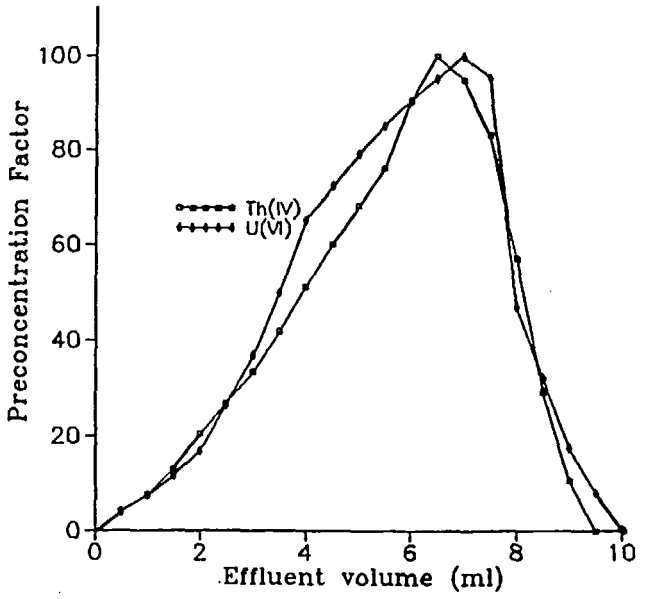


FIG. 7 Profile of thorium(IV) and uranium(VI) elution from Amberlite XAD-2-*o*-VTSC.

Effect of Electrolytes and Foreign Ions

The effect of various electrolytes like KCl, NaCl, NaF, NaBr, $NaNO_3$, Na_2SO_4, Na_3PO_4, and CH_3COONa on the sorption of Th(IV) and U(VI) with Amberlite XAD-2-*o*-VTSC resin was studied. It was found that all the electrolytics were tolerable in the 0.5–2 M concentration range except for sodium phosphate where it was only 0.12 M for both metal ions. Their limit of tolerance was defined as the amount of electrolyte (anion)/foreign ion

TABLE 2
Preconcentration Factor for Thorium(IV) and Uranium(VI)[a]

Metal ion	Feed solution (mL)	Concentration ($ng \cdot mL^{-1}$)	Stripping solution (mL)	Recovery (%)	Preconcentration factor
Thorium(IV)	1000	100	9.5	98	105
Uranium(VI)	1000	100	10.0	97	100

[a] Experimental conditions: Amberlite XAD-2-*o*-VTSC = 1 g; thorium(IV) = 100 μg, pH 3.0; uranium(VI) = 100 μg, pH 6.5.

TABLE 3
Tolerance Limits of Electrolytes on the Sorption of Thorium(IV) and Uranium(VI) on Amberlite XAD-2-*o*-VTSC[a]

	Electrolytes ($mol \cdot L^{-1}$)							
Metal ion	NaF, 100 mL	NaCl, 100 mL	NaBr, 100 mL	$NaNO_3$, 100 mL	$NaNO_2$, 100 mL	Na_2SO_4, 100 mL	Na_3PO_4, 100 mL	CH_3COONa, 100 mL
Thorium(IV) (100 μg)	1.0	2.0	1.5	2.0	2.0	0.5	0.12	1.0
Uranium(VI) (100 μg)	1.0	1.5	1.0	1.5	1.5	0.5	0.12	1.0

[a] Experimental conditions: Amberlite XAD-2-*o*-VTSC = 1.0 g.

(cation) that caused an error of 2–3% in the recovery of metal ions. The results are given in Table 3.

The effects of commonly occurring cations in water samples like Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), etc. and those of Y, La, Ce, and other rare earths present in geological material on the sorption of Th(IV) and U(VI) by Amberlite XAD-2-*o*-VTSC have been studied. The alkali and alkaline earth metal ions do not affect the recovery of both metal ions up to a 200-fold excess.

In the sorption of 100 μg of thorium at pH 2.5, 250 μg of Mn(II); 300 μg each of Fe(III), Co(II), and Ni(II); 200 μg of Cu(II); and 450 μg of Zn(II) and Pb(II) did not interfere. Almost no interference of Y, La, Ce, and other rare earths was observed up to a fivefold excess in the sorption of thorium (100 μg, pH 2.5) when measured at 283.73 nm by ICAP-AES, since they have a higher pH of sorption (6.0–9.0).

However, for 100 μg of uranium at pH 6.0, the tolerance limits for various intefering ions were 225 μg Mn(II); 250 μg each of Fe(III), Co(II), and Ni(II); 400 μg of Cu(II); and 150 μg each of Zn(II) and Pb(II). At pH 6, Y, La, Ce, and other rare earths did interfere in the sorption of uranium. However, the separation of uranium(VI) from lanthanum(III) was achieved by sequential acid elution when taken in the same concentration ratio (100 μg/25 mL) and measured at 358.5 nm by GF-AAS. At higher concentrations the sorption was not quantitative and with low recoveries.

The effect of actinides was not studied in the present investigations.

Chromatographic Separations

The synthesized resin was found to exhibit high selectivity for thorium and uranium as shown by the breakthrough curves, the pH of maximum sorption,

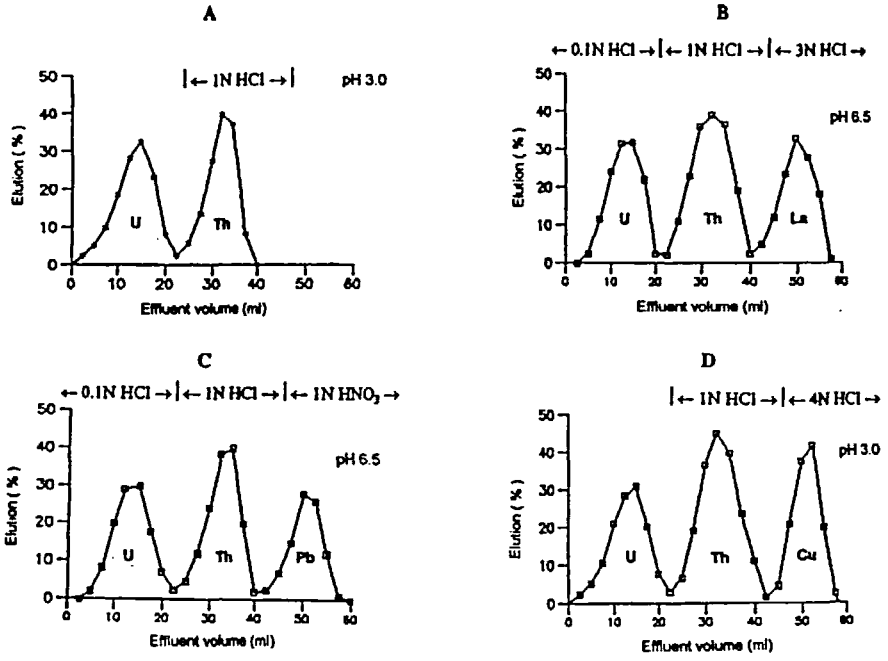


FIG. 8 (A) Separation of Th and U. (B) Separation of Th, U, and La. (C) Separation of Th, U, and Pb. (D) Separation of Th, U, and Cu.

and elution studies. Further, favorable kinetics makes the resin useful for separating them from mixtures on a column. Hence, the following synthetic mixtures (each 100 μg in 25 cm^3 of buffer solution) were passed through the column at a flow rate of 2 $mL \cdot min^{-1}$: 1) thorium and uranium; 2) thorium,

TABLE 4
Preconcentration and Determination of Uranium(VI) in Simulated River and Groundwater[a] Samples

Sample	Amount present (μg)	Amount added (μg)[b]	Amount found (μg)	Recovery (%)
Sabarmati River, Ahmedabad	11	100	110 ± 2	97
Groundwater, Navrangpura, Ahmedabad	18	100	117 ± 2	98

[a] One-liter sample.
[b] Average of three determinations.

TABLE 5
Determination of Thorium and Uranium in Indian Monazite Sand and in US Geological Survey Standards

	Monazite sand, Travancore, India (%)		USGS:BCR-1 ($\mu g \cdot g^{-1}$)		USGS:GSP-1 ($\mu g \cdot g^{-1}$)	
Metal ion	Present	Found[a]	Present[b]	Found[a]	Present[b]	Found[a]
Thorium	8.52	8.41 ± 0.25	6.1	6.05 ± 0.16	105	105.1 ± 1.2
Uranium	0.018	0.019 ± 0.002	1.7	1.68 ± 0.08	2.1	2.12 ± 0.09

[a] Average and standard deviation, from triplicate runs conducted with a single column.
[b] Reference 33.

uranium, and lanthanum; 3) thorium, uranium, and lead; and 4) thorium, uranium, and copper. The column effluents were analyzed for each metal ion in the mixture. Quantitative separations were achieved in all four mixtures as shown in their separation patterns in Fig. 8.

Application to Analysis of Water Samples, Monazite Sand, and Geological Materials

To check the applicability of the proposed method for preconcentration and determination of thorium and uranium, the resin was subjected to various water samples, monazite sand, and rock samples. Water samples were collected from the Sabarmati River near a thermal power station, Ahmedabad, and ground water samples from the Navrangpura region of Ahmedabad, India. The uranium contents found were 10 and 17 μg/1000 mL sample analyzed, respectively. However to bring the concentrations up to the detection level, the samples were spiked with 100 μg standard uranium. The geological materials were obtained from United States Geological Survey USGS:BCR-1 and USGR:GSP-1, and were decomposed in a mixture of acids as described earlier (31, 32). The results are tabulated in Tables 4 and 5.

CONCLUSIONS

Amberlite XAD-2-*o*-VTSC resin shows good potential for trace enrichment of thorium and uranium with high preconcentration factors, and their separation is possible in the presence of various interfering ions. The results obtained for a variety of geological reference materials demonstrate that the procedure allows precise and accurate analysis of geological samples for their thorium and uranium contents. Since it has negligible affinity for alkali and alkaline

earth cations, it has proved to be highly useful in the analysis of natural water samples.

The synthesized resin was recycled many times without affecting its sorption capacity. The method also requires smaller eluent volumes and is therefore very rapid. However, the proposed method fails to achieve complete separation of uranium from known interfering cation like Y, La, and Ce when they are present in more than a 1:1 concentration ratio.

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