SYNTHESIS OF QUINALDINIC ACID AMIDE DERIVATIVE OF STYRENE-DIVINYLBENZENE COPOLYMER AND ITS APPLICATION IN PRECONCENTRATION OF MERCURY(II)

KEY WORDS: Quinaldic acid amide, styrene-divinyl benzene, mercury(II), selective sorption, preconcentration.

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ABSTRACT
A new chelating resin has been synthesized by introducing a quinaldic acid amide group into styrene-divinyl benzene(9%) copolymer beads. The resin is stable in fairly strong acids or alkali and has been characterized by elemental analysis for nitrogen and from i.r. spectra. The water regain value is 0.37g/g. The sorption patterns of Na(I), K(I), Ca(II), Mg(II), Pb(II), Cu(II), Ni(II), Zn(II), Cd(II), Hg(II) and Fe(III) on the chelating resin have been studied as a function of pH. The resin selectively sorbs Hg(II) over a wide pH-range of 2.5 - 7.6 with high efficiency. The maximum exchange capacity for Hg(II) is 1.98 mmols g⁻¹ at pH 5.5. Over 99% of Hg(II) sorbed has been recovered by using 10% thiourea in 1M HClO₄ both by batch and column operations. The method has been utilized in the preconcentration and recovery of Hg(II) from industrial and laboratory waste water.
INTRODUCTION

Direct determination of mercury in natural water samples by conventional atomic absorption spectrometry (AAS) is not generally possible as the mercury contents are often below the limit of detection. Many procedures have been developed for preconcentrating mercury in water. One of the prevailing techniques is a gas-stripping procedure based on the reduction-aeration method.

Many chelating ion-exchangers containing functional groups like oxine and thioureido, azathiopyrine disulphonic acid, mercapto and azo, dithizone and thiazole and its derivatives have recently been developed for the preconcentration of mercury. Such resins containing histidine and dithiocarbamate have mercury exchange capacity of 1.5 mmol g⁻¹ or higher but separation of mercury(II) from other metal ions is not very efficient. Chelating exchangers containing polymeric phosphoric acid or phosphine oxide and Sumichellite O-10R have even been recommended for treatment of waste water.

This communication describes the synthesis of a new chelating resin with a quinaldinic acid amido group introduced into macroreticular styrene-DVB copolymer beads and its application to preconcentration of mercury(II) and separation from allied metal ions. The synthesis is easy and the exchange capacity of mercury (II) is higher than most of the chelating resins reported. Mercury(II) can be recovered easily from the resin, it desired and the method has been extended to the determination after preconcentration of the metal ions from industrial and laboratory waste water. The resin has the potential for use as a sewage water treatment material.

EXPERIMENTAL

Apparatus

A Shimadzu Atomic Absorption/Flame Emission Spectrophotometer (Model 646) and a Beckman UV-Visible DB Spectrophotometer (Model 26) were used for the determination of metal ion concentrations. Infra-red spectra were recorded in a Beckman instrument (Acculab 10). Nitrogen was determined by a standard Micro-Duma apparatus. A gravity flow column with appropriate reservoir was used as holder of the resin.

Reagents

All the metal ion solutions were prepared from their salts and oxides (analytical grade) and metal contents were determined by the standard methods. Hg(II) and Ni(II) were determined gravimetrically using thionalide and dimethylglyoxime respectively while Fe(III) was determined by titration with dichromate. The other metal ions, viz., Ca(II), Mg(II), Pb(II), Zn(II) and Cd(II) were determined by titration with Na₂EDTA. Buffer solutions were prepared by mixing different proportions of standard solutions of sodium chloride and hydrochloric acid (for pH 0.5 to 3.9), Sodium acetate - acetic acid (for pH 4.0 to 6.0) and potassium dihydrogen phosphate - disodium hydrogen phosphate (above pH 6.0). For lead, the pH was adjusted with sodium hydroxide and nitric acid.

Synthesis of the resin

The amino derivative of styrene DVB copolymer (80-100 mesh) was prepared by nitration followed by amination of the nitrated polymer. It was then N-acylated by treating it with quinaldiny1 chloride in toluene medium on a boiling water bath. The resin was first washed with methanol to free it from excess quinaldiny1
chloride and then with water. It was immersed in 2N HCl for 24 hr and washed free of chloride, air dried and stored. The steps of synthesis are illustrated below:

\[
\text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2 \rightarrow \text{Sn/HCl} \rightarrow \text{NH}_2
\]
\[
\text{C}_{10}\text{H}_6\text{ONCl} \rightarrow \text{NH}-\overset{\text{C}}{\mid} \text{N} \text{O}
\]

Procedure for determination of metal exchange capacity:
Batch operation

A known amount of the air dried resin (~0.5 g) was mixed with the desired metal ion of known concentration and volume which was magnetically stirred for 24 hr. The pH of the solution was controlled by a suitable buffer. Finally, the resin was filtered and washed with the same buffer until free of unabsorbed metal ions. The chance of loss of metal ions during washing was negligible as only strong acids or another chelating agent was capable of eluting the metal ions from the resin.

The metal ions sorbed were then eluted with appropriate reagents. The concentrations of eluted as well as unabsorbed metal ions were determined by standard methods. The entire process was repeated with buffered solutions of different pH-values for each of the metal ions studied (Fig. 1).

\[\text{FIG. 1. EXCHANGE CAPACITY OF THE RESIN FOR DIFFERENT METAL IONS AS A FUNCTION OF pH}\]


Inset: b to g on an enlarged scale
Standard AAS methods\(^{13}\) were employed to determine the concentrations of Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II), Fe(III) and flame emission mode was employed for Na(I) and K(I), while visible spectrophotometry with dithizone was applied in the case of Pb(II). Cold-vapor AAS with standard reduction/aeration system was used for determining the concentration of Hg(II).

**Column operation**

A glass column (1cm i.d., 30cm length) was packed with 20g of resin, previously swollen in water to a height of 22cm. The column was equilibrated with a desired buffer solution. An excess of the metal ion at a pH controlled by the same buffer was allowed to percolate through the resin. The rate of flow was controlled at 0.5 - 1 ml min\(^{-1}\). The column was washed with the same buffer solution. The sorbed metal ions were eluted with a suitable acid or reagent and the concentration was determined.

**Preconcentration and Determination of Hg(II) in waste water**

Samples of waste water were collected in pre-cleaned\(^{14}\) polyethylene bottles. A 3-litre aliquot was filtered through Whatman No. 42 filter paper. The pH was adjusted to 5.5 and then passed through the resin column adjusted to the same pH at the rate of 1 ml min\(^{-1}\). The sorbed mercury(II) was eluted with 50 ml of 10\% thiourea in 1N HClO\(_4\). The metal content was determined by the cold vapor AAS technique.

**RESULTS AND DISCUSSION**

**Eluting agents**

The eluting solutions used for different metal

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**TABLE 1**

<table>
<thead>
<tr>
<th>Eluting agent</th>
<th>Metal Ion(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)SO(_4) (2N)</td>
<td>Na(I), K(I), Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II), Fe(III)</td>
</tr>
<tr>
<td>HNO(_3) (3N)</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>Thiourea (10%) in HClO(_4) (1N)</td>
<td>Hg(II)</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Hg(II) recovered, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N H(_2)SO(_4)</td>
<td>17 ± 0.5</td>
</tr>
<tr>
<td>4N H(_2)SO(_4)</td>
<td>39 ± 0.8</td>
</tr>
<tr>
<td>2N HCl</td>
<td>51 ± 2</td>
</tr>
<tr>
<td>4N HCl</td>
<td>92 ± 2</td>
</tr>
<tr>
<td>2N HNO(_3)</td>
<td>15 ± 0.5</td>
</tr>
<tr>
<td>4N HNO(_3)</td>
<td>33 ± 1</td>
</tr>
<tr>
<td>Citric acid &amp; ammonium citrate</td>
<td>16.3 ± 1.5</td>
</tr>
<tr>
<td>10% Thiourea &amp; 0.1M HClO(_4)</td>
<td>57 ± 1</td>
</tr>
<tr>
<td>10% Thiourea &amp; 1.0M HClO(_4)</td>
<td>99.5 ± 0.5</td>
</tr>
</tbody>
</table>
ions are presented in Table 1, which lists only the most suitable of the eluting agents examined.

Recovery of mercury(II) with various eluting agents were studied in detail. Mercury was found to be strongly absorbed by the resin as the recovery with common acids is incomplete. The results of these studies are given in Table 2.

Metal ion exchange capacity as a function of pH

The results of the studies on sorption patterns for different metal ions are presented in Fig. 1. Mercury(II) is sorbed between pH 2 and 7, with the maximum capacity of 1.98 mmols g\(^{-1}\) at pH ~5.5, whereas the other metals have low capacity (the maximum among them being 0.2 for lead(II) at pH 4.0). None of the metal ions tested are sorbed at or above pH 6.0.

Separations

Mercury was separated from synthetic mixtures containing one or more of Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Pb(II), Cu(II), Ni(II) and Fe(III). The resin absorbed Hg(II) strongly between pH 5.0 - 6.0, while Na(I), K(I), Ca(II), Mg(II) and Zn(II) passed unabsorbed. Thus on percolating the mixture through the column at pH 5.0 - 6.0 only mercury was absorbed and recovered as described earlier. The results of these separations are given in Table 3.

Other separations are also possible, e.g. from Fe(III), Cd(II), Pb(II) and Ni(II). Iron(III) is not absorbed by the resin at pH 5.5, but it hydrolyses. Phosphoric acid was added to keep Fe(III) in solution. Hg(II) was separated from Cd(II), Pb(II) and Ni(II) at pH 5.5 as these ions have negligible sorption at

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### Table 3

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Amount, (\mu g) ml(^{-1})</th>
<th>Hg(II) recovered, (\mu g) ml(^{-1})</th>
<th>Average Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(I)</td>
<td>50, 150, 200</td>
<td>74.0, 73.9, 74.0</td>
<td>99.9</td>
</tr>
<tr>
<td>K(I)</td>
<td>70, 140, 210</td>
<td>73.7, 73.9, 73.8</td>
<td>99.7</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>40, 120, 160</td>
<td>73.7, 74.0, 73.9</td>
<td>99.8</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>82, 164, 246</td>
<td>74.0, 73.9, 73.8</td>
<td>99.9</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>111, 222, 333</td>
<td>73.3, 73.7, 71.1</td>
<td>98.2</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Amount, (\mu g) ml(^{-1})</th>
<th>Hg(II) recovered, (\mu g) ml(^{-1})</th>
<th>Average Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>181, 362, 543</td>
<td>73.4, 73.1, 73.9</td>
<td>99.3</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>11, 22, 34</td>
<td>73.8, 73.9, 73.7</td>
<td>99.7</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>41, 205, 328</td>
<td>73.1, 73.5, 73.9</td>
<td>99.3</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>56, 112, 168</td>
<td>73.8, 72.9, 73.9</td>
<td>99.4</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>49, 98, 490</td>
<td>73.8, 73.4, 73.6</td>
<td>99.5</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>64, 128, 192</td>
<td>73.8, 73.4, 73.7</td>
<td>99.4</td>
</tr>
</tbody>
</table>
this pH, while for Cd\(^{2+}\) and Fe\(^{3+}\) the pH was maintained around 2.0. Hg(II) was preferentially sorbed at pH 6.5 in presence of Na\(_2\)HPO\(_4\) - citric acid buffer and this has been utilised in the separation of Hg(II) from Cu (II). The results are presented in Table 4.

**Determination of Hg(II) in waste water**

Six samples of water were collected from different points of the moat surrounding the campus of University of Burdwan where the waste water from the laboratories is discharged. The Hg(II) content was determined by preconcentration using the resin column method and a mean value 6 ± 0.8 ng ml\(^{-1}\) of mercury was determined. Similarly, six samples of water were collected over the same period from Tamla Nallah, a small ditch where the effluents of the industrial belt at Durgapur city, are discharged. The mean mercury content was found to be 42 ± 1.0 ng ml\(^{-1}\).

These values were checked by an independent method\(^{12}\) using AAS technique after preconcentration of inorganic mercury on Dowex 1 - X8 resin(chloride form). The results were slightly lower 4.5 ± 0.9 and 38 ± 1 ng ml\(^{-1}\) respectively for laboratory waste water and industrial effluents.

**Characterization of the resin**

Being a new resin its water regain value was determined and found to be 0.37 g/g. The resin was stable for at least 7 days in common acids like sulfuric, nitric, hydrochloric and perchloric (all of 4N strength) as well as in 2N sodium hydroxide. The stability was determined by analysis of nitrogen content before and after treatment.

**TABLE 5**

| Ring Breathing Bands in i.r. Spectra |
|-----------------|-----------------|-----------------|
| Quinaldinic acid (cm\(^{-1}\)) | Chelating resin (cm\(^{-1}\)) | Chelating resin with Hg(II)\(_{sorbed}\) (cm\(^{-1}\)) |
| 1615 m | 1615 m | 1620, 1610 m, br |
| 1595 m | 1600 m | |
| 1465 m | 1505 m | 1505 w |
| 1440 m | 1438 m | 1440 w |

m = medium, br = broad, w = weak

The infra-red spectra of the chelating resin, before and after sorption of mercury as well as of quinaldinic acid were recorded. The presence of the vital ring breathing bands\(^{15}\) in all the three samples, as presented in Table 5 indicates the incorporation of the quinaldinic acid amide group into the styrene - DVB matrix. The spectra were recorded in KBr discs.

The nitrated polymer contains 11.31% nitrogen. The total nitrogen of the aminated polymer is 11.46% of which 6.1% is due to amino-group determined by titration in non-aqueous medium\(^{16}\), indicating 54% conversion in the reduction process. The final resin contains 9.26% nitrogen and the exchange capacity of the nitro or amino group is negligible.

**CONCLUSION**

The method of synthesis of the chelating ion-exchanger is simple and the resin is stable. Mercury
DAS AND DAS

(II) is selectively sorbed on it over a wide pH range, having high exchange capacity. Thus, it can freely compete with all such resins reported for preconcentration of mercury(II) from natural water samples. The resin has the potential to be used for treatment of waste water.

ACKNOWLEDGEMENTS

Support for the research from the University Grants Commission, New Delhi is gratefully acknowledged. Thanks are also due to Thermax Pvt. Ltd., Poona, India for the gift samples of styrene - DVB beads.

REFERENCES


Received February 26, 1988
Accepted May 9, 1988
Selective Separation of Uranium(VI) on a Chelating Styrene-DVB Based Resin Containing Quinaldinic Acid Amide Group

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Received 21 January 1988; revised and accepted 11 May 1988

A new chelating styrene-DVB based resin containing quinaldinic acid amide functional group has been synthesised and characterised. The sorption patterns of Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Bi(III), Fe(III), Ti(IV) and U(VI) have been studied as a function of pH. The resin sorbs U(VI) over a wide range of pH (1.0 to 4.0) with a maximum sorption of 0.32 mmol/g at pH 3.5 to 4.0. Zn(II), Cd(II), Cu(II), Ni(II), Pb(II), Fe(III) and Ti(IV) are also sorbed to different extents by the resin while Na(I), K(I), Be(II), Ca(II), Mg(II) and Bi(III) are not sorbed. Conditions for separation of U(VI) from these metal ions have been identified. The eluting agent used for U(VI) is 3 M HNO₃, and the recovery recorded is about 99.9%.

Very few chelating ion exchangers⁴ ⁵ ⁶ have been used for the separation and preconcentration of U(VI), among which N-phenyl and N-methyl substituted hydroxamic acid resins⁷ are worth special mention. The aim of the present investigation was to develop a chelating ion-exchanger for the selective and rapid separation of the trace amounts of U(VI) from other metal ions. In this work a new styrene-DVB (8%) based chelating resin containing quinaldinic acid amide as a functional group has been synthesised and used for the preconcentration and separation of U(VI) from various metal ions.

The resin reported in this work has a much higher sorption capacity for uranyl ion compared with those of the other resins developed so far. Exhibits a smooth peak of sorption and does not require any gradient elution.

Materials and Methods

An atomic absorption spectrophotometer (Shimadzu AA-646) and a double beam UV-visible spectrophotometer (Shimadzu Acculab 20) were used for measurement of the concentrations of the metal ions. A digital pH meter (Sambros-233S) was used for adjustment of pH. Infra-red spectrum was recorded in KBr matrix on a Beckmann Acculab-10 IR spectrophotometer. Nitrogen was determined by a standard Micro-Dumas apparatus. A gravity-flow column with an appropriate reservoir was used as holder of the ion exchange resin.

Uranium solution was prepared from uranyl nitrate (E. Merck) and the metal content was determined by the standard method. The stock solutions of various metal ions were prepared from their salts or oxides and estimated following standard methods.

Buffer solutions were prepared by mixing different proportions of standard solutions of sodium chloride and hydrochloric acid (pH 0.5 to 3.5), acetic acid and sodium acetate (pH 3.5 to 5.9) and Na₃HPO₄ and K₂HPO₄ (pH 5.9 to 8.0). During studies on separation from lead, HNO₃ and NaOH were used to control the pH.

Synthesis of the resin

Styrene-DVB polymer beads (80-100 mesh size) containing 8% DVB (Thermax Private Ltd., Poona, India) was nitrated using a mixture of H₂SO₄ and HNO₃. After washing the nitrated product with water, it was reduced to aminopolystyrene by tin (E. Merck) and conc. hydrochloric acid. The 'aminated' product was then condensed with quinaldyl chloride by refluxing the mixture in toluene medium or a waterbath for 24 hr. A schematic diagram of the synthesis of the resin is given below:

Determination of sorption capacity of the resin for U(VI) and other metal ions

The sorption capacity of the resin for different metal ions was determined by batch and column operations. In batch operation, 0.5 g of the air-dried resin was stirred on a magnetic stirrer for 24 hr with an excess of the desired metal ion solution of known strength 0.1 M and volume (10 ml); the
pH was controlled by a suitable buffer. The sorbed metal ions were eluted by using appropriate eluting agents [2N H₂SO₄ for Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Ni(II) and Fe(III)], 4N HCl for Ti(IV), 3N HNO₃ for Be(II), Pb(II), Bi(III) and U(VI)]. The whole process was repeated for different pH values. The eluted metal ions and also the metal ions left in the wash solution were determined following standard methods. The sorption capacity of each of these metal ions against pH has been shown in Fig. 1.

In column operation, a glass column (1 cm i.d., 30 cm length) was packed with ~22 g resin. The resin was initially swollen with 2N HCl and then washed with deionised water. The packed column was washed with appropriate buffer. The flow rate was adjusted at 0.5-1.5 ml/min. Calculated excess amount of the desired metal ion (150 ml, 0.1 M), at desired pH, was passed through the column, washed with appropriate buffer and eluted with suitable eluting agents as stated earlier. The sorption capacity in column operation was slightly lower than the capacity in batch operation. Concentrations of different metal ions left in the washings and after elution from the resin were determined by an appropriate method, e.g., for Ca(II), and Mg(II) by titration with EDTA, for Na(I), K(I), Zn(II), Cd(II), Cu(II), Ni(II), and Fe(III) by atomic absorption flame emission spectrometry and for Be(II), Pb(II), Bi(III) and U(VI) by colorimetry using standard organic reagents. The results of the determination of maximum sorption capacities of uranium VI studied by both batch and column operations are given in Table 1.

Separation and determination of uranium in uraninite ore

A weighed amount of the ore (200-400 mg) was treated first with dil. HNO₃ and then with 5 ml of conc. H₂SO₄ following a standard procedure. Finally, the volume was made up to 250 ml. The solution was adjusted to pH ~ 1.0, and 10 ml EDTA (~1 M) was added. The pH of the solution was raised to ~ 4.0. Excess of EDTA did not affect the sorption capacity of U(VI) around pH ~ 4.0 but suppressed the exchange of other metal ions present in the solution and also prevented precipitation due to hydrolysis. The solution was then percolated through the resin column and uranium was eluted with 3N HNO₃, as described earlier.

Results and Discussion

Characterisation of the resin

The resin being a new one, was characterised by its water regain value, infrared spectrum, its stability towards acids and alkali, elemental analysis and metal exchange capacity.

Where regain value was observed to be 0.37 g/g indicating appreciable sorption capacity of the resin. Infrared spectrum of the resin showed a band at 1500 cm⁻¹ indicating the presence of -CONH - groups. In addition to this sharp band, the IR spectra exhibited medium bands at 1615, 1600, and 1430 cm⁻¹ which are very close to the ring breathing bands of quinoline acid. The resin was found to be stable for at least 7 days in 4 N H₂SO₄, 4 N HNO₃, 4 N HCl, 4 N HClO₄ and 2 N NaOH because no appreciable changes in nitrogen content and sorption capacity were found after treatment with the above mentioned reagents.

The thermogravimetric analysis (TGA) showed that the dried resin started decomposing at 260°C and loss in weight (20.2%) was attributed to the loss of quinaldine acid group.

The resin was also found to be quite stable to radiation. There was no loss of activity on exposure to a 5.12 or 9.36 M rad source for 24-22 hr. However, on exposure to 16.72 M rad source for 144 hr, the activity of the resin was measured by the sorption capacity of U(VI) before and after exposing the resin to radiation.

The nitrogen content of the nitrated polymer was found to be 11.31%. After reduction, the resin contained 11.46% nitrogen. Amino group was estimated by titration in nonaqueous medium which indicated about 68% conversion of nitro-resin to amino-resin. The nitrogen content of the final chelating resin was found to be 9.22%. The conversion of amino group to quinaldine acid amide group was calculated as 85%. Thus the final resin contained about 21.5% of quinaldine acid amide group and this value agrees with the TGA result which is slightly lower as the TGA experiment was carried out in presence of air. The metal exchange capacity of both nitrated and aminated polymer was found to be negligible; hence the free amino and nitro groups present in the final resin are not the active sites of the resin.

Metal absorption capacity and separation

Conditions for separation of U(VI) from the metal ions Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Zn(II), Pb(II), Ni(II), Fe(III), and Ti(IV) were studied.

Among the above metal ions, Ti(IV) and Zn(II) showed different sorption forms in the pH region ~ 2.0-5.0, but at pH ~ 4.0 they were not sorbed by the resin and instead U(VI) was sorbed by the resin in the pH region ~ 1.0 to 4.0. So, for the separation of U(VI) from these metal
ions the mixture was maintained at pH~ 1.0, the resin column was washed with the same buffer and the mixture was passed through the column when only U(VI) was sorbed by the resin.

Separation of Zn(II), Cd(II) and Ni(II) from U(VI) was also achieved between pH 3.5 and 4.0. But, as the resin sorbs Zn(II), Cd(II) and Ni(II) in small amounts, EDTA was used to suppress the chelation of these metal ions. At pH ~ 1.0 sorption capacity of U(VI) is small. Hence, when uranium(VI) was present in small amounts and other metals in larger amounts the first method was followed but when U(VI) was present in larger amount and the others in smaller quantities, separation was performed following the latter method at pH 3.5 to 4.0.

Copper(II) was sorbed in the pH range 1.0-4.0. So, before separation, it was marked by EDTA (10 ml 1.0 M solution). NaI, KI, Be(II), Ca(II) and Mg(II) were not sorbed by the resin. But Bi(III) was hydrolysed above pH ~ 1.0. Hence, thiourea was added to keep Bi(III) in solution, the mixture was maintained at pH ~ 3.5 and was percolated through the column and eluted as before Fe(III) and Th(IV) are also hydrolysed above pH ~ 2.0 and pH ~ 2.5 respectively hence the pH mentioned they are sorbed by the resin to some extent. So EDTA and F- were used as masking agents for Fe(III) and Th(IV) respectively. When separation of U(VI) and Th(IV) was studied, polythene containers were used.

Pb II showed absorption peaks similar to that of UVI. Hence, EDTA was used as masking agent during the separation of U VI from Pb II. Alternatively, both of these ions could be sorbed on the resin and Pb II eluted first with EDTA though this process was more time consuming.

In each case, amount of uranium VI taken was 0.23 mg. Each separation was carried out three times; in the first instance the amount of foreign ion taken was close to that of U VI, followed by experiments with larger amounts. In each case the recovery of uranium was over 99%.

When uranium present in uraninite ore was separated and determined using this resin, uranium found was 0.15% against the reported value of 0.16%.

A few other separations, e.g., Fe(III) from Cu(II), Zn(II) or Cd(II), can also be effected using this resin. However, these separations are not reported as they are of limited practical utility due to low sorption capacities of the metal ions.

Acknowledgement
The authors are indebted to the UGC, New Delhi, for the financial support and to Thermax Private Ltd., Poona, India for the gift sample of styrene-DVB polymer beads.

Table 1 - Sorption Capacity of Uranium(VI) on Quinidanic Acid Amide Resin

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount of resin (g)</th>
<th>Capacity (mmol g⁻¹)</th>
<th>pH</th>
<th>Amount of resin (g)</th>
<th>Capacity (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.59385</td>
<td>0.05</td>
<td>2.0</td>
<td>0.6139</td>
<td>0.08</td>
</tr>
<tr>
<td>2.5</td>
<td>0.6522</td>
<td>0.22</td>
<td>3.0</td>
<td>0.6552</td>
<td>0.22</td>
</tr>
<tr>
<td>3.5</td>
<td>0.6518</td>
<td>0.22</td>
<td>3.7</td>
<td>0.5622</td>
<td>0.22</td>
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<tr>
<td>4.0</td>
<td>0.5222</td>
<td>0.22</td>
<td></td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>

*U(VI) taken = 10 ml of 0.1 M solution; U(VI) taken = 15 ml of 0.1 M solution.

Table 2 - Separation of Uranium(VI) from Diverse Ions

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount (mg)</th>
<th>U(VI) recovered (mg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI</td>
<td>0.50</td>
<td>0.23</td>
<td>23</td>
</tr>
<tr>
<td>KI</td>
<td>0.10</td>
<td>0.23</td>
<td>23</td>
</tr>
<tr>
<td>BeII</td>
<td>0.222</td>
<td>0.229</td>
<td>99.8</td>
</tr>
<tr>
<td>CaII</td>
<td>0.20</td>
<td>0.23</td>
<td>100</td>
</tr>
<tr>
<td>MgII</td>
<td>0.15</td>
<td>0.23</td>
<td>100</td>
</tr>
<tr>
<td>ZnII</td>
<td>0.20</td>
<td>0.228</td>
<td>99.1</td>
</tr>
<tr>
<td>CdII</td>
<td>0.20</td>
<td>0.229</td>
<td>99.8</td>
</tr>
</tbody>
</table>

Table 3 - Separation of Uranium(VI) from Diverse Ions Using Masking Agents

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount (mg)</th>
<th>U(VI) recovered (mg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuII</td>
<td>0.65</td>
<td>0.227</td>
<td>99.3</td>
</tr>
<tr>
<td>PbII</td>
<td>1.30</td>
<td>0.228</td>
<td>98.3</td>
</tr>
</tbody>
</table>

Table 4 - Separation of Uranium(VI) from Diverse Ions Using Masking Agents

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount (mg)</th>
<th>U(VI) recovered (mg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaII</td>
<td>0.20</td>
<td>0.229</td>
<td>99.8</td>
</tr>
</tbody>
</table>

Table 5 - Separation of Uranium(VI) from Diverse Ions Using Masking Agents

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount (mg)</th>
<th>U(VI) recovered (mg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnII</td>
<td>0.20</td>
<td>0.228</td>
<td>99.1</td>
</tr>
<tr>
<td>CdII</td>
<td>0.20</td>
<td>0.229</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Pb(II)  0.60  0.228
      1.20  0.23  0.229  99.7
      1.80  0.23
      1.45  0.227
Bi(III)  2.90  0.229  0.228  99.1
      4.34  0.229
      0.222
Fe(III)  0.444  0.229  0.228  99.1
      0.666  0.229
      0.75  0.229
Ti(IV)  1.50  0.229  0.229  99.7
      2.25  0.228

In presence of (a) EDTA (b) thiourea (c) fluoride

References

Fig. 1—Sorption capacity of the resin for different metal ions as a function of pH [(a) U(VI), (b) Pb(II), (c) Cu(II), (d) Cd(II), (e) Fe(III), (f) Ti(IV), (g) Ni(II) and (h) Zn(II)].