# Silica Gel-Bonded Cationic Polyelectrolyte with Ferron as Counterion. Application to Preconcentration or Elimination of Trace Metals

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An integral N-based cationic polymer, poly[*N*-xylylene *N*,*N*′-dicyclohexylethylenediammonium dibromide], was immobilized through hydrogen bonding on the surface of silica gel. The chelating ligand, 7-iodo-8-hydroxyquinolino 5-sulfonic acid (Ferron), was subsequently attached to the matrix by ion-exchange method; this renders an extremely stable stationary phase, free from leaching complications, under electrostatic (salt) bond interactions. Analytical characteristics of this sorbent were studied. The optimum sorption conditions for $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Fe^{3+}$ under static and dynamic (column) methods were ascertained. The chelator was found to be selective for the retention of $Cu^{2+}$, $Pb^{2+}$, and $Fe^{3+}$ from multi-element mixtures. The relatively fast kinetics of the sorbent with the time required to reach half of the maximum sorption ($t_{1/2}$ value 2 min) and the percentage attainment of equilibrium in 2 min ($P_{2\ \mathrm{min}}$ value > 50%) for most of the heavy metals, excluding $Ni^{2+}$, reveal the suitability of the chelating resin in column operation, especially in single column ion-chromatography. The specific applications of the sorbent in purification of supporting electrolyte/buffers required for voltammetric detection are also explored.

Chelating sorbents obtained via immobilization of complexing agents on solid supports have received much attention in preconcentration and separation of elements.[1)] These materials provide simple and efficient methods of chromatographic analysis and may be combined with a variety of highly sensitive methods of determination. However, the usual complications of leaching of the ligands and/or preswelling of the solid support which effects the locking of chelating anions in the inner core of resin, resulting in high capacity and slow exchange rate, cause problems in column operation with such sorbents.[2)] The use of polymeric supports instead suffers from the drawback of having lower mechanical strength as compared to silica.[3)] But when silica-based polymer bonded phases with attached ion-exchange and complex forming groups are used, the chelators have shown considerable promise as the stationary phase in chromatographic separations, owing to their robust, non-swelling and highly efficient nature. The surface modification of silica gel through chemical reactions has often led to an incomplete immobilization and involves very tedious chemical approaches of silylation, amidization of bound amines, diazotization and ligand coupling in multiple steps.[4,5)]

The separation of transition and heavy metals with high sensitivity has been extensively studied by Dionex method[6)] followed with spectrophotometric detection, since the introduction of ion-chromatography.[7)] However, post-column determinations by suitable colouring reagent (e.g., 4-(2-pyridylazo)resorcinol; PAR) suffers from poor specificity.[8—10)] Therefore, our prime intention is to offer an easier method than chemical immobilization for the modification of chelating functionalities over silica gel matrix to attain the required stability and selectivity. Interest in the present work also lies in the search for a low-capacity resin as packing material in single-column ion chromatography. A low capacity resin, particularly with chelating groups on the outer surface of packing material, is reportedly advantageous in achieving favourable sorption kinetics and avoids the use of a second ion-exchange suppressor column in the conventional ion-chromatography.[2)]

## Experimental

**Reagents.** All reagents were analytical grade or better. Triply distilled deionised water, with conductivity ranging between $0.06\times10^{-6}$ and $0.07\times10^{-6}$ s cm$^{-1}$ at 25 °C, was used for the preparation of analyte metal ions by the sequential dilution method.

The preparation of polymer matrix, Poly[*N*-xylylene-*N*,*N*′-dicyclohexylethylenediamine dibromide] (abbreviated hereafter as $C_2EXBr_2$), is reported elsewhere.[11)]

Silica gel (Merck TLC grade, ca. 20—60 mesh) was activated with concentrated HCl and $HNO_3$; residual acids were subsequently washed off with water. The gel was dried at ca. 120 °C for a day and then stored in a desiccator after cooling, prior to use.

**Immobilization on Silica Gel.** The compound, Poly[*N*-xylylene-*N*,*N*′-dicyclohexylethylenediammonium diiodohydroxyquinoline sulfonate] (abbreviated hereafter as $C_2EX(IHQS)_2$, Fig. 1), could not be isolated in solid form. The green-colored solution of $C_2EX(IHQS)_2$ turned yellowish-brown upon heating, indicating thermal instability. Moreover, the addition of water into the DMF solution of $C_2EX(IHQS)_2$ caused salting out of the white original polymer leaving 7-iodo-8-hydroxyquinoline-5-sulfonate (Ferron) anions ($IHQS^-$) in the solution phase. Therefore, as an alternative approach to obtain stable silica-$C_2EX(IHQS)_2$ adsorbate, the polymer matrix was first immobilized over silica gel and the corresponding counterions were exchanged later with IHQS anions. This procedure is analogous to those of Weetall et al.[12—14)] and Hill[15)] where some modifications of the procedure for ligand coupling are deliberately made by anionic exchange method. For this, silica gel was concentrated with a solution of $C_2EXBr_2$ polymer matrix (0.1061 g/30 ml DMF) and then treated with a DMF solution (0.1770 g/10 ml) of sodium salt of 7-iodo-8-hydroxyquinoline-5-sulfonic acid. An instant green colouration over the surface of silica gel indicated the ion replacement of $Br^-$ anions by $IHQS^-$ anions. The product was dried enough to get rid off the solvent and finally washed with DMF–$H_2O$ mixture to remove $Br^-$ ions or the residual reagents.

The loading of chelating ligand onto the matrix depends on the absolute amount of polyelectrolyte bound to the silica gel surface as well as on the chemical and physical states of the polyelectrolytic resin. The extent of $IHQS^-$ loading over the chelating resin–silica gel was calculated as 16.1 $\mu mol\,g^{-1}$ of silica gel after the estimation of unreacted IHQS ligand in the filtrate by the colourimetric method of Iron(III)–Ferron complexation. A 100% loading of $IHQS^-$ anion on the polymer matrix was also verified separately by stripping off the materials from the surface of immobilized silica gel by acid digestion, which did not respond to any halogen test.

The sorption of $C_2EX(IHQS)_2$ on silica gel was measured under static conditions by varying the concentrations of chelating polymer in the range 0.16—$2.7\times10^{-4}$ M (1 M=1 $mol\,dm^{-3}$) and shaking for 12 h (without evaporating DMF). The chelating polymer left in the solution was measured by $Fe^{3+}$–Ferron complexation spectrophotometrically to obtain the corresponding adsorption isotherm.

**Experimental Techniques.** The static method was employed to determine the optimum pH, equilibration time and leaching effect; the dynamic method revealed other sorption conditions such as flow rate, breakthrough volume, pH and desorption condition through column. In the batch method, the extent of sorption of metal ion was monitored by differential pulse anodic stripping voltammetry (DPASV) with comparisons of metal ion numbers before and after the sorption. However in the column procedure, 50 ml volume of the test solution was loaded at an appropriate pH and flow rate with the help of peristaltic pump. Sorbed metal ion was stripped off in the column by 0.1 M HCl solution after 15 min equilibration time, this was followed with water washings, to allow DPASV measurements.

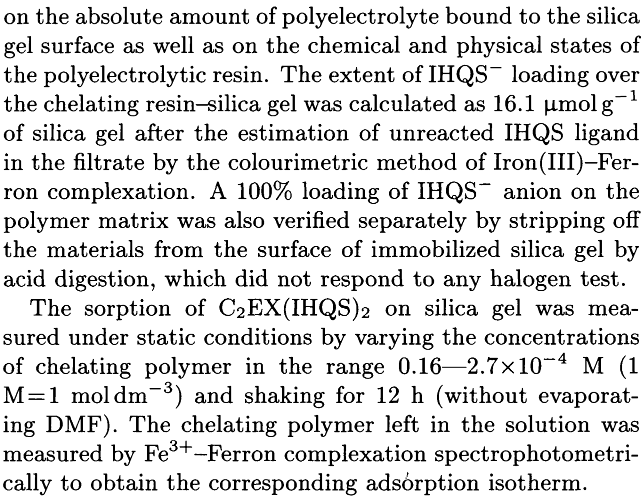

Fig. 1. Structure of chelating polymer, Poly[*N*-xylylene-*N*,*N*′-dicyclohexylethylenediammonium di-iodohydroxyquinoline sulfonate].

A PAR model 264A voltammetry analyzer was employed in all determinations of metal ions at ca. 25 °C in the conventional manner of the standard addition method. The buffers used were: 0.2 M ammonium citrate (pH 3.0) for $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, and $Pb^{2+}$; 0.01 M sodium tartrate (pH 11.0) for $Fe^{3+}$; and 0.1 M KCl for $Co^{2+}$ and $Ni^{2+}$. The purification of these buffers was made in a separate column of silica bound $C_2EX(IHQS)_2$ resin; the related discussion follows in this article.

**Optimum pH.** The percentage sorption of metal ions as a function of pH was determined by equilibrating 0.1 g immobilized silica gel with a fixed amount (1.6 µg/25 ml water) of target metal ion for 2 h in static conditions at different pH values ranging from 2.0 to 7.0.

**Sorption Kinetics.** The samples (0.16 µmol/25 ml) of $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Fe^{3+}$ were mechanically shaken at room temperature (ca. 25 °C) with 0.1 g immobilized silica gel for 5, 10, 20, 30, and 60 min at their optimum pH values. The amount of sorbed metal ion was evaluated by monitoring the amount of metal ion left in the filtrate after sorption. Equilibrium capacities were expressed as µmol/g of the sorbent. The exchange rate of resin, i.e., the time needed to reach the half of the maximal sorption of a metal ($t_{1/2}$) and the measurement of capacity for metal sorption after a period of 2 min, i.e., the percentage attainment of equilibrium in 2 min (the $P_{2\ \mathrm{min}}$) by immobilized silica gel (60 mesh, large surface area) could be taken as a practical measure of exchange rate for satisfactory column operation.[2)] The time condition of 2 min for the measurement is not arbitrary, since $t_{1/2}$ greater than 2 min may cause poor efficiency, tailing and difficult elution from column.

**Column Operations.** A glass column (13 cm long and 1.4 cm in diameter) fitted with a G-1 sintered coarse glass frit as a bottom support was loosely packed (1 cm height) in the usual manner with 1.5 g chelating sorbent (60—20 mesh). The effect of different flow rates (1.5—5.0 $ml\,min^{-1}$) on sorption, breakthrough volume and pH-dependence of selective chelation were studied. To determine the maximal sorption capacity of the sorbent bed (1.5 g), the number of moles of metal ions taken was 24.2 µmol (this is equal to the total number of available chelating agents ($IHQS^-$) present in the column bed).

## Results and Discussion

A close comparison amongst infrared spectra (Fig. 5) recorded for $C_2EXBr_2$ (curve 1, KBr pellet) silica–$C_2EXBr_2$ (curve 2, immobilized silica gel-KBr pellet) silica–$C_2EX(IHQS)_2$ (curve 3, immobilized silica gel-KBr pellet) shows that all N–H vibrations in curve 1 (i.e., N–H stretching ca. 3483 $cm^{-1}$ due to the terminal secondary amine group, N–H stretching ca. 3153 cm$^{-1}$, and N–H bending, ca. 1573 cm$^{-1}$, for amine salt) are absent in curves 2 and 3. However, the presence of C–N vibrations at ca. 1385 cm$^{-1}$ (terminal secondary amine group) and C–Br at ca. 667 cm$^{-1}$ (terminal $-CH_2Br$) in curves 2 and 3 supports the immobilization of polymer matrix. In curve 3, a weak O–H bending and C–O stretching at ca. 1350 cm$^{-1}$ due to phenolic -OH, along with the typical ring vibrations at ca. 1600 cm$^{-1}$, indicate the anion exchange with IHQS$^-$ onto the polymer-modified silica gel surface.

The adsorption of polymer onto silica surface is identified from the restricted N–H stretching vibrations due to the hydrogen bonding of the type $>NH\cdots O$[16,17] which gives no reliable peak for $-NH$[5] in the modified sorbent (Fig. 5). The proposed immobilization is initially involved with the proton transfer from silanol group to the medium (DMF) leading to the existence of an "ion-pair" surface adsorbate at the solid/liquid interface through hydrogen bonding.[17] The existence of hydrogen bonding is evident from the fact that $C_2EX(IHQS)_2$ as such could not be obtained in the solid form via the ion-exchange approach, owing to thermal instability; the same was readily obtained, however, over the surface of silica gel solely due to the electron withdrawing effect of the oxygen atom of the silanol group through hydrogen bond. This imparts additional positive charge density to the respective quaternized nitrogens, to withhold bulkier IHQS$^-$ counterions. The silica modified resin produced is found thermally stable up to 300 °C, apparently due to the strong electrostatic interactions. Also, leaching of IHQS$^-$ anion and/or polymer matrix from silica gel surface is totally absent, even in strong acidic medium as high as 0.6 M, in contrast to the earlier work of Lee et al.[18] The structure of immobilized $C_2EX(IHQS)_2$ in Fig. 6 could be thus tentatively suggested, where all the counterions are outwardly exposed for chelation, as is evident from 100% loading of the chelating ligand, and the parent polycations are firmly held on the solid support, without any steric clogging of the matrix, in accordance with Grahame's modification of Stern–Gouy–Chapmans' electrical double layer theory.[19]

**Sorption under Static Conditions.** The immobilized resin is completely free from any leaching of the anion (IHQS$^-$) by common anion (e.g. Cl$^-$, $NO_3^-$, $ClO_4^-$, $SO_4^{2-}$, $HCO_3^-$, $CH_3COO^-$ etc.) exchange upto 0.6 M concentrations. However, leachings in silica–$C_2EX(IHQS)_2$ above 0.6 M concentrations are found in the order: $ClO_4^- > NO_3^- > SO^{2-} > CH_3COO^-$. The adsorption isotherm (Fig. 2), as stated in the experimental section, revealed the extent of loading of the chelating polymer to be 0.38 µmol g$^{-1}$ of the silica gel.

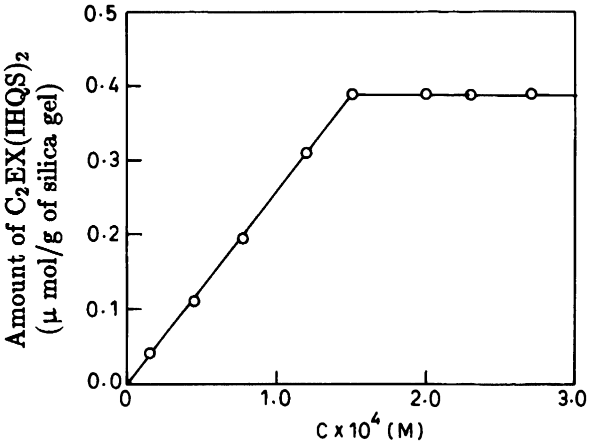

Fig. 2. Adsorption isotherm of 7-iodo-8-hydroxyquinoline-5-sulfonate loaded chelating polymer of varying concentrations ($C$) on the surface of silica gel.

The results for sorption of a group of metals ($Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Fe^{3+}$, $Co^{2+}$, and $Ni^{2+}$) at different pH values (Fig. 3) suggest that the dynamic method is more efficient than the static method. All metal ions except $Ni^{2+}$ are quantitatively sorbed (98—100%) at their optimum pH values in the column between pH 2.0 to 7.0. The relative sorption of metal ions increases till the optimum pH is reached and decreases thereafter. The major loss in observed sorption (Fig. 3) and $K_D$ values (Table 1) may be attributed to the competitive hydroxide formation[3] of respective metal ions beyond pH >5. The ferric ions showed 100% sorption between pH 2.0 to 7.0 due to the higher stability constant of $Fe^{3+}$–IHQS complex.[20] Thus, the present sorbent is very selective for iron(III), irrespective of pH (2—7).

Figure 4 shows that the equilibration time required to attain maximum sorption under static conditions was 10 min for $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$; 20 min for $Cd^{2+}$; and 60 min for $Pb^{2+}$ and $Co^{2+}$. Thus the resin showed fast kinetics for all metal ions studied except $Ni^{2+}$, which required contact time greater than 60 min. The relationship between contact time and equilibrium capacities (Fig. 4) further showed that silica–$C_2EX(IHQS)_2$ has a $t_{1/2}$ value of 2 min and $P_{2\ \mathrm{min}}$ value about 50% for all metal ions studied (except $Ni^{2+}$, $t_{1/2}$=11 min). This indicates that the resin meets the requirements for satisfactory column operations with fast rate of sorption by low-capacity resin, for all metal ions (excluding $Ni^{2+}$) studied (the high-capacity resins take a longer time to

Table 1. Distribution Coefficient ($K_D$) of Metal Ions as a Function of pH[a]

| pH | $K_D^*$ Distribution coefficient of metal ions | | | | | |
|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Pb^{2+}$ | $Fe^{3+}$ | $Co^{2+}$ |
| 2.0 | 213 | 343 | 71 | 156 | V. H. | 0 |
| 3.0 | 260 | 879 | 797 | 789 | V. H. | 0 |
| 4.0 | 346 | 31000 | 1813 | 612 | 2250 | 161 |
| 5.0 | 89034 | 970 | V. H. | 404 | 1406 | 1020 |
| 7.0 | 1535 | 791 | 2 | 410 | 1213 | 274 |

a) Error=±4%; 1.6 µg of metal ion in 25 ml volume; 25 °C; 1 h (equilibrium state); V. H.=very high.

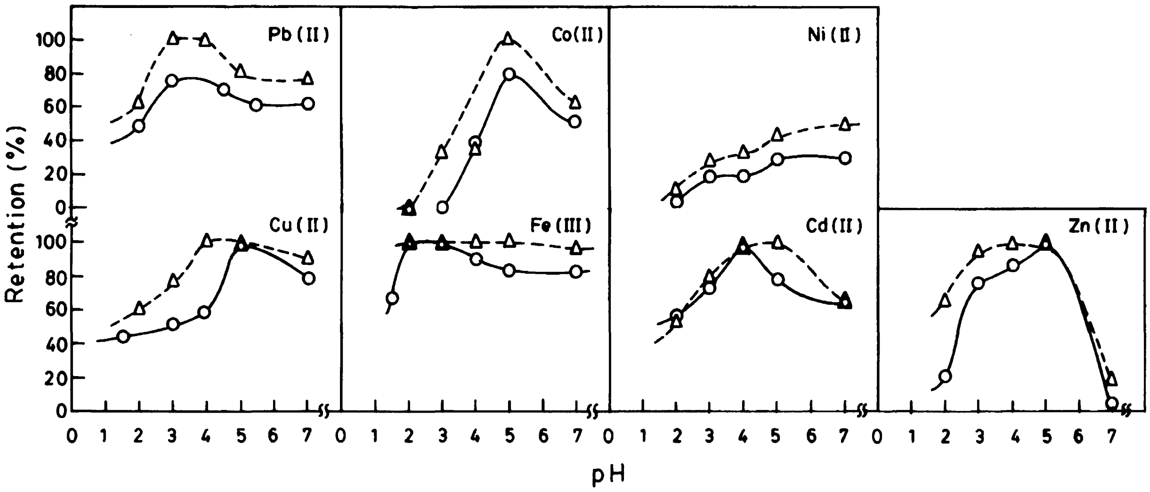

Fig. 3. Retention of metal ions on silica gel immobilized chelating sorbent as a function of solution pH (○ Batch and △ dynamic method). [Metal ion concentration=1.6 μg/25 ml water; Amount of modified sorbent=0.1 g].

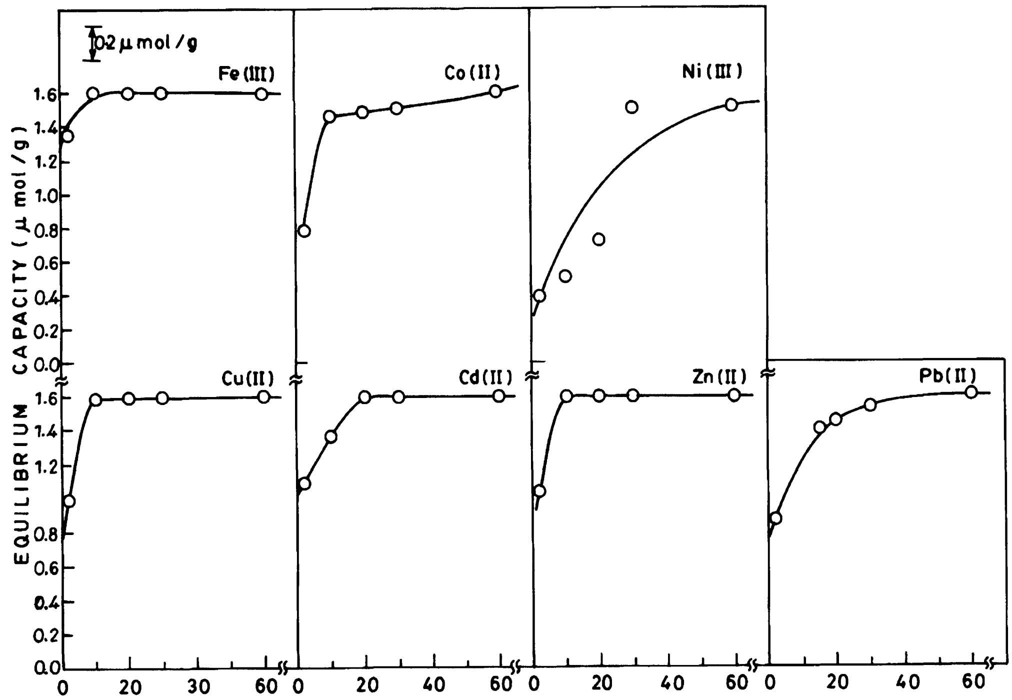

Fig. 4. Relationship between equilibrium capacity of silica gel immobilized chelating sorbent and contact time. Metal ion concentration=0.16 μmol/25 ml; Amount of modified sorbent=0.1 g; Optimum pH 5 for all metals except $Pb^{2+}$ (pH 4.0) and $Fe^{3+}$ (pH 2—7).

reach equilibrium).

**Sorption under Dynamic Conditions.** The maximum sorption capacity of chelating resin was found to be 16.1 $\mu mol\,g^{-1}$ (100% metal sorption) for all metal ions studied at their respective pH values. This is equivalent to the total number of ($IHQS^-$) of polymer matrix coated over silica gel surface, contrary to the earlier observations[18] where all loaded $IHQS^-$ anions were not fully available for chelation. It may be pointed out here that similar modified silica gel stationary supports, where the ligand 8-hydroxyquinoline was directly immobilized onto silica gel, could not avoid the severe hydrolysis at high pH and cleavage of the bonded phase during the prolonged column operation.[20—22] However, silica gel in the present work appears as a preferred support material for polymer coating, which renders favorable metal sorption kinetics without any leaching or decomposition complications even at extreme pH values.

As is evident from the breakthrough volume results (Table 2), $Cu^{2+}$ and $Cd^{2+}$ were desorbed at 2000 ml sample volume while $Zn^{2+}$, $Pb^{2+}$, and $Co^{2+}$ had breakthrough at 1000 ml. Interestingly, $Fe^{3+}$ had shown no effect of physical desorption for excessive sample volume (>2000 ml).

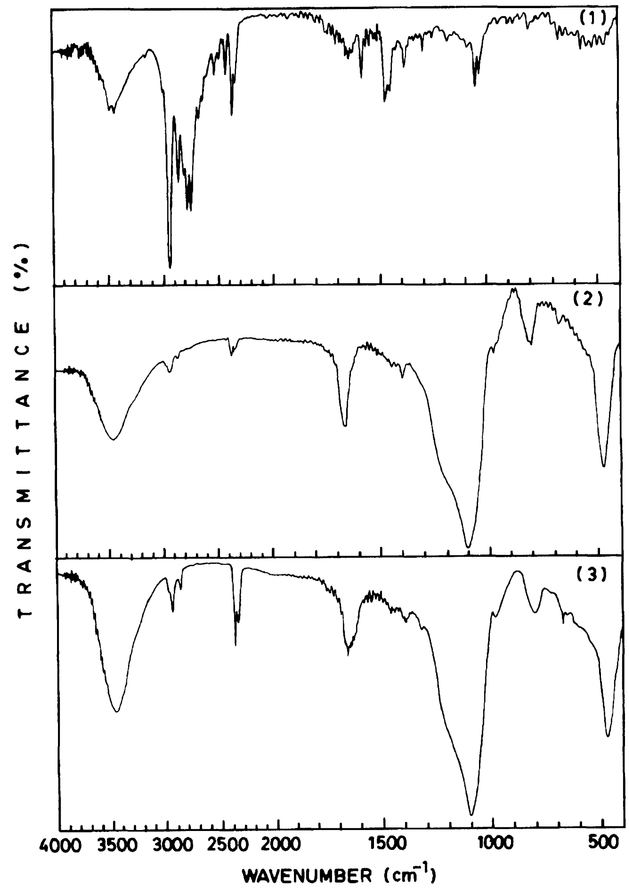

Fig. 5. Infrared (KBr pellet) spectra: 1. Polymer matrix $C_2EXBr_2$; 2. Silica–$C_2EXBr_2$; 3. Silica–$C_2EX(IHQS)_2$.

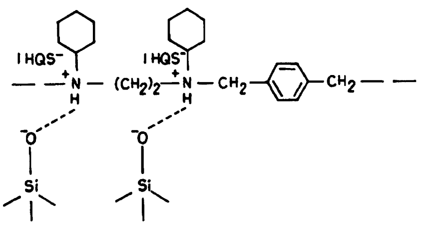

Fig. 6. Structure of silica–$C_2EX(IHQS)_2$ sorbent.

Table 2. The Influence of Sample Volume on Degree of Sorption

| Sample volume ml | Sorption^a)/% | | | | | |
|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Pb^{2+}$ | $Fe^{3+}$ | $Co^{2+}$ |
| 50 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 100 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 200 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 500 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1000 | 100.0 | 100.0 | 89.9 | 53.36 | 100.0 | 85.6 |
| 2000 | 52.7 | 63.4 | 81.1 | 45.4 | 100.0 | 58.9 |

a) Optimum pH≈5.0 ($Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Co^{2+}$); <7.0 ($Fe^{3+}$); 4.0 ($Pb^{2+}$) Sorbent bed 1.5 g ($C_2EX(IHQS)_2$–silica); Flow rate 5 ml min$^{-1}$; 24.2 µmol of metal ions.

Table 3. The Influence of Flow Rate on Degree of Sorption of Metal Ions (100 µg/50 ml) as a Function of pH

| pH | Flow rate ml min$^{-1}$ | Sorption^a)/% | | | | | |
|---|---|---|---|---|---|---|---|
| | | $Cu^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Pb^{2+}$ | $Fe^{3+}$ | $Co^{2+}$ |
| 2.0 | 1.5 | 60.0 | 54.4 | 67.9 | 62.0 | 100.0 | 0 |
| | 3.0 | 35.2 | 11.5 | 35.8 | 24.1 | 100.0 | 0 |
| | 5.0 | 21.3 | 7.0 | 27.5 | 11.2 | 100.0 | 0 |
| 3.0 | 1.5 | 76.8 | 79.5 | 95.2 | 100.0 | 100.0 | 32.9 |
| | 3.0 | 35.2 | 38.9 | 55.0 | 100.0 | 100.0 | 20.1 |
| | 5.0 | 21.7 | 17.6 | 21.8 | 30.2 | 100.0 | 9.3 |
| 4.0 | 1.5 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 33.6 |
| | 3.0 | 51.9 | 67.2 | 91.6 | 100.0 | 100.0 | 20.2 |
| | 5.0 | 40.2 | 23.3 | 35.8 | 100.0 | 100.0 | 7.2 |
| 5.0 | 1.5 | 100.0 | 100.0 | 100.0 | 80.8 | 100.0 | 100.0 |
| | 3.0 | 100.0 | 51.1 | 91.6 | 21.0 | 100.0 | 76.4 |
| | 5.0 | 100.0 | 14.1 | 39.7 | 7.9 | 100.0 | 32.5 |
| 7.0 | 1.5 | 90.0 | 67.5 | 19.8 | 76.9 | 100.0 | 61.5 |
| | 3.0 | 79.3 | 19.1 | 15.2 | 24.1 | 100.0 | 25.1 |
| | 5.0 | 42.8 | 2.7 | 6.8 | 12.6 | 100.0 | 10.7 |

Table 4. The Influence of Acid Concentration on Percentage Recovery of Metal Ions

| Eluent | Recovery^a)/% | |
|---|---|---|
| | $Cu^{2+}$ | $Fe^{3+}$ |
| 0.1 M HCl | 100.0 | 100.0 |
| 0.05 M HCl | 73.7 | 50.0 |
| 0.1 M $HNO_3$ | 81.9 | 56.22 |
| 0.05 M $HNO_3$ | 63.0 | 48.1 |

a) Error±5%, 100 µg of metal ion in 50 ml volume; 25 °C. Equilibration time 15 min; eluent volume 10 ml.

The correlation of results of percentage sorption at varying pH values and flow rates (Table 3) formulates a strategy for the selective sorption and separation of target metal ions from the host of other metal ions. The $Fe^{3+}$-chelation is independent of pH and flow rate studied indicating its stability is higher than that of other metal ions.[23)] Table 3 further suggests that $Fe^{3+}$ is an interfering ion for other heavy metals, irrespective of pH value. This necessiates the isolation of iron prior to the speciation of other metal ions. The pH values for the selective separation of $Pb^{2+}$ and $Cu^{2+}$ from the mixture of other metals are 4.0 and 5.0, respectively. However, the flow rate of 5 ml min$^{-1}$ is preferred in all separations, as the sorptions of all metal ions other than analyte ion are found drastically diminished at this particular flow rate (Table 3). The sorbent, however, could not be used for the selective separations of $Cd^{2+}$, $Zn^{2+}$, and $Co^{2+}$ ions from the multi-element samples due to the unfavorable conditions of operational pH and flow rate. The other limitation particularly is the separation of $Fe^{2+}$ and $Fe^{3+}$ in the present instance, where the polymer matrix instantaneously oxidises $Fe^{2+}$ to $Fe^{3+}$ because of the polycationic chain-bearing amine salt structure.

The relative efficacy of 10 ml aliquot of 0.1 M HCl, 0.05 M HCl, 0.1 M $HNO_3$, and 0.05 M $HNO_3$ in stripping off $Cu^{2+}$ and $Fe^{3+}$ after 15 min equilibration time is compared in Table 4. Here, 0.1 M HCl was found to have a higher efficiency (100% recovery) than 0.1 M $HNO_3$. Furthermore, the recovery efficiency of the most selective metal ions ($Fe^{3+}$ and $Cu^{2+}$) which have higher formation constants than other metals, is studied from their normalized elution curves (Fig. 7) obtained at their respective optimum pH values. Results show that all trace metals having stability constants less than or equal to that of $Fe^{3+}$ could be quantitatively recovered using a maximum 10 ml of 0.1 M HCl as eluent. The initial two milliliters of the effluent apparently represent dead volume of the column, as no metals are detected.

**Analysis of Synthetic Water Samples.** Two synthetic water samples (50 ml) with the composition: $Cu^{2+}$, $Pb^{2+}$, $Fe^{3+}$, $Cd^{2+}$, $Co^{2+}$, and $Zn^{2+}$ (sample 1) and $Cu^{2+}$, $Pb^{2+}$, $Fe^{2+}$, $Cd^{2+}$, $Co^{2+}$, and $Zn^{2+}$ (sample 2) (50 μg each metal) were passed through the column at pH 3.0 and flow rate of 5 ml $min^{-1}$—the most suitable conditions to separate $Fe^{3+}$ (or $Fe^{2+}$) in a multicomponent mixture. The iron-free effluent thus obtained was adjusted to pH 4.0 and subjected to the column for the separation of $Pb^{2+}$ ion. The effluent collected after this separation was readjusted to pH 5.0 for further analysis of $Cu^{2+}$ through column procedure. The accompanying metals were obviously not retained at the optimized conditions of pH and flow rate in these separations. The retained metal ions were finally eluted; the corresponding DPASV results are portrayed in Table 5.

**Purification of Supporting Electrolytes.** A number of heavy metals viz., $Cu^{2+}$; $Cd^{2+}$; $Zn^{2+}$; $Pb^{2+}$ are observed to be quantitatively sorbed at pH 4.0 and $Fe^{3+}$ at pH 2.0—7.0 with a slow flow rate of 1.5 ml $min^{-1}$. Thus the sorbent can find application in the purification of the supporting electrolytes (buffers) used in DPASV experiments. Voltamperograms for 0.2

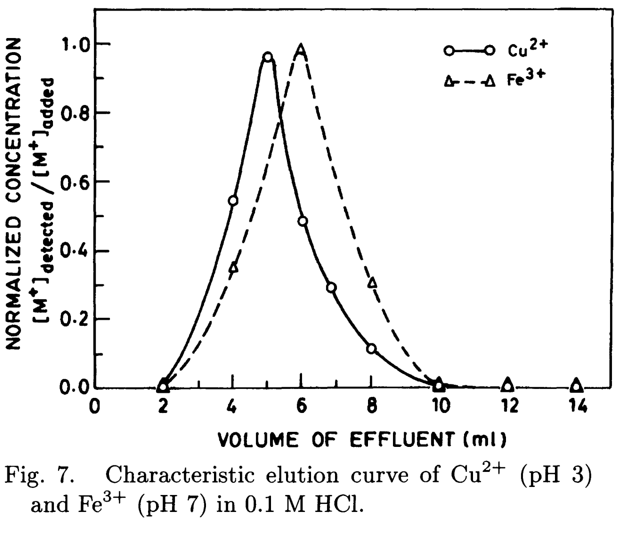

Fig. 7. Characteristic elution curve of $Cu^{2+}$ (pH 3) and $Fe^{3+}$ (pH 7) in 0.1 M HCl.

Table 5. Analysis of Synthetic Water (Sample 50 ml)

| Metal | Optimum pH | Flow rate | Sample 1 | | Sample 2 | |
|---|---|---|---|---|---|---|
| | | | Added | Found[a] | Added | Found[a] |
| | | ml $min^{-1}$ | μg | μg | μg | μg |
| $Fe^{3+}$ | 3.0 | 5.0 | 50.0 | 49.7±0.2 | 50.0 | 49.7±0.2 |
| $Pb^{2+}$ | 4.0 | 5.0 | 50.0 | 49.6±0.4 | 50.0 | 49.6±0.4 |
| $Cu^{2+}$ | 5.0 | 5.0 | 50.0 | 49.8±0.1 | 50.0 | 49.8±0.1 |

a) Standard deviation for 3 determinations.

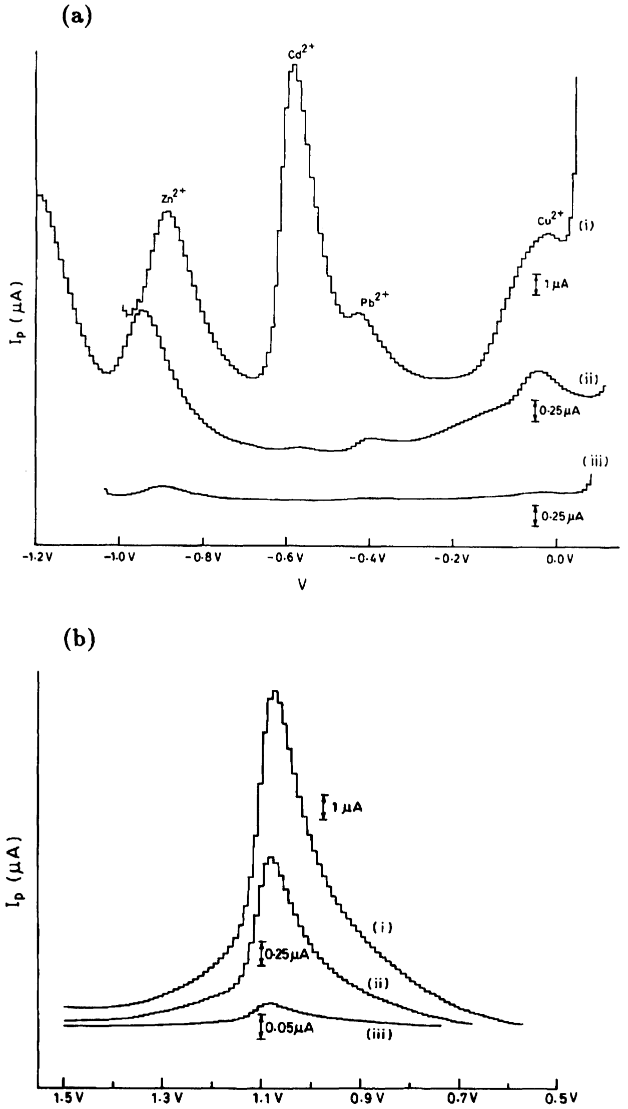

Fig. 8. (a) Voltamperograms for 0.2 M ammonium citrate (pH 3.0; 60 min deposition time; scan rate 10 mV $s^{-1}$; pulse 25 mV): (i) spike to (ii), (ii) 0.2 M ammonium citrate (10 ml), (iii) 0.2 M ammonium citrate after passing through column (10 ml). (b) Voltamperogram of 0.001 M sodium tartrate (pH 11.0; 60 min deposition time; scan rate 10 mV $s^{-1}$; pulse 25 mV): (i) spike to (ii), (ii) 0.001 M sodium tartrate (10 ml), (iii) 0.001 M sodium tartrate after passing through column (10 ml).

M ammonium citrate pH 3.0 (Fig. 8a) show that sufficient number of metal ions ($Zn^{2+}$ 10 ppb, $Cd^{2+}$ 0.1 ppb, $Pb^{2+}$ 2 ppb, $Cu^{2+}$ 10 ppb) were present in the supporting electrolytes. After passing 0.2 M ammonium citrate buffer at pH 4.0 and a flow rate of 1.5 ml $min^{-1}$ through the column, almost all metal contents are removed and whatever traces of $Zn^{2+}$ and $Cu^{2+}$ remained were due only to the contamination introduced through pH-adjustment as required for DPASV monitoring. Similarly, $Fe^{3+}$ contents (29 ppb) in 0.001 M sodium tartrate buffer of pH 11.0 (Fig. 8b) were minimized by passing it through the column, at pH 7.0 with a flow rate of 1.5 ml $min^{-1}$. A repeat of the column operations stated above completely removed all the metal traces from supporting electrolyte prior to the DPASV runs. The small fractions of $Fe^{3+}$ in the test run in this case also are due to the addition of KOH for pH-adjustment for recording DPASV.

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