

**CHROMATOGRAPHIC SEPARATIONS  
OF METAL IONS  
ON STRONG ACID CATION-EXCHANGE RESIN  
LOADED WITH NEUTRAL RED**

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**SUMMARY**

The cation-exchange resin Amberlite IR-120 has been modified by adsorption of neutral red at pH 3.0. Several binary and ternary separations of important metal ions were achieved on the basis of their  $K_d$  values when chromatographed with different mobile phases. To demonstrate its practical utility  $Zn^{2+}$  and  $Zr^{4+}$  were selectively separated from a synthetic mixtures of metal ions on a column of the material.  $Zn^{2+}$  and  $Ca^{2+}$  ions were quantitatively separated and determined in the pharmaceutical preparation Zevit.

**INTRODUCTION**

Much effort is devoted to the removal of heavy metals from industrial effluents and wastewater, mainly because of increasing environmental problems resulting from excessive and indiscriminate industrialization. The potential of chelating ion-exchange resins for separation and preconcentration of metal ions has been firmly established [1–6]. These materials, which bear chelate-forming groups and ion-exchange groups are usually prepared by incorporation of complexing groups on the ion-exchange resin. The selectivity of these modified resins for metal ions depends on the nature of the functional groups of the complexing agents.

Another way of preparing a chelating resin is by chemical reaction. Griesbach and Lieser [7] described the synthesis of fifteen adsorbents. Dowex 1-X8 containing adsorbed sulfonated azo dyes [8] has been found useful for separation of copper and nickel. Azothiopyrine disulfonic acid [9] has been incorporated on to an anion-exchange resin and the product has been used for uptake of mercury, copper, and cadmium from aqueous

solutions; similar use of pyrogallolsulfonic acid [10] enabled the separation and enrichment of  $\text{Mo}^{6+}$ , and  $\text{Fe}^{3+}$ . Incorporation of the thiol [11] functional group resulted in a chelating resin with high selectivity toward heavy metal ions. Nabi et al. synthesized a variety of chelate-forming resins by incorporating complexing agents such as bromophenol blue [12], eriochrome black T [13], Congo red [14], alizarin red [15], crystal violet [16], and toluidine blue [17] and explored their potential for separation of metal ions. In addition to their use for the separation of metal ions, these chelating ion-exchange resins have been applied to the adsorption of bile salts [18] and the decoloration of lactic acid [19].

This work was undertaken to develop a new modified ion-exchange resin using different chelating reagents. The strong acid cation-exchange resin Amberlite IR-120 was modified by adsorption of neutral red, a compound with two aromatic rings, which might bind to the resin matrix (styrene-divinylbenzene), and two nitrogen donor atoms, which might react selectively with metal ions. The analytical applications of the material have been explored.  $\text{Zr}^{4+}$  and  $\text{Zn}^{2+}$  have been selectively separated from a synthetic mixture of other metal ions. Another aim of the work was to establish an effective analytical method for separation and determination of  $\text{Zn}^{2+}$  and  $\text{Ca}^{2+}$  in a commercially available pharmaceutical preparation.

## EXPERIMENTAL

### Reagents

Amberlite IR-120 resin (mesh size 16–45, 8% divinylbenzene by weight) in the protonated form was obtained from BDH (UK). Amberlite IRA-400 (mesh size 20–50, 8% divinylbenzene by weight) in  $\text{Cl}^-$  form was obtained from Loba Chemie. Neutral Red was from E. Merck (Germany) and the disodium salt of EDTA was from S.D. Fine Chemicals (India). Acetic acid, sodium acetate, citric acid, formic acid, and other reagents were AR grade. Zevit in capsule form was used as pharmaceutical preparation and was obtained from SmithKline–Glaxo Pharmaceutical Company (India).

Ethanolic solutions (1%) of 1-[1-hydroxy-2-naphtholazo]-5-nitro-2-naphthol-4-sulphonic acid sodium salt (Eriochrome Black-T) and 1-[2-pyridylazo]-2-naphthol (PAN), and an aqueous solution (1%) of *o*-cresol-sulphonaphthalein-3',3''-bis[methyliminodiacetic acid sodium salt] (xylenol orange) were used as indicators. A 0.01 M solution of the disodium salt of ethylenediaminetetracetic acid (EDTA) was used for titration.

A list of the metal ions investigated is given in Table I.

**Table I**

The cations studied

Cation	Salt used (0.1 M aqueous solution)
Mg <sup>2+</sup>	Magnesium nitrate
Ca <sup>2+</sup>	Calcium nitrate
Ba <sup>2+</sup>	Barium nitrate
Sr <sup>2+</sup>	Strontium nitrate
Hg <sup>2+</sup>	Mercurous nitrate
Pb <sup>2+</sup>	Lead nitrate
Cd <sup>2+</sup>	Cadmium nitrate
Zn <sup>2+</sup>	Zinc nitrate
Mn <sup>2+</sup>	Manganese chloride
Cu <sup>2+</sup>	Copper nitrate
Co <sup>2+</sup>	Cobalt nitrate
Ni <sup>2+</sup>	Nickel nitrate
Fe <sup>3+</sup>	Ferric nitrate
Al <sup>3+</sup>	Aluminium nitrate
Bi <sup>3+</sup>	Bismuth nitrate
La <sup>3+</sup>	Lanthanum nitrate
Zr <sup>4+</sup>	Zirconium oxychloride

**Preparation of modified resin**

Cation and anion-exchange resins (Table II) were each treated separately (1.0 g) with neutral red solution (1000 ppm, 20.00 mL) in 100-mL conical flasks for 4 h. The resins were separated from the solution. The colour of the Amberlite IR-120 resin changes from golden yellow to brick

**Table II**

Types of ion-exchange resin used

Type of Exchanger	Functional group	Trade Name	Ion exchange capacity (meq g <sup>-1</sup> )
Cation, strong acid	Sulfonic acid	Amberlite IR-120	5.35
Anion, strong base	Quaternary ammonium ion	Amberlite IRA-400	3.50

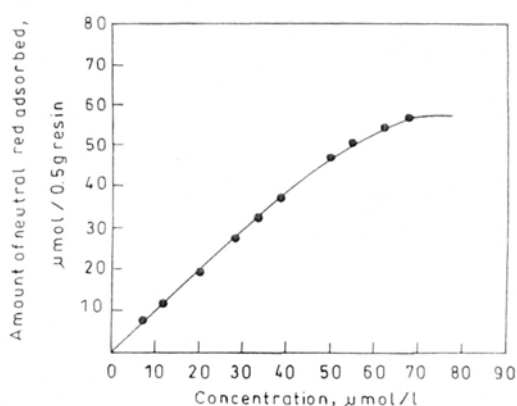
red; that of Amberlite IRA-400 from brown to red. The treated resins were washed several times with demineralized water. It was observed qualitatively during washing that Amberlite IR-120 retained its colour strongly whereas the Amberlite IRA-400 loses colour gradually on washing and was therefore not studied further. For this reason only Amberlite IR-120 resin was chosen for detailed study.

Amberlite IR-120 modified with neutral red was also prepared by treating the resin with a  $68.0\text{-}\mu\text{mol L}^{-1}$  solution of neutral red at pH 3.0 for 24 h. (pH was measured with an Elico India (Delhi, India) LI-10 T digital pH meter.) The resin was washed several times with demineralized water to remove excess reagent. The resin with adsorbed neutral red was finally dried in an oven at  $60^\circ\text{C}$  to remove moisture.

### Study of the Adsorption Isotherm

#### *Effect of Reagent Concentration*

To study the sorption of neutral red under static conditions, resin in the protonated form (0.5 g) was equilibrated with neutral red solutions (50 mL) of different concentration ( $10\text{--}68\ \mu\text{mol L}^{-1}$ ) in a temperature controlled electronic shaker–incubator (MSW-275, Delhi, India, with a stainless body) at constant pH 3.0 for 4 h. The equilibrium concentration of the reagent was then determined spectrometrically at 540 nm by means of a Bausch and Lomb (USA) Spectronic 1001 spectrophotometer. The adsorption isotherm shown in Fig. 1.

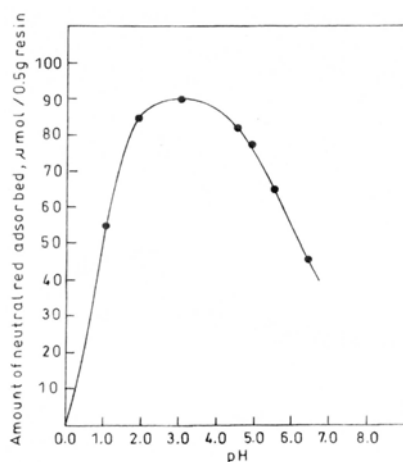


**Fig. 1**

Effect of neutral red concentration on the amount of dye adsorbed by Amberlite IR-120 resin

### *Effect of pH*

To determine the effect of pH on the adsorption of neutral red, 0.5 g resin was shaken continuously with 50 mL  $68 \mu\text{mol L}^{-1}$  neutral red solution of different pH (adjusted by adding appropriate acid, base, or buffer) for 4 h. The equilibrium concentration of the reagent in the supernatant liquid was determined spectrophotometrically at 540 nm (Fig. 2).



**Fig. 2**

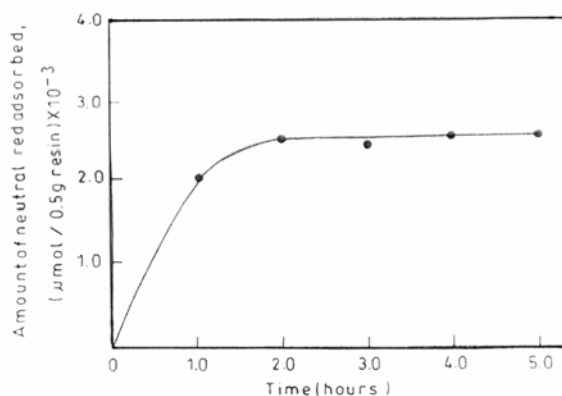
Effect of pH on the amount of neutral red dye adsorbed by Amberlite IR-120 resin

### *Effect of Time*

The equilibration time for adsorption of neutral red by the resin was established by performing a series of adsorption experiments at constant pH 3.0. A constant mass (0.5 g) of Amberlite IR-120 was stirred with an aqueous solution of neutral red (50 mL) for different times. The amount of neutral red taken up by the resin was determined by analyzing the supernatant solution spectrophotometrically at 540 nm. (Fig. 3).

### **Distribution Coefficients ( $K_d$ ) of Metal Ions**

Modified resin beads (0.4 g) were loaded with 1.0 mL of 0.10 M metal ion solution and 39 mL of an appropriate solvent in a 250-mL Erlenmeyer flask. The solvent systems studied for determination of the  $K_d$  values are listed in Table III. The mixture was shaken continuously in a shaker at  $25 \pm 2^\circ\text{C}$  for 4 h. The amount of cation in solution before and



**Fig. 3**

Effect of equilibration time on the amount of neutral red dye adsorbed by Amberlite IR-120 resin

**Table III**

Solvent systems used for determination of distribution coefficients of metal ions

Solvent System	Composition (v/v)	Notation
0.05 M acetic acid	–	S <sub>1</sub>
0.50 M sodium acetate	–	S <sub>2</sub>
0.05 M acetic acid–0.01 M sodium acetate	1:1	S <sub>3</sub>
0.05 M acetic acid–0.05 M sodium acetate	1:1	S <sub>4</sub>
0.05 M acetic acid–0.50 M sodium acetate	1:1	S <sub>5</sub>
0.05 M acetic acid–1.00 M sodium acetate	1:1	S <sub>6</sub>
0.10 M citric acid	–	S <sub>7</sub>
0.10 M formic acid	–	S <sub>8</sub>

after equilibration was determined by EDTA titrations using a standard method and an appropriate metal ion indicator. The  $K_d$  value for each metal ion was then calculated by use of the formula:

$$K_d = \frac{(\text{Amount of metal ion in resin (g)})/(\text{Mass of resin (g)})}{(\text{Amount of metal ion in solution (g)})/(\text{Volume of solution (mL)})} = \frac{(I - F)/0.4 \text{ g}}{F/40 \text{ mL}} = \frac{I - F}{F} \times 100 \text{ mL g}^{-1}$$

where  $I$  (mL) is the volume of EDTA used before treatment with the resin,  $F$  (mL) is the volume of EDTA used after treatment with the resin,  $I - F$  (mL) is the amount of metal ion in the resin phase (mL).  $K_d$  values for the metal ions in the different solvent systems are presented in Table IV.

**Table IV**

Distribution coefficients of metal ions in the different solvent systems

Metal ion	Distribution coefficient (mL g <sup>-1</sup> )							
	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>	S <sub>8</sub>
Mg <sup>2+</sup>	445	95	450	440	95	18	459	990
Ca <sup>2+</sup>	930	158	950	945	158	43	20500	25500
Ba <sup>2+</sup>	3900	400	3900	3900	405	150	15900	19000
Sr <sup>2+</sup>	2350	308	4800	4800	300	75	19500	48000
Hg <sup>2+</sup>	1917	78	1400	1400	75	50	24100	5950
Pb <sup>2+</sup>	1666	77	5200	5200	76	0	21100	6967
Cd <sup>2+</sup>	1237	435	4180	4176	435	7	21300	197
Zn <sup>2+</sup>	5300	23	5300	5300	23	59	21500	5300
Mn <sup>2+</sup>	692	98	690	688	96	48	18900	4650
Bi <sup>2+</sup>	1263	1716	1260	1259	1700	800	21700	21700
Cu <sup>2+</sup>	200	14	400	350	14	4	31000	30000
Al <sup>3+</sup>	4650	0	4650	4650	0	0	18900	18900
Fe <sup>2+</sup>	1163	4950	1112	1011	4950	2370	20100	20100
Co <sup>2+</sup>	102	21	101	100	20	10	47500	19300
Ni <sup>2+</sup>	2475	0	2000	2040	0	0	20500	20500
Zr <sup>4+</sup>	1400	17900	1400	1300	17900	17900	17900	17900
La <sup>3+</sup>	5150	0	5150	5150	0	0	20900	20900

### Quantitative Separations of Metal Ions

Separation of the metal ions was performed by an elution technique. Modified resin (2 g) was packed into a glass column of 0.60 cm i.d., with a glass-wool support at the end, and washed 2–3 times with demineralized water. Binary solutions of the metal ions were prepared by mixing 0.1 M solution of each ion. The binary mixture (2.0 mL) was then poured on to the top of the column and the solution was left to flow slowly (8–10 drops min<sup>-1</sup>) through the column until a small amount remained above the surface of the resin. The column was then rinsed with demineralized water. The effluent collected was recycled through the column to ensure complete

**Table V**

Aqueous solutions used as mobile phases

No.	Name	Formula	Concn (M)	pH
1.	Acetic acid	CH <sub>3</sub> COOH	0.05	–
2.	Citric acid	HOOC(OH)C(CH <sub>2</sub> COOH) <sub>2</sub>	0.10	–
3.	Ethylenediaminetetraacetic acid	(COOH) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N(COOH) <sub>2</sub>	0.01	–
4.	Formic acid	HCOOH	0.10	–
5.	Nitric acid	HNO <sub>3</sub>	1.00	–
6.	Sodium acetate	CH <sub>3</sub> COONa	0.50	–
7.	Neutral red (Stock solution)	–	1000 ppm	–
8.	Acetic acid–sodium acetate buffer	CH <sub>3</sub> COOH–CH <sub>3</sub> COONa	–	3.75
9.	Ammonium hydroxide–ammonium chloride buffer	NH <sub>4</sub> OH–NH <sub>4</sub> Cl	–	10.00
10.	Sodium acetate–hydrochloric acid buffer	CH <sub>3</sub> COONa–HCl	–	1.09–6.40

absorption of metal ions. The metal ions were then eluted with an appropriate mobile phase (Table V) and the effluent was collected in 10-mL fractions. The metal ion content of each 10 mL fraction was determined titrimetrically using disodium salt of EDTA solutions as titrant. The total volume of an eluent used for complete removal of a particular metal ion and the quantities separated are given in Table VI.

#### Selective Separation of Zr<sup>4+</sup> and Zn<sup>2+</sup> From Other Metals in a Synthetic Mixture

For selective separation of Zr<sup>4+</sup> from a mixture of other metal ions a synthetic mixture was prepared by mixing 0.1 M magnesium nitrate, calcium nitrate, strontium nitrate, manganese chloride, cadmium nitrate, and zirconium oxychloride. A known volume of the mixture (1.0, 1.5, or 2.0 mL) was poured on to the column using the same procedure as described for binary separation of metal ions. Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Mn<sup>2+</sup>, and Cd<sup>2+</sup> were eluted together by use of 0.50 M sodium acetate. Zr<sup>4+</sup> was strongly retained by the ion-exchange resin and was eluted with 1.0 M nitric acid solution. The amount of zirconium eluted was then determined by titration using 0.01 M disodium solution of EDTA. A similar procedure was adopted for selective separation of Zn<sup>2+</sup> ion from a synthetic mixture of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, and Zn<sup>2+</sup> (Tables VII and VIII).



**Table VI**

Binary separations of  $Zr^{4+}$  and of  $Zn^{2+}$  from other cations on neutral red modified Amberlite IR-120 cation-exchange resin

Binary mixture	Amount loaded (mg)	Amount found (mg)	Recovery (%)	Volume of eluent (mL)	Eluent used
$Zr^{4+}$	9.21	9.16	99.45	40	1.00 M Nitric acid
$Mg^{2+}$	2.72	2.61	95.95	40	0.50 M Sodium acetate
$Zr^{4+}$	9.21	9.12	99.02	40	1.00 M Nitric acid
$Ca^{2+}$	4.12	4.02	97.57	40	0.50 M Sodium acetate
$Zr^{4+}$	9.21	9.21	100.00	50	1.00 M Nitric acid
$Sr^{2+}$	8.42	8.32	98.81	60	0.50 M Sodium acetate
$Zr^{4+}$	9.21	9.16	99.45	50	1.00 M Nitric acid
$Cd^{2+}$	11.07	11.07	100.00	60	0.50 M Sodium acetate
$Zr^{4+}$	9.21	9.21	100.00	50	1.00 M Nitric acid
$Mn^{2+}$	5.90	5.81	98.47	50	0.50 M Sodium acetate
$Zn^{2+}$	7.05	6.85	97.16	60	1.00 M Nitric acid
$Mg^{2+}$	2.58	2.58	100.00	50	0.50 M Sodium acetate
$Zn^{2+}$	7.05	6.88	97.58	60	1.00 M Nitric acid
$Ca^{2+}$	4.06	4.06	100.00	50	0.50 M Sodium acetate
$Zn^{2+}$	7.05	6.88	97.58	60	1.00 M Nitric acid
$Co^{2+}$	5.98	5.91	98.82	60	0.50 M Sodium acetate
$Zn^{2+}$	7.05	7.05	100.00	60	1.00 M Nitric acid
$Cu^{2+}$	6.11	6.09	99.67	60	0.50 M Sodium acetate
$Zn^{2+}$	7.05	6.92	98.15	60	1.00 M Nitric acid
$Mn^{2+}$	5.60	5.57	99.46	50	0.50 M Sodium acetate

**Table VII**

Selective separation of  $Zr^{4+}$  from a synthetic mixture of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$  on a column of neutral red-loaded Amberlite IR-120 resin

No.	Amount of $Zr^{4+}$ loaded (mg)	Amount of $Zr^{4+}$ found (mg)	Recovery (%)	Eluent used	Volume of eluent (mL)
1.	9.21	9.12	99.02	1.0 M Nitric acid	50
2.	13.8	13.6	98.55	1.0 M Nitric acid	60
3.	18.4	18.4	100.00	1.0 M Nitric acid	80

**Table VIII**

Selective separation of  $Zn^{2+}$  from a synthetic mixture of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$  on a column of neutral red-loaded Amberlite IR-120 resin

No.	Amount of $Zr^{4+}$ loaded (mg)	Amount of $Zr^{4+}$ found (mg)	Recovery (%)	Eluent used	Volume of eluent (mL)
1.	7.05	6.98	99.00	1.0 M Nitric acid	60
2.	10.5	10.5	100.00	1.0 M Nitric acid	70
3.	14.1	13.8	97.87	1.0 M Nitric acid	80

### Separation and determination of $Zn^{2+}$ and $Ca^{2+}$ in pharmaceutical preparation

For separation and determination of  $Zn^{2+}$  and  $Ca^{2+}$  in a pharmaceutical preparation, four commercially available Zevit capsules were treated with a mixture of 12 mL HCl and 4 mL  $HNO_3$ . The mixture was heated until nitric acid fumes disappeared. It was then filtered and the clear solution obtained was diluted to 100 mL with demineralized water. A small portion of the mixture was added to a column packed with 2.0 g modified

**Table IX**

Separation and determination of  $Zn^{2+}$  and  $Ca^{2+}$  present in a pharmaceutical sample (Zevit) on a column of neutral red loaded Amberlite IR-120 resin

No.	Amount loaded (mg)		Amount found (mg)		Recovery (%)		Eluent used	
	$Zn^{2+}$	$Ca^{2+}$	$Zn^{2+}$	$Ca^{2+}$	$Zn^{2+}$	$Ca^{2+}$	$Zn^{2+}$	$Ca^{2+}$
1 <sup>a</sup>	0.240	0.672	0.239	0.670	99.58	99.70	1.00 M Nitric acid	0.05 M Acetic acid
2 <sup>a</sup>	0.240	0.672	0.239	0.670	99.58	99.70	1.00 M Nitric acid	0.05 M Acetic acid
3 <sup>a</sup>	0.240	0.672	0.238	0.671	99.16	99.85	1.00 M Nitric acid	0.05 M Acetic acid
4 <sup>a</sup>	0.240	0.672	0.238	0.671	99.16	99.85	1.00 M Nitric acid	0.05 M Acetic acid
5 <sup>a</sup>	0.240	0.672	0.239	0.670	99.58	99.70	1.00 M Nitric acid	0.05 M Acetic acid
6 <sup>b</sup>	0.300	0.840	0.300	0.839	100.00	99.88	1.00 M Nitric acid	0.05 M Acetic acid
7 <sup>b</sup>	0.300	0.840	0.299	0.839	99.66	99.88	1.00 M Nitric acid	0.05 M Acetic acid
8 <sup>b</sup>	0.300	0.840	0.298	0.838	99.33	99.76	1.00 M Nitric acid	0.05 M Acetic acid
9 <sup>b</sup>	0.300	0.840	0.298	0.839	99.33	99.88	1.00 M Nitric acid	0.05 M Acetic acid
10 <sup>b</sup>	0.300	0.840	0.299	0.838	99.66	99.76	1.00 M Nitric acid	0.05 M Acetic acid

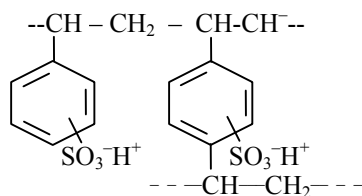
<sup>a</sup>The standard deviation was 0.0005 for both  $Zn^{2+}$  and  $Ca^{2+}$ ; the coefficient of variance was 0.22 for  $Zn^{2+}$  and 0.07 for  $Ca^{2+}$

<sup>b</sup>The standard deviation was 0.0008 for  $Zn^{2+}$  and 0.0005 for  $Ca^{2+}$ ; the coefficient of variance was 0.26 for  $Zn^{2+}$  and 0.06 for  $Ca^{2+}$

resin.  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  ions were eluted with 0.05 M acetic acid and 1.0 M nitric acid, respectively, and determined titrimetrically against a standard solution of the disodium salt of EDTA. The results of these separations are listed in Table IX.

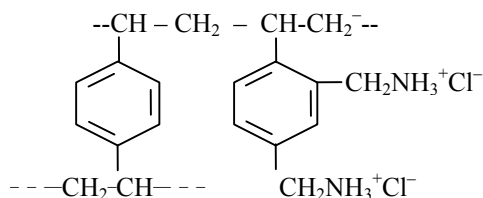
## RESULTS AND DISCUSSION

Both cation (Amberlite IR-120; Fig. 4) and anion-exchange resins (Amberlite IRA-400; Fig. 5) were tested for adsorption of neutral red (Fig. 6) but a positive result was achieved only with the cation-exchange resin



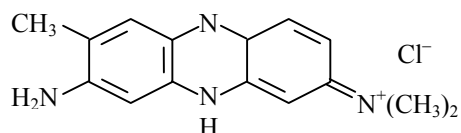
**Fig. 4**

The structure of Amberlite IR-120



**Fig. 5**

The structure of Amberlite IRA-400



**Fig. 6**

The structure of neutral red

Amberlite IR-120 in  $H^+$  form. Equilibrium conditions such as concentration of neutral red, pH, and adsorption time were studied. The adsorption isotherm of neutral red is a straight line and follows Langmuir's adsorption isotherm (Fig. 1). The maximum uptake of neutral red was found to be 57  $\mu\text{mol}/0.5\text{ g resin}$  at pH 3.0 (Fig. 2). The time required to reach equilibrium for adsorption of neutral red by the resin was found to be 4 h. No further adsorption occurs on increasing the time. An equilibration time of 4 h was therefore chosen to ensure complete adsorption throughout these experiments (Fig. 3).

It can be concluded that neutral red, which contains two aromatic rings, was attached to the polystyrene skeleton by physical adsorption;  $\pi$ - $\pi$  dispersion forces arising from the aromatic nature of the resin and neutral red seem to be responsible for this adsorption. The presence of two nitrogen donor atoms of the neutral red facilitates its selective interaction with metal ions.

It is apparent from the distribution coefficients given in Table IV that the neutral red resin has differential selectivity for metal ions, possibly because of the formation of metal complexes with different stability constants. The type of solvent used will also affect the ease of complexation. Studies of the adsorption of different metal ions in diverse solvent systems revealed many interesting features. It was observed (Table IV) that almost all the metal ions except zirconium(IV) had low  $K_d$  values in 0.50 M sodium acetate ( $S_2$ ), possibly because of the greater tendency of zirconium (IV) to complex with neutral red. The exceptionally high  $K_d$  value for zinc (II) in 0.05 M acetic acid ( $S_1$ ) made it possible to separate it from other metal ions. It is interesting to note that  $K_d$  values of the metal ions decrease with increasing sodium acetate content in the mixed sodium acetate-acetic acid system.

It is also interesting to note that  $K_d$  values for most of the metal ions are exceptionally high when citric acid or formic acid are used as solvents. This behaviour of metal ions may again be because of the formation of more stable metal complexes with neutral red. On the basis of the different  $K_d$  values several binary separations of metal ions were achieved on columns packed with this material, by selecting appropriate mobile phases (Table VI). The exceptionally high  $K_d$  value of  $Zr^{4+}$  enables its separation from a mixture of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$ .  $Zr^{4+}$  was strongly held by the resin and eluted with 1.0 M  $HNO_3$  whereas the other metal ions were eluted together with 0.50 M sodium acetate. Similarly,  $Zn^{2+}$  was strongly retained and eluted with  $HNO_3$  whereas other metal ions were eluted with

0.05 M acetic acid. The practical utility of these separations were demonstrated quantitatively by achieving separation of  $Zn^{2+}$  and  $Zr^{4+}$  from other metal ions in synthetic mixtures (Tables VII and VIII).

The further utility of this material was explored by determination of  $Zn^{2+}$  and  $Ca^{2+}$ , after separation, in the pharmaceutical preparation Zevit (Table IX). The validity of the method was checked by performing five replicate analysis. The method seems precise and accurate, as is evident from the standard deviation data. The separation of zirconium can be used for isolation and determination of the metal in its alloys zircon, nohlite, and uranite, and from igneous rocks.

## CONCLUSION

Neutral red loaded IR-120 resin has differential selectivity for metal ions. It can also be used as a packing material in column chromatography and for preconcentration and recovery of metals from industrial effluents and wastewater. This method can also be adopted for the determination of composition of alloys.

## ACKNOWLEDGEMENT

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