CHAPTER 4

ANALYTICAL APPLICATIONS

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4.0 ANALYTICAL APPLICATIONS

Column chromatography is a technique in which resolution of a mixture is achieved by the virtue of difference in migration rates of the components in a packed column[1]. Column separations are achieved through elution, displacement and frontal techniques. In the frontal technique, the weakly bound exchangeable counter ions of the resin will be displaced by the ions of the electrolyte solutions and a sharp boundary line will be formed. On the continuous feeding of the electrolyte solution into the column the different ions from the resin will appear in the effluent in the order of increasing affinity. Where as in the displacement technique, a mixture of different components gets adsorbed on the column forming different bands depending on the distribution coefficients (Kd). On addition of displacing agent into the column the bands move downwards and components are separated. Both frontal and displacement techniques can be carried out easily, but they can not be used either for quantitative analytical or preparative purposes. Where as elution methods make it possible to obtain ions separately in adequate purity for quantitative analytical purposes. For selective elutions, there is no cross contamination at any level during separations.

In the present study separations of metal ions are carried out using mainly selective elution techniques. The details of the column separations are discussed below.

4.1 Column characterisation

The column was prepared from the swollen resin as discussed in section 2.5.1. The specifications of the column are given in Table 4.1. The column utility[2] which is the characteristic value of the column depends on the flow rate, length of the column and metal ion concentration. Column utility can be studied at a known constant flow rate and column length. Isoplanes are plotted, as the ratios of the metal observed in column effluent (C) to the metal added to column (Co) versus volume of effluent at constant flow rate (Fig.4.1 and 4.2).

Column utility which is the ratio of break through capacity (BTC) and total capacity (TC) was calculated from the isoplanes. The observations are recorded in Table-4.1. The results show that the column prepared from the resin has good metal retention capacity and can be used as one of the analytical tools for the study of ion exchange chromatography in analytical procedures.

Separations of various binary and ternary mixtures were carried out and results are given in Tables 4.2 - 4.6 and Figs. 4.3 - 4.21.

4.2 Separation of binary mixtures

4.2.1 Separation of Copper (II) and Nickel (II)

A 30 cm^3 solution of 1:1 mixture of copper and nickel containing 10 mg of each metal ion was passed at pH 5 using 0.2 M acetate buffer through the column at the flow rate of 1 $cm^3\ min^{-1}$. The column was washed with deionised water to remove unexchanged metal ions. However, no metal was observed in the column effluent, indicating complete exchange of metal ions on the resin. Separation of metal ions was achieved with the help of selective elution technique by passing first 60 cm^3 of 0.2 M acetic acid as an eluting reagent for nickel followed by 70 cm^3 of 0.1 M hydrochloric acid for elution of copper. 5 cm^3 fractions of column effluent were collected and were analysed for the metal ion content by EDTA titrations[3]. The

Table 4.1 : Column characterisation

Sr. No.	Metal	Column length cm	Interstitial volume (Vo) cm^3	Break through capacity BTC mM g^{-1}	Total column capacity TC mM g^{-1}	Degree of utilization BTC/TC
1.	Cu(II)	15.0	2.1	0.61	1.16	0.53
2.	Ni(II)	15.0	2.1	0.12	0.89	0.13
3.	Zn(II)	15.0	2.1	0.16	0.91	0.18
4.	Cd(II)	15.0	2.1	0.05	0.19	0.26
5.	Hg(II)	15.0	2.1	0.26	0.75	0.35

Weight of the resin taken for column preparation ~3 g.

Fig. 4·1

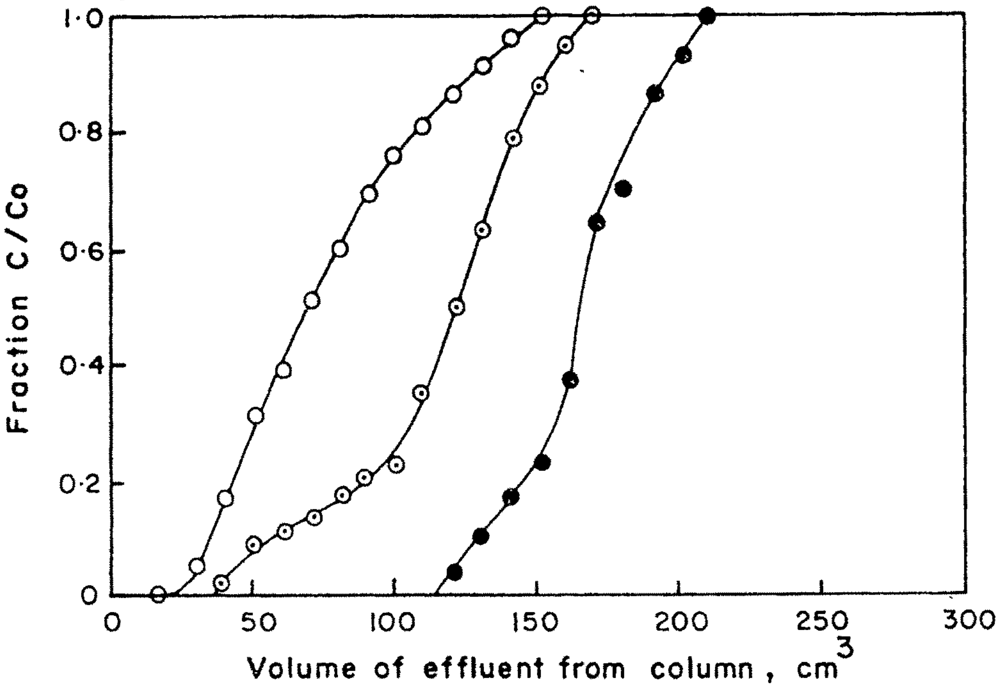
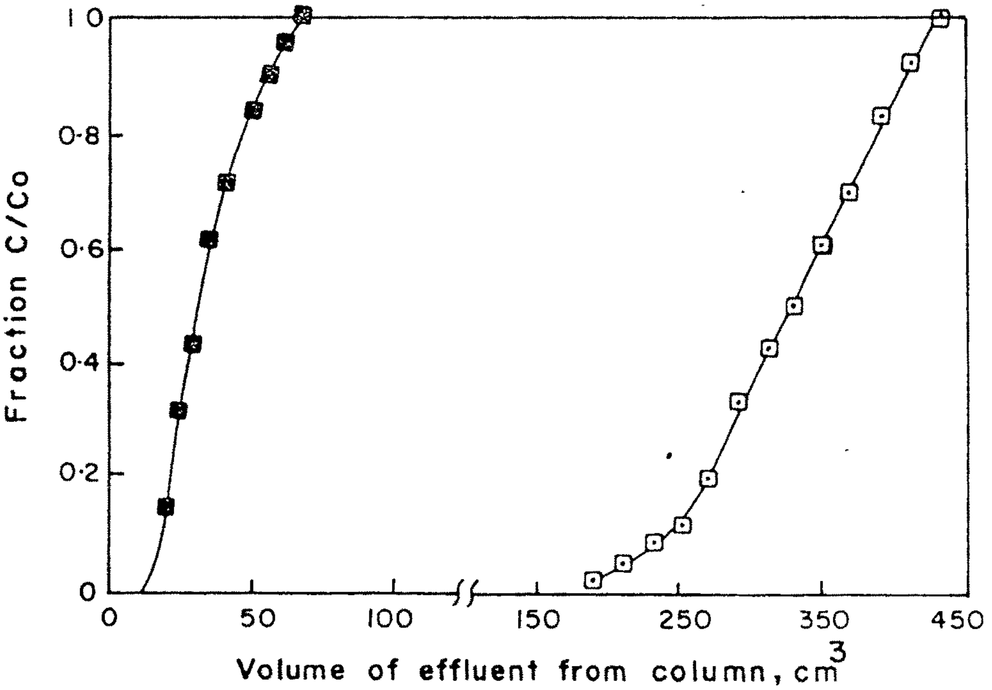


Fig. 4·2



Metal concentration 1 mg cm^{-3}, flow rate 1 cm^3 min^{-1}, bulk of column effluent tested 10 cm^3 for Cu, Ni, Zn and Hg, and 5 cm^3 for Cd.

● Cu, ○ Ni, ⊙ Zn, ■ Cd, ⊡ Hg.

results are given in Fig. 4.3. % Recovery of each of the metal ion is given in Table 4.2. No cross contamination was observed in any of the separations.

4.2.2. Separation of Copper (II) and Zinc (II); and Nickel (II) and Zinc (II)

A 30 cm^3 mixtures of Cu (II) and Zn (II) or Ni (II) and Zn (II) containing 10 mg of each metal ion in 1:1 ratio were passed through the column at a flow rate of 1 cm^3 min^{-1}. The pH of mixtures was maintained at 5 using 0.2 M acetate buffer. At this condition exchange of zinc did not take place and hence a first few fractions of column effluent showed complete leaching of zinc. The column was further washed with deionised water and copper and nickel were eluted as discussed in sec.4.2.1. The presence of metal ion was examined in each fraction through appropriate EDTA titrations[3]. The results for the separation of Cu (II) and Zn (II); and Ni (II) and Zn (II) are shown in Fig.4.4 and 4.5. % Recovery of each metal in both the mixtures is given in Table 4.2.

4.2.3 Separation of Nickel (II) and Palladium (II);and Nickel (II) and Platinum (IV)

In these separations 30 cm^3 solutions containing 1:1 mixtures of Ni (II) and Pd (II) or Ni (II) and Pt (IV) were passed through the column at pH 5 using 0.2 M acetate buffer at a flow rate of 1 cm^3 min^{-1}. The mixtures contained 10 mg of each metal ion. The column was further washed with deionised water. The column effluents showed absence of metal ions indicating complete exchange of metal ions with the resin. Nickel was eluted as discussed earlier (sec.4.2.1). Palladium and platinum were eluted with (i) a mixture of 0.1 M hydrochloric acid and 1.0 % thiourea and (ii) a mixture of 0.1 M hydrochloric acid and 5.0 % thiourea respectively. Palladium and Platinum were estimated complexometrically using EDTA and

Fig. 4·3

Separation of Copper and Nickle

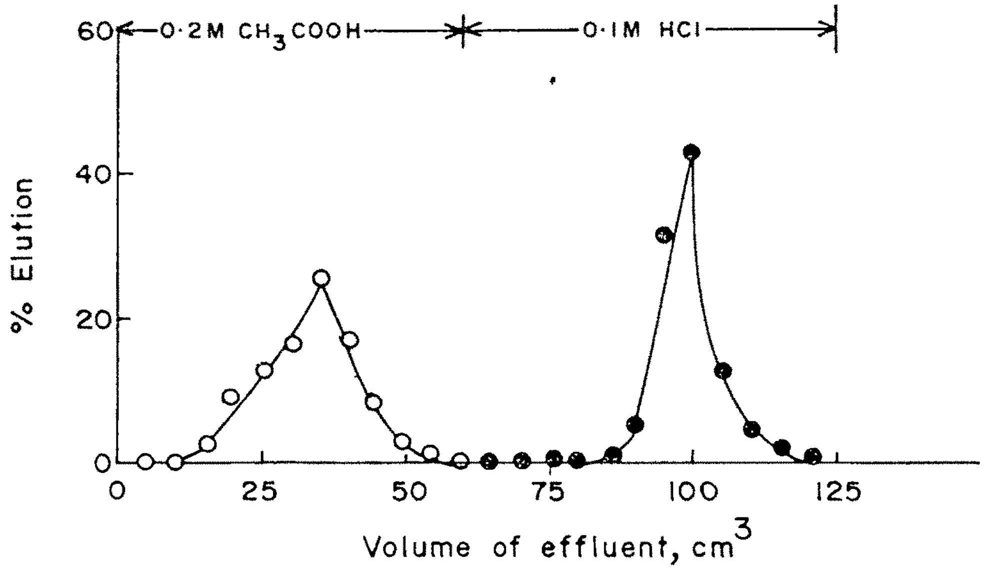
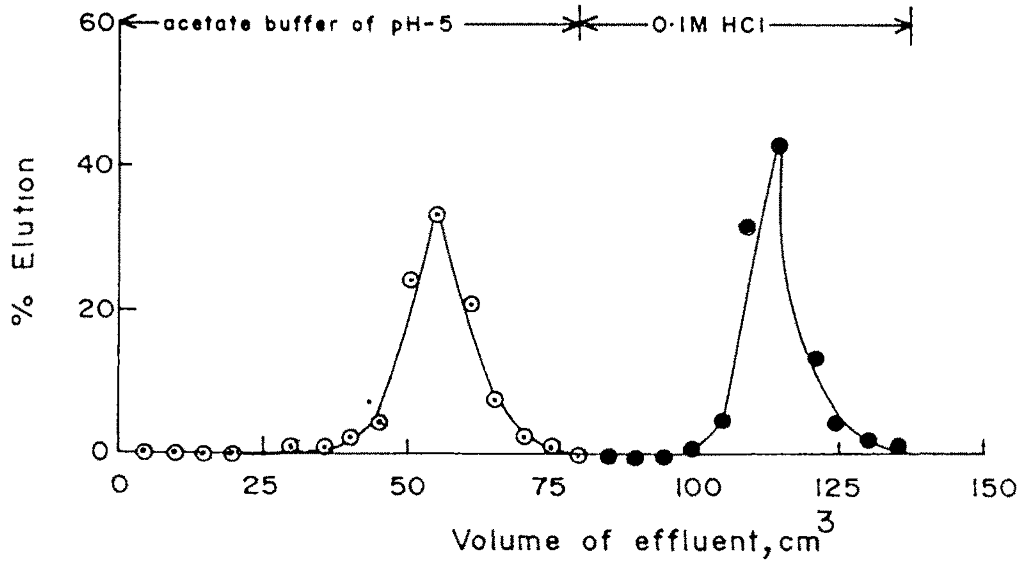


Fig. 4·4

Separation of Copper and Zinc



Metal taken 10mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}

○ Nickle, ● Copper, ⊙ Zinc

iodometrically using $Na_2S_2O_3$ respectively after decomposing thiourea complexes with H_2O_2 in the column effluent. The separation patterns for Ni (II) and Pd (II); and Ni (II) and Pt (IV) are given in Fig.4.6 and 4.7. % Recovery of each metal in both the mixtures is given in Table 4.2. No cross contamination was observed in any of these separations.

4.2.4 Separation of Copper (II) and Gold (III)

A 30 cm^3 mixture of Cu (II) and Au (III) containing 10 mg of each metal ion in 1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Copper was eluted and analysed as discussed in sec.4.2.1. Gold was eluted with a mixture of 0.1 M hydrochloric acid and 1.0 % thiourea. The estimation of gold was done colourimetrically[4] using sodium diethyl dithio carbamate. The results obtained are given in Fig.4.8. The recovery of the metal ions is given in Table 4.2. No cross contamination was observed in this separation.

4.2.5 Separation of Zinc (II) and Cadmium (II)

A 30 cm^3 mixture of Zn (II) and Cd (II) containing 10 mg of each metal in 1:1 ratio was passed through the column at pH 5 using 0.2 M citrate-phosphate buffer at a flow rate of 1 cm^3 min^{-1}. The column was washed with deionised water. No metal was observed in column effluent. Zinc was eluted with 0.2 M HCl followed by the elution of cadmium with 0.5 M CH_3COOH. The estimation of zinc and cadmium was done titrimetrically using EDTA[3]. The results are given in Fig.4.9. %Recovery of metal ions is given in Table 4.3. No cross contamination was observed.

Fig.4·5

Separation of Nickel and Zinc

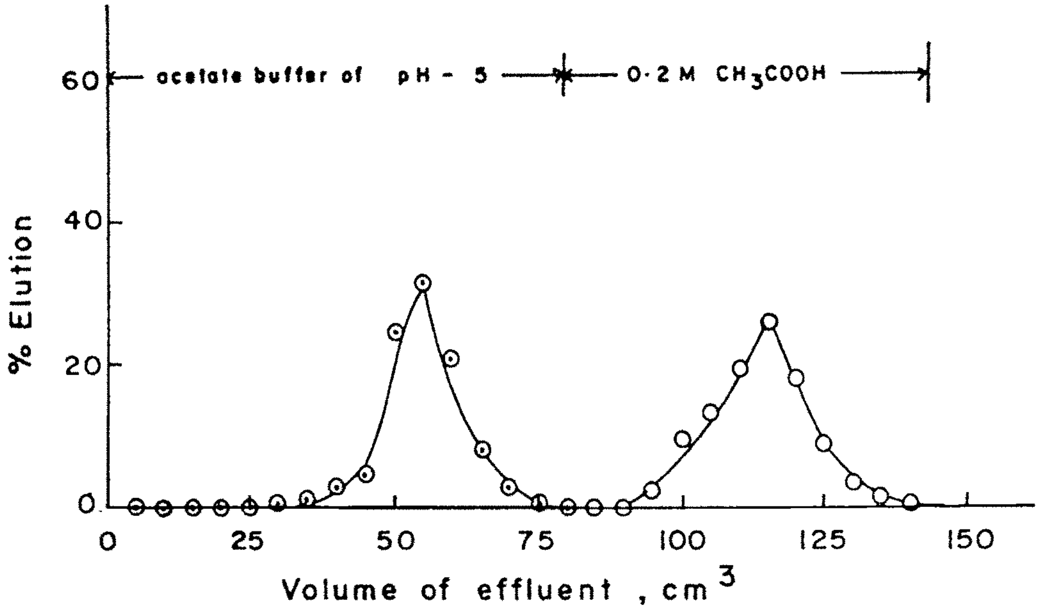
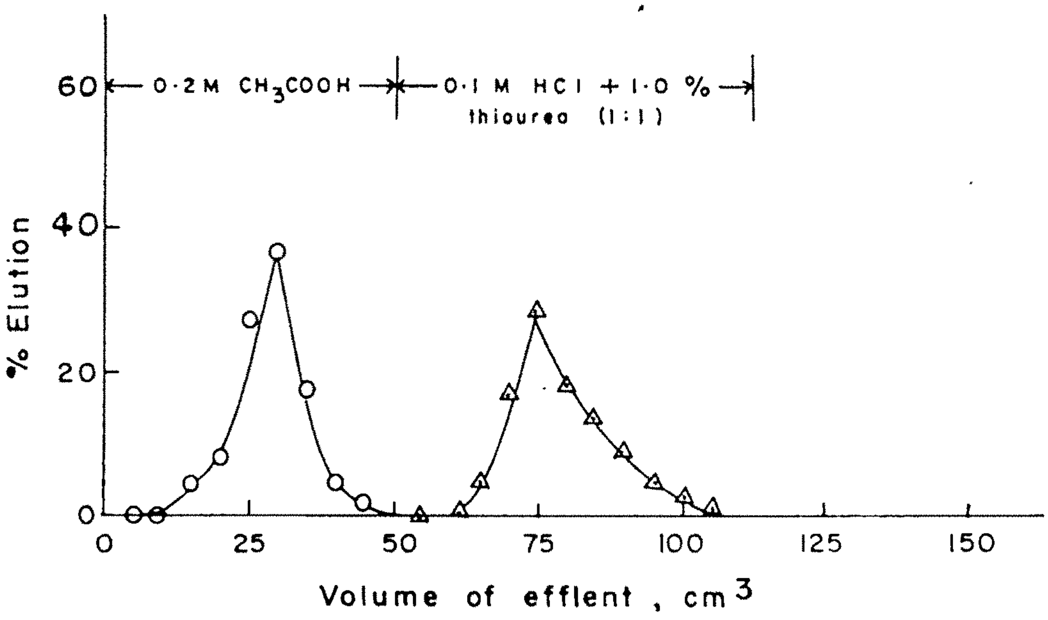


Fig.4·6

Separation of Nickle and Palladium



Metal taken 10 mg each , metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}.

○ Nickel, ⊙ Zinc, △ Palladium

Fig.4·7

Separation of Nickel and Platinum

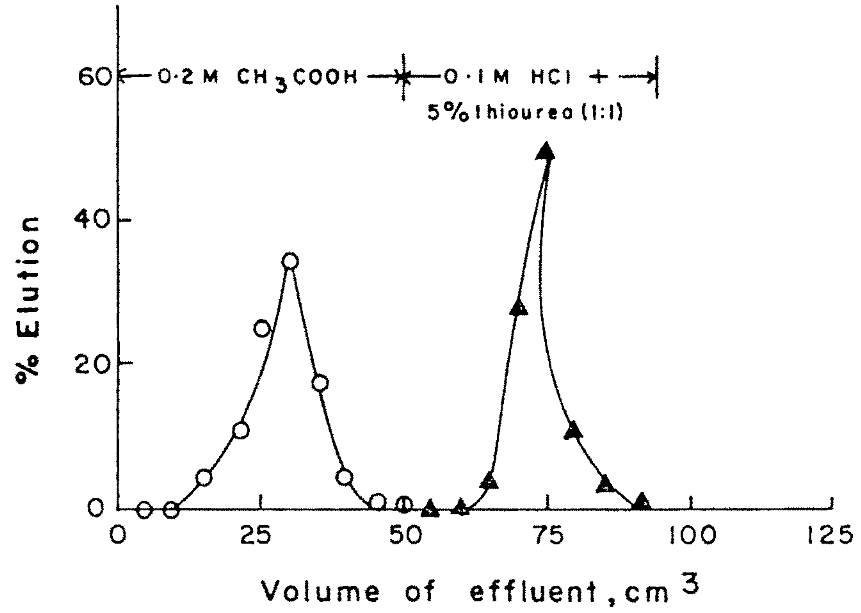
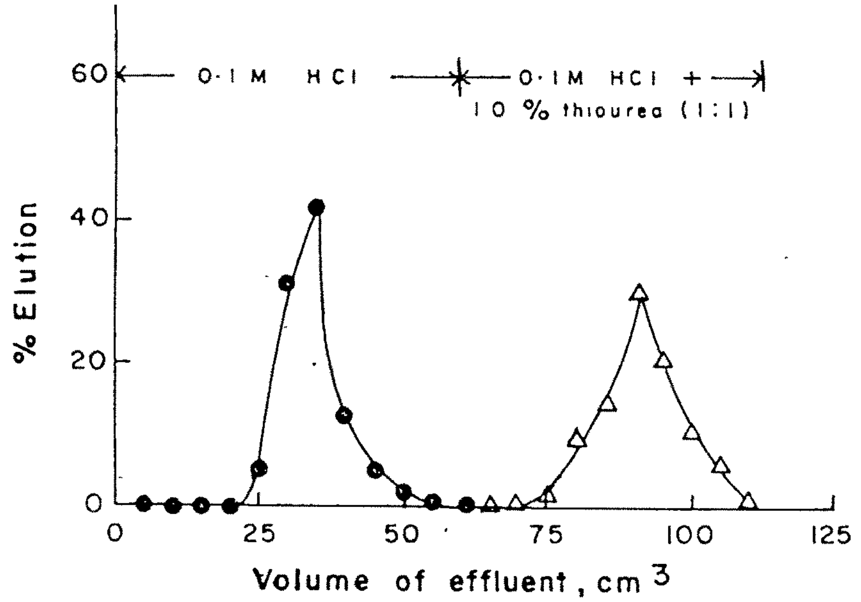


Fig. 4·8

Separation of Copper and Gold



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}

○ Nickel, ▲ Platinum, ● Copper, △ Gold.

Table 4.2 : Efficiency of recovery of metals from binary mixtures

Amount of metal			Amount of metal		
mg taken	mg * recovered	% recovery	mg taken	mg * recovered	% recovery
10.0	10.11	101.1	10.0	10.06	100.6
(Copper)			(Nickel)		
10.0	10.13	101.3	10.0	9.88	98.8
(Copper)			(Zinc)		
10.0	10.13	101.3	10.0	9.81	98.1
(Nickel)			(Zinc)		
10.0	9.99	99.9	10.0	9.93	99.3
(Nickel)			(Palladium)		
10.0	9.96	99.6	10.0	9.73	97.3
(Nickel)			(Platinum)		
10.0	10.03	100.3	10.0	9.99	99.9
(Copper)			(Gold)		

* mean of 3 determinaitons with s.d. = ±0.62 to 1.35

4.2.6 Separation of Cadmium (II) and Mercury (II); and Zinc (II) and Mercury(II)

The 30 cm^3 mixtures of Cd (II) and Hg (II) or Zn (II) and Hg (II), each containing 10 mg of metal ion in 1:1 ratio were passed through the column at pH 5 using 0.2 M acetate buffer. At this condition exchange of cadmium and zinc did not take place and hence a first few fractions of column effluent showed complete leaching of cadmium or zinc. In both the separations, mercury was eluted with a mixture of 0.5 M HNO_3 and 2 % NH_4NO_3. The estimation of cadmium, zinc and mercury was done titrimetrically using EDTA[3]. The separation patterns for Cd (II) and Hg (II); and Zn (II) and Hg(II) are given in Fig.4.10 and 4.11. % Recovery of metal ion is given in Table 4.3. No cross contamination was observed.

4.2.7 Separation of Mercury (II) and Gold (III); and Mercury (II) and Platinum (IV)

The 30 cm^3 solutions containing mixtures of Hg (II) and Au (III) or Hg (II) and Pt (IV) with 10 mg of each metal ion in 1:1 ratio were passed through the column at pH 5 using 0.2 M acetate buffer. Analysis of mercury, gold and platinum from column effluent was done as described earlier. The results are given in Fig.4.12 and 4.13. % Recovery of the metal ions is given in Table 4.3. No cross contamination was observed.

4.2.8 Separation of Gold (III)and Platinum (IV)

A 30 cm^3 mixture of 10 mg of Au (III) and Pt (IV) in 1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Gold was eluted with a 1·1 mixture of 5.0 M HCl and 1.0 M HNO_3 followed by the elution of platinum as described

Fig. 4·9

Separation of Zinc and Cadmium

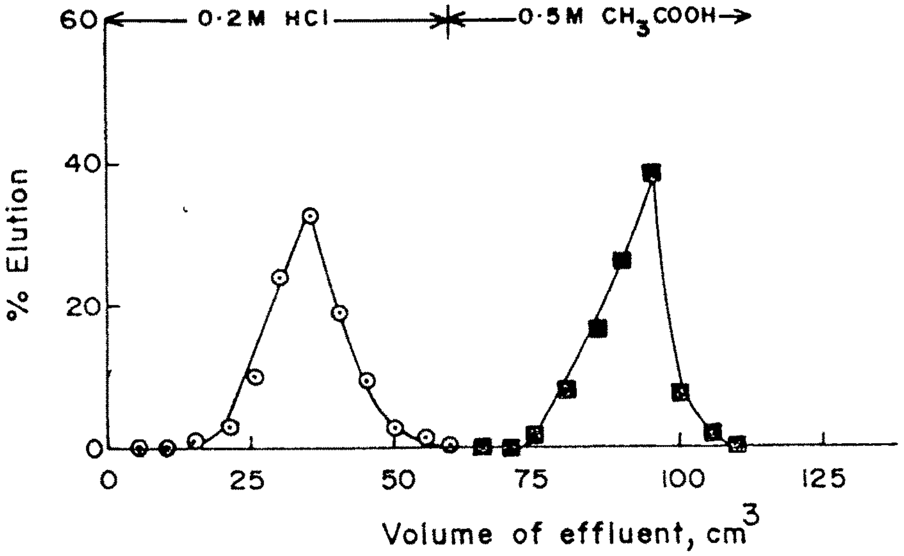
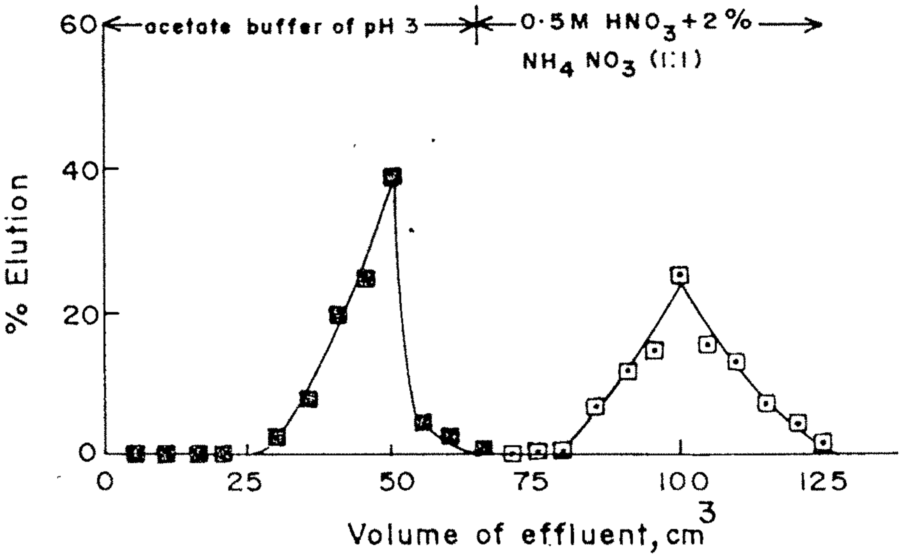


Fig. 4·10

Separation of Cadmium and Mercury



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}

⊙ Zinc, ▣ Cadmium, ⊡ Mercury

Fig. 4·11

Separation of Zinc and Mercury

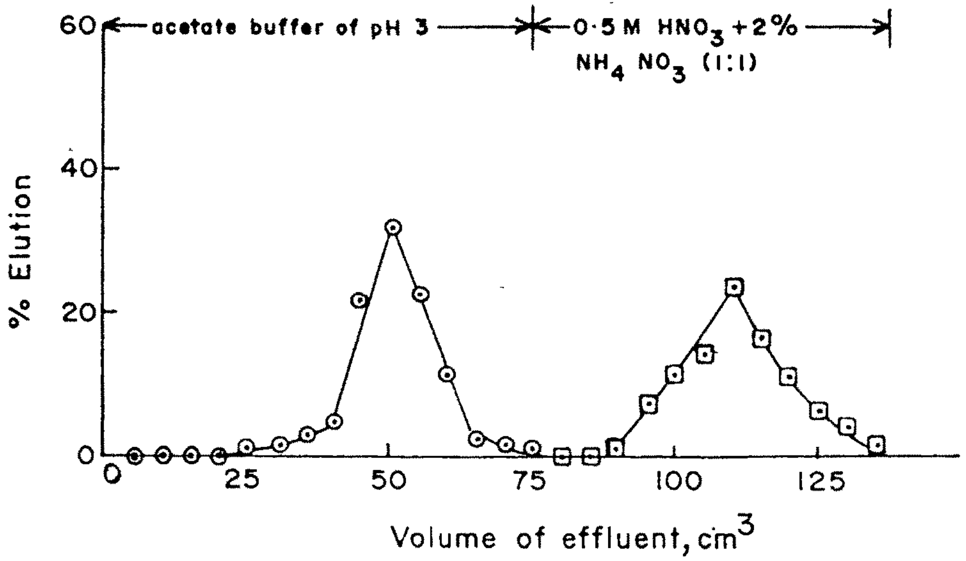
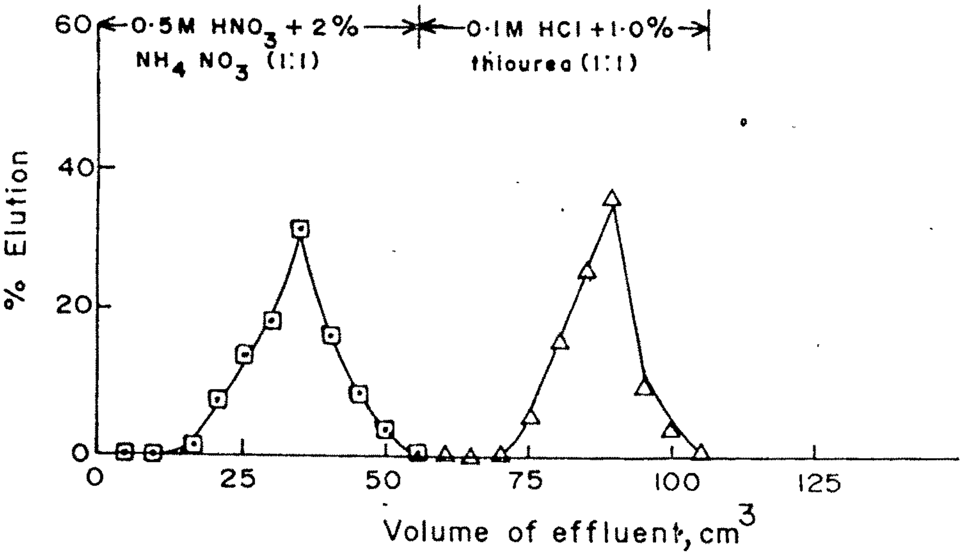


Fig. 4.12

Separation of Mercury and Gold



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}

⊙ Zinc, ⊡ Mercury, △ Gold,

Table 4.3 : Efficiency of recovery of metals from binary mixtures

Amount of metal			Amount of metal		
mg taken	mg * recovered	% recovery	mg taken	mg * recovered	% recovery
10.0	9.88	98.8	10.0	9.98	99.8
(Zinc)			(Cadmium)		
10.0	9.99	99.9	10.0	9.99	99.9
(Cadmium)			(Mercury)		
10.0	10.02	100.2	10.0	9.80	98.0
(Zinc)			(Mercury)		
10.0	10.02	100.2	10.0	9.91	99.1
(Mercury)			(Gold)		
10.0	10.01	100.1	10.0	9.80	98.0
(Mercury)			(Platinum)		
10.0	10.09	100.9	10.0	10.02	100.2
(Gold)			(Platinum)		
10.0	9.99	99.9	10.0	10.03	100.3
(Mercury)			(Lead)		

* mean of 3 determinations with s.d. = ± 0.69 ot 0.90

earlier. The results are given in Fig. 4.14. % Recovery of the metal ions is given in Table 4.3. No cross contamination was observed and recovery was quantitative.

4.2.9 Separation of Mercury (II) and Lead (II)

A 30 cm^3 mixture of 10 mg of Hg (II) and Pb (II) in 1:1 ratio was passed through the column at pH 3 using 0.2 M acetate buffer. Lead was completely leached out. Analysis of mercury was done as described earlier. The separation pattern for mercury and lead is given in Fig.4.15.

4.3 Separation of ternary mixtures

4.3.1 Separation of Copper (II), Nickel (II) and Zinc (II)

A 30 cm^3 mixture containing 10 mg each of Cu(II), Ni(II) and Zn(II) in 1:1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Zinc was not exchanged at this condition and was observed in the first few fractions of column effluent. Copper and nickel were quantitatively exchanged on the column and were eluted and estimated as discussed earlier. The results are given in Fig.4.16 and Table 4.4. No cross contamination was observed.

4.3.2 Separation of Nickel (II), Palladium (II) and Platinum(IV)

A 30 cm^3 mixture of Ni(II), Pd(II) and Pt(IV), containing 10 mg of each metal in 1:1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Nickel was eluted with 0.2 M CH_3COOH. Where as palladium and platinum were eluted with a mixture of 0.1 M HCl and 5 % thiourea. However, separation of

Fig. 4·13

Separation of Mercury and Platinum

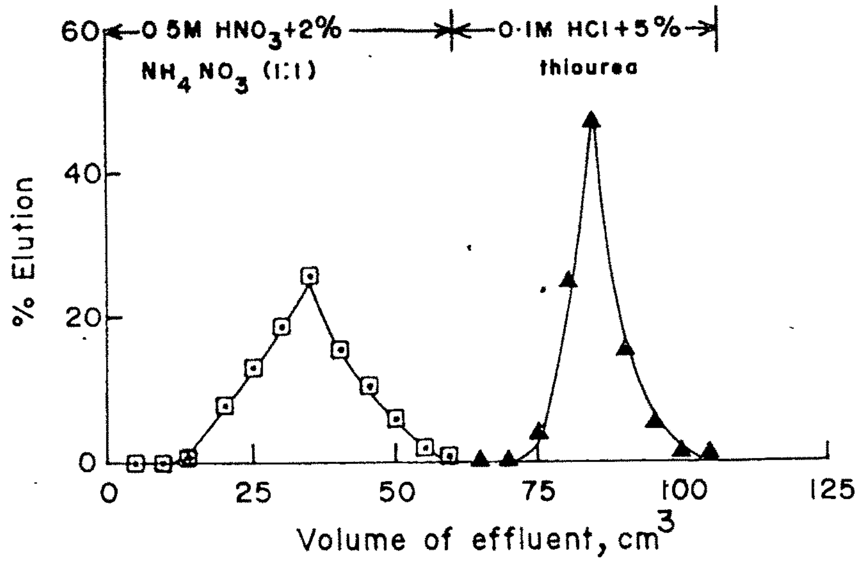
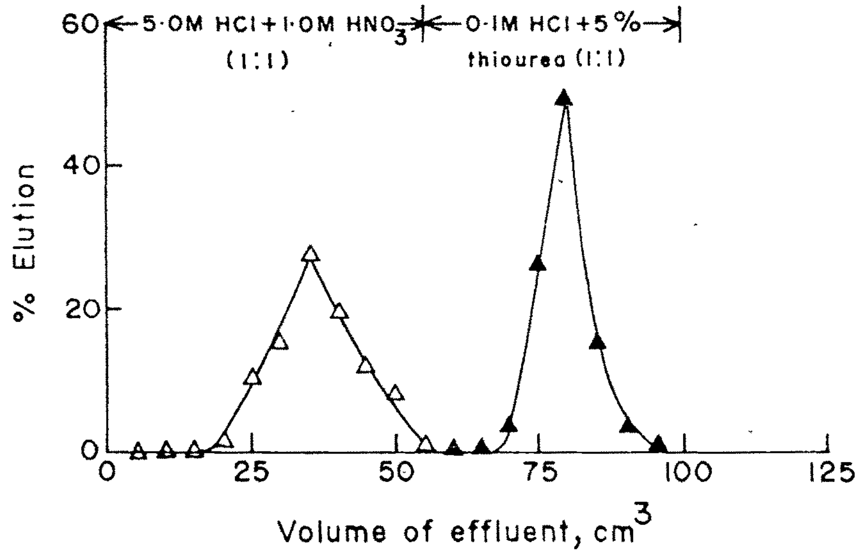


Fig. 4·14

Sepration of Gold and Platinum

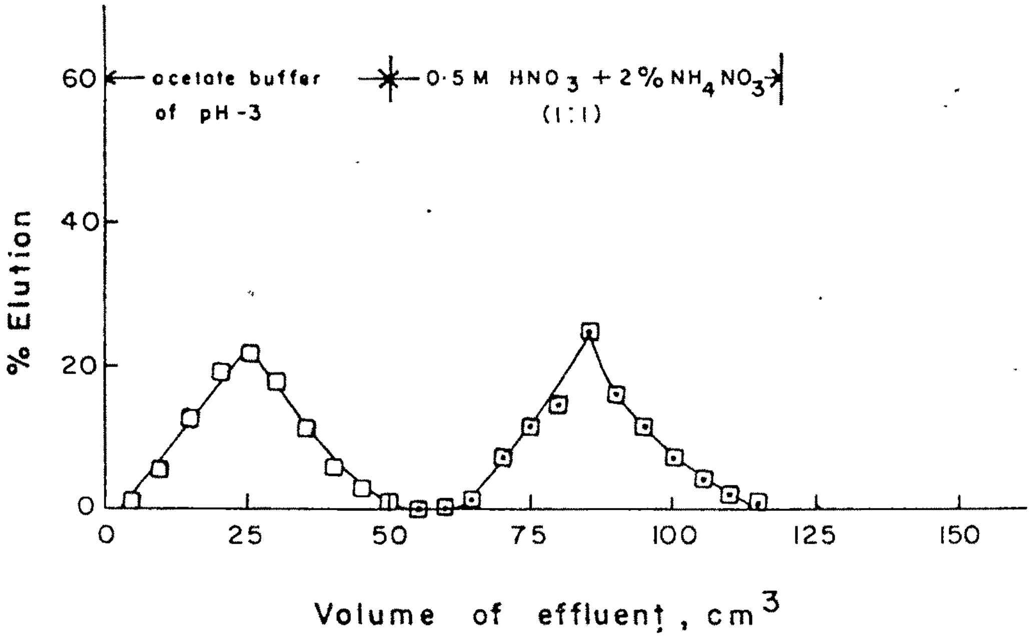


Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}.

⊡ Mercury, ▲ Platinum, △ Gold

Fig. 4·15

Separation of Mercury and Lead



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}.

□ Lead, ⊡ Mercury

Pd(II) and Pt(IV) was not achieved. The results are given in Fig.4.17 and Table 4.4.

4.3.3 Separation of Zinc (II), Cadmium (II) and Mercury (II)

A 30 cm^3 mixture of Zn(II), Cd(II) and Hg(II) containing 10 mg of each metal ion in 1:1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Mercury was retained on the column quantitatively and was analysed as discussed earlier. The column effluent containing unretained zinc and cadmium was again passed through the column in 0.2 M citrate-phosphate buffer of pH 5. Both cadmium and zinc were retained on the column quantitatively at this condition and were analysed as discussed earlier. The results are given in Fig.4.18 and Table 4.4.

4.3.4 Separation of Platinum (IV), Gold (III) and Mercury (II); and Platinum(IV), Gold (III) and Copper (II)

The 30 cm^3 mixtures of Pt(IV), Au(III) and Hg(II) or Pt(IV), Au(III) and Cu(II), each containing 10 mg of each metal ion in 1:1:1 ratio were passed through the column at pH 5 using 0.2 M acetate buffer. In the separation of Pt(IV), Au(III) and Hg(II), mercury was eluted with a mixture of 0.5 M HNO_3 and 2 % NH_4NO_3 followed by the elution of gold and platinum with a mixture of 5 M HCl and 1 M HNO_3 and 0.1 M HCl and 5 % thiourea respectively. Where as in the separation of Pt(IV), Au(III) and Cu(II), copper was first eluted with 0.1 M HCl followed by the elution of gold and platinum as described earlier. The separation patterns for Pt(IV), Au(III) and Hg(II); and Pt(IV), Au(III) and Cu(II) are given in the Fig. 4.19 and 4.20.

Fig. 4·16

Separation of Copper, Nickel and Zinc

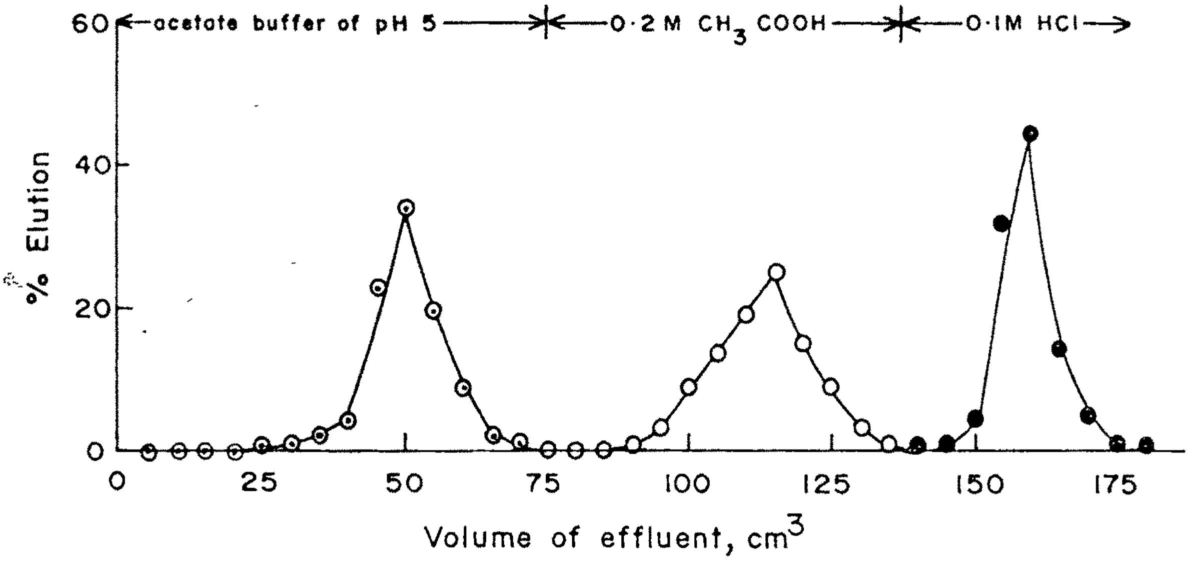
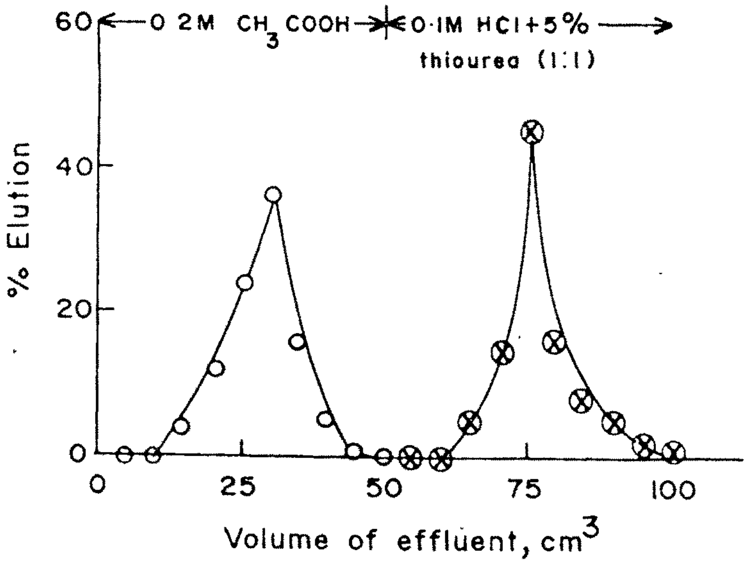


Fig. 4·17

Separation of Nickel, Palladium & Platinum



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}.

⊙ Zinc, ○ Nickel, ● Copper, ⊗ Palladium + Platium

Fig. 4·18

Separation of Zinc, Cadmium and Mercury

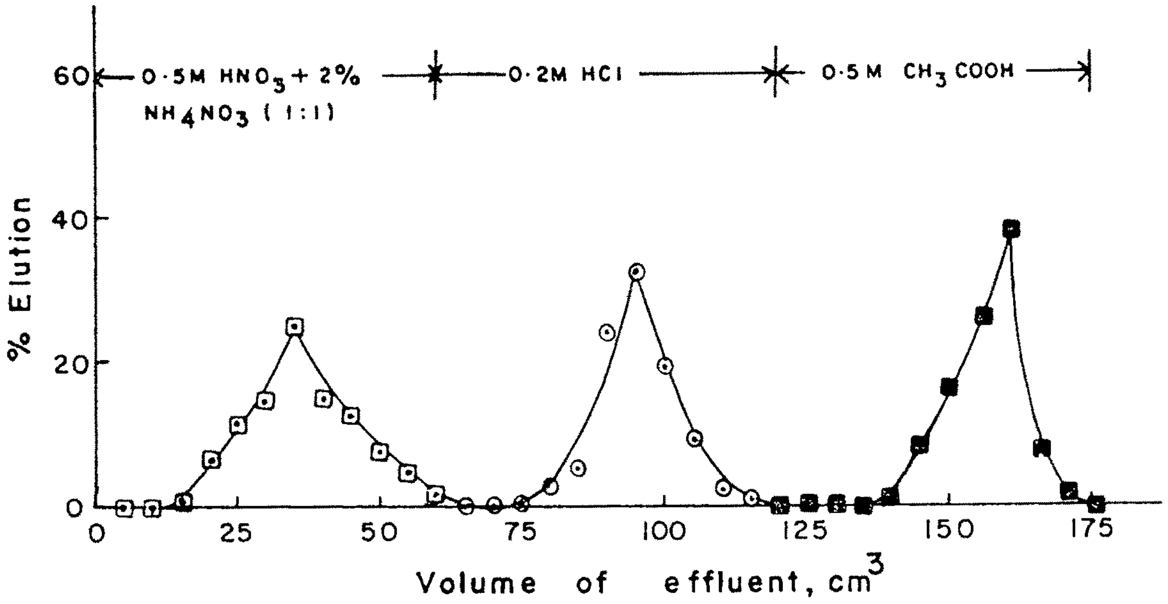
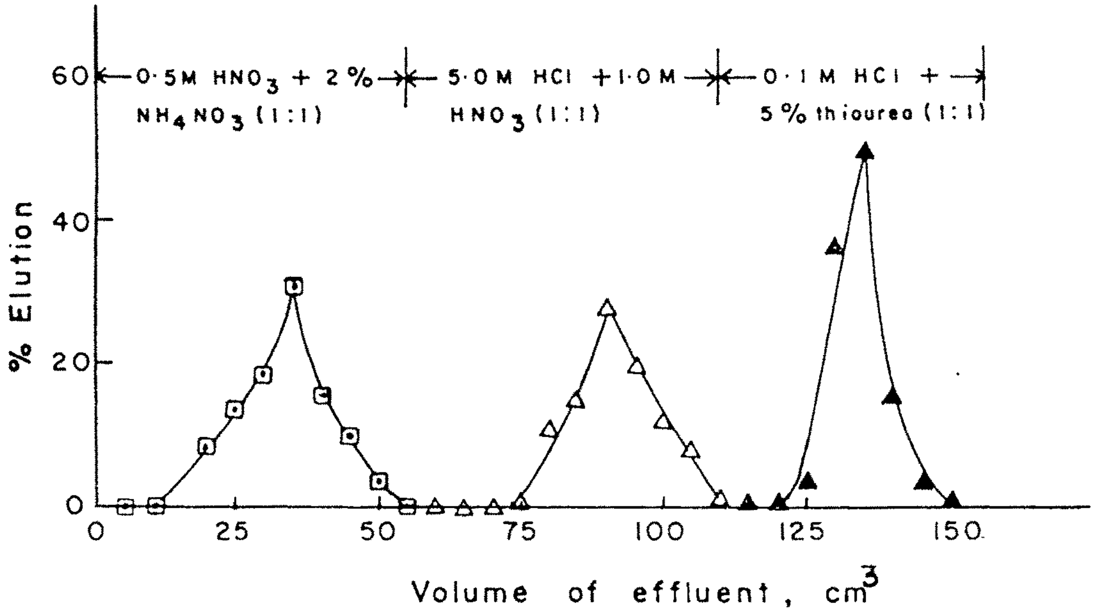


Fig. 4·19

Separation of Platinum, Gold and Mercury



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 $cm^3\,min^{-1}$.

⊡ Mercury, ⊙ Zinc, ■ Cadmium, △ Gold, ▲ Platinum

Table 4.4 : Efficiency of recovery of metals from ternary mixtures

Amount of metal			Amount of metal			Amount of metal		
mg taken	mg* recovered	% recovery	mg taken	mg* recovered	% recovery	mg taken	mg * recovered	% recovery
10 0	10.11	101.1	10.0	10.1	101.0	10.0	9.94	99.4
(Copper)			(Nickel)			(Zinc)		
10.0	9.86	98.6	10 0	9.98	99.8	10.0	9.99	99.9
(Zinc)			(Cadmium)			(Mercury)		
10.0	10.01	100.1	10.0	10.09	100.9	10.0	9.99	99.9
(Platinum)			(Gold)			(Mercury)		
10.0	10.0	100.0	10 0	9.96	99 6	10.0	9.99	99 9
(Platinum)			(Gold)			(Copper)		

* mean of 3 determinations with s.d. = ±0.57 to 1.17

4.3.5 Separation of Palladium (II), Platinum (IV) and Gold (III)

A 30 cm^3 mixture of Pd(II), Pt(IV) and Au(III) containing 10 mg of each metal ion in 1:1:1 ratio was passed through the column at pH 5 using 0.2 M acetate buffer. Gold was eluted with a mixture of 5 M HCl and 1 M HNO_3 where as Pd(II) and Pt(IV) were eluted together with a mixture of 0.1 M HCl and 5 % thiourea and were analysed as described earlier. The results are given in Fig.4.21 and Table 4.4. Separation of Pd(II) and Pt(IV) was not possible.

Separation of Cu(II) - Ni(II), Cu(II) - Au(III), Au(III) - Pt(IV), Zn(II) - Cd(II), Pd(II) - Ni(II), Cd(II) - Hg(II) and Cu(II) - Zn(II) were tried with 1:10 and 10:1 ratios. For all separations with different ratios, % recovery was observed to be quantitative. % Recoveries for 1:10 and 10:1 ratios are given in Table 4.5 and 4.6.

Fig. 4·20

Separation of Platinum, Gold and Copper

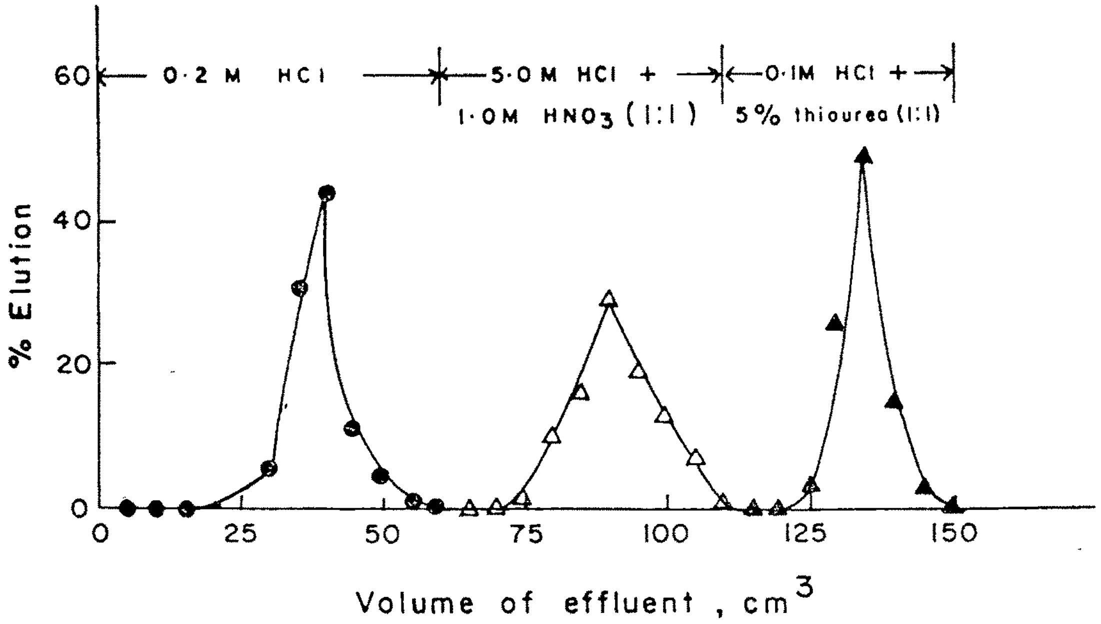
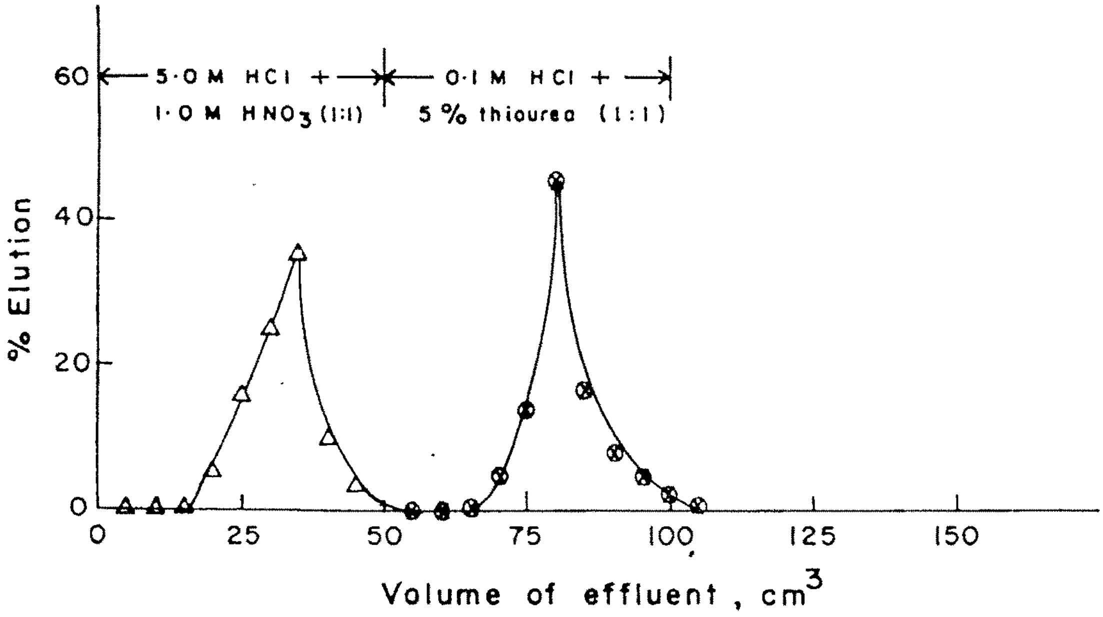


Fig. 4·21

Separation of Palladium, Platinum, and Gold



Metal taken 10 mg each, metal solution taken 30 cm^3, flow rate 1 cm^3 min^{-1}

● Copper, △ Gold, ▲ Platinum, ⊗ Palladium + Platinum

Table 4.5 : Efficiency of recovery of metals from binary mixtures

Amount of metal			Amount of metal		
mg taken	mg * recovered	% recovery	mg taken	mg * recovered	% recovery
1.0	0.98.	98.0	10.0	9.9	99.0
(Copper)			(Nickel)		
1.0	0.95	95.0	10.0	9.85	98.5
(Copper)			(Gold)		
1.0	0.90	90.0	10.0	10.05	100.5
(Gold)			(Platinum)		
1.0	0.98	98.0	10.0	9.95	99.5
(Zinc)			(Cadmium)		
1.0	1.08	108.0	10.0	9.87	98.7
(Palladium)			(Nickel)		
1.0	0.95	95.0	10.0	10.01	100.1
(Cadmium)			(Mercury)		
1.0	1.0	100.0	10.0	9.8	98.0
(Copper)			(Zinc)		

* mean of 3 determinations with s.d. = ±1.27 to 1.87

Table 4.6 : Efficiency of recovery of metals from binary mixtures

Amount of metal			Amount of metal		
mg taken	mg * recovered	% recovery	mg taken	mg * recovered	% recovery
10.0 (Copper)	0.05	100.5	1.0 (Nickel)	0.93	93.0
10.0 (Copper)	9.98	99.8	1.0 (Gold)	0.91	91.0
10.0 (Gold)	9.75	97.5	1.0 (Platinum)	1.05	105.0
10.0 (Zinc)	10.01	100.1	1.0 (Cadmium)	0.95	95.0
10.0 (Palladium)	9.99	99.9	1.0 (Nickel)	0.98	98.0
10.0 (Cadmium)	10.2	102.0	1.0 (Mercury)	0.97	97.0
10.0 (Copper)	10.01	100.1	1.0 (Zinc)	1.02	102.0

* mean of 3 determinations with s.d. = ±0.49 to 0.68

Reference

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