

ION EXCHANGE SEPARATION OF TRANSITION ELEMENTS OF THE PERIODIC TABLE. PART II

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Copper, iron and zinc have been separated from one another by ion exchange method. A mixture of the three cations was run over an anion exchange resin and each cation was successively eluted with hydrochloric acid. The eluants were studied polarographically using step height-concentration calibration group method.¹

The separation of metal ions by anion-exchange resins is based on the transformation of metal ions into anionic complexes. This technique is applicable to cases where extremely stable complexes are formed. In cases where hydrolysis occurs in rinsing with water it is advantageous to work the column with the complexing agent like HCl after the sorption step. Thus a separation of different metals from one another can be obtained by percolating the solution to be analysed through an anion exchanger with anions which give strong complexes with certain metal ions present in the solutions. Those metals which form strong complexes are quantitatively retained, whereas other metals pass quantitatively into the effluent.²

Since Cu^{++} , Fe^{+++} , Zn^{++} form strongly stable anionic chloro complexes in hydrochloric acid medium and since their stability decreases with decreasing strengths of the acid, it is possible to separate them quantitatively from a mixture.

Cu^{++} and Zn^{++} were estimated in the eluant polarographically from neutral solutions. Since a neutral solution of Fe^{+++} could not be prepared under similar conditions it was determined titrimetrically.

Apparatus and Reagents

Amberlite IRA-400 (Cl) (L. Light & Co. Ltd., Colnbrook, England) anion exchanger was employed. The resin was first put in distilled water till maximum swelling was obtained. The resin-slurry was then fed to a Pyrex column (1.3 cm dia, 68 cm high) taking care that no air bubble was entrained because that would decrease the efficiency of the resin. The column was loaded to a height of 26 cm, and glass wool plug inserted. The resin in the column was then repeatedly washed with distilled water. Lastly the column was washed with strong HCl to reactivate the resin and to provide complexing media for subsequent separation of the three cations.

CuCl_2 (1.345 g) was dissolved in a small quantity of concd HCl and the volume made up to 100 ml. 1 ml of the solution = 6.37 mg Cu.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.70g) was dissolved in a small amount of concd HCl and the volume made up to 100 ml. 1 ml of the solution = 6.44 mg Fe.

ZnCl_2 (1.364 g) was dissolved in a small amount of concd HCl and the volume made up to 100 ml. 1 ml of the solution = 6.538 mg Zn.

Other reagents used for identification of Cu^{++} , Fe^{+++} and Zn^{++} were potassium ferrocyanide (E. Merck, Germany), hydrogen sulfide gas, potassium sulfocyanide (B.D.H., England), and quinaldic acid (B.D.H., England).

Cambridge Pen-writing polarograph was used for recording the polarograms. One ml test solution plus 1 ml 0.1 M KCl (base electrolyte) and 1 ml 0.2% Triton X-100 was put into the polarograph cell. Nitrogen was bubbled through the solution to remove dissolved oxygen. The capillary was then lowered into the cell to dip about 0.5 cm in the solution. The reservoir of Hg was raised to a constant height (from tip of capillary to the mercury level in the reservoir) and the polarograph switched on to record the polarogram. According to Ilkovic equation, concentration of the test solution is directly proportional to diffusion current provided the temperature, composition of base electrolyte, rate of flow of Hg and the drop time are kept constant.³ The polarograms were taken under these constant conditions, and concentrations were directly calculated from the diffusion current.

Experimental

Column Experiments with Cu^{++} .—Three solutions of CuCl_2 were made by dissolving 0.135 g salt in 3N, 3.5N and 4N HCl respectively and the volume made up to 10 ml. One ml of each solution was separately evaporated to dryness and the

dried mass taken up with distilled water to make 10 ml of each solution. One ml of each of these three solutions was taken separately in the polarographic cell and their polarograms recorded wherefrom the diffusion currents were calculated.

Column Experiment with Cu⁺⁺ in 3N HCl.—The column was washed with 3N HCl to provide the complexing media for Cu⁺⁺ in 3N HCl. One ml CuCl₂ solution in 3N HCl was then fed to the column at a flow rate of 1 ml/min. The column was then washed with 3N HCl solution 26 ml of the said acid was sufficient to completely elute the unadsorbed Cu⁺⁺. The eluate thus obtained was carefully evaporated to dryness and the mass taken up with distilled water to make 10 ml of the solution. One ml of this solution was put into the polarographic cell and the polarogram taken. From the original polarogram of Cu⁺⁺ in 3N HCl and that obtained from the unadsorbed Cu⁺⁺ in 3N HCl as indicated in Fig. 1a the per cent adsorption of Cu⁺⁺ was calculated from the diffusion current (Table 1).

Column Experiment with Cu⁺⁺ in 3.5N HCl.—The column was washed thoroughly with distilled water till the washings were neutral. Then 3.5N HCl was run through the column to provide the necessary complexing media for Cu⁺⁺ in 3.5N HCl. One ml CuCl₂ solution in 3.5N HCl was adsorbed, and then it was observed that 30 ml 3.5N HCl was used for complete removal of unadsorbed Cu⁺⁺. The polarograms of the original CuCl₂ in 3.5N HCl and the unadsorbed Cu⁺⁺ are indicated in Fig. 1b their diffusion current obtained and per cent adsorption calculated (Table 1).

Column Experiment with Cu⁺⁺ in 4N HCl.—The column was washed thoroughly with distilled water till washings were free from any trace of acid. Then 4N HCl was run through the column

to provide the complexing media for 3Cu⁺⁺ in 4N HCl. After that one ml solution was adsorbed into the column at the flow rate of 1 ml/min and was then washed with the said acid. It was observed that 10 ml 4N HCl was used for complete removal of unadsorbed Cu⁺⁺. The polarograms of the Cu⁺⁺ in 4N HCl and that obtained after adsorption through the column were recorded as previously and indicated in Fig. 1c and, from their diffusion currents thus obtained, per cent adsorption was calculated (Table 1).

TABLE I

HCl	Cu taken/ ml soln (mg)	Cu adsorbed (mg)	% adsorption
3N	6.37	0.00	Nil
3.5 N	6.37	0.85	13.33
4.0 N	6.37	6.3578	99.80

Column Experiments with Fe⁺⁺⁺.—0.27 g FeCl₃·6H₂O was dissolved separately in 1N, 2N, 3N, 4N and 5N HCl, and the volume made up to 10 ml. One ml of each of these solution was adsorbed in the column after providing the proper complexing media. The unadsorbed Fe⁺⁺⁺ from each adsorption was collected and determined titrimetrically with N/10 K₂Cr₂O₇ using diphenylamine as internal indicator. It was observed that approximately 40 ml of each acid was sufficient for complete removal of unadsorbed Fe⁺⁺⁺ in each case. From the quantities of Fe⁺⁺⁺ obtained from literature of the unadsorbed Fe⁺⁺⁺, per cent adsorption was calculated (Table 2).

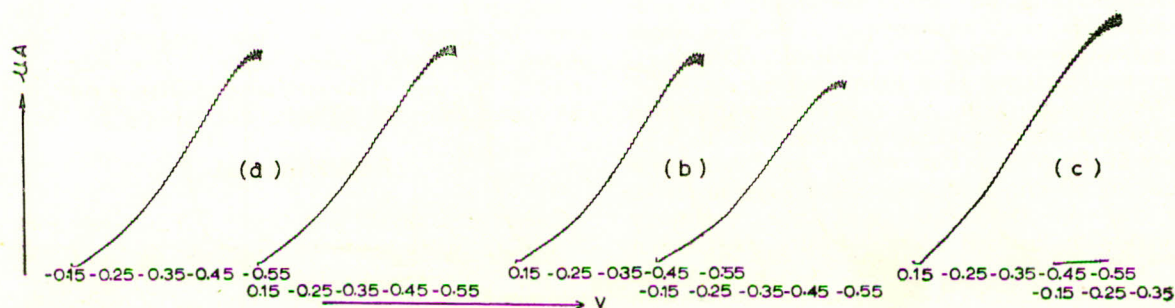


Fig. 1.—Polarograms showing the adsorption of Cu⁺⁺ in (a) 3N HCl, (b) 3.5N HCl, (c) 4N HCl at sensitivity 1/100 and damping 3.

TABLE 2

HCl	Fe taken/ ml soln (mg)	Fe adsorbed(mg)	% adsorption
1N	6.44	0.00	nil
2N	6.44	0.66	10.25
3N	6.44	3.52	54.60
4N	6.44	5.45	84.64
5N	6.44	6.44	100.00

Column Experiments with Zn⁺⁺.—0.136 g ZnCl₂ was dissolved in each of 0.025N, 0.05N, 0.5N, 1N HCl and the volumes made up to 10 ml. One ml of each of the four solutions was evaporated to dryness taken up with distilled water and the volume made to 10 ml. Then one ml of each of these solutions were taken into polarographic cell separately, and their polarograms recorded.

One ml of each of the acid solutions was separately adsorbed in the column as described under copper, providing, of course, the required complexing media in each case. The unadsorbed Zn⁺⁺ was washed out using the respective acid in each case. It was observed that 25 ml of each acid was sufficient for complete removal of Zn⁺⁺ from the column.

The solutions containing unadsorbed Zn⁺⁺, from each of the above column experiments, was evaporated to dryness, taken up with distilled water and the volumes made up to 10 ml. One ml of each of these neutral solutions was separately subjected to polarographic determination. From the diffusion currents obtained in case of the polarograms of original solutions and those obtained from the polarograms of unadsorbed Zn⁺⁺ solution, as indicated in Fig. 2 (a-d) the per cent adsorption was calculated as given in Table 3.

TABLE 3

HCl	Zn taken/ ml soln (mg)	Zn adsorbed(mg)	% adsorption
0.005 N	6.5380	0.0000	nil
0.025 N	6.5380	1.6345	25.10
0.050 N	6.5380	2.6980	41.27
0.500 N	6.5380	6.4359	98.44
1.000 N	6.5380	6.5380	100.00

Separation of Cu-Fe-Zn

One ml each of the three standard solutions was taken in a 100-ml beaker and shaken to mix them well. The column was washed with concd HCl (9N HCl) to provide the complexing media. The mixture was then fed to the column through the thistle funnel at the rate of 1 ml/min. The beaker was rinsed repeatedly with concd HCl and the washings poured into the thistle funnel. When nearly all of the mixture and washings had passed through resin bed, selective elution of the three cations was carried out.

Elution of Copper.—From previous observations on the adsorption of Cu⁺⁺, as indicated in Table 1, it was concluded that Cu⁺⁺ should be eluted with 3N HCl. Hence, 3N HCl was employed for the elution of Cu⁺⁺; 35 ml 3N HCl was used for complete removal of Cu⁺⁺ from the column. The eluate so obtained was carefully evaporated to dryness, the dried mass taken up with distilled water and the volume made up to 10 ml. One ml from this solution was put into the polarograph cell and its polarogram recorded. From the comparison of the polarograms of the standard CuCl₂ solution and of the Cu⁺⁺ eluate after separation as

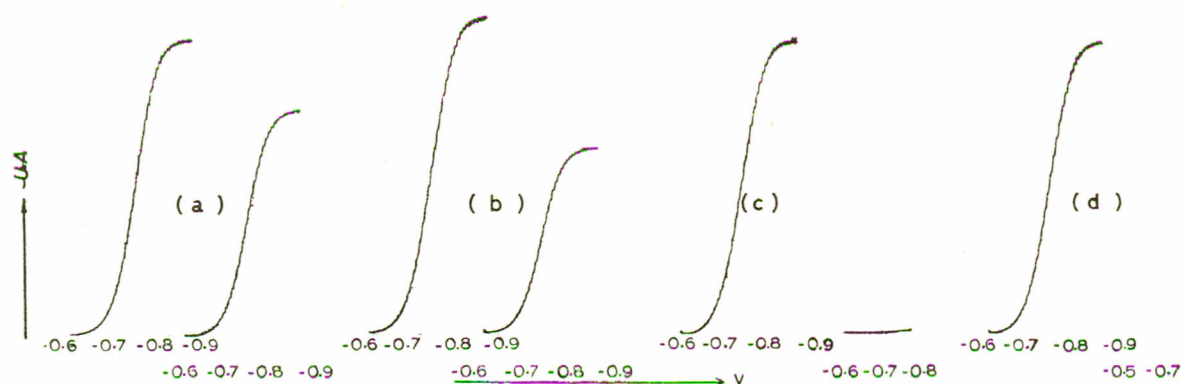


Fig. 2.—Polarograms showing the adsorption of Zn⁺⁺ in (a) 0.025N HCl, (b) 0.05N HCl, (c) 0.5N HCl, (d) 1N HCl at sensitivity 1/100 and damping 3.

shown in Fig 3(a,b) and Fig. 5 it was observed that whole of the Cu^{++} fed to the column was eluted (Table 4) and that neither Fe^{+++} nor Zn^{++} was affected by 3N HCl.

Elution of Iron.—It is observed from Table 2 that Fe^{+++} should be eluted with 1N HCl without breaking the chloro complex made by Zn^{++} . Hence, after the removal of Cu^{++} from the column, 1N HCl was allowed to percolate through the column and the effluent collected. 40 ml 1N HCl was required for complete removal of Fe^{+++} (Table 4). The eluate of Fe^{+++} was titrated with N/10 $\text{K}_2\text{Cr}_2\text{O}_7$ using diphenylamine as internal indicator (error 2.6%).

Elution of Zinc.—Table 3 shows that adsorption of Zn^{++} is zero at 0.005N HCl concentration. Hence, the elution of Zn^{++} was carried out with 0.005N HCl. 50 ml of this acid was used for complete elution of Zn^{++} . This also suggests that Zn^{++} forms the strongest anionic chloro complex in a very low HCl concentration. The eluate so obtained was carefully evaporated to dryness, taken up with distilled H_2O and the volume made up to 10 ml. Then 1 ml of this solution was taken into the polarographic cell and its polarogram was recorded. From the polarograms of the standard ZnCl_2 solution and of the eluate after separation as indicated from Fig. 4 (a, b) and Fig. 5 it was clear that Zn^{++} was quantitatively eluted (Table 4).

TABLE 4

Cations	Taken (mg)	Found (mg)	Error %
Cu^{++}	0.6357	0.6357	nil
Fe^{+++}	6.44	6.272	2.60
Zn^{++}	0.6538	0.6538	nil

Discussion

In the present communication quantitative separation and determination of Cu, Fe and Zn has been described. The polarograms indicate that the separation is complete in the hydrochloric acid medium. The present study and earlier work in this medium forms the basis of the separation of various cations in presence of each other. This has already been briefly taken up in the discussion of Part I.

Apart from HCl other known media are oxalate, citrate and HCl-HF, and less commonly employed are nitrate and sulphate. Since the basis of group separations of complicated mixtures are (i) selective complex formation and (ii) difference in charge,

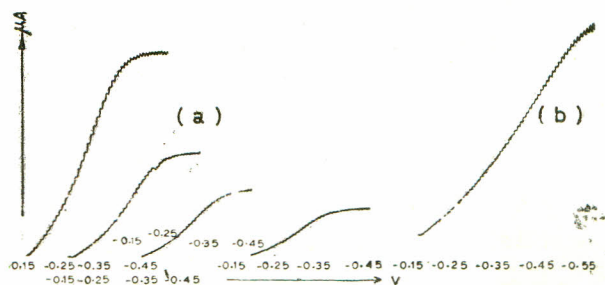


Fig. 3.—Polarograms of Cu^{++} showing (a) calibration curves of standard CuCl_2 solution; (b) after separation from Cu^{++} - Fe^{+++} - Zn^{++} at sensitivity 1/100 and damping 3.

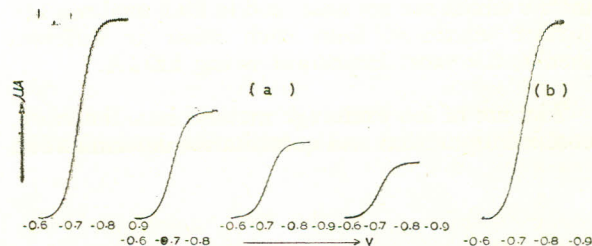


Fig. 4.—Polarograms of Zn^{++} showing (a) calibration curves of standard ZnCl_2 solution; (b) after separation from Cu^{++} - Fe^{+++} - Zn^{++} at sensitivity 1/100 and damping 3.

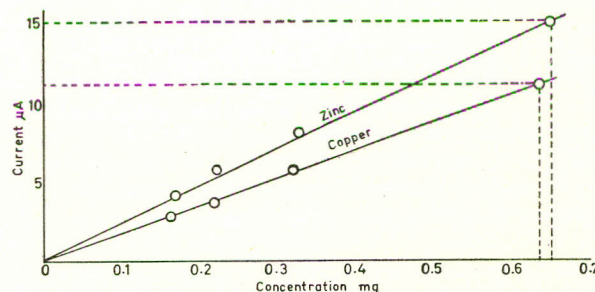


Fig. 5.—Calibration curves for Cu^{++} and Zn^{++} current vs. connection.

Russell⁴ explained the formation of extremely strong complexes and selective elution of zirconium and niobium in oxalic acid media. Similarly tri-, di- and monovalent ions have been separated from each other by means of citrate buffers at pH 3 and pH 5.

Kraus and Moore⁵ used a mixture of HCl-HF for elements which tend to polymerize, e.g. Zr (iv), Hf (iv), Nb(v), Ta(v) and Pa(v).

In group separations based upon difference in charge, the eluant should be such that it does not give strong complexes with the elements to be separated. It has been found by Fritz and Karraker⁶ that with perchlorate solutions the separations are fairly rapid and accurate.

The investigations carried out by the authors and separation methods reported in the literature are undoubtedly of great assistance but much help can be derived from the published distribution coefficients in different media. Although it is possible to separate large number of elements from a single column with only one eluant, it is reliable and simple to make the separation in several steps by employing several eluants.

Interfering anions are removed as usual, by passing the solution over strongly acidic cation exchange resin and later eluting the cations with HCl. Cations like Al, Ni, alkali and alkaline earth metals which are not adsorbed in HCl medium are further separated from each other in different media, the most important being EDTA.

The use of ion exchange method has, therefore, enabled separation and quantitative determination

of elements from alloys, ores etc. The techniques also find application for reclaiming metals from alloys, purifying industrial wastes solutions and electrolytes.

References

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