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

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The separation of the cations Ni^{++}, Mn^{++} and Co^{++} has been carried out using the ion exchange method. The mixture of these cations in 9N HCl is added to an anion exchanger and eluted with 6N NHCl to remove Co and Mn while Ni is not adsorbed at all.   The concentration of the separated cations has been determined polarographically using the step-height-concentration calibration group method.[1]

Hydrochloric acid has been considered one of the most versatile media for ion exchange seperations,[2] because of the formation of anionic chloro complexes with various cations. These anionic chloro complexes differ in their stability constants towards elution.   On the basis of the difference in stability constants it is, therefore, possible to separate various cations from one another under proper working conditions.

Nickel and aluminium are among the non-sorbable elements[3] whereas manganese and cobalt are effectively taken up by the anion-exchange resin in chloride media.   The latter two elements exhibit large difference in their distribution co-efficients in HCl and, therefore, no tailing effect is noticeable under proper   washing conditions.

In order to be sure of the freeness of any element in the eluants, the eluants have been subjected to polorographic determination for any infinitesimal contamination.

Apparatus and Reagents

Ion Exchange Resin.—Amberlite I RA-400 (Cl) (Light and Co. Ltd., Colnbrook, England) anion exchanger was used. The resin was first put in distilled water to allow maximum swelling and later transferred to a Pyrex glass column (1.3 cm dia and 68 cm high) and up to a height of 26 cm. The column was washed with distilled water and then with 9N HCl in order to completely regenerate the chloride ions and to remove any mechanically held metallic ions. The resin was then thoroughly washed with distilled water and a glass wool plug inserted.

Standard   Solution   of   Nickel.—$NiCl_2$. $6H_2O$ (2.377 g) was dissolved in a small quantity of 9N HCl and the volume made up to 100 ml with 9N HCl. 1 ml of the solution=5.87 mg of Ni.

Standards Solution of Manganese.—$MnCl_2.4H_2O$ (1.98 g) was dissolved in a small amount of 9N HCl and the volume made up to 100 ml with 9N HCl. 1 ml of solution=5.5 mg of Mn.

Standard   Solution   of   Cobalt.—$CoCl_2.6H_2O$ (2.38 g) was dissolved in a small amount of 9N HCl and then volume made up to 100 ml with 9N HCl.   One ml of the solution=9 mg Co.

Reagents used for Identification of Ni, Mn, Co.—Dimethylglyoxime (E. Merck, W. Germany); sodium bismuthate (May & Baker, England); α-nitroso-β-naphthol (E. Merck. W. Germany).

Polarograms.—Cambridge pen-writing polarograph was used for recording the polarograms. One ml of the 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 gas was bubbled through the solution for 10 min to remove dissolved oxygen. The capillary was then lowered into the cell to dip about 0.5 cm in the solution.   The mercury reservoir was then raised to a constant height of 71.5 cm (from the tip of the capillary to the Hg 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 the diffusion current provided the temperature, composition of base electrolyte, rate of flow of Hg and the drop time are kept constant.[4] The polarograms were taken under these constant conditions and concentrations were directly calculated from diffusion current.

Experimental

Column Experiments with Ni^{++}.—Since nickel is nonsorbable in any HCl concentration, it passes through the column as such.   This is shown by the polarogram of the original Ni^{++} solution and that obtained after passing through the column (Figs. 3a, b and Fig. 6).

Column Experiments with Co^{++}.—$CoCl_2.6H_2O$ (0.3g) was used each time and its solution prepared using 5N, 6N, 7N and 8N HCl and volume made up to 10.0 ml.

One ml of each solution (prepared in 5, 6, 7 and 8N HCl) was evaporated separately to remove HCl and then redissolved in distilled water to make 10 ml of the solution. One ml of this solution was taken in the polarograph cell and the polarogram obtained in each case.

One ml of each solution (prepared in 5, 6, 7 and 8N HCl) was separately passed through the column and effluents collected. The effluents were evaporated to dryness and then taken up with distilled water to make 10 ml of the solution. One ml of each of these solutions was then put into the polarograph cell separately and their polarograms obtained, as indicated in Fig. 1a–d. From the diffusion currents obtained from the above polarograms, per cent adsorption of Co was calculated as given in Table 1.

Column Experiments with Mn^{++}.—$MnCl_2.4H_2O$ (0.5 g) was dissolved in 6N, 7N, 8N, 9N and 10N HCl separately and the volume made up to 25 ml. One ml of each solution was evaporated to dryness and redissolved in distilled water and the volume made to 10 ml. One ml of each solution

TABLE 1

HCl	Co taken/ ml soln (mg)	Co adsorbed (mg)	% adsorption
4N	6.9	nil	nil
5N	6.9	0.500	7.2
6N	6.9	1.830	26.5
7N	6.9	5.175	75.0
8N	6.9	6.658	97.0

was taken and polarograms obtained. Then 1 ml of each solution was passed through the column separately and the polarograms of the unadsorbed Mn obtained. From the diffusion current in each case from Fig. 2a–d, the percentage adsorption was calculated as given in Table 2.

TABLE 2

HCl	Mn taken/ ml soln (mg)	Mn adsorbed (mg)	% adsorption
6N	5.552	nil	nil
7N	5.552	0.252	4.54
8N	5.552	0.182	3.30
9N	5.552	2.602	47.00
10N	5.552	0.142	2.40

The % adsorption of Mn is low because, as reported,[5] elution constant for Mn is fairly high.

It is concluded from the above tables that the separation of these cations from each other is possible and can be effected by eluting manganese at 6N HCl and eluting Co at 4N HCl. Maximum adsorption is achieved at 9N hydrochloric acid concentration.

Separation of Ni, Mn, Co.—One ml of the solution of each cation was taken in a 100-ml beaker and shaken to mix the three solutions. The mixture was then fed to the column through a thistle funnel, with a stopcock, at the rate of 1 ml/min. The beaker was washed repeatedly and the washings also transferred to the column. Care was taken that the resin was closely packed and there was no air bubble entrained in the resin bed because the presence of air causes tailing effects.

Elution of Nickel.—Since nickle is nonsorbable, it forms no anionic chloro complexes. It was not
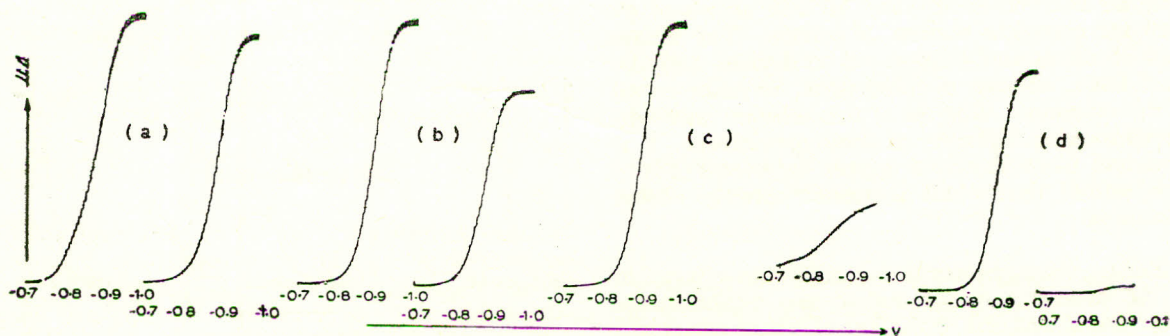

Fig. 1.—Polarograms showing the adsorption of cobalt in (a) 5N HCl, (b) 6N HCl, (c) 7N HCl (d) 8N HCl at sensitivity 1/100 and damping 2.
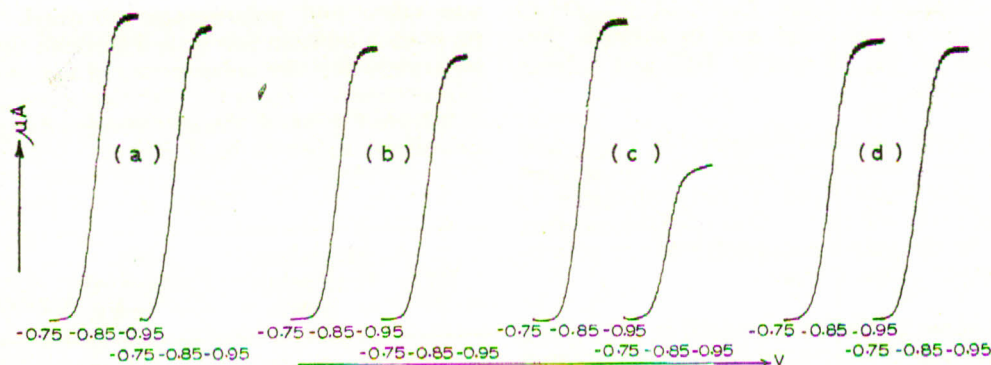
Fig. 2.—Polarograms showing the adsorption of manganese in (a) 7N HCl, (b) 8N HCl (c) 9N HCl, (d) 10N HCl at sensitivity 1/100 and damping 2.

adsorbed and was eluted forthwith. 50 ml 9N HCl would be used for complete elution of nickel from the column. The eluate thus obtained was carefully evaporated to dryness and the volume (10 ml) made up with distilled water. One ml of this solution was taken into the polarographic cell and its polarogram taken. From the standard graph for Ni (Figs. 3a, b and 6) it was observed that almost all of the Ni was eluted (Table 3).

Elution of Manganese.—From Table 2 it is clear that Mn is eluted at 6N HCl concentration. Hence, after the complete elution of Ni with 9N HCl the concentration of the acid was reduced to 6N. It took 25 ml of 6N HCl for complete elution of Mn. The eluate was carefully evaporated to dryness and the dried mass taken up with distilled water to make 10 ml of the solution. One ml of this solution was taken in the polarograph cell and the polarogram taken. From the standard graph for Mn (Fig. 4 a,b, and 6) it is observed that nearly all of Mn was eluted (Table 3).

Elution of Cobalt.—As seen from Table 1, cobalt is not adsorbed on the anion exchange resin in 4N HCl. Hence, after complete removal of Mn from the mixture fed to the column, 4N acid was used for the elution of Co. It took 40 ml of 4N HCl for complete elution of cobalt. The eluate thus obtained was evaporated to dryness and the mass taken up with distilled water to make 10 ml of the solution. One ml of this solution was subjected to prolarography as done previously. It is observed from standard graph for cobalt (Figs 5 (a,b) and 6) that cobalt is almost entirely eluted (Table 3).

The percentage error occurring in the separation of the cations was not due to any experimental error but it was due to the loss of eluate consumed for qualitative testing during the collection of eluate.
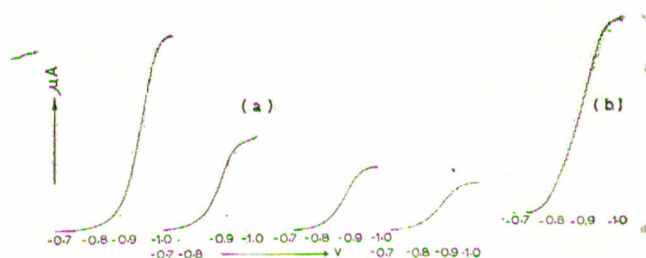

Fig. 3.—Polarograms of Ni++ showing (a) calibration curves of standard NiCl₂ solution; (b) after separation from Ni–Mn–Co++ at sensitivity 1/100 and damping 2.
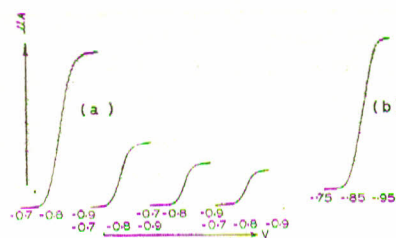

Fig. 4.—Polarograms of Mn++ showing (a) calibration curves of standard MnCl₂ solution; (b) after separation from Ni–Mn–Co++ at sensitivity 1/200 and damping 2.
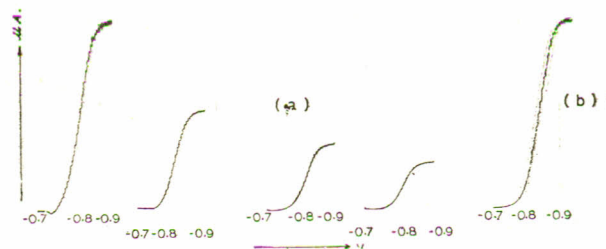

Fig. 5.—Polarograms of Co++ showing (a) calibration curves of standard MnCl₂ solution; (b) after separation from Ni++–Mn++–Co++ at sensitivity 1/100 and damping 2.
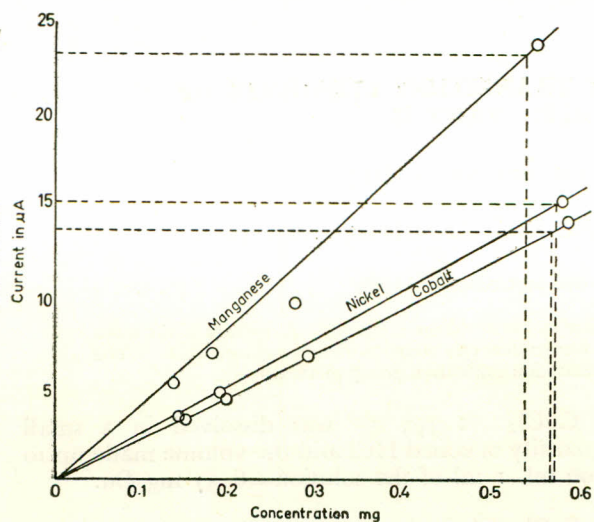
Fig. 6.—Calibration curves for Ni,$^{++}$ Mn^{++} and Co^{++}.

TABLE 3

Cation	Taken (mg)	Found (mg)	Eerror %
Ni^{++}	0.587	0.573	2.4
Mn^{++}	0.550	0.540	1.81
Co^{++}	0.5894	0.5720	2.9

Discussion

It has been mentioned earlier that distribution coefficients and adsorbabilities of cations are among the many factors responsible for bringing about their separations. Kraus and his coworkers[6] have measured the distribution coefficients of various elements from solutions containing different amounts of hydrochloric acid on a strongly basic anion exchange resin (Dowex 1 × 10) and plotted against hydrochloric acid concentration. From these investigations it is collected that certain cations (Al, alkali and alkaline earth metals) are not absorbed at all from solutions containing hydrochloric acid. There are ions like gold, mercury, silver and iridium which are strongly absorbed for which the distribution coefficient decreases with increasing hydrochloric acid concentration. There are still more ions like titanium, iron, cobalt, uranium and many others which show increase in distribution coefficient with increasing hydrochloric acid concentration. It can, therefore, be easily concluded from the very different behaviour of ions that they can be separated from each other on an anion exchange resin by using solutions of suitable hydrochloric acid concentration as eluting agent.

The separation of Ni, Mn and Co was based on the above observations and it could be seen from the polarograms that the separations were complete and that the eluate for each cation is free from any contamination.

Samuelson[7] has described a scheme of separation of different cations which may interfere with each other in a particular medium. From unknown solutions of, say, spent electrolytes, ore solutions or solutions obtained by dissolution of industrial wastes, metals and alloys, anions like phosphates, tungstates, oxalates and sulphates may interfere with the separation and quantitative determination of cations. These are, therefore, first removed by passing the solution under examination over a strongly acidic cation exchange resin which retains the cations, and the anions are collected in the effluent. The cations can be stripped off the column with hydrochloric acid and subjected to separation by using different eluants and more than one columns (strongly basic), if necessary.

The principles and procedures discussed above find wide applications in the analysis of industrial samples. Wilkins[8] has reported the separation of the constituents of alloy consisting of Al, Mn, Ni, Cr, Co, Fe, Ti, W, Mo and Ta on a strongly basic anion exchange resin using various eluants.

References

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