

Application of Cation Exchange for the Separation of Metals in Mixed Solvent Media

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Abstract

The use of ethanol and methanol separately in admixture with hydrochloric acid for the selective elution of cations on the ion-exchange resin Dowex 50 x 8-200 H⁺ form is investigated. The distribution co-efficient of metal ions were measured in ethanol-water-hydrochloric acid and methanol-water-hydrochloric acid mixtures. By applying distribution co-efficient data the metals from the mixtures have been separated one after another with different compositions of ethanol-water-hydrochloric acid and methanol-water-hydrochloric acid solutions. The average recovery for all separations was within 97%-99% and the standard deviation for all data was $\pm 2.5\%$. The developed analytical methodology can be applied for the separation and quantification of metal ions from natural water.

I. Introduction

Ion-exchange is one of the most important chromatographic techniques for the separation of metal ions¹⁻⁶. In recent years, the use of ion exchange for the removal and separation of metal ions is of wide interest due to its simplicity, elegance and range of variable experimental conditions⁷. Several previous works have been carried out by ion-exchange methods for the separation and determination of elements¹⁻⁸. F. W. E. Strelow⁹ separated the tetravalent rare earth metals and Scandium from Aluminium, Gallium, Indium, Thallium, Iron, Titanium, Uranium and other elements by cation exchange. A.G. Gaikwad and S.M. Khopker^[10] separated Lead from mixed solvents by cation exchanger. Moreover, Alam *et al.*¹¹⁻¹⁶ separated metal ions in acetone, isopropanol, ethylene glycol, 1, 4-Dioxan with cation exchange resin Zeocarb 225 and Dowex 50 x 8, 100-200 mesh.

F. W. E. Strelow and F. S. Von¹⁷ separated metal ions by anion exchange in mixed solvents. Santoyo *et al.*⁸ determined Lead, Copper, Cadmium, Cobalt, Zinc, Nickel ion in ground water using ionic separation column system including HPIC-CS2 of Dionex as cationic column, HPIC-AS4 of Dionex as anionic column and IonPac CS5 of Dionex as bifunctional ion-exchange column. Moreover, S. A. Nabi *et al.*⁷ separated Cu(II) and Zn(II) with modified Amberlite IR-400 anion exchange (Cl⁻ form) with nephthol blue-black. Recently Alam *et al.*¹⁸ started to work with anion exchange resin and separated few metals using formic acid. The information received from the thorough survey of literature shows that some work have been done on cation exchanger in H⁺ forms of Dowex, Dionex, Amberlite IRC 718 (Na⁺ form) and anion exchanger with modified Amberlite IR-400 (Cl⁻ form)⁷⁻¹⁶. There has been negligible report in the literature on any successful, complete separation and comparison of their separation efficiency of metal ions using cation-exchange resin in H⁺ form with ethanol-water-hydrochloric and methanol-water-hydrochloric admixture. Therefore, it would be interesting to develop a separation technique with cation-exchange resin which can completely separate metal ions from a mixture.

This work was undertaken in an attempt to develop a separation technique of metal ions using ethanol - hydrochloric acid-water and methanol-hydrochloric acid-water admixtures. For this purpose, strongly acidic cation-exchange resin of the type Dowex 50 x 8-200 H⁺ was employed. The metals investigated were chosen on the basis of their biological, environmental and industrial importance.

II. Experimental Apparatus

The spectrophotometric measurements were carried out with an UV-Visible recording spectrometer (160A Shimadzu, Japan) with 1 cm quartz cells.

Reagents and Materials

An air dried pretreated cation exchange resin (1.0 g) 'Dowex 50 x 8-200 H⁺ form, strongly acidic cation, 100-200 dry mesh size (Aldrich Chemical Co.) was used in the measurement of distribution co-efficient and column separations. The ion exchange capacity of 'Dowex 50 x 8-200 H⁺ was determined with following procedure reported elsewhere⁵ and the exchange capacity for Cu(II), Fe(II), Cr(III) and Pb(II) were found to be 2.2, 2.7, 2.5 and 4.2 meq g⁻¹ respectively. The EDTA, sodium thiosulphate and potassium dichromate solutions (0.05M, 0.01M and 0.01M respectively) from analytical grade reagent (E Merck) were prepared for the complexometric, iodometric and oxidation-reduction methods respectively¹⁹. These methods were applied for the determination of distribution co-efficient of metals in different ethanol/methanol-water-hydrochloric acid systems. Metal salts solutions (0.05M) were also prepared from analytical grade reagents. Each of the metal salt solution was standardized by appropriate complexometric, iodometric and oxidation-reduction method, using standard EDTA, sodium thiosulphate and potassium dichromate solutions. 1-2 mL of mineral acid was added to the metal solution to prevent hydrolysis. After separation of metals by ethanol-water-hydrochloric acid, the trace metals were analysed by UV-Visible Spectrophotometer^{19, 20}. All the aqueous solutions employed in this work were made with deionized water.

General Procedure for Metal Separation and Determination

An air dried pretreated cation exchange resin 'Dowex 50 x 8-200 H⁺' (1.0 g) was taken into a 100 mL glass stoppered bottle. To the bottle, metal salt solution (4mL, 0.05M) and appropriate amount of ethanol/methanol-water-hydrochloric acid mixture (50 mL) was added. The bottle was stoppered and shaken for 10 hours. A definite amount of aliquot from the supernatant was then withdrawn and after evaporation of the acid and organic solvent to dryness, the metal ion content was determined by an appropriate complexometric/iodometric/oxidation-reduction method¹⁹. The distribution coefficient on a dry weight basis was calculated with the following equation^{19, 20}.

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$$D = \frac{\text{(Amount of solute on resin/ Weight of the resin, gm)}}{\text{(Amount of solute in solution/Volume of solution, mL)}}$$

Depending on the distribution coefficient of the metal ions, the separation of the mixture into components was effected by varying the composition of the eluting agent. In this work, batch distribution co-efficient served as valuable guide in selecting conditions for column separations. The separated metals were analyzed at trace level by UV-Visible spectrophotometer²⁰.

III. Results and Discussion

Distribution co-efficient

The distribution co-efficient of all metal ions (Mn(II), Cu(II), Pb(II), Fe(III), Cr(III) & Al(III)) were studied in 0.5M hydrochloric acid. It was found that the distributions co-efficient of most of the metal ions were decreased with increasing percentage of ethanol and methanol in 0.5 M hydrochloric acid as shown in Table 1 and Table 2. The distribution co-efficient of Pb(II) was zero at 90% and 95% ethanol. However, the distribution co-efficient of Mn(II), Pb(II), Fe(II) and Al(III) were zero at 2.0 molarity of hydrochloric acid as shown in Table 3 and Table 4. The distribution co-efficient values of different metals in variable ethanol-water-formic acid medium were varied. However the variations were significant in various molar concentration of hydrochloric acid at 50% ethanol as shown in Table 3 and Table 4. This might be the presence of organic acid in the solvent would bring about some dissociation of the resin-cation complexes depending upon their relative affinities for the resin. Moreover, the cation produced by the dissociation would form in some cases complexes with ethanol whose movement down the column would be dependent upon the stability of the complexes with respect to both water and acid.

Separation of Mixtures

In ethanol–water–hydrochloric acid system a Pb(II)-Fe(III)-Cr(III) and two Al(III)-Mn(II)-Cu(II)-Cr(III), Pb(II)-Fe(III)-Cu(II)-Cr(III) four component synthetic mixtures have been successfully separated and analyzed quantitatively as shown in Table 5. Moreover, in methanol–water–hydrochloric acid system three Al(III)-Cu(II)-Pb(II), Al(III)-Fe(III)-Mn(II)-Cr(III), Al(III)-Pb(II)-Fe(II)-Cr(III) four component synthetic mixtures have been successfully separated and analyzed quantitatively as shown in Table 5. The average recovery for all separations (Table 3 & Table 4) was within 95.0-98.5% and the standard deviation for all data was $\pm 0.5\%$. UV-Visible Spectrophotometric methods were applied for the quantitative estimation of metals. In order to separate metals ions from the mixtures on cation exchange resin column, solvent composition and hydrochloric acid concentration were chosen such that metal would rapidly eluted from the column one after another. In this case, hydrochloric acid concentration was constant (0.5M) but the ethanol or methanol concentration was varied. From the Table 5, it was found that the separations using eluting agents were affected by distribution co-efficient data. The elution curves of the metals were represented in the Fig.1 and Fig. 2. However, a slight tailing was observed in the elution curve in the separation of Al, Fe, Mn and Cu the Fig. 1 & 2 respectively. Tailing can be reduced by decreasing the flow rate^{18, 20}. Moreover, a convenient balance between flow rate and the time required to elute a metal ion must be found. A normal flow rate of 0.2 mL to 0.3 mL per minute gives the most satisfactory result and this flow rate has been maintained in all measurements. Tailing can also be reduced by using finer mesh resin^{18, 20}, but this alternative type of resin has not been tried. Transformation from a partially non-aqueous elution medium to an aqueous medium and from aqueous medium to partially non-aqueous medium does not hinder the performance of the column.

Table. 1. Distribution co-efficient of metal ions in various percent concentrations of ethanol in 0.5 M hydrochloric acid.

Metal ions	% concentration of ethanol					
	30%	50%	70%	80%	90%	95%
Mn(II)	142.2	43.0	25.0	11.3	2.0	0
Cu(II)	87.0	52.0	47.0	38.2	12.3	0
Pb(II)	76.62	43.0	39.0	11.32	0	0
Fe(III)	156.0	86.0	50.1	16.0	11.6	6.0
Cr(III)	180.0	100.0	66.0	54.0	39.2	36.0
Al(III)	12.0	8.0	4.2	2.6	1.0	0

Table. 2. Distribution co-efficient of metal ions in various percent concentrations of methanol in 0.5 M hydrochloric acid.

Metal ions	% concentration of methanol					
	30%	50%	70%	80%	90%	95%
Mn(II)	76.2	44.0	27.6	11.5	2.0	0
Cu(II)	63.6	46.0	35.0	16.6	6.5	0
Pb(II)	54.8	43.0	30.0	24.3	11.3	0
Fe(III)	156.0	86.0	51.0	30.0	16.0	0
Cr(III)	171.0	100.2	81.0	65.0	44.2	23.2
Al(III)	10.0	6.0	4.2	0	0	0

Table. 3. Distribution co-efficient of metal ions in various molar concentrations of hydrochloric acid in 50% ethanol.

Metal ions	Molarity of hydrochloric acid				
	0.3M	0.5M	1.0M	1.5M	2.0M
Mn(II)	76.6	44.0	11.3	7.2	0
Cu(II)	87.0	52.0	42.2	31.0	6.5
Pb(II)	55.0	44.2	11.3	2.0	0
Fe(III)	86.0	81.0	29.2	16.0	0
Cr(III)	161.2	100.0	81.0	66.0	54.0
Al(III)	1.0	8.0	0	0	0

Table. 4. Distribution co-efficient of metal ions in various molar concentrations of hydrochloric acid in 50% methanol.

Metal ions	Molarity of hydrochloric acid				
	0.3M	0.5M	1.0M	1.5M	2.0M
Mn(II)	55.0	43.5	24.3	12.3	0
Cu(II)	43.0	30.0	24.4	0	0
Pb(II)	87.0	46.0	6.5	0	0
Fe(III)	107.2	85.0	21.0	10.0	0
Cr(II)	125.2	100.2	44.2	36.2	21.0
Al(III)	0	0	0	0	0

Table. 5. Separation and analysis of synthetic metal ion mixture on Dowex 50 x 8-200 H⁺ form, 100- 200 dry mesh (metals appear in the order of elution with the amount of wash solution included with the first eluted metal). Column dimension (12.5cmx1.5cm)

No.of series	Eluting agent	Taken (mg)	Found (mg)	Recovery%
1	Pb(II)-Fe(III)-Cr(III)			
	Pb(II): 90ml; 90% ethanol, 0.5M HCl	9.62	9.62	99.9
	Fe(III): 90 ml; 95% ethanol, 0.5M HCl	5.86	5.84	99.65
	Cr(III): 80 ml; Aqueous 3M HCl	4.52	4.51	99.77
2	Al(III)-Mn(II)-Cu(II)-Cr(III)			
	Al(III): 70 ml; 50% ethanol, 1.0 M HCl	2.67	2.66	99.6
	Mn(II): 80 ml; 50% ethanol, 2.0 M HCl	6.22	6.17	99.2
	Cu(II): 90 ml; 95% ethanol, 0.5M HCl	6.23	6.19	99.5
	Cr(III): 70 ml; Aqueous 3M HCl	4.52	4.52	100.0
3	Pb(II)-Fe(III)- Cu(II)- Cr(III)			
	Pb(II):90 ml; 90% ethanol, 0.5M HCl	9.6	9.6	99.0
	Fe(III):80 ml; 95% ethanol, 0.5M HCl	5.8	5.7	99.8
	Cu(II):90 ml; 50% ethanol, 2.5M HCl	6.2	6.1	99.2
	Cr(III): 80 ml; Aqueous 3M HCl	4.5	4.4	99.0
4	Al(III)- Cu(II)- Pb(II)- Cr(III)			
	Al(III):70 ml; 80% methanol, 0.5M HCl	2.6	2.6	99.9
	Cu(II):70 ml; 50% methanol, 0.5M HCl	6.2	6.1	99.0
	Pb(II):80 ml; 95% methanol, 0.5M HCl	9.6	9.6	99.4
	Cr(III):70 ml; Aqueous 3M HCl	4.5	4.4	98.0

5	Al(III)- Fe(III)- Mn(II)- Cr(III)			
	Al(III):70 ml; 80% methanol, 0.5M HCl	2.6	2.6	99.0
	Fe(III):90 ml; 95% methanol, 0.5M HCl	5.8	5.8	99.0
	Mn(II):80 ml; 95% methanol, 0.5M HCl	6.2	6.1	99.0
	Cr(III):80 ml; Aqueous 3M HCl	4.5	4.4	98.0
6	Al(III)- Pb(II)- Fe(II)- Cr(III)			
	Al(III):80 ml; 80% methanol, 0.5M HCl	2.6	2.6	99.0
	Pb(II):80 ml; 50% methanol, 1.5M HCl	9.6	9.6	99.0
	Fe(III):80 ml; 95% methanol, 0.5M HCl	5.8	5.8	99.0
	Cr(III):70 ml; Aqueous 3M HCl	4.5	4.5	99.5

Application

Sample water was collected from Shadarghat point of the river Buriganga. In the preconcentration studies, one litre of filtered sample water was passed through the resin column at a flow rate of 0.20-0.30/min. The respective eluting agent for Fe(II), Cu(II) and Cr(III) were passed through the column and effluents were collected for each of the above

metal. The fractions of effluent for Fe(III), Cu(II) and Cr(III) were diluted and treated with respective coloring agents and were determined with UV- Visible spectrophotometer^{19, 20}. Thus the amount of Fe(II), Cu(II) and Cr(III) in surface water of Buriganga river have been determined.

Table. 6. Separation and analysis of surface water of the river Buriganga

Location	Eluting agent	Method	Found $\mu\text{g/L}$
Buriganga river at Shadarghat point	<u>Ethanol-water-HCl admixture system</u> Al(III): 70 ml; 50% ethanol, 1.0 M HCl Mn(II): 80 ml; 50% ethanol, 2.0 M HCl Cu(II): 90 ml; 95% ethanol, 0.5 M HCl Cr(III): 70 ml; Aqueous 3M HCl	UV-Visible	1.5
		UV-Visible	2.8
		UV-Visible	4.2
		UV-Visible	6.3
Buriganga river at Shadarghat point	<u>Methanol-water-HCl admixture system</u> Al(III)- Fe(II)- Mn(II)- Cr(III) Al(III):70 ml; 80% methanol, 0.5M HCl Fe(III):90 ml; 95% methanol, 0.5M HCl Mn(II):80 ml; 95% methanol, 0.5M HCl Cr(III):80 ml; Aqueous 3M HCl	UV-Visible	1.3
		UV-Visible	5.1
		UV-Visible	2.7
		UV-Visible	6.5

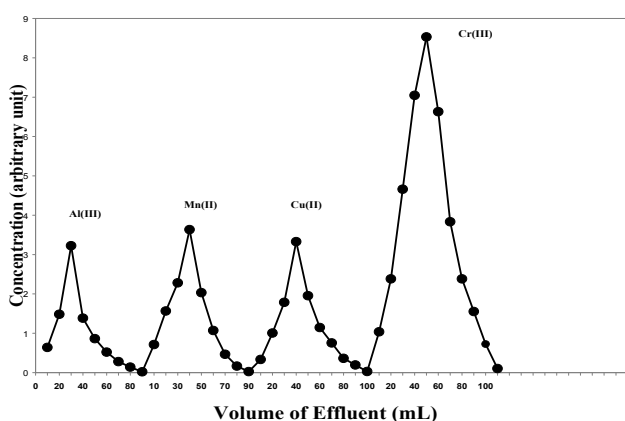


Fig. 1. Elution curve for Al(III)-Mn(II)-Cu(II)-Cr(III) in ethanol- water - hydrochloric acid system.

Eluting agent: Al(III): 70 ml; 50% ethanol, 1.0 M HCl
Mn(II): 80 ml; 50% ethanol, 2.0 M HCl
Cu(II): 90 ml; 95% ethanol, 0.5M HCl
Cr(III): 70 ml; Aqueous 3M HCl

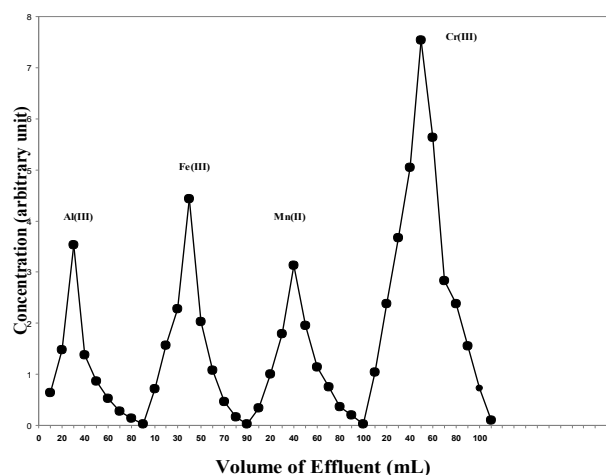


Fig. 2. Elution curve for Al(III)-Fe(III)-Mn(II)-Cr(III) in methanol- water - HCl system.

Eluting agent: Al(III):70 ml; 80% methanol, 0.5M HCl
Fe(III):90 ml; 95% methanol, 0.5M HCl
Mn(II):80 ml; 95% methanol, 0.5M HCl
Cr(III):80 ml; Aqueous 3M HCl

IV. Separation Mechanism

The separation of metal ions as halogen complexes by elution from a cation exchange column with an aqueous hydrochloric acid solution is now an established technique. It has been shown that the metal ions are taken up more strongly at lower hydrochloric acid concentration by cation exchange resin if appreciable amount of water miscible organic solvent is added to the aqueous hydrochloric acid¹⁰. Hydrochloric acid is a strong acid. It exchanges the metal ions which are already absorbed on the resin surface. Each metal is absorbed over a well defined range of pH and this property was used as the basis of a method of separation. Those metals, which do not absorb or exchange H⁺ on the resin surfaces, are not retained by the resin²⁻³. Generally, the resin prefers to a polar solvent than a less polar one. The ethanol and methanol are polar solvents. Water, however, is by no means the only solvent, which allows ion-exchange to take place. The combination of two polar solvents with hydrochloric acid helps to separate metals from the metals mixture.

V. Conclusion

The important achievement of this piece of work is the separation and quantitative determination of Al(III)-Mn(II)-Cu(II)-Cr(III), Pb(II)-Fe(III)-Cu(II)-Cr(III) and Al(III)-Fe(III)-Mn(II)-Cr(III) with selective elution from a cation exchanger followed by spectrophotometric methods at trace level. Cr(III)-Cu(II) and Mn(II)-Cr(III) could not be separated in acetone-water-hydrochloric acid system, ethylene glycol -water-hydrochloric acid system and 2-propanol -water-hydrochloric acid system on cation exchanger. The above system can easily be separated in ethanol-water-hydrochloric acid and methanol-water-hydrochloric acid system on cation exchanger due to the different polarity and physical properties of ethanol and methanol.

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