

## Application of Anion Exchange for the Separation of Metals in 1,4-Dioxan- Water- Formic Acid Medium

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### Abstract

The use of 1,4-Dioxan in admixture with formic acid for the selective elution of cations on the anion-exchange resin Dowex 1x 8 in Cl<sup>-</sup> form is investigated. The elution technique was coupled with UV-Visible spectrophotometry and AAS. The distribution co-efficient of metal ions were measured in 1, 4-Dioxan-water-formic acid mixture. By applying distribution co-efficient data, the metals from the mixtures have been separated one after another with different compositions of 1,4-Dioxan-water-formic acid solution. The average recovery for all separations (n =26) were within 95.05%-99.04% and the standard deviation for all data was  $\pm 0.73\%$ . The developed analytical methodology was successfully applied for the separation and quantification of metal ions in the microgram range from the real samples collecting from natural water using UV-Visible and AAS technique.

### I. Introduction

Ion-exchange is one of the most important chromatographic techniques for the separation of metal ions [1-6]. In recent years, the use of anion exchange for the removal and separation of metal ions is of wide interest due to its simplicity, elegance and range of variable experimental conditions [7]. Several previous works have been carried out by ion-exchange methods for the separation and determination of elements in milligram level [1-8]. F. W. E. Strelow [9] 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 ethanol, methanol, 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. Von [17] 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<sup>-</sup> 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<sup>+</sup> forms of Dowex, Dionex, Amberlite IRC 718 (Na<sup>+</sup> form) and anion exchanger with modified Amberlite IR-400 (Cl<sup>-</sup> form) [7-16]. To our knowledge, there has been no report in the literature on any successful and complete separation of metal ions using anion-exchange resin in Cl<sup>-</sup> form, strongly basic anion, 100-200 dry mesh with Dioxan as organic solvent. Therefore, it would be interesting to develop a separation technique with anion-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 Dioxan admixture with formic acid and water. For this purpose, strongly basic anion-exchange resin of the type Dowex (1x 8) in Cl<sup>-</sup> 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 and some samples were also analyzed by atomic absorption spectrophotometer(model AA -680 Shimadzu, Japan).

### Reagents and Materials

An air dried pretreated anion exchange resin (1.0 g) 'Dowex (1x 8)', chloride form, strongly basic anion, 8% cross-linking, 0.30–1.2 mm particle size, 14–52 dry mesh, (BDH Laboratory Supplies, England) was used in the measurement of distribution co-efficient and column separations. The ion exchange capacity of 'Dowex'-1-Chloride was determined following the procedure reported elsewhere [5] and the exchange capacity for Ca(II), Fe(II), Ni(II) and Pb(II) were found to be 2.3, 2.7, 2.6 and 4.2 meq g<sup>-1</sup> 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 respectively [19]. These methods were applied for the determination of distribution co-efficient of metals in different dioxan-water-formic 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 dioxan-water-formic acid the trace metals were analysed by UV-Visible and Atomic Absorption Spectrophotometric methods [21]. All the aqueous solutions employed in this work were made with deionized water.

### General Procedure for Metals Separation and Determination

An air dried pretreated anion exchange resin 'Dowex-1-Chloride' (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 Dioxane–water-formic

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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 method [19]. The distribution coefficient on a dry weight basis was calculated with the following equation [19].

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

Depending on the values of 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 absorption spectrophotometry and atomic absorption spectrophotometry.

### III. Results and Discussion

#### Distribution co-efficient

The distribution co-efficient of all metal ions were studied in 0.5M formic acid. It was found that the distribution co-efficient of most of the metal ions were increased with increasing percentage of Dioxan in 0.5 M formic acid as shown in Table-1. The distribution co-efficient of Mn(II), Ni(II), Co(II) and Al(III) were zero at all concentrations of formic acid presented in Table-2. However, the distribution co-efficient of Zn(II), Fe(III), Cd(II) and Cr(III) were increased with increasing of molarity of formic acid. The distribution co-efficient values of different metals in variable Dioxan-water-formic acid medium were varied. However the variations were significant in various molar concentrations of formic acid at 50% 1,4-Dioxan as shown in Table-2. This might be the presence of organic acid in the solvent would bring about some dissociation of the resin-anion complexes depending upon their relative affinities for the resin. Moreover, the cation produced by the dissociation would form in some case complexes with Dioxan 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 Dioxan–water–formic acid system a four component mixture Cr(III)-Ni(II)-Fe(III)-Zn(II), Co(II)-Ni(II)-Cr(III)-Cu(II), Mn(II)-Ni(II)- Pb(II)- Zn(II), Co(II)- Ni(II)- Fe(III)- Zn(II) and five Cr(III)- Co(II)- Cu(II)-Fe(III)-Zn(II) and Cr(III)-Mn(II)-Ni(II)-Fe(III)-Zn(II) synthetic mixtures have been successfully separated and analyzed quantitatively as shown in Table-3. Atomic Absorption Spectrophotometric and UV-Visible Spectrophotometric methods were applied for the quantitative estimation of (Cu, Mn, Zn, Pb & Co) and (for Cr, Ni & Fe) respectively. In order to separate metal ions from the mixtures on an anion exchange resin column, solvent composition and formic acid concentration were chosen such that metals would rapidly eluted from the column one after another. In this case, formic acid concentration was constant (0.5M) but the dioxan concentration was varied. From the Table-3 it was found that the separations using eluting agents were affected by distribution co-efficient data.

Synthetic metal ion mixtures Co(II)-Ni(II)-Cr(III)-Cu(II), Cr(III)-Co(II)-Cu(II)-Fe(III)-Zn(II) and Cr(III)-Mn(II)-Ni(II)-Fe(III)-Zn(II) were again prepared for the separation and recovery experiment with variation of the molarity of formic acid and analysed with Atomic Absorption (Cu, Mn, Zn & Co) and UV-Visible Spectrophotometric (Cr, Ni & Fe) method as presented in Table-4. The average recoveries for all separations (Table-3 & Table-4) were within 95.0-98.5% and the standard deviation for all data was  $\pm 0.8\%$ .

However, a slight tailing was observed in the elution curve in the separation of Cr, Mn, Ni, Fe and Zn as shown in Fig.1. 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 1,4 - Dioxan in 0.5 M formic acid.**

Metal ions	% concentration of 1,4 – Dioxan					
	30	50	70	80	90	95
Cu(II)	0	0	0	36.2	75.9	132.6
Zn(II)	0	50.7	612.2	941.6	1276.8	1940.0
Mn(II)	0	0	0	0	37.8	118.4
Fe(III)	0	2.1	190.5	596.6	926.0	1901.5
Ni(II)	0	0	3.5	33.7	129.2	1325.6
Pb(II)	0	0	66.0	337.67	926.0	1905.7
Co(II)	0	0	0	0	52.1	231.3
Cd(II)	65.1	272.2	599.6	925.3	1910.6	1912.0
Al(III)	0	0	0	0	0	0
Cr(III)	0	2.9	79.0	183.25	12.1	0

**Table. 2. Distribution co-efficient of metal ions in various molar concentrations of formic acid in 50% 1,4-Dioxan.**

Metal ions	Molarity of formic acid					
	0. 5M	1. 0M	1. 5M	2. 0M	2. 5M	3. 0M
Cu(II)	0	0	0	0	14.5	48.5
Zn(II)	50.7	63.2	71.0	88.7	112.7	146.0
Mn(II)	0	0	0	0	0	0
Fe(III)	2.1	7.2	9.2	11.3	3.6	0
Ni(II)	0	0	0	0	0	0
Pb(II)	0	24.4	35.1	39.3	49.2	54.8
Co(II)	0	0	0	0	0	0
Cd(II)	272.2	419.8	637.6	796.8	924.6	1921.5
Al(III)	0	0	0	0	0	0
Cr(III)	3.0	68.6	116.5	121.6	129.4	147.2

**Table. 3. Separation and analysis of synthetic metal ion mixture on Dowex 1X8 in Cl<sup>-</sup> 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)**

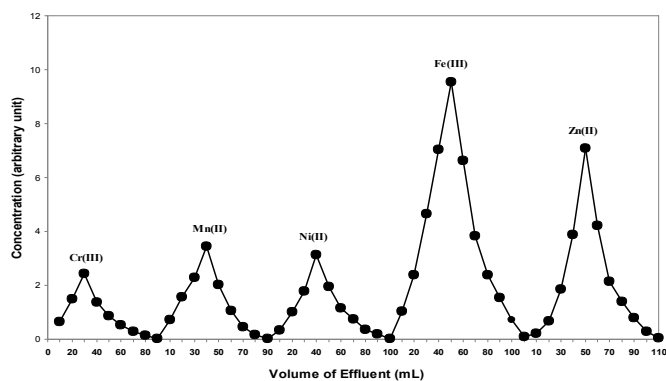
No.of series	Eluting agent	Taken (mg)	Found (mg)	Recovery%
1	Cr(III)-Ni(II)-Fe(III)- Zn(II)			
	Cr(III): 90mL; 95% 1,4 - Dioxan, 0.5M HCOOH	15.9	15.5	97.0
	Ni (II): 70 mL; 70% 1,4 - Dioxan, 0.5M HCOOH	12.0	11.6	96.2
	Fe(III):80 mL; 50% 1,4 – Dioxan, 3M HCOOH	11.1	11.0	97.9
	Zn(II): 80 mL; 30% 1,4 - Dioxan, 0.5M HCOOH	13.5	13.2	97.4
2	Co(II)-Ni(II)-Cr(III)-Cu(II)			
	Co(II): 70 mL; 80% 1,4 - Dioxan, 0.5M HCOOH	12.0	11.6	97.2
	Ni(II): 80 mL; 50% 1,4 - Dioxan, 3M HCOOH	12.0	12.0	98.5
	Cr(III):80 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	16.0	15.7	98.4
	Cu(II): 80 mL; 50% 1,4 - Dioxan, 0.5M HCOOH	13.3	13.0	97.5
3	Mn(II)-Ni(II)- Pb(II)- Zn(II)			
	Mn(II):80 mL; 80% 1,4 - Dioxan, 0.5M HCOOH	11.5	11.1	96.1
	Ni(II):70 mL; 50% 1,4 - Dioxan, 1.5M HCOOH	12.0	11.7	97.0
	Pb(II):90 mL; 50%1,4 - Dioxan, 0.5M HCOOH	45.4	43.7	96.3
	Zn(II): 80 mL; 30% 1,4 - Dioxan, 0.5M HCOOH	13.5	13.2	97.5
4	Co(II)- Ni(II)- Fe(III)- Zn(II)			
	Co(II):70 mL; 80% 1,4 - Dioxan, 0.5M HCOOH	12.0	11.4	96.2
	Ni(II):70 mL; 70% 1,4 - Dioxan, 0.5M HCOOH	12.0	11.4	95.1
	Fe(III):80 mL; 50% 1,4 - Dioxan, 3M HCOOH	11.1	10.8	97.4
	Zn(II):80 mL; 30% 1,4 - Dioxan, 0.5M HCOOH	13.5	13.3	98.0
5	Cr(III)- Co(II)- Cu(II)- Fe(III)- Zn(II)			
	Cr(III):90 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	15.9	15.5	96.1
	Co(II):80 mL; 80% 1,4 - Dioxan, 0.5M HCOOH	12.0	11.3	97.1
	Cu(II):80 mL; 70% 1,4 - Dioxan, 0.5M HCOOH	13.1	13.0	98.1
	Fe(III):80 mL; 50% 1,4 - Dioxan, 3M HCOOH	11.1	10.8	98.4
Zn(II): 80 mL; 30% 1,4 - Dioxan, 0.5M HCOOH	13.5	13.0	97.0	
6	Cr(III)- Mn(II)- Ni(II)- Fe(III)- Zn(II)			
	Cr(III):70 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	15.9	15.3	96.0
	Mn(II):80 mL;80% 1,4 – Dioxan, 0.5M HCOOH	11.5	11.2	97.1
	Ni(II):80 mL; 70% 1,4 – Dioxan, 0.5M HCOOH	12.0	11.8	98.0
	Fe(III):80 mL; 50% 1,4 – Dioxan, 3M HCOOH	11.1	10.9	98.4
Zn(II):70 mL; 30% 1,4 – Dioxan, 0.5M HCOOH	13.5	13.1	97.0	

**Table. 4. Separation and recovery of synthetic metal ion mixtures on Dowex 1X8 by visible spectrophotometric and atomic absorption spectrophotometric techniques. Metals appear in the order of elution with the amount of wash solution included with the first eluted metal. Column dimension 2.5 cm X 0.74 cm**

No. of series	Eluting agent	Taken (mg)	Found (mg)	Recovery%
1	Co(II)- Ni(II)-Cr(III)- Cu(II)			
	Co(II): 70 mL; 80% 1,4 - Dioxan, 0.5M HCOOH	26.9	26.5	98.3
	Ni(II): 80 mL; 50% 1,4 – Dioxan, 3M HCOOH	29.9	29.4	98.4
	Cr(III):80 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	90.1	89.2	99.0
	Cu(II): 80 mL; 50% 1,4 - Dioxan, 0.5M HCOOH	30.1	29.5	97.8
2	Cr(III)- Co(II)- Cu(II)- Fe(III)- Zn(II)			
	Cr(III):90 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	75.1	73.5	98.0
	Co(II):80 mL; 80% 1,4 – Dioxan, 0.5M HCOOH	27.0	26.3	97.7
	Cu(II):80 mL; 70% 1,4 – Dioxan, 0.5M HCOOH	40.1	39.6	98.7
	Fe(III):80 mL; 50% 1,4 - Dioxan, 3M HCOOH	40.0	39.0	97.3
	Zn(II): 80 mL; 30% 1,4 - Dioxan, 0.5M HCOOH	17.6	17.4	99.0
3	Cr(III)- Mn(II)- Ni(II)- Fe(III)- Zn(II)			
	Cr(III):70 mL; 95% 1,4 - Dioxan, 0.5M HCOOH	90.1	88.5	98.2
	Mn(II):80 mL;80% 1,4 – Dioxan, 0.5M HCOOH	28.0	27.3	99.0
	Ni(II):80 mL; 70% 1,4 – Dioxan, 0.5M HCOOH	30.0	29.2	98.0
	Fe(III):80 mL; 50% 1,4 - Dioxan, 3M HCOOH	50.0	49.3	99.0
	Zn(II):70 mL; 30% 1,4 – Dioxan, 0.5M HCOOH	18.0	17.3	99.0

### 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. The respective eluting agent for Cr(III), Mn(II), Ni(II), Fe(III) and Zn(II) were passed through the column and effluents were collected for each of the above metal. The fractions of effluent for Cr(III), Ni(II) and Fe(II) were diluted and treated with respective coloring agents and were determined with UV- Visible spectrophotometer where Mn(II) and Zn(II) were determined by AAS. Thus the amount of Cr(III), Mn(II), Ni(II),Fe(III) and Zn(II) in surface water of the Buriganga river have been determined.



**Fig. 1 . Elution curve for Cr(III)–Mn(II)–Ni(II)–Fe(III)–Zn(II) in 1,4-Dioxan– water – formic acid system.**

Eluting agent for Cr(III): 95% Dioxan; Mn(II): 80% Dioxan; Ni(II): 70% Dioxan; Fe(III):50% Dioxan; Zn(II): 30% Dioxan in 0.5M formic acid.

### 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 anion exchange resin if appreciable amount of water miscible organic solvent is added to the aqueous hydrochloric acid [10]. Formic acid is the strongest acid among all the members of homologous series of organic acids. It forms negatively charged formate complexes with metals. The negative formate complex exchanged with anion-exchanger and strongly retained in the resin bed. 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 form complexes, are not retained by the resin, because the resin is anionic form [2-3]. Generally, the resin prefers to a polar solvent to a less polar one. The 1,4-Dioxan is polar solvent. Water, however, is by no means the only solvent, which allows ion-exchange to take place. The combination of two polar solvents with formic acid helps to separate metals from the metals mixture.

**Table. 5. Separation and analysis of surface water of the river Buriganga**

Location	Eluting agent	Method	Found µg/L
Buriganga river at Shadarghat point	Cr(III)- Mn(II)- Ni(II)- Fe(III)- Zn(II)		
	Cr(III):70 mL; 95% 1,4 – Dioxan, 0.5M HCOOH	UV-Visible	1.5
	Mn(II):80 mL;80% 1,4 – Dioxan, 0.5M HCOOH	AAS	0.8
	Ni(II):80 mL; 70% 1,4 – Dioxan, 0.5M HCOOH	UV-Visible	4.6
	Fe(III):80 mL; 50% 1,4 – Dioxan, 3M HCOOH	UV-Visible	6.3
Zn(II):70 mL; 30% 1,4 – Dioxan, 0.5M HCOOH	AAS	2.8	

#### IV. Conclusion

The outstanding achievement of this piece of work is the separation and quantitative determination of Co(II)-Ni(II)-Cr(III)-Cu(II), Cr(III)-Co(II)-Cu(II)-Fe(III)-Zn(II) and Cr(III)-Mn(II)-Ni(II)-Fe(III)-Zn(II) with selective elution from an anion exchanger followed by spectrophotometric methods at trace level. Cr(III)-Zn(II) and Co(II)-Cr(III) could not be separated in absolute alcohol-water-formic acid system, ethylene glycol -water-formic acid system and 2-propanol -water-formic acid system on anion exchanger. The above system can easily be separated in 1,4-Dioxan-water-formic acid system on anion exchanger due to the different polarity and physical properties of 1,4-Dioxan.

- Nabi S. A, K. N. Sheeba and M. A. Khan, 2005, *Acta Chromatographica*, 15, 206.
- Nabi S. A., A. M. T, Khan, 2002, *Acta Chromatographica*, 12,129.
- Nabi, S. A, E. Laiq and A. Islam, 2001, *Acta Chromatographica*, 11, 118.
- Nabi S. A, M. A. Khan and A. Islam, 2001, *Acta Chromatographica*, 11, 130.
- Agrawal A, K. K. Shaha, 2006, *J. Hazard. Mat. B* 133, 299.
- Atia A. A, A. M. Donia and K. Z. Elwakeel, .2005, *ReactFunct. Polym.* 65, 267.

- Nabi S. A., M. Naushad and A. M. Khan, 2006, *Collod. Surf. A: Physicochem. Eng. Aspects*, 280.
- Santoyo E, S. S. Gutierrez and P. V. Surendra, 2000, *J. Chromatogr. A*, 88 229.
- Strelow F.W.E., 1966, *Analytical Chem. Acta.* **34(4)** 387-393.
- Gaikwad A. G, Khopker S. M., 1985, *J. Liq. Chromatograph.*, **8(14)** 2706-2718.
- Alam A. M. S., M. S. T. Bhuyan, 1983 *J. Bangladesh Acad. Sci.*, 7, 75.
- Alam A. M. S, Bhuyan, 1984, *J., Dhaka Uni. Stud.*, **32(2)**, 9.
- Alam A. M. S., A. N. M. E. Haq, S. A. Tarafdar and A. H. Khan, 1984, *J. Bangladesh Acad. Sci.*, **10(1)**, 5-12.
- Alam A. M. S., S. P. Paul, 1988, *J. Bangladesh Chem. Soci.*, **1(2)**, 127-133.
- Alam A. M. S., B. Roy, 1989, *J. Bangladesh Acad. Sci.*, **13(1)**,49-54.
- Alam A. M. S., A.K.M.A Hossain, M. A. Quyser, and A. Etmna, 1993, *J. Bangladesh Acad. Sci.*, **6(23)**, 161-166.
- Strelow F.W.E, Von F. S, 1966, *Analyst*, **38(4)**, 545-548.
- Alam A. M. S, S. Parvin and M. A. Quyser, 2000, *Chem. Environ. Res (India)*, **9(1&2)**, 17-23.
- Vogel A. I, 1978, *A Text Book of Quantitative Inorganic Analysis*, 4th edition, E.L.B.S. Longmans. pp. 173, 309, 433-436, 441-447.
- Shaibal I. A. M., F. Khanom, M. A. Rahman, A. M. S. Alam, 2005. *Pak. J. Anal. Chem.*, 6, 35-41.