

## Application of Anion Exchange Resin for the Separation of Metals in Tert-butyl Alcohol - Water-Formic Acid Medium

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### Abstract

The use of tertiary butyl alcohol in admixture with formic acid for the selective elution of cations on the ion exchange resin Amberlite IRA-420 in Cl<sup>-</sup> form is investigated. The elution technique was coupled with absorption spectrometry and atomic absorption spectrophotometry. The distribution coefficients of metal ions were measured in tertiary butyl alcohol -water-formic acid mixture. By applying distribution co-efficient data, the metals from the mixtures have been separated one after another by eluting with tertiary butyl alcohol-water-formic acid solution of different compositions. The average recovery for all separations (n = 18) was within 94.6 – 98.2 % and the standard deviation for all data was  $\pm 0.96$ . 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 and industrial effluents using UV-Visible and AAS techniques.

### I. Introduction

Ion-exchange is one of the most important chromatographic techniques for the separation of metal ions<sup>1-6</sup>. 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<sup>7</sup>. Several previous works were done by ion-exchange for separation and determination of the elements in milligram level<sup>1-8</sup>. F. W. E. Strelow<sup>9</sup> separated the tetravalent rare earth metals and Scandium from Aluminium, Gallium, Indium, Thallium, Iron, Titanium, Uranium and other elements by cation exchanger. A. G. Gaikwad and S. M. Khopker<sup>10</sup> separated Lead from mixed solvents by cation exchanger. Moreover, Alam *et al.*<sup>11-16</sup> 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<sup>17</sup> separated metal ions by anion exchange resin in mixed solvents. Santoyo *et al.*<sup>8</sup> determined Lead, Copper, Cadmium, Cobalt, Zinc, and Nickel 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.*<sup>7</sup> separated Cu (II) and Zn (II) with modified Amberlite IR-400 anion exchange resin (Cl<sup>-</sup> form) with naphthol blue-black. Recently Alam *et al.*<sup>18</sup> have started to work with anion exchange resin and separated few metals using formic acid.

This work was undertaken in an attempt to develop a separation technique of metal ions using tert-butyl alcohol admixture with formic acid and water and strongly basic anion-exchange resin of the type Dowex (1 x 8) in Cl<sup>-</sup> form was chosen. The metals were chosen on the basis of their

biological, environmental and industrial importance. The concentration of formic acid was so chosen that the metals remained as anionic complex.

### 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) 'Amberlite IRA-420', chloride form, strongly basic anion, 8% cross-linking, 0.30–1.2 mm particle size, 14–52 dry mesh, (BDH, England) was used in the measurement of distribution co-efficients and column separations. The ion exchange capacity of 'Amberlite IRA-420'-1-Chloride was determined following the procedure reported elsewhere<sup>5</sup> and the exchange capacity for Ca(II), Fe(II), Ni(II) and Pb(II) in tert-butyl alcohol-formic acid mixtures were found to be 2.6, 2.9 and 2.5 meq g<sup>-1</sup> respectively. The EDTA, sodium thiosulphate and potassium dichromate solutions (0.05 M, 0.01 M and 0.01 M respectively) from analytical grade reagent (E Merck) were prepared for the complexometric, iodometric and oxidation-reduction methods respectively<sup>19</sup>. These methods were applied for the determination of distribution co-efficient of metals in different acetone-water-formic acid systems. Metal salts solutions (0.05 M) 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 respectively. 1-2 mL of

mineral acid was added to the metal solution to prevent hydrolysis. After separation of metals by acetone-water-formic acid the trace metals were analysed by UV-Visible and Atomic Absorption Spectrophotometric methods<sup>21</sup>. The calibration curves for the analysis of metals by AAS and UV-Visible Spectrophotometric methods were presented in Fig. 1 and Fig. 2. All the aqueous solutions employed in this work were made with deionized water.

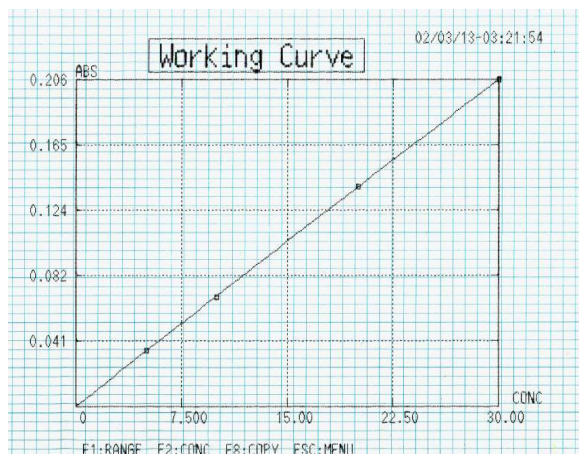


Fig. 1. Calibration curve of AAS

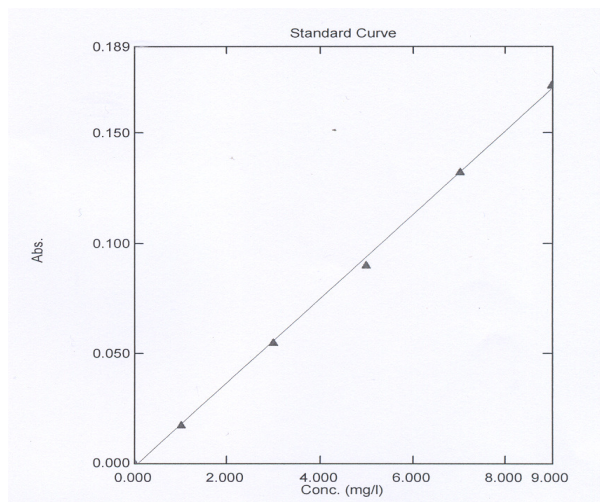


Fig. 2. Calibration curve of UV-Visible Spectrophotometer

### General procedure for metal separation and determination

An air dried pretreated anion exchange resin ‘Amberlite IRA-420’ (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 tert-butyl alcohol–water–formic 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. The distribution coefficient (D) on a dry weight basis was calculated with the following equation<sup>19</sup>.

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

Depending on the distribution coefficients 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 a valuable guide in selecting conditions for column separations. The separated metals were analyzed at trace level by absorption spectrophotometry and atomic absorption spectrometry.

## III. Results and Discussion

### Distribution Coefficient

The distribution co-efficients of all metal ions were increased with increasing percentage of tertiary butyl alcohol in 0.5M formic acid as shown in the Table 1. The distribution co-efficient of Mn(II) had the value zero at 50% tertiary butyl alcohol and were increased with increasing percentage of tertiary butyl alcohol. At 50% tertiary butyl alcohol the distribution co-efficient of Ni(II), Zn(II), Fe(II) and Co(II) were very low. The distribution co-efficient of Cd(II) were high at all percentages of tertiary butyl alcohol except 20%. So this eluting condition was chosen for the separation of Cd(II) ion. On the other hand, the distribution co-efficient of Co(II) were very low compared to other metal ions at all percentage of tertiary butyl alcohol.

The distribution co-efficients of the metal ions Cu(II), Ni(II), Zn(II), Pb(II) and Fe(III) were gradually decreased with higher acid concentration at 50% tert-butanol as shown in Table 2. Whereas the distribution co-efficients of Cd(II) was gradually increased with the higher concentration of formic acid at 50% tert-butanol. On the other hand, the distribution co-efficient of Mn(II) were zero in 50% tert-butanol at all molar concentrations of formic acid. For Co(II) the distribution co-efficient was very low at 0.5M formic acid and the values are about zero from 2.0M to all the next higher molar concentrations of formic acid. The distribution co-efficient of Cu(II) were very low at 2.0M and 2.5M formic acid and zero at 3.0M formic acid. The values of distribution co-efficient of Cd(II) and Pb(II) were always high at 50% tert-butanol.

**Table. 1. Distribution co-efficient of metal ions in various percent concentrations of tertiary butyl alcohol at 0.5M formic acid.**

Metal ions	% Concentration of tertiary butyl alcohol						
	20%	30%	50%	70%	80%	90%	95%
Cu(II)	-	-	5.16	9.51	20.09	39.06	128.02
Mn(II)	-	-	0.00	3.15	24.60	105.98	181.46
Ni(II)	-	-	3.15	6.6	16.20	26.04	106.09
Co(II)	-	-	2.30	12.63	18.0	43.52	80.0
Pb(II)	-	-	34.89	94.11	145.98	279.46	346.27
Fe(III)	-	-	4.59	17.89	44.07	149.77	215.27
Sn(II)	-	-	24.07	41.23	57.11	127.83	168.56
Zn(II)	-	-	1.29	35.08	213.28	674.98	1282.48
Cd(II)	9.48	20.06	60.23	99.85	212.79	327.62	612.96

**Table. 2. Distribution co-efficient of metal ions in various molar concentrations of formic acid at 50% tert- butanol.**

Metal ions	% Concentration of tertiary butyl alcohol					
	0.5M	1.0M	1.5M	2.0M	2.5M	3.0M
Cu(II)	5.16	2.35	1.57	0.81	0.07	0.00
Ni(II)	3.15	2.34	1.54	0.78	0.0	0.0
Mn(II)	0.00	0.00	0.00	0.00	0.00	0.00
Zn(II)	1.29	1.29	0.91	0.17	0.00	0.00
Sn(II)	24.07	22.93	20.0	16.18	10.51	3.14
Co(II)	2.30	1.51	0.75	0.01	0.01	0.00
Pb(II)	34.89	32.95	29.31	24.42	14.64	3.14
Fe(III)	2.68	2.31	1.59	1.23	1.23	0.14
Cd(II)	60.23	63.74	71.0	79.39	91.40	99.85

### Separation of Mixtures

In tertiary butyl alcohol-water-formic acid mixture, two four component mixture of [Mn(II)-Cu(II)-Sn(II)-Cd(II), [Mn(II)-Cu(II)-Pb(II)-Cd(II)] and two five component mixture of [Mn(II)-Cu(II)-Sn(II)-Pb(II)-Cd(II), Zn(II)-Cu(II)-Sn(II)-Pb(II)-Cd(II)] have been prepared, successfully separated and analyzed quantitatively as shown in Table 3. The average recovery for all separations (n=18) was within 94.6 – 98.2 % and the standard deviation for all data was  $\pm 0.96$ . The individual metal ion was determined quantitatively by complexometric methods. Here the concentration was in mg level. It was found that the separations using eluting agents were affected by distribution co-efficient data. 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 the species containing metal would rapidly eluted from the column one after another.

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 and industrial effluents using UV-Visible and AAS techniques. The elution curve of five component mixtures was shown in (Fig. 1).

Separation of more than five component mixture was not possible in the present work, as the separation of the mixture Zn(II)-Mn(II), Co(II)-Ni(II), Cu(II)-Fe(III), could not be worked out, because they have almost the same values of distribution co-efficient at most eluting conditions.

Slight tailing is observed in the elution of Pb(II) and Cd(II). Tailing can be reduced by decreasing the flow rate. However, 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 instruments. Tailing can also be reduced by using finer mesh resin<sup>18, 20</sup>, 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. 3. Separation and recovery of synthetic metal ion mixtures on Amberlite IRA-420 in Cl<sup>-</sup> form, 14 – 52 dry mash (metal appears in the order of elution with the amount of wash solution included with the first eluted metal) and analysis with suitable complexometric method. Column dimension: 22.0 cm X 0.74 cm (Resin 6.0g)**

No of series	Eluting agent	Taken mg	Found mg	Recovery %
1	<b>Mn(II)–Cu(II)–Sn(II)–Cd(II)</b>			
	<b>Mn(II):</b> 110 mL; 50% tert- butanol, 0.5M HCOOH	10.99	10.79	98.2
	<b>Cu(II):</b> 100 mL; 50% tert- butanol, 1.5M HCOOH	12.71	12.32	96.9
	<b>Sn(II):</b> 90 mL; 50% tert- butanol, 2.5M HCOOH	23.74	23.14	97.5
	<b>Cd(II):</b> 100 mL; 20% tert- butanol, 0.5M HCOOH	22.48	21.61	96.1
2	<b>Mn(II)–Cu(II)–Pb(II)–Cd(II)</b>			
	<b>Mn(II):</b> 100 mL; 50% tert- butanol, 0.5M HCOOH	10.99	10.63	96.7
	<b>Cu(II):</b> 100 mL; 50% tert- butanol, 1.5M HCOOH	12.71	11.97	94.1
	<b>Pb(II):</b> 110 mL; 50% tert- butanol, 3.0M HCOOH	41.44	40.09	96.8
	<b>Cd(II):</b> 110 mL; 20% tert- butanol, 0.5M HCOOH	22.48	21.45	95.4
3	<b>Mn(II)–Cu(II)–Sn(II)–Pb(II)–Cd(II)</b>			
	<b>Mn(II):</b> 110 mL; 50% tert- butanol, 0.5M HCOOH	10.99	10.82	98.48
	<b>Cu(II):</b> 100 mL; 50% tert- butanol, 1.5M HCOOH	12.712	12.35	97.2
	<b>Sn(II):</b> 90 mL; 50% tert- butanol, 2.5M HCOOH	23.74	23.04	97.1
	<b>Pb(II):</b> 110 mL; 50% tert- butanol, 3.0M HCOOH	41.44	39.99	96.5
	<b>Cd(II):</b> 100 mL; 20% tert- butanol, 0.5M HCOOH	22.48	21.77	96.8
4	<b>Zn(II)–Cu(II)–Sn(II)–Pb(II)–Cd(II)</b>			
	<b>Zn(II):</b> 100 mL; 50% tert- butanol, 0.5M HCOOH	13.06	12.68	97.04
	<b>Cu(II):</b> 100 mL; 50% tert- butanol, 1.5M HCOOH	12.71	12.23	96.2
	<b>Sn(II):</b> 90 mL; 50% tert- butanol, 2.5M HCOOH	23.74	23.02	97.1
	<b>Pb(II):</b> 110 mL; 50% tert- butanol, 3.0M HCOOH	41.44	40.09	96.7
	<b>Cd(II):</b> 100 mL; 20% tert- butanol, 0.5M HCOOH	22.48	21.87	97.1

#### Application

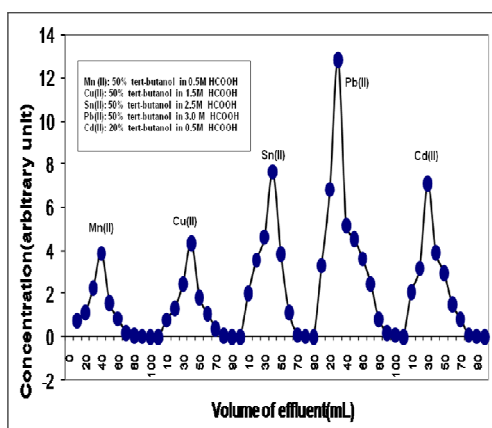
Sample water from the River Balu was collected at rainy season and its pH and conductivity were measured (Table 4). In the preconcentration studies, one liter sample water was passed through the resin column. The respective eluting agent for the series [Mn(II)–Cu(II)–Sn(II)– Pb(II)–Cd(II)] was passed through the column and the effluents were

collected for each of the above metal. Organic solvent and acid were evaporated from the effluent. The fractions of effluent for the above metals were diluted and preserved in well-cleaned polythene container into a refrigerator for the determination of the quantity by Atomic Absorption Spectrophotometer (AAS).

**Table. 4. Location, pH, specific conductivity and time taken for the preconcentration of one liter sample water of the river Balu.**

River	Season of sample collection	Date of collection	Location	pH	Specific Conductance mS/cm	Time taken for preconcentration
Balu	Rainy Season	July16, 2008	Middle of the river at Demra	7.53	1.26 x 0.1	11 hours and 15 minutes

The usual method of using Atomic Absorption Spectrophotometer (AAS) requires the construction of a calibration curve for constituent being determined. So for every element a calibration curve was prepared using standard solution of the constituent within the proper linear range. In this work, all the metal ions at trace level were determined by AAS. The amount of Mn(II), Cu(II), Sn(II), Pb(II) and Cd(II) was found in the water of the river Balu is represented in Table 5.



**Fig. 1.** Elution curve for Mn(II)–Cu(II)–Sn(II)–Pb(II)–Cd(II) in tertiary butanol–water–formic acid system.

For the determination of the metal ion Mn(II), Cu(II), Sn(II), Pb(II) and Cd(II) by AAS, a calibration curve with the standard solutions for each of the respective metal was

made before the analysis of the sample solutions. From the data presented in Table 5, it has been observed that the amounts of Mn(II), Cu(II), and Pb(II) are not significantly higher in the surface water collected from the river Balu at Demra. Water of the river at Demra is highly contaminated with the waste of industries located in this area. The composition of the industrial waste may consist of many toxic chemicals with different metal ions.

**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<sup>10</sup>. Formic acid is the strongest acid among all the members of homologous series of organic acid. 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<sup>2-3</sup>. Generally the resin prefers more a polar solvent to a less polar one. The combination tertiary butyl alcohol and along with formic acid seems to work ideally in this present investigation.

**Table. 5. Separation and analysis of surface water of the river Balu for a series of metals on Amberlite IRA-420 in Cl<sup>-</sup> form, 14 – 52 dry mesh with atomic absorption spectrophotometric technique. Column dimension: 7.5 cm X 0.74 cm (Resin 1.5g).**

No of series	Eluting agent	Found ( µg / liter )
		Balu river in rainy season
1	<b>Mn(II)–Cu(II)–Sn(II)–Pb(II)–Cd(II)</b>	
	<b>Mn(II):</b> 110 mL; 50% tert- butanol,0.5M HCOOH	11.17 ± 0.15
	<b>Cu(II):</b> 100 mL; 50% tert- butanol, 1.5M HCOOH	8.19 ± 0.11
	<b>Sn(II):</b> 90 mL; 50% tert- butanol, 2.5M HCOOH	BDL
	<b>Pb(II):</b> 110 mL; 50% tert- butanol, 3.0M HCOOH	5.31 ± 0.08
	<b>Cd(II):</b> 100 mL; 20% tert- butanol, 0.5M HCOOH	1.24 ± 0.05

BDL: Below detection limit (<0.5 µg / liter)

#### IV. Conclusion

On the basis of distribution co-efficient data, a number of metal ion mixtures can be separated and analyzed successfully after selective elution from an anion exchange resin column in tert-butanol – water – formic acid system. Mn(II)–Cd(II) mixture could not be separated in absolute alcohol – water – formic acid system on anion exchanger. Again Sn(II)–Pb(II) and Cu(II)–Pb(II) mixtures could not be separated in acetonitrile–water–formic acid system on anion exchanger. Moreover, Sn(II)–Pb(II), mixture could not be worked out in absolute alcohol, ethylene glycol, 1,4-Dioxan and acetonitrile – water – formic acid system. But all these mixtures can be easily separated in tert-butanol – water–formic acid system on anion exchanger. So, tert-butanol has been proved to be useful solvent compared to absolute alcohol, acetone, ethylene glycol, 1,4-Dioxan and acetonitrile for the separation of above-mentioned mixtures of metal ions. The most useful achievement of this piece of work is the success of separation and quantification of metal ions in a mixture with selective elution from an anion exchanger followed by atomic absorption spectrophotometric method at trace level. Since ion-exchange is a continuous technique, this method (in combination with AAS) may be easily applied for the separation and determination of trace metals in natural water. This method can also be used in elemental trace analysis for biological system, clinical samples and in pharmaceutical analysis and monitoring of industrial effluents.

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