CHAPTER-THREE

Anion Exchange Separation of Mg, Ca, Sr, Ba, Zn, Cd Hg, Pb, Mn, Cô, Ni, Al

In Aqueous Acetone Tartaric Acid Medium

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CHAPTER -III

Introduction :

Water is invariably the most important of all the resources. Man's unplanned activities are measurab(i)ly changing the chemical quality of air and water. The Socioeconomic condition resulting prodigal growth of population which in turn increases the per capita demand for energy and materials, has brought such changes tomore alarming situation. Everything that man injects into the biosphere-inorganic, organic or biological may directly or indirectly reach finally to natural water course. In this respect, inorganic trace elements are of special concern because they are nondegradeble and therefore, persistent, some of them, particularly heavy metals are highly toxic and even in low concentrations they can affect the aquatic life and the food webs. The increased use of water for public supply contaminated with industrial effuent has raised concern of pollutants in water on the public health. The concern relates to the harm that might be produced by long term and continued injection of toxic pollutants both in terms of chronic toxic manifestation and carcinogenicity.

The presence of heavy metals such as Ca^{2+} , Pb^{2+} , $2n^{2+}$, Cd^{+2} and Hg^{2+} in waste waters has been a matter of considerable concern in recent year because of their toxic properties even when present in traces. Many methods including precipitation, adsorption and ion exchange have been used with varying degree of success for containing more toxic heavy metal ions from industrial effluents.

Mercury has proved tobe the most dangerous aquatic pollutant because it is always rapidly methylated in the aqueatic environment and in this form it becomes accumalated in the food chains¹. In Minerata, values upto 20 mg/kg of fish weight were measured in fish and shel fish. In the USA and Canada max values of 10-K mg/kg, in Sweden and Norway 8-9/KS and Finland about 6 mg/kg have been reported in polluted waters.

Historical Review :

The tendency of metal ions to form the complexes with carboxylic acids was observed and many difficult seperations were possible in these media. The seperation potential has been proved to be of practical use by achieving some binary seperations on ion exchange columns.

The first application of tartrate as complexing agents for the seperation of elements by ion exchange chromatography is probably found in a paper by Tompking and Mayer(1) who determined cation exchange separation factors for the lanthanide pair promethium-enropium with various complexing agents and showed that the factor in tartrate was layer than separation in those days. Relatively few paper, most of them describing the seperation of only a few elements by cation exchange in tartrate media have appeared sporadically since then. Copper has been retained as cationic ammine complex from tartrate solutions containing excess ammonia and separated from aluminum (2) lead (3) and tin (IV) and antimony (III) 4. Copper (II), Zinc and nickel (II) 5 and also gallium. Antimony (III) has been seperated from Hn (II)by selective elution with 2 % tartaric acid of pH 1 (adjust with copper (II), Cobalt (II) and cadmium by elution with 20 % tartaric acid (8), iron (III) from magnesium by elution with 20 %. tartaric acid tartrate of pH 3 (9) and lead from tin (IV) antimony (V) niobium (V), tantalum(V), tungsten(VI) and molybdenum (VI) by eluting these elements with 0.25 M tartaric acid containing 0.01 M nitric acid while lead is retained (10)

The first systematic study of cation exchange distribution coefficients in tartrate media has probably been presented by Qureshi et.al¹¹. Only the elements Ti(IV), V(V), Fe(III), Nb(II) and U(VI) were included and there is some uncertainly in the results later studies by Dadone et.al¹² Simek¹³ also investigated a limited number of elements (seven and five respectively). A study of a large number of element was presented by Rouchand and Revel¹⁴. Unlartunately the results were presented as curves which allow only, and approximate estimation of the actual values of the Coellicients were determined as a function of tartaric acid concentration at a single concentration (0.3 M) of nitric acid. Numberous elements e.g. V, Nb, Th, Pn, Bi, Fb, were complexes.

Methods were applied to the analysis of Wood's metal, and the separations were also carried out with liquid anion exchangers, Amberlite LA-1 in Xylene.

A new nitrite media was used by Bhatnagar et.al.¹⁶ for studying the distribution of some metal ions in aqueous and mixed ethanol media. In contination to this anion exchange equilibrium distribution of 14 metal ions have been studied¹⁷ in aqueous nitrite and aqueous, methanol nitrite

media using Dowex 21-K in nitrate form. The ions such as Hg(II), Cd(II), and Pb(II) which were expected to form stable metal nitrite complexes gave high K_D values, suggesting separation possibilities for many metal ions by ions exclusion technique.

The anion exchange behaviour of several elements in systems containing tartaric acid was studied and the separations of metal ions were carried out. Husain and Charandabi¹⁵ investigated the adsorption characterstics and seperation possibilities of 27 elements by using Amberlite C-400 (HCOO⁻ forms), the strongly basic anion exchange resin in media containing aqueous tartaric acid and mixture of tartaric acid with sodium formate, hydrochloric acid, sodium nitrite, acetone, and methanol. The qualitative seperations achieved were Sr-La, Zn-Cd-Hg.

Investigation of the isolation of uranium and its seperation from other elements by employing anion exchange resins in combination with mono-carboxylic acid acting a complexing agents for Uranium have been carried out in the past $^{13-14}$ for this purpose, buffered aqueous solution of acetic acid^{18,19} were successfully employed. The ascorbic acid proved to be a valuable complexing agents for Uranium and thorium in mixed and non-aqueous solvents²⁰⁻²², in which the use of some organic acids has been investigated for the seperation of uranium from other elements. The anion exchange behaviour of hexavalents uranium and of a number of other elements in organic solvents containing organicacid is also studied²²; The solvents employed included aliphatic alcohols, acetone and dioxan. As organic acids the monocarboxylic acids i.e. formic acid and propionic acid and also chloro derivatives of acetic acid have been investigated.

Ton exchange studies of Zirconium in citrate systems have been done by Khopkar et.al²³. The strongly basic quatenary ammonium type of anion exchanger Dowex 21 K was utilised. Nitric acid hydrochloric acid, perchloric acid, and ammonium chloride, were studied as eluants, Zirconium was also seperated from the important fission product elements like barium, strongium, casium, cadmium and also from lead and molybdate. The formation of Zirconium anionic citrate (pH 2.7) complex in 5 % citric acid solution was reported by Tompkins, Khym et.al²⁴ and used this complex for the elution of zirconium in presence of fission product, such as cerium, barium, and strontium the seperation of Sr from Ba was carried out by using Dowex 2 anion exchanger. The anion exchange seperation ^{30,31} of Ca and Mg in ores and minerals was carried out by using complex forming agents such as ammonium acetate²⁵ ammonium lactate^{26,27} ammonium formate²⁸, and EDTA²⁹. The seperation of Fe(III) from Cr(VI) by both cation exchange ^{32,33} and anion exchange resin have been investigated. When Cr(III) was present it was either oxidised to Cr(VI)³⁶ or complexed with a suitable reagent. Trilon³⁷ ß or potassium thiocyanate from form anionic complex which at a suitable pH passed unadsorbed through the cation exchanger Fe(III) was separated from Cr(III) on anion exchange resin by using tartarate³⁸ solutions.

The anion exchange characteristics of Co, Ni, Zn, Mn, Mg, Ca, Cu and Cd metal ions in aqueous acetone acetic acid³⁹. Chloroacetic acid⁴⁰, dichloroacetic acid⁴¹ and trichloroacetic acid⁴² media were investigated in our laboratories. The synthetic mixtures were separated at suitable elution conditions.

Present Work :

The adsorption characteristics of Co. Mg, Ca, Cd, Zn, Ni, Fb, Al, Hg, Mn, Sr, Ba, Cu metal¹ ions on Dowex 21-K (Cl⁻ form) in aqueous acetone fartaric acid were studied. The distribution coefficients of these ions were found out at various percentage of acetone and at various concentrations of tartaric acid. The probable seperation of metal ions were predicted from the distribution coefficient data. The results of seperation of binary, ternary mixtures are presented in this chapter. The elution characteristics are discussed from the elution curves. The seperation limits are recorded which suggest the efficiency of the seperation by ion exchange chromatography technique.

EXPERIMENTAL

A) Measurement of Distribution Coefficient :

The metal chloride solutions of Co, Mg, Ca,Cu,Od,Zn, Ni, Al, Mn, Sr, Ba and Pb and nitrate solutions of Bi and Hg were prepared by dissolving the appropriate amounts of chloride and nitrate (Chapter-I) in distrilled water. Dowex 21-K in Cl⁻ form was used.

l g of air dried anion exchange resin and taken in 250 ml glass stoppered flask 4 ml of 0.05 M metal ion solution and 50 ml of the appropriate acetone water tartaric acid mixture was taken. The flask was stoppered and kept for 24 hrs. An aliquol from supernant liquid was pipetted out and acetone was evaporated. The metal ion content was determined by suitable titration method.

B) Ion.Exchange Separation of Metal Ions :

The pyrex glass chromatographic columns of 50 ml capacity were used. The columns were provided with safely device to maintain the ion exchanger under liquid. The column was packed with a small wad of glass wool at the bottom and a slurry of 10 g soaked resin was poured and was allowed to settle by occassional taping. A Care was taken to prevent the formation of air pockets or strate of the ion exchange resin.

Procedure :

The column was equilibrated with the resin by passing 20 ml of acetone water tartaric acid mixture at maximum flow rate. The binary, ternary mixture of various metal ions were prepared.

It was allowed to pass down the column slowly without allowing the level of the liquid to droup below the surface of the exchanger. The requisite amount of eluting agent was added. After about an hour the effluent fractions were collected in test tubes by maintaining a flow rate of 2 ml/min. The presence of metal ion was tested by suitable analytical reagents in the effluent fractions.

Under specified experimental conditions the first metal ion starts eluting and it is completely removed in a series of fractions collected. The second metal ion starts eluting and gets completely eluted at a particular fraction.After complete removal of the two metals elution is stopped. The metal ions contents in the collected fractions were estimated by standard volumetric procedures and total metal ion concentration was calculated.

In case of fernary and quanternary mixture the first two and first three metal ion respectively were eluted by suitable eluting agents and finally the last metal is eluted by proper eluting agent. The experimental details were the same as described above. The concentration of metal ion versus effluent volumes are plotted.

Metal	Acetone % (v/v)						
Ion	0	20	40	60	80		
Mg	65.690	57.818	54.50.4	70.838	75.00		
Ca	17.48	15.03	6.209	17.48	165.2		
sr	т.А.*	T.A.	T.A.	T.A.	T.A.		
Ba	31.77	20.25	14.79	11.42	9.371		
3n	0.8437	11.00	20.69	45.37	2047		
Cd	0.8437	11.00	20.69	45.37	204孝7		
Hg	т.А.	T.A.	T.A.	T.A.	T.A.		
Pb	0.0000	T.A.	3456	T .A.	T.A.		
Mn	6.674	19.972	112.153	378	461		
Co	1.390	2.854	21.09	56.36	176.6		
Cu	0.5454	1.958	2.842	18.07	27 .8 6		
Ni	0.0000	8,526	5.940	12.6	38.215		
Bi	ppt*	ppt	ppt	ppt	ppt		
Al(III)	2.75	3.25	4.50	7.717	9.80		

Table 3.1 : Distribution Coefficients (K_D) in aqueous acetone tartaric acid (0.05 M) media on Dowex 21 K-(Cl⁻) form

T.A. = Total Adsorption

ppt = Precipitation

Metal	Acetone % (v/v)						
10n ~	0	20	40	60	80		
Mg(II)	62.00	59.82	93.705	64.469	75		
Ca(II)	12.02	15.32	17.46	22.90	T.A.		
Sr(II)	T.A.	Т.А.	T.A.	T.A.	T.A.		
Ba(II)	20.37	20,18	14.19	9.397	T.A.		
Zn (II)	7.941	11.12	18.62	34.12	5212		
Ca(II)	21.18	106.2	124.2	281.2	5184		
Hg(II)	1262.25	T.A.	T.A.	T.A.	T.A.		
Pb(II)	9.817	1698	2056	2934	3456		
Mn (II)	21.00	25.411	246	278	460		
Co(II)	13.5	10.33	39.26	57.54	83.00		
Cu(II)	2.70	3.454	5.400	18.6	367.2		
N1(II)	20.925	17.018	22.60	58,52	83.00		
Bi(III)	116.00	117.2	221.00	279.25	303.2		
Al (III)	2.48	6.70	9.80	11.90	15.95		

Table 3.2 Distribution Coefficients (K_D) in aqueous-acetone tartaric acid (0.1 M)media on Dowex 21 K(Cl⁻)form

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Metal					
TOI1	0	20	40	60	80
Mg(II)	82.58	76.45	68.210	54.5	64
Ca(II)	15.10	13.50	T.A.	T.A.	T.A.
Sr(II)	T.A.	Τ.Α.	T.A.	T.A.	T.A.
Ba(II)	53.95	64.6	125.3	125.3	T.A.
Zn (II)	20.48	46.28	168.44	421.3	T.A.
ca(11)	T.A.	T.A.	T.A.	T.A.	T.A.
Hg(II)	T.A.	T.A.	T.A.	T.A.	Τ.Α.
Pb(II)	26.98	T.A.	T.A.	3436	T.A.
Mn(II)	22.595	21.6	238.736	246	462
C ₀ (II)	33.19	45.20	264.2	T.A.	T.A.
Cu(II)	4.378	4.064	5.400	42.82	216
Ni(II)	35.10	81.00	91.00	94.8	546.
Bi(III)	120.5	210.2	216.00	290.9	540
Al(III)	9.90	24.00	34.40	45.20	54.0

Table 3.3 Distribution coefficients (K_D) in aqueous acetone tartaric acid (0.5 M)media on Dowex 21 K (Cl⁻) form

Metal		Acetone %	(v/v)	میں میں انتقابا الیل میں میں اسے میں اسی میں اسی کا این ال	
10n	0	20	40	60	80
Mg(II)	77.93	111.8	T.A.	T.A.	PPt
Ca(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Sr(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Ba(II)	180.00	186	41 4	647	PPt
$z_n(II)$	945	1450	2578	T.A.	T.A.
Cd(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Hg(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Pb(II)	T.A.	T .A.	PPt	PPt	PPt
Mn(II)	67.500	306	486	331 .71	1 026
$C_{0}(II)$	319.20	T .A.	T.A.	T.A.	T.A.
Cu(II)	4.3	T.A.	T.A.	T.A.	T.A.
Ni(II)	315.20	T.A.	T.A.	T.A.	T.A.
Bi(III)	39.90	86.24	149.7	263.7	717.3
A1(III)	43.25	77.00	102.25	184.00	415.00

Table 3.4 Distribution coefficients (K_D) in aqueous-acetone tartaric acid (1.0 M)media on Dowex 21 K(Cl⁻) form





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Fig. 3-2

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RESULTS AND DISCUSSION

A) Distribution Coefficients in Aqueous Acetone Tartaric Acid Medium

The distribution Coefficients of Mg, Ca, Sr, Ba, Zn, Cd, Hg, Pb, Mn, Co, Cu, Ni, Bi and Al were found out in 0.05, 0.1, 0.5, 1 M tartaric acid at 0, 20, 40, 60 and 80 percentages of acetone and the values are presented in tables 3.1, 3.2, 3.3 and 3.4. The values of distribution coefficients of Ca, Mn, and Co are low at 0, 10, 40 percentage of acetone and 0.05, 0.1 M tartaric acid indicating less't' complexing tendency. K_D values seem to be large at higher percentages of acetone and at higher (0.5 M, 1 M) concentration of tartaric acid Ba, Cu, Ni and Al containing 0.05 M tartaric acid. The tendency of forming tartarate complexes increase with the rise in concentration of tartaric acid. The values are large at higher bercentages of acetone in 0.1, 0.5 and 1 M tartaric acid. The behaviour of Al towards acetone and tartaric acid is affected to less extent. The distribution coefficients of Zn and Cd are low at 0.05, 0.1 M of tartaric acid except 80 percent acetone, cadmium shows total adsorption at 0.5 and 1M tartaric acid where as Zinc indicates higher tendency of adsorption at lMiltartaric acid, Pb shows lower values of

Kp at 0.05, 0.1 and 0.5 M tartaric acid without acetone and higher values at all percentages of acetone and all concentration of the acid. It indicates that the presence of acetone is well preferred in complexation.

The tendency of adsorption of Hg and Sr on resin is very high at 0, 20, 40, 60 percentage of acetone and at 0.05, 0.1, 0.5 and 1.0 M of tartaric acid. A precipitation is observed with Bi in 0.05 M tartaric acid at all percentages of acetone. This tendency is decreased at higher concentration of the acid, Mg, Ba and Pb get precipitated at 1.0 M acid and high percentages of acetone, Hg and Sr thus form anionic tartarate complexes which exchange Cl ions on the resin.

From the K_D data of the metal ions in Tables 3.1 and 3.4 following selectivity sequences for the anion exchange can be given.

1) Tartaric Acid = 0.05 M

a) Acetone % = 0 Hg \rightarrow Sr \rightarrow Mg \rightarrow Ba \rightarrow Ca \rightarrow Mn \rightarrow Al \rightarrow Co Zn \rightarrow Cd \rightarrow Cu \rightarrow Ni \rightarrow Pb

b) Acetone % = 80 Hg \geq Sr \geq Zn \geq Cd \geq Mn \geq Co \geq Ca Mg \geq Ni \geq Cu \geq Ba \geq Al

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ь)	Acetone	≥ % = 80				
	нд 🍌	sr 🏹	РЪ 涛	ca 🍃	Zn 🍃	Ca 🍃
	co 🍃	Cu 🍃	Ni >	mn >	ві >	Al

It is seen that the distribution coefficients very with the change in concentration of acetone and tartaric acid. The role of acetone and acid on the distribution coefficients is discussed below.

Effect of Concentration of Acetone :

It is observed that the values of distribution coefficients of metal ions under study increase with the rise in concentration of acetone at 0.05, 0.1, 0.5 and 1 M concentration of tartaric acid.

Ion exchange between a solid and a solution can only occur if certain requirements are met. A solvent must be used in which exchanging species are soluble. There must be ions in both the solution and the solid. The solute and the functional groups of the solid (resin) must be dissociate atleast partially. The ions must be free to remove to exchange with one another. This requires porous structures of the resin which is expanded by Swelling in the solvent water, because of its high dielectric constant, is an excellent solvent for most inorganic and quite number of Organic acids, bases and salts. There are other solutions with high dielectric constants in which electrolytes can dissolve and dissociate and in which most of the common ion exchangers are stable. Such solvents are formamide (f = 126) anhydrous ammonia (f = 22), ethylene glycol ($\xi = 41$) methanol ($\xi = 32$) ethanol (t = 26) and acetone (t = 27). These solvents can be used with or without addition of water. Many organic acids, are more readily dissolved in these solvents than in water. The nature of the solvent like acetone affects the solubility, dissociation and the soluation of the solutes and the behaviour of the ion exchanger and certain pecularities and side effects are more pronounced with acetone than with water.

The metal ions under study are preferred at higher percentage of acetone because of the variation in dielectric constant. It is reported that the distribution coefficients 42 increase with decreasing dielectric constant. Akerlof has determined the dielectric constant of a number of aquecus organic solvent mixtures.

Table 3.5

The dielectric constants of acetone-water

mixtures v/v

adh 11mg adh 40mg ang 2015 Ann 400 Ann 405 Ann dag						
Acetone %	100	70	30	20	10	0
Dielectric constant	21.1	35.7	61	67	73	78.4

A similar charge in distribution coefficients of some metal ions in aqueous acetone carboxylic acid using cation and anion exchangers are reported earlier.

A fairly reliable measure for the affinity is the extent of Swelling of the resin in the solvent. The Swelling by the total solution, water and organic solvent as a function of the mole fraction of organic solvent can be described as moles of solution per equivalent resin. The mole of organic solvent taken up by the resin as a function of their mole fractions vary somehow in proportion to their polarities, giving a relatively large increase with the more polar solvents like methanol, glycol, acetic acid and little or no increase with the less polar solvents like dioxane, acetone, n-propanol, isopropanol, t-butanol, propionic acid. The decrease in the total absorbed solution as a function of the mole fraction of organic solvent shows that the mixed solvent in general becomes a poorer solvating agent for ions in the resin. The quanternary amine bound to a poly-styrene skeleton probably behaves much like a large organic ion with a low density of surface charge and only react with the less polar, more organic component of This conclusion is based on the experia mixed solvent. mental evidance of the uptake of solvent, dioxane, acetone, isopropanol and n-propanol by the resin, when a very small change in the uptake of organic solvent is observed for substantial change in its mole fraction in the outer solution (from Xs = 0.1 to Xs = 0.9). It is quite probable that this large ion retains nearly a constant solution shell irrespective of the solution composition. In support of this view, there are a number of examples where a carbonium ion attracts the more organic component of a mixed solvent 44,45 on the evidence we may suppose that the resin particle is solucted by one or two less polar organic solvents like acetone, dioxane, n-propanol, etc.

The more polar organic solvents like methanol, acetic acid, glycol probably solvate the cation as well as the anion in the functional resin group.

When the counter ion is a Simple Inorganic anion as in the present case Cl, there is strong evidance that this anion is primarily surrounded by water molecules regardless of which responable model is used to interprete 45 the results . On this basis one must suppose that the water and organic solvent molecules in the resin phase are somehow partly separated from each other at the resin functional group. Such an occurance is in fact not improbable in view of the behaviour of salts in a mixed solvent. In the mixed aquepus organic solvent with less polar solvents like acetone, dioxane, propanol, etc. the salting out effect of NaCl or KCl separate the water from organdc solvent; resulting in phase separations whereas with a perchlorate, such seperation does not take place because of the small affinity of the perchlorate ion for water molecules. In another mixed solvent with a molar organic solvent like methanol, or even ethanol, phase seperation does not become possible by addition of a chloride. However, a sulphate separates water and ethanol, which show the necessity of supposing a large excess of the more polar component in the viscinity of the anion. The hydration number of

the sulphate ion in aqueous solution is known to be 8 to 11^{46} . These data demonstrate that in a mixed solvent the affinity for water molecule is greater for an anion that for a cation.

In the water rich region, the uptake of organic ion is in general much preferred compared with other solution compositions. This preterential uptake of organic solvent is more polar organic solvents than with the less polar. It is seen that, where as the cations are in a sate of lower free energy of transfer in mixed aqueous methanol than in water, the reverse in the case for the anions⁴⁸.

The Quanternary methyl amine fixed to polystyrene attracts methanol molecules to form a complex structures - C $(CH_3)_3 N (ROH)_n$ in which the number of methanol molecules remains nearly constant irrespective of change in the solution composition. The same is true for the case of other organic solvents, the values being different, depending on the nature of the solvent.

The degree of cross linking affects the total swelling of the resin, the lower the cross linking the greater the uptake of the solution. The resin in Cl⁻ from of low cross linking shows a high exchange capacity in aqueous n-propanol⁴⁷. The sorption and elution of metal ions on an exchanger from mixed aqueous organic solvents are complex processes. The pertial substitution of aqueous solution by organic solvent produces a number of changes in an exchange system such as, change in the solution structure due to the interaction between water and organic solvent, change in the hydration and solvation of the electrolyte, change in the solvent composition in the resin phase, change in the activity coefficient of the electrolyte in the solution phase as well as in the resin phase, change in the complexation of metal ion and change in the extent of invasion by an electrolyte. All these change are mutually dependant and affect the distribution of the metal ions.

The ions, acetone, water and carboxylic acid, remains in contact with the resin while deciding distribution coefficients. The exact mechanism of the process is unknown. The role of each of these individual factors will help in predicting the process. The sorption of acids on the resin is discussed below.

The acid molecules interact strongly with one of the constituents of resin. In order to obtain the information about the selectivity sorption of acid from aqueous solutions, the acid concentration inside the resin beads was determined as a function of the external concentration. The solvent uptake is negligible at higher concentration of acid.

The sorption of the acid the resin may be due to the exchange between the citrate ions and the resin ion because the acids have relatively large ionization constants. This sorption, based on ion exchange, could be varified by determining the concentration of the chloride ion removed from the resin bed. It is observed that the distribution coefficients of the zinc, cadmium, mercury, and stronsium, lead are higher than the other metal ions at corresponding acid concentrations, showing that the citrate or titrate complex ions of Zn, Cd, Hg, Sr and Pb are sorbed on the resin, the acid might have been sorbed to the very small extent. The removal of Cl⁻ ions from the resin bed was observed experimentally.

Effect of Cocentration of tartaric acid :

From the data of distribution coefficients (Tables 3-1 to 3.4) it is observed that the K_D values of metal ions under study increases with the increase in concentration of tartaric acid. This suggests that at higher concentration of tartaric acid most of the metal ions from stable anionic titrate complexes.

A survey literature⁵⁰⁻⁶¹ reveals that simple complexes of Cd(II) with a number of carboxylate ions such as formate, oxalate, tartrate, have been studied polarographically, Shivhare and Singh⁶² studied the behaviour of Cd(II) in tartrate and imidazole tartrate media by using polarographic technique. In Cd(II) - tartrate system the plot of E ½ versus log [(Tart)]² was t a straight line thereby showing the formation of a simplex complex. The composition and the stability constant were determined by Linganes method. This gave the complex species as [Cd (Tart)₂]²⁻ with the stability constant log B₀₂ = 3.7 A comprehensive polarographic studies on the mixed complexes of Cd(II) with B and r-picolines, and some carboxylate ions like oxalate, malonate, succinate and tartrate was undertaken by Singh et al⁶⁴. The plot of E ½ Vs log (Tart²⁻)was found to be a straight line indicating the formation of a single complex. This gave the complex species $[Cd(Tart)_2]^{2-}$ with the stability constant log $B_2 = 2.84$.

The formation of tartrate complex may be indicated $CHCOO^-$ H⁺

$$+ ca^{2+} = [ca(chcoo)_{2}]^{2-} + 2h^{+}$$

This negative complex of Cd exchanges with Cl ions from Dowex 21 K(Cl) resin. The reaction be # ig ,

as

 $2R-N^{+}(CH_{3})_{3}C1^{-} + [Cd(Tart)_{2}]^{2} \longrightarrow [R-N^{+}(CH_{3})_{3}]_{2} [Cd(Tart)_{2}]^{2} + 2C1$

A similar polarographic study of the formate complexes 65 of Cd,Cu, Pb, Tl and Zn showed that Cd, Pb, Zn, form weak but definite complexes of the type $M(HCOO)^+$, $M(HCOO)_2$, $M(HCOO)_3^-$, and $M(HCOO)_4^{2^-}$ with formate concentrations ranging from 0 to 1.98M solutions, held at a constant ionic strength of 2.0 with perchlorate. Cu forms similar complexes which appear to be more stable, while Tl shows no complexing tendency except at very high formate concentrations.

Table No. 3.5 : Quantitative separation of binary mixture (First ion in the mixture is eluted, while the second ion is retained)

Mixture	Metal ion eluted	Bluting agent	m moles taken	m moles found
1	2	3	4	5
Ma + Ha	Ma	a	0.215	0.220
<i></i>	Hg	c	0.215	0.205
Ca + Hg	Ca	a	0.215	0.220
	Hg	C	0.215	0.220
Ba + Hg	Ba	a	0.225	0.205
	Hg	с	0.215	0.220
2n + Hg	Zn	a	0.240	0.245
	Hg	C	0.215	0,220
Mn + Hg	Mn	a	0.205	0.225
	Hg	c	0.215	0.220
Co + Hg	Co	a	0.225	0.210
	Hg	с	0.215	0,205
Cu + Hg	Cu	a	0.200	0.205
	Hg	c	0.215	0.230
Ni + Hg	Ni	a	0.195	0.195
	Hg	С	0.215	0.220
Mg + Sr	Mg	a	0.215	0,225
	Sr	b	0.215	0.215
Ca + Sr	Ca	a	0.250	0.255
	Sr	b	0,205	0,225
Ba + Sr	Ba	a	0.225	STAL OLAL
	Sr	ъ	0.215	6 (0.210) * LIB3 734

1	2	3	4	5
2n + Sr	 Zn	a	0.200	0.200
	Sr	b	0.205	0.205
Mn + Sr	Mn	a	0.225	0.220
	Sr	b	0.205	0.200
Co + Sr	Co	a	0.235	0.240
	Sr	b	0.205	0.205
Cu + Sr	Cu	a	0.250	0.245
	Sr	Ъ	0.200	0.210
Ni + Sr	Ni	a	0.250	0.250
	Sr	b	0.210	0.215
Mg + Cđ	Mg	đ	0.215	0.220
	Cđ	a	0.240	0.235
Ca + Cd	Ca	đ	0.230	0.250
	Ca	a	0.235	0,235
Zn + Cđ	Zn	đ	0.240	0.245
	Cđ	a	0.240	0.240
Mn + Cd	Mn	đ	0.250	0.250
	Cđ	a	0.240	0.240
Co + Cd	Co	đ	0.250	0.250
	ca	a	0,240	0.240
Cu + Cd	Cu	đ	0.240	0.245
	ca	a	0.240	0.240
Ni + Ca	Ni	đ	0.250	0,245
	Cđ	a	0.235	0.238
Mg + Pb	Mg	đ	0.215	0.220
	Pb	а	0.215	0.210

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-		2	3	4	5
Ca +	+ Pb	Ca	đ	0.250	0.252
		Pb	a	0.210	0.215
Zn -	+ Pb	Zn	đ	0.240	0.245
		Pb	a	0.215	0.220
Mn -	+ Pb	Mn	đ	0.225	0.215
		Pb	a	0.215	0.215
Co +	+ Pb	Co	đ	0.250	0.258
		Pb	a	0.215	0.215
Cu +	+ Pb	Cu	đ	0.250	0.245
		Pb	a	0.200	0.210
Ni -	+ Pb	Ni	đ	0.250	0.250
		Pb	a	0.210	0.215

a) 0 % Acetone + 0.05 M Tartaric Acid

b) 3 M formic Acid

c) 2 M Perchloric Acid

- d) 20 % Acetone + 0.5 M Tartaric Acid
- e) 80% Acetone + 0.05 M Tartaric Acid



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Fig. 3.8 - Elution Curves of Mn/Cu/Mg/Ca - Cd.



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Fig. 3.10-Elution Curves of Mn/Mg/Co - Pb.



Mixture	Metal ion eluted	Eluting agent	m moles taken	m moles found	
1	2	3	4	5	
Ca+Cd+Hg	Ca	e	0.250	0.255	
	Cđ	а	0.230	0.235	
	Hg	С	0.225	0.225	
CO+Cd+Hg	Co	е	0.250	0.255	
	Ca	а	0.225	0.225	
	Hg	с	0.225	0.225	
Cu+Cd+Hg	Cu	e	0.205	0.225	
	Cg	а	0.225	0.225	
	Hg	С	0.225	0.225	
Mg+Cd+Hg	Mg	e	0.220	0.220	
	Cđ	a	0.210	0.205	
	Hg	С	0.225	0.225	
Ni+Cd+Hg	Ni	e	0.205	0.255	
	Cđ	a	0.235	0.245	
	Hg	с	0.215	0.235	
Mn+Cd+Hg	Mn	е	0.225	0.245	
	Cđ	a	0.235	0.235	
	Hg	с	0.225	0.220	
Cu+2n+Hg	Cu	e	0.250	0.260	

a

С

Zn

Hg

0.205

0.225

0.210

0.225

Table 3.6 : Quantitative Separation of Ternary Mixture

an - and	an a	والمراجع والمراجع والمراجع والمراجع والمراجع والمحافي والمراجع والمراجع والمراجع والمراجع والمراجع		
1	2	3	4	5
	34		0.005	0.225
mg+2n+Hg	rig	e	9.225	0.235
	Zn	a	0,235	0.235
	Hg	С	0.225	0.225
Mn+2n+Hg	Mn	a	0.225	0.240
	Zn	a	0.200	0.205
	Hg	С	0,225	0.225
Co+zn+Hg	Co	e	0.250	0.250
	Zn	a	0.215	0.215
	Hg	с	0.225	0.225
Ca+2n+Hg	Ca	е	0.250	0.260
	Zn	a	0.205	0.210
	Hg	с	0.225	0.230
Ba+Zn+Hg	Ba	е	0.200	0.205
	Zn	a	0,205	0.215
	Hg	C	0.225	0.230
Cu+Pb+Hg	Cu	е	0.200	0.235
	Pb	a	0.245	0.255
	Hg	с	0.220	0.225
Ni+Pb+Hg	Ni	e	0.215	0.235
	Pb	a	0.215	0.215
	Hg	с	0.225	0.225
Co+Pb+Hg	Co	е	0,250	0.255
	Pb	a	0.225	0.225
	Hg	с	0.225	0.225

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1	2	3	4	5
Ca+Pb+Hg	Ca	e	0.250	0.265
	Pb	a	0.215	0.215
	Hg	с	0.225	0.225
Mn+Pb+Hg	Mn	e	0.225	0.230
	Pb	a	0.200	0.205
	Hg	c	0.225	0.225
Mg+Pb+Hg	Mg	е	0.225	0.230
	Pb	a	0.200	0.205
	Hg	c	0,225	0.225
Mn+Cd+Sr	Mn	e	0.225	0.240
	Ca	a	0.235	0.235
	Sr	b	0.205	0.205
Mg+Cd+Sr	Mg	е	0.225	0.230
	ca	a	0.235	0.235
	Sr	ъ	0.205	0.205
Co+Cd+Sr	Co	e	0.250	0.255
	Ca	a	0.225	0.225
	Sr	b	0.205	0.205
Cu+Cd+Sr	Cu	e	0.250	0.255
	Ca	a	0.235	0.255
	Sr	b	0.205	0.210

1	2	3	4	5 -
Autonter	Cu	•	0.225	0 230
Cutzinior	Cu 7n	a	0.240	0.235
	Sr	b	0.205	0.205
Ni+Zn+Sr	Ni	е	0.225	0.230
	Zn	a	0.235	0.240
	Sr	b	0.205	0.206
Mg+zn+Sr	Mg	e	0.225	0.230
	Zn	a	0.235	0.235
	Sr	b	0.205	0.205
Co+2n+Sr	Co	e	0.250	0.245
	Zn	a	0.215	0.215
	Sr	b	0.205	0.207
Mn+2n+Sr	Mn	e	0.225	0.245
	Zn	a	0.235	0.245
	Sr	b	0.205	0.210
Ca+2n7Sr	Ca	e	0.250	0.255
	Zn	a	0.205	0.210
	Sr	b	0.205	0.215

1	2	3	4	5
Ba+2n+Sr	Ba	e	0.225	0.215
	Zn	a	0.200	0.215
	Sr	b	0.205	0.205
Mn+Pb+Sr	Mn	e	0,225	0.235
	Pb	a	0.200	0.205
	Sr	b	0.205	0.205
Mg+Pb+Sr	Mg	e	0,225	0.235
	Pb	a	0.205	0.210
	Sr	b	0.205	0.205
Cu+Pb+Sr	Cu	e	0.200	0.210
	Pb	a	0.200	0.235
	Sr	b	0.205	0.205
			0.045	
Co+Pb+Sr	Co	e	0.245	0.250
	Pb	a	0.205	0.205
	Sr	b	0.205	0.215

- a) % Acetone + 0.05 M TA
- b) 3 M formic Acid
- c) 2 M perchloric Acid
- d) 20 % Acetone + 0.5 M TA
- e) 80% Acetone + 0.05 M TA

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Fig. 3-13 - Elution Curves of Ca/Co/Cu/Mg - Cd - Hg.





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Fig. 3-18 - Elution Curves of Mn / Mg - Pb



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Separation :

The results of the qualitative separation of Synthetic binary, ternary mixtures in aqueous acetone tartaric acid are presented in Tables 3.1 to 3.6.

a) Binary Mixtures :

1) Separation of Hg from Mg/Ca/Ba/Zn/Mn/Co/Cu/Ni:

As Hg is totally adsorbed on resin in 0.05 M tartaric acid without acetone it was retained on the resin column. Zn, Cd, Mn, Co, Cu, Ni, show no measurable adsorption on the resin Ba, Ca, and mg show little tendency to get adsorbed on the resin. All these cp=ions are eluted by 0.05 M acid. After complete removal of these ions Hg was stripped off by 2 M perchloric acid.

2) Separation of Sr from Mg/Ca/Ba/Zn/Mn/Co/Cu/Ni

As Hg, Sr also shows very high tendency of compleexation with tartaric acid at all percentages of acetone and at all concentrations of acid it is strongly held up by the resin at 0.05 M tartaric acid. The other Co-ion from the binary mixture is eluted first and Sr was collected by adding 3 M formic acid solution on the resin column. The amount collected was estimated titrimetrically.

3) Separation of Mg/Ca/Zn/Mn/Co/Cu/Ni-Cd/Pb

Cd and Pb show total adsorption in 20 % acetone -0.5 M tartaric acid and hence Cd or Pb is retained on the column leaving its Co-ion in the binary mixture . Ca, Mn, Cu, were easily removed from the column as these ions show very low K_D values Mg, Zn, Co, Ni were eluted by the above solution little bit slowly. Cd or Pb being remained unadsorbed in 0.05 Mtartaric acid without acetone was stripped off in this medium.

4) Separation of Cd/Co/Cu/Mg/Ni/Mn-Cd/Zn/Pb-Hg

Cd, Zn, Pb and Hg show high K_D values in 80% Acetone - 0.05 M tartaric acid and therefore these ions are remained strongly adsorbed on the resin, the other Co-ion Ca, Co, Cu, Mg, Ni, Mn is eluted and estimated. Cd, Zn, Pb show no measurable adsorption in 0.05 M tartaric acid solution and Hg is totally adsorbed. The Co ion Cd or Zn or Pb is eluted by 0.05 M tartaric acid solution. Hg was stripped off by 2M perchloric acid solution.

5) Separation of Mn/Mg/Co/Cu-Cd/Pb-Sr

Cu/Ni/Mg/Co/Mn/Ca/Ba-Zn-Sr In a tertiary mixture containing Cd, Pb, Zn, Sr are adsorbed on the resin in 80% acetone - 0.05 M tartaric acid and other Co ion is eluted first.After the complete elution of Cd, Pb, Zn by 0.05 M tartaric acid Sr was eluted by 3 M formic acid solution. Elution Curves :

Two component and three component elution curves are presented in Figs. 3.3 to 3.12, 3.13 to 3.22. The curves. The curves indicate how the systematic information contained in the Tables of distribution coefficients can be applied to develop analytical separation procedure. The clear cut separations of metal ions indicated by no overlap of the elution curves. From the binary mixtures containing Hg, Sr the metal ions Ni, Zn, Ca, Mn, Cu, Co, Ba are eluted by 20 % Acetone - 0.5 M tartaric acid. The elution curves for these metal ions show slight tailing. From the mixtures Mn/Mg/Co - Pb the elution curves for Mn/Mg/Co show slight failing whereas that of Pb shows tronting. In tertiary mixtures the elution curves for Cd, Zn, Pb show slight failing. From binary and tertiary mixtures the metal ion eluted first shows some amount of tailing as the other Co ion interferes in the separation, but fronting is not observed. The elution curves for the most of the metal ions show the bell shaped Gaussion distribution curves indicating good column chromatographic separations.

Sr.No.	Metal ion	BTV ml	VEP ml	TEV ml	Eluent*
1	2	3	4	5	6
1	Ni(II)	10	20	60	đ
2	2n (II)	10	20	60	đ
3	Ca(II)	10	30	65	đ
4	Mn(II)	10	30	60	đ
5	Cu(II)	10	30	60	đ
6	Co(II)	10	30	70	đ
7	Ba(II)	9	30	50	đ
8	Cu(II)	10	20	60	đ
9	Ni(II)	10	20	70	đ
10	Ca(II)	10	20	80	đ
11	Co(II)	9	20	60	a
12	Zn(II)	5	20	70	a
13	Mg(II)	10	20	65	a
14	Sr(II)	10	20	100	b
15	Hg(II)	10	30	80	c
16	Ni(II)	5	30	60	đ
17	Co(II)	7	30	50	đ

Table 3.7 Elution Characteristics of metal ions in aqueous acetone tartaric acid media

18	Zn (II)	7	25	60	đ
19	Ca(II)	5	20	100	a
20	Mn(II)	8	30	70	a
21	Cu(II)	7	30	70	a
22	Mg(II)	7	20	70	a
23	Cu(II)	7	25	65	a
24	Pb(II)	5	110	160	a
25	Zn (II)	9	20	80	đ
26	Cu(II)	9	20	60	đ
27	Ni(II)	7	20	60	đ
28	Ca(II)	7	20	50	đ
29	Mn(II)	7	20	60	đ
30	Mg(II)	7	20	75	đ
31	C ₀ (II)	10	20	80	đ
32	Cu(II)	10	20	65	đ
33	Hg(II)	10	50	80	a
34	2n (II)	10	20	85	a
35	Pb(II)	10	50	80	a
36	Ni(II)	10	40	80	a
37	C ₀ (II)	10	40	80	a

a = 0% Acetone + 0.05M TA

b = 3M formic Acid

c = 2 M perchloric Acid d = 20 % Acetone + 0.5 M TA e = 80 % Acetone + 0.05M TA

109

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