CHAPTER I

GENERAL INTRODUCTION

-: INTRODUCTION :-

The industrial and academic uses of ion-exchange have been broadened to such an extent that the term now signifies a unit operation that as analogous to such classic operations as adsorption, distillation and filtration. Most ion exchange applications are transformation, fractionation, concentration and removal of ionic substances. All over the world, numerous plants are in operation, accomplishing tasks that range from the recovery of metals from industrial wastes to the separation of rare earths and from catalysis of organic reactions to decontamination of water in cooling systems of nuclear reactors. In the laboratory, ion exchangers are used as an aid in analytical and preparative chemistry. The aims of scientific research with ion-exchange membranes extend far into physiological chemistry and biophysics. However, the prominent use of ion exchange chromatography is still the purification and demineralization of water, a perennial challenge and a task with the growth of population and industries has made more pressing than ever. The heavy metal ions such as copper, lead, zinc, cadmium and mercury have received greater attention in recent years because of their toxic properties even in traces in sewage, industrial and mining wastes streams. Many agricultural waste materials are capable of binding heavy metal ions by ion exchange, adsorption or chelation mechanism.

Chromatography is often referred to as an art of separation. It deals with phenomenon involved in separating and resolving different constitutents of mixtures by virtue of certain physical and chemical properties and forces of interaction. The impact of chromatography has been very great on almost all areas of analysis and therefore on the general progress of science. The principles of chromatography and their wide applicability were discovered by Michael Tswett in 1906. The phenomenon of ion exchange was first observed and studies by two British agricultural chemistrs[2,3] in 1850. Although the phenomenon of ion exchange and the principles of chromatography had been recognized and utilized separately for many years, their amalgmation as Ion-Exchange chromatography could be considered to date from the work of Adams and Holmes[4] in 1935. Chromatography is further branched as gas, column, thin layer, paper and ion-exchange chromatography.

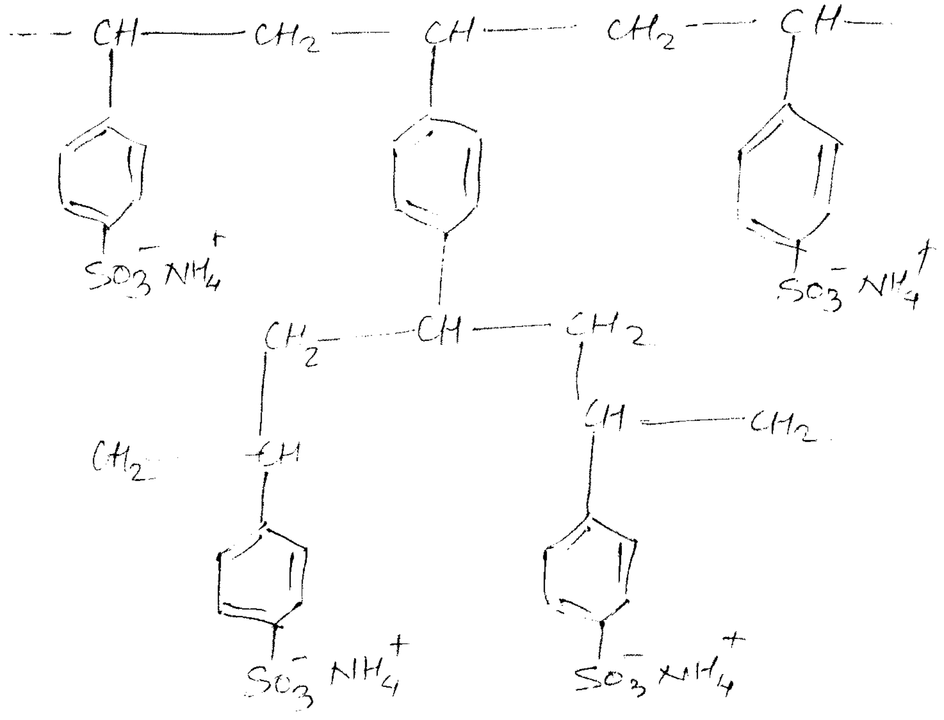
ION EXCHANGE MATERIALS

Ion exchange separations are limited to samples containing ionised or partially ionised solutes. Ion exchange is a chemical reaction in which free mobile ions of a solid, the ion exchanger, are exchanged for different ions of similar charge in solution. The ion exchangers are insoluble in the solvent containing ions to be exchanged, and they are resistant to chemicals at temperatures below 100°C. Among their basic physical properties, hardness and resistance to abrasion are the most desirable.

All ion exchangers have the same basic structure. This fundamental frame work is a three dimensional network that is fixed and chemically insensitive to the surrounding electrolytes. It acts like a semipermeable membrane through which charged species can diffuse. The site of exchange is attached to this inert matrix. The site of exchange is hydrophilic and contains functional groups that are ionisable and mobile counter ions. These counter ions can be replaced when brought in contact with an external solution containing ions of suitable charge and size. The fixed functional groups determine the nature of the exchange process. Thus the ion exchange materials are categorised as cation exchangers and anion exchangers. The cation exchangers are capable at exchanging cations and the anion exchangers can exchange anions with the surrounding electrolytes.

Ion Thus a cation exchanger consists of a polymeric anion and active cations, while an anion exchanger is a polymeric cation with active anions.

A widely used cation exchange resin is that obtained by the copolymerisation of styrene and a small proportion of divinylbenzene, followed by sulphonation[3]. It may be represented as



The formula enables us to visualise a typical cation exchange resin. It consists of a polymeric skeleton, held together by linkings crossing from one polymer chain to the next, the ion exchange groups are carried on this skeleton. The solid granules of resin swell when placed in water, but the swelling is limited by the cross-linking. The resulting structure is a vast sponge-like network with negatively charges sulphonate ions attached firmly to the framework. These fixed negative charge are balanced by an equivalent number of cations. These ions move freely within the water filled pores and are sometimes called mobile ions; they are the ions which exchange with other ions. When a cation exchanger containing mobile ions C^+ is brought into contact with a solution containing A^+ the latter diffuse into the resin structure and cations C^+ diffuse out until equilibrium is attained. The solid and the solution then contain both cations C^+ and A^+ in numbers depending upon the position of equilibrium.

ACTION OF ION EXCHANGE RESINS.

Cation exchange resins contain free cations which can be exchanged for cations in solution (Soln.)

$(Res.A^-)B^+ + C^+$ (solution) $\rightleftharpoons$ $(Res.A^-)C^+ + B^+$(solution).——(1)

If the experimental conditionsare such that the equilibrium is completely displaced from left to right the ion C^+ is completely fixed on the cation exchanger. If the solution contains several ions (C^+, B^+, and E^+) the exchanger may show different affinities for them, thus making separations possible. A typical example is the displacement of sodium ions in a sulphonate resin by calcium ions.

$2(Res.SO_3^-)\ Na^+ + Ca^{2+}$ (soln) $\rightleftharpoons$ $(Res.SO_3^-)_2\ Ca^{2+} + 2\ Na^+$(soln)——(2)

The reaction is reversible, by passing a solution containing sodium ions through the product, the calcium ions may be removed from the resin and the original sodium form regenerated. Similarly, by passing a solution of a neutral salt through the hydrogen form of a sulphonic resin, an equivalent quantity of the corresponding acid is produced by the following typical reaction.

$$(\mathrm{Res.SO_3^-})\mathrm{H^+} + \mathrm{NaCl}\ (\mathrm{Soln}) \rightleftharpoons (\mathrm{Res.SO_3^-})\mathrm{Na^+} + \mathrm{H^+Cl^-}(\mathrm{soln}) \text{------} (3)$$

For strongly acidic cation exchange resins, the exchange capacity is virtually independent of the pH of the solution. For weak acid cation exchangers, such as those containing the carboxylate group, ionisation occurs to an appreciable extent only in alkaline solution, i.e. in their salt form, consequently the carboxylic resins have very little action in solutions below pH 7. These carboxylic exchangers in the hydrogen form will absorb strong bases from solution.

$$(\mathrm{Res.COO^-})\mathrm{H^+} + \mathrm{Na^+OH^-}\ (\mathrm{soln}) \rightleftharpoons (\mathrm{Res.COO^-})\mathrm{Na^+} + \mathrm{H_2O} \text{------} (4)$$

but will have little action upon, say, sodium chloride; hydrolysis of the salt form of the resin occurs so that the base may not be completely absorbed even if an excess of resin is present.

Earlier Work

Carboxylic acid media have shown a great potential for the separation of metal ions which are otherwise very difficult to separate. Firdman and Yudinazh[5] extracted and separated Nb^{5+} and Ti^{4+} form oxalic acid solution using cation exchanger KY-2 in protonated form. The use of ion exchange separations in determining trace elemtns by neutron activation analysis is described by Brooksbank and Leddicotte[6].

Lanthanides were separated on the column of Dowex 50 using ammonium citrate as eluent at pH 3.26. Tartaric acid,[7] citric acid and formic acid[8] have proved to be very effective for metal ion separations. Boron and magnesium were separated from iron by a simple procedure with a cation exchange resin, ' Diaron K'. H_3BO_3 in an acidic solution of the sample is passed through the resin, and iron or other cations are absorbed. Boron was detected titrimetrically or colorimetrically. Magnesium was adsorbed quantitatively by the resin even in the presence of tartaric acid, but iron is passed into the eluate through the resin by 20% tartaric acid.

The cation exchanoe characteristics of a large number of elements towards the strongly acidic cation exchange resin Dowex 50W-X8 in media containing varying concentrations of formic acid and mixtures of formic acid with aqueous dioxan were investigaged by Qureshi et al.[8] The mixture of bismuth and copper solutions was separated. Bismuth was eluted by passing 23 M formic acid through the column at a flow rate of 3 ml/min, copper was then eluted with 2.5 M hydrochloric acid at a flow rate of 1.5 ml/min. Also the separations of the mixtures of lead and copper, barium and lanthanum, cadmium and copper were predicted.

Attempts were made to employ addition of water-acetone to promote metal-carboxylate complex formation for the selective elution of Ni, Cu, Co and Zn ions from Dowex 50W-X8 resion.[9] The distribution coefficients of Ni, Cu, Co and Zn ions in aqueous acetone-acetic, chloroacetic, dichloroacetic and trichloroacetic acids were found out at various compositions of the latter. The data were used for working out the optimum conditions for metal ion separations. Results on the separation of binary and ternary mixtures of metal ions were presented.

Cation exchange chromatographic studies of manganese on Dowex 50W-X8 are recently reported in out laboratory.[10] The distribution coefficients for Cu, Zn, Mg, Ni, Cd, Co, Mn, Ca, Pb, Th, Al, Hg, Sr and Ba were found out in aqueous acetone - succinic acid media. The effect of varying concentrations of acetone and the acid on distribution coefficients were studied to find out the suitable conditions for the separations. The quantitative separations of manganese from other elements were carrid out.

A systematic study of the cation exchange behaviour of metals on $R-NH_4$ type resin in aqueous-ammonium acetate and ammonium acetate containing other solvents (mixed media) has been reported by some workers. Minami and Ishimori[11] explored the possibility of separating barium from lead on a cation-exchanger by first eluting the absorbed lead with ammonium acetate at pH 6 and then barium, with 10% , ammonium chloride solution. The difference in the stability of the anionic complexes of barium and lead with ethylenediaminetetraacetic acid at pH 4.5 and 10.5 respectively has been utilised for their separation.[12] Lead (pH = 4.5) passed out of bed and adsorbed barium was eluted with EDTA (disodium salt) at pH 10.5 Khopkar and De[13] studied the cation exchange behaviour of barium on Dowex 50W-X8 (H^+). Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA has been used as the eluting agents. Barium has been separated from U(VI), Cu(II), Hg(II), Cs, Zn, Cd, Ag, Ce(IV), Zr, Th, Fe(III) and Bi(III) by 4 M ammonium acetate. Kemula and co-workers[14] developed a procedure for the separation of silver from the copper based on the adsorption of both ions on the cation exchanger, Welfatit KPS-200. Copper was eluted as the complex $CuCl_4^{-2}$ by hydrochloric acid, while silver was precipitated on the column. A method[15] had been developed for separation of silver, lead and mercury (II) in their mixtures at the milligram level, based on their differences in ion exchange potential on a cation exchanger, Dowex 50W-X8 (H^+). Out of the two common eluting agents nitric acid and ammonium acetate[16,17] the latter is preferable in view of the more favourable separation factors. It was observed that 300 ml of 0.25 in ammonium acetate eluted lead alone, the effluent was free from silver and mercury. Further 0.5 M ammonium acetate offers a good separation of silver from mercury, 150 ml of this eluent removed silver alone and the effluent was free from mercury. Finally mercury was removed from the resin bed by 100 ml of 4 M ammonium acetate.

Janauer et. al. separated barium from other metal ions by means of cation exchange in an aqueous 20%, v/v DMSO medium containing 0.25 mol/l of thiocyanate.[18,19] As the DMSO offers numerous advantages as an eluent in cation-exchange chromatography because of its complex forming tendency with almost all metal ions, it is used as solvent in many analytical procedures. Diehl et al.[20] studied the behaviour of Bi^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} & Ag^+, Sn^{4+} and Zn^{2+} on a cation exchange resin (Bio Rad AG 50-X8) in DMSO-hydrochloric acid - water systems. On the basis of KD values they predicted the possibility of separating these cations from mixtures. The anion-exchange behaviour of several cations in methanol-hydrochloric acid-DMSO-water systems has been explored by Fritz and Lehoczky,[21] who showed the usefulness of these systems by separating various mixtures of metal ions.

Phipps[22] has studied the selectivity sequence of monovalent anions on an anion exchange resin in [illegible] systems. Earlier studies[23,24] have shown that formic acid offers unusual possibilities in cation-exchange chromatography and zirconium can be separated from thorium and hafnium by cation-exchange in formic acid media.

PRESENT WORK

The thesis mainly comprises the studies in ion exchange seperations of some metal ions. The work done on different aspects of ion exchange is divided into three chapters.

First chapter covers the theory of ion exchange chromatography and the general experimental procedure.

Second chapter consists of the studies of kinetics of exchange of copper, magnesium and lead on Amberlite IR-120$(NH_4)^+$ in aqueous acetone Amonium tartarate medium. Various kinetic parameters such as half exchange time ($t^{1/2}$), interdiffusion coefficients(D), parabolic diffusion constants (k) and rate constants (K) are computed and the results are examined in view point of various exchange isotherms. The effect of temperature over these exchange processes was studied and the values of energy of activation [E_a] entropy of activation (S) are reported.

Chapter three deals with column chromatographic seperations of binary and multicomponent mixtures of different metal ions such as Th^{4+}, Al^{3+}, Fe^{3+}, Zn, Mn, Co, Ni, Cu, Pb, Sr, Ba, Ca, Cd, Hg and Mg by using cation exchanger Amberlite IR 120 $(NH_4)^+$ The distribution coefficients (K_D) were calculated at various concentrations of Ammonium tartrate and at various percentages of acetone. The optimum conditions such as concentration of metal ions, composition of mixed solvents, the strength of the acids were determined from the values of distribution coefficients. The results of all the seperations are presented inthis chapter. The elution characteristics such as BTV, VEP and TEV were found out from elution curves.

EXPERIMENTAL :-

Reagents, Solutions and Apparatus

Ion Exchange Resin :

The ion exchanger used for all experiments is a strongly acidic cation exchange resin in ammonia form. The cation exchanger, commercially known as Amberlite IR 120 (20-50 mesh) in ammonia form is in the form of beads of golden yellow colour. The resin had a moisture content of ~ 8%. The air dried resin had a capacity of 3.6 m.eq/g.

Prior to use, the cation exchange resin was washed with 2 M HCl for several times and then with distilled water until the resin in free from free chloride ions. The resin got swollen when placed in water.

When the resin is used for any exchange experiment, the chloride ions get replaced by other negatively charged metal ion complexes. The resin in then brought to original NH_4^+ chloride form by washing it with excess of 2 MNH_4Cl, followed by washing with distilled water. The resin then comes back in the NH_4^+ ~~chloride~~ form which can be used again for other exchange processes. This process is called as regeneration.

THE GLASS COLUMN

For all seperation work corning glass columns are used. The resin is filled in the glass columns, by preparing a slury of it in water. The column is open on one end and at the other end there is a nozzle with a stop cock, with the help of which one can control the drop rate of the effluent. The glass column has a length of ~10 Cm and uniform inner diameter of 14 mm. A column of resins bed can rest easily on a sintered glass porous support at the bottom. The height of the resin bed can be varied easily. A care is always taken that the resin bed will always remain bneath the water level at the top.

Solutions

All BDH chemicals of Analytical grade are used.

E.D.T.A.

0.1 M, 0.01 M and 0.001 M standard solutions of E D T A were prepared by dissolving 37.225 g. 3.723 g and 0.372 g of A.R. grade E D T A per litre.

Metal salts

0.05 M solutions of calcium, magnesium, manganese, nichel, cobalt, copper, cadmium, zinc, strontium , barium, aluminium, mercury, iron chlorides and thorium and lead nitrates were prepared by using A.R. grade salts as follows.

1)	$COCl_26H_2O$	11.896 g. :	
2)	$CdCl_2$ 2.5 H_2O	11.42 g. :	
3)	$CuCl_2$ 2 H_2O	8.524 g. :	
4)	$HgCl_2$	13.575 g. :	
5)	$NiCl_26H_2O$	11.885 g. :	
6)	$ZnCl_2$	6.814 g. :	
7)	$Mn\ Cl_2$ 4 H_2O	9.896 g. :	
8)	$CaCl_2.2H_2O$	7.351 g. :	were dissolved in 1000 ml distilled water
9)	$BaCl_22H_2O$	12.215 g. :	
10)	$SrCl_2$ $6H_2O$	13.331 g. :	
11)	$AlCl_36H_2O$	12.072 g. :	
12)	$MgCl_26H_2O$	10.165 g. :	
13)	$Pb(NO_3)_2$	16.560 g. :	

14)	$Th(NO_3)_4 \cdot 4H_2O$	27.600 g. :	
15)	$FeCl_3 \cdot 6H_2O$	13.510 g. :	Few drops HCl added and then diluted to 1000 ml.

The solutions were standardised by using literature methods.

Buffer solutions (pH = 10)

70.0 g of A.R. Ammonium chloride was dissolved in 568 ml of concentrated Ammonia and diluted to 1000 ml with distilled water.

INDICATORS

1) **ERIOCHROME BLACK-T.** :- The indicator solution was prepared by dissolving 0.2 g of dyestuff in 15 ml of triethenolamine with the addition of 5 ml of absolute alcohol to reduce the viscosity.

2) **XYLENOL ORANGE** : The indicator solution was prepared by dissolving 0.5 g of xylenol orange in 100 ml of water.

3) **PAN 1-(2-pyridylazo)-2-naphthol** : The indicator solution was prepared by dissolving 0.1 g of PAN in 100 ml of methyl alcohol.

4) **Phthalein complexone** : The indicator solution was prepared by dissolving 0.1 g of phthalein complexone in 100 ml of water containing a little ammonium hydroxide.

5) **Murexide Indicator** : The indicator solution was prepared by dissolving one g of murexide in 50 ml of distilled water.

6) **Ammonium thiocyanate** : 40% solution in disttiled water.

Ammonium tartrate (2 M)

Tartaric acid of 4 M was mixed with 4 M NH_3 soln. The temp. of reaction was controlled by flow of water and allowed to cool in the reactor.

Ammonium tartrate in Acetone-water mixture : The solutions of ammonium tartrate of the derived molarities were prepared in various compositions of acetone-water mixture (v/v) and the molar strengths of the stock solutions were determined volumetrically.

Estimation of Metal Ions :

1) **Estimation of Calcium**[25] : The calcium ions were estimated titrimetrically using standard EDTA solution. 10 ml of calcium chloride solution was pipetted out in a conical flask and it was diluted to 50 ml with distilled water. 4 ml of buffer solution and a few drops of Eriochrome black-T indicator was then added and the mixture was titrated with 0.1 M EDTA solution until the colour changes from wine red to blue. The amount of calcium was calculated by using the relation :

1 ml 0.1 M EDTA = 4.008 mg Ca

2) **Estimation of Magnesium**[25] : The magnesium ions were estimated titrimetrically using standard EDTA solution. The procedure for estimation of magnesium ions is the same as that of calcium ions. The amount of magnesium was calculated by using the relation :

1 ml. 0.1 M EDTA = 2.432 mg Mg

3) **Estimation of Manganese**[25] : 10 ml of manganese chloride solution was pipetted out in a conical flask, 0.5 g of hydroxyl ammonium chloride was added to prevent oxidation of manganese ion. The solution was then diluted to 50 ml. with distilled water. 3 ml. of triethanol amine, 2 ml of buffer solution (pH=10) and few drops of Erio-T indicator were added and the mixture was titrated with 0.1 M EDTA solution until the colour changes from wine red to sky blue. The amount of manganese was calculated by using the relation :

1 ml 0.1 M EDTA = 5.494 mg Mn

4) ESTIMATION OF CADMIUM[25] : The cadmium ions were estimated titrimetrically using standard EDTA solution. 10 ml of cadmium chloride solution was pipetted out in a conical flask and it was diluted to 50 ml with distilled water, three drops of xylenol orange indicator were added. If the colour of the solution is red, dil. H_2SO_4 is added until the solution acquires yellow colour, powdered hexamine is added in order to change yellow colour of solution to intensely red. This step ensures that the solution has the correct pH (about 0.6). The mixture was titrated with 0.1 M EDTA solution until the colour changes from red to yellow. The amount of cadmium was calculated by using the relation.

1 ml 0.1 M EDTA = 11.242 Mg Cd

5) Estimation of Cobalt[25] : 10 ml of the cobalt chloride solution was diluted to 25 ml with distilled water and 3 drops of xylenol orange indicator were added followed by very dilute sulphuric acid until the colour just changes from red to yellow. To this solution powdered hexamine was added with shaking until the deep red colour was restored (pH = 6). The solution was warmed to about 40° C and titrated with standard EDTA solution until the colour changes from red to yellow orange, the addition of titrant should be made dropwise near the end point, since the colour change is normally not altogether sharp. The amount of cobalt was calculated by using the relation.

1 ml 0.1 M EDTA = 5.8933 mg Co

6) Estimation of Thorium[25] : 10 ml of thorium nitrate solution was pipetted in a 250 ml conical flask and diluted with about 25 ml. distilled water. The pH was adjusted to a value of 2-3 by the addition of dilute nitric acid. To the solution added 3 drops of xylenol orange indicator solution and the solution was titrated with staneard EDTA solution, until the colour changes from red to lemon yellow. 1 ml 0.1 EDTA = 23.205 mg Th

7) Estimation of Zinc[25] : 10 ml of the zinc chloride solution was diluted to about 75 ml with distilled water and 3 drops of xylenol drange indicator solution were added. To this solution powdered hexamine was added with shaking until it acquires an intense red colour. The solution was titrated wity the standard EDTA solution until the colour changes sharply from red to ~~he~~ yellow.

1 ml 0.1 M EDTA = 6.538 mg Zn

8) Estimation of Lead[25] : The lead ions were estimated titrimetrically using standard EDTA solution. The procedure for the estimation of lead ions is the same as that of the cadmium ions. The amount of lead was calculated by using the relation :

1 ml 0.1 M EDTA = 20.721 mg Pb

9) Estimation ~~sof~~ of copper[26] : 10 ml of nearly neutral solution of copper chloride was pipetted in a 250 ml conical flask. One ml. of glacial acetic acid and 3-4 drops 0.1 percent PAN indicator solution were added. The solution was titrated with 0.1 M EDTA solution. The end point indicated by a colour change from red to yellowish-green. Before the end point reddish brown colour appears if more than few milligrams of copper are present.

1 ml 0.1 M EDTA = 6.354 mg Cu

10) Estimation of Nickel[25] : Nickel was determined by a direct titration with EDTA, using muroxide as an indicator. Ammonium hydroxide was added to the 10 ml of solution of nickel until the nickel ion is converted to the tetramine complex. Diluted mixture and 3-6 drops of a saturated aqueous solution of muroxide was added for each 100 ml of solution. The solution

titrated with staneard 0.1 M EDTA solution. The end point is indicated by a colour change from orange-yellow to purple.

1 ml 0.1 M EDTA = 5.869 mg Ni

11) Estimation of strontium[26] : The solution containing the strontium was mixed with an equal volume of alcohol and for each 100 ml of the mixture 2-3 drops of 0.1 percent aqueous solution of phthaleincomplexone containing a little ammonium hydroxide and 5 ml of conceentrated ammonium hydroxide was added. The solution was titrated immediately with 0.1 M EDTA solution. At the end point, the red colour of the mixture disappears abruptly.

1 ml of 0.1 M EDTA = 8.763 mg Sr

12) Estimation of Barium[26] : The titration of barium with phthaleincomplexone was carried out at pH 11. At pH = 10, the colour of the indicator is substantielly weaker. At higher concentration the colour change is not sharp, due to small difference in stabilities of metal-indicator and metal EDTA complexes. The dtermination is improved by adding 30-50% alcohol. In the presence of alcohol the carbonates of the metals may precipitate. For this reason a back titration is recommended. An excess of EDTA is added and the excess titrated with standard barium chloride solution. The indicator is coloured in basic solution, with the result that, at the end point of the titration, the solution remians rose coloured.

1 ml 0.1 M EDTA = 13.738 mg Ba

13) Estimation of Aluminium[25] : To 10 ml of the aluminium chloride silution run from a burette a slight excess of 0.1 N EDTA solution and adjusted the pH between 7 and 8 by the addition of ammonia solution. The solution was boiled for a few minutes to ensure complete complexation of the aluminium. The solution was cooled to room temperature and adjusted the pH to 7 to 8. Then a few drops

of Eriochrome Black-T indicator were added and the solution was titrated xmmudkt wutx rapidally with standard 0.01 M Zinc sulphate solution until the colour changes from blue to wine red.

Every ml difference between the volume of 0.01 M EDTA added and the 0.01 M zinc sulphate solution used in the back titration corresponds to 0.2698 mg Al.

14) <u>Estimation of Mercury</u>^{26} : To the 10 ml of mercury chloride solution ran from burette a small excess of standard EDTA solution. Buffer (pH = 10) 5 ml. , and Eriochrome black-T indicator were added. The excess EDTA titrated with standard zinc or magnesium sulphate solution. Mercury also determined by adding an excess of magnesium EDTA complex in an amount of at least equivalent to mercury present, and then after adding the buffer and indicator the magnesium formed in the replacement reaction was titrated with standard EDTA solution.

1 Ml. 0.1 M EDTA = 20.061 mg Mg

15) <u>Estimation of Iron</u>^{26} : 10 ml ferric chloride solution was pipetted out in a conical flask. The solution was neutralised by the addition of 0.1 N NaOH. Then 1-2 drops of 40% ammonium thiocyanate solution was added and the solution was titrated against standard EDTA solution. The end point is indicated by the colour change from red to colourless.

1 ml 0.1 M EDTA = 5.585 mg Fe

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