
CHAPTER - III

ANION EXCHANGE CHROMATOGRAPHIC SEPARATION OF

Mg, Ca, Sr, Ba,

Pb, Zn, Cd, Hg,

Cu, Mn, Co, Ni,

Th AND Bi.

**ON
AMBERLITE IR-45 (Cl)
IN
AQUEOUS-ACETONE-MALEIC ACID MEDIA**

There are many factors affecting the distribution of metal ions between aqueous solutions and an anion exchanger. They include the formation of additional species by side reactions, the application of a constant ionic medium, the salt effect connected with it, the secondary cation effect and the effect of acid, the effect of metal loading, the influence of temperature and the effects of resin structure, such as capacity and crosslinking.

HISTORICAL REVIEW

The separation of metals as chloro-complexes from aqueous hydrochloric acid solutions using anion exchange columns is now a well established and valuable analytical procedure¹⁻⁸. In this method the metals that form anionic chlorocomplexes are taken up from strongly hydrochloric acid solutions, other metals pass through the column. Then the metals on the columns are eluted one or two at a time using aqueous solutions of hydrochloric acid that are progressively more dilute.

It is observed that metals are taken up more strongly and at lower hydrochloric acid concentrations if an appreciable amount of water-miscible organic solvent is added to the aqueous hydrochloric acid. Ketzin and Gebert⁹ studied the adsorption of lithium chloride, lithium nitrate, cobalt chloride and nickel nitrate on Cl^- and NO_3^- form anion

exchange resins from acetone solution. They noted that the whole salt is adsorbed and suggested that the salts might be taken up as complex anions. On the other hand Davis and Owen¹⁰ postulated that the salts are adsorbed by the resin by a solvent extraction process. Tuck and Welch¹¹ found that the uptake of Pu(IV) by an anion exchange resins from a nitric acid - diethylene glycodebutyl ether solution is the result of anionic complex formation.

In the anion exchange separation of sulphate, sulphite, thiosulphate, sulphide, selenite and tellurite, Iguchi^{12,13} found that the addition of alcohol to the eluting agent increased the adsoribilities of all except the selenite and tellurite. Burstall et al¹⁴ eluted gold in the form of $\text{Au}(\text{CN})_2^-$ from an anion exchange column using an acetone eluent containing 5% HCl and 5% water. Korkisch et al¹⁵. Separated U(VI) from certain other metals on a chloride form anion exchange column using a solution of HCl in the mixed water and ethyl alcohol. The addition of 10-25% CH_3OH to an aqueous HCl eluent has been found to improve the anion exchange separation of Zn and Cd¹⁶. Kojima^{17,18} and Yoshino and Kurimura¹⁹ studied the anion exchange behaviour of several of the transition elements in mixed solvents containing HCl. Distribution coefficients in mixed media were compared with those in aqueous HCl solutions. The anion exchange behaviour of Cd, Co, Cu, Ni, Zn, Mn(II), Pb(II), Th(IV), Se, Bi, Zr(IV), Ca and Mg ions in water

isopropyl/ethyl/methyl alcohol - HCl media was studied by Fritz and Peterzyk²⁰. Column separations of metal ion mixtures were carried out by eluting with alcohol-water-hydrochloric acid mixtures of different compositions. About 24 multicomponent mixtures of metal ions were separated.

Hazan and Korkisch²¹ investigated a large number of hydrochloric acid-organic solvent mixtures in order to find a medium in which a cobalt and nickel but not iron can be adsorbed on an anion exchange resin. Iron was eluted from cobalt and nickel by using 90% acetone-10% 6 M hydrochloric acid solution and further adsorption of cobalt and nickel was achieved in 70% acetone-30% 2 M HCl solution, nickel was eluted before cobalt.

In connection with environmental studies concerning the distribution of trace constituents in natural waters, it is frequently necessary to determine very low concentrations of elements such as cadmium, lead and copper.

A method²² is described for the determination of Cd, Cu and Pb in samples of natural ion-saline waters. After acidification with HBr, the water sample is filtered and following the addition of ascorbic acid, passed through a column of the strongly basic anion exchange resin Dowex 1 - X8 (Br⁻ form). On this exchanger Cd(II), Cu(II) and Pb(II) are adsorbed as anionic bromide complexes. After elution of

these elements with 1 M HNO_3 , the determination by atomic absorption spectrometry were carried out in a medium of 90% (v/v) CH_3OH and 10% (v/v) 1.5 M HBr .

In the radio-active decay of uranium, certain intermediate procedures are useful in geological dating. Among these ^{230}Th , ^{231}Pa have found many uses in dating deep-sea sediment horizon fossils, corals and marine mollusc shells. The selective separation²³ of Th(IV) , Pa(V) and $\text{UO}_2(\text{II})$ ions from each other was carried out by using Dowex 1 as anion-exchanger and $\text{HCl-CH}_3\text{COOH}$ mixtures of various compositions as eluents.

Many theoretical investigations²⁴⁻²⁸ have dealt with the anion exchange behaviour of elements in organic and in mixed organic-inorganic solutions of very low water content. The suitability of anhydrous CH_3COOH as a medium for the separation of some lanthanides like Nd(III) , Sm(III) , Tb(III) and Tm(III) on anion exchange resins, Dowex 1 - X8 in Cl^- and NO_3^- forms, was investigated by Kraus²⁹. The results indicated that although transfer to the anhydrous solvent does not influence the distribution coefficients of these elements in this medium, the addition of anions drastically changes their adsorption behaviour so that their separations become possible.

Anion exchange behaviour of Bi , Cd , Pb , Zn and In in the HBr-HNO_3 acid mixtures was studied by Strelow



et al³⁰⁻³². The distribution coefficients in 0.03 M HBr with various concentrations of HNO₃(0-2M) were obtained by using Bio-Rad AG 1 - X8 anion exchange resin. The K_D values decrease with increase in the molarities of HNO₃. Selectivities of elements in HBr-HNO₃ mixtures upto 2 M HNO₃ follow the sequence³², Bi(III), Cd(II), Pb(II), Zn(II), In(III), Cu(II), similar to the sequence in pure HBr. The elements are less strongly adsorbed from the mixed acid, but the separation factors are often large and some times even larger than in the pure acid.

Carboxylic acids and their salts as media for ion exchange separations seem to be quite attractive because ion exchange resins are widely used for practical purposes ranging from analytical chemistry to large scale industrial processes. Qureshi et al³³ have shown that carboxylic acid media are useful for ion separation of cations, and successful binary separations of Ti(IV) - UO₂(II), Ti(IV) - V(V), Nb(V) - V(V) and Ti(IV) - Fe(III) on cation exchange columns were achieved. The ion exchange behaviour of Pb, Cu(II), Fe(II), Th, V, Fe(III), UO₂(II), Th(IV) and rare earth metal ions in formic acid, sodium formate, oxalic acid, potassium oxalate, citric acid, potassium citrate, tartaric acid and potassium tartarate solution was studied³⁴ on anion and cation exchange resins. The tendency of metal ions to form the complexes with carboxylic acids was

observed and many difficult separations were possible in these media. The separation potential has been proved to be of practical use by achieving some binary separations on ion exchange columns. The separations achieved were in good agreement with electrophoretic movements.

Ion exchange behaviour of Bi(III) has been extensively studied in mineral acid media as both anionic and cationic complexes³⁵⁻³⁷. Limited use has been made of EDTA³⁸, oxalate³⁹⁻⁴⁰, and formate⁴¹ solutions. Gerdes and Rieman³⁹ investigated a method of analysis of brass by ion exchange chromatography. The sample solution of brass alloy in HCl is passed over Dowex 1 - X8 resin. When 185 ml of 3-4 M HCl was eluted at 1.5 ml per min, the first 25 ml of elute was found to contain Ni, the next 80 ml Cu and the remainder lead. Fe was eluted with 0.5 M HCl (30 ml) and then 0.5 oxalic acid (100 ml) was added to the column. Zinc was collected in 61 - 131 ml \sim 70 ml and Sn was collected in (151 - 200 \sim 50 ml) solution.

Maines⁴² has described an ion exchange procedure for silicate analysis. He employed adsorption of the sulphosalicylate complexes of Fe(III), Ti(IV) and Al(III) on Dowex 1 - X8 anion exchange resin for the separation of these elements from Mn(II), Mg, Ca, K and Na.

Systematic studies on the anion exchange behaviour of Bi(III) in maleic acid and succinic acid solutions on

Amberlite IRA-401 were carried out by Sobhana et al⁴³.

HNO₃ and HClO₄ at different concentrations were tried as eluents in the two systems. Methods have been developed for the separation of Bi(III) from Th(IV), Fe, Pb, Zn, Cd, CO, Ni, Mg and Mn metal ions. Methods were applied to the analysis of Wood's metal, separations were also carried out with liquid anion exchanger, Amberlite LA-1 in xylene.

A new nitrite media was used by Bhatnagar et al⁴⁴ for studying the distribution of some metal ions in aqueous and mixed ethanol media. In continuation to this anion exchange equilibrium distribution of 15 metal ions have been studied⁴⁵ in aqueous nitrite and aqueous methanol nitrite media using Dowex 21K in nitrate form. The ions such as Hg(II), Cd(II) and Ag(I) which were expected to form stable metal nitrite complexes gave high K_D values, separation possibilities for many metal ions by ion exclusion technique have been suggested.

PRESENT WORK

Selective sorption and elution of metal complexes on anion exchangers has been shown in recent years to be an extremely powerful tool for metal ion separations. Carboxylic acids, are known to form complexes with many metal ions and use has been made of some of them to

facilitate separations. However, only a few studies on the adsorption of metal maleate complexes on anion exchange resins have been reported. The aim of the present work is to investigate the adsorption characteristics and separation possibilities of elements in systems containing carboxylic acids. The distribution coefficients of fourteen metal ions in aqueous - acetone - maleic acid were found out at various concentrations of acetone and acids too. The data has been procured on a new commercially available exchanger Amberlite IR-45 in chloride form. The optimum conditions for analytical separations were decided from the values of distribution coefficients. The results of synthetic binary, tertiary and quaternary mixtures are presented.

EXPERIMENTAL

MEASUREMENT OF DISTRIBUTION COEFFICIENTS

1 g of air dried anion exchange resin was taken in 250 ml glass stoppered erlynmeyer flask. 4 ml of 0.05 M metal ion solution and 50 ml of appropriate acetone-water-maleic acid mixture was taken. The flask was stoppered and kept for 24 hours. An aliquot from supernatent liquid was pipetted out and acetone was evaporated. The metal ion content was determined by suitable titration method.

ION-EXCHANGE SEPARATION OF METAL IONS

The Pyrex glass chromatographic columns of 50 ml capacity were used. The columns were provided with safety 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 20 g soaked resin was passed and was allowed to settle by occasional tapping. A care was taken to prevent the formation of air pockets or strata of the ion exchange resin.

PROCEDURE

The column was equilibrated with the resin by passing 20 ml of acetone-water-maleic acid mixture at maximum flow rate⁹⁷⁻⁹⁸. The binary, tertiary and quaternary mixtures of various metal ions were prepared.

It was allowed to pass down the column slowly without allowing the level of the liquid to drop 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 1 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 and the fractions were collected. The metal ion contents of the two mixtures were carried out by standard titrimetric procedures.

In case of tertiary mixtures the first and second metal ion is eluted by suitable eluting agents and third metal is eluted finally by proper eluting agent. The experimental details for tertiary and also for quaternary mixtures were the same as described above. The concentration of metal versus effluent volumes were plotted and from the nature of the curves the quantities of respective metal ions and extent of separation was determined.

Table 3.1: Distribution Coefficients (K_D) in Aqueous-Acetone-Maleic Acid (0.05M) Media on Amberlite IR-45 - (Cl^-) form.

Metal Ion	Acetone % V/V				
	00	20	40	60	80
Mg(II)	2.6	N.A.	N.A.	N.A.	N.A.
Ca(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Sr(II)	2.4	3.0	2.4	3.3	2.7
Ba(II)	2.8	4.8	5.6	6.9	7.2
Pb(II)	4.9	7.6	23.3	127.8	441.8
Zn(II)	3.37	1.7	4.2	28.8	77.0
Cd(II)	7.6	22.6	83.1	442.2	1104.0
Hg(II)	450.0	810.0	1097.0	T.A.	T.A.
Cu(II)	5.6	7.2	11.1	23.1	37.8
Mn(II)	2.9	2.2	1.7	2.2	2.2
Co(II)	3.1	N.A.	N.A.	N.A.	2.1
Ni(II)	3.4	1.6	1.3	2.2	2.2
Th(IV)	7.5	7.5	7.1	9.0	9.2
Bi(III)	Ppt	Ppt	Ppt	Ppt	1790.0

N.A. = No adsorption

T.A. = Total adsorption

Ppt = Precipitation

Table 3.2: Distribution Coefficients (K_D) in Aqueous-Acetone-Maleic Acid (0.1M) Media on Amberlite IR-45 - (Cl⁻) form.

Metal Ion	Acetone % V/V				
	00	20	40	60	80
Mg(II)	3.5	3.5	N.A.	N.A.	N.A.
Ca(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Sr(II)	3.0	3.6	3.9	4.5	5.1
Ba(II)	2.5	4.8	5.4	5.6	5.9
Pb(II)	6.2	8.3	26.2	140.7	627.7
Zn(II)	1.7	2.0	3.9	26.6	75.7
Cd(II)	9.1	23.2	86.8	399.0	1683.0
Hg(II)	1097.0	T.A.	T.A.	T.A.	T.A.
Cu(II)	3.7	6.0	8.0	19.4	32.6
Mn(II)	3.2	3.5	2.5	1.7	1.1
Co(II)	2.1	2.4	2.1	1.8	1.8
Ni(II)	1.9	3.7	1.9	1.3	3.4
Th(IV)	9.0	8.2	8.2	9.7	Ppt
Bi(III)	Ppt	Ppt	Ppt	Ppt	2160.0

N.A. = No adsorption

T.A. = Total adsorption

Ppt = Precipitation

Table 3.3: Distribution Coefficients (K_D) in Aqueous-Acetone-Maleic Acid (0.5M) Media on Amberlite IR-45 - (Cl⁻) form.

Metal Ion	Acetone % V/V				
	00	20	40	60	80
Mg(II)	2.0	2.3	1.4	1.7	1.4
Ca(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Sr(II)	2.7	2.4	2.7	3.3	4.8
Ba(II)	4.2	9.8	12.7	13.1	24.1
Pb(II)	2.8	5.2	17.2	108.8	420.2
Zn(II)	2.8	2.2	4.7	24.5	86.4
Cd(II)	1104.0	T.A.	T.A.	T.A.	T.A.
Hg(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Cu(II)	4.1	3.3	4.8	8.0	18.8
Mn(II)	2.9	3.5	2.9	3.0	3.5
Co(II)	8.5	7.0	5.1	4.8	6.2
Ni(II)	3.2	2.2	2.8	3.0	3.7
Th(IV)	14.7	17.0	16.5	16.0	12.9
Bi(III)	111.2	303.0	404.0	597.1	683.9

N.A. = No adsorption

T.A. = Total adsorption

Ppt = Precipitation

Table 3.4: Distribution Coefficients (K_D) in Aqueous-Acetone-Maleic Acid (1.0M) Media on Amberlite IR-45 - (Cl^-) form.

Metal Ion	Acetone % V/V				
	00	20	40	60	70
Mg(II)	2.0	3.9	2.6	2.0	2.5
Ca(II)	N.A.	N.A.	2.2	2.8	3.2
Sr(II)	3.9	3.9	4.5	4.8	5.9
Ba(II)	4.8	10.5	12.3	17.9	23.6
Pb(II)	5.9	16.9	60.7	227.8	1036.8
Zn(II)	3.3	3.1	5.0	38.5	65.1
Cd(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Hg(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Cu(II)	4.8	5.2	5.2	8.8	15.5
Mn(II)	3.8	3.2	3.8	3.2	4.5
Co(II)	8.1	12.7	13.6	31.9	33.2
Ni(II)	3.0	2.8	3.8	4.7	5.2
Th(IV)	26.1	27.4	28.6	27.4	30.2
Bi(III)	58.9	276.6	560.9	952.3	1329.7

N.A. = No adsorption

T.A. = Total adsorption

Ppt = Precipitation

RESULTS AND DISCUSSION

DISTRIBUTION COEFFICIENTS IN AQUEOUS-ACETONE-MALEIC ACID MEDIUM

The distribution coefficient of Mg, Ca, Sr, Ba, Pb, Zn Cd, Hg, Cu, Mn, Co, Ni, Th(IV) and Bi(III) were found out at 0, 20, 40, 60 and 80 percentages of acetone and at 0.05, 0.1, 0.5 and 1 M concentrations of maleic acid. The values are presented in Table 3.1 to 3.4.

The distribution coefficients of Mg, Ca, Sr, Ba, Cu, Mn, Co, Ni, Zn and Th are low at all concentrations of maleic acid and at all percentages of acetone. Mg, Ca, Sr, Cu, Mn and Ni show no adsorption, indicating that these metals have no tendency of complex formation. Ba, Zn, Co and Th show the very little tendency of formation of maleate complex anions at 0.5 and 1 M maleic acid and at more than 40 percentage of acetone.

The distribution coefficients of Pb are low at all concentrations of maleic acid, up to 40% acetone. These values are high at 60 and 80% acetone at all concentrations of acid and it is very high at 1 M maleic acid - 80% acetone (1036).

The tendency of complete adsorption of Hg on resin is indicated by highest measurable values of K_D (T.A.). This

indicates the behaviour of forming very stable anionic complex of Hg.

The values of distribution coefficients of Cd are low at 0, 20 percentages of acetone at 0.05 M, 0.1 M maleic acid. The tendency of exchanging anionic maleate complex of Cd with the resin is favoured at higher percentages of acetone and higher concentrations (0.5 and 1 M) of acid as well.

For Bismuth, the precipitation is seen at 0.05, 0.1 M maleic acid upto 60 percent of acetone. It may be due to the formation of oxycompounds. Bismuth maleate, formed at 80% acetone - 0.05, 0.1M acid and at all percentages of acetone at 0.5, 1 M of the acid, exchange Cl^- ions of Amberlite IR-45. The formation of anionic maleate complex is as reported earlier⁴³⁻⁴⁵.

As most of the separations are carried out at 0.1 M MA (0% acetone), 0.5 M MA (60% acetone) and 1 M MA (20 and 70% acetone), the selectivity sequence is given for these systems.

0.1 M maleic acid, 0% acetone

$\text{Hg} > \text{Cd} > \text{Th} > \text{Pb} > \text{Cu} > \text{Mg} > \text{Mn} > \text{Sr} > \text{Ba} > \text{Co} > \text{Ni} > \text{Zn} > \text{Ca}$.

0.5 M maleic acid 60% acetone

$\text{Hg} > \text{Cd} > \text{Bi} > \text{Pb} > \text{Zn} > \text{Th} > \text{Ba} > \text{Cu} > \text{Co} > \text{Sr} > \text{Mn} > \text{Ni} > \text{Mg} > \text{Ca}$

1 M maleic acid 20% acetone

Hg>Cd>Bi>Pb>Th>Co>Ba>Cu>Mg>Sr>Mn>Zn>Ni>Ca

1 M maleic acid 70% acetone

Hg>Cd>Bi>Pb>Zn>Co>Th>Ba>Cu>Sr>Ni>Mn>Ca>Mg

EFFECT OF CONCENTRATION OF ACETONE

The dielectric constant of a solvent, and the polarity and polarizability of solvent molecules are the properties which affect strongly their interactions with solutes and hence their solvent power. Onsagar and Kirkwood⁴⁸ gave the relationship between dielectric constant and dipole moment as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{g\epsilon} = \frac{4\pi}{3} N (\alpha + g\mu^2/3KT)$$

where α is the polarizability, μ the dipole moment, g coefficient, K the Boltzmann constant and T absolute temperature. The solvents are classified as nonpolar and highly polarizable ($\alpha \geq 10A^3$). The symmetrical molecules such as cyclohexane, p-xylene and carbon tetrachloride are nonpolar, the molecules of lower symmetry (toluence, p-dioxane), show a small dipole moment and the very unsymmetrical molecules, with functional groups such as C=O, -NO₂, -CN show high dipole moments, e.g. acetone (2.72 Debye), nitrobenzene (3.99 Debye). Multiple bonds and bonds

between carbon and the heavier halogen and sulphur atoms highly contribute to the polarizability of organic molecules, where as single C-C bonds, C-N and C-F bonds contribute less.

The solvents like acetic acid or dibutyl phosphoric acid are hydrogen bonded chains or larger aggregates. Cyclic aggregates have a low dipole moment, while chain polymers have a high dipole moment respectively⁴⁷.

It is observed that the distribution coefficients of Pb, Cd, Hg increase with the rise in concentration of acetone. In other metal ions the increase in K_D values are observed slowly at higher percentages of acetone. It is therefore reported that the distribution coefficients increase with the decreasing dielectric constant. Akerlof⁴⁹ has determined the dielectric constants of a number of aqueous organic solvent mixtures.

Table 3.5: The Dielectric Constants of Acetone-Water Mixtures V/V

Acetone	100.0	70.0	30	20	10	0.0
Dielectric Constant	21.1	35.7	61	67	73	78.4

Mixtures of such polar solvents as alcohol, water and acetone follow Kirkwood's equation⁴⁸.

$$\epsilon = \epsilon_1 - \delta_2 C_2$$

Where δ_2 is the molar dielectric decrement for dilute solutions of the less polar component 2 (acetone $\epsilon = 21.1$) in the highly polar component 1 (water $\epsilon = 78.4$).

Mixing an organic solvent, like alcohol or acetone with water lowers the dielectric constant and increases the electrical forces between ions. Complex ions become more stable, and ion pairing is favoured. The difference between the resin and solvent environments is magnified, because resins that have ionic groups take up water in preference to less polar organic solvent. Organic solvents, therefore, have profound effects on the distribution of metal ions in both anion and cation exchange. J. S. Fritz^{50,51} showed that the binding of divalent metal ions to an anion exchanger in hydrochloric acid solutions was strengthened by adding alcohol, and that isopropyl alcohol was more effective than ethyl or methyl alcohol.

A similar change in distribution coefficients of uranium in methanol-water mixtures containing 10% of 6 M nitric acid has been reported earlier⁵².

The system under study, is metal ions like Zn, Cd, Hg, Co, Ni, Cu, Ca, Mg, Pb, Th, Bi, Ba, Sr, Mn as the nitrates or chlorides in water-acetone medium. The dielectric constants are lowered by acetone ($\epsilon = 21.1$), and hence it can be concluded that there is great probability of

ion association. Ion pair formation is favoured and three dimensional water structure is broken down in presence of the cations and anions.

The dissolution of a salt in an organic solvent is furthered by a favourable entropy and heat of solution, the former is always positive and the latter is within the range of ± 10 Kcal/mole. The heat of solution depends strongly on whether the salt is anhydrous, a hydrate or a solvate with the solvent employed, as does the solubility itself. The solubility of anhydrous lithium perchlorate in diethyl ether (5321 weight %) was found to be more than that of trihydrate (0.196 weight %)⁵³. The solubility of anhydrous thorium nitrate⁵⁴ or cobalt chloride⁴⁶ in acetone was found to be slight compared with the appreciable solubilities of the hydrates in acetone⁵⁴.

When the counter ion is a simple inorganic anion as in the present case of Cl^- , there is strong evidence that this anion is primarily surrounded by water molecules regardless of which reasonable model is used to interpret the results⁵⁵.

The ions, acetone, water and carboxylic acids remain 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 acetic acid molecules interact strongly with one of the constituents of resin. In order to obtain the information about the selective sorption of acetic acid from aqueous solutions, the acid concentration inside the resin bead was determined as a function of the external concentration. It was observed that the solvent uptake (H_2O) was 0.643 gms/g of dry resin when there was no acetic acid outside the resin. As the concentration of acetic acid increases from 0 to 17.14 M solvent uptake rises only from 0.643 to 0.821 i.e. the solvent uptake is negligible at higher concentration of acetic acid. When K_a , i.e. the ratios of internal to external acid concentrations were calculated, it was observed that K_a is quite high at low external acid molarities, tending to unity at high concentration.

Using the model of Gregor, we can assume that the internal solution of anion exchange resin consists of two different parts: Firstly, the hydration and solvation molecules of water and acetic acid respectively, with no solvent power for which there is no reason to accept a composition different from that of outside. The strong interaction between the acetic acid molecules and the ionogenic groups of the resin has been proved⁵⁶ and hence it

is plausible to accept a higher mole fraction of the acetic acid in the solvating solution than in the free solution. These considerations explain the increased overall molarity of the acid inside the exchanger, when equilibrated with an aqueous acetic acid solution of a given composition. It was further stated that the internal volume of free solution tends to zero at high acetic acid molarities, whereas the solvation number reaches a maximum value of about four at 17.38 M acetic acid. This means that, in the case of glacial acetic acid, the swelling of the resin is due only to the tendency of the ionogenic groups of the exchanger to be surrounded each by four acetic acid molecules. This conclusion seems reasonable, since it is logical to assume that the forces causing the distortion of resin skeleton can only result in the case of such a high swelling from the very strong affinity of the acetic acid molecules towards the ionogenic groups, leaving no space for free solution.

EFFECT OF CONCENTRATION OF MALEIC ACID

From the data of distribution coefficients (Tables 3.1 to 3.4) it is observed that K_D values of metal ions under study increases with the increase in concentration of maleic acid. This suggests that at higher concentration of maleic acid most of the metal ions form stable anionic maleate complexes.

Eventhough the exact mechanism of the uptake of metal ions on the resin is not known it is essential to know the different processes in exchange reactions that take place in the presence of weak acid in aqueous or mixed media.

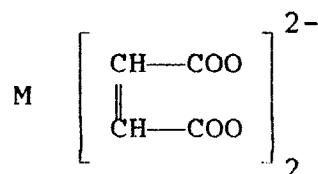
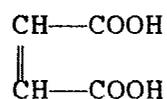
In the citric acid medium, both negatively and positively charged complexes are formed with Fe^{+3} .⁵⁷

Cupric ions⁵⁸ react with the oxalate ions to form $\text{CuHC}_2\text{O}_4^+$, CuC_2O_4 and $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$ with association constants 3.1×10^2 , 7.0×10^4 , and 2.3×10^4 at ionic strength (μ) 0.1. All three types of complexes with varying stability are possible and hence, the ion-exchange behaviour of copper in metal-oxalic acid medium is rather complicated.

In the oxalic acid medium Fe^{2+} forms a negatively charged complex. Hence, it has a low K_D on the cation exchanger while it has a high K_D on the anion exchanger. The formation of the negatively charged complex is confirmed by the electrophoretic studies.

In the tartaric acid medium, titanium⁵⁹ forms a negatively charged complex ($\text{TiOC}_4\text{H}_3\text{O}_6^-$).

In the present studies, maleic acid is a dibasic acid and hence it may be concluded that it forms a negatively charged maleate complex.



Maleic acid

Metal maleate complex $[\text{M}(\text{Ma})_2]^{2-}$
Where M = Cd, Hg, Pb.

The exchange of the negatively charged complex $\text{M}(\text{Ma})_2^{2-}$ takes place with Cl^- ions of the anion exchange resin, Amberlite IR-45.

SEPARATIONS

The results of the quantitative separation of synthetic binary tertiary and quaternary mixtures in aqueous-Acetone-maleic acid are presented in Table 3.6 to 3.8 and by figure 3.1 to 3.23.

ANION EXCHANGE SEPARATION OF METAL IONS IN AQUEOUS ACETONE MALEIC ACID

Separation of Binary Mixtures

The results of separations are presented in table 3.6 and by figs 3.1 to 3.14.

Separation of Cd from

Ni/Th/Ca/Cu/Mn/Sr/Ba/Mg/Co/Zn/Pb.

As the distribution coefficient of Cd in 60% acetone - 0.5 M maleic acid is higher than those of Ni, Th,

Ca, Cu, Mn, Sr, Ba, Mg, and Co, Cd was retained on the column and Ni, Th, Ca, Cu, Mn, Sr, Ba, Mg and Co were eluted. Cd was then stripped off from the column by 0.1 M maleic acid. The K_D values of Zn and Pb are less than Cd, in 20% acetone 1 M MA. These metal ions were separated by 20% acetone and 1 M maleic acid. Cd was then stripped off from the column by 0.1 M maleic acid.

Separation of Pb from

Ni/Sr/Ca/Cu/Co/Ba/Mg/Mn/Th

Ni, Sr, Ca, Cu, Co, Ba, Mg, Mn and Th are weakly bound to the resin in 70% acetone - 1M maleic acid and hence these metal ions were eluted in this medium. Pb was then eluted by 0.1 M maleic acid. The first metal ion was eluted at higher acid concentration having high acetone content and second one was eluted at lower acid concentration with zero percent acetone.

Separation of Hg from.

Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg/Zn/Pb

60% acetone - 0.5 M maleic acid is a poor eluent for Hg but not for Ni, Th, Co, Cu, Ca, Mn, Sr, Ba and Mg ions and hence these ions were eluted first from the column. Hg was removed by 0.5 M perchloric acid. Zn and Pb were eluted from the column by using 20% acetone - 1 M MA. Hg was removed by 0.5 M perchloric acid as it is strongly adsorbed in maleic acid media.

Separation of Bi from

Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg

It is seen that 70% acetone - 1 M MA is the best eluent for above mentioned ions except Bi. These ions were eluted with 70% acetone - 1 M MA. The elution of Bi was followed with 2 M sulphuric acid, as it is strongly adsorbed in maleic acid media.

SEPARATION OF TERTIARY MIXTURES

Separation of Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg/Zn/Pb-Cd-Hg

The results of separations of tertiary mixtures are presented in table 3.7 and figures 3.15 to 3.20.

The values of distribution coefficients of Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg are low in 60% acetone 0.5 M MA. Zn and Pb show lower K_D in 20% acetone - 1M MA. In above mentioned media distribution coefficients of Cd and Hg are very high. Hence Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg was eluted first with 60% acetone 0.5 M maleic acid and Zn and Pb were eluted by 20% acetone 1 M MA. Cd and Hg ions remain adsorbed on the resin column. Cd was then eluted by using 0.1 M MA. Hg was finally stripped off by using 0.5 M perchloric acid.

Separation of Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg-Pb-Hg

It is found that Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg ion has least tendency to form anionic maleate complexes and hence negligible tendency to exchange with Cl^- of resin, the above metal ions were eluted by 70% acetone - 1 M MA. Pb was then collected by passing 0.1 M MA as eluent. Hg was finally driven away by 0.5 M perchloric acid from the column.

SEPARATION OF QUATERNARY MIXTURES

The results of the separations are presented in table 3.8 and figures 3.21 to 3.23.

Separation of Ba/Th/Ca/Cu/Ni/Sr/Mg/Mn/Co-Pb-Cd-Hg

In 70% acetone - 1 M MA, Ba/Th/Ca/Cu/Ni/Sr/Mg/Mn/Co was weakly bound in comparison to Pb, Cd and Hg. Ba/Th/Ca/Cu/Ni/Sr/Mg/Mn/Co was eluted first with 70% acetone - 1 M MA. Pb was eluted later with 20% acetone - 1 M MA, in this medium distribution coefficients of Cd and Hg are very high. Cd was then eluted with 0.1 M MA. Hg was finally eluted with 0.5 M perchloric acid.

Table 3.6: Quantitative Separation of Binary Mixtures
(First Ion in Mixture is Eluted While the
Second Ion is Retained)

Mixture	Metal Ion eluted	Eluting agent	m Moles taken	m Moles found
1	2	3	4	5
Ni(II)+Cd(II)	Ni(II)	a	0.245	0.244
	Cd(II)	b	0.240	0.232
Th(IV)+Cd(II)	Th(IV)	a	0.240	0.230
	Cd(II)	b	0.240	0.232
Ca(II)+Cd(II)	Ca(II)	a	0.230	0.223
	Cd(II)	b	0.240	0.232
Cu(II)+Cd(II)	Cu(II)	a	0.245	0.245
	Cd(II)	b	0.240	0.232
Mn(II)+Cd(II)	Mn(II)	a	0.235	0.235
	Cd(II)	b	0.240	0.232
Zn(II)+Cd(II)	Zn(II)	c	0.245	0.245
	Cd(II)	b	0.240	0.232
Sr(II)+Cd(II)	Sr(II)	a	0.240	0.225
	Cd(II)	b	0.240	0.232
Ba(II)+Cd(II)	Ba(II)	a	0.240	0.230
	Cd(II)	b	0.240	0.232
Pb(II)+Cd(II)	Pb(II)	c	0.245	0.245
	Cd(II)	b	0.240	0.232
Mg(II)+Cd(II)	Mg(II)	a	0.227	0.224
	Cd(II)	b	0.240	0.232
Co(II)+Cd(II)	Co(II)	a	0.231	0.229
	Cd(II)	b	0.240	0.232
Ni(II)+Pb(II)	Ni(II)	d	0.235	0.224
	Pb(II)	b	0.242	0.242
Sr(II)+Pb(II)	Sr(II)	d	0.240	0.225
	Pb(II)	b	0.242	0.242

Table 3.6: Contd....

1	2	3	4	5
Ca(II)+Pb(II)	Ca(II)	d	0.230	0.226
	Pb(II)	b	0.242	0.242
Cu(II)+Pb(II)	Cu(II)	d	0.245	0.245
	Pb(II)	b	0.242	0.242
Co(II)+Pb(II)	Co(II)	d	0.231	0.225
	Pb(II)	b	0.242	0.242
Ba(II)+Pb(II)	Ba(II)	d	0.240	0.230
	Pb(II)	b	0.242	0.242
Mg(II)+Pb(II)	Mg(II)	d	0.227	0.221
	Pb(II)	b	0.242	0.242
Mn(II)+Pb(II)	Mn(II)	d	0.235	0.235
	Pb(II)	b	0.242	0.242
Th(IV)+Pb(II)	Th(IV)	d	0.240	0.233
	Pb(II)	b	0.242	0.242
Mn(II)+Hg(II)	Mn(II)	a	0.235	0.235
	Hg(II)	e	0.222	0.222
Ca(II)+Hg(II)	Ca(II)	a	0.230	0.223
	Hg(II)	e	0.222	0.222
Zn(II)+Hg(II)	Zn(II)	c	0.245	0.245
	Hg(II)	e	0.222	0.222
Ni(II)+Hg(II)	Ni(II)	a	0.245	0.244
	Hg(II)	e	0.222	0.222
Co(II)+Hg(II)	Co(II)	a	0.231	0.229
	Hg(II)	e	0.222	0.222
Cu(II)+Hg(II)	Cu(II)	a	0.245	0.245
	Hg(II)	e	0.222	0.222
Ba(II)+Hg(II)	Ba(II)	a	0.240	0.230
	Hg(II)	e	0.222	0.222
Th(IV)+Hg(II)	Th(IV)	a	0.240	0.230
	Hg(II)	e	0.222	0.222

Table 3.6: Contd....

1	2	3	4	5
Sr(II)+Hg(II)	Sr(II)	a	0.240	0.225
	Hg(II)	e	0.222	0.222
Mg(II)+Hg(II)	Mg(II)	a	0.227	0.224
	Hg(II)	e	0.222	0.222
Pb(II)+Hg(II)	Pb(II)	c	0.245	0.245
	Hg(II)	e	0.222	0.222
Ni(II)+Bi(III)	Ni(II)	d	0.235	0.224
	Bi(III)	f	0.230	0.226
Sr(II)+Bi(III)	Sr(II)	d	0.240	0.225
	Bi(III)	f	0.230	0.226
Th(IV)+Bi(III)	Th(IV)	d	0.240	0.233
	Bi(III)	f	0.230	0.226
Ca(II)+Bi(III)	Ca(II)	d	0.230	0.226
	Bi(III)	f	0.230	0.226
Ba(II)+Bi(III)	Ba(II)	d	0.240	0.230
	Bi(III)	f	0.230	0.226
Cu(II)+Bi(III)	Cu(II)	d	0.245	0.245
	Bi(III)	f	0.230	0.226
Mg(II)+Bi(III)	Mg(II)	d	0.227	0.221
	Bi(III)	f	0.230	0.226
Mn(II)+Bi(III)	Mn(II)	d	0.235	0.235
	Bi(III)	f	0.230	0.226
Co(II)+Bi(III)	Co(II)	d	0.231	0.225
	Bi(III)	f	0.230	0.226

a = 60% acetone + 0.5 M maleic acid.

b = 0.1 M maleic acid.

c = 20% acetone + 1 M maleic acid

d = 70% acetone + 1 M maleic acid.

e = 0.5 M perchloric acid.

f = 2 M sulphuric acid.

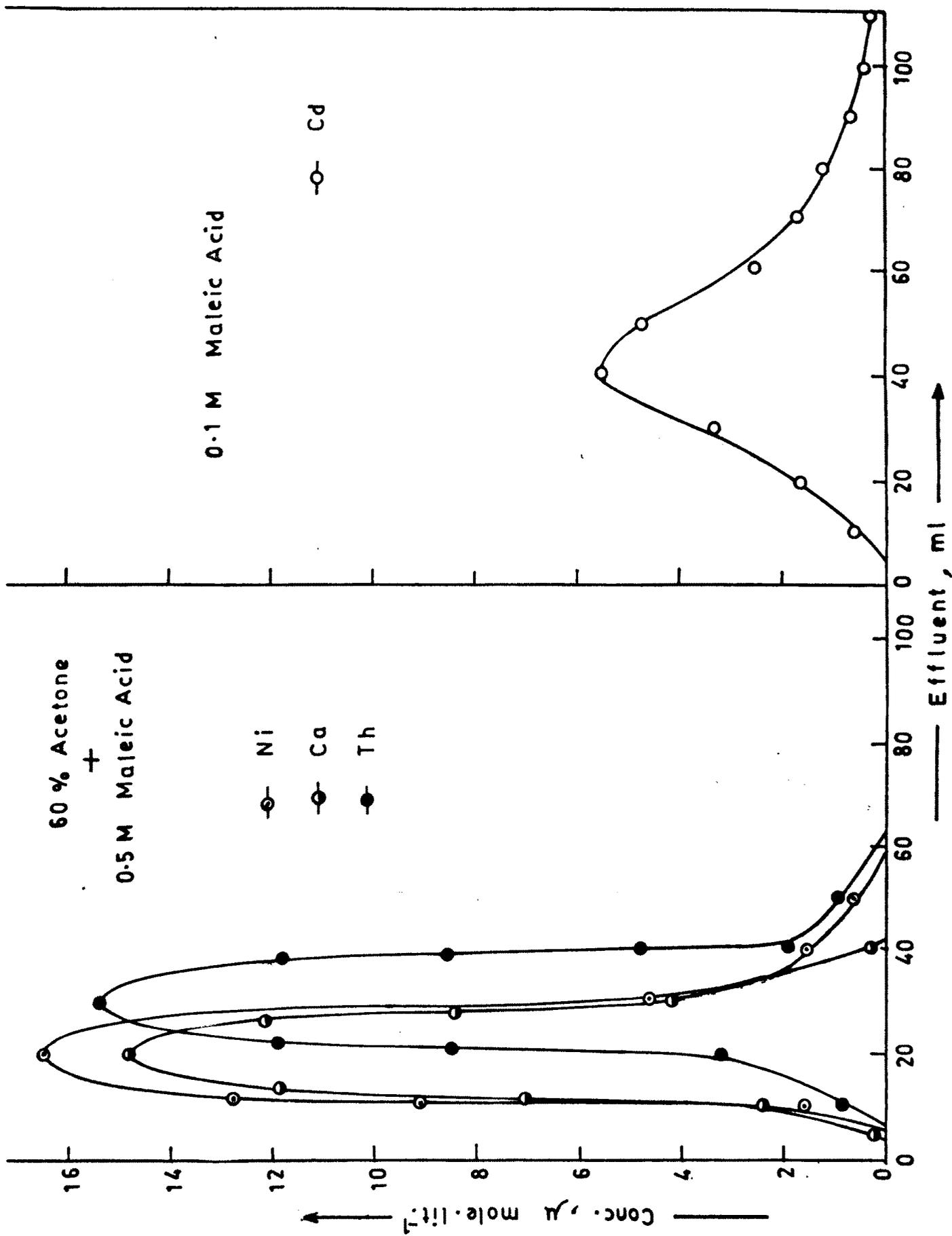


Fig. 3.1 — Elution Curves of Ni/Ca/Th — Cd.



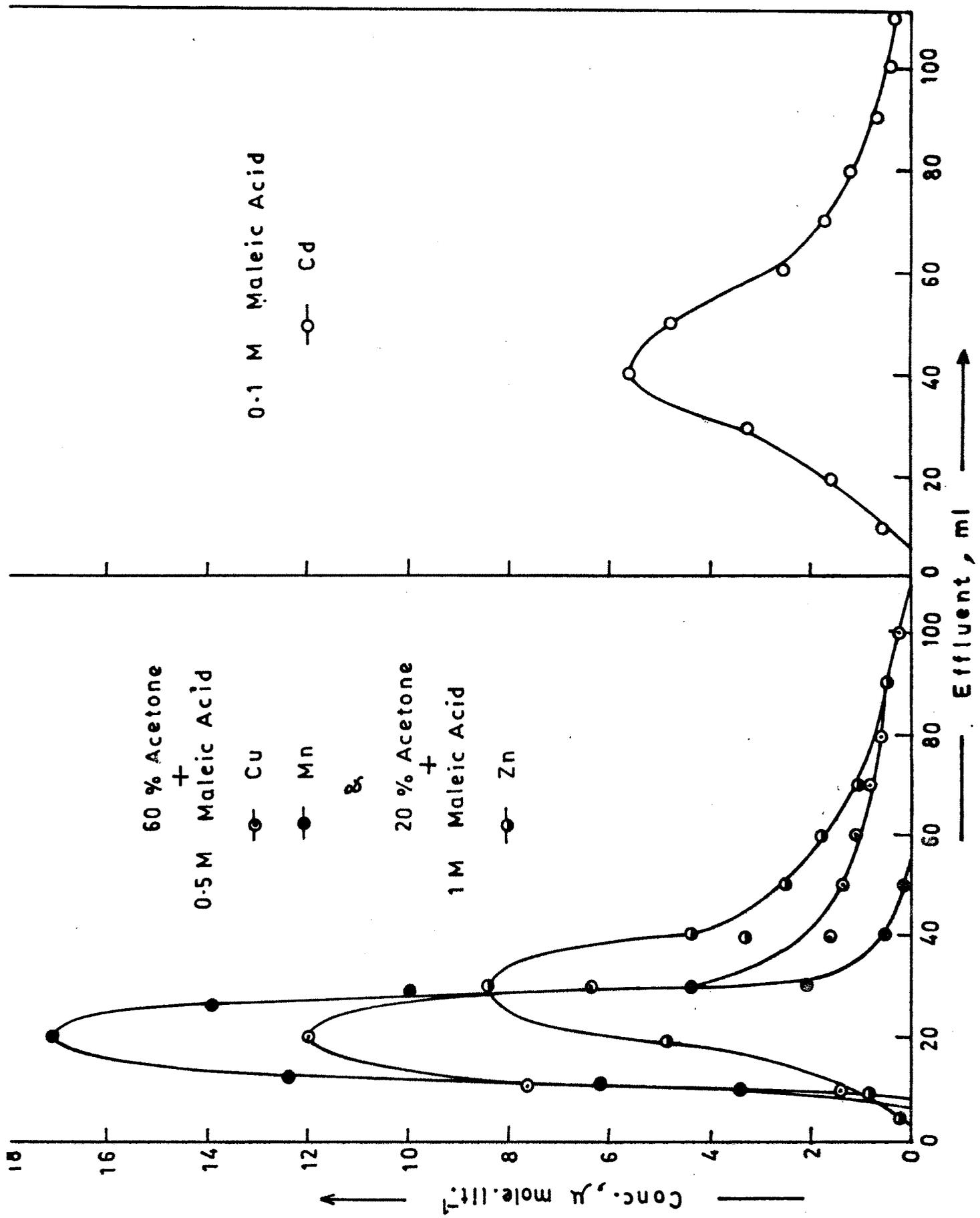


Fig. 3.2 — Elution Curves of Zn/Cu/Mn — Cd.

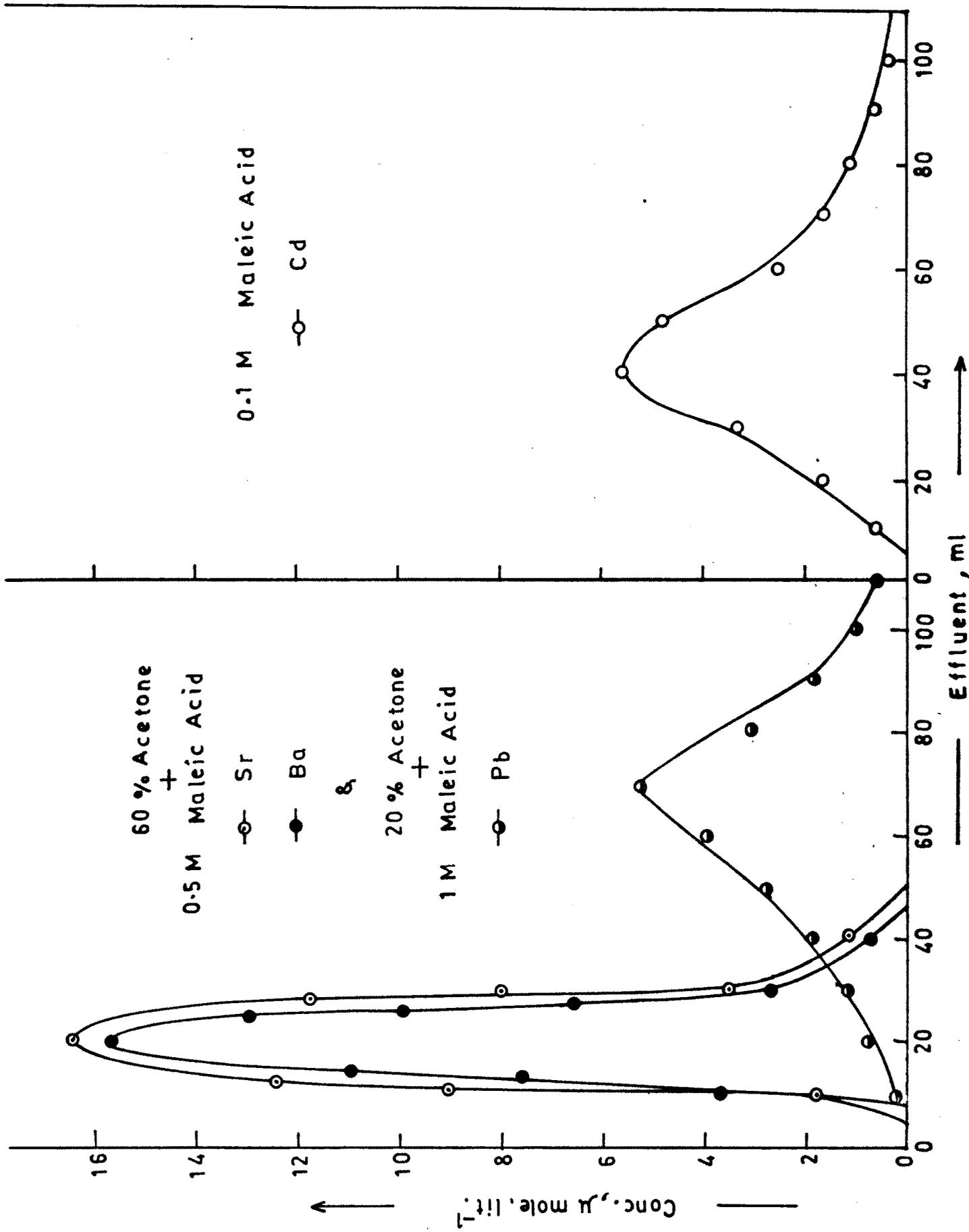


Fig. 3-3 — Elution Curves of Sr/Ba/Pb — Cd.

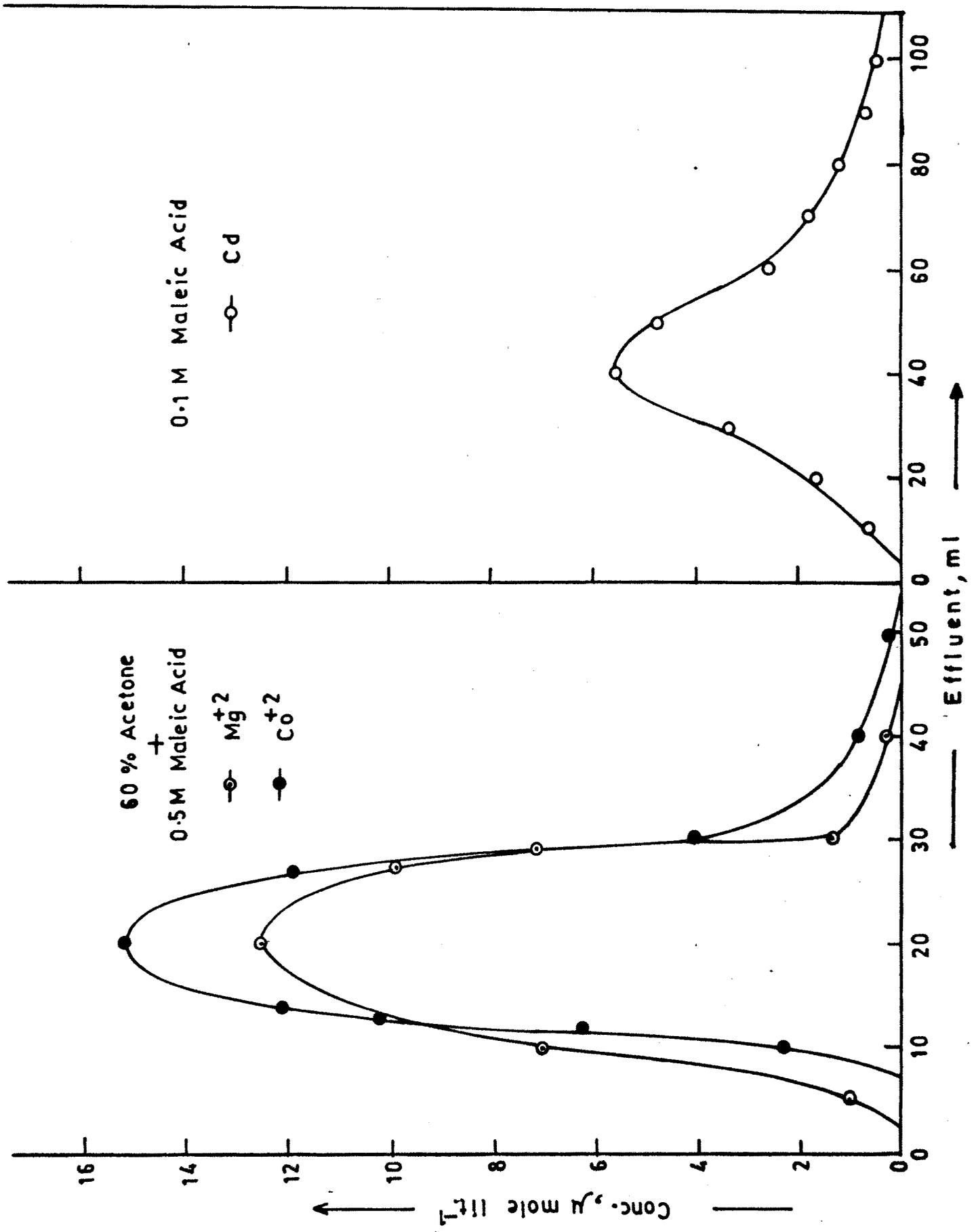


Fig. 3.4 — Elution Curves of Mg / Co — Cd .

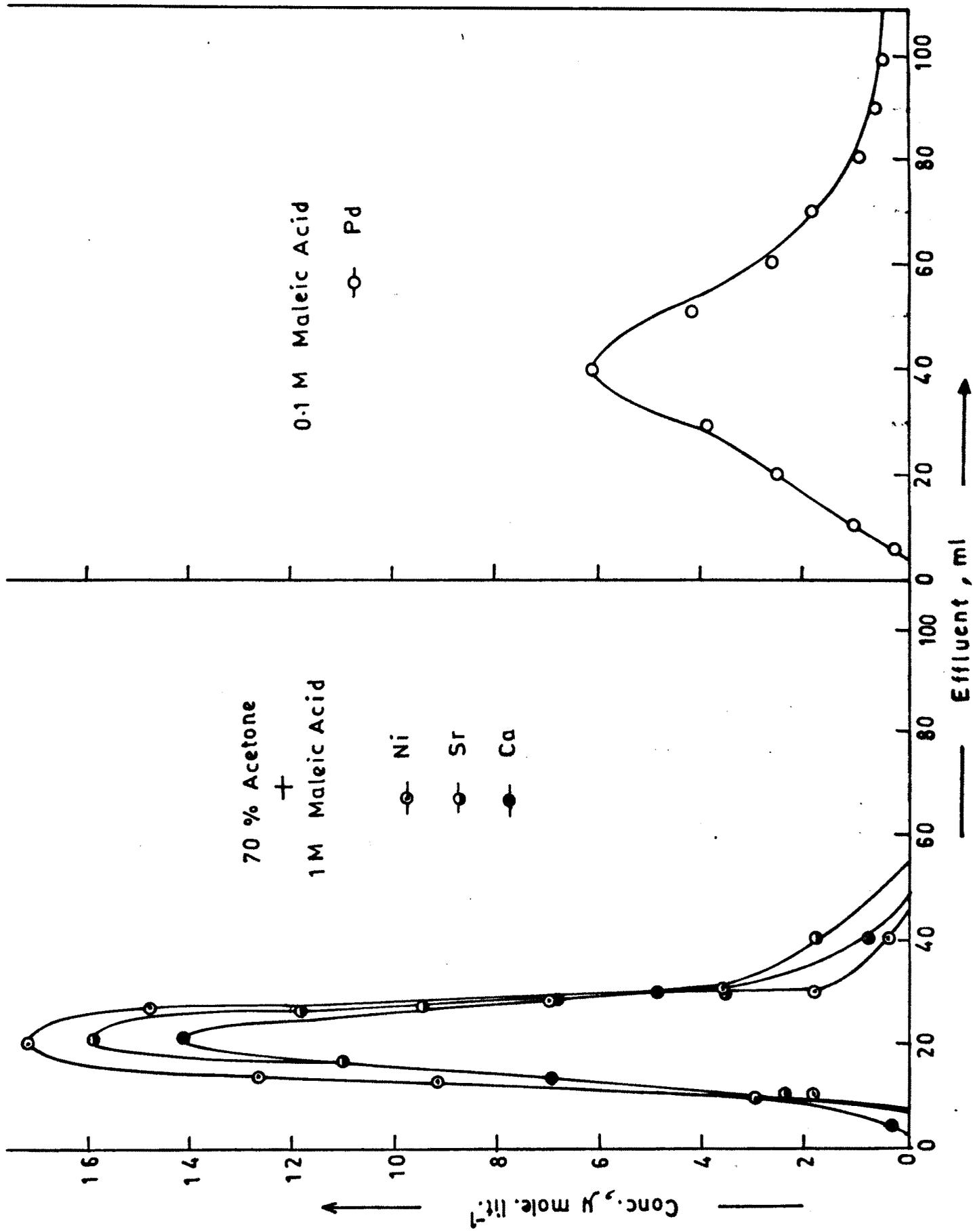


Fig. 3.5 — Elution Curves of Ni/Sr/Ca — Pb.

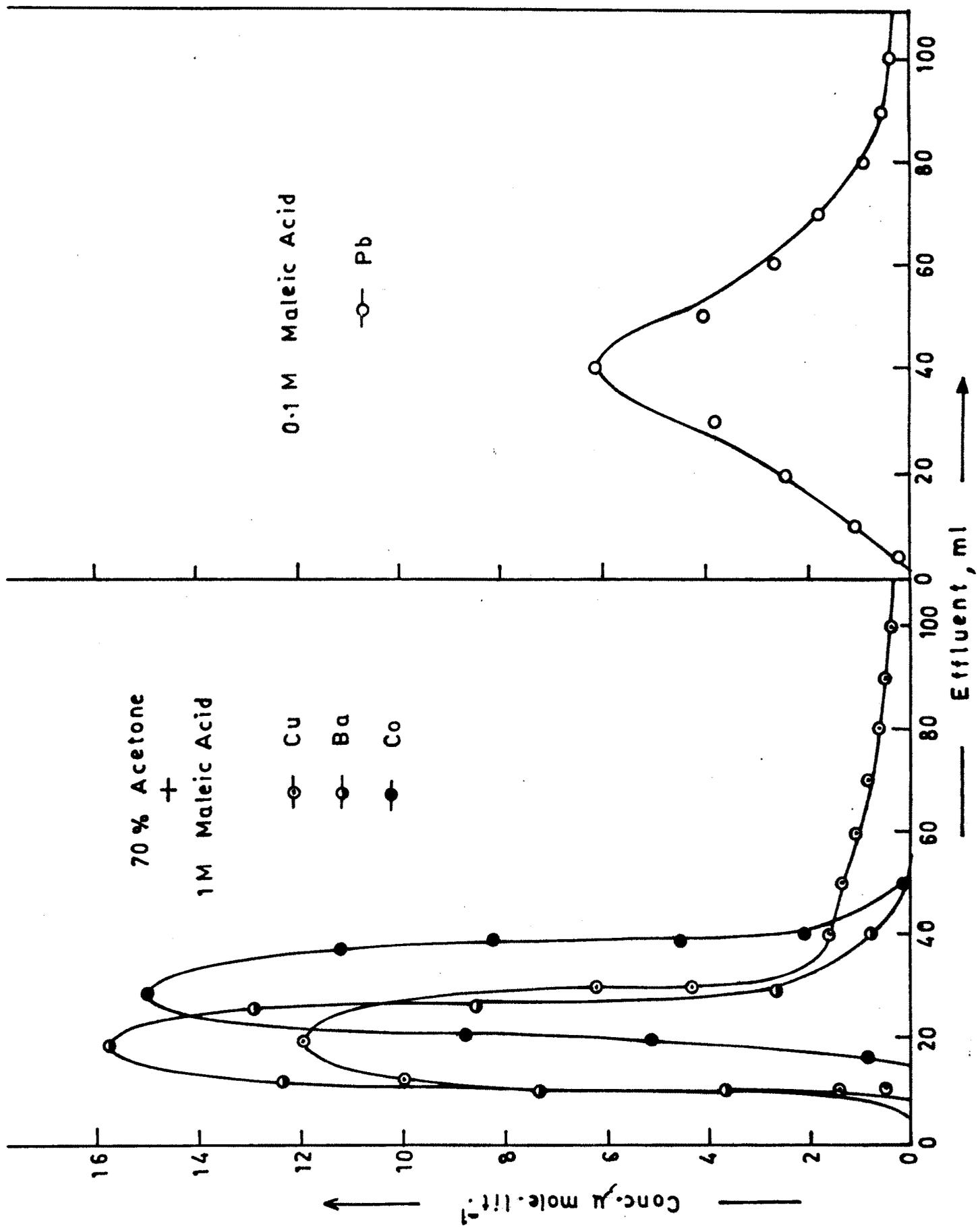


Fig. 3.6 — Elution Curves of Cu / Ba / Co — Pb .

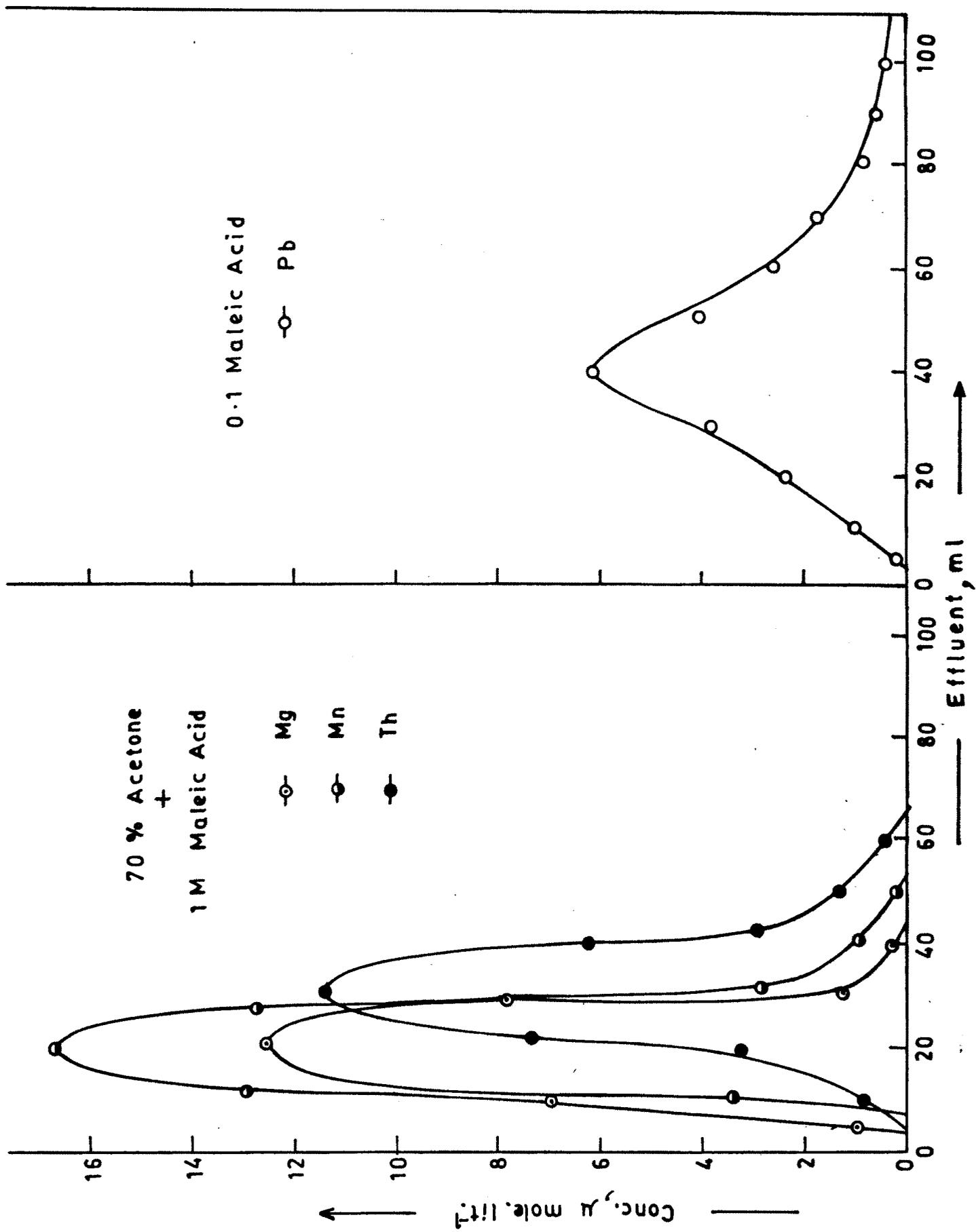


Fig. 3.7 — Elution Curves of Mg/Mn/Th — Pb.

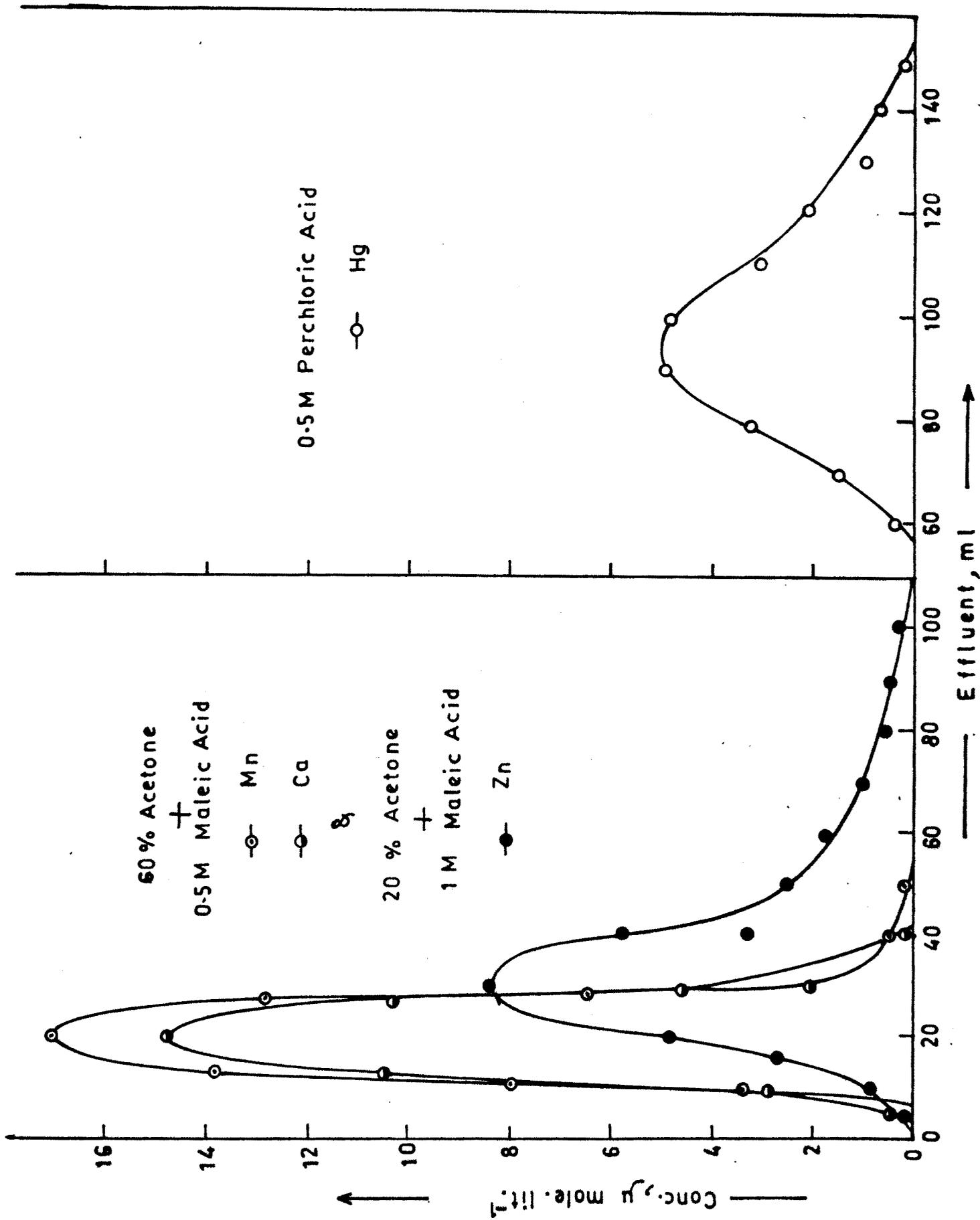


Fig. 3.8 — Elution Curves of Mn/Zn/Ca — Hg.

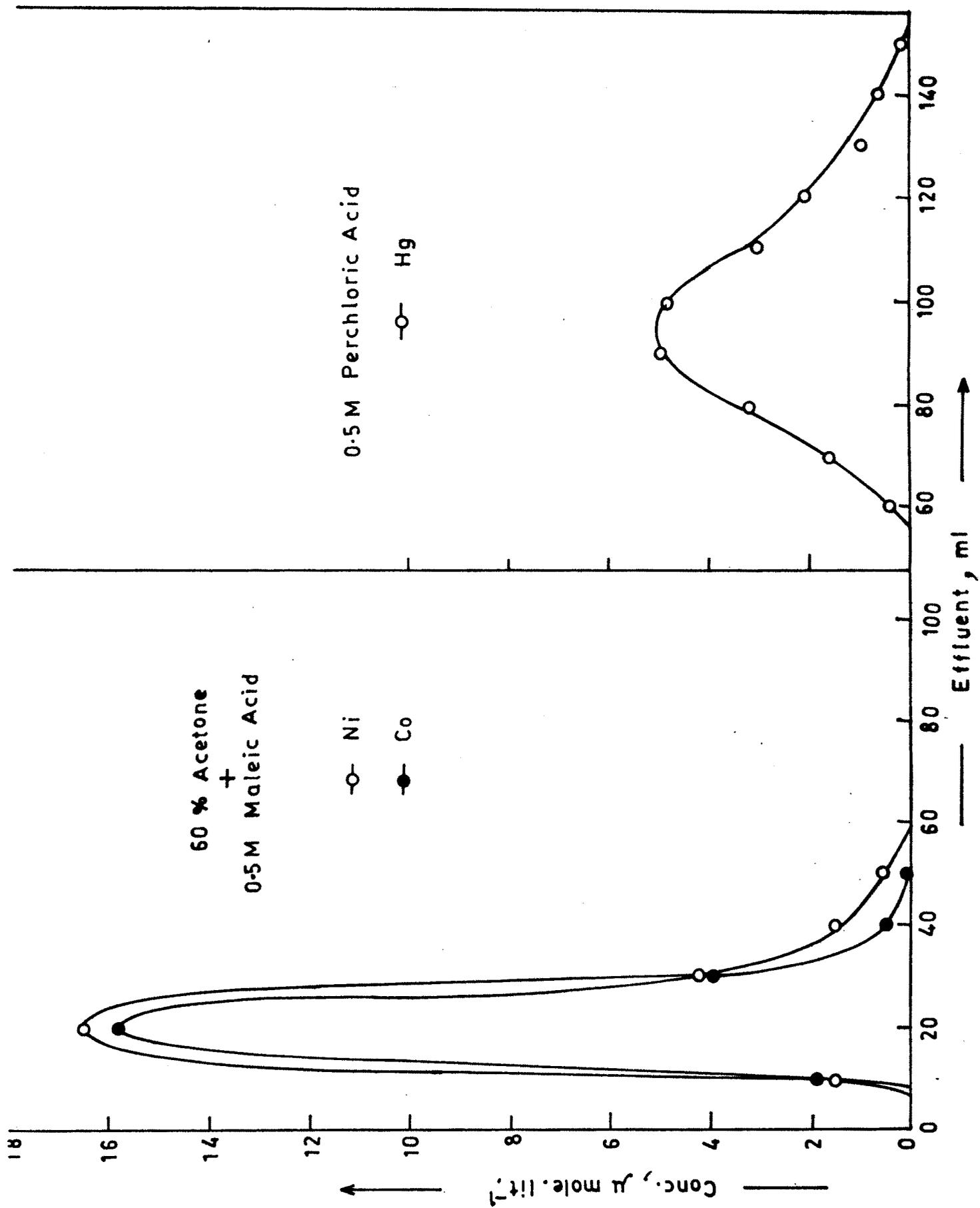


Fig. 3.9 — Elution Curves of Ni/Co — Hg.

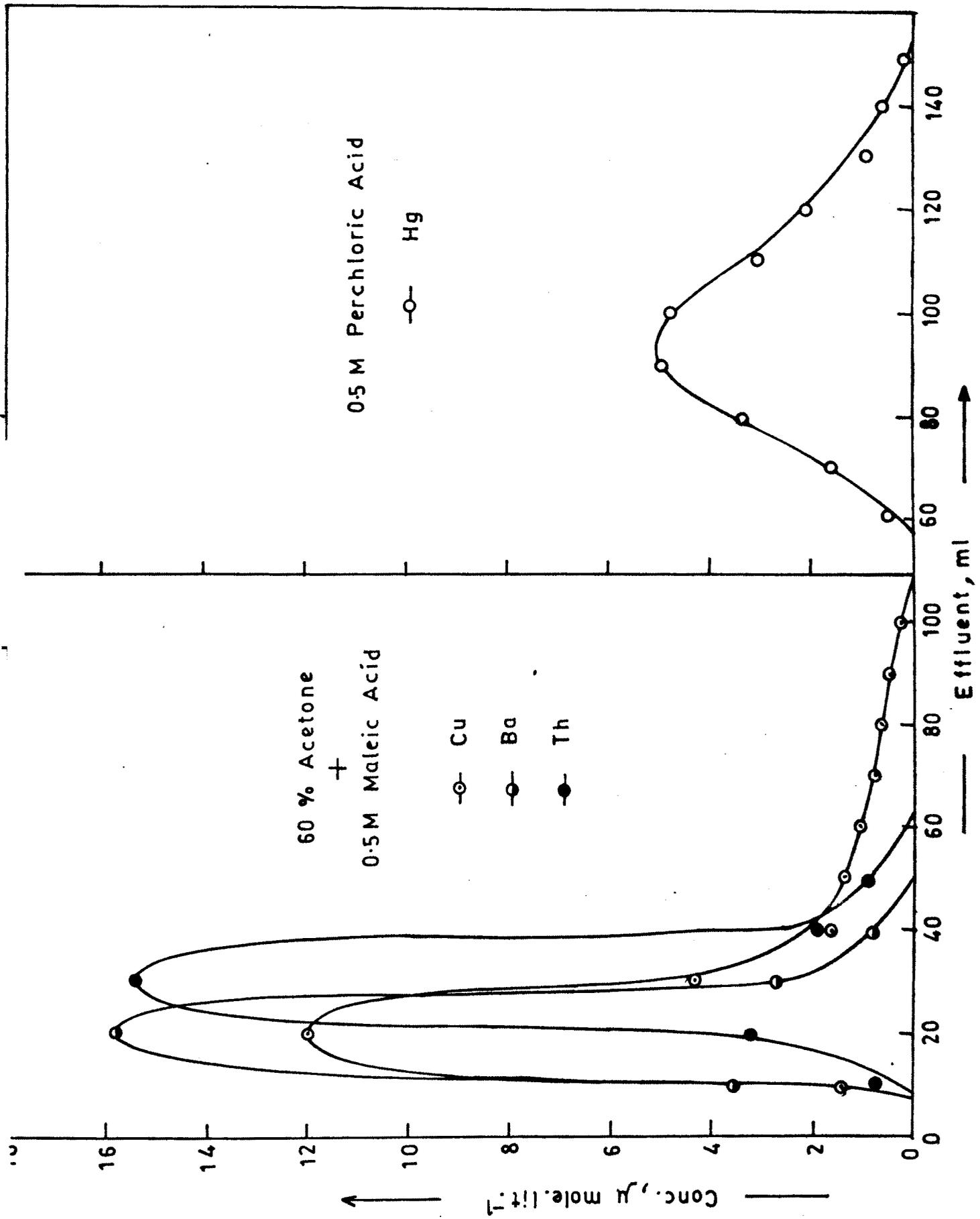


Fig. 3.10 — Elution Curves of Cu/Ba/Th — Hg.

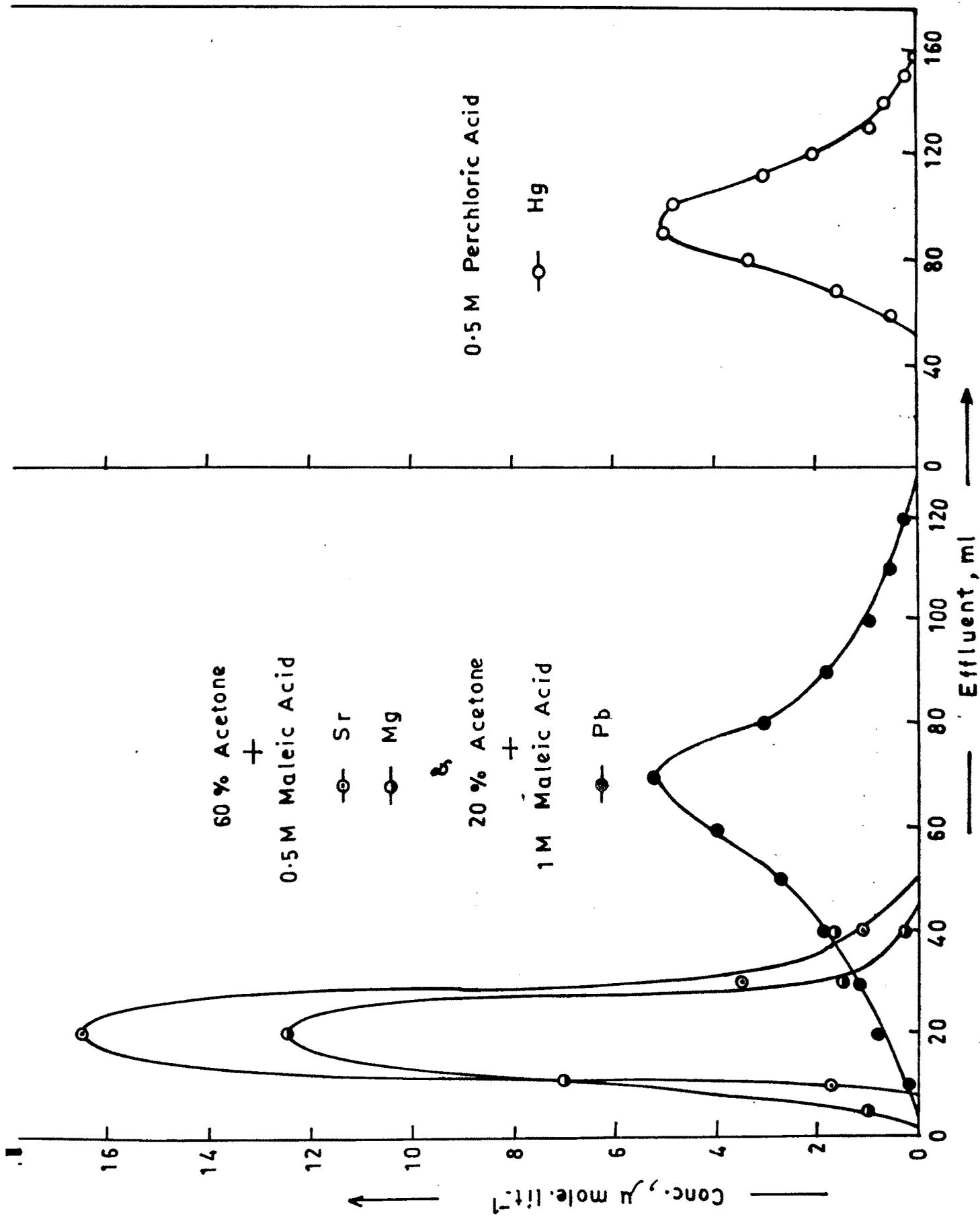


Fig. 3.11 — Elution Curves of Sr/Mg/Pb — Hg.

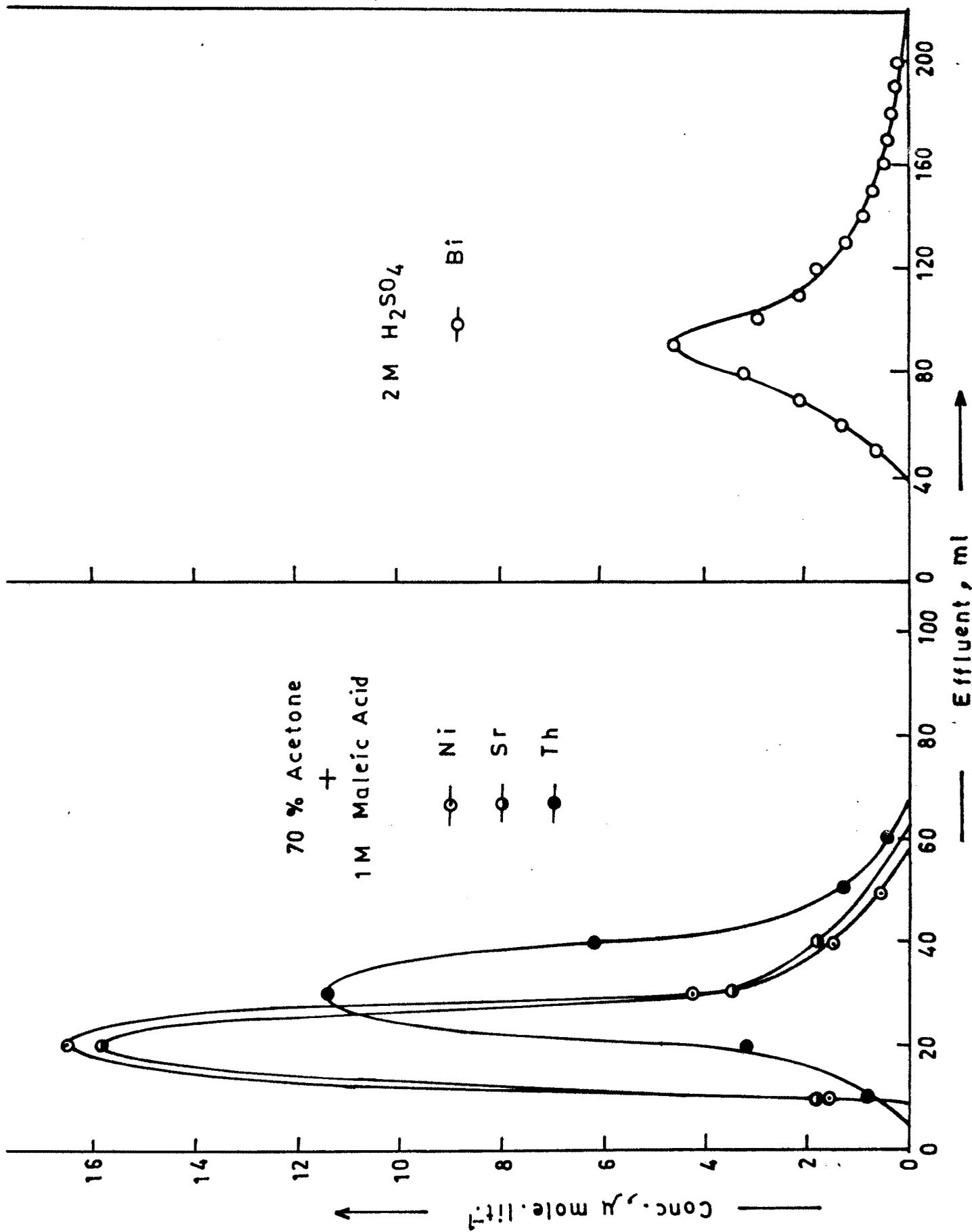


Fig. 3.12 — Elution Curves of Ni/Sr/Th — Bi.

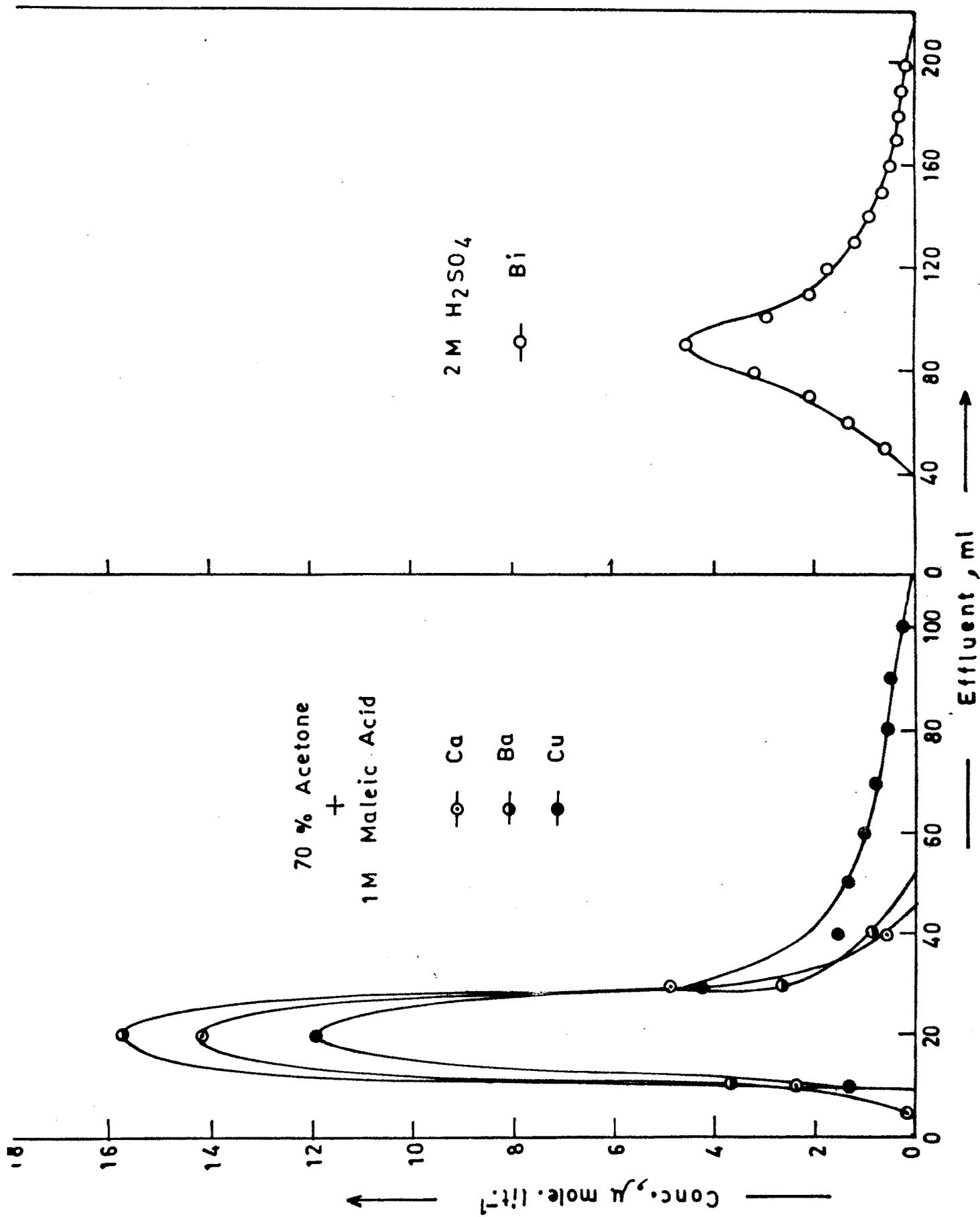


Fig. 3-13 — Elution Curves of Ca/Ba/Cu — Bi.

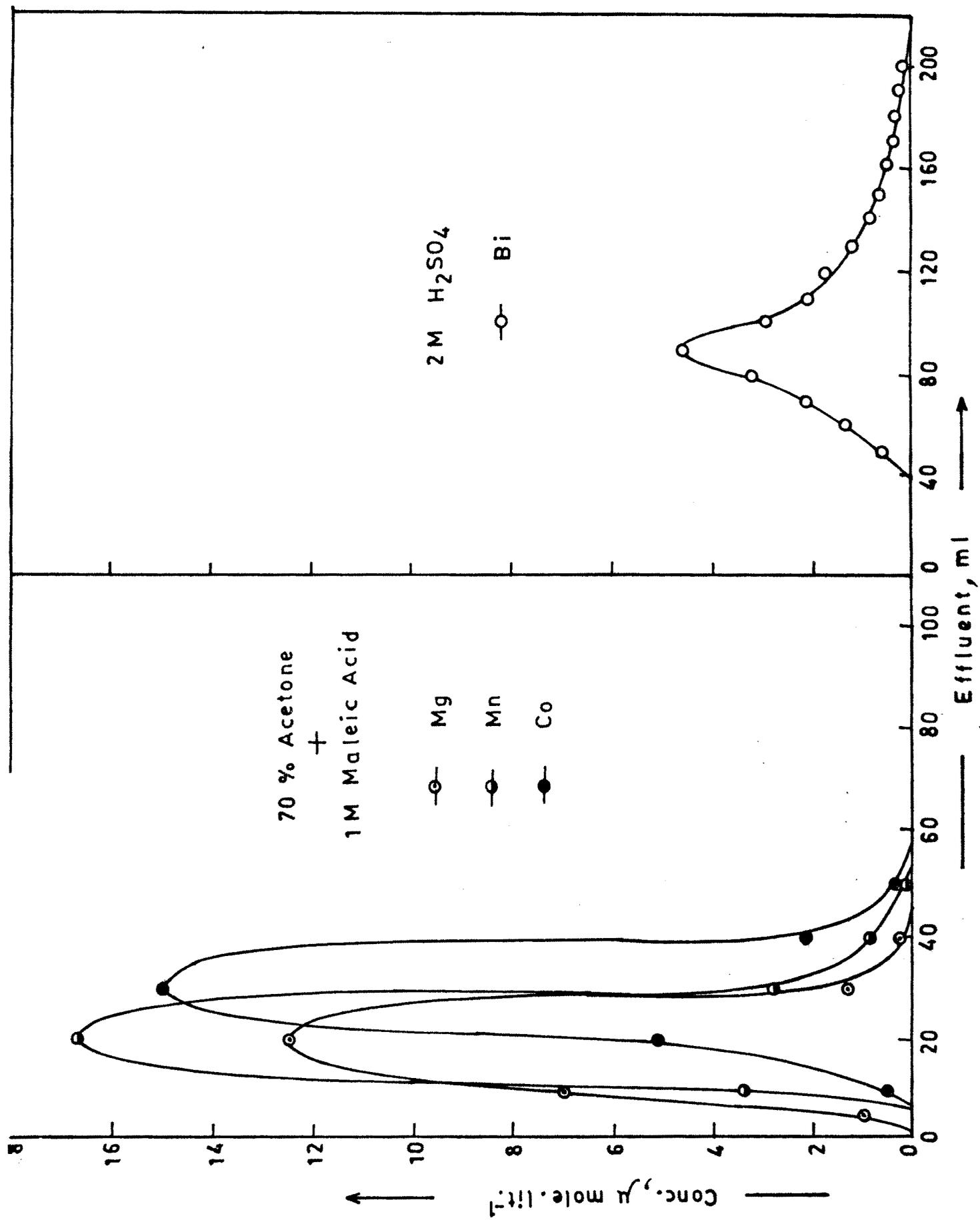


Fig. 3.14 — Elution Curves of Mg/Mn/Co — Bi .

Table 3.7: Quantitative Separation of Synthetic Tertiary Mixtures.

Mixture	Metal Ion eluted	Eluting agent	m Moles taken	m Moles found
1	2	3	4	5
Ni(II)+Cd(II)+Hg(II)	Ni(II)	a	0.245	0.240
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Co(II)+Cd(II)+Hg(II)	Co(II)	a	0.231	0.225
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Ca(II)+Cd(II)+Hg(II)	Ca(II)	a	0.230	0.220
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Zn(II)+Cd(II)+Hg(II)	Zn(II)	d	0.245	0.245
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Ba(II)+Cd(II)+Hg(II)	Ba(II)	a	0.240	0.226
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Sr(II)+Cd(II)+Hg(II)	Sr(II)	a	0.240	0.225
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Th(IV)+Cd(II)+Hg(II)	Th(IV)	a	0.240	0.230
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Mn(II)+Cd(II)+Hg(II)	Mn(II)	a	0.235	0.233
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Mg(II)+Cd(II)+Hg(II)	Mg(II)	a	0.227	0.220
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Cu(II)+Cd(II)+Hg(II)	Cu(II)	a	0.245	0.245
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222



Table 3.7 : Contd....

1	2	3	4	5
Pb(II)+Cd(II)+Hg(II)	Pb(II)	d	0.245	0.245
	Cd(II)	b	0.240	0.232
	Hg(II)	c	0.222	0.222
Cu(II)+Pb(II)+Hg(II)	Cu(II)	e	0.245	0.245
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Mn(II)+Pb(II)+Hg(II)	Mn(II)	e	0.235	0.230
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Ca(II)+Pb(II)+Hg(II)	Ca(II)	e	0.230	0.224
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Ba(II)+Pb(II)+Hg(II)	Ba(II)	e	0.240	0.230
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Sr(II)+Pb(II)+Hg(II)	Sr(II)	e	0.240	0.225
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Th(IV)+Pb(II)+Hg(II)	Th(IV)	e	0.240	0.233
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Ni(II)+Pb(II)+Hg(II)	Ni(II)	e	0.235	0.224
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Mg(II)+Pb(II)+Hg(II)	Mg(II)	e	0.227	0.221
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222
Co(II)+Pb(II)+Hg(II)	Co(II)	e	0.231	0.223
	Pb(II)	b	0.242	0.242
	Hg(II)	c	0.222	0.222

a = 60% acetone + 0.5 M maleic acid.

b = 0.1 M maleic acid.

c = 0.5 M perchloric acid.

d = 20% acetone + 1 M maleic acid.

e = 70% acetone + 1 M maleic acid.

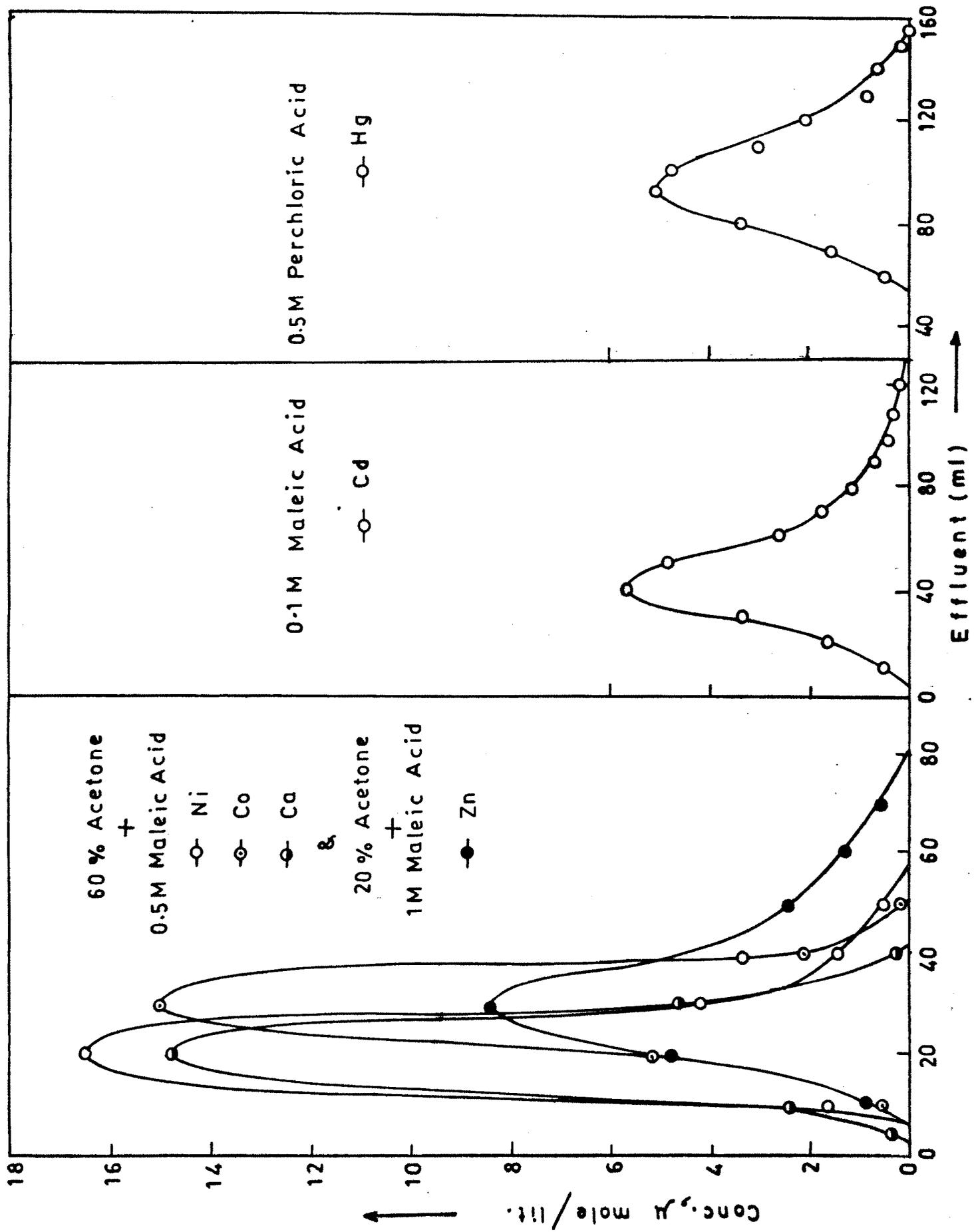


Fig. 3-15 — Elution Curves of Ni/Co/Ca/Zn — Cd — Hg .

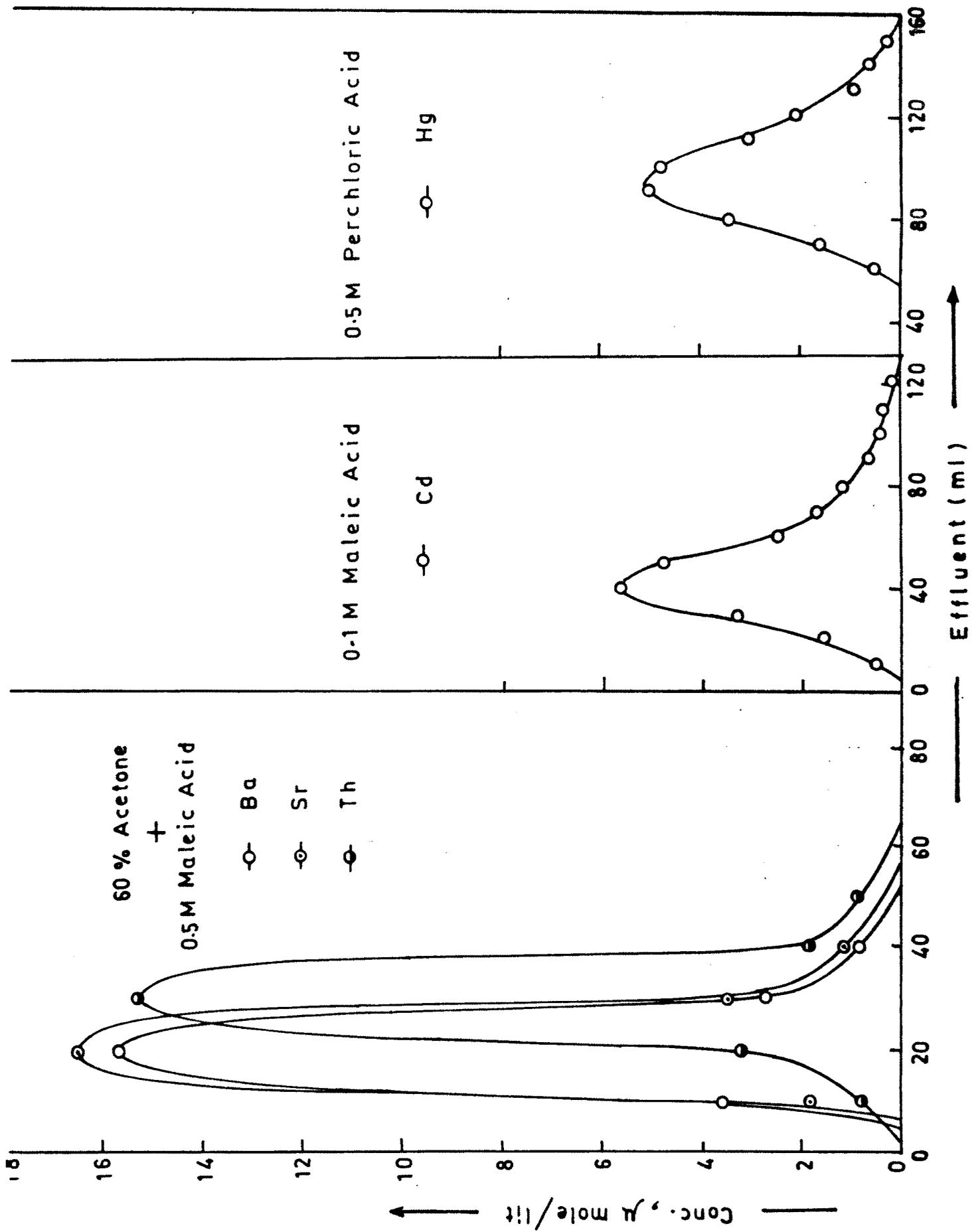


Fig. 3.16 — Elution Curves of Ba/Sr/Th — Cd — Hg .

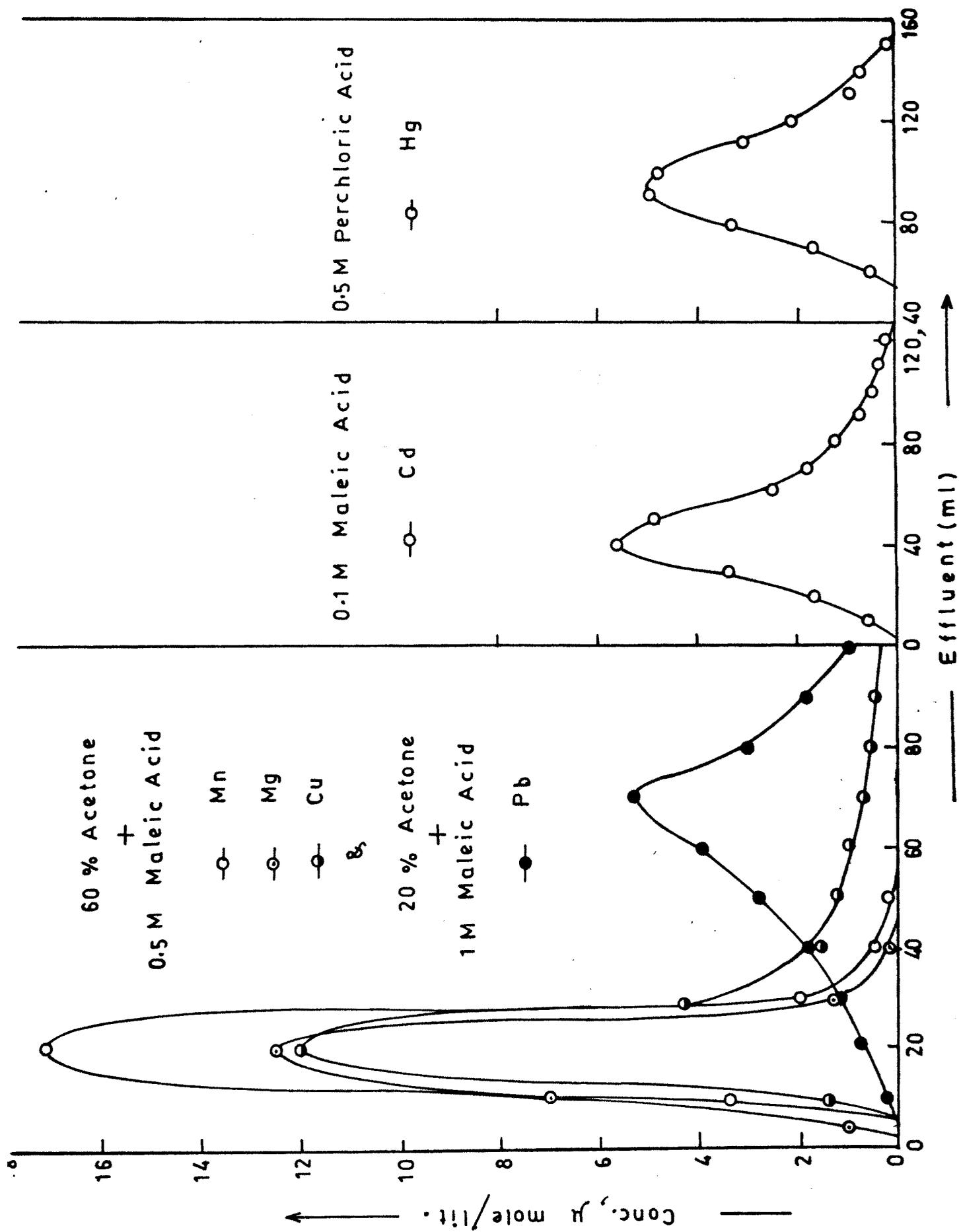


Fig. 3.17 — Elution Curves of Mn/Mg/Cu/Pb — Cd — Hg .

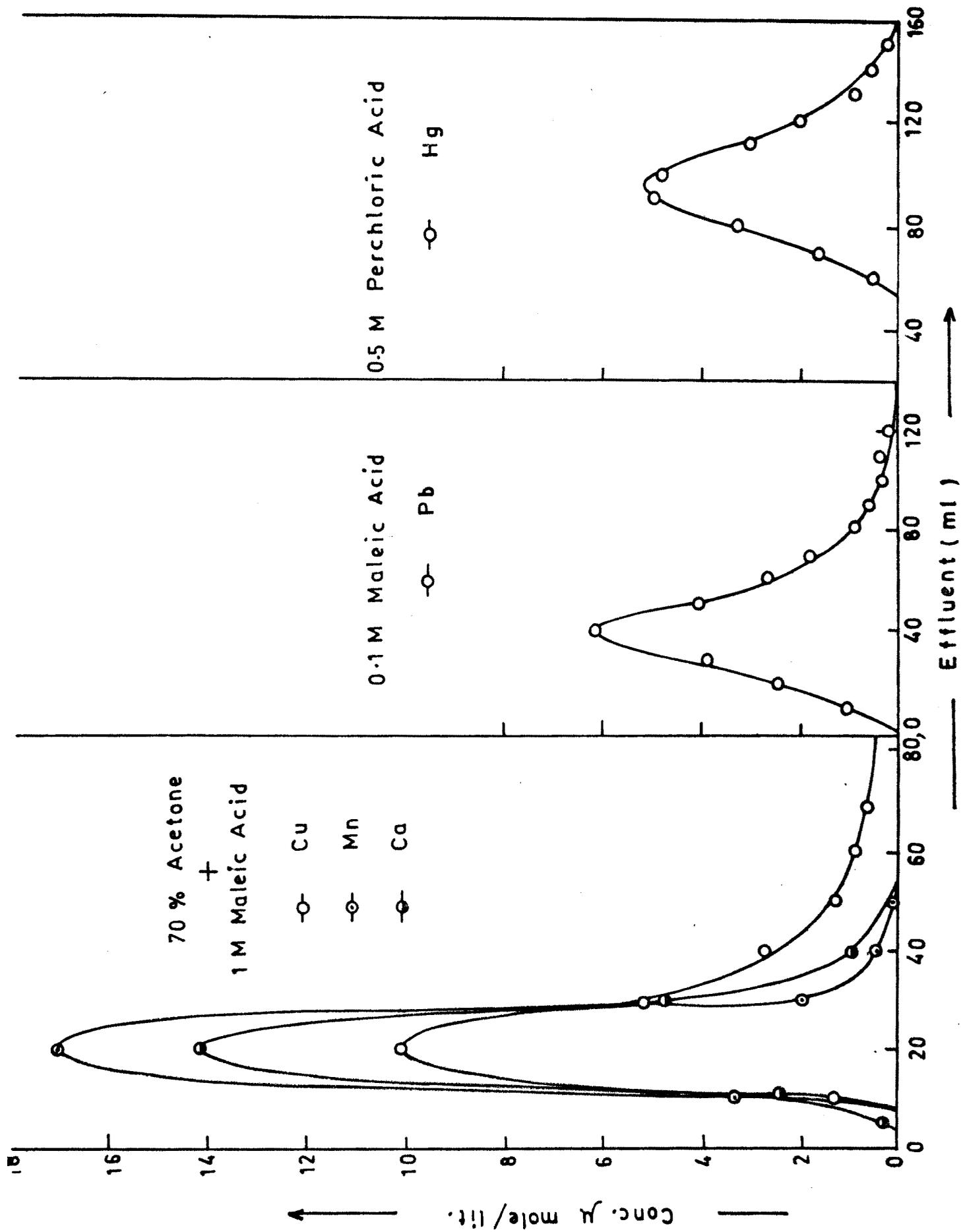


Fig. 3-18 — Elution Curves of Cu/Mn/Ca — Pb — Hg .

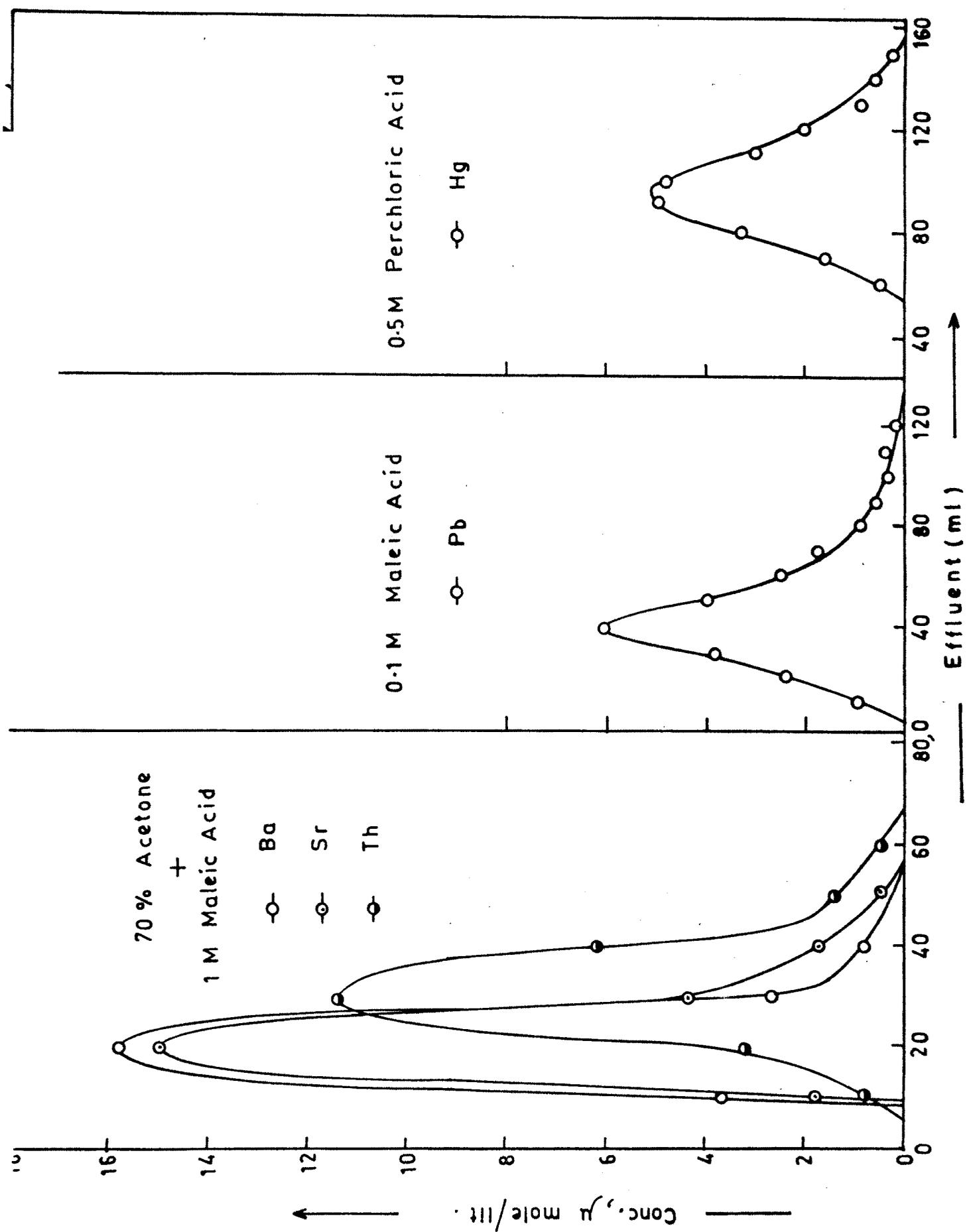


Fig. 3-19 — Elution Curves of Ba / Sr / Th — Pb — Hg .

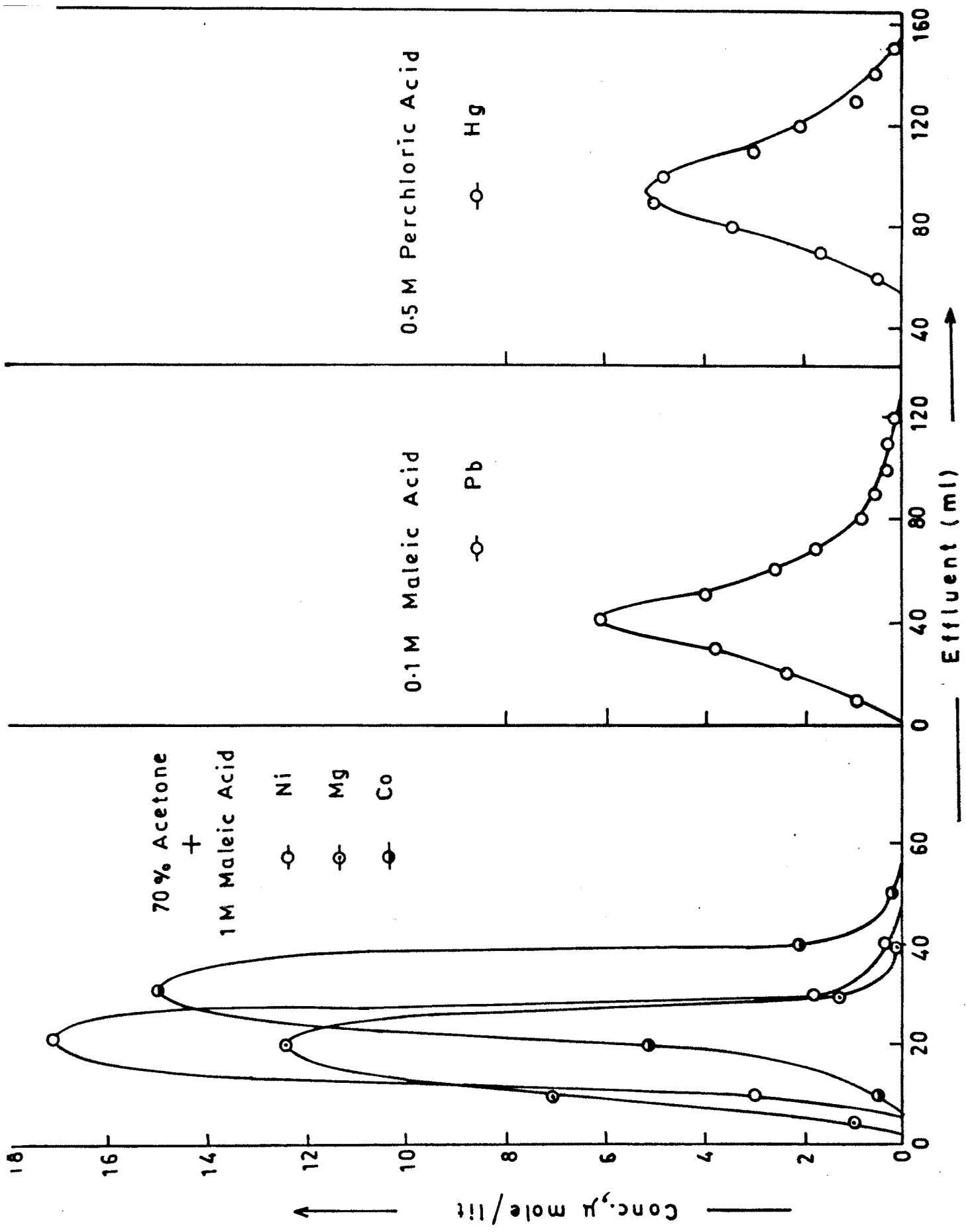


Fig. 3-20 — Elution Curves of Ni/Mg/Co — Pb — Hg .

Table 3.8: Quantitative Separation of Synthetic Quaternary Mixtures.

Mixture	Metal Ion eluted	Eluting agent	m Moles taken	m Moles found
Ba(II)+Pb(II)+Cd(II)+Hg(II)	Ba(II)	a	0.240	0.226
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Th(IV)+Pb(II)+Cd(II)+Hg(II)	Th(IV)	a	0.240	0.230
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Ca(II)+Pb(II)+Cd(II)+Hg(II)	Ca(II)	a	0.230	0.226
	Pb(II)	b	0.242	0.232
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Cu(II)+Pb(II)+Cd(II)+Hg(II)	Cu(II)	a	0.245	0.245
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Ni(II)+Pb(II)+Cd(II)+Hg(II)	Ni(II)	a	0.235	0.224
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Sr(II)+Pb(II)+Cd(II)+Hg(II)	Sr(II)	a	0.240	0.225
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Mg(II)+Pb(II)+Cd(II)+Hg(II)	Mg(II)	a	0.227	0.220
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222

Table 3.8 : Contd....

Mixture	Metal Ion eluted	Eluting agent	m Moles taken	m Moles found
Mn(II)+Pb(II)+Cd(II)+Hg(II)	Mn(II)	a	0.235	0.235
	Pb(II)	b	0.242	0.232
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222
Co(II)+Pb(II)+Cd(II)+Hg(II)	Co(II)	a	0.231	0.225
	Pb(II)	b	0.242	0.233
	Cd(II)	c	0.240	0.240
	Hg(II)	d	0.222	0.222

a = 70% acetone + 1 M maleic acid.

b = 20% acetone + 1 M maleic acid

c = 0.1 M maleic acid.

d = 0.5 M perchloric acid.

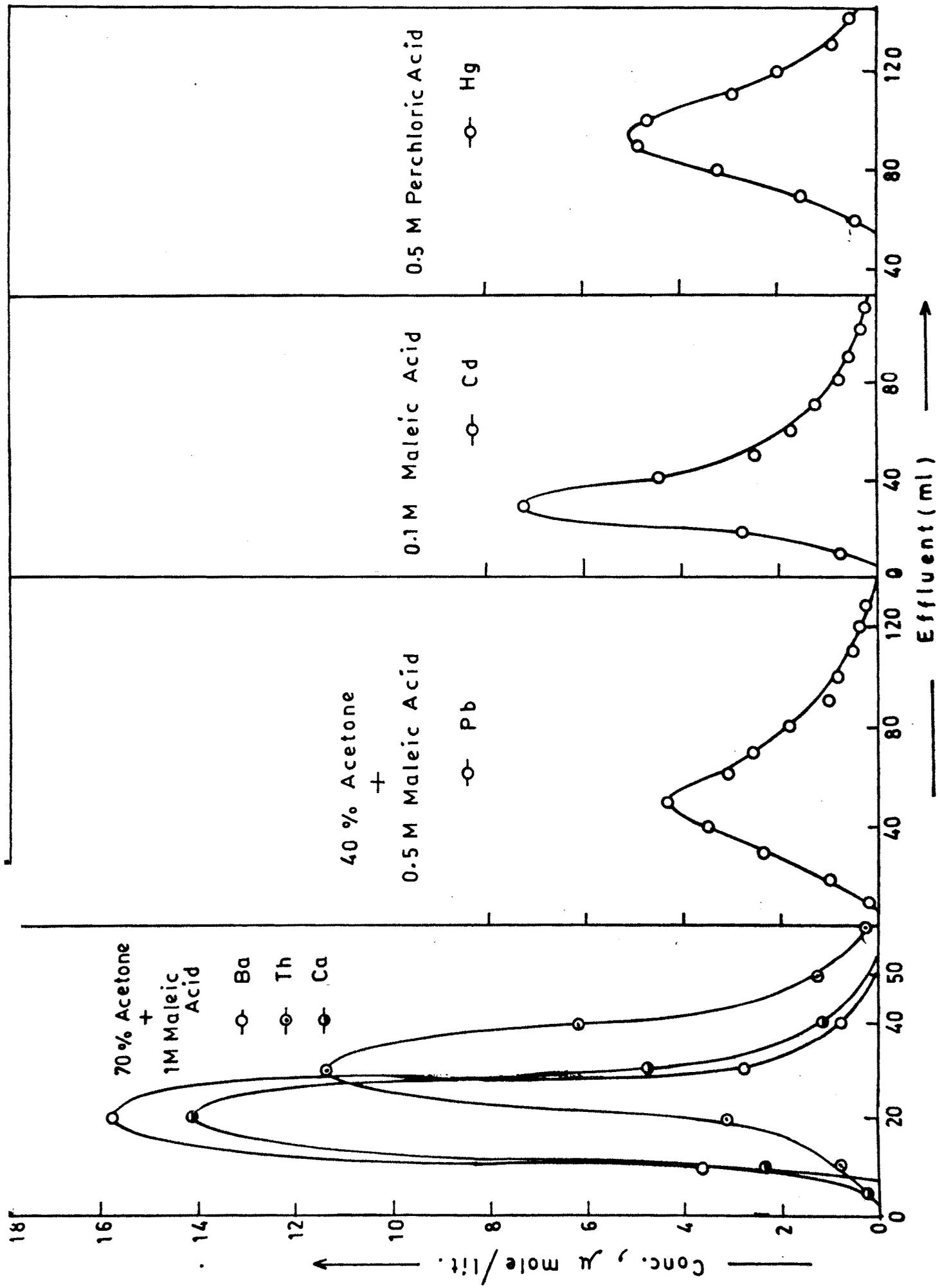


Fig. 3-21 — Elution Curves of Ba/Th/Ca — Pb — Cd — Hg.

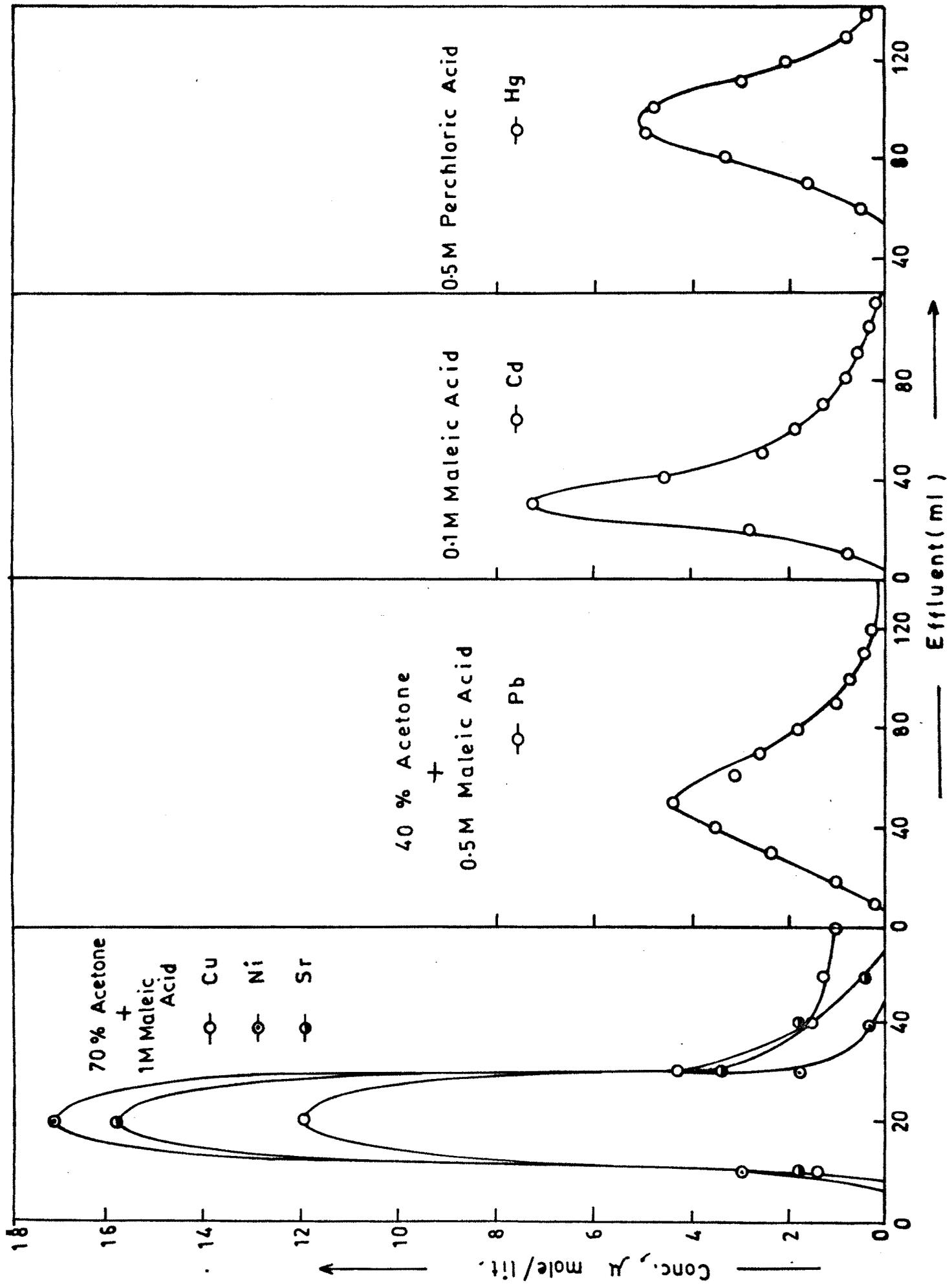


Fig. 3-22 — Elution Curves of Cu/Ni/Sr — Pb — Cd — Hg .

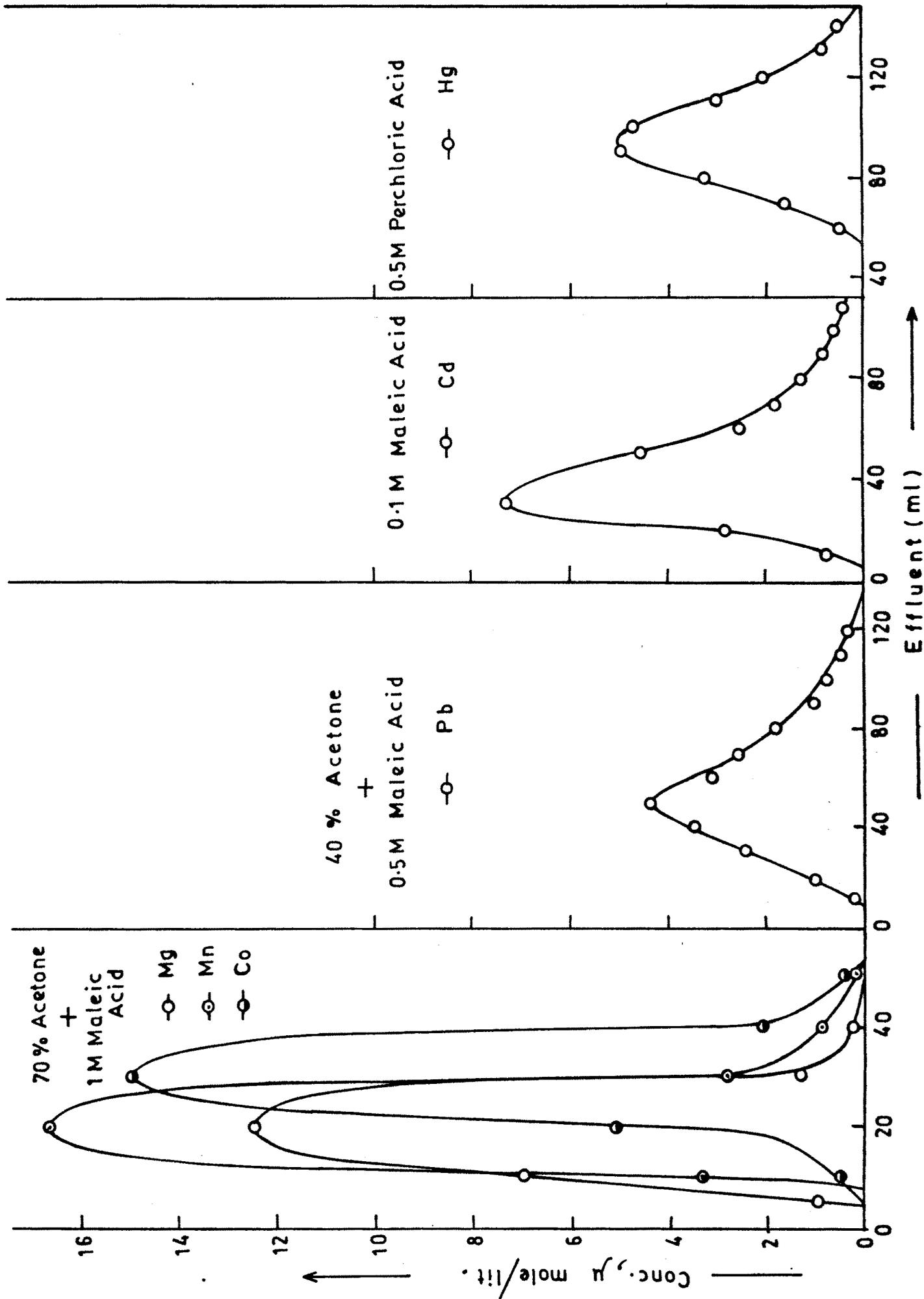


Fig. 3.23 — Elution Curves of Mg/Mn/Co — Pb — Cd — Hg .

ELUTION CURVES

Two component, three component and four component elution curves are presented in figs 3.1 to 3.23. The curves indicates how the systematic information contained in tables of distribution coefficients can be applied to develop analytical separation procedures. The clear-cut separations of metal ions are indicated by no overlap of the elution curves.

It is observed that the nature of the curves of the first metal ion eluted except Pb is bell shaped showing that the other co-ion does not interfere in the process. In the case of Pb fronting and tailing is observed. The elution of Cd, Pb, Hg and Bi show slight fronting and little bit more tailing. These metals are strongly adsorbed on the resin and hence to break the stable anionic complex more eluting agent is required and the time for elution is also more.

Table 3.9 : Elution Characteristics of Metal Ions in Binary Mixtures in Aqueous-Acetone-Maleic Acid Media.

Sr.No.	Metal Ion	BTV(ml)	VEP(ml)	TEV(ml)	Eluent
1	2	3	4	5	6
A) Ni/Th/Ca/Cu/Mn/Sr/Ba/Mg/Co/Zn/Pb-Cd (Figs 3.1 to 3.4)					
1	Ni	7	20	60	a
2	Th	7	30	62	a
3	Ca	4	20	42	a
4	Cu	10	20	105	a
5	Mn	8	20	56	a
6	Sr	5	20	50	a
7	Ba	8	20	47	a
8	Mg	3	20	45	a
9	Co	7	20	53	a
10	Zn	4	30	107	c
11	Pb	8	70	125	c
12	Cd	5	40	130	b

Table 3.9 : Contd...

1	2	3	4	5	6
B) Ni/Sr/Ca/Cu/Co/Ba/Mg/Mn/Th - Pb (Figs 3.5 to 3.7)					
13	Ni	8	20	45	d
14	Sr	8	20	55	d
15	Ca	3	20	47	d
16	Cu	5	20	110	d
17	Co	6	30	52	d
18	Ba	8	20	50	d
19	Mg	4	20	45	d
20	Mn	7	20	53	d
21	Th	5	30	65	d
22	Pb	5	40	130	b
C) Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg/Co/Zn/Pb-Hg (Figs 3.8-3.11)					
23	Ni	8	20	62	a
24	Th	7	30	63	a
25	Co	8	20	51	a
26	Cu	10	20	107	a
27	Ca	4	20	44	a
28	Mn	8	20	56	a
29	Sr	5	20	53	a
30	Ba	7	20	45	a
31	Mg	3	20	46	a
32	Zn	4	30	109	c
33	Pb	8	70	127	c
34	Hg	54	94	160	e

Table 3.9 : Contd...

1	2	3	4	5	6
D) Ni/Th/Co/Cu/Ca/Mn/Sr/Ba/Mg - Bi (Figs 3.11 to 3.14)					
35	Ni	8	20	56	d
36	Th	8	30	65	d
37	Co	7	30	53	d
38	Cu	10	20	110	d
39	Ca	4	20	45	d
40	Mn	7	20	53	d
41	Sr	10	20	60	d
42	Ba	10	20	54	d
43	Mg	3	20	45	d
44	Bi	40	90	210	f

a = 60% acetone + 0.5 M maleic acid

b = 0.1 M maleic acid

c = 20% acetone + 1 M maleic acid

d = 70% acetone + 1 M maleic acid

e = 0.5 M perchloric acid

f = 2 M sulphuric acid.

Table 3.10: Elution Characteristics of Metal Ions in Tertiary Mixtures in Aqueous-Acetone-Maleic Acid Media.

Sr.No.	Metal Ion	BTV(ml)	VEP(ml)	TEV(ml)	Eluent
1	2	3	4	5	6
A) Ni/Co/Ca/Zn/Ba/Sr/Th/Mn/Mg/Cu/Pb-Cd-Hg (Fig 3.15-3.17)					
1	Ni	8	20	56	a
2	Co	7	30	53	a
3	Ca	4	20	44	a
4	Zn	5	30	107	d
5	Ba	8	20	51	a
6	Sr	7	20	55	a
7	Th	4	30	62	a
8	Mn	7	20	56	a
9	Mg	3	20	45	a
10	Cu	8	20	105	a
11	Pb	8	70	125	d
12	Cd	5	40	130	b
13	Hg	54	94	160	c

Table 3.10: Contd....

1	2	3	4	5	6
B) Cu/Mn/Ca/Ba/Sr/Th/Ni/Mg/Co/-Pb-Hg (Figs 3.18 to 3.20)					
14	Cu	7	20	110	e
15	Mn	8	20	54	e
16	Ca	3	20	53	e
17	Ba	8	20	55	e
18	Sr	8	20	57	e
19	Th	6	30	65	e
20	Ni	6	20	47	e
21	Mg	3	20	43	e
22	Co	8	30	67	e
23	Pb	5	40	130	b
24	Hg	54	94	160	c

a = 60% acetone + 0.5 M maleic acid

b = 0.1 M maleic acid

c = 0.5 M perchloric acid

d = 20% acetone + 1 M maleic acid

e = 70% acetone + 1 M maleic acid.

f = 2 M sulphuric acid.

Table 3.11: Elution Characteristics of Metal Ions in Quaternary mixtures in Aqueous-Acetone-Maleic Acid Media.

Sr.No.	Metal Ion	BTV(ml)	VEP(ml)	TEV(ml)	Eluent
1	2	3	4	5	6
Ba/Th/Ca/Cu/Ni/Sr/Mg/Mn/Co-Pb-Cd-Hg (Figs 3.21 to 3.23)					
1	Ba	8	20	50	a
2	Th	5	30	65	a
3	Ca	4	20	52	a
4	Cu	8	20	110	a
5	Ni	7	20	45	a
6	Sr	8	20	55	a
7	Mg	5	20	45	a
8	Mn	7	20	55	a
9	Co	5	20	55	a
10	Pb	8	50	135	b
11	Cd	5	30	125	c
12	Hg	55	95	162	d

a = 70% acetone + 1 M maleic acid

b = 20% acetone + 1 M maleic acid

c = 0.1 M maleic acid

d = 0.5 M perchloric acid

ELUTION CHARACTERISTICS**BREAK THROUGH VOLUME (BTV)**

During separation, ions require some amount of initial eluting agent to come out through the column. This volume of eluting agent is known as break through volume.

PEAK ELUTION VOLUME (PEV)

The volume of eluting agents required to obtain the peak in the elution curve of the metal ions is said to be peak elution volume (PEV).

TERMINAL ELUTION VOLUME (TEV)

After eluting maximum amount of metal ion as eluate, the ion exchange rates become lower. The volume of eluting agents required for completion of the elution of metal ions is represented by Terminal Elution Volume (TEV).

The values of break through volume (BTV), volume elution peak (VEP) and terminal elution volume (TEV) for the metal ion separations of Mg, Ca, Ba, Sr, Zn, Cd, Hg, Pb, Mn, Co, Cu, Ni, Th and Bi in aqueous - acetone - maleic acid are presented in tables 3.9 to 3.11. Generally it is observed that BTV values are \sim 3 - 10 ml for elution of metal ions. This indicates that the initial period required to start the separation is low. The BTV values of Hg and Bi are higher than other metal ions (Hg \sim 55 and Bi = 40). The values of VEP are 20 - 40 ml indicating the speedy separation. The

values of VEP of Hg (VEP = 94 ml), Pb (VEP = 70 ml), Bi (VEP = 90) are higher than the other metal ions showing that these metal ions require comparatively more quantity of the eluents. The values, TEV, represent the total volume of eluent and the time required for the completion of the separation processes. Generally it is observed that TEV are \sim 40 - 70 ml, indicating that the separations are completed in 40-70 minutes. The flow rate for the metal ion separation were maintained as 1 ml/min. TEV values of Cu (TEV \sim 110), Zn (TEV \sim 110), Pb (TEV \sim 125), Cd (TEV \sim 130), Hg (TEV \sim 160), Bi (TEV \sim 210 ml) are high showing that these metal ions require more time for the separation.

It is generally observed that the values of BTV, VEP and TEV for the first metal ion to be eluted in the mixture are lower than those of second metal ion indicating the negligible interference of second metal ion due to wide difference in K_D values.

SEPARATION LIMITS

The separation of metal ions from binary, ternary and quaternary mixtures in aqueous acetone maleic acid media were carried out at equal quantities (\sim 0.250 m moles each). The separations were further carried out at 0.125 and 0.062 m moles of the metal ions. It is generally observed that the recovery of all metal ions is more than 85%, indicating that the separations were possible at low concentrations.

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