CHAPTER - III

COLUMN CHROMATOGRAPHIC SEPARATION OF

Mg, Ca, Sr, Ba,

Pb, Zn, Cd, Hg,

Cu, Mn, Co, Ni,

Th AND Al.

ON
AMBERLITE IR-120 (NH_4^+)
IN
AQUEOUS ACETONE-AMMONIUM CITRATE MEDIA

EARLIER WORK

A variety of complexing media have been used to study the metal ion exchange on cation exchangers, and their use has been done in many analytical separations. Amongst these mineral acids and their salts form a class of complexing agents which has been used by many workers. As the presence of water miscible polar solvents proved to be advantageous in the metal ion exchange in complexing media, the use of mineral acids and their salts has been done in a variety of non-aqueous and mixed-aqueous solvent.

Carboxylic acid media have shown great potential for the separation of metal ions which are otherwise very difficult to separate. Fridman and Yudinazh[1] extracted and separated Nb^{5+} and Ti^{4+} from oxalic acid solution using cation exchanger Ky-2 in protonated form.

Lanthanides were separated on the column of Dowex-50 using ammonium citrate as eluent at pH 3.26. Tartaric acid[2], citric and formic acid[3] 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 a acidic solution of the sample is passed through the resin, and iron or other cations are adsorbed. 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.

A selective study of titanium, vanadium, iron, niobium and uranium in formaic, oxalic, tartaric and citric acid media was carried out by Qureshi, Varshney and Kaushik[4]. The distribution coefficients in these media at various concentrations were calculated and mixtures of titanium and uranium, titanium and vanadium were separated, tartaric acid was used as eluent for titanium, formic acid for niobium and nitric acid for vanadium, uranium and iron. Eletrophoretic movements of these metal ions were studied in 2% tartaric acid, 10% tartaric acid and 2M nitric acid in order to ascertain the nature of the charged species of these metals.

Cation exchange studies of yttrium and its separation from various other elements were carried out by Khopkar[5] using malonic acid and tartaric acid as eluting agents. In malonic acid and succinic acid media bismuth can be separated from several other metal ions.

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 50 Wx8 resin[6]. 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 50 Wx8 are recently reported in our laboratory[7]. The distribution coefficients for Cu, Zn, Mg, Ni, Cd, Co, Mn, Ca, Pb, Th(IV), Al(III), Hg, Sr and Ba were found out in aqueous aceton-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 carried out.

Ion exchange chromatography has been used to separate mixtures of calcium and magnesium or of iron and chromium, that occur together in the qualitative scheme of analysis and also in minerals and ores, such as limestone, dolomite and chrome iron ore. The separation of calcium and magnesium were carried out by using complex forming agents such as ammonium acetate[8], ⓐ ammonium lactate[9-10], ammonium formate[11], ethylenediamine tetraacetic acid (EDTA)[12].

H. Tsubota and Kitano[13] reported that the fission products could be separately eluted more easily and rapidly by using a buffer solution of formic acid and ammonium formate as the elutriant than by using any other elutriants. The separation of Ca and Mg[13] was possible by using 1M formic acid and 1M ammonium formate (the formate buffer solution) at pH=4. Ca and Sr were separated by using the formate buffer solution at pH = 4.1. To separate Sr and Ba, sr was first eluted by the buffer solution at pH = 4.5, and then Ba was eluted by 2M ammonium formate solution.

A systematic study of the cation exchange behaviour of metals on R-$\overset{+}{\mathrm{N}}$H type resin in aqueous-ammonium acetate and ammonium acetate containing other solvents (mixed media) has been reported by some workers. Minami and Ishimori[14] explored the possibility of separating barium from lead on a cation exchanger by first eluting the adsorbed 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 EDTA at pH 4.5 and 10.5 respectively has been utilised for their separation. Lead (pH = 4.5) passed out of bed and adsorbed barium was eluted with EDTA (disodium salt) at pH 10.5 Khopkar and Dey[15] studied the cation exchange behaviour of barium on Dowex 50 Wx8 (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 4M ammonium acetate.

The cation exchange (Dowex 50 Wx8 $\overset{+}{NH_4}$ form) characteristic of 19 metal ions in various concentrations (0.02 - 1.60 M) of ammonium acetate were reported[16]. At low concentration of ammonium acetate the separation of cerium(IV) is low, where as other metal ions showed appreciable sorption. Through the determination of distribution coefficient and separation factors as a function of ammonium acetate concentration, separation of Ce(IV) from its binary mixtures with Ce(III), La(III), Co(II), Ni(II), Cu(II), Zn(II), or Pb(II) has been achieved.

The cation exchange by Dowex 50 W - x 4 $\overset{+}{NH_4}$ form characteristics of 17 metal ions in media consisting of 40% DMF and varying concentrations (0.02 - 1M) of NH_4 OAC were reported[17]. The values of distribution coefficients were evaluated, and some of the separations such as Cu(II), Th(IV), Al(III), Cu(II)/Zn(II)/Cd(II), Hg(II)-Zn(II)/Cd(II)/Pd(II) were achieved using column chromatography.

EXPERIMENTAL

A) Measurement of Distribution Coefficients

The distribution coefficient, K_D was determined by batch equilibrium method. 1 g of air dried Amberlite IR-120

(NH_4^+ form) resin was taken in 250 ml glass stoppered erlynmeyer flask. 4 ml of 0.05 M metal ion solution and 50 ml of the appropriate aqueous acetone-ammonium citrate was taken. The flask was stoppered and kept for 24 hrs. After 24 hrs. an aliguot from the supernatent 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 50ml capacity were used. The columns were provided with safety device to maintain the ion exchanger under liquid. The column was packed with a small bed of glass wool at the bottom and a slurry of $\sim$ 10 g soaked resin was passed and was allowed to settle by occassional tapping. A care was taken to prevent the formation of air pockets or strata of the ion exchange resin.

PROCEDURE

The column was equilibriated with the resin by passing 20 ml of aqueous-acetone ammonium citrate solution at maximum flow rate. The binary or tertiary 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. The effluent fractions were collected in test tubes by maintaining a flow rate of 3ml/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 of fractions collected. The second metal ion starts eluting and gets completely eluted at a particular fractions. After complete removal of the two metals elution is stopped. The metal ion contents in the collected fractions were estimated by standard volumetric procedures.

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

PRESENT WORK

The adsorption characteristics of Co, Mg, Ca, Cd, Zn, Th, Ni, Pb, Al, Mn, Sr, Ba, Cu and Hg metal ions on Amberlite IR-120 (NH_4^+ form) in Aqueous Acetone Ammonium citrate were studied. The distribution coefficients of these ions were found out at various percentages of acetone and at various concentrations of Ammonium citrate, The probable separations of metal ions were predicted from the distribution coefficient data. The results of separation of binary and tertiary mixtures are presented in this chapter. The elution characteristics are discussed from the elution curves. The separation limits are recorded which suggest the efficiency of the separations by ion exchange chromatography technique.

Table 3.1 : Distribution Coefficients (K_D) in Aqueous-Acetone Ammonium Citrate (0.02M) Media on Amberlite IR-120 ($\overset{+}{NH_4}$)

Metal Ion	Acetone %, V/V				
	00	20	40	60	80
Mg(II)	T.A.	T.A.	627.23	412.10	206.47
Ca(II)	1638.00	T.A.	T.A.	T.A.	T.A.
Sr(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Ba(II)	1905.42	1470.00	2232.00	860.40	396.00
Pb(II)	391.50	357.20	540.00	290.90	768.46
Zn(II)	358.56	137.00	49.14	24.73	74.92
Cd(II)	810.00	522.00	394.00	151.00	97.20
Hg(II)	255.90	321.15	365.29	231.12	255.90
Cu(II)	87.84	34.65	6.443	4.450	7.848
Mn(II)	705.17	560.57	209.38	127.77	161.10
Co(II)	134.20	170.52	149.14	102.07	50.048
Ni(II)	560.25	211.62	97.20	44.28	30.00
Th(IV)	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
Al(III)	46.20	30.50	25.20	22.10	15.09

T.A. = Total Adsorption

Ppt. = Precipitation

Table 3.2 : Distribution Coefficients (K_D) in Aqueous-Acetone Ammonium Citrate (0.06M) Media on Amberlite IR-120 (NH_4^+)

Metal Ion	Acetone %, V/V				
	00	20	40	60	80
Mg(II)	231.60	38.24	27.24	17.419	13.603
Ca(II)	16.99	72.90	284.39	352.08	352.08
Sr(II)	100.40	16.5857	N.A.	N.A.	Ppt.
Ba(II)	100.67	47.96	177.03	Ppt.	Ppt.
Pb(II)	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
Zn(II)	21.099	21.099	2.984	1.04	0.519
Cd(II)	285.40	150.82	100.28	Ppt.	Ppt.
Hg(II)	54.93	54.93	432.00	246.85	96.42
Cu(II)	7.55	3.15	1.358	N.A.	2.063
Mn(II)	325.50	201.46	90.39	85.83	78.84
Co(II)	92.93	52.18	39.59	27.52	21.66
Ni(II)	20.00	21.68	0.590	N.A.	N.A.
Th(IV)	T.A.	T.A.	T.A.	T.A.	T.A.
Al(III)	25.87	14.46	14.46	18.33	25.87

N.A. = No Adsorption

T.A. = Total Adsorption

Ppt. = Precipitation

Table 3.3 : Distribution Coefficients (K_D) in Aqueous-Acetone Ammonium Citrate (0.1M) Media on Amberlite IR-120 (NH_4^+)

Metal Ion	Acetone %, V/V				
	00	20	40	60	80
Mg(II)	T.A.	300.24	142.80	21.692	15.73
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)	90.37	90.37	174.60	2232.00	2232.00
Pb(II)	110.49	78.00	270.00	614.25	1282.50
Zn(II)	22.40	9.276	2.054	0.5714	175.20
Cd(II)	158.14	92.66	49.304	Ppt.	Ppt.
Hg(II)	365.29	T.A.	255.90	285.42	342.00
Cu(II)	2.88	2.88	N.A.	1.98	278.43
Mn(II)	115.815	63.32	54.00	214.87	462.24
Co(II)	47.088	96.428	114.48	114.48	86.40
Ni(II)	11.52	3.139	3.139	N.A.	N.A.
Th(IV)	851.53	T.A.	T.A.	T.A.	Ppt.
Al(III)	110.08	100.42	90.23	70.19	50.71

N.A. = No Adsorption

T.A. = Total Adsorption

Ppt. = Precipitation

Table 3.4 : Distribution Coefficients (K_D) in Aqueous-Acetone Ammonium Citrate (0.2M) Media on Amberlite IR-120 (NH_4^+)

Metal Ion	Acetone %, V/V				
	00	20	40	60	80
Mg(II)	38.71	38.71	18.264	6.666	T.A.
Ca(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Sr(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Ba(II)	T.A.	T.A.	T.A.	T.A.	T.A.
Pb(II)	42.22	585.90	585.90	187.40	T.A.
Zn(II)	37.25	30.69	11.76	11.76	927.00
Cd(II)	138.00	138.00	220.90	264.31	T.A.
Hg(II)	270.00	T.A.	162.00	200.67	285.42
Cu(II)	1.98	N.A.	N.A.	N.A.	705.857
Mn(II)	35.00	32.04	21.03	161.10	938.76
Co(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Ni(II)	N.A.	11.59	10.40	10.40	T.A.
Th(IV)	T.A.	T.A.	T.A.	T.A.	T.A.
Al(III)	122.45	99.88	47.41	22.40	15.50

N.A. = No Adsorption

T.A. = Total Adsorption

RESULTS AND DISCUSSIONS

The distribution coefficients of Mg, Ca, Sr, Ba, Pb, Zn, Cd, Hg, Cu, Mn, Co, Ni, Th and Al were found out at 0, 20, 40, 60 and 80 percentages of acetone at 0.02, 0.06, 0.1 and 0.2 M ammonium citrate solutions, the values are given in tables from 3.1 to 3.4.

The distribution coefficients of all metal ions are high at all percentages of acetone at 0.02 M solution of ammonium citrate. The values are maximum at 0 and 20 percent acetone and go on decreasing with the rise in percentage of acetone. The uptake of thorium on the resin is maximum at 0.06, 0.1, 0.2 M ammonium citrate at all percentages of acetone. Thorium forms a precipitate at 0.02 M ammonium citrate at all percentages of acetone. Calcium and strontium show maximum values of distribution coefficients i.e. total adsorption at 0.02, 0.1 M ammonium citrate solutions. Magnesium shows total adsorption at 0.02 and 0.1 M ammonium citrate solution. It shows adsorption without any content of acetone.

K_D values of barium are high at 0.02 and 0.2 M ammonium citrate solutions at all percentages of acetone. The values of distribution coefficient of Mg, Ca, Sr, Ba, Pb and Cd are maximum i.e. total adsorption at 80 percentage of acetone and at 0.2 M ammonium citrate solutions.

Very high values of K_D for all metal ions at 0.02M ammonium citrate indicate the formation of stable cationic citrate complexes which exchange NH_4^+ ions on the resin.

The behaviour of Mg, Ca, Sr, Ba is different from other metal ions. The distribution coefficients are high at 0.02 and 0.1 M ammonium citrate solutions but are comparatively low in 0.06 and 0.2 M medium. From the K_D data of metal ions in Table 3.1 to 3.4 following selectivity sequences for the cation exchange can be given.

AMMONIUM CITRATE = 0.02 M

a) Acetone percentage = 0

Sr ≃ Mg>Ba>Ca>Cd>Mn>Ni>Pb>Zn>Hg>Co>Cu>Al

b) Acetone percentage = 40

Sr≃ Ca>Ba>Mg>Pb>Cd>Hg>Mn>Co>Ni>Zn>Al>Cu

c) Acetone percentage = 80

Sr ≃ Ca>Pb>Ba>Hg>Mg>Mn>Cd>Zn>Co>Ni>Al>Cu

AMMONIUM CITRATE = 0.06 M

a) Acetone percentage = 0

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

b) Acetone percentage = 40

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

c) Acetone percentage = 80

Th>Ca>Hg>Mn>Co>Mg>Al>Cu>Zn>Ni

AMMONIUM CITRATE = 0.1 M

a) Acetone percentage = 0

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

b) Acetone percentage = 40

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

c) Acetone percentage = 80

Sr ≃ Ca ≃ >Ba>Pb>Mn>Hg>Cu>Zn>Co>Al>Mg>Ni

AMMONIUM CITRATE = 0.2 M

a) Acetone percentage = 0

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

b) Acetone percentage = 40

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

c) Acetone percentage = 80

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

It is seen that the distribution coefficients vary with the change in the concentration of acetone and ammonium citrate solutions. The role of acetone and citrate salt on the distribution coefficients is discussed below.

EFFECT OF CONCENTRATION OF ACETONE

The dielectric constant of a solvent, and the polarity and polarizability of solvent molecules are the properties which affect strongely their interactions with the properties which affect strongely their interactions with solutes and hence their solvent power. Onsager[18] and Kirkwood[19-20] gave the relationship between dielectric constant and dipole moment as

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

Where α is the polarizability, μ is the dipole moment, g = coefficient, K is the Boltzmann constant and T absolute temperature. The solvents are classified as non-polar (μ = 0), polar (μ>0), slightly polarizable (α<2A°) and highly polarizable ($\alpha \geq$ 10°A). The symmetrical molecules such as cyclohexane, p-xylene and carbon tetrachloride are non polar, the molecules of lower symmetry (toluene p-dioxane), show a small dipole moment and the very unsymmetrical molecules with functional groups such as C=O, —NO_2, —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 sulpher atoms highly contribute to the polarizability of organic molecules, where as single C—C or C—O bonds, C—N and C—F bonds contribute less.

The solvents like acetic acid or dibutylphosphoric acid are hydrogen bonded dimers and alcohols and water are hydrogen bonded chains or larger aggregates. Cyclic aggregates and a low dipole moment, while chain polymers have a low and high dipole moments respectively[21].

It is observed that the distribution coefficients of all metal ions decrease with the rise in percentages of acetone.

The present findings are similar to those reported earlier by piters and Flore[22]. The distribution coefficients for Zn(II), Ca(II), Se(IV), Sb(III), Ba(II) and Sc(III) decrease with the increasing acetone content.

Akerlof[23] has determined the dielectric constants of a number of aqueous organic solvent mixtures.

THE DIELECTRIC CONSTANTS OF ACETONE-WATER MIXTURES V/V

Acetone %	100	70	30	20	10	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 equation[19-20].

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

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

A similar change in distribution coefficients of In(III), Cd, Rh(III), Hg and Pb in ethanol-water mixtures at various percentages of acetone and at 0.1, 0.2, 0.5 and 1 M HCl has been reported.

Ionic dissociation leading to electrical conductivity is the most important distinguishing feature of electrolyte solutions and this makes the dielectric constant of the solvent a property of prime importance. Active solvents, being usually highly polar, have appreciable dielectric constants, so that some ionic dissociation occurs (e.g. acetone ϵ = 21.1). Active solvents permit strong ion-dipole interactions, having in many cases atoms with donar properties, so that they can co-ordinate and solvate the metal ions. oxygen and nitrogen atoms with unshared electron pairs are the most important donar atoms. The solvation reaction can be envisaged as a generised acid base reaction. Solvation is thus one of the main features of electrolyte solutions in active solvents.

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 K Cal/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

(53-21 weight %) was found to be more than that of the trihydrate (0.196 weight %)[24].

The solubility of anhydrous thorium nitrate[25] in acetone was found to be slight compared with the appreciable solubilities of the hydrates in acetone.

It has been stated that the solubility of an electrolyte in a series of solvents is correlated with the dielectric constant of the solvents and mixtures of solvents too.

The relative binding energies of water and the organic solvent in mixed solvents were obtained from measurements of the heat of solution of metal salt, hydrates in the organic solvents and in their mixtures with water[26].

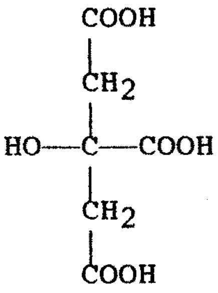
It was shown that the uptake of organic solvent was greater by the hydrogen resinate than by the silver or sodium resinate[27-34]. The affinity of the hydroxonium ion (H_3O^+) was found to be greater for the less polar solvent than for the polar solvent, and therefore the hydrogen resinate cation exchanger absorbs most of the solvents such as acetone, dioxane, propanol.

In the water rich region, the uptake of organic ion is in general much preferred compared with other solution compositions.

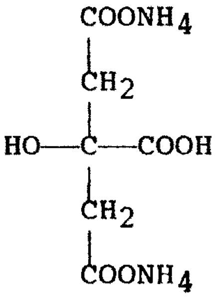
EFFECT OF CONCENTRATION OF AMMONIUM CITRATE

The distribution coefficient (K_D) of the cations are reported in tables 3.1 to 3.4. In all the cases the sorption of metal ions decreases with increasing the concentrations of ammonium citrate solutions. Generally the metal ion forms a complex with the citrate ion and the sorption depends upon the nature of complex formed. If the charge on the complex is positive, zero or negative, the sorption will be less[16].

As the concentration of ammonium citrate is increased, citrate ion replaces the co-ordinating water molecules resulting in the formation of complex species of a small positive charge and consequently K_D is lowered. A further increase in the concentration of ammonium citrate leads to the fomation of a neutral species and this also results in a decrease of K_D. When the concentration of ammonium citrate is higher, and a neutral metal citrate is likely to be present in the solution, the predominent species in the resin phase would be M^{II} (H cit)$^+$ or M^{III} (H cit)$^{2+}$. The chemical formula of citric acid is $H_3C_6H_5O_7$. The structural formula of citric acid is (a) and that of ammonium citrate is (b)



(a)



(b)

$[H(NH_4)_2C_6H_5O_7]$

Where, M— Metalion and cit = citrate = $C_6H_5O_7$ ion.

The presence of M^{II} $(oAC)^+$ or M^{III} $(oAC)^{2+}$ was reported by Ghosh[17] and earlier workers[37,38]. Lowere K_D values for alkali salts[39] and ammonium salts [40,41] of carboxylic acid are due to increased complexation at higher pH.

The resin in NH_4^+ form is equilibriated with the metal ion and citrate ligand solutions. It was assumed that a single cationic complex is sorbed on the resin along with excess ligand. In the citric acid medium[42] Fe^{3+} forms both negatively and positively charged complexes cupric ions[43] react with the oxalate ions to form $CuHC_2O_4^+$, CuC_2O_4 and $Cu(C_2O_4)^{2-}$ with association constants 3.1×10^2, 7.0×10^4 and 2.3×10^4.

From the above discussion it can be concluded that the cationic complexes such as M^{II} (H cit)$^+$ and M^{III} (H cit)$^{2+}$ are formed with divalent, trivalent and M^{IV} (H cit)$^{3+}$ quadrivalent metal ions. In general M^{n}[(H cit)$^{n-1}$]$^{+}$ species are formed. The cationic citrate complexes thus formed exchange NH_4^+ ions from Amberlite IR 120 resin. The negatively charged complexes and the neutral complexes elute from the column as they are not adsorbed on the resin.

COLUMN CHROMATOGRAPHIC SEPARATIONS

The results of the quatitative separation of synthetic multicomponent mixtures in aqueous acetone ammonium citrate media are presented in tables 3.5 to 3.6 and by figures 3.10 to 3.14.

SEPARATION OF Mg FROM

Pb/Mn/Ba/Cu/Co/Zn/Ni

Mg is strongly bound to the resin, Amberlite IR 120 (NH_4^+) in comparision to Pb/Mn/Ba/Cu/Co/Zn/Ni. Pb/Mn/Ba/Cu ions are eluted by 0% acetone - 0.1 M ammonium citrate solution, Co/Zn/Ni ions are eluted by 20% acetone - 0.02 M ammonium citrate medium. Mg is then stripped off from the column by 60% acetone - 0.06 M ammonium citrate solution.

SEPARATION OF Ca FROM

Pb/Co/Zn/Mn/Ba/Cu/Ni

As the distribution coefficient of Pb/Co/Zn/Mn/Ba/Cu/Ni is lower than that of Ca in 0.1 M ammonium citrate without acetone, the metal is eluted first in this medium. Ca is then eluted by 0.06 M ammonium citrate not containing acetone.

SEPARATION OF Sr FROM
Pb/Co/Zn/Mn/Ba/Cu/Ni

From the distribution studies it is observed that 0% acetone - 0.1 M ammonium citrate is the best eluent for Pb/Co/Zn/Mn/Ba/Cu/Ni metal ion and hence Pb/Co/Zn/Mn/Ba/Cu/Ni are removed from the column in this medium and Sr is retained. Sr is finally eluted by 20% acetone - 0.06 M ammonium citrate.

SEPARATION OF Th FROM
Pb/Co/Zn/Cu/Ni/Mg/Cd/Ba

Pb/Co/Zn/Cu/Ni/Mg/Cd/Ba is weakly bound to the resin in comparision to Th. Pb/Co/Zn/Cu/Ni is eluted by 20% acetone - 0.1 M ammonium citrate medium, Mg is stripped off by 60% acetone - 0.1M ammonium citrate and Cd/Ba is eluted by 40% acetone - 0.1 M ammonium citrate solution. Th was then removed by 60% acetone - 0.4 M ammonium butarate.

SEPARATION OF Zn/Co/Cu/Ni - Mg - Ca/Th

Zn/Ni/Co/Cu show lower distribution coefficient than Mg and Ca/Th. Zn/Ni is eluted by 20% acetone - 0.02 M ammonium citrate, Co/Cu is removed by 0% Acetone - 0.1 M ammonium citrate. Mg is then stripped off by 60% acetone - 0.06 M ammonium citrate and Ca is desorbed by 0% acetone - 0.06M ammonium citrate and Th is removed last by 60% acetone - 0.4 M ammonium butarate solution.

SEPARATION OF Zn/Co/Cu/Ni - Ca - Th

0% Acetone - 0.1 M ammonium citrate is found to be suitable eluent for Zn/Co/Cu/Ni and not for Ca and Th. Ca and Th is retained on the column and Zn/Co/Cu/Ni is eluted by 0% Acetone - 0.1 M ammonium citrate. Ca was collected by using 0.06 M ammonium citrate eluent and Th is stripped off by 60% acetone - 0.4 M ammonium butarate.

It is generally observed that the elution curves presented in fig. 3.2 of Mn, Ba. Cu, Ni are bell shaped. The ions which are eluted first does not have any interference of the Co - ion. The ions coming in second or third order of preference in binary and tertiary mixtures are comparatively strongly adsobed on the resin. These require slightly higher amount of eluent and hence slight fronting is expected initially, once the maximum amount of metal ions is exchanged by eluent the removal of last traces require large amount of eluent and hence some tailing in the process is expected. Zn, Co, Pb (fig. 3.1) Mg (fig. 3.1, 3.2, 3.3, 3.4). Show slight tailing and Sr shows negligible fronting and tailing.

The most of the elution curves tends to show bell shape indicating that the satisfactory separations are possible.

Table 3.5 : Quantitative Separation of Binary Mixtures (First ion in the 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
Pb(II)+Mg(II)	Pb(II)	b	0.236	0.208
	Mg(II)	c	0.227	0.219
Co(II)+Mg(II)	Co(II)	a	0.245	0.243
	Mg(II)	c	0.227	0.219
Zn(II)+Mg(II)	Zn(II)	a	0.242	0.226
	Mg(II)	c	0.227	0.219
Mn(II)+Mg(II)	Mn(II)	b	0.245	0.244
	Mg(II)	c	0.227	0.219
Ba(II)+Mg(II)	Ba(II)	b	0.268	0.266
	Mg(II)	c	0.227	0.219
Cu(II)+Mg(II)	Cu(II)	b	0.242	0.192
	Mg(II)	c	0.227	0.219
Ni(II)+Mg(II)	Ni(II)	a	0.192	0.189
	Mg(II)	c	0.227	0.219
Pb(II)+Ca(II)	Pb(II)	b	0.236	0.199
	Ca(II)	d	0.222	0.141
Co(II)+Ca(II)	Co(II)	b	0.231	0.195
	Ca(II)	d	0.222	0.141
Zn(II)+Ca(II)	Zn(II)	b	0.242	0.207
	Ca(II)	d	0.222	0.141
Mn(II)+Ca(II)	Mn(II)	b	0.235	0.201
	Ca(II)	d	0.222	0.141

Table 3.5 : Contd....

1	2	3	4	5
Ba(II)+Ca(II)	Ba(II)	b	0.254	0.239
	Ca(II)	d	0.222	0.241
Cu(II)+Ca(II)	Cu(II)	b	0.242	0.192
	Ca(II)	d	0.222	0.141
Ni(II)+Ca(II)	Ni(II)	b	0.244	0.207
	Ca(II)	d	0.222	0.141
Pb(II)+Sr(II)	Pb(II)	b	0.236	0.193
	Sr(II)	i	0.248	0.151
Co(II)+Sr(II)	Co(II)	b	0.231	0.229
	Sr(II)	i	0.248	0.151
Zn(II)+Sr(II)	Zn(II)	b	0.242	0.217
	Sr(II)	i	0.248	0.151
Mn(II)+Sr(II)	Mn(II)	b	0.235	0.235
	Sr(II)	i	0.248	0.151
Ba(II)+Sr(II)	Ba(II)	b	0.255	0.055
	Sr(II)	i	0.248	0.151
Cu(II)+Sr(II)	Cu(II)	b	0.242	0.207
	Sr(II)	i	0.248	0.151
Ni(II)+Sr(II)	Ni(II)	b	0.248	0.160
	Sr(II)	i	0.248	0.151
Pb(II)+Th(IV)	Pb(II)	e	0.236	0.186
	Th(IV)	f	0.200	0.195
Co(II)+Th(II)	Co(II)	e	0.231	0.230
	Th(II)	f	0.200	0.195
Zn(II)+Th(IV)	Zn(II)	e	0.242	0.208
	Th(IV)	f	0.200	0.195
Cu(II)+Th(IV)	Cu(II)	e	0.242	0.198
	Th(IV)	f	0.200	0.195
Ni(II)+Th(IV)	Ni(II)	e	0.244	0.154
	Th(IV)	f	0.200	0.195

Table 3.5 : Contd....

1	2	3	4	5
Mg(II)+Th(IV)	Mg(II)	g	0.227	0.213
	Th(IV)	f	0.200	0.195
Cd(II)+Th(IV)	Cd(II)	h	0.241	0.211
	Th(IV)	f	0.200	0.195
Ba(II)+Th(IV)	Ba(II)	h	0.254	0.244
	Th(IV)	f	0.200	0.195

a = 20% Acetone - 0.02 M Ammonium citrate

b = 0% Acetone - 0.1 M Ammonium citrate

c = 60% Acetone - 0.06 M Ammonium citrate

d = 0% Acetone - 0.06 M Ammonium citrate

e = 20% Acetone - 0.1 M Ammonium citrate

f = 60% Acetone - 0.4 M Ammonium butarate

g = 60% Acetone - 0.1 M Ammonium citrate

h = 40% Acetone - 0.1 M Ammonium citrate

i = 20% Acetone - 0.06 M Ammonium citrate

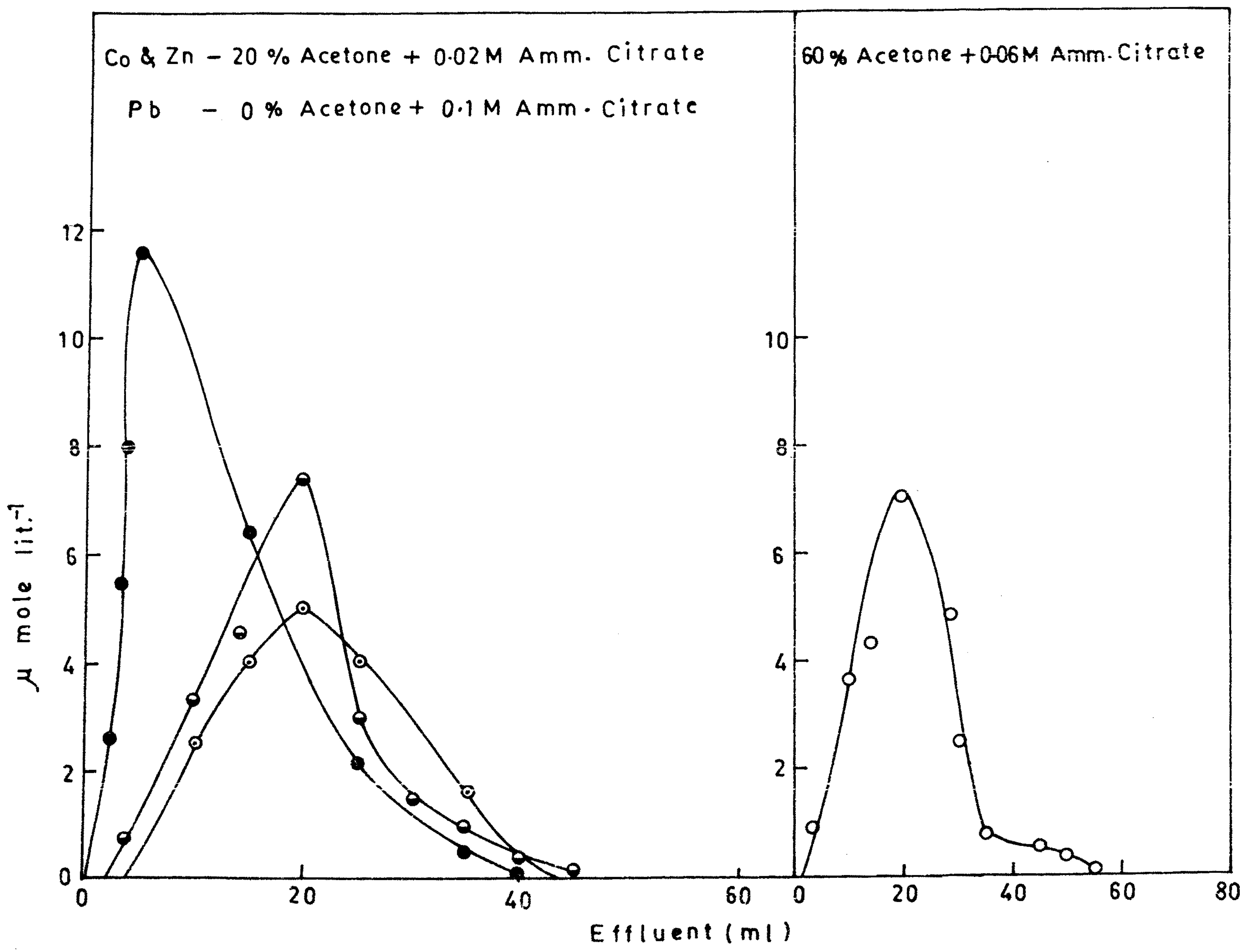


Fig. 3·1 — Elution curves of Zn (⊙)/Co (◑)/Pb (●) — Mg (○)

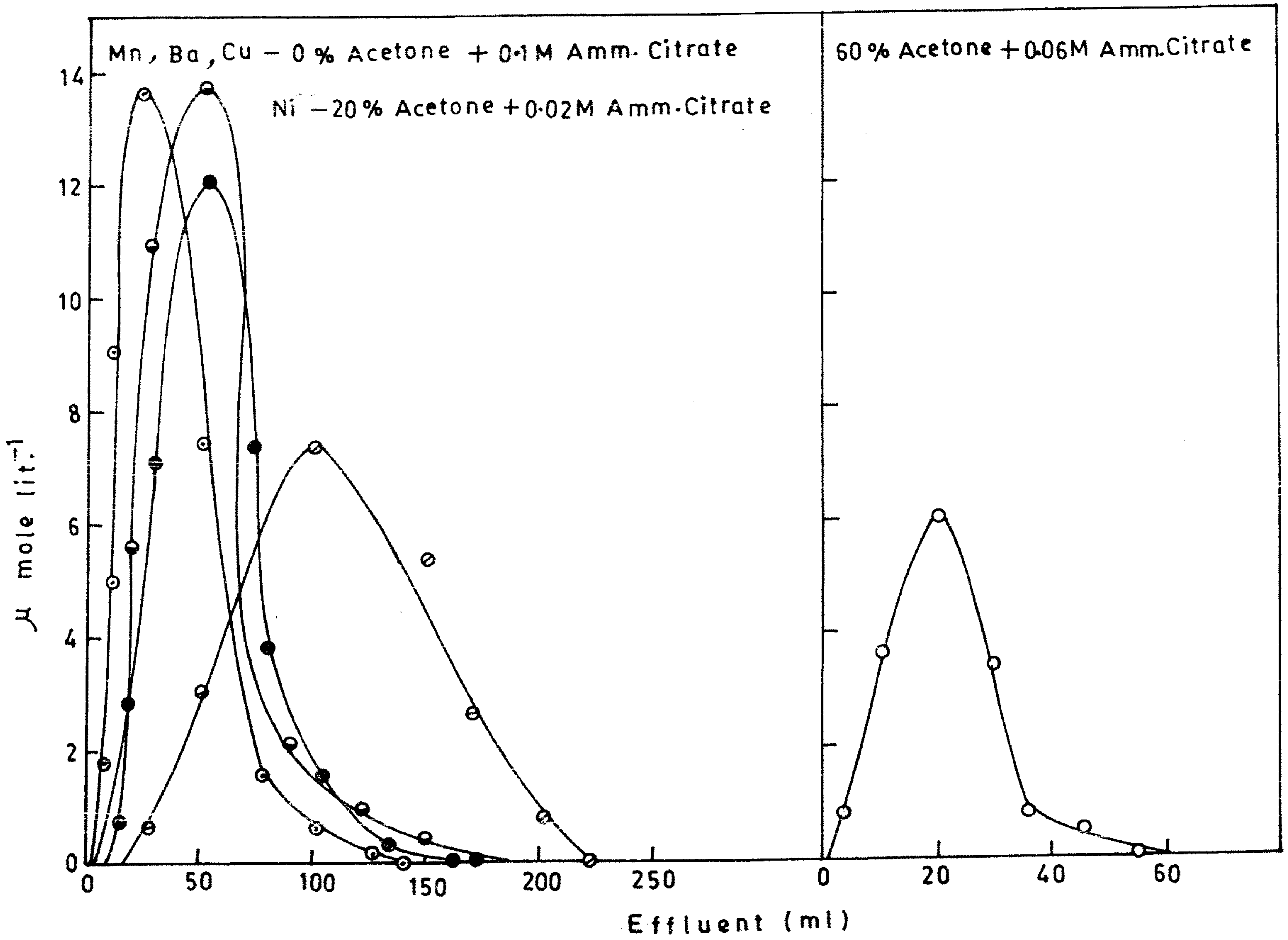


Fig. 3·2 — Elution curves of Mn (⊙)/ Ba (⊖)/ Cu (●)/Ni (⊘) — Mg (○)

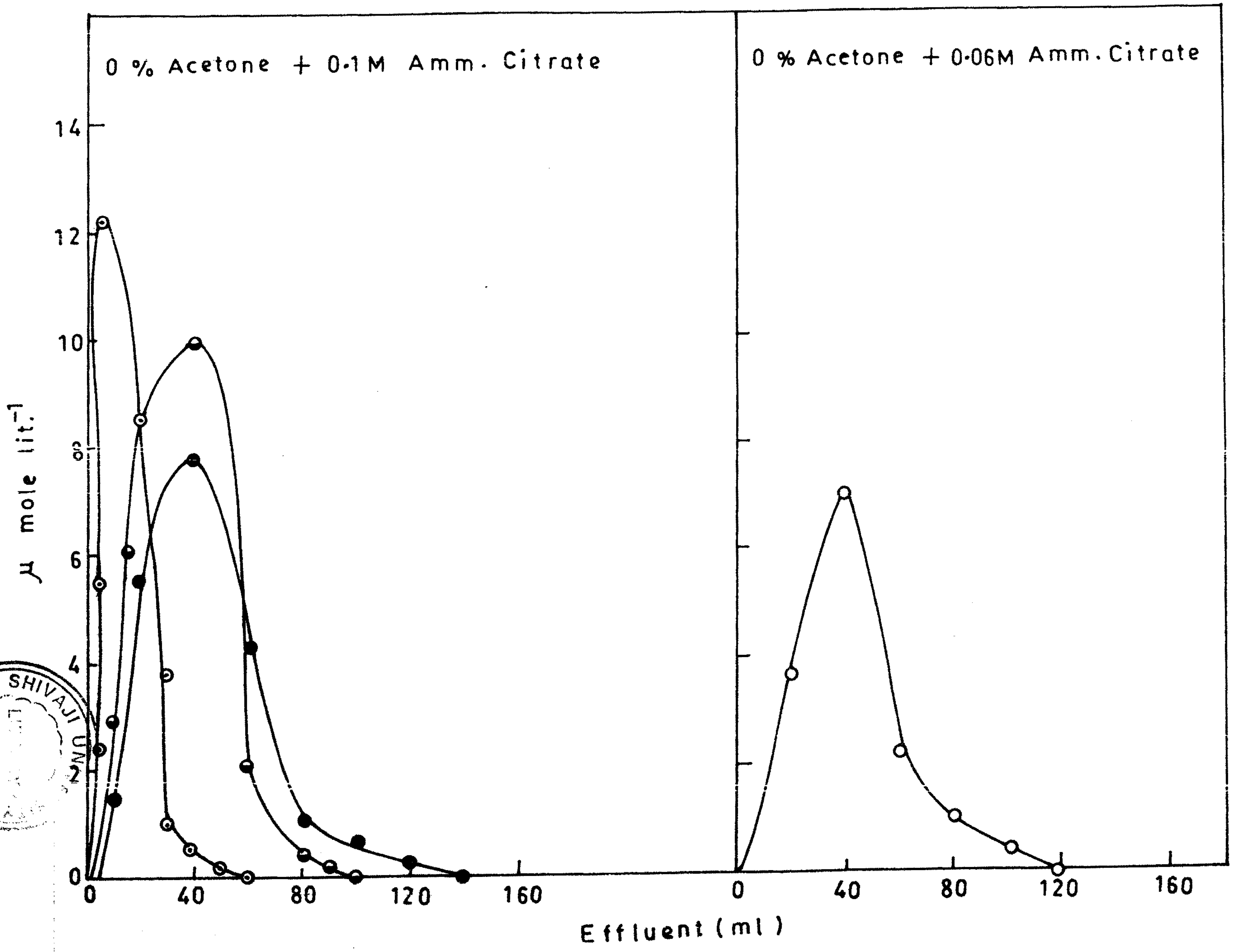


Fig. 3·3 — Elution curves of Pb (⊙)/Zn (⊖)/Co (●) — Ca (○).

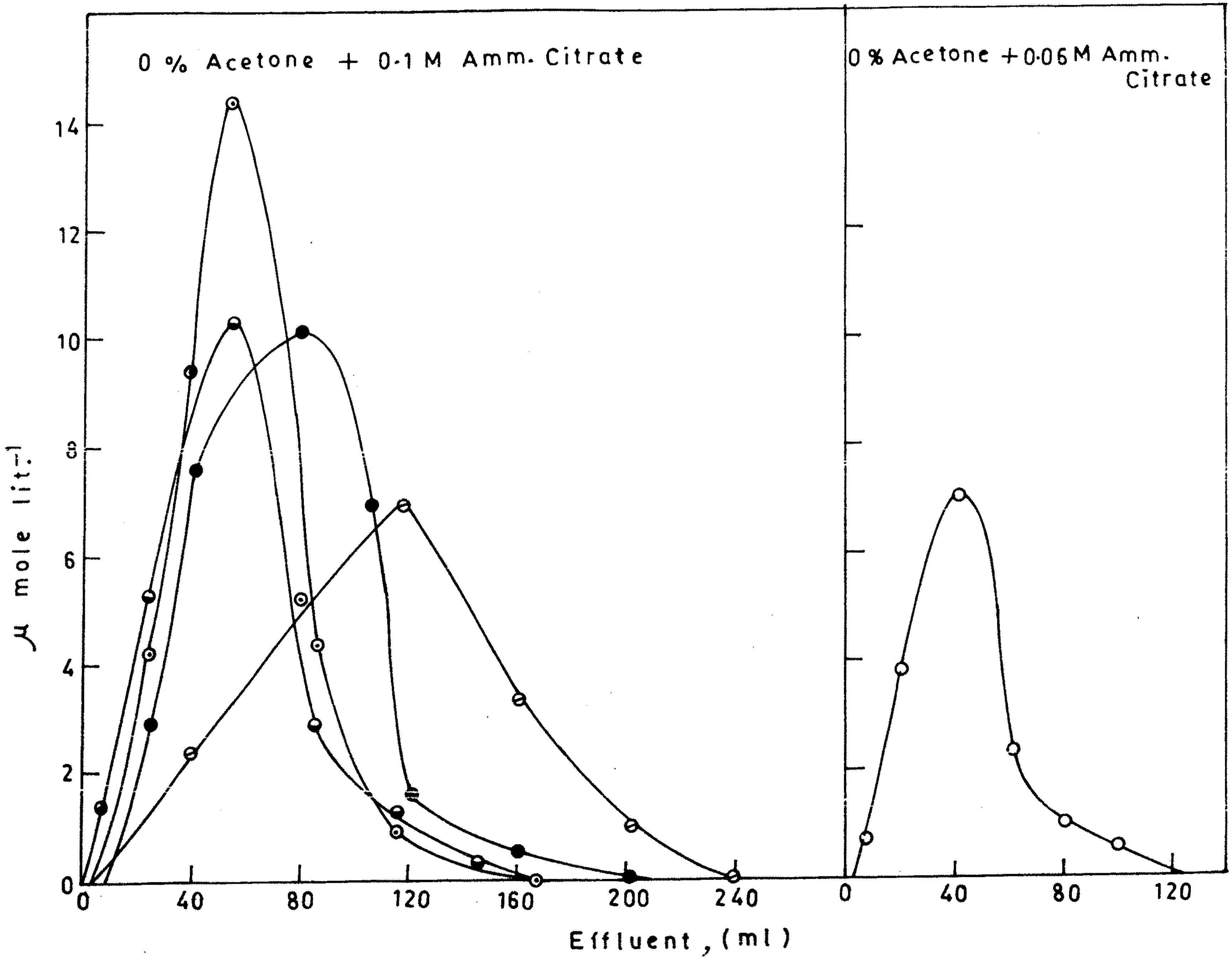


Fig. 3·4 — Elution curves of Ba (⊙)/Mn (⊖)/Cu (●)/Ni (⊘) — Ca (○).

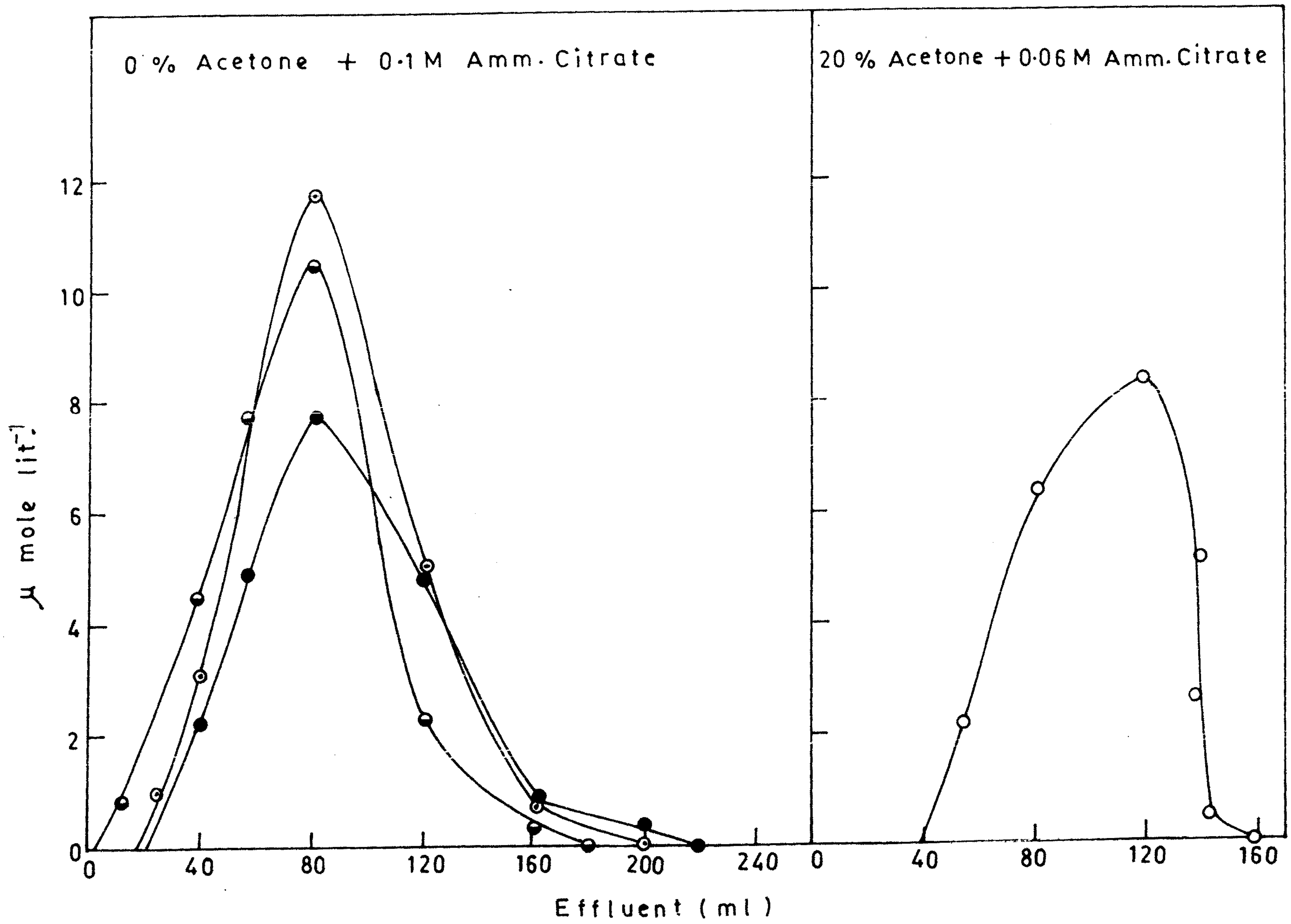


Fig. 3·5a— Elution curves of Cu (⊙)/Co (◒)/Ni (●) — Sr (○) .

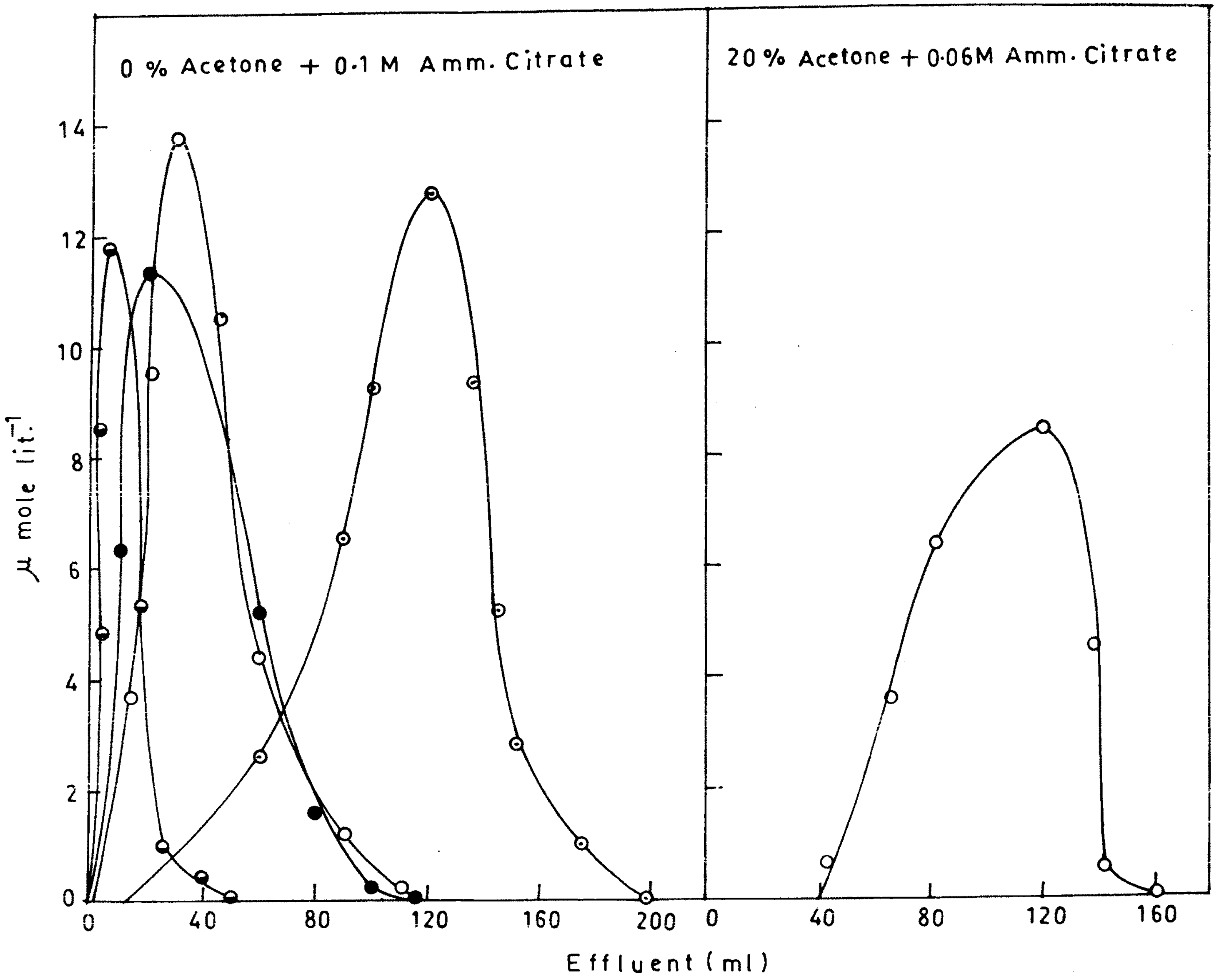


Fig. 3·5b— Elution curves of Mn(○)/Ba(⊙)/Pb(◒)/Zn(●) — Sr(○).

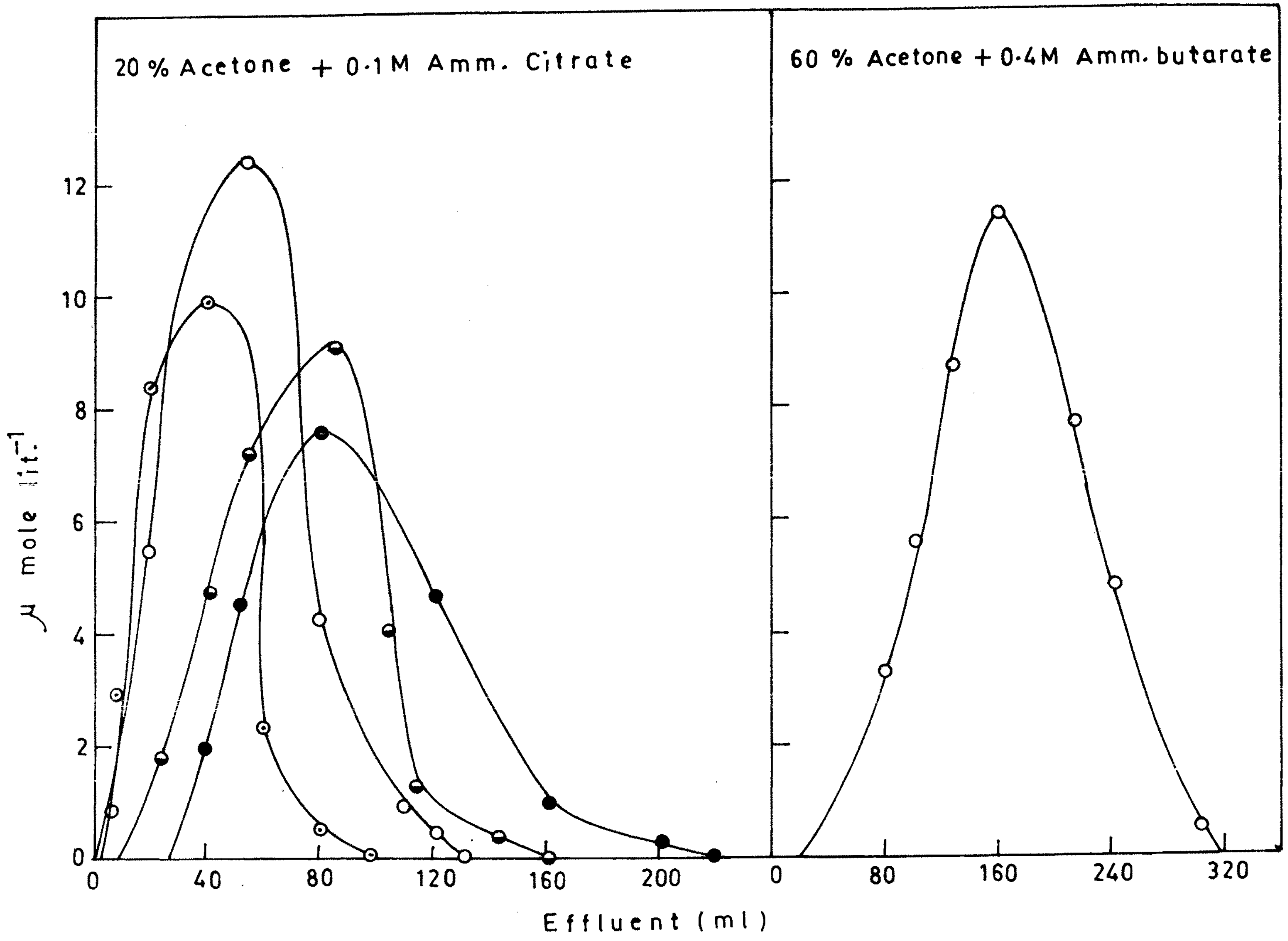


Fig. 3·6 — Elution curves of Co(○)/Zn (⊙)/Cu(◒)/Ni (●) — Th (○).

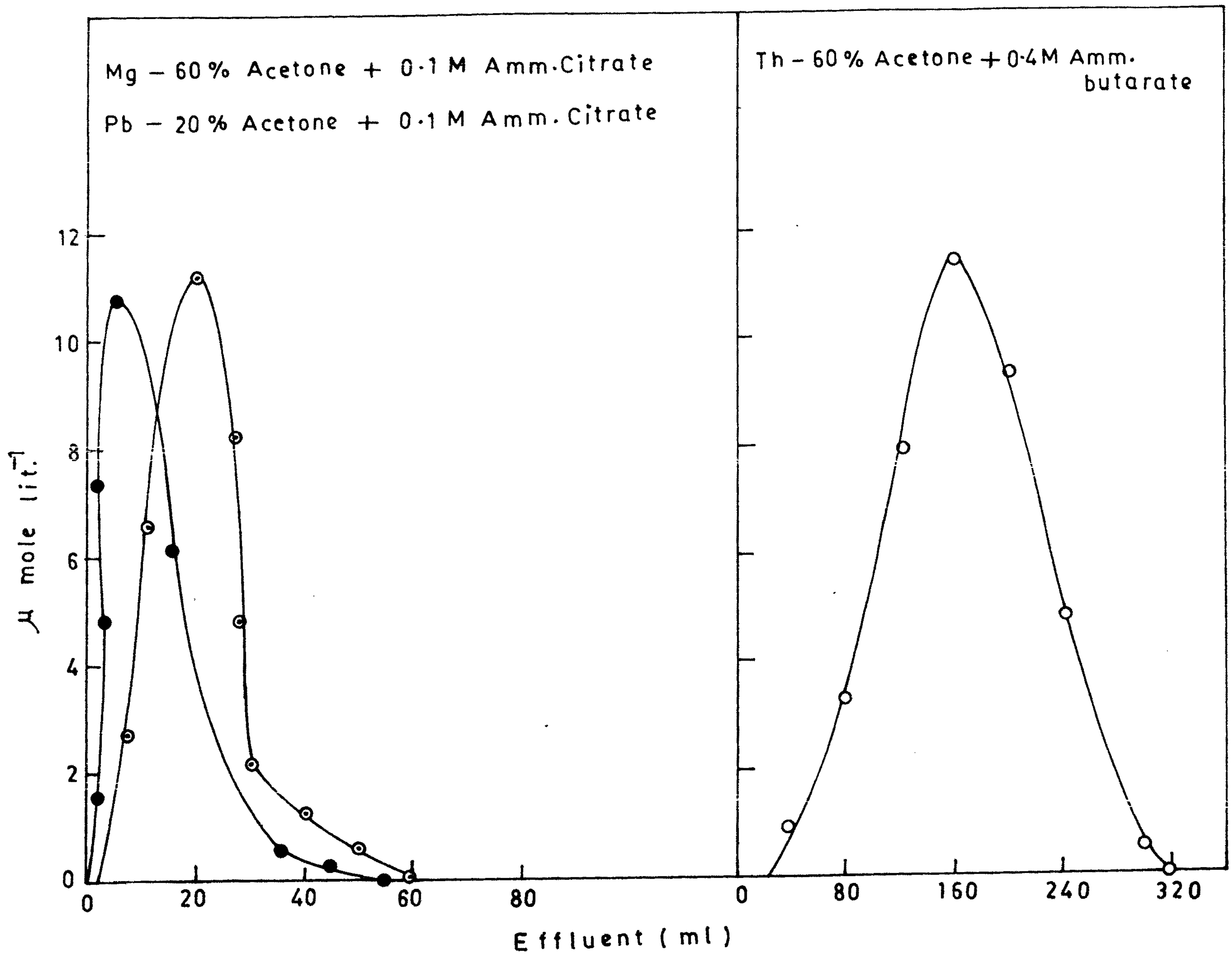


Fig. 3·7 — Elution curves of Mg (⊙) / Pb (●) — Th (o) .

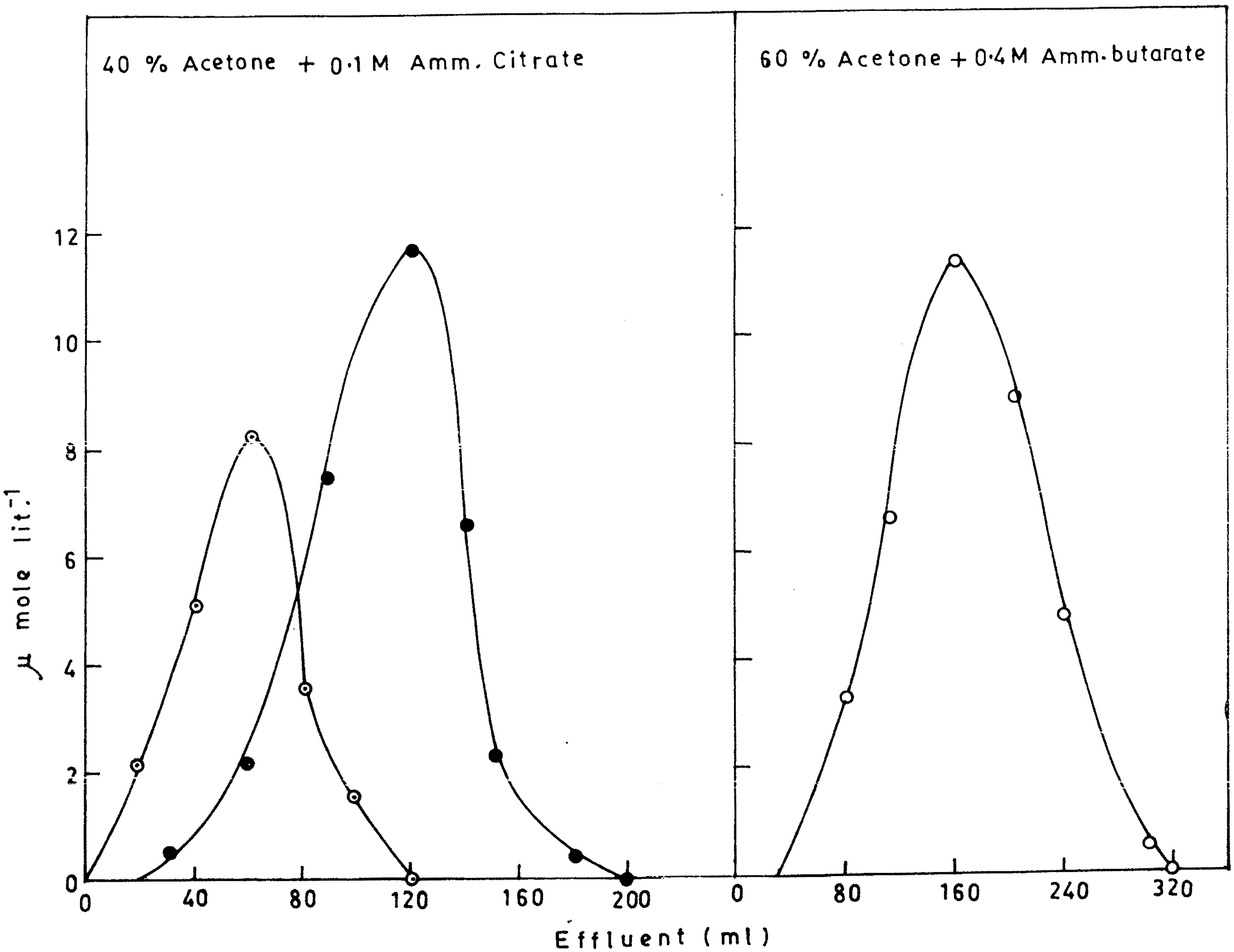


Fig. 3·8 — Elution curves of Cd (⊙) / Ba (●) — Th (○).

Table 3.6 : Quantitative Separation of Tertiary Mixtures

Mixture	Metal ion eluted	Eluting agent	M moles taken	M moles found
1	2	3	4	5
Zn(II)+Mg(II)+Ca(II)	Zn(II)	b	0.242	0.226
	Mg(II)	c	0.227	0.219
	Ca(II)	d	0.222	0.141
Co(II)+Mg(II)+Ca(II)	Co(II)	b	0.231	0.195
	Mg(II)	c	0.227	0.219
	Ca(II)	d	0.222	0.141
Cu(II)+Mg(II)+Ca(II)	Cu(II)	b	0.242	0.192
	Mg(II)	c	0.227	0.219
	Ca(II)	d	0.222	0.141
Ni(II)+Mg(II)+Ca(II)	Ni(II)	a	0.192	0.189
	Mg(II)	c	0.227	0.219
	Ca(II)	d	0.222	0.141
Zn(II)+Mg(II)+Th(IV)	Zn(II)	a	0.242	0.226
	Mg(II)	c	0.227	0.219
	Th(IV)	f	0.200	0.195
Co(II)+Mg(II)+Th(IV)	Co(II)	b	0.231	0.195
	Mg(II)	c	0.227	0.219
	Th(IV)	f	0.200	0.195
Cu(II)+Mg(II)+Th(IV)	Cu(II)	b	0.242	0.192
	Mg(II)	c	0.227	0.219
	Th(IV)	f	0.200	0.195
Ni(II)+Mg(II)+Th(IV)	Ni(II)	a	0.192	0.189
	Mg(II)	c	0.227	0.219
	Th(IV)	f	0.200	0.195
Zn(II)+Ca(II)+Th(IV)	Zn(II)	b	0.242	0.207
	Ca(II)	d	0.222	0.141
	Th(IV)	f	0.200	0.195
Co(II)+Ca(II)+Th(IV)	Co(II)	b	0.231	0.195
	Ca(II)	d	0.222	0.141
	Th(IV)	f	0.200	0.195

Table 3.6 : Contd...

1	2	3	4	5
Cu(II)+Ca(II)+Th(IV)	Cu(II)	b	0.242	0.192
	Ca(II)	d	0.222	0.141
	Th(IV)	f	0.200	0.195
Ni(II)+Ca(II)+Th(IV)	Ni(II)	b	0.244	0.207
	Ca(II)	d	0.222	0.141
	Th(IV)	f	0.200	0.195

a = 20% Acetone - 0.02 M Ammonium citrate

b = 0% Acetone - 0.1 M Ammonium citrate

c = 60% Acetone - 0.06 M Ammonium citrate

d = 0% Acetone - 0.06 M Ammonium citrate

f = 60% Acetone - 0.4 M Ammonium butarate

In binary and tertiary mixture separations it is observed that the values of break through volume (BTV) are low. Zn, Co, Pb, Mn, Ba, Cu, Mg Metal ions start eluting by 2-10 ml of respective eluting agent. The values being very small indicate the quick elution. The maximum elution of the metal ions are obtained by 20-100 ml of the eluting agent and the elution process is completed by 40 to 240 ml of the eluting mixture. As the elution rate is maintained at 3ml/minute. The metal ion Zn, Co, Pb, Mg are separated in 20-60 minutes and Sr, Th and Ca are totally eluted in 40-110 minutes. It can be concluded that generally the mixture is separated in 3 hours. The eluent required is in the range 40 ml minimum and 400 ml maximum.

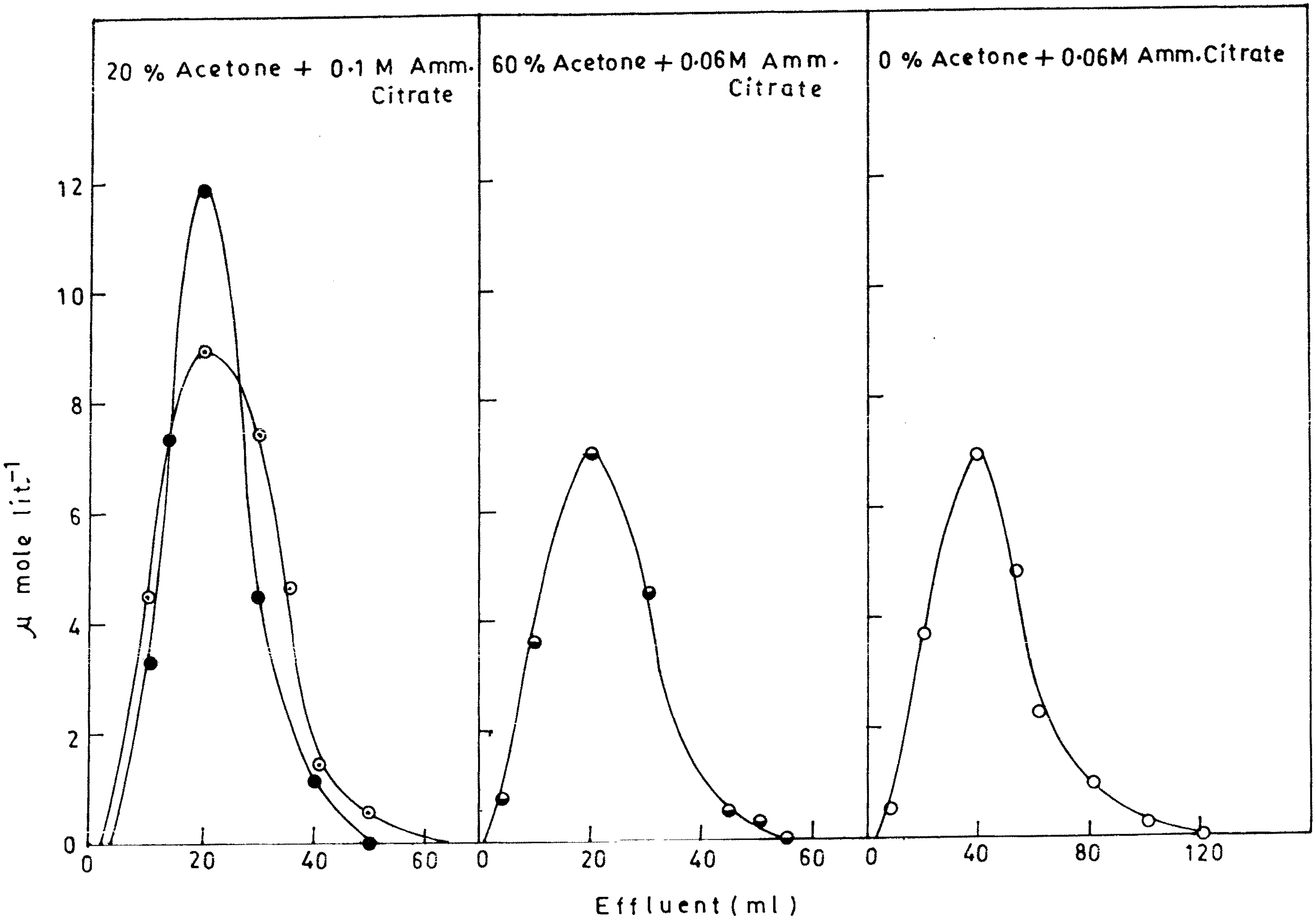


Fig. 3·9 — Elution curves of Zn (⊙)/Co (●) — Mg (◒) — Ca (○) .

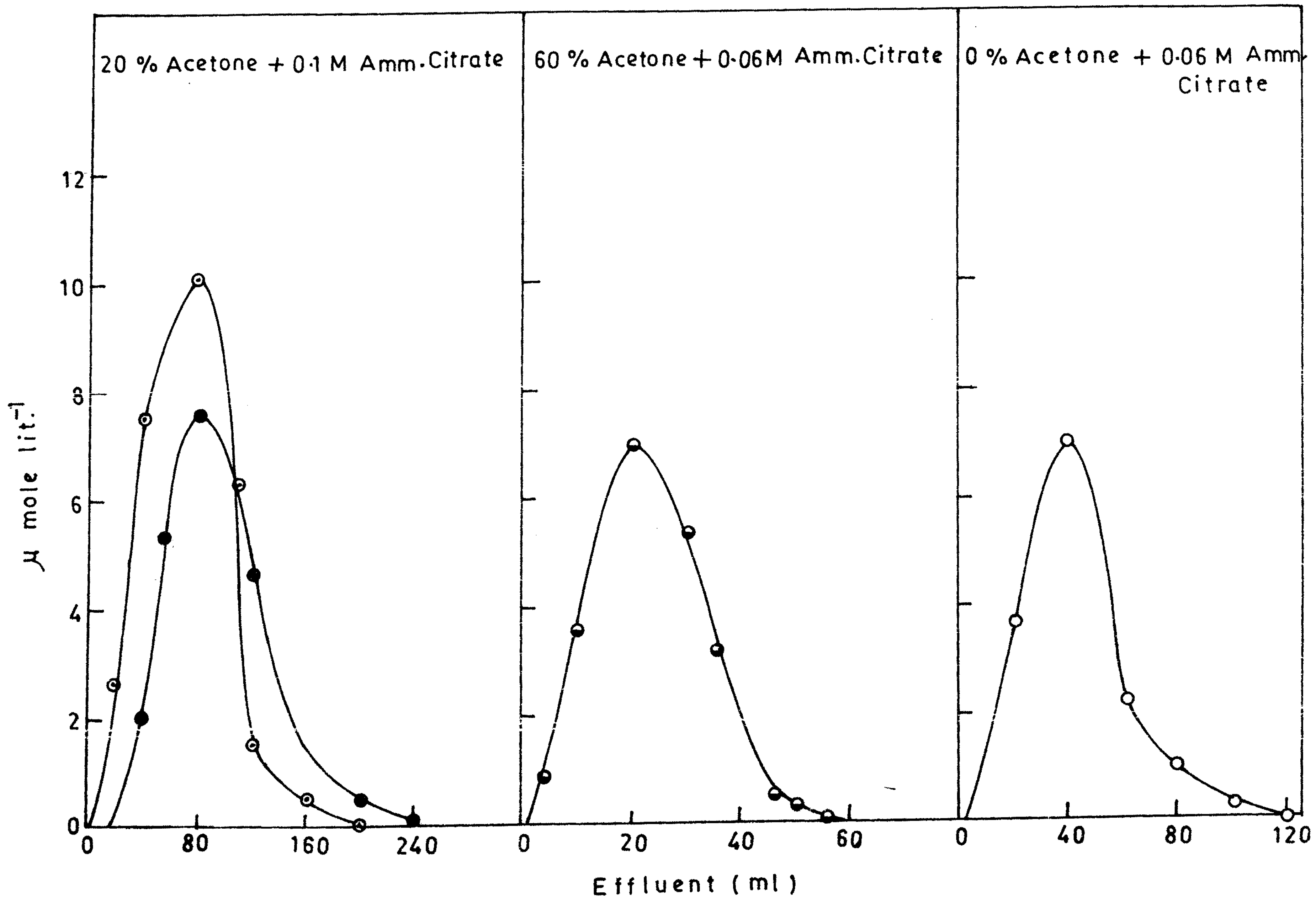


Fig. 3·10 — Elution curves of Cu (⊙) / Ni (●) — Mg (◒) — Ca (○).

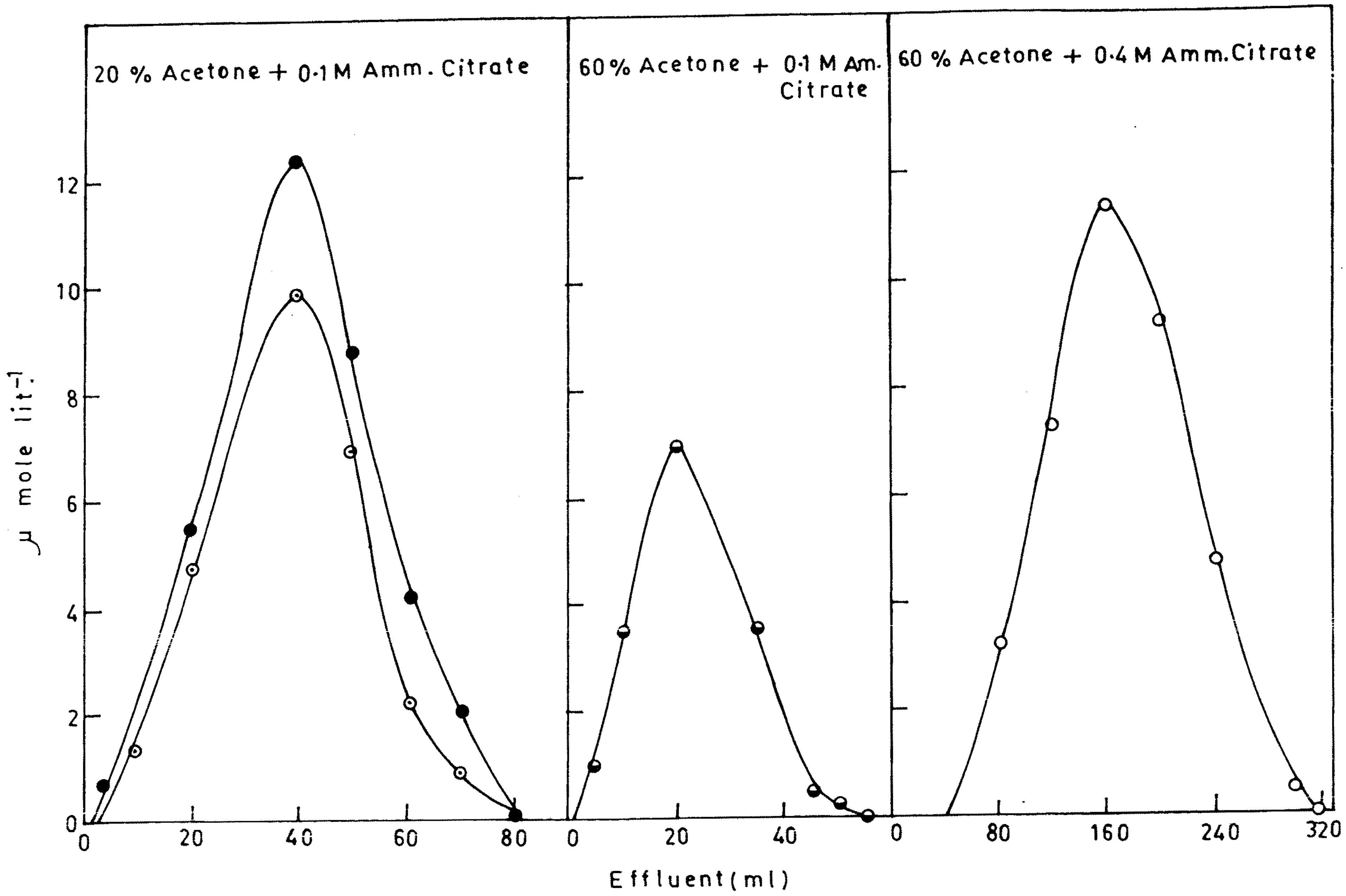


Fig. 3·11 — Elution curves of Zn (⊙) / Co (●) — Mg (◒) — Th (○) .

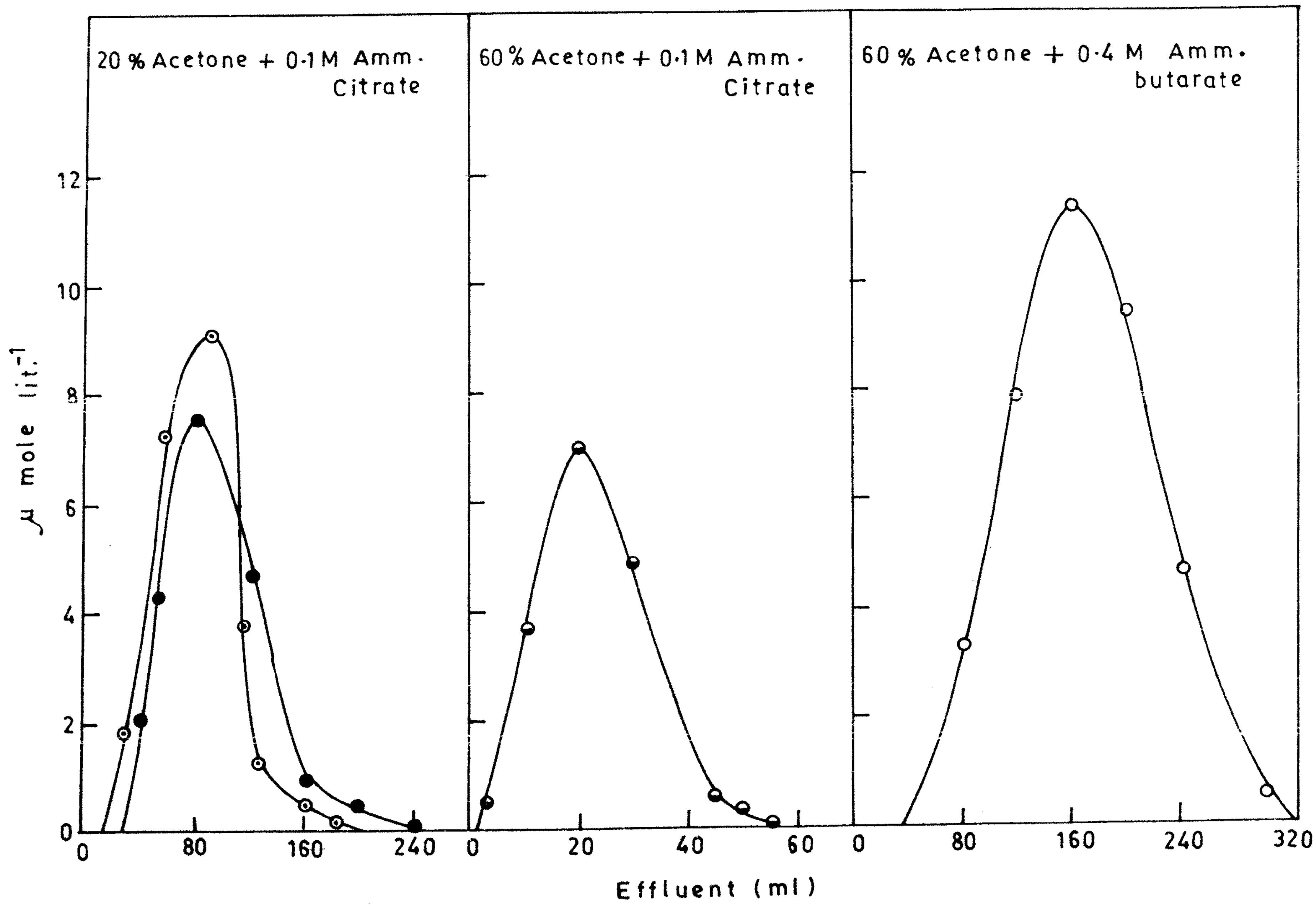


Fig. 3·12 – Elution curves of Cu (⊙) / Ni (●) — Mg (◐) — Th (○).

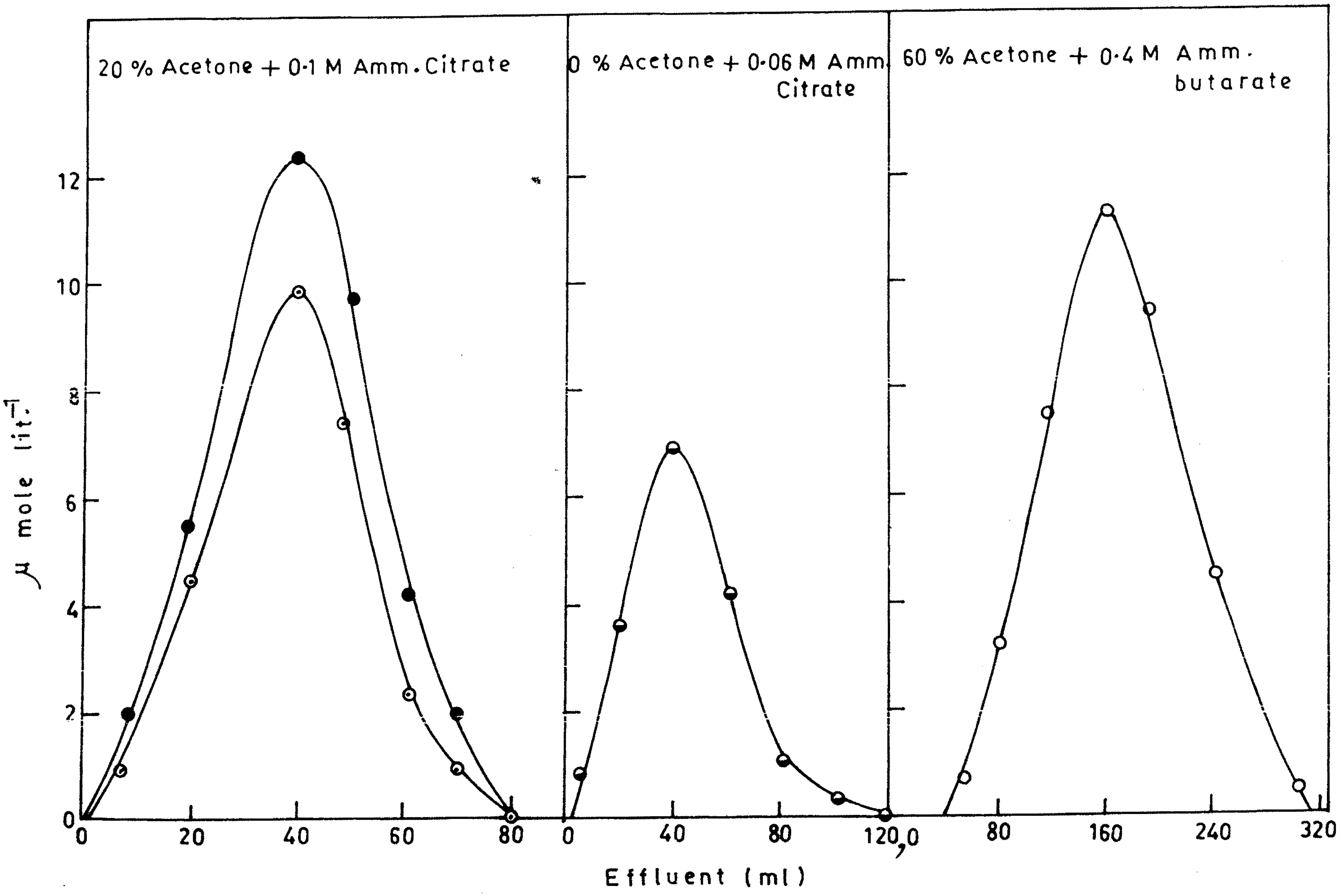


Fig. 3·13 — Elution curves of Zn (⊙) / Co (●) — Ca (◒) — Th (○) .

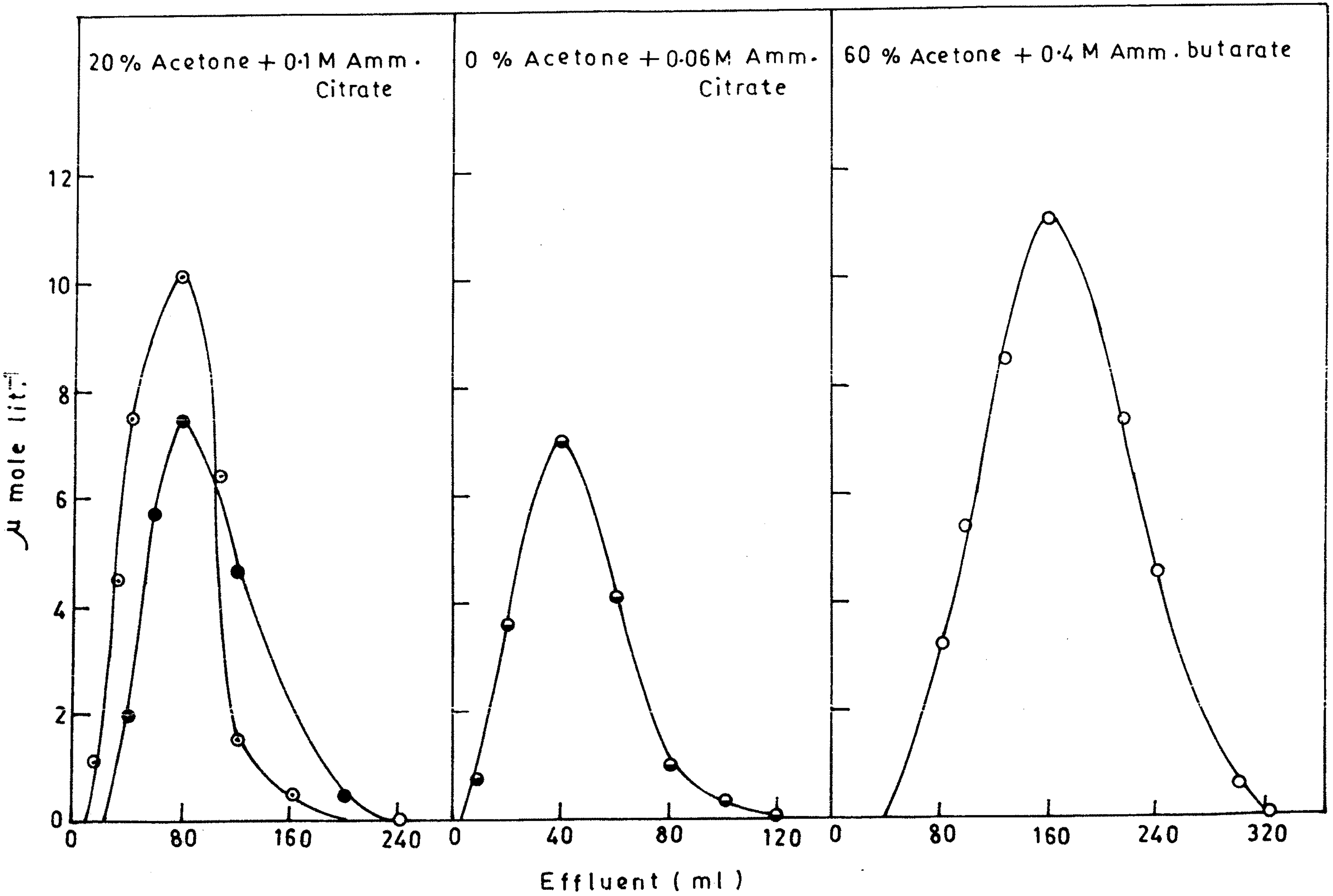


Fig. 3·14 — Elution curves of Cu (⊙) / Ni (●) — Ca (⊖) — Th (○).

ELUTION CURVES

Two component and three component elution curves are presented in figs. 3.1 to 3.15. The curves indicate how the systematic information contained in the 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. The various shapes of elution curves are discussed below.

Ideally the concentration profile of a solute in the direction of movement of the mobile phase should remain Gaussian at all concentrations as it moves through the system. However, sorption characteristics of change at high concentrations resulting in the changes in the distribution ratio. If no such changes occurred, a plot of the concentration of solute in the mobile phase as a function of that in the stationary phase at constant temperature would be linear and the concentration profile symmetrical plots of this type are known as sorption isotherms, can show curvature towards either axis under which circumstances the concentration profile will show tailing or fronting. Both these effects are undesirable as they lead poor separations and unreliable quantitative data. Fronting, which produces peaks with slopping front and sharp near boundaries is more likely to occur in systems where partition forms the basis of separation process, and where the soulte has the small distribution ratio. Tailing produces peaks with sharp leading edges and long sloping near boundaries. It is particularly likely to occur where adsorption is involved in the separation process. Both effects become pronounced at high concentrations and are therefore sympomatic of overloading the column or surface with sample. Restricting the sample size so as to operate over a linear region of the sorption isotherm is a recognized means of preventing fronting and tailing.

Table 3.7 : Elution characteristics of metal ions in aqueous acetone Ammonium citrate media (binary mixtures).

Sr.No.	Metal ion	BTV ml	VEP ml	TEV ml	Eluent
1	2	3	4	5	6
1.	Zn(II)	2	5	40	a
2.	Co(II)	5	20	45	a
3.	Pb(II)	6	20	35	b
4.	Mn(II)	5	30	140	b
5.	Ba(II)	10	50	155	b
6.	Cu(II)	7	50	150	b
7.	Ni(II)	15	100	225	a
8.	Mg(II)	3	20	55	c
9.	Pb(II)	1	5	60	b
10.	Zn(II)	5	40	100	a
11.	Co(II)	8	40	140	a
12.	Ba(II)	5	50	170	b
13.	Mn(II)	2	45	160	b
14.	Cu(II)	12	80	200	b
15.	Ni(II)	3	120	240	a
16.	Ca(II)	5	40	120	d
17.	Sr(II)	40	120	160	i
18.	Th(IV)	20	180	320	f

a = 20% Acetone - 0.02 M Ammonium citrate

b = 0% Acetone - 0.1 M Ammonium citrate

c = 60% Acetone - 0.06 M Ammonium citrate

d = 0% Acetone - 0.06 M Ammonium citrate

f = 60% Acetone - 0.4 M Ammonium butarate

i = 20% Acetone - 0.06 M Ammonium citrate

Table 3.8 : Elution characteristics of metal ions in aqueous acetone Ammonium citrate media (Ternary mixtures).

Sr.No.	Metal ion	BTV ml	VEP ml	TEV ml	Eluent
1	2	3	4	5	6
1.	Zn(II)	5	20	60	a
2.	Co(II)	7	20	50	b
3.	Mg(II)	3	20	55	c
4.	Ca(II)	5	40	120	d
5.	Cu(II)	5	80	200	b
6.	Ni(II)	20	80	240	b
7.	Th(II)	50	160	320	f

a = 20% Acetone - 0.02 M Ammonium citrate

b = 0% Acetone - 0.1 M Ammonium citrate

c = 60% Acetone - 0.06 M Ammonium citrate

d = 0% Acetone - 0.06 M Ammonium citrate

f = 60% Acetone - 0.4 M Ammonium butarate

ELUTION CHARACTERISTICS

BREAK THROUGH VOLUME

Ion exchange is often used for removing a certain ion from a solution or for replacing it by another ion. Let us assume that the ion B in an electrolyte BY should be replaced by another ion A. When an electrolyte BY is poured on the column which is packed with A, the solution BY goes automatically through a series of bath equilibriations. Thus all B ions eventually replaced by A before the solution appears in the effluent.

When the solution is fed to the column it will exchange all its ions B for A in a comparatively narrow zone at the top of the bed. The solution, now containing the electrolyte AT, passes through the lower part of the column without further change in composition. As the feed is continued, the top layers of the bed are constantly exposed to fresh solution BY eventually, they are completely converted to B form and loose their efficiency, they become exhausted. The one in which the ion exchange occurs is thus displaced down stream. In due course, this zone reaches the bottom of the column. This is the break through of B, now, ions B first appear in the effluent.

In the present studies species of A ions do not form cationic complexes with ammonium citrate of a particular concentration and these pass away through Amberlite IR-120 containing NH_4^+ ions. These 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. After the elution of A, another eluting agent which breaks the cationic complex of companion ion B, is passed on the column. The initial volume of this eluting agent is the break through volume for the elution of B (BTV).

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). High selectivity of the ion exchanger guarantees large differences in the migration rates of the various peaks and thus facilitates the separation.

TERMINAL ELUTION VOLUME (TEV)

After eluting the maximum amount of metal ion as eluate the ion exchange rate becomes slow. The volume of eluting agent 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 Th, Cu, Co, Cd, Pb, Mn, Mg, Ni, Zn, Ca, Ba and Sr in aqueous acetone ammonium citrate are presented in tables 3.1 to 3.15.

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