Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Thin-Layer Chromatography of Metal Ions. I. The Quantitative Separation of Cd^{2+} from Zn^{2+}, Cu^{2+}, and Pb^{2+}. The Quantitative Separation of Cu^{2+} from $Ni^{2+}$and Co^{2+}

Mohsin Qureshi[a]; Jagat S. Thakur[a]
[a] Chemistry Section, Zakir Husain Engineering College, Aligarh Muslim University, Aligarh, U.P., India

To cite this Article Qureshi, Mohsin and Thakur, Jagat S.(1976) 'Thin-Layer Chromatography of Metal Ions. I. The Quantitative Separation of Cd^{2+} from Zn^{2+}, Cu^{2+}, and Pb^{2+}. The Quantitative Separation of Cu^{2+} from $Ni^{2+}$and Co^{2+}', Separation Science and Technology, 11: 5, 467 — 482
To link to this Article: DOI: 10.1080/01496397608085336
URL: http://dx.doi.org/10.1080/01496397608085336

SEPARATION SCIENCE, 11(5), pp. 467–482, 1976

Thin-Layer Chromatography of Metal Ions. I. The Quantitative Separation of Cd^{2+} from Zn^{2+}, Cu^{2+}, and Pb^{2+}. The Quantitative Separation of Cu^{2+} from Ni^{2+} and Co^{2+}

MOHSIN QURESHI and JAGAT S. THAKUR

CHEMISTRY SECTION
ZAKIR HUSAIN ENGINEERING COLLEGE
ALIGARH MUSLIM UNIVERSITY
ALIGARH (U.P.), INDIA

Abstract

The quantitative separations of Cd^{2+} from Cu^{2+}, Zn^{2+}, and Pb^{2+}, and of Cu^{2+} from Ni^{2+} and Co^{2+} have been studied in details using varying concentrations of NaCl solution in acetone. In order to find the optimum conditions for the separation of these metal ions, a systematic study was made of various important factors, such as sample concentrations, eluent concentrations, pH, and ionic strength. The chromatographic behavior of 47 metal ions was also investigated using 1.0 *M* NaCl solution in 30% acetone.

INTRODUCTION

Thin-layer chromatography is very efficient for the separation of metal ions. Recent work done up to 1972 has been admirably summarized by Brinkman (*1*). After 1972 only a few studies have been made on the thin-layer chromatography of metal ions on silica gel G (*2, 3*). Soljic and coworkers (*4*) separated Cu, Pb, Bi, Cd, Hg, As, Sb, and Sn by thin-layer chromatography on cellulose using 25:5 BuOH—3 *M* HCl.

All these studies suffer from the following limitations:

(a) The quantitative aspects of the separations have not been examined.

(b) The effect of various factors such as sample concentrations, eluent concentrations, pH, and ionic strength has not been systematically studied.

Without the study of these factors, the separation cannot be put to much practical use. The present work was therefore undertaken to remove these limitations. The chromatographic behavior of 47 metal ions was investigated using 1.0 *M* NaCl solution in 30% acetone.

Sodium chloride was chosen because it enables one to study the effect of Cl^- concentration on the separations. In the earlier studies HCl was invariably chosen. However, if the HCl concentration varies, then the $[H^+]$ and $[Cl^-]$ are both simultaneously varied. Acetone was used because it does not solvate the ions and it suppresses hydrolysis to give more compact spots. The results obtained are summarized in the form of two papers.

Paper I deals with the following separations:

Cd^{2+} from Cu^{2+}, Zn^{2+}, and Pb^{2+}.
Cu^{2+} from Ni^{2+} and Co^{2+}.

Paper II deals with

Fe^{2+} from Ni^{2+} and Co^{2+}.
Hg^{2+} from Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, and Bi^{3+}.

All the separations are quantitative.

EXPERIMENTAL

Apparatus

Thin-layer chromatography apparatus (Toshniwal, India) for the preparation of silica gel plates on 20 × 3.5 cm glass plates was used. The chromatography was performed in 24 × 6 cm glass jars. Elico pH meter Model LI-10, Bausch and Lomb Spectronic 20 Colorimeter were used for pH and spectrophotometric measurements, respectively.

Reagents

Silica gel G (E. Merck), cadmium sulfate, cadmium nitrate (made in Poland), zinc sulfate (B.D.H.) cobalt sulfate (Sarabhai M. Chemical, India), lead nitrate (B.D.H.), cobalt sulfate (B.D.H.), nickel sulfate (B.D.H.), sodium chloride (B.D.H.), dithizone (B.D.H.), sodium diethyldithiocarbamate (made in Hungary), acetone (B.D.H.), chloroform (B.D.H.), and carbon tetrachloride (B.D.H.) were used. All other reagents were of AnalaR grade.

Test Solutions

Sulfates of Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and nitrates of Cd^{2+} and Pb^{2+} were used. The solutions (0.1 *M*) of chlorides, nitrates, and sulfates of most of the cations were prepared in 0.1 *M* solutions of the corresponding acids. The 0.1 *M* antimony and bismuth chloride solutions were prepared in 30% v/v and 4 *M* hydrochloric acid, respectively. Niobium pentachloride solution (1%) was prepared in 10% tartaric acid. Selenium dioxide was dissolved in water and made alkaline with 1 *M* potassium hydroxide. The 1% solution of gold chloride was prepared in 4 *M* hydrochloric acid. Tantalum pentaoxide was dissolved in concentrated sulfuric acid and ammonium sulfate. 0.1% Pt solution was prepared by dissolving Pt wire in aqua regia. Sodium molybdate, sodium tungstate, potassium chloride, and rubidium chloride solutions were prepared in water. Ceric sulfate (0.1 *M*) was prepared in 3.6 *N* sulfuric acid. Stannous chloride (0.1 *M*) was prepared in 4 *M* hydrochloric acid.

Detection

Ag^{+}, Tl^{+}, Hg^{+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Bi^{3+}, As^{5+}, and Sb^{5+} were detected with yellow ammonium sulfide solution. A 1% aqueous solution of aluminon was used to detect Al^{3+}, Ga^{3+}, and Be^{2+}, and 0.1% alcoholic alizarin red-S solution was used for La^{3+}, Y^{3+}, Pr^{3+}, Lu^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Zr^{4+}, Th^{4+} Ce^{4+}, Sn^{2+}, Sn^{4+}, and Nb^{5+} spots. To detect Zn^{2+} and Cr^{3+} a 1% alcoholic diphenyl carbazide solution was used. Ni^{2+} and Co^{2+} spots were detected with 1% alcoholic dimethylglyoxime solution, and Fe^{3+}, VO^{2+}, and $UO_2{}^{2+}$ were detected with 2% aqueous potassium ferrocyanide solution. A 1% alcoholic solution of pyrogallol was used to detect W^{6+}, and Ta^{5+}, Mo^{6+}, Pt^{4+}, Se^{4+}, and Au^{3+} spots were detected with 0.1 *M* stannous chloride solution in 4 *M* hydrochloric acid. Aqueous potassium ferricyanide solution was used to detect Fe^{2+}, and 1% alcoholic chromotropic acid solution was used to detect Ti^{4+}.

Preparation of Silica Gel Plates

The slurry used was prepared by mixing the silica gel with constant shaking for 5 min in conductivity water in the ratio of 1 : 3. This slurry was used immediately to coat the clean glass plates with the help of an applicator to give a layer of 0.25 mm thickness for qualitative studies and 0.50 mm thickness for quantitative studies. These plates were first dried at room temperature and then in an electrically controlled oven at 100 ± 5 °C for 2 hr for complete drying. They were then stored in an oven at room temperature until used.

Procedure

Approximately 3 μl of the test solutions (0.1 *M*) were applied on each silica gel plate by using a micropipette. The solvent was allowed to ascend 10 cm from the starting line on the plate in all cases. After the development was over, the plates were dried in an air oven and the cations were detected with the usual reagents. For the quantitative separation, each metal ion was eluted with 0.1 *N* sulfuric acid from silica gel and determined spectrophotometrically. Dithizone (8 mg in 100 ml chloroform) and a 1% solution of sodium diethyldithiocarbamate were used as color reagents for the spectrophotometric determination of Cd^{2+} and Cu^{2+}, respectively (*5*, *6*).

Electrophoresis

In order to explain the R_F values, electrophoresis studies were performed in a NaCl system using the Shandon Electrophoresis Apparatus (Shandon Scientific Company, London).

RESULTS AND DISCUSSION

The chromatographic behavior of 47 metal ions was first studied in a solution which was 1.0 *M* in NaCl and 30% in acetone. The results are summarized in Table 1. From this study a number of separations were found to be possible. These were then studied more thoroughly and the effect of various factors was investigated.

The Separation of Cd^{2+} from Cu^{2+}, Zn^{2+}, and Pb^{2+}

In order to find the optimum conditions for the separation of Cd^{2+}

TABLE 1

Chromatographic Behavior of 47 Metal Ions in 1.0 *M* NaCl and 30% Acetone

Tl^+ (0.00)
Fe^{2+} (0.0–0.84)
Cd^{2+} (0.87)
Ni^{2+} (0.90)
Zn^{2+} (0.0–0.48)
Cr^{3+} (0.0–0.88)
Ga^{3+} (0.0–0.08)
La^{3+} (0.0)
Lu^{3+} (0.0–0.68)
Eu^{3+} (0.0–0.42)
Dy^{3+} (0.0–0.44)
Tm^{3+} (0.0–0.48)
Ti^{4+} (0.0–0.99)
Se^{4+} (0.00)
As^{5+} (0.0–0.78)
Mo^{6+} (0.00)
Ag^+ (0.00–0.56)
Hg^{2+} (0.89)
$UO_2{}^{2+}$ (0.0–0.39)
Co^{2+} (0.94)
Pb^{2+} (0.00)
Fe^{3+} (0.0–0.88)
Al^{3+} (0.0–0.49)
Pr^{3+} (0.0–0.91)
Nd^{3+} (0.0–0.40)
Gd^{3+} (0.0–0.40)
Ho^{3+} (0.0–0.63)
Zr^{4+} (0.0–0.57)
Th^{4+} (0.0–0.22)
Pt^{4+} (0.93)
Ta^{5+} (0.0–1.00)
W^{6+} (0.00)
$Hg_2{}^{2+}$ (0.50–1.00)
Cu^{2+} (0.0–0.21)
VO^{2+} (0.0–0.92)
Sn^{2+} (0.0–0.80)
Be^{2+} (0.0–0.88)
Bi^{3+} (0.0–0.87)
Au^{3+} (0.97)
Y^{3+} (0.0–0.44)
Sm^{3+} (0.0–0.47)
Tb^{3+} (0.0–0.40)
Er^{3+} (0.0–0.47)
Ce^{4+} (0.00)
Sn^{4+} (0.0–0.82)
Sb^{5+} (0.0–0.87)
Nb^{5+} (0.0)

from Cu^{2+}, Zn^{2+}, and Pb^{2+}, a systematic study was made of the various important factors as given below.

Effect of Cl^- Concentration (Figs. 1a, b, and c)

The Cl^- concentration was varied from 0.1 *M* NaCl-saturated NaCl. In all of these solutions Cd^{2+} has a high R_F and it can be separated from Cu^{2+}, Zn^{2+}, and Pb^{2+} using dilute solutions of sodium chloride. The best results are obtained with 0.35 *M* NaCl for Zn^{2+}, 0.50 *M* for Cu^{2+}, and 0.10 *M* for Pb^{2+}. The R_F values of Zn^{2+} and Pb^{2+} increase as the chloride ion concentration increases until in the saturated solution these ions have R_F values very close to that of Cd^{2+}. However, because the spots are compact, separation is still possible, but the plates are deformed on drying. At a high Cl^- concentration Zn^{2+} and Pb^{2+} form anionic complexes such as $ZnCl_4{}^{2-}$ and $PbCl_4{}^{2-}$, while copper forms complexes of low stability; hence there is no effect of Cl^- concentration on the R_F value of Cu^{2+}. It is interesting to compare these results with the work of Kraus and Moore (*7*). In this comparison it must be noted that we have studied concentrations from 0.0 to 2.0 *M* in greater detail.

Cd^{2+} forms the strongest complex, and in 1 *M* HCl it is completely in the anionic form, leading to maximum adsorption at this point. However, as the HCl concentration is increased the chlorocomplex is unable to compete successfully with the chloride ion, and there is a decrease in the

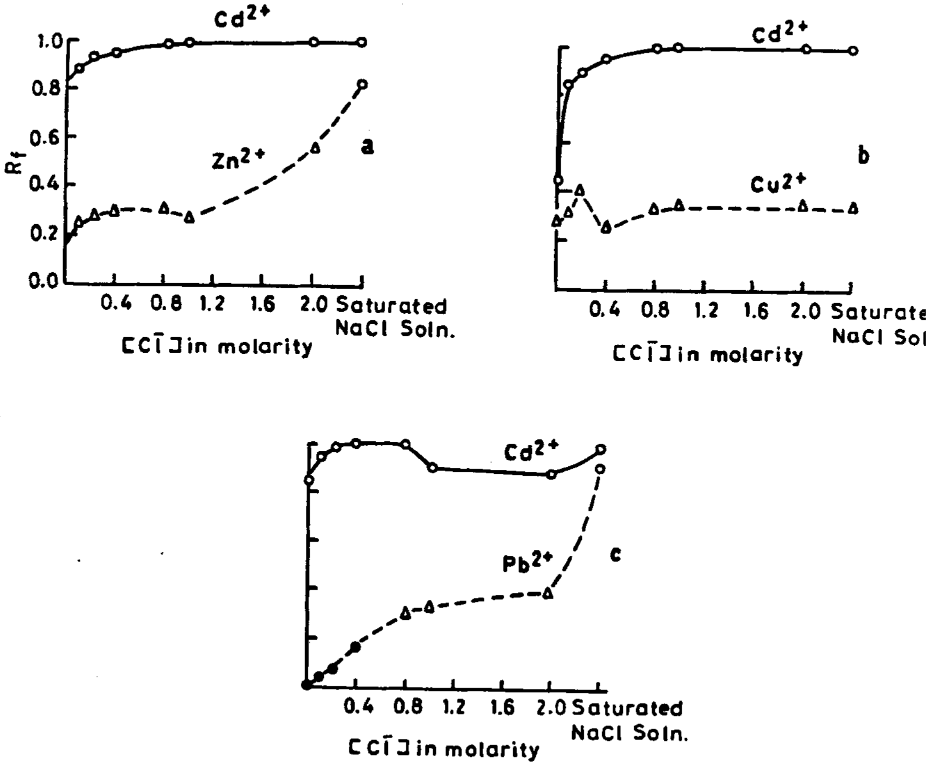


FIG. 1. (○) Compact spots; (●) tailing spots with RL − RT < 4; (△) tailing spots with RL − RT > 4.

K_d value. In our case the minimum NaCl concentration used was 0.01 M. This is apparently able to complex most of the Cd^{2+} ions. Hence the R_F of Cd^{2+} is very large. As silica acts as a weak cation exchanger (see Eq. 1), the anionic chlorocomplex is not adsorbed, thus leading to a high R_F.

$$2m(\equiv Si-OH) + mCd^{2+} \rightleftarrows m(\equiv Si-O)_2Cd^{2+} + 2mH^+ \qquad (1)$$

As the Cl^- concentration reaches 1 M the complex formation is complete and there is no further increase in R_F. Zn^{2+} also forms the very stable $ZnCl_4^{2-}$ complex, but it is slightly less stable than that of Cd^{2+}. Hence at lower Cl^- concentrations the K_d value of Zn^{2+} is smaller than that of

Cd^{2+}. We also find that in our case at low Cl^- concentrations that the R_F value of Zn^{2+} is smaller than the R_F value of Cd^{2+}, making the Cd–Zn separation possible.

According to Kraus (*7*), Cu^{2+} is only slightly adsorbed, even from 2 *M* HCl. We also found that the R_F of Cu^{2+} is low and unaffected by the Cl^- concentration.

According to Kraus (*7*), complex formation of Pb^{2+} increases with an increase in chloride ion concentration until it reaches a maximum at 1.0 *M* HCl. However, we found that as the Cl^- concentration increases the R_F increases until it becomes a maximum in saturated NaCl solution.

Thus it is apparent that TLC on silica gel is more effective than anion exchange chromatography on Dowex 1-X10 as it is possible to separate Cd^{2+} and Zn^{2+} by TLC but not by anion exchange chromatography.

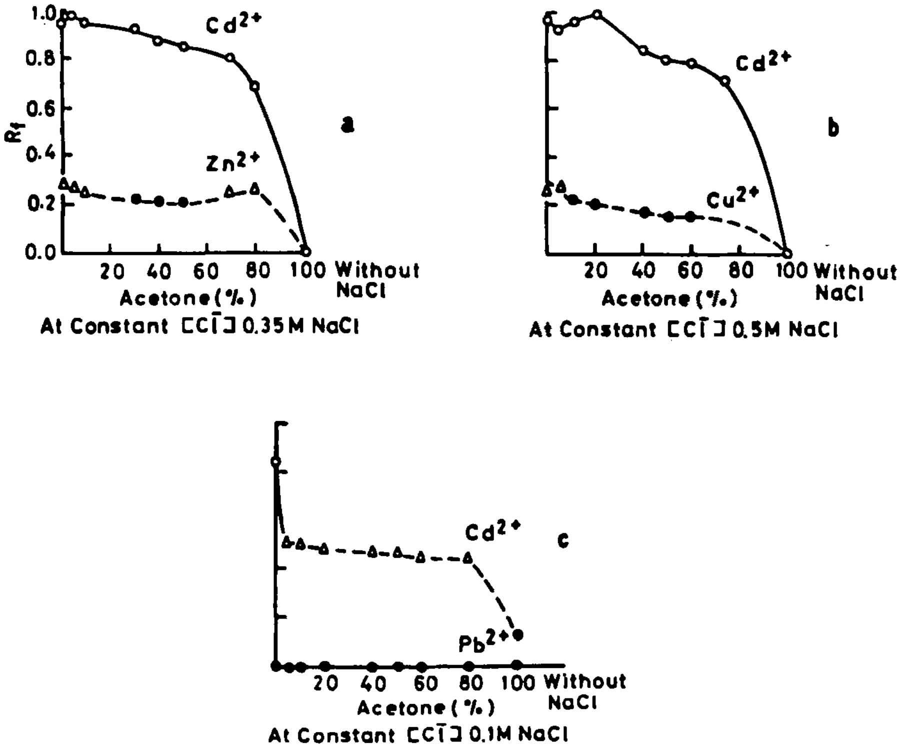


FIG. 2. See Fig. 1 for key to symbols.

Effect of the Addition of Acetone

As the acetone concentration increases there is a considerable decrease in the tailing of Zn^{2+}, Cu^{2+}, and Pb^{2+}. The Cd^{2+} spot remains compact but there is a slight decrease in the R_F value of Cd^{2+} as the acetone concentration increases from 0 to 80%. The R_F values of Zn^{2+} and Cu^{2+} remain almost constant up to 80% acetone concentration and then there is a sharp decrease in R_F values. In 100% acetone (i.e., Cl^- is absent) the R_F values of Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} are zero. The best solvent for the separation of Cd^{2+} from Zn^{2+} is found to be a solution which is 0.35 *M* in sodium chloride and 30% in acetone. For Cd^{2+}–Pb^{2+} and Cd^{2+}–Cu^{2+} separations, 0.1 *M* NaCl (without acetone) and 0.5 *M* NaCl in 20% acetone are best. The results are given in Figs. 2a, b, and c.

Effect of pH

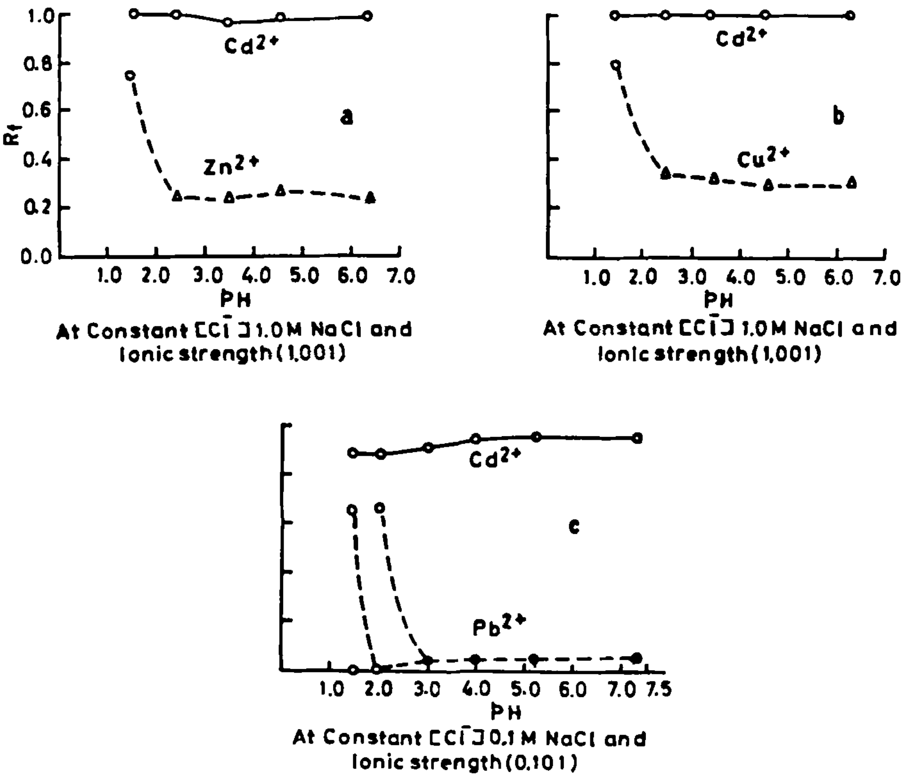
At a low pH (i.e., 1.5) the Zn^{2+} and Cu^{2+} spots are in the form of fine streaks. As the pH increases (i.e., 1.5 to 6.30) the R_F values of Cu^{2+} and Zn^{2+} become almost constant. There is no effect of pH on the R_F value of Cd^{2+}. The optimum pH for the separation of Cd^{2+} from Zn^{2+} and of Cd^{2+} from Cu^{2+} is 3.3 ± 0.5 where the spots are comparatively compact.

At pH < 2 the spot of Pb^{2+} splits into two subspots: the lower one is compact and the upper one is in the form of a fine streak. These two spots are clearly separated from each other. This behavior may be due to the formation of two chlorocomplexes of Pb^{2+}, with one being more strongly adsorbed than the other.

Cu^{2+} and Zn^{2+} have high R_F values at low pH. This is because at low pH a large number of H^+ ions compete with Cu^{2+} and Zn^{2+} ions for the exchange sites and the equilibrium is shifted to the left (Eq. 1). The results are given in Figs. 3a, b, and c. In the case of Cd^{2+}, the R_F is already very high, so it cannot increase further.

Effect of Ionic Strengths

There is no effect of ionic strength on the R_F value of Cd^{2+}. The Cd^{2+} spot remains very compact as the ionic strength increases from 1 to 6. The R_F of Zn^{2+} and Cd^{2+} decreases slightly as the ionic strength increases from 2 to 3 and then remains constant, but the R_F of Pb^{2+} increases with the ionic strength and then becomes constant. The separation of Cd^{2+} from Zn^{2+}, Cu^{2+}, and Pb^{2+} is possible even at higher ionic strengths, but the plates are deformed on drying. The results are given in Figs. 4a, b, and c.



At Constant [Cl^-] 1.0M NaCl and Ionic strength (1.001)

At Constant [Cl^-] 1.0M NaCl and Ionic strength (1.001)

At Constant [Cl^-] 0.1 M NaCl and Ionic strength (0.101)

FIG. 3. See Fig. 1 for key to symbols.

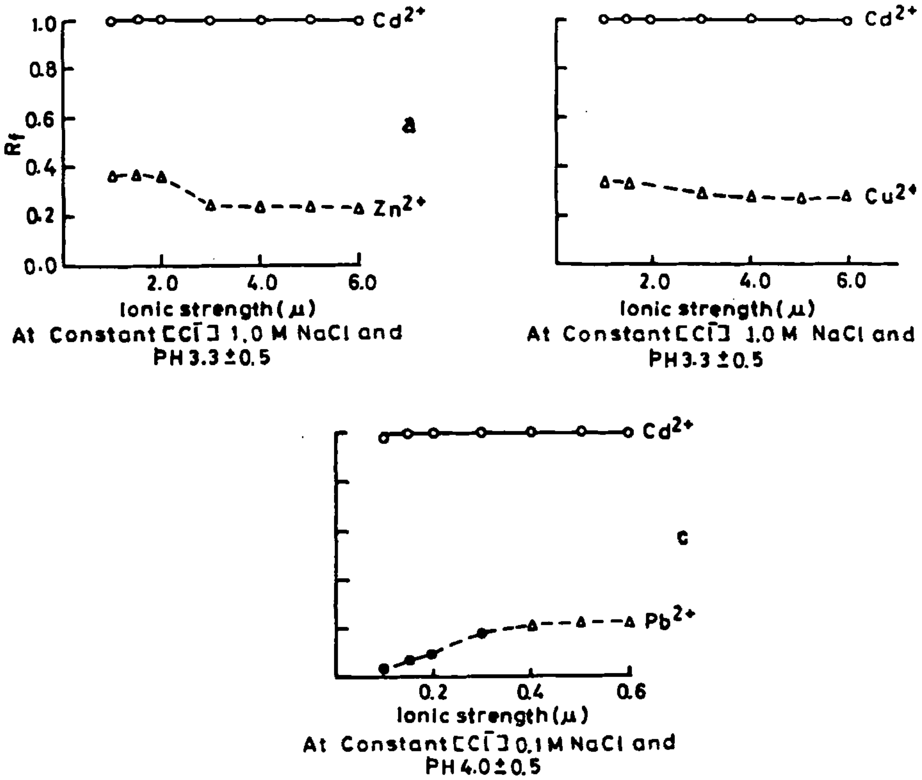


FIG. 4. See Fig. 1 for key to symbols.

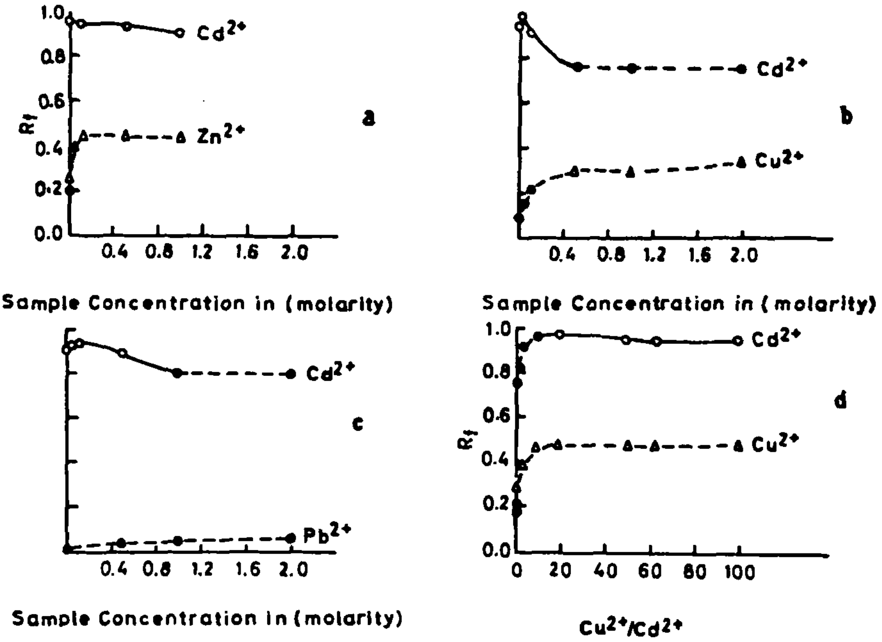


FIG. 5. See Fig. 1 for key to symbols.

TABLE 2

The Quantitative Separation of Cd^{2+} from Zn^{2+}, Cu^{2+}, and Pb^{2+} by Thin-Layer Chromatography

Amount of Cd^{2+} loaded (μg)	Amount of interferring metal ions loaded (μg)	Amount of Cd^{2+} found (μg)	Percent error
	Zn^{2+}		
337.00	0.98	330.00	−2.07
1.70	2.70	1.85	+8.82
2.70	2.70	2.65	−1.85
	Cu^{2+}		
674.00	1.00	670.00	−0.59
2.70	20.00	2.80	+3.70
4.40	4.40	4.20	−4.54
	Pb^{2+}		
674.00	3.11	670.00	−0.59
2.70	1244.00	2.65	−1.85
4.40	4.40	4.30	−2.27

Loading Effect

The R_F value of Zn^{2+} increases abruptly as the concentration of the applied solution becomes greater than 0.01 *M*, and it becomes constant after 0.05 *M*. Thus one cannot separate Zn^{2+} at a higher concentration (>2 μg) from Cd^{2+}. The applied solution increases and separation is possible only up to 0.15 *M* of Cu^{2+}. As the sample concentrations are increased there is very little effect on the R_F values of Pb^{2+} and Cd^{2+}. The separation of these metals is possible up to a 2.0 *M* concentration of each metal ion.

Thus 2.70 to 337.00 μg of Cd^{2+} can be separated from 0.98 to 2.70 μg of Zn^{2+}. 2.70 to 674.00 μg of Cd^{2+} can be separated from 1.00 to 20.00 μg of Cu^{2+} and 3.11 to 1244.00 μg of Pb^{2+}. The results are given in Figs. 5a, b, c, and d and Table 2.

The Separation of Cu^{2+} from Ni^{2+} and Co^{2+}

In order to find the optimum conditions for the separation of these metal ons, a systematic study was made of the various important factors. The behavior of Cd^{2+} and Cu^{2+} has been discussed earlier.

Effect of Cl^- Concentration

The R_F values of Ni^{2+} and Co^{2+} are almost independent of the Cl^- concentration. In the saturated solution of sodium chloride the Cu^{2+} spot goes along that of Ni^{2+} and separation is not possible. The separation of Cu^{2+} from Co^{2+} is possible even in saturated solutions of sodium chloride, but the deformation of plates takes place. The results are given in Figs. 6a and b.

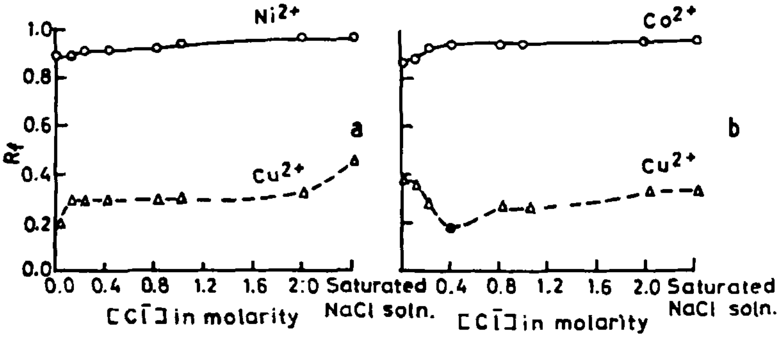


FIG. 6. See Fig. 1 for key to symbols.

TABLE 3

Electronegativity, Hydrated Ionic Radii in Aqueous Solution at 25 °C (a^0 in A^0) of Metal Ions, and Favorable pH Values at Which Certain Ions Begin to Precipitate as Hydrous Oxides

Metal ions	Electronegativity (*8*)	Hydrated (*9*) ionic radii	pH (*10*)
Ag^+	1.42	1.25	9
Cd^{2+}	1.46	2.50	8
Ni^{2+}	1.75	3.00	8
Co^{2+}	1.70	3.00	8
Zn^{2+}	1.66	3.00	6
Cu^{2+}	1.75	3.00	6
Fe^{2+}	1.64	3.00	–
Hg^{2+}	1.44	2.50	–
Pb^{2+}	1.55	2.25	–
Bi^{3+}	1.67	–	–

It is difficult to explain why Cu^{2+} has a lower R_F than do Ni^{2+} and Co^{2+}. Cu^{2+}, Ni^{2+}, and Co^{2+} have almost the same electronegativity. Their hydrated radii are also the same, as shown in Table 3.

According to Kraus and Moore (*7*), Cu^{2+}, Ni^{2+}, and Co^{2+} in 2 *M* HCl do not form any chlorocomplex and hence their R_F should be low. But Ni^{2+} and Co^{2+} have high R_F values while Cu^{2+} has a low R_F value.

It appears that NaCl behaves differently than HCl. It is possible that when the pH of the solution is 6, copper is hydrolyzed and precipitated as $Cu(OH)_2$. However, Ni^{2+} and Co^{2+} are precipitated at pH 8 and hence they are still in the form of ions. Since the NaCl concentration is high, the Na^+ ions compete with the Ni^{2+} and Co^{2+} ions and hence these ions have high R_F values.

Effect of the Addition of Acetone

The R_F values of Cu^{2+}, Ni^{2+}, and Co^{2+} decrease as the acetone concentration increases. In 100% acetone (i.e., Cl^- absent) the R_F values of these metal ions are zero. The optimum solvents for the separation of Cu^{2+} from Ni^{2+} and Co^{2+} are 0.20 *M* NaCl in 50% acetone and 0.50 *M* NaCl in 50% acetone, respectively. The results are given in Figs. 7a and b.

Effect of pH

The spot of Cu^{2+} is in the form of a streak at pH 1.45 to 2.00. The R_F value of Cu^{2+} decreases as the pH increases, but the R_F values of Ni^{2+} and Co^{2+} are not affected throughout this pH range. The optimum pH

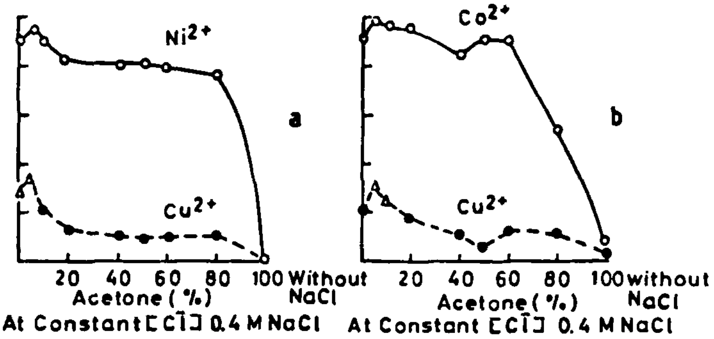


FIG. 7. See Fig. 1 for key to symbols.

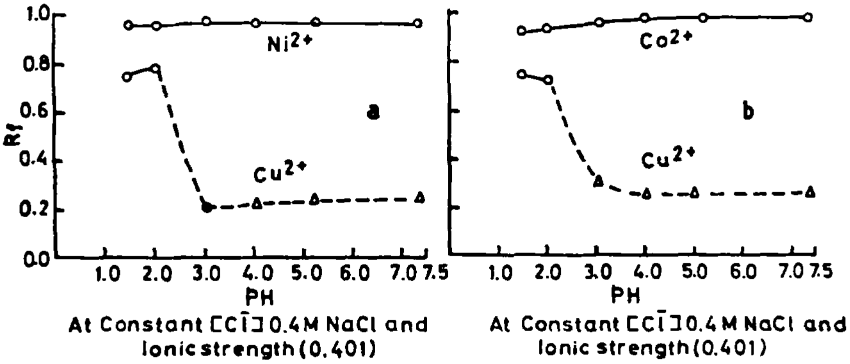


FIG. 8. See Fig. 1 for key to symbols.

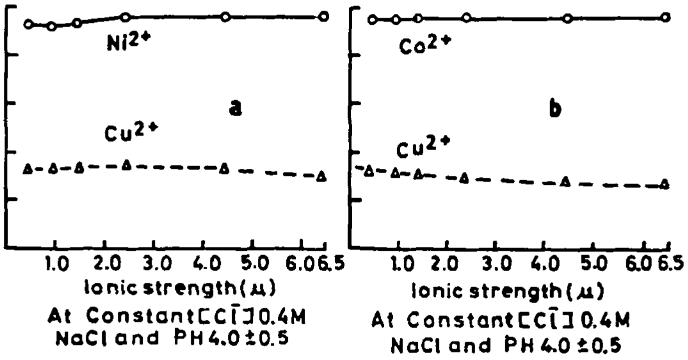


FIG. 9. See Fig. 1 for key to symbols.

for the separation of Cu^{2+} from Ni^{2+} and Co^{2+} is 4.0 ± 0.5. The results are shown in Figs. 8a and b. The R_F values of Ni^{2+} and Co^{2+} cannot be increased further at low pH because they are already high.

Effect of Ionic Strength

There was little effect on the R_F values of Cu^{2+}, Ni^{2+}, and Co^{2+}. Separation is possible even at higher ionic strength (i.e., 6.40) but the plates are deformed on drying. The results are shown in Figs. 9a and b.

Loading Effect

The R_F value of Cu^{2+} increases and those of Ni^{2+} and Co^{2+} decrease as the concentration of metal ions increases. At higher concentrations of metal ions, the spot of Cu^{2+} moves with the spots of Ni^{2+} and Co^{2+}. Thus 5.00 to 20.00 μg of Cu^{2+} can be separated from 1.00 to 360.00 μg of Ni^{2+}, and 5 to 19.06 μg of Cu^{2+} can be separated from 1.00 to 180.00 μg of Co^{2+}. The results are given in Figs. 10a, b, c and Table 4.

TABLE 4

The Quantitative Separation of Cu^{2+} from Ni^{2+}, Co^{2+}, and Cd^{2+}

Amount of Cu^{2+} loaded (μg)	Amount of interfering metal ions (μg)	Amount of Cu^{2+} found (μg)	Percent error
	Ni^{2+}		
20.00	1.00	20.50	+2.50
10.00	10.00	10.00	0.00
5.00	180.00	5.00	0.00
5.00	360.00	5.00	0.00
	Co^{2+}		
19.06	1.00	20.00	+4.93
10.00	10.00	10.00	0.00
5.00	18.00	5.00	0.00
5.00	180.00	5.20	+4.00
	Cd^{2+}		
20.00	2.00	19.00	−5.00
10.00	10.00	10.00	0.00
5.00	168.00	5.00	0.00
5.00	674.00	4.85	−3.00

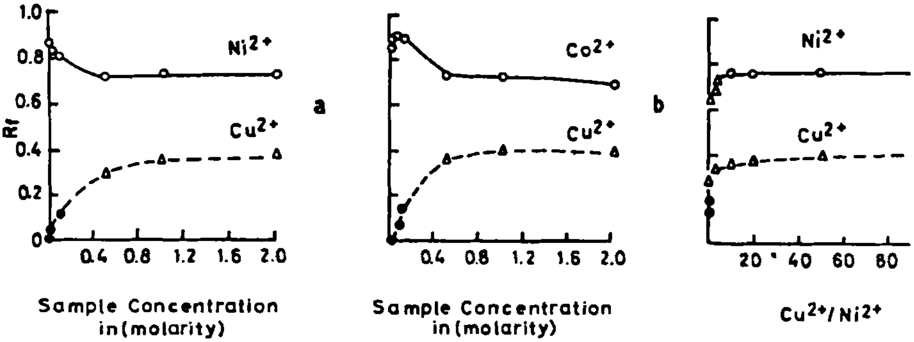


Fig. 10. See Fig. 1 for key to symbols.

Acknowledgments

The authors thank Dr. W. Rahman for research facilities and the University Grants Commission (India) for financial assistance to J.S.T.

REFERENCES

1. U. A. Th. Brinkman, G. De Vries, and R. Kauroda, *J. Chromatogr.*, *85*, 187–526. (1973)
2. H. Mueller and R. Rother, *Anal. Chim. Acta*, *66*(1), 49–55 (1973).
3. R. Olsina, R. Dapas, and C. Marone, *J. Chromatogr.*, *75*(1), 93–99 (1973).
4. Z. Soljic, S. Turina, and V. Marjanovic, *Fresenius Z. Anal. Chem.*, *31*, 258 (1972).
5. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959, p. 354.
6. Ref. *5*, p. 469.
7. I. M. Kolthoff and J. P. Elving, *Treatise on Analytical Chemistry*, Part I, Vol. 3, Interscience, New York, 1961, p. 1546.
8. M. C. Day, Jr. and J. Selbin, *Theoretical Inorganic Chemistry*, Reinhold, New York; Chapman and Hall, London, 1967, p. 114.
9. *Lange's Handbook of Chemistry*, 11th ed., McGraw-Hill, New York 1973, p. 55.
10. H. H. Willard, N. H. Furman, and K. E. Bacon, *A Short Course in Quantitative Analysis*, Van Nostrand, New York, 1968, p. 148.

Received by editor January 31, 1976