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# Separation Studies of Transition Metal Ions with Cationic Micellar Eluents in Normal Phase Thin-Layer Chromatography

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## SUMMARY

The analytical potential of surfactant-mediated mobile phase in thin layer chromatographic separation and identification of metal cations has been investigated. Effects of (a) concentration of surfactant in the mobile phase, (b) acidity or basicity of surfactant-containing developer medium, and (c) the presence of electrolyte and non electrolyte additives in the mobile phase systems on the mobility of metal cations were examined. Better chromatographic performance of hybrid-mobile phase systems comprising of micelle (3% CTAB) –water–alcohol (methanol, ethanol, propanol or butanol) over aqueous micellar mobile phase systems was observed. The thin layer chromatographic (TLC) system comprising silica gel G as stationary phase and 3% aqueous cetyltrimethylammonium bromide (CTAB) + propanol (80+20) as mobile phase was identified as the most favourable for the separation of mixtures of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ . Semiquantitative determination of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  by visual comparison of colour intensities on the TLC plates as well as by measurement of spot area was attempted. Identification of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  from river water, industrial wastewater and sulphide sludge with preliminary separation has been achieved. The method has been successfully applied for identification of Hg, Zn and Cd in synthetic ores such as cinnabar ( $HgS$ ), zinc blende ( $ZnS$ ) and greenockite ( $CdS$ ). The dilution and detection limits of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  on silica gel layers have also been evaluated.

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## INTRODUCTION

Over the years, thin layer chromatography (TLC) has become a preferred analytical technique for the separation of closely related inorganic species using aqueous (acidic, neutral and alkaline solvents) and mixed organic or aqueous–organic solvent systems as chromatographic eluents. It has been successfully utilized in the analysis of wastewater for total heavy metal contents [1], characterization of hazardous wastes [2], estimation of toxic metals in industrial sewage [3] and the recovery of thiocyanate from photogenic wastewater [4]. Incorporation of aqueous micellar solutions pioneered by Armstrong and Terrill [5] as mobile phase systems has further accentuated the importance of TLC where simultaneous separation of ionic or non-ionic species in a variety of matrices is required. Micellar liquid chromatography (MLC) where the concentration of a surfactant in mobile phase is kept above the critical micelle concentration (CMC) of the surfactant has gained immense

popularity and wider applicability due to operational simplicity, cost effectiveness, relatively non-toxicity and enhanced separation efficiency [6–10].

We recently reported [11–14] the chromatographic separation of inorganic species on silica gel and alumina layer, with surfactant-mediated mobile phase systems. It was found that better separation possibilities for cationic and anionic species were on silica gel and alumina layers, respectively. As regards to the nature of surfactant in the mobile phase, uncommon separation selectivity for cations was realized with cationic surfactant eluents. Conversely, eluents containing anionic surfactant were found most suitable for selective separation of anionic species. In continuation of our earlier studies, we have used cetyl trimethylammonium bromide (CTAB), a cationic surfactant as eluent to achieve rapid separation of coexisting  $Hg^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  ions from aqueous solutions on silica layer. Simultaneous separation of  $Hg^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  bears envi-

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ronmental, biological and metallurgical importance because zinc is frequently associated with cadmium and one metal contain small quantities of the others with deleterious effects on performance. It is therefore not surprising that several analytical techniques including ion-exchange chromatography [15], reversed-phase paper chromatography [16], solvent extraction [17] and TLC [11,18] have been used for the separation of  $\text{Cd}^{2+}$  from  $\text{Zn}^{2+}$ . However, none of these studies involve the use of surfactant-mediated mobile

phase systems. The present work was therefore undertaken to utilize the chromatographic performance of cationic surfactant in the separation of heavy metal cations.

## EXPERIMENTAL

**Chemicals and Reagents:** Silica gel 'G', sodium dodecyl sulfate (SDS), dimethylglyoxime, methanol, ethanol, propanol and butanol were of Qualigens, India; alumina, cetyltrimethylammonium

### Mobile Phase

**Table 1.** List of solvent systems used as mobile phase

No.	Symbol	Composition
(a)	M 1	Water
(b)	<b>Aqueous surfactant solutions</b>	
	M 2	1% aqueous CTAB
	M 3 <sup>a</sup>	3% aqueous CTAB
	M 4	5% aqueous CTAB
	M 5	7% aqueous CTAB
	M 6	1% aqueous SDS
	M 7	3% aqueous SDS
	M 8	5% aqueous SDS
	M 9	7% aqueous SDS
(c)	<b>Buffered micellar solutions</b>	
	M 10	3% CTAB in buffer solution of pH 2.3
	M 11	3% CTAB in buffer solution of pH 4.0
	M 12	3% CTAB in buffer solution of pH 5.7
	M 13	3% CTAB in buffer solution of pH 9.0
	M 14	3% CTAB in buffer solution of pH 11.9
(d)	<b>Aqueous micellar solutions with added NaCl</b>	
	M 15	3% aqueous CTAB containing 1 g NaCl per 100 mL
	M 16	3% aqueous CTAB containing 5 g NaCl per 100 mL
	M 17	3% aqueous CTAB containing 10 g NaCl per 100 mL
	M 18	3% aqueous CTAB containing 15 g NaCl per 100 mL
(e)	<b>Aqueous micellar solution with added urea</b>	
	M 19	3% aqueous CTAB containing 1 g urea per 100 mL
	M 20	3% aqueous CTAB containing 5 g urea per 100 mL
	M 21	3% aqueous CTAB containing 10 g urea per 100 mL
	M 22	3% aqueous CTAB containing 15 g urea per 100 mL
(f)	<b>Aqueous micellar solution with added alcohol</b>	
	M 23	3% aqueous CTAB + methanol (20+80)*
	M 24	3% aqueous CTAB + methanol (50+50)
	M 25	3% aqueous CTAB + methanol (80+20)
	M 26	3% aqueous CTAB + ethanol (20+80)
	M 27	3% aqueous CTAB + ethanol (50+50)
	M 28	3% aqueous CTAB + ethanol (80+20)
	M 29 <sup>b</sup>	3% aqueous CTAB + propanol (20+80)
	M 30	3% aqueous CTAB + propanol (50+50)
	M 31 <sup>c</sup>	3% aqueous CTAB + propanol (80+20)
	M 32	3% aqueous CTAB + butanol (90+10)
	M 33	3% aqueous CTAB + butanol (95+5)

\*Mobile phase proportions for multi-solvent systems are in parts by volume

a) CMC = 0.46%, b) CMC = 0.34%, c) CMC = 0.36%

bromide (CTAB), potassium ferrocyanide, dithizone and 1,10-phenanthroline were of CDH, India. All other chemicals were also of Analytical Reagent grade.

**Metal Ions Studied:**  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Hg}^{2+}$ .

**Test Solutions:** Chromatography was performed using standard aqueous solutions (1%) of the chloride, nitrate or sulphate salts of the above mentioned metal ions.

**Detection:**  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  with 1% aqueous potassium ferrocyanide;  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  with 1% solution of alcoholic dimethylglyoxime;  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Hg}^{2+}$  with 0.5% dithizone in  $\text{CCl}_4$  were detected.

**Stationary Phase:** Silica gel 'G'

## CHROMATOGRAPHY

(a) **Preparation of TLC Plates:** The TLC plates were prepared by mixing silica gel with demineralized water in 1:3 ratio by weight with constant shaking to obtain a homogeneous slurry. The resultant slurry was applied on the glass plates with the help of an applicator to give a 0.25 mm-thick layer. The plates were first dried at room temperature and then activated at  $100 \pm 5$  by heating in an electrically controlled oven for 1 h. The activated plates were stored in a close chamber at room temperature until used.

(b) **Preparation of Spiked, Industrial Wastewater and River Water:** A 20 mL of industrial wastewater (pH, 2.97) collected from lock industries, Aligarh, India or river water (pH, 7.48) obtained from Ganga river at Naraura, India or sea water (pH, 8.47) obtained from Anjana beach, Goa, India was spiked with 100  $\mu\text{g}$  each of Zn, Cd and Hg salts. About 20 mL of 0.5% thioacetamide solution was added into spiked sample. The resultant precipitate of Zn, Cd and Hg sulfides was washed with distilled water, centrifuged and dissolved in minimum possible volume of concentrated HCl. The acid was completely dissolved in 5 mL of distilled water. An aliquot (10  $\mu\text{L}$ ) of each sample was applied on TLC plate and chromatography was performed as done for the standard samples.

(c) **Preparation of Synthetic Ores:** Cinnabar ( $\text{HgS}$ ), zinc blende ( $\text{ZnS}$ ) and greenockite ( $\text{CdS}$ ) were synthetically prepared by spiking 50 mL of distilled water (pH 5.6) with Zn, Cd and Hg salt solutions following the same procedure as described above in (b).

**Procedure:** Test solutions (10  $\mu\text{L}$ ) were spotted on thin layer plates with the help of a micropipette about 2.0 cm above the lower edge of the TLC plates. The spots were dried in air and then plates were developed with chosen mobile phase by one dimensional ascending technique in 24 x 6 cm glass jars. The development distance was fixed to 10 cm in all cases. After development, the plates

were dried again and the spots of cations were visualized as coloured spots using the appropriate spraying reagent.  $R_L$  ( $R_F$  of the leading edge) and  $R_T$  ( $R_F$  of trailing edge) values for the detected spots were determined.  $R_F$  values for metal ions were calculated by use of the formula  $R_F = (R_L + R_T) / 2$ .

**Separation:** For the separation, equal amounts of metal ions to be separated were mixed and 10  $\mu\text{L}$  of the resultant mixture was spotted on the activated TLC plate which was then dried in air. The plates were developed to a distance of 10 cm, the spots were detected and the separated metal cations were identified on the basis of  $R_F$  values.

**Limits of Detection:** The limits of detection of metal cations were determined by spotting different amounts of metal ion on the TLC plates, developing the plates and detecting the spot. The method was repeated with successive lowering of the amount of metal ion until no spot was detected. The minimum amount detectable on the TLC plates was taken as the limit of detection.

**Recovery of Cadmium by Spot-Area Method:** To determine recovery of cadmium by spot-area measurement method, 0.01 mL from a series of standard solutions of  $\text{Cd}^{2+}$  (0.5–2.5%) were spotted on silica layers. The plates were developed with M 31. After detection, the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated. The recovery of cadmium was studied by analyzing various samples spiked with  $\text{Cd}^{2+}$ . For this purpose, experiments were performed by spotting 0.01 mL of sample solution containing 100  $\mu\text{g}$  cadmium. The recovery of  $\text{Cd}^{2+}$  was  $82 \pm 2\%$ .

## RESULTS AND DISCUSSION

The results of this study have been summarized in Tables 2–6 and Figures 1–2. The mobility of ten metal cations was examined on silica gel layer using aqueous solutions of SDS and CTAB. In order to optimize the experimental conditions, effect of various factors, such as (a) concentration of the surfactants, (b) acidity and basicity of the medium, (c) the presence of urea and NaCl in the surfactant-containing mobile phase and (d) nature of the added alkanols in the micellar mobile phase on the mobility of cations was examined.

### (a) Effect of Concentration of Surfactants:

To understand the effect of concentration of cationic (CTAB) or anionic (SDS) surfactant on the mobility of metal cations, chromatography was performed on silica layers using different concentrations of surfactant – mediated mobile phase systems (M 2–M 9) as developers. The  $R_F$  values of metal cations obtained in pure water (*i.e.*, zero surfactant concentration, M 1) and in aqueous solutions of CTAB and SDS at different concentration levels (M 2–M 9) are listed in Table 2. From the data listed in Table 2, following conclusions may be drawn:

**Table 2.**  $R_F$  value of metal cations obtained on silica layers developed with pure water (M 1) and aqueous solutions of CTAB (M 2–M 5) and SDS (M 6–M 9) at different concentration levels.

Metal Ions	$R_F$ value								
	Water	CTAB				SDS			
	M 1	M 2	M 3	M 4	M 5	M 6	M 7	M 8	M 9
Fe <sup>3+</sup>	0.10	0.05	0.06	0.07	0.10	0.06	0.05	0.02	0.05
Cu <sup>2+</sup>	0.10	0.07	0.27	0.32	0.37	0.05	0.07	0.07	0.10
Ni <sup>2+</sup>	0.90	0.85 T	0.85 T	0.85 T	0.85 T	0.87	0.90	0.87 T	0.85 T
Co <sup>2+</sup>	0.85	0.72	0.72	0.77	0.80	0.87	0.90	0.90	0.85 T
Cd <sup>2+</sup>	0.40	0.45 T	0.63 T	0.80 T	0.85 T	0.45 T	0.80 T	0.82 T	0.82 T
Zn <sup>2+</sup>	0.05	0.06	0.15	0.20 T	0.20	0.07	0.10	0.10	0.10
Ag <sup>+</sup>	0.30 T	0.00	0.11	0.15 T	0.17 T	0.07	0.10	0.07	0.02
Pb <sup>2+</sup>	0.02	0.02	0.07	0.10	0.15 T	0.02	0.05	0.00	0.02
Bi <sup>3+</sup>	0.04	0.07	0.12	0.15 T	0.16 T	0.15 T	0.15 T	0.15 T	0.10
Hg <sup>2+</sup>	0.02	0.95	0.95	0.95	0.95	0.33 T	0.65 T	0.65 T	0.64 T

T = Tailed Spot ( $R_L - R_T > 0.30$ )

- (1) In pure water, all metal ions except Ni<sup>2+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> show little mobility and Ag<sup>+</sup> was found to produce tailed spot. The higher mobility of Ni<sup>2+</sup> ( $R_F = 0.90$ ) and Co<sup>2+</sup> ( $R_F = 0.85$ ) facilitates their separations from all other metal ions studied whereas the mid  $R_F$  ( $R_F = 0.40$ ) of Cd<sup>2+</sup> opens opportunities for its selective separation from multicomponent mixture of metal cations.
- (2) When aqueous surfactant (SDS or CTAB) solutions at different concentration levels (1, 3, 5 and 7%) were used as mobile phase, metal ions such as Fe<sup>3+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup>, Zn<sup>2+</sup> and Ag<sup>+</sup> stayed very close to the point of application. Conversely, Ni<sup>2+</sup> and Co<sup>2+</sup> show higher mobility ( $R_F \approx 0.85$ ).
- (3) Metal ions such as Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ag<sup>+</sup> and Bi<sup>3+</sup> show occasional tailing ( $R_L - R_T > 0.3$ ) and their spots appear as elliptical extension in the direction of solvent flow.
- (4) Cu<sup>2+</sup> shows higher mobility in CTAB (M 3–M 5) compared to its mobility in SDS (M 6–M 9).
- (5) Cd<sup>2+</sup> produces badly tailed spots at all concentration levels of surfactant irrespective of the nature of the surfactant (cationic or anionic).
- (6) Hg<sup>2+</sup> shows higher mobility in the presence of cationic surfactant, but in case of SDS it produces tailed spot.
- (7) 3% aqueous CTAB solution (M 3) was judged to be favourable for further studies as more compact spots for cations were realized with this mobile phase system.

#### (b) Effect of Acidity and Basicity of the Medium:

Thin layer chromatography of metal ions was performed using

**Table 3.** Mobility of metal cation developed with buffered surfactant solutions of different pH values.

Metal ions	$R_F$ value				
	M 10	M 11	M 12	M 13	M 14
Fe <sup>3+</sup>	0.07	0.10	0.11	0.07	0.10
Cu <sup>2+</sup>	0.32	0.22	0.05	0.15	0.02
Ni <sup>2+</sup>	0.88	0.85 T	0.85 T	0.86	0.82
Co <sup>2+</sup>	0.81	0.85	0.85 T	0.86	0.75
Cd <sup>2+</sup>	0.32, 0.69	0.85 T	0.79	0.82	0.89
Zn <sup>2+</sup>	0.12	0.04	0.07	0.16	0.11
Ag <sup>+</sup>	0.08	0.05	0.05	0.07	0.10
Pb <sup>2+</sup>	0.05	0.05	0.05	0.05	0.09
Bi <sup>3+</sup>	0.32 T	0.40 T	0.30 T	0.20 T	0.35 T
Hg <sup>2+</sup>	0.88	0.95	0.96	0.95	0.96

3% CTAB solution prepared in borate–phosphate buffers of different pH values (pH = 2.3, 4.0, 5.7, 9.0 and 11.9). The results obtained with the buffered surfactant solutions have been summarized in Table 3. The following conclusions may be drawn from these results:

- (1) Change in pH of mobile phase system had little effect on the mobilities of Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Zn<sup>2+</sup>, Bi<sup>3+</sup> and Pb<sup>2+</sup>. Except Bi<sup>3+</sup> and Hg<sup>2+</sup>, all these metal ions remained near the point of application ( $R_F = 0.10$ ) irrespective of the fact whether mobile phase medium used was of acidic or basic in nature. Bi<sup>3+</sup> produced tailed spots at all pH values and Hg<sup>2+</sup> showed higher mobility ( $R_F = 0.88$ – $0.96$ ).
- (2) With strongly acidic mobile phase (M 10–M 11) Cu<sup>2+</sup> showed relatively higher mobility ( $R_F$ , 0.32 at pH 2.3 and 0.22 at pH 4.0) while it remained near the point of application with weakly acidic (M 12) or alkaline (M 13–M 14) mobile phase systems.
- (3) Cd<sup>2+</sup> exhibited a peculiar behaviour as it gave double spots ( $R_F = 0.32, 0.69$ ) with mobile phase M 10 (pH = 2.3), tailed spot ( $R_F = 0.85$ ) with M 11 (pH = 4.0) and exceptionally well formed compact spots with relatively higher  $R_F$  value with M 12 ( $R_F = 0.79$ ), M 13 ( $R_F = 0.82$ ) and M 14 ( $R_F = 0.89$ ).
- (4) Compact spots of Ni<sup>2+</sup> and Co<sup>2+</sup> were visualized in highly acidic (M 10) or basic medium (M 13–M 14). However, when the nature of the mobile phase was less acidic (pH = 4.0 or 5.7) both these metal ions gave elongated spots ( $R_F = 0.85$ ).

#### (c) Effect of Non-electrolyte and Electrolyte Additives:

The effect of addition of urea (organic non electrolyte) and NaCl (inorganic electrolyte) at different concentration levels in the eluent M 3 (3% aqueous CTAB) on the mobility of metal ions was examined. The results obtained with NaCl added mobile phases (M 15 – M 18) and urea added mobile phase systems (M 19–M 22) are

**Table 4.** Mobility of metal cations on 3% aqueous CTAB containing different concentrations of electrolyte and non-electrolyte additives

Metal Ions	R <sub>F</sub>							
	NaCl added mobile phase				Urea added mobile phase			
	M 15	M 16	M 17	M 18	M 19	M 20	M 21	M 22
Fe <sup>3+</sup>	0.05	0.06	0.06	0.06	0.05	0.07	0.05	0.05
Cu <sup>2+</sup>	0.22	0.27	0.20 T	0.20 T	0.22	0.22	0.22	0.27
Ni <sup>2+</sup>	0.92	0.92	0.90	0.92	0.85 T	0.84 T	0.85 T	0.85 T
Co <sup>2+</sup>	0.92	0.92	0.90	0.95	0.70	0.77	0.80	0.82
Cd <sup>2+</sup>	0.90	0.92	0.92	0.94	0.55 T	0.57 T	0.60 T	0.65 T
Zn <sup>2+</sup>	0.10	0.07	0.20 T	0.20 T	0.07	0.12	0.10	0.12
Ag <sup>+</sup>	0.00	0.06	0.25 T	0.37	0.10	0.10	0.06	0.11
Pb <sup>2+</sup>	0.07	0.22 T	0.87	0.65 T	0.05	0.04	0.02	0.02
Bi <sup>3+</sup>	0.06	0.09	0.12	0.15 T	0.06	0.05	0.10	0.12
Hg <sup>2+</sup>	0.92	0.92	0.90	0.90	0.92	0.92	0.95	0.90

T = Tailed Spot ( $R_L - R_T > 0.30$ )

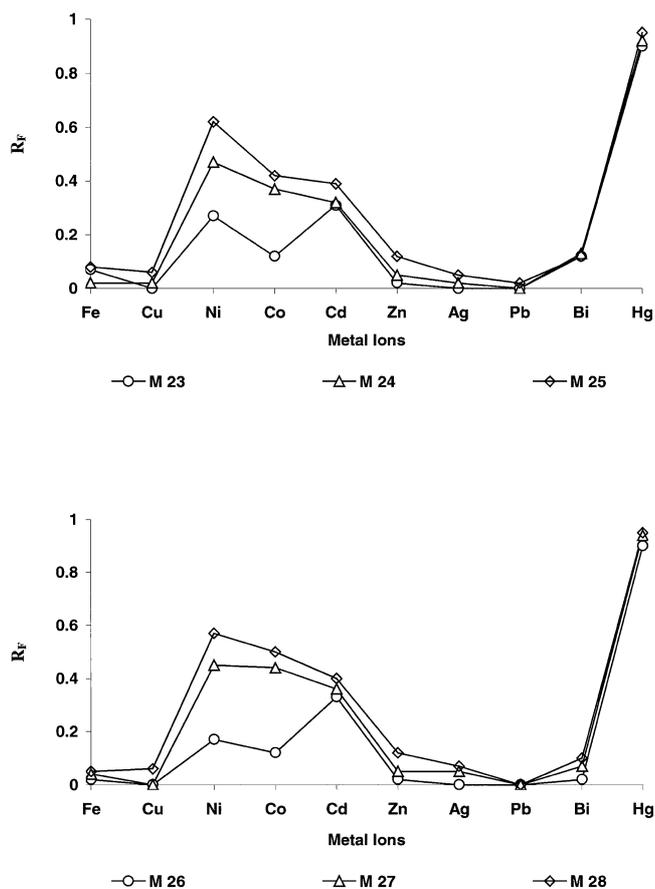
summarized in Table 4. From the available data, following trends are noticeable:

- (1) The mobility of Fe<sup>3+</sup> remained almost unaffected at all concentration levels of urea and NaCl. The mobility of Ag<sup>+</sup> was found to increase with the increase in NaCl concentration. However, their mobilities in the presence of urea remained almost unchanged.
- (2) Co<sup>2+</sup> exhibited slight increase in mobility with the increase of urea concentration in the mobile phase. However, the presence of NaCl caused no effect on the mobility of this metal ion (R<sub>F</sub> (0.95)).
- (3) Ni<sup>2+</sup> and Cd<sup>2+</sup> produced tailed spots at all concentration levels of urea in contrast to the formation of highly compact spots with NaCl added mobile phases regardless of the NaCl concentration.

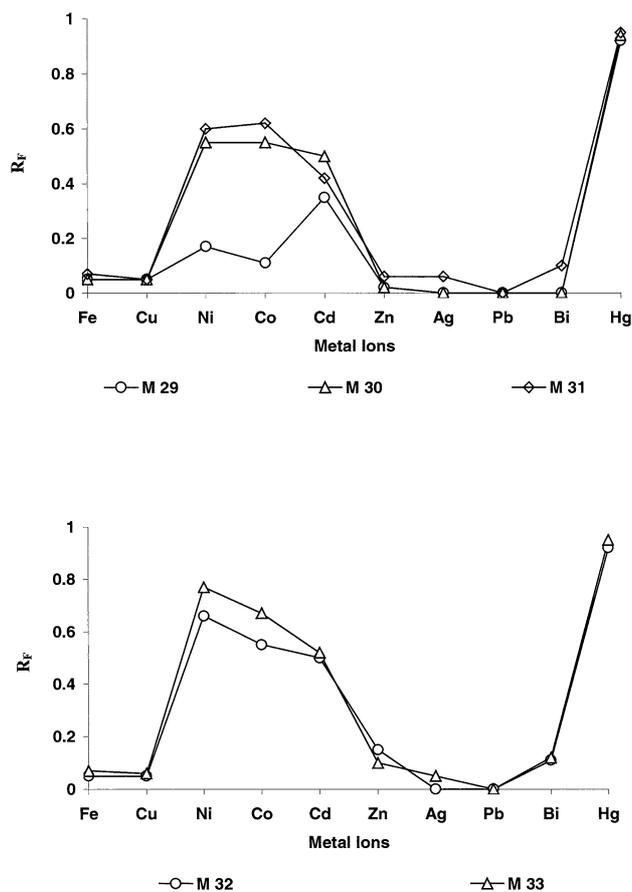
#### (d) Effect of Alkanols:

To investigate the retention of metal cations on silica layer, hybrid-mobile phase systems comprising of micelle (3% CTAB) – water–alcohol (methanol, ethanol, propanol or butanol) were also used and better chromatographic performance in terms of promotion of differential migration of metal ions by these mobile phases over aqueous micellar mobile phase systems was observed. The values of CMC determined for M 3 (3% aqueous CTAB), M 29 (3% aqueous CTAB + 80% propanol) and M 31 (3% aqueous CTAB + 20% propanol) were 0.46%, 0.34% and 0.36% respectively. It shows that propanol decreases the CMC value of CTAB from 0.46% to 0.34%. Hence, CTAB is present in the form of micelles. The R<sub>F</sub> values of metal cations were determined with micelle–water–alcohol mobile phases (M 23–M 33) consisting of methanol (20, 50 or 80%), ethanol (20, 50 or 80%), propanol (20,

50 or 80%) or butanol (5 or 10%) and 3% aqueous CTAB. In all cases, a general trend of decreasing R<sub>F</sub> value with the increase in alcohol concentration was noticed. The representative's plots are given in Figures 1(a) and (b). The retention mechanism is connected with the adsorption of surfactant on the surface of the stationary phase. As long as the surface of the silica gel layer is saturated by the adsorbed surfactant i.e., there are no more free silanol groups on the layer for the interaction, metal ions move faster showing higher R<sub>F</sub> value. The addition of alcohol to the mobile phase leads to the reduction in the adsorbed amount of surfactant on the stationary phase [19], which causes an increase in retention of solutes and a change in selectivity. Thus, in the presence of alcohol the silica layers are not completely saturated by adsorbed surfactant and there are still free silanol groups, the interaction between them and the metal cations affects the retention pattern. In these cases, the nature and the polarity of alcohol play an important role in the separation. In general, the better separation possibilities were realized with mobile phase containing 20% propanol (M 31). Successful separation of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> can be achieved with any of the mobile phase containing alcohols. However, mobile



**Figure 1(a).** Mobility of heavy metal cations on silica gel layers developed with 3% aqueous CTAB containing different amounts of alcohols.



**Figure 1(b).** Mobility of heavy metal cations on silica gel layers developed with 3% aqueous CTAB containing different amounts of alcohols.

phase M 31 is most favourable. We successfully separated coexisting  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  on silica layer using M 31 as mobile phase. The  $R_f$  values of the resolved spots were in the order  $Hg^{2+}$  (0.95),  $Cd^{2+}$  (0.47) and  $Zn^{2+}$  (0.07). Thus, moderately polar alcohol (e.g. propanol) provides superior separation of metal cations compared to more polar alcohol (e.g. methanol).

It has been reported [20] that the microenvironment of micellar system is greatly influenced by the presence of added organic substance and inorganic electrolytes. To examine this aspect, inorganic (NaCl, NaBr,  $NaNO_3$ , HCOONa,  $NaHCO_3$ ,  $NH_4Cl$ ,  $NH_4Br$  and  $NH_4NO_3$ ) and organic (oxalic, citric, tartaric acid, urea, L-arginine, L-valine, L-tryptophan, L-methionine, L-serine and L-glutamic acid) impurities were added in M 31 to obtain mobile phase systems containing 1% of each foreign substance. The resultant mobile phase systems were used to examine the effect of impurities in the eluent on simultaneous separation of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ . The results presented in Table 5 clearly demonstrate that mutual separation of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  could not be achieved with mobile phases containing 1% citric, oxalic or tartaric acid because of the co-migration of  $Zn^{2+}$  and  $Cd^{2+}$  with  $Hg^{2+}$ . Similarly, with

**Table 5.** Separation of coexisting  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  in the presence of inorganic and organic impurities.

Additives (1%)	Separation ( $R_f$ )		
	$Zn^{2+}$	$Cd^{2+}$	$Hg^{2+}$
NaCl	0.07	0.90	0.95
NaBr	0.08	0.80	0.95
$NaNO_3$	0.09	0.60	0.95
HCOONa	0.10	0.71	0.98
$NaHCO_3$	0.02	0.20 T	0.97
$NH_4Cl$	0.08	0.67	0.95
$NH_4Br$	0.07	0.70	0.95
$NH_4NO_3$	0.07	0.70	0.95
Oxalic acid	0.69	0.92	0.95
Citric acid	0.71	0.80	0.95
Tartaric acid	0.72	0.95	0.97
Urea	0.10	0.40	0.95
L-arginine	0.07	0.50	0.95
L-valine	0.11	0.56	0.94
L-tryptophan	0.07	0.62	0.95
L-methionine	0.11	0.57	0.95
L-serine	0.09	0.45	0.94
L-glutamic acid	0.50	0.67	0.92
Without additives	0.07	0.47	0.95

Stationary phase: silica gel

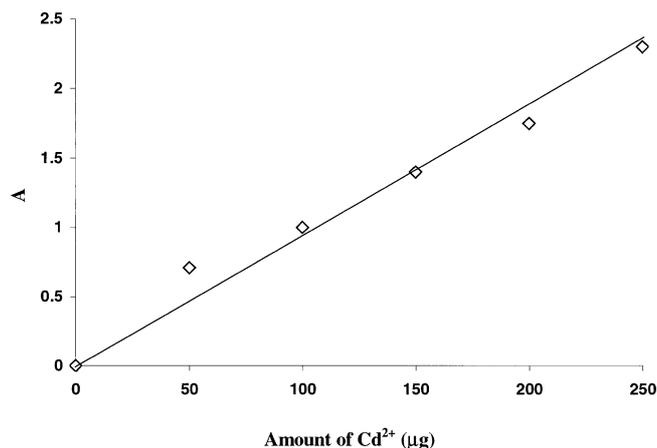
Mobile phase: M 31

other mobile phase systems the separation of  $Cd^{2+}$  from  $Hg^{2+}$  is hampered. Conversely, its separation from  $Zn^{2+}$  is improved because of the enhanced mobility of  $Cd^{2+}$ . This observation suggests that the presence of organic or inorganic impurities in water-micelle-alcohol hybrid mobile phase systems have serious adverse effects on chromatographic performance of micellar mobile phases in regards to the separation of metal cations.

The lowest possible detectable microgram amount along with dilution limit of metal cation (given in parenthesis) on silica gel layer were,  $Zn^{2+}$  (0.017, 1:  $5.8 \times 10^5$ ),  $Cd^{2+}$  (0.50, 1:  $2 \times 10^4$ ) and  $Hg^{2+}$  (0.05, 1:  $2 \times 10^5$ ).

#### Semiquantitative estimation of $Cd^{2+}$

An attempt has been made to determine the recovery of cadmium spiked into water using spot-area measurement method. A linear relationship obtained when the amount of sample spotted was plotted against area of the spot follows the empirical equation  $\zeta = km$ , where  $\zeta$  is the area of the spot,  $m$  is the amount of the solute and  $k$  is a constant. Representative plot for  $Cd^{2+}$  has been shown in Figure 2. The linearity is maintained upto 250  $\mu g$  /spot. At higher concentration a positive deviation from linear law was observed. The accuracy and precision was around  $\pm 12\%$ .



**Figure 2.** Calibration curve for semiquantitative determination of Cd<sup>2+</sup>

Stationary phase: silica gel

Mobile phase: M 31

**Table 6.** Recovery and separation of coexisting Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> ions from spiked water and synthetically prepared metal ores and heavy metal sludge samples

Spiked/Synthetic Samples	R <sub>F</sub>		
	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
River water	0.05	0.46	0.95
Sea Water	0.03	0.46	0.95
Sulfides	0.14	0.56	0.96
Distilled water	0.07	0.47	0.95

Stationally phase: sillca gel

Mobile phase: M 31

#### Application:

The proposed method was applied for identification of zinc, cadmium and mercury in spiked industrial wastewater, river and sea water samples as well as in metal sulphide ores after separation on silica layer. The results listed in Table 6 clearly demonstrate that Hg, Cd and Zn which are spiked in the various samples can be recovered and separated on silica TLC plates developed with M 31.

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#### REFERENCES

- [1] Volynets, M. P. ; Kitaeva, L. P. ; Timerbaev, A. P. *Zh. Anal. Khim.*, **1986**, *41*, 1989–1995.
- [2] Stephenes, R. D. ; Chan, J. J. in J. C. Touchstone and D. Rogers (eds.) *Thin-layer chromatography: Quantitative Environmental and Clinical Applications*, Wiley, New York p. 363 (1980).
- [3] Thielemann, H. *Acta Hydrochem. Hydrobio.*, **1977**, *5*, 191–193.
- [4] Mohammad, A. ; Khan, M. A. *Indian J. Environ. Hlth.*, **1996**, *38*, 100–104.
- [5] Armstrong, D. W. ; Terrill R. Q. *Anal. Chem.*, **1979**, *51*, 2160–2163.
- [6] Borgerding, M. F. ; Williams (Jr.), R. L. ; Hinze, W. L. ; Quina, *J. Liq. Chromatogr.*, **1989**, *12*, 1367–1406.
- [7] Kord, A. S. ; Khaledi, M. G. *Anal. Chem.*, **1992**, *64*, 1901–1907.
- [8] Szymanski, A. ; Szczepaniak, W. *Chem. Anal. (Warsaw)*, **1998**, *43*, 346–349.
- [9] Khaledi, M. G. ; Strasters, J. K. ; Rodgers, A. H. ; Breyer, E. D. *Anal. Chem.*, **1990**, *62*, 130–136.
- [10] Walker, T. A. *J. Liq. Chromatogr.*, **1996**, *19*, 1715–1727.
- [11] Mohammad, A. ; Agrawal, V. *J. Planar Chromatogr. Mod. –TLC*, **2000**, *13*, 210–216.
- [12] Shtykov, S. N. ; Sumina, E. G. ; Tyurina, N. V. C. *J. Planar Chromatogr. –Mod. TLC*, **2000**, *13*, 266–270
- [13] Mohammad, A. ; Syed, S. ; Sharma, L. M. ; Syed, A. A. *Acta Chromatographia*, **2001**, *11*, 183–195.
- [14] Mohammad, A. ; Sirwal, Y. H. *J. Planar Chromatogr. – Mod TLC*, **2001**, *15*, 107–115.
- [15] Dingmi, S. ; Suya, L. ; Taohui, L. *Fenxi Huaxue*, **1984**, *12*, 934; C. A., **1985**, *102*, 7195 V.
- [16] Yeole, C. G. ; Shinde, V. M., *Analyst.*, **1983**, *104*, 1102–1107.
- [17] Yoshiaki, S. *Anal. Chem. Acta*, **1981**, *127*, 209–212.
- [18] Mohammad, A. ; Fatima, N. *Chromatographia*, **1987**, *23*, 653–655.
- [19] Dorsey, J. G. ; De Etchegaray, M. T. ; Landy, J. S. *Anal. Chem.*, **1983**, *55*, 924–928
- [20] Borgerding, M. F. ; Hinze, W. L. *Anal. Chem.*, **1985**, *57*, 2183–2190.