CETYLPYRIDINIUM CHLORIDE
MICELLE-MEDIATED MUTUAL SEPARATION
OF ZINC, CADMIUM, AND MERCURY IONS
BY THIN-LAYER CHROMATOGRAPHY

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SUMMARY

Cationic surfactant-mediated systems containing different concentrations of cetylpyridinium chloride have been used as mobile phases in thin-layer chromatographic separation of metal cations on silica layers. The effect of surfactant concentrations below and above the critical micelle concentration (CMC) on the retention behaviour of metal ions was examined. The best TLC system for rapid mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} was unmodified silica as stationary phase and 5% aqueous cetylpyridinium chloride as mobile phase. The effects of pH (acidity or basicity), inorganic electrolytes (the acetate, formate, chloride, bromide, and carbonate of sodium and the chloride and nitrate of calcium), and organic compounds (urea) in the cetylpyridinium chloride solution on the mobility and separation efficiency of Zn^{2+}, Cd^{2+}, and Hg^{2+} were assessed. The limits of detection for these metal cations were also determined. The method is well suited to identification and separation of Hg^{2+}, Zn^{2+}, and Cd^{2+} from synthetically prepared ores, for example cinnabar (HgS), zinc blende (ZnS), and greenoekite (CdS), and from hydroxide sludge.

INTRODUCTION

Micellar liquid chromatography involving use of surfactant ions above their critical micellar concentration (CMC) as mobile phase to control the retention of a solute has been the focus of numerous studies [1–5] since it was first proposed by Armstrong and coworkers in 1977 [6]. The multiplicity of interactions (hydrophobic, electrostatic, and hydrogen bonding) associated with micellar systems provides unique separation possibilities for structurally similar solutes. Micelles are capable of differential dis-

solution and binding of a variety of solutes, leading to their potential use to achieve several new separations including resolution of optical isomers. Thin-layer chromatography (TLC), an efficient analytical technique, has been used for identification of total heavy metals in industrial wastewaters [7], transition metals in seawater and wastewater [8], polyphosphates in soft drinks [9], and determination of Ag(I) in synthetically prepared horn silver [10]. The usefulness of TLC has been further increased by the use of micellar systems as mobile phases. Micellar mobile phases have been extensively used in reverse-phase liquid chromatographic separations of biologically active organic compounds [11,12]. In contrast, there have been few reports of studies of the use of these systems as mobile phases in chromatographic separations of metal cations [13–15]. Micellar chromatography of inorganic compounds has been reviewed by Okada [16].

This communication reports a reliable micellar TLC method for rapid mutual separation and identification of Zn^{2+}, Cd^{2+}, and Hg^{2+} on silica layers using cationic surfactant aqueous solutions of cetylpyridinium chloride (CPC) as mobile phases. Separation and identification of Zn^{2+}, Cd^{2+}, and Hg^{2+} is very important because:

(a) these metals belong to the same group (IIB) of the periodic table and are fairly toxic;
(b) Hg^{2+} and Cd^{2+} act as effective enzyme inhibitors;
(c) Zn^{2+} in some metalloenzymes can be substituted by Cd^{2+} which leads to cadmium toxicity;
(d) cadmium is usually associated with zinc minerals; and
(e) the mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} is analytically difficult because of their similar physicochemical properties.

In addition to semiquantitative determination of Zn^{2+}, Cd^{2+}, and Hg^{2+}, the method was also used for identification of Zn^{2+}, Cd^{2+}, and Hg^{2+} in synthetic sulphide ores and hydroxide sludge samples. As far as we are aware this is the first report of the use of CPC in mobile phases for TLC analysis of inorganic species.

EXPERIMENTAL

Chemicals and Reagents

Silica gel G and urea were from E. Merck (India); dimethylglyoxime was from Qualigens (India); cetylpyridinium chloride (CPC), potassium ferrocyanide, dithizone, sodium chloride, sodium bromide, calcium nitrate,

calcium chloride, sodium acetate, and sodium formate were from CDH (India). All chemicals were of analytical reagent grade.

The metal cations studied were Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Pb^{2+}, Bi^{3+}, and Hg^{2+}. Chromatography was performed using standard aqueous solutions (1%) of the chloride, nitrate, or sulphate salts of these metal ions. Fe^{3+} and Cu^{2+} were detected with 1% aqueous potassium ferrocyanide, Ni^{2+} and Co^{2+} with a 1% alcoholic solution of dimethylglyoxime, and Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Bi^{3+}, and Hg^{2+} with a 0.5% solution of dithizone in CCl_4.

The buffer solutions used to prepare 5% CPC solutions are listed in Table I. The mobile phases used are listed in Table II.

Table I

Buffer solutions used as solvents to prepare mobile phases containing 5% CPC

No.	Composition	Volume ratio	pH
1	0.04 M Boric acid + 0.04 M phosphoric acid	50:50	2.3
2	0.04 M Boric acid + 0.04 M phosphoric acid + 0.24 M NaOH	50:50:8	3.4
3	Buffer capsules		4.0
4	0.04 M Boric acid + 0.04 M phosphoric acid + 0.24 M NaOH	50:50:10	5.7
5	0.04 M Boric acid + 0.04 M phosphoric acid + 0.24 M NaOH	50:50:14	7.0
6	0.04 M Boric acid + 0.04 M phosphoric acid + 0.24 M NaOH	50:50:20	8.0
7	Buffer capsules		9.2
8	0.04 M Boric acid + 0.04 M phosphoric acid + 0.24 M NaOH	50:50:60	11.9

Table II

The mobile phases used

Symbol	Composition
M_1	0.01–10% Solutions of CPC in distilled water
M_2	5% Solutions of CPC in borate–phosphate buffer of pH 2.3, 3.4, 4.0, 5.7, 7.0, 8.0, 9.2, or 11.9
M_3	5% Solutions of CPC in aqueous solutions (0.2–5%) of NaCl, NaBr, $Ca(NO_3)_2$, $CaCl_2$, $NaHCO_3$, CH_3COONa, HCOONa, or urea

Preparation of Sulphide Ores

Cinnabar (HgS), zinc blende (ZnS), and greenoekite (CdS) were prepared synthetically by spiking 50 mL distilled water (pH 6.7) with Zn^{2+},

Cd^{2+}, or Hg^{2+} salt solutions. Approximately 20 mL 0.5% thioacetamide solution was added to spiked samples. The resulting precipitates of Zn^{2+}, Cd^{2+}, or Hg^{2+} sulphides were washed with distilled water, centrifuged, and dissolved in the minimum possible volume of concentrated HCl. The acid was completely evaporated, the residue was dissolved in 5 mL distilled water, and TLC was performed using 10 μL sample solution.

Preparation of Heavy Metal Hydroxide Sludge

Synthetic heavy metal sludge containing Zn^{2+}, Cd^{2+}, and Hg^{2+} was prepared by adding sufficient NaOH solution (1%) to a solution of the metal salts (1% of each). The metal hydroxide precipitate was filtered, dried, and dissolved in a minimum volume of concentrated hydrochloric acid. The acid was completely evaporated, the residue was dissolved in 5 mL distilled water, and TLC was performed using 10 μL sample solution.

Chromatography

TLC was performed on silica gel G. Plates were prepared by mixing silica gel with demineralized water in the ratio 1:3 (*w/w*), with constant shaking, to obtain a homogeneous slurry. The slurry was applied to 20 cm × 3 cm glass plates coated by means of a Toshniwal (India) TLC applicator to give 0.25-mm layers. The plates were first dried at room temperature then activated at $100 \pm 2°C$ by heating in an electrically controlled oven for 1 h. The activated plates were stored in a closed chamber at room temperature until used.

Test solutions (10 μL) were spotted on the thin-layer plates, by means of a micropipette, approximately 2.0 cm above the lower edge of the plates. The spots were dried in air and the plates were then developed with the chosen mobile phase, by the ascending one-dimensional technique, in 24 cm × 6 cm glass jars. The development distance was always 10 cm. After development, the plates were dried again and the spots of cations were visualized as coloured spots by using a glass sprayer to apply the appropriate chromogenic reagent. R_L (R_F of the leading edge) and R_T (R_F of the trailing edge) values were determined for the detected spots and R_F values for the metal ions were calculated by use of the formula $R_F = 0.5(R_L + R_T)$.

For separations, equal volumes of metal ions to be separated were mixed and 10 μL of the resulting mixture was spotted at the same position on an activated TLC plate. The plate was dried in air then developed, and

the spots detected, as described above. The separated metal cations were identified on the basis of R_F values

For examining the effect of impurities, one drop (5 μL) of each of Zn^{2+}, Cd^{2+}, Hg^{2+} and the impurity solution was spotted successively at the same position on an activated TLC plate. The spot was completely dried after each application. After final drying, the TLC plate was developed with 5% CPC and the spots were detected as described above.

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

To examine the effect of ageing of the mobile and stationery phases on the separation, two approaches were followed:

(a) A sample containing a mixture of Zn^{2+}, Cd^{2+}, and Hg^{2+} was applied each day to a freshly prepared TLC plate and the plate was developed with 5% CPC (prepared on the first day and used continuously for 7 days) as mobile phase. The R_F values of the separated cations were determined each day.

(b) A sample containing a mixture of Zn^{2+}, Cd^{2+}, and Hg^{2+} was applied to a set of TLC plates prepared on day one and developed with the selected mobile phase (5% CPC). Other TLC plates prepared on the same day (i.e. day one) were used for seven days and developed each day with freshly prepared mobile phase (5% CPC). The R_F values of separated metal cations obtained on each set of TLC plates were determined.

To examine the effect of temperature on separation, TLC plates spotted with a mixture of Zn^{2+}, Cd^{2+}, and Hg^{2+} were developed with 5% CPC with the mobile phase at temperatures in the range 5–80°C. After detection, the R_F values of the metal cations were evaluated. Similarly, to investigate the effect of UV radiation, the mobile phase (5% CPC) was exposed to ultraviolet radiation continuously for 24 h. During exposure a portion of mobile phase was taken out at intervals of 2 h and used for separation of Zn^{2+}, Cd^{2+}, and Hg^{2+}.

RESULTS AND DISCUSSION

This investigation was performed with a system in which the stationary phase is known for its weak cation-exchange properties, the mobile

phase contains a cationic surfactant, and the analytes are positively charged species. It is assumed that during chromatography of the cations with aqueous micellar solutions processes such as:

(a) cation exchange between the analyte and the protons of silanol groups,
(b) analyte–micelles interactions, and
(c) adsorption of surfactant by the silica gel surface

occur, and affect the mobility of metal cations in a peculiar manner which enables novel separations.

Effect of Surfactant Concentration

The R_F values of metal cations obtained on silica gel with mobile phases containing different concentrations of cationic surfactant (CPC) are listed in Table III.

Table III

R_F values of metal cations obtained on silica developed with distilled water and with CPC-containing mobile phases

Metal ion	Distilled water	Aqueous CPC						
		0.01%	0.1%	1%	3%	5%	7%	10%
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Cu^{2+}	0.10	0.05	0.07	0.02	0.00	0.02	0.02	0.07
Ni^{2+}	0.90T	0.85T	0.72T	0.68T	0.75T	0.65T	0.62T	0.80
Co^{2+}	0.85T	0.70T	0.65T	0.59T	0.65T	0.66T	0.60T	0.77
Cd^{2+}	0.40	0.35T	0.25T	0.27T	0.45T	0.57	0.59	0.62
Zn^{2+}	0.05	0.04	0.07	0.02	0.05	0.06	0.07	0.06
Ag^{+}	0.20T	0.05	0.10	0.10	0.05	0.05	0.07	0.06
Pb^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Bi^{3+}	0.04	0.15	0.25T	0.15T	0.17T	0.17T	0.10	0.20T
Hg^{2+}	0.40	0.30T	0.50T	0.40T	0.92	0.95	0.9	0.97

T denotes tailing spot ($R_L - R_T > 0.30$)

The concentrations of surfactant in the mobile phases were maintained below and above the critical micelle concentration (CMC) of CPC (CMC = 0.042%) to examine the effect on the mobility of the metal cations. This was done intentionally, because below the CMC surfactants remain mostly in the monomeric (anionic or cationic) form and behave like electrolytes whereas above the CMC surfactants form micelles in dynamic equilibrium with a smaller number of free monomers in solution. At dif-

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ferent concentrations the same surfactant molecules can therefore behave differently, thus modifying the retention behaviour of the metal cations. The data listed in Table III show the following trends.

(a) At low surfactant concentrations (0.01–0.1%) in the mobile phase, i.e. below or near the CMC of the surfactant, mutual separation of Cd^{2+}, Hg^{2+}, and Zn^{2+} is not possible because of the formation of diffuse (or tailing, $R_L - R_T > 0.3$) spots for Cd^{2+} and Hg^{2+}.

(b) At higher surfactant concentrations, e.g. 5–10%, which is much above the CMC, excellent separation of the metal ions from their mixtures is possible, as a result of modified interactions of the metal cations with the mobile phase or with the micelles. For example, mutual separation of Hg^{2+}, Cd^{2+}, and Zn^{2+} is always possible with eluents containing surfactant concentrations ≥5%.

(c) In pure water (zero surfactant) mutual separation of Hg^{2+}, Cd^{2+}, and Zn^{2+} from their mixtures is not possible because Hg^{2+} and Cd^{2+} co-migrate (the R_F of both the cations is 0.40)

Taking into consideration the shorter development time and better spot detection, we used mobile phase containing 5% CPC to achieve mutual separation of Hg^{2+}, Cd^{2+}, and Zn^{2+} ions. The order of mobility was $Hg^{2+} > Cd^{2+} > Zn^{2+}$. It seems that Hg^{2+} (high R_F) is easily eluted by the mobile phase (or specifically by the micelles) whereas Zn^{2+} is strongly retained by the stationary phase. The mobility of Cd^{2+} is intermediate.

To optimize the experimental conditions for simultaneous separation of Cd^{2+}, Hg^{2+}, and Zn^{2+} ions the effect of mobile phase pH, mobile phase impurities, impurities in the sample, temperature, UV irradiation, and the age of the mobile and stationary phases were also examined.

Effect of Mobile Phase pH

The results presented in Table IV reveal that mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} is readily possible in the pH range 4.0–9.2.

Effect of Impurities Added to the Mobile Phase

To examine the effect on the mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} of addition of inorganic electrolytes (sodium or calcium salts) and organic compounds to the micellar mobile phases, aqueous solutions (2–5%) of these additives were prepared by dissolving the required amounts in distilled water. These solutions were then used as solvents to prepare CPC micellar solutions (5%). The R_F values (average of triplicate determinations) of resolved spots of Zn^{2+}, Cd^{2+}, and Hg^{2+} from their mixtures,

Table IV

Effect on the mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} of the pH of the micellar mobile phase (5% CPC)

pH	Separation (R_F)		
	Zn^{2+}	Cd^{2+}	Hg^{2+}
2.3	0.20T	0.63	0.95
3.4	0.17T	0.60	0.92
4.0	0.11	0.62	0.92
5.7	0.07	0.58	0.92
7.0	0.07	0.57	0.91
8.0	0.06	0.65	0.95
9.2	0.07	0.67	0.92
Without buffer	0.05	0.58	0.95

T denotes tailing spot ($R_L - R_T > 0.30$)

obtained in the presence of added impurities in the micellar mobile phase (5% CPC), are listed in Table V.

Table V

Effect on the mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} of additives in the micellar mobile phase (5% CPC)

Aqueous solution of different impurities (%)		Separation (R_F)		
		Zn^{2+}	Cd^{2+}	Hg^{2+}
NaCl	1	0.05	0.80	0.95
	1.5	0.02	0.85	0.95
NaBr	1	0.05	0.65	0.90
	1.4	0.05	0.78	0.90
CaNO$_3$	1.5	0.05	0.70	0.95
	2	0.06	0.79	0.96
CaCl$_2$	0.5	0.03	0.68	0.95
	0.9	0.07	0.78	0.95
NaHCO$_3$	1.8	0.05	0.68	0.96
	2.2	0.03	0.76	0.97
CH$_3$COONa	1	0.07	0.70	0.95
	1.2	0.07	0.78	0.94
HCOONa	0.7	0.06	0.65	0.92
	0.9	0.04	0.74	0.95
Urea	3	0.08	0.63	0.92
	5	0.08	0.72	0.95
Without additives		0.05	0.58	0.95

The added organic and inorganic compounds are supposed to affect the CMC, the aggregation number, the partial specific volume of the surfactant, and the structure of the micellar assembly [17,18]. It is clear from Table V that Zn^{2+} is firmly retained near the point of application ($R_F < 0.07$) irrespective of the nature of additives in the mobile phase, and Hg^{2+} migrates near the solvent front ($R_F > 0.92$). The additives affect the mobility of Cd^{2+}. The R_F value of Cd^{2+} in the presence of organic and inorganic impurities varied in the range 0.70–0.85. Thus the mobility of Cd^{2+} is increased by the presence of additives. Although it is always possible to achieve good binary separations of Zn^{2+} from Hg^{2+} or Cd^{2+}, irrespective of the concentrations of the additives in the 5% CPC, mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} could not be achieved in the presence of these additives if present above the threshold values given in Table V because of enhancement of the R_F value of Cd^{2+}.

Effect of Impurities Added to the Sample

Table VI summarizes the effect of a variety of impurities on mutual separation of Cd^{2+}, Hg^{2+}, and Zn^{2+}. Amines do not effect the separation although the R_F value of Cd^{2+} is slightly changed from its standard value (0.58) by the presence of impurities in the sample. Nitrite and acetate have

Table VI

Mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} in the presence of anions and amines as impurities in the sample

Impurity added to the sample	Separation (R_F)		
	Zn^{2+}	Cd^{2+}	Hg^{2+}
SCN^-	0.05	0.49	0.92
PO_4^{3-}	0.07	0.55	0.95
MnO_4^-	0.05	0.55	0.95
$Mo_7O_{24}^{2-}$	0.07	0.52	0.95
NO_2^-	0.08	0.90	0.95
CH_3COO^-	0.04	0.86	0.97
IO_3^-	0.03	0.51	0.94
o-Chloroaniline	0.07	0.60	0.94
o-Nitroaniline	0.07	0.58	0.92
Methylamine	0.03	0.59	0.93
Dimethylamine	0.03	0.59	0.93
Dimethylamine	0.05	0.50	0.92
Trimethylamine	0.07	0.57	0.95
Without impurities	0.05	0.58	0.95

a substantial effect on the mutual separation of Cd^{2+}, Hg^{2+}, and Zn^{2+}. The Cd^{2+} co-migrates with Hg^{2+} in the presence of NO_2^- and CH_3COO^- ions in the sample.

Effect of Ageing of the Mobile Phase

The mobile phase (5%, CPC) can be used continuously for seven days without any change in the mobility of Zn^{2+}, Cd^{2+}, and Hg^{2+} in their mixtures when chromatographed daily on freshly prepared silica gel TLC plates.

Effect of Ageing of the Silica Gel TLC Plate

The best separation was achieved on freshly prepared TLC plates. The quality of the plates deteriorates with time and diffuse spots of Cd^{2+}, Hg^{2+}, and Zn^{2+} were obtained on older TLC plates.

Effect of Development Temperature

Mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} was possible for development temperatures up to 50°C (Fig. 1). Above 50°C the Hg^{2+} spot merged with the Cd^{2+} spot, restricting the separation of these ions. Zn^{2+} remained near the point of application over the entire range of development temperature (5–80°C) and hence could be separated from both Cd^{2+}, and Hg^{2+}.
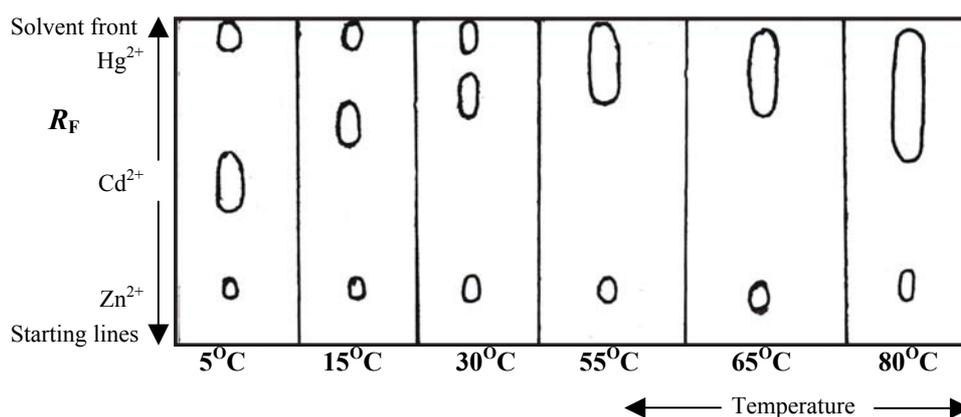
Fig. 1

Separation of mixtures of Zn^{2+}, Cd^{2+}, and Hg^{2+} on silica gel developed with 5% CPC at different temperatures (5–80°C)

Effect of UV Radiation

No significant change of the R_F values of Cd^{2+}, Zn^{2+} and Hg^{2+} was observed when the sample mixture was chromatographed with 5% aqueous CPC exposed to UV radiation for 24 h. If, however, after detection of the spots, the plates were exposed to UV radiation for 6 h, the colour of the detected spots of Zn^{2+}, Cd^{2+}, and Hg^{2+} disappeared.

Limits of Detection

This method enables highly sensitive detection of these metal cations. The sensitivity (given in parentheses) obtained by TLC with silica–aqueous CPC (5%) is Cd^{2+} (0.30 μg), Zn^{2+} (0.019 μg), and Hg^{2+} (0.024 μg). This high sensitivity may be because a significant fraction of these metal cations resides close to the micelle–water surface.

Application

The method was used for identification and separation of heavy metal cations in synthetic metal hydroxide sludge and metal sulphide ore samples. The results listed in Table VII clearly reveal that the method is useful for detection and separation of Hg in cinnabar (HgS), Cd in greenoekite (CdS), and Zn in zinc blend (ZnS), and for separation of the metals from hydroxide sludge samples.

Table VII

Separation of mixtures of Zn^{2+}, Cd^{2+}, and Hg^{2+} ions from synthetically prepared metal sludge and from heavy metal sulphide ores

Synthetic sample	Separation (R_F)		
	Zn^{2+}	Cd^{2+}	Hg^{2+}
Sulphide ores	0.06	0.60	0.95
Hydroxide sludge	0.05	0.52	0.93
Distilled water	0.05	0.06	0.95

CONCLUSION

Mutual separation of Zn^{2+}, Cd^{2+}, and Hg^{2+} was achieved experimentally on silica gel layers developed with 5% aqueous cetylpyridinium chloride as mobile phase. The method was used for successful separation and identification of these metal cations in synthetic ores and metal hydroxide sludge.

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