Chromatographic Separation of Heavy Metal by Used of Aminoplast as a Stationary Phase.

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Abstract

The chromatographic behavior of heavy metal ions have been studied on aminoplast polymer as stationary phase using anionic surfactant Sodium laureth sulfate (SLS) as mobile phase. Effect of (a) concentration of surfactant in the mobile phase,(b) acidity or basicity of surfactant containing developer medium and (c) the presence of strong and weak electrolytes additives in the mobile phase system. Semiquntatative determination of Cd^{2+} and Zn^{2+} by measurement of spot area was attempted. Identification of Zn^{2+} and Hg^{2+} from river water, industrial waste water with preliminary separation has been achieved.

Introduction

Thin layer chromatography (TLC) is considered to be superior to other chromatographic techniques, because of its simplicity and relatively low cost. Success in TLC depends to great extent upon the proper selection of the mobile phase. The separation possibilities in TLC are greatly enhanced when chromatoplates are developed with mixed solvent systems. TLC has been successfully utilized for various purposes, such as the separation of metal ions from a water sample [1], the characterization of the mobility of metal [2].The use of aqueous surfactant solution as a mobile phase in TLC was pioneered by Armstrong and Terrill [3]. Using a surfactant as the mobile phase gained popularity and became more widely applied due to its operational simplicity, cost effectiveness, relative non-toxicity and enhanced separation efficiency [4-8]. The use of silica gel and an alumina layer with surfactant –mediated mobile phase systems [9-14] has been used to separate various inorganic

species. Numbers of metal ions were systematically chromatographed on thin layer of aminoplast [15].

   In the present study a new mobile phase solvent system was developed, implanting a anionic surfactants Sodium laureth sulfate (SLS) when employed as a mobile phase, SLS may be used to separate various metal ions under a range of different conditions. We herein describe the continuation of earlier work on TLC [1-2] and discuss our systematic study of separation and selectivity of mobile phase for different metal ions using TLC with aminoplast in thin layer.

Experimental

Chemicals and Reagents: Urea, formalin solution, Sodium laureth sulfate (SLS) was obtained from Merk, dimethylglyoxime, dithizone, potassium ferrocyanide, carbon tetrachloride, NaCl, acetic acid methanol and ethanol were obtained from SD Fine India. All other chemicals were of analytical reagent grade.

Metal ion Studied: Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Ag^+ and As^{3+}.

Test Solution: TLC was performed using a standard aqueous solution (1%) of the chloride, nitrate or sulphate salts of the metal ions listed.

Detection: Fe^{3+} and Cu^{2+} were detected using 1% aqueous potassium ferrocyanide; Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+ and As^{3+} using 0.5% dithizone in carbon tetrachloride; and Ni^{2+} and Co^{2+} using a 1% solution of alcoholic dimethylglyoxime.

Stationary Phase: Aminoplast

Mobile Phase: The various solvent systems that were used as the mobile phases are listed in Table No.1

Table 1: Mobile phase systems.

S.No.	Symbol	Compositions
1	M1	Pure water mobile phase system
2	Aqueous surfactant solution	
	M2	1% aqueous SLS
	M3	3% aqueous SLS
	M4	5% aqueous SLS
	M5	7% aqueous SLS
3	Buffered surfactant solution	
	M6	3% SLS in buffer solution of pH 2.3
	M7	3% SLS in buffer solution of pH 4.0
	M8	3% SLS in buffer solution of pH 5.7
	M9	3% SLS in buffer solution of pH 9.0

	M10	3% SLS in buffer solution of pH 11.9
4		Aqueous surfactant solution with added Strong and weak electrolyte
	M11	3% aqueous SLS containing 1g NaCl per 100ml
	M12	3% aqueous SLS containing 3g NaCl per 100ml
	M13	3% aqueous SLS containing 5g NaCl per 100ml
	M14	3% aqueous SLS containing 1ml CH_3COOH per 100ml
	M15	3% aqueous SLS containing 3ml CH_3COOH per 100ml
	M16	3% aqueous SLS containing 5ml CH_3COOH per 100ml

Thin - layer chromatography

Preparation of Plates: Aminoplast was prepared in the laboratory using urea and formalin solution. The TLC plates were prepared by mixing mixture of aminoplast with deminerlised water in 1:2 ratio by weight with constant stirring to obtain homogeneous slurry. It was then immediately applied on the glass plates by dipping method. The plates were allowed to dry over night at room temperature and were used next day for TLC.

Procedure: Test solutions were spotted onto thin- layer plates with the help of a micropipette positioned about 1.0 cm above the lower edge of the TLC plates. The spots were air dried and the plates were then developed with the given mobile phase using by the one dimensional ascending technique in glass jars. The development distance was fixed at 10 cm in all cases. Following development, the plates were again air dried and the spots of the cations were visualized as coloring spots using the appropriate spraying reagent. R_F values were then calculated.

Separation: For the separation, the metal ions to be separated were mixed in equal amounts. A test solution of the resultant mixture was spotted onto the activated TLC plate, and was then air dried. The plates were developed to a distance of 10 cm. The spots were detected and the separated metal cations were identified by their R_F values.

Limits of Detection: The limits of detection of the metal cations were determined by spotting different amounts of metal ion onto the TLC plates, developing the plates using the method describe above, and then detecting the spots. This method was repeated with a successive decrease in the amount of metal ion used until spots were not detected. The minimum detectable amount on the TLC plates was taken as the limit of detection.

Recover of Cd^{2+} and Zn^{2+} by Spot area Method: To determine recovery of Cd^{2+} and Zn^{2+} by spot area measurement method, 0.01mL from series of standard solution of Cd^{2+} and Zn^{2+} were spotted on thin layer. The plates were developed with M15. After detection, the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated. The recovery of Cd^{2+} and Zn^{2+} were studied by analyzing various samples. For this purpose, experiments were performed by spotting 0.01mL of sample of solution containing 100μg Cd^{2+}, Zn^{2+} and Co^{2+}. The recovery of Cd^{2+} was 78± 3% and Zn^{2+} was 50± 3%.

Results and discussion

The results of the study describe herein are summarized in Table 2 to 5 and in Figures 1 to 3. The mobility of 10 metal cations was examined on aminoplast layers, using aqueous solutions of SLS. In order to optimize the experimental conditions, effect of various factors such as (a) concentration of surfactants and (b) basicity and acidity of medium on mobility of metal ion was examined.

A.1. Effect of Concentration of Surfactants: To understand the effect of concentration of anionic (SLS) surfactant on the mobility of metal cations, chromatography was performed on aminoplast layer using different concentration of surfactant − mediated mobile phase system (M2 − M5) as developers. The R_F values of metal cations obtained in pure water (*i. e., zero surfactant concentration,* M1) and in aqueous solution of SLS at different concentration levels (M2-M5) are listed in table 2.

Table 2: R_F values of metal cations obtained on aminoplast layer developed with pure water (M1) and aqueous solution SLS (M2-M5) at different concentration levels.

Metal ions	Water	SLS			
	M1	M2	M3	M4	M5
Zn^{2+}	0.12	0.15	0.30	0.22	0.10T
Cd^{2+}	0.40	0.45T	0.66	0.58	0.23T
Hg^{2+}	0.23	0.95	0.95	0.95	0.95
Fe^{3+}	0.12	0.16	0.25	0.20	0.15T
Ni^{2+}	0.75	0.80T	0.90	0.80	0.80
Co^{2+}	0.77	0.80	0.87	0.82	0.75
Cu^{2+}	0.32	0.08	0.20	0.12	0.05
Pb^{2+}	0.02T	0.04	0.06	0.04	0.03
Ag^+	0.30T	0.04	0.24	0.13	0.08
As^{3+}	0.11	0.12	0.22	0.15T	0.11T

T- tailed spot.

From the data listed in table 2, following conclusion may be drawn:

In pure water, all metal except As^{3+}, Pb^{2+} Fe^{3+} and Zn^{2+} show maximum mobilities and Pb^{2+} and Ag^{2+} were found to produce tailed spot. The higher mobility of Co^{2+} ($R_F \approx 0.77$) and Ni^{2+} ($R_F \approx 0.75$) facilitates their separation from all other metal ions studied whereas the mid retention factor of Hg^{2+} and Cu^{2+} opens opportunities for its selectivity separation from mulicomponnent mixture of metal cations.

When aqueous surfactant SLS solution at different concentration level (1%,3%, 5% and 7%) were used as mobile phase, metal ions such as Ni^{2+}, Co^{2+} and Hg^{2+} show higher mobility.

There were increasing mobilities in all metal cations in SLS addition mobile phase system as compared to pure water mobile phase system. In SLS addition mobile phase

system there were increasing mobility from concentration increases from 1% to 3%, but later on there were decreasing mobility when concentration increases from 3% to 5% to 7%.

In M 5(7% aqueous SLS) mobile phase system, metal cation such as Cu^{2+}, Pb^{2+} and Ag^+ show lower mobility as compared to pure water mobile phase system.

In M 3 (3% aqueous SLS) mobile phase system less time required for separation of metal ions as compared to other mobile system. Good and compact spot were obtained in M 3 mobile phase system so M 3 mobile phase was the used in further analysis.

A.2. Effect of Acidity and basicity of the medium: Thin layer chromatography of metal ions was performed using 3% SLS solution prepared in borate-phosphate buffers of different pH values (pH=2.3, 4.0, 5.7, 9.0 and 11.9). The result obtained with buffered surfactant solutions have been summarized in table 3.The following conclusions may be drawn from these results:

Table 3: Mobility of metal cations developed with buffered surfactant solution of different pH values.

Metal ions	R_F value				
	M6	M7	M8	M9	M10
Zn^{2+}	0.23T	0.34	0.45	0.28	0.15T
Cd^{2+}	0.11T	0.23T	0.66	0.34	0.18T
Hg^{2+}	0.23	0.78	0.95	0.76	0.32T
Fe^{3+}	0.12T	0.21	0.35	0.15	0.09
Ni^{2+}	0.14	0.78	0.9	0.56	0.45T
Co^{2+}	0.23T	0.45	0.88	0.56	0.13T
Cu^{2+}	0.55T	0.45	0.35	0.24	0.16
Pb^{2+}	0.09	0.11	0.22	0.11	0.04
Ag^+	0.04	0.20	0.34	0.12	0.11
As^{3+}	0.05	0.12	0.34	0.3	0.03

T- tailed spot.

Change in pH of mobile phase system had maximum effect on the mobilities of all metal cations. Hg^{2+}, Ni^{2+} and Co^{2+} showed higher mobility as compared to other metal cations.

With weakly acidic pH mobile phase system (M8), all metal cations showed relatively higher mobilities as copampred to aqueous mobile phase system (M3). In M8 mobile phase system Hg^{2+} , Ni^{2+} and Co^{2+} showed higher mobility ($R_F \approx 0.95$-0.88) facilitates their separation from all other metal ions studied.

With strongly acidic mobile phase (M6-M7) all metal ions except Cu^{2+} showed relatively lower mobility as soon there were increasing acidic pH of mobile phase.

With strongly alkaline pH (M9-M10) all metal ions showed relatively lower mobility. Mobility decreases as soon as alkaline pH of mobile phase increases.

Metal ions such as Pb^{2+}, As^{3+} and Ag^+ remained near the point of application at

higher acidic (M6) and higher alkaline (M10) pH of mobile phase system.

Some metal cations produced tailed spot at higher acidic and at higher alkaline pH.

Mobility of various metal cations was decreases with increasing acidic and alkaline pH of mobile phase system. So that higher alkaline and acidic SLS cannot use for separation of various metal ions from various sample. In M8 mobile phase system, metal ions gives higher mobility and well formed compact spot so that pH 5.7 that is weak alkaline SLS good mobile phase for separation metal cations.

A.2. Effect of strong and weak electrolyte additives: The effect of Strong electrolyte NaCl and weak electrolyte CH_3COOH at different concentration level in the eluent M3 (3%aqueous SLS) on the mobility of metal ions was examined. The results obtained with NaCl added mobile phase (M11-M13) and CH_3COOH added mobile phase system (M14-M16) are summarized in Table 4.

Table 4: Mobility of metal cations on 3% SLS containing different concentration of weak electrolyte & strong electrolyte admixture.

Metal ions	NaCl			CH_3COOH		
	M11	M12	M13	M14	M15	M16
Zn^{2+}	0.3	0.34	0.36	0.31	0.35	0.40T
Cd^{2+}	0.66	0.58	0.57	0.66	0.68	0.75
Hg^{2+}	0.95	0.9	0.91	0.95	0.97	0.95
Fe^{3+}	0.3	0.31	0.32	0.34	0.45	0.50T
Ni^{2+}	0.9	0.88	0.89	0.89	0.95	0.94
Co^{2+}	0.87	0.85	0.86	0.89	0.95	0.94T
Cu^{2+}	0.2	0.22	0.24	0.3	0.34	0.38
Pb^{2+}	0.07	0.05	0.06	0.07	0.1	0.15T
Ag^+	0.24	0.27	0.28	0.31	0.41	0.45
As^{3+}	0.22	0.21	0.2	0.24	0.3	0.33T

T- tailed spot.

The following conclusions may be drawn from these results:

Mobility of all metal ions almost unaffected at all concentration level of strong electrolyte that is in NaCl added mobile phase systems (M11-M13).

In case of weak electrolyte added mobile phase systems (M14-M16), mobility of all metal cations were increase as soon as there was increasing concentration of CH_3COOH.

At M16 mobile phase system, metal ions such as Zn^{2+}, Fe^{3+}, Co^{2+}, Pb^{2+} and As^{3+} produced tailed spot.

In weak electrolyte added mobile phase system good and compact spot were obtained within short period of time as compared to NaCl added mobile phase systems.

A.3. Semiquantitative estimation of Cd^{2+} and Zn^{2+}: An attempt has been made to determine the recovery of Cd^{2+} and Zn^{2+} spiked into water using spot area

measurement method by using M15 mobile phase system. A linear relationship obtained when the amount of sample spotted was plotted against area of the spot follows the empirical equation $\zeta = km$, where ζ is the area of the spot, m is the amount of solute and k is a constant. Representative plot for Cd^{2+} and Zn^{2+} has been shown in Figure 1-2 respectively. The linearity is maintained upto 250 µg/spot. At higher concentration a positive deviation from linear law was observed. The accuracy and precision was around $Cd^{2+} = \pm78\%$ and $Zn^{2+} = \pm50\%$.
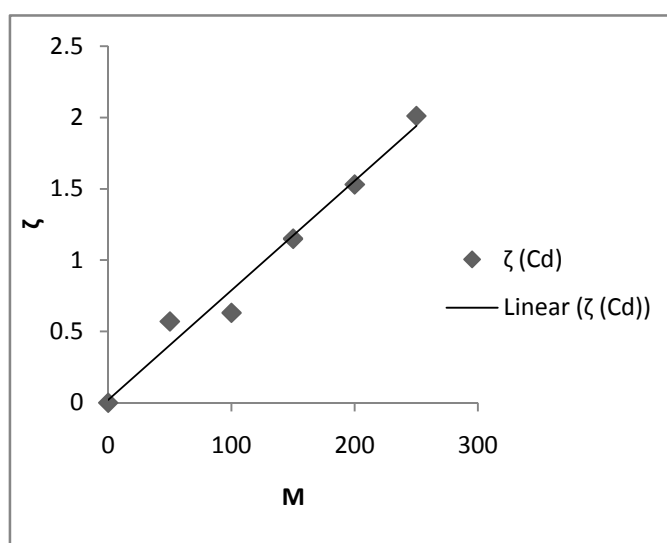
Figure 1: Calibration curve for semiquantitaive determination of Cd^{2+}
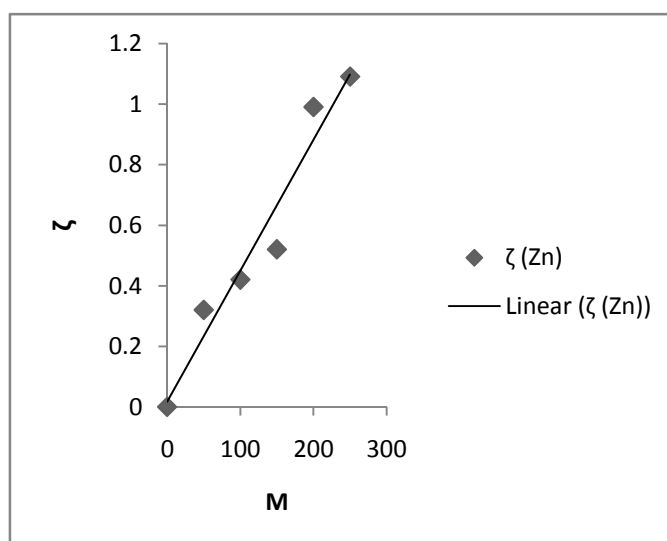
Figure 2: Calibration curve for semiquantitaive determination of Zn^{2+}

Table 5: Recovery and separation of coexisting Hg^{2+} and Zn^{2+} ions from spiked water and synthetically prepared metal ores heavy metal sludge samples.

Spiked/Synthetic samples	R_F	
	Hg^{2+}	Zn^{2+}
River water	0.89	0.76
Power plant ash	0.56	0.23
Industrial waste	0.34	0.11

Stationary Phase:-aminoplast layer
Mobile phase : M15

Application

The proposed method was applied for identification of zinc and mercury in spiked industrial waste water, river and power plant ash after separation on aminoplast layer. The result listed in Table 5 clearly demonstrated that Hg and Zn which spiked in the various sample can be recovered and separated on Aminoplast plates developed with M15.

Acknowledgement

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