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Rapid Chromatographic Separation of Heavy Metal Cations on Bismuth Silicate Layer

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ABSTRACT

The chromatographic behavior of various heavy metal ions have been studied by bismuth silicate layer as the stationary phase, with mobile phase system containing formic acid. The effect of protic and aprotic organic modifiers (methanol, ethanol, acetone, acetonitrile, DMSO and dioxane) and surfactant (SDS, BAC and Tween 80) on the retention behavior of the metal cations was examined. A novel mobile phase system comprising of 0.1M HCOOH and 1 M HCOONa in volume ratio 7:3 was identified as the best mobile phase for rapid separation and identification of mixtures of Cu^{2+} , Cd^{2+} and Hg^{2+} . Semiquantitative determination of Ni^{2+} , Pb^{2+} and Fe^{3+} by spot area measurement was attempted. The proposed method was successfully applied for identification and separation of copper, cadmium and mercury from river water, industrial waste water as well as from hydroxide sludge samples.

Keywords Bismuth silicate, DMSO, mobile phase, metal cations, CMC.

INTRODUCTION

Because of unique properties, bismuth silicate has been used as novel sorbent layer for chromatographic separation of metal cations by thin layer chromatography [1]. The use of aqueous surfactant solution as a mobile phase in TLC was pioneered by Armstrong and Terril [2]. 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 [3-7]. The use of silica gel and alumina layer with surfactant mediated mobile phase system [8-13] has been used to separate various inorganic species.

Considering the interdisciplinary and wide analytical utilization of chromatography techniques, in the present study, bismuth silicate and formic acid containing eluents were used for separation of various metal cations from multicomponent mixture as well as from various river and industrial wastewater.

MATERIALS AND METHODS

Chemicals and reagents- Bismuth nitrate, sodium silicate, silica gel-G, benzalkonium chloride, sodium dodecyl sulfate and tween80 (Merk), dimethyl glyoxime, dithiozone, potassium ferrocynide, methanol, ethanol and acetone (Loba chemie, India), 1-4 dioxane, formaic acid, DMSO, acetonitrile and inorganic salts (CDH, India) were used. All the reagents used were of analytical regent grade.

Test solutions- 1.0% aqueous solutions of following salts were used as test solution:

- i. Nitrates of Cd^{2+} , Pb^{2+} , Tl^{4+} , Al^{3+} and Ag^+ ii. Chlorides of Ni^{2+} , Co^{2+} , Fe^{3+} , Hg^{2+} and Ti^{4+}

iii. Sulfates of Cu^{2+} , VO^{2+} and UO_2^{2+} .

All the solutions were prepared in double distilled water. The solution of nitrates of lead, silver and the chlorides of mercury contained small quantities of corresponding acid to limit the extent of hydrolysis.

Detection Reagents-

For the detection of various cations, the following reagents were used:

- i. Yellow ammonium sulphide for Cd^{2+} , Ag^+ , Pb^{2+} , Tl^{4+} and Hg^{2+}
- ii. Aqueous potassium ferrocynide for Fe^{3+} , Cu^{2+} , UO_2^{2+} , VO^{2+} and Ti^{4+}
- iii. Dimethylglyoxime in ethanol for Ni^{2+} and Co^{2+}
- iv. Aluminon (1%) for Al^{3+} .

Stationary phase - Bismuth silicate.

Mobile phase- various solvent systems that were used as the mobile phases are listed in table1.

Symbol	Composition
M1	1.0M HCOONa
M2	1.0M HCOOH
M3	1.0M HCOOH +1.0M HCOONa (3:7)
M4	1.0M HCOOH +1.0M HCOONa (1:1)
M5	1.0M HCOOH +1.0M HCOONa (7:3)
M6	0.01M HCOOH
M7	0.01M HCOONa
M8	$1.0M HCOOH + CH_3OH (7:3)$
M9	$1.0M HCOOH + C_2H_5OH (7:3)$
M10	1.0M HCOOH + acetone (7:3)
M11	1.0M HCOOH + acetonitrile (7:3)
M12	1.0M HCOOH + DMSO (7:3)
M13	1.0M HCOOH + 1,4 dioxane (7:3)
M14	1.0M HCOOH + 0.1M aq.SDS (7:3)
M15	1.0M HCOOH +0.1M aq. BAC (7:3)
M16	1.0M HCOOH + 0.1M aq. Tween 80 (7;3)
M17	1.0M HCOOH + 0.0001M aq. SDS (7:3)
M18	1.0M HCOOH + 0.0001M aq. BAC (7:3)
M19	1.0M HCOOH + 0.0001M aq. Tween 80 (7:3)

Preparation of spiked industrial waste water and river water – A 50ml volume of industrial waste water (pH 4.1) collected from metal industries, Nagpur, India or river water (pH7.48)obtained from Chandrabhaga river, Dhapewada, India was spiked with $100\mu g$ each of Cu^{2+} , Cd^{2+} and Hg^{2+} salts. About 30ml of 0.5% thioacetamide solution was added into the spiked sample. The resultant precipitate of Cu^{2+} , Cd^{2+} and Hg^{2+} sulphides was washed with distilled water, centrifuged and dissolved in minimum possible volume of concentrated HCl. The acid was completely removed by evaporation and the residue was dissolved in 5ml of distilled water. An aliquot (5µl) of each sample was applied on TLC plate and chromatography was performed as done for standard samples.

Preparation of heavy metal hydroxide sludge- Synthetic heavy metal sludge of Cu^{2+} , Cd^{2+} and Hg^{2+} was prepared by adding sufficient volume of 1% NaOH solution into a mixture containing 1% solution of these metal salts in equal volumes. The metal hydroxide precipitate so obtained was filtered dried and dissolved in a minimum volume of concentrated HCl. The acid was completely evaporated, the residue was dissolved in 5 ml of distilled waters and TLC was performed having 5µl sample.

Thin - layer chromatography:

Preparation of bismuth silicate plates- Five hundred milliliters of a 0.1M solution of bismuth nitrate in $2M \text{ HNO}_3$ and 500ml of a 0.1M solution sodium silicate in 2M NaOH were simultaneously added drop wise with constant stirring to 30ml of distilled water in flask. The rate of addition of the reactants was so adjusted that the contents of the flask were just neutral to methyl red indicator. The reaction mixture was allowed to coagulate over night and the formed gel was washed several times with distilled water by decantation until the supernatant was free of ions. The supernatant was completely removed. A slurry prepared by mixing the gel (75 ml) with a powder of silica gel G

(20gm) as a binder was used to coat 20×20 cm glass plates. The plates were dried in an oven at 80°C for 3hrs and then stored at room temperature inside desiccators.

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.

Semi- quantitative determination by spot- area measurement- For semi quantitative determination by spot- area measurement method, 0.01ml volume from a series of standard solution (0.5-2%) of Ni²⁺, Pb²⁺, Fe³⁺ and Tl⁺ were spotted on thin layer plates. The plates were developed with M5 (1.0M HCOOH + 1.0M HCOONa (7:3)). After detection the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated.

RESULT AND DISCUSSION

Table1.- Mobility of heavy metal cations on bismuth silicate plates developed with formate ion containing mobile phase

Matal ions	Mobile phases				
Metal Ions	M1	M2	M3	M4	M5
Cu^{2+}	0.02	0.70	0.65	0.30T	0.53
Ni ²⁺	0.30	0.87	0.76	0.70	0.84
Co^{2+}	0.32	0.87	0.54	0.70	0.83
Cd^{2+}	0.00	0.58	0.36	0.50	0.47
Pb^{2+}	0.04	0.40T	0.03	0.12	0.28T
$T1^+$	0.70	0.64	0.65	0.50	0.32
Hg^{2+}	0.12	0.41T	0.00	0.00	0.19
Al^{3+}	0.00	0.35T	0.00	0.00	0.24T
Fe ³⁺	0.00	0.05	0.05	0.05	0.05
$\mathrm{UO_2}^{2+}$	0.02	0.02	0.02	0.02	0.02
VO^{2+}	0.04	0.04	0.04	0.04	0.04
Ag^+	0.00	0.04	0.04	0.04	0.04
Ti ⁴⁺	0.03	0.03	0.03	0.03	0.03
T- tailed spot($R_L - R_T > 0.30$)					

The R_F values of metal cations obtained on bismuth silicate layer plates developed with 1.0M HCOOH (pH \approx 2.3), 0.01M HCOONa (pH > 7.0) and 1.0M HCOOH – 1.0M HCOONa (3:7, 1:1, 7:3) are summarized in table 2. With 1.0 M HCOONa (M1), most of the cations remains near the point of application, whereas metal ion Tl⁺ shows appreciable mobility and thus can be selectively separated from other metal ions on bismuth silicate plates developed with 1.0M HCOONa. Conversely, Cu²⁺ and Cd²⁺ have much higher mobility in 1.0 M HCOOH (M2) compared to 1.0M HCOONa and can be separated from Fe³⁺, UO₂²⁺, VO²⁺ and Ti⁴⁺. The combination of these two solvent systems in different proportions further increases the separation potentially of formic acid by modifying the retention behavior of cations and several metal cations can be selectively separated with M3 – M5 mobile phases. The lowering of HCOOH or HCOONa concentration (M6, M7) from 1.0M to 0.01M results in decreasing in R_F values of cations. The result presented in Fig. 1 as ΔR_F (R_F in 1.0M HCOOH or HCOONa- R_F in 0.01M HCOOH or HCOOH or HCOONa versus metal cations) plots clearly indicate this effect.



Fig. 1. Plot of $\Delta \mathbf{R}_{\mathrm{F}}$ versus metal ions $\Delta R_F(A) = (R_F \text{ in } 1.0M \text{ HCOOH}) - (R_F \text{ in } 0.01M \text{ COOH})$ $\Delta R_F(B) = (R_F \text{ in } 1.0M \text{ HCOONa}) - (R_F \text{ in } 0.01M \text{ COONa})$

Table2- Effect of added organic solvents in 1.0M HCOOH on the mobility of metal is	ons
$\Delta R_F = (R_F \text{ in } 1.0M \text{ HCOOH} + \text{ organic solvents } (7:3)) - (R_F \text{ in } 1.0 \text{ M HCOOH})$	

Metal Ions	Methanol	Ethanol	Acetone	Acetonitrile	DMSO	Dioxane	
Cu ²⁺	-0.67	-0.64	-0.50	-0.14	-0.02	-0.07	
Ni ²⁺	-0.63	-0.26	-0.22	+0.06	-0.11	-0.11	
Co^{2+}	-0.63	-0.16	-0.20	+0.08	+0.10	+0.11	
$\mathrm{UO_2}^{2+}$	+0.05	+0.30	+0.25	+0.21	+0.40	+0.48	
VO^{2+}	-0.10	+0.06	-0.05	+0.35	+0.04	+0.29	
Cd^{2+}	+0.06	-0.05	-0.48	+0.08	+0.21	+0.12	
Ag^+	-0.13	-0.18	-0.18	-0.18	-0.18	-0.18	
Pb^{2+}	-0.12	-0.29	-0.25	+0.20	+0.13	+01.8	
Tl^+	+0.09	-0.18	+0.09	+0.07	+0.02	+0.10	
Hg^{2+}	-0.08	-0.46	-0.46	+0.30	+0.03	+0.36	
Al^{3+}	+0.17	+0.07	+0.02	0.00	+0.20	+0.20	

 Pb^{2+} , UO_2^{2+} , Cu^{2+} and VO^{2+} in 1.0 M HCOOH + methanol, ethanol, acetone or dioxane (7:3); Ag^+ , Pb^{2+} , Hg^{2+} in 1.0M HCOOH and Al^{3+} in all mobile phase (M8- M13) produced taied spot. No effect of added organic solvents was observed on the mobility of Fe^{3+} and Ti^{4+} .

Effect of added organic solvents:

In order to understand the role of organic solvents on the mobility of metal ions, the R_F values of metal cations were determined with mobile phase M8-M13 obtained by mixing methanol, ethanol, acetone, DMSO, Dioxane and acetonitrile with 1.0M aqueous formic acid respectively in 7:3 ratios by volume. The R_F values (obtained by subtracting R_F values realized with 1.0M formic acid from the R_F values realized with 1.0M formic acid plus organic additives) are presented in table 2. The positive and negative values of ΔR_F clearly demonstrate the effect of added organic solvents on the mobility trend of metal cations. Amongst these, DMSO is aprotic dipolar; MeOH and EtOH are polar proton donor; dioxane is proton acceptor; acetone being non polar favors the formation of non dissociated metal complexes and acetonitrile bearing CN group is an useful complexing agent. Thus, the inherent diverse properties of the added organic solvents influence the mobility pattern of metal cations opening new possibilities for their separations. The mobility of heavy metals decreases upon the addition of alcohols and ketones (examples. MeOH, EtOH and acetone) in the mobile phase as indicative by negative value of ΔR_F for the most of the metal cations. Conversely, the addition of 1,4-dioxane, DMSO and acetonitrile in the mobile phase enhances the mobility of cations as indicative by positive ΔR_F value. None of the organic modifires exerts any influences on the mobility of Fe³⁺ and Ti⁴⁺.

Effect of added surfactants:

The use of surfactant mediated systems, as mobile phase in liquid chromatography has been the choice of analytical chemists because of their advantages of enhanced selectivity, low cost and reduced toxicity. We have used cationic (BAC), anionic (SDS) and nonionic (Tween 80) surfactant in combination with 1.0M formic acid as eluents. From retention behavior of metal cations on bismuth silicate plates developed with surfactant containing formic acid mobile phase systems (M14- M19), following conclusion are drawn.

- i. Fe^{3+} , Ag^+ and Ti^{4+} remain near the point of application irrespective of the nature of surfactant (cationic, anionic and non ionic) and the concentration of surfactant.
- ii. Al^{3+} produce tailed spot at all concentrations of the surfactants.
- iii. Pb^{2+} show occasional tailing.
- iv. Most of the metal cations $(Cu^{2+}, Ni^{2+}, Co^{2+} VO^{2+}, Tl^+, Cd^{2+} and UO_2^{2+})$ show higher mobility in mobile phases comprising volume ratio 7:3 of formic acid and surfactant solution compared to the mobile phase consisting of formic acid surfactant in 3:7 volume ratio.
- v. Lowering of surfactant concentration from 0.1 M (M14- M16) to 0.0001M (M17- M19) in the mobile phase leads to minor change in mobility of metal cations.

Table3- Experimentally achieved separations of metal cations on bismuth silicate plates developed with different mobile phases

Mobile phase	Separation (R _F)
1.0 M HCOOH	Ni^{2+} or $Co^{2+}(0.86) / Cu^{2+}(0.75) - Fe^{3+}(0.08) / UO_2^{2+}$, $Ti^{4+}(0.0) / VO^{2+}(0.13)$
1.0M HCOOH + 1.0M HCOONa (7:3)	Ni ²⁺ , Co ²⁺ (0.84)/Cu ²⁺ (0.67) – Fe ³⁺ or Ti ⁴⁺ (0.0)/UO ₂ ²⁺ , VO ²⁺ (0.05) Ni ²⁺ (0.84) – Cd ²⁺ (0.46) – Ag ⁺ (0.0)
$1.0M HCOOH + CH_3OH (7:3)$	$Cd^{2+}(0.60), Hg^{2+}(0.35) - Fe^{3+} \text{ or } Ti^{4+}(0.00) / Cu^{2+}(0.10) / UO_2^{-2+} \text{ or } VO^{2+}(0.06).$
$1.0M HCOOH + C_2H_5OH (7:3)$	$\text{Co}^{2+}(0.70)$ - $\text{Cd}^{2+}(0.51)$ or $\text{Tl}^+(0.42)$ – Fe^{3+} , Ag^+ , Bi^{3+} or $\text{Ti}^{4+}(0.0)/\text{Cu}^{2+}$ or $\text{Pb}^{2+}(0.10)$
1.0M HCOOH + Acetone (7:3)	Ni ²⁺ or Co ²⁺ (0.66), Tl ⁺ (0.70) – Fe ³⁺ , Ag ⁺ , Hg ²⁺ or Ti ⁴⁺ (0.00)/ UO ₂ ²⁺ (0.23) / VO ²⁺ or Cd ²⁺ (0.09) and Pb ²⁺ (0.14)
1.0M HCOOH + DMSO (7:3)	Cd ²⁺ , Ni ²⁺ , Co ²⁺ or Cu ²⁺ (0.76) – UO ₂ ²⁺ (0.38)/ Pb ²⁺ or Hg ²⁺ (0.50) – Fe ³⁺ (0.05) / Ag ⁺ or Ti ⁴⁺ (0.0)
1.0M HCOOH + 1,4- Dioxane (7:3)	Hg ²⁺ (0.80) / Ni ²⁺ or Co ²⁺ (0.75) / Cu ²⁺ , Cd ²⁺ or Tl ⁺ (0.71) – UO ₂ ²⁺ (0.45) – Fe ³⁺ or Cu ²⁺ (0.05).
1.0M HCOOH + 0.1M SDS (7:3)	Hg^{2+} , Ni^{2+} , Co^{2+} or Cu^{2+} (0.76) – UO_2^{2+} (0.33) – Fe^{3+} , Ag^+ or Ti^{4+} (0.12).
1.0M HCOOH + 0.1M BAC (7:3)	Hg^{2+} , Ni^{2+} or $Co^{2+}(0.89) - UO_2^{2+}(0.33) - Fe^{3+}$, Ag^+ or $Ti^{4+}(0.0)$.
1.0M HCOOH + 0.1M Tween 80 (7:3)	$Hg^{2+}(0.70)$, Ni^{2+} or $Co^{2+}(0.63) / Cu^{2+}(0.76) - UO_2^{2+}(0.33) - Fe^{3+}$, Ag^+ or $Ti^{4+}(0.12)$.

The formic acid containing mobile phases was found capable to resolve several metal cations from their multicomponent mixtures. As a result, some important cations separation realized experimentally have been summarized in table 3.





Semiquantitative determination of Ni²⁺, Pb²⁺ Tl⁺ and Fe³⁺- A relatively less accurate but the simplest method for quantitaion is based on the measurement of the size of the size the spot by drawing the outline of the spot on a piece of tracing paper. Therefore, an attempt was made to achieve semiquantitative determination of metal ions by measuring the spot area of the spot follows the empirical equation $\xi = \text{km}$ where ξ is the area of the spot, m is the amount of the solute and k is a constant. The linearity maintained up to $200 \mu g/\text{spot of Ni}^{2+}$, Pb²⁺ Tl⁺ and Fe³⁺. At higher all the cases were observed. The standard curve constructed for semiquantitative determination of Pb²⁺ in Fig 2 was used to find out the amount of lead present in industrial wastewater samples. The accuracy and precision were below $\pm 15\%$.

Applications

Amongst TLC systems examined, the system comprising bismuth silicate plates developed with M5 that is 1.0 M HCOOH + 1M HCOONa (7:3) mobile phase was identified as the most useful for the analysis of heavy metal cations. This system was applied for identification and separation of certain metal cations from industrial waste and metal hydroxide sludge. The results summarized in Table 4 clearly demonstrate the applicability of the method for identification as well as separation of Cu^{2+} , Cd^{2+} and Hg^{2+} from their mixtures.

Table 4- Identification and separation of mixtures from spiked water and heavy metal sludge

Spiked/Synthetic		R _F values	
samples	Cu ²⁺	Cd^{2+}	Hg^{2+}
River water	0.12	0.32	0.87
Industrial waste water	0.14	0.34	0.89
Sludge	0.16	0.32	0.88

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REFERENCES

[1] V. Ghoulipour, S. W. Husain, Analytical Science, 2000, Vol. 16,1079.

[2] D.Armstrong, R. Q. W. Terrill, Anal. Chem., 1979, 51, 2160-2163.

[3] D.Armstrong, R. Q. W. Terrill, Anal. Chem., **1979**, 51, 2160-2163.

[4] M. F. Borgerding, Williams (Jr), R. L.; Hinze, W. L.; Quina, New J. Liq. Chromatography, 1989,12, 1367-1406.

[5] A.S. Kord, M. G. Khaledi, Anal, Chem., 1992, 64, 1901-1907.

[6] A.Mohammad, Nahed Jabeen; Acta. Chromatographia, 2003, 13, 135-153.

[7] M. G.K haledi, J. K.Strasters, A.H. Rodgers, E. D. Breyer, Anal. Chem., 1990, 62,130-136.

[8] A. Mohammad, V.J. Agrawal, J. Quimica Analytica, 2000,254, 20-25.

[9] A. Mohammad, Y. H. Sirwal, J. Planar Chromatography-Mod.TLC, 2002,15, 107-115.

[10] A Mohammad, Eram Iraqi, and Iftkhar Alam Khan, J. of Surfactant and Detergent, 1999, Vol.2; No.4, 523-529.

[11] A. Mohammad, V. Agrawal, Nahed Jabeen. Chromatography, 2003, 24, 2 1-7.

[12] C. G.Yeole, V. M.Shinde, Analyst, 1983, 104, 1102-1107.

[13] T. Okada, Anal Chem., **1988**, 60, 2116