

RESEARCH ARTICLE

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Layer**

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Separation and Identification of Heavy Metal Ions by Thin Layer Chromatography on Stannous Silicate Layer

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Abstract

Thin layer of stannous silicate was used to study the chromatographic behavior of 18 metal ions in surfactant mixed solvents. Effect of presence of alcohol at various concentrations, presence of strong and weak electrolytes, effect of concentration of surfactant, effect of acidity and basicity of aqueous surfactant on mobility of metal cations were also studied. By using surfactant and with various additives mixed in mobile phase, metal ions such as Cu^{2+} - Hg^{2+} and UO_2^{2+} - Ni^{2+} were separated from their binary mixture. Semi-quantitative determination of Ni^{2+} by measurement of spot area was attempted.

Keywords: Thin layer; stannous silicate; surfactant; alcohol.

1. Introduction

Thin layer chromatography (TLC) is a very convenient and effective technique for the separation and identification of inorganic ions. It permits selective separations, simple detection and easy manipulation of the mobile phase. As a result, numerous sorbents and even greater number of mobile phases have been developed for achieving improved chromatographic performance in terms of selectivity, resolution, rapidity and reproducibility. From literature [1-3], the mobile phases used in inorganic solvents; or aqueous solution of acids, bases and salts. Although organic solvents such as benzene, chloroform, acetone, methanol, acetonitrile, carbon tetrachloride, dioxane, acetic acid, phenols, cyclohexane and hexane are quickly removed from the sorbent layer after development, most of these toxic to some extent. However, aqueous micellar solutions of surfactants are almost non-toxic, non-flammable and odorless. Aqueous micellar systems capable of mimicking certain properties of organic solvents (solubilizing non polar solutes) have been considered as an attractive alternative to organic solvents as the mobile phase in the chromatographic analysis of complex mixtures. The highly selective partitioning of solutes to micelles results in unique separation possibilities for both ionic and non-ionic solutes.

Surfactants have long been used as mobile phase components in ion pair chromatography (IPC) and micellar liquid chromatography (MLC) [4-9]. Since the first report by Armstrong and Henry [10], interest in MLC has grown rapidly and it is now being used as substitute for traditional liquid chromatography with reversed phases [11-14]. The fascinating feature of micellar systems is the presence of three phases (micellarmicropseudo phase, bulk mobile phase and the stationary phase) that provides of multiple interactions, resulting in unique simultaneous separation capabilities of hydrophobic and hydrophilic compounds. The applicability of a quadratic relationship between the time of mobile phase motion and the distance from the solvent entry position of mobile phase and front of the mobile phase was validated for micellar TLC [15]. The use of micellar solution as the mobile phase in TLC was first reported in 1979 by Armstrong and Terrill [16, 17]. Despite distinct advantages, micellar systems have not been extensively used in TLC compared with their use in reversed phase high performance liquid chromatography [18-21] and micellarelectrokinetic capillary chromatography [22-24]. Metal ions were successfully separated using anionic surfactant SDS containing amino acids [25] and SDS with iodides and chlorides from pure soil sample [26]. Various metal ions have been separated on Titan-Yellow modified resin surfactant solvents [27]. Micellar electrokinetic chromatographic separation and analysis of uranium, gold and mercury in environmental ore sample also carried out using SDS surfactant [28]. Spectrometric estimation of cations was carried out by MLC [29]. The various metal ions were separated using aminoplast [30], lanthanum silicate [31], stannous arsenate [32] using various organic solvent systems. Drugs and metal ions were separated on bismuth silicate layer [33, 34].

The aim of this work was to explore the possibility of using BAC (cationic surfactant) and stannous silicate as a stationary phase in the separation of heavy metal cations. The role of various factors such as surfactant concentration, pH of the medium, and addition of organic modifiers (alkanols) and of electrolytes (NaCl and CH₃COOH) on the retention behavior of metal ions was examined.

2. Methods

2.1 Reagents: Stannous chloride, sodium silicate, SDS (Sodium Dodecyl Sulfate) and BAC (Benzalkonium Chloride) were obtained from Merck; Dimethylglyoxime, dithizone, potassium ferrocyanide, carbon tetrachloride, methanol, ethanol, propanol, butanol, glacial acetic acid, and HCl were obtained from SD Fine (India). All other chemicals were of analytical reagent grade.

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

2.3 Detection: Fe³⁺, Cu²⁺, U⁶⁺, V⁵⁺, Zr⁴⁺, and Th⁴⁺ were detected using 1% aqueous potassium ferrocyanide; Zn²⁺, Cd²⁺, Hg²⁺, Bi³⁺, Sb³⁺, Pb²⁺, Ag⁺, Mo⁶⁺, As³⁺, and W⁶⁺ using 0.5% dithizone in carbon tetrachloride; and Ni²⁺, and Co²⁺ using a 1% solution of alcoholic dimethylglyoxime.

2.4 Stationary phase: Mixture of stannous silicate and silica gel 'G' was used as the stationary phase. Five hundred milliliters of an aqueous 0.05M solution of stannous chloride and 500ml of an aqueous 0.1M solution of sodium silicate were mixed. The mixture was thoroughly stirred during which white gel was formed. The pH of gel was adjusted to 1, by adding dilute nitric acid. The gel was kept overnight and 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 (50cm) with a powder of silica gel G (20g) as a binder was used to coat 20×20cm glass plates. The plates were dried in an oven at 80°C for 3hrs and then stored at room temperature inside desiccators.

2.5 Buffer solutions: Buffer solutions at pH 2.3, 4.0, 5.7, 9.0 and 11.9 were prepared by adding 0, 8.2, 10, 20 and 60ml of 0.24M NaOH, respectively, into a 100ml mixture consisting of equal volumes of boric acid (0.04M) and phosphoric acid (0.4M).

2.6 Mobile phase: The various solvent systems used are found in Table 1.

Thin-layer chromatography

2.7 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 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.

2.8 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.

2.9 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.

2.10 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⁺ was spotted on thin layer plates. The plates were developed with 1% aqueous BAC:Ethanol 8:2 (v/v).

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

No.	Symbol	Composition
A	H1	Water
B	Aqueous Surfactant Solutions	
	M1	1% Aqueous BAC (Benzalkonium chloride)
	M2	3% Aqueous BAC (Benzalkonium chloride)
	M3	5% Aqueous BAC (Benzalkonium chloride)
	M4	7% Aqueous BAC (Benzalkonium chloride)
	M5	1% Aqueous SDS (sodium dodecyl sulfate)
	M6	3% Aqueous SDS (sodium dodecyl sulfate)
C	Buffered Surfactant Solutions	
	M7	1% Aqueous BAC in buffer solution of pH 2.3
	M8	1% Aqueous BAC in buffer solution of pH 4.0
	M9	1% Aqueous BAC in buffer solution of pH 5.7
	M10	1% Aqueous BAC in buffer solution of pH 9.0
	M11	1% Aqueous BAC in buffer solution of pH 11.9
D	Addition of Alcohol	
	M12	1% Aq. BAC : Methanol (9:1) (V/V)
	M13	1% Aq. BAC : Methanol (8:2) (V/V)
	M14	1% Aq. BAC : Methanol (7:3) (V/V)
	M15	1% Aq. BAC : Ethanol (9:1) (V/V)
	M16	1% Aq. BAC : Ethanol (8:2) (V/V)
	M17	1% Aq. BAC : Ethanol (7:3) (V/V)
	M18	1% Aq. BAC : Propanol (9:1) (V/V)
	M19	1% Aq. BAC : Propanol (8:2) (V/V)
	M20	1% Aq. BAC : Butanol(9:1) (V/V)
	M21	1% Aq. BAC : Butanol(8:2) (V/V)
D	Addition of Electrolyte	
	1. NaCl (Strong Electrolyte)	
	M22	1% aqueous BAC containing 1g NaCl per 100ml
	M23	1% aqueous BAC containing 3g NaCl per 100ml
	2. Acetic Acid (Weak Electrolyte)	
	M24	1% aqueous BAC containing 1ml acetic acid per 100ml
	M25	1% aqueous BAC containing 3ml acetic acid per 100ml

3. Results and Discussion

The results of this study have been summarized in Tables 2, 3 and Figures 1-4. The mobility of eighteen metal cations was examined on stannous silicate layer using aqueous solution BAC. In order to optimize the experimental conditions, the effect of various factors such as the concentration of the surfactant, the acidity and basicity of the medium, the nature of alkanols in the surfactant mobile phase and the presence of NaCl and CH₃COOH in the surfactant mobile phase on the mobility of cations was examined.

3.1 Effect of the concentration of surfactants

In order to understand the effect of surfactant concentration, the mobility of an individual metal on stannous silicate layer was determined using wide concentration range (1%, 3%, 5% and 7%) of BAC and (1% and 3%) of SDS. From data in Table 2, the following trends were noticed.

- 1) In pure water, all metal ions except Th⁴⁺, W⁶⁺ and Mo⁶⁺ show low mobility and all these metals were found to produce tailed spot.
- 2) In aqueous surfactant mobile phase systems, negligible changes were observed in mobilities of metal cations.
- 3) Mobilities were decreased in aqueous anionic surfactant SDS (M5-M6) mobile systems as compared to pure water and aqueous cationic surfactant BAC mobile systems.

- 4) Aqueous BAC mobile systems (M1-M4), higher mobility was obtained as compared to pure water mobile systems. All metal cations except Sb^{3+} , As^{3+} , Pb^{2+} , Th^{4+} , W^{6+} and Mo^{6+} show same R_F values at all concentrations of BAC.
- 5) The behavior of Sb^{3+} and As^{3+} was peculiar. It shows higher mobility ($R_F = 0.70$) with mobile phase containing a surfactant concentration 1% and above this concentration (3% to 7%) mobility of Sb^{3+} and As^{3+} suddenly decreases ($R_F = 0.10$). Certain metal ions (Zn^{2+} , Ni^{2+} , UO_2^{2+} , Hg^{2+} , Zr^{4+} and Bi^{3+}) showed occasional tailing.
- 6) Pb^{2+} , Th^{4+} , W^{6+} and Mo^{6+} were strongly retained by stannous silicate and remained at the point of application.
- 7) In BAC mobile phase systems, the higher mobility of Ni^{2+} ($R_F = 0.67-0.69$) and Hg^{2+} ($R_F = 0.69-0.70$) facilitates their separation from all other metal ions studied, whereas the mid R_F ($R_F = 0.40-0.45$) of Cu^{2+} , Zn^{2+} , Zr^{4+} and Cd^{2+} opens opportunities for its selective separation from multi component mixture metal ions.
- 8) The increase in concentration of BAC from 1% to 7% results in minor changes in the mobility of metal ions which indicate that the various types of concentration dependent structures formed by surfactant molecules with comitant change in their aggregates [35] do not effectively influence the mobility of metal ions.

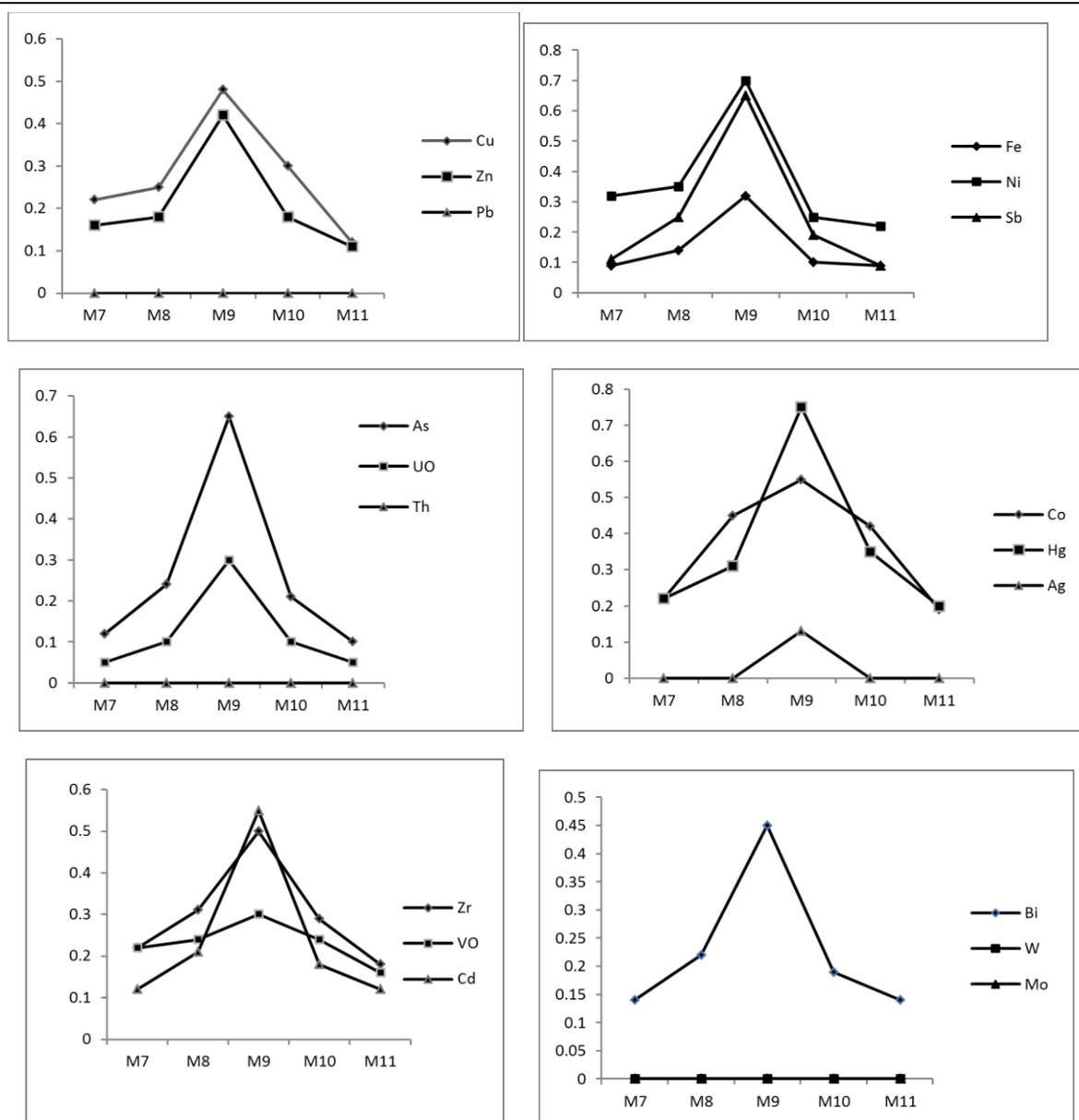
Table 2: R_F value of the metal cations obtained on stannous silicate layer developed with pure water and aqueous solution of BAC and SDS as different concentration level.

Metal Ions	R_F Value						
	Water	BAC				SDS	
	H1	M1	M2	M3	M4	M5	M6
Cu^{2+}	0.28T	0.45	0.43	0.41	0.43	0.11 T	0.12 T
Zn^{2+}	0.21T	0.40 T	0.38	0.38 T	0.39	0.10	0.12 T
Pb^{2+}	0.04	0	0	0	0	0	0
Fe^{3+}	0.15T	0.20	0.21	0.24	0.22	0.15 T	0.14 T
Ni^{2+}	0.29T	0.67	0.70 T	0.69	0.67 T	0.17 T	0.17 T
Sb^{3+}	0.14T	0.70	0.10	0.11	0.11	0.09	0.10
As^{3+}	0.15T	0.70	0.10	0.11	0.10	0	0
UO_2^{2+}	0.17T	0.25	0.23 T	0.25	0.24 T	0.05	0.07
Th^{4+}	0	0	0	0	0	0	0
Co^{2+}	0.31T	0.50	0.51	0.53	0.54	0.16 T	0.14 T
Hg^{2+}	0.35T	0.70	0.71 T	0.71 T	0.69 T	0.11 T	0.11 T
Ag^+	0.17T	0.12	0.11	0.09	0.11	0	0
Zr^{4+}	0.15T	0.45 T	0.50	0.43 T	0.48	0.05 T	0.06 T
VO^{2+}	0.14T	0.25	0.24	0.25	0.27	0.11 T	0.10
Cd^{2+}	0.35T	0.45	0.48	0.48	0.47	0.17 T	0.18 T
Bi^{3+}	0.31T	0.40 T	0.41 T	0.40	0.41	0.11 T	0.11
W^{6+}	0	0	0	0	0	0	0
Mo^{6+}	0	0	0	0	0	0	0

T-tailed spot [$R_L - R_T > 0.3$]

3.2 Effect of acidity and basicity of medium

Thin layer chromatography of metal ions was performed using 1% aqueous BAC solution prepared in phosphate-borate buffer solutions of different pH values (2.3, 4.0, 5.7, 9.0 and 11.9). The results obtained with the buffered surface solutions are shown in Figure 1. It is apparent from Figure 1 that changes in pH of mobile phase systems had little effect on the mobility of metal ions. Metal ions such as Pb^{2+} , Th^{4+} , W^{6+} , Ag^+ and Mo^{6+} remained near point of application irrespective of the fact whether mobile phase medium used was acidic or basic in nature. At acidic (pH-2.3 and pH-4.0) and basic (pH-9.0 and pH-11.9) metal ion gave spread spot with low mobility. However, better separation possibilities were observed at pH-5.7.



M7 - 1% Aqueous BAC in buffer solution of pH 2.3,

M8 - 1% Aqueous BAC in buffer solution of pH-4.0,

M9 - 1% Aqueous BAC in buffer solution of pH 5.7,

M10 - 1% Aqueous BAC in buffer solution of pH - 9.0,

M11 - 1% Aqueous BAC in buffer solution of pH -11.9

Figure 1: Mobility of metal ions on stannous silicate layer developed in buffer solutions.

3.3 Effect of addition of alcohol

The effect of an alcohol chain length on the mobility of metal ions was examined using mobile phase consisting of aqueous 1% BAC solutions with various alcohols (methanol, ethanol, propanol and butanol) in various ratios (9:1, 8:2, and 7:3 v/v). The mobility of metal ions was the lowest in case of butanol and propanol (M18-M21).

The organic solvents (alcohols) modified the retention mechanism and controlled the relative mobility of metal ions. The added alcohols can affect the CMC, the aggregation number, and the actual strength of the micelle assembly. The results shown in Figure 2 indicate that upon increasing the added methanol concentration from 10ml to 30ml, the following trends in the mobility of metal ions were observed. A sharp decrease in the R_F values of UO_2^{2+} , VO^{2+} , Ni^{2+} and Co^{2+} from 0.8 to 0.5 and sharp increase in R_F values of Fe^{3+} , Zr^{4+} , Hg^{2+} , Cu^{2+} and Zn^{2+} from 0.1 to 0.4 were observed on increasing the concentration of added methanol from 10ml to 30ml. The mobility of Sb^{3+} , As^{3+} , Cd^{2+} and Bi^{3+} remained unaltered irrespective of the concentration of added methanol (10ml to 30ml). Nearly same trends of R_F values were observed in all concentration range of ethanol (M15-M17).

R_F value of metal ions decreases as soon as chain length of alcohol increases from ethanol to butanol. Time required for separation was also more in case of propanol and butanol mobile phase at all concentrations. Metal ions such as Pb^{2+} , Th^{4+} , W^{6+} and Mo^{6+} were strongly retained by stannous silicate and remained at the point of application.

3.4 Effect of addition of strong and weak electrolyte

The effect of addition of weak electrolyte (CH_3COOH) and strong electrolyte ($NaCl$) at different concentration levels in the eluent 1% aqueous BAC on the mobility of metal cations was examined. The R_F values of metal cations were determined with surfactant–water–electrolyte mobile phase consisting of $NaCl$ (1g and 3g) and CH_3COOH (1ml and 3ml) and 1% BAC. From the available data in Table 3, following trends are noticeable.

- 1) Higher mobility and compact spots were obtained in mobile phase containing weak electrolytes CH_3COOH as compared to mobile phase containing strong electrolyte $NaCl$.
- 2) In acetic acid added mobile phase system, mobility was found to increase as soon as concentration of acetic acid increases from 1ml to 3ml.
- 3) Pb^{2+} , Th^{4+} , Ag^+ , W^{6+} and Mo^{6+} did not show any mobility in all cases of mobile phase containing both electrolytes.

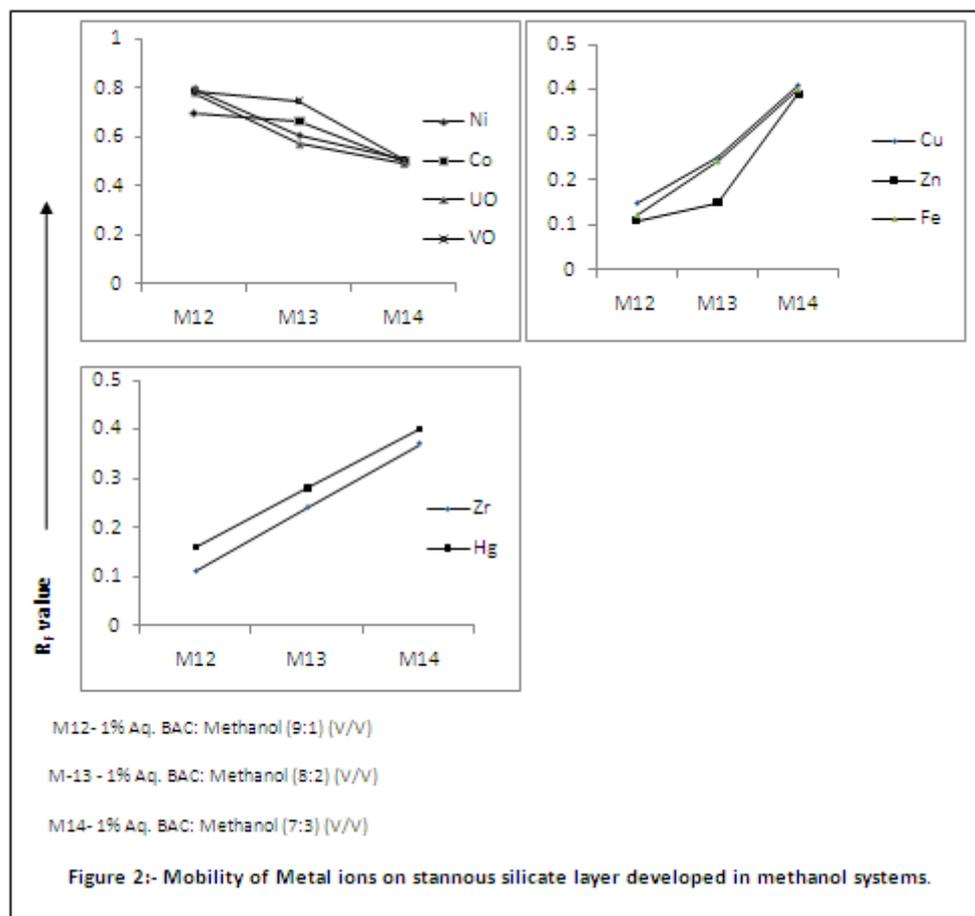
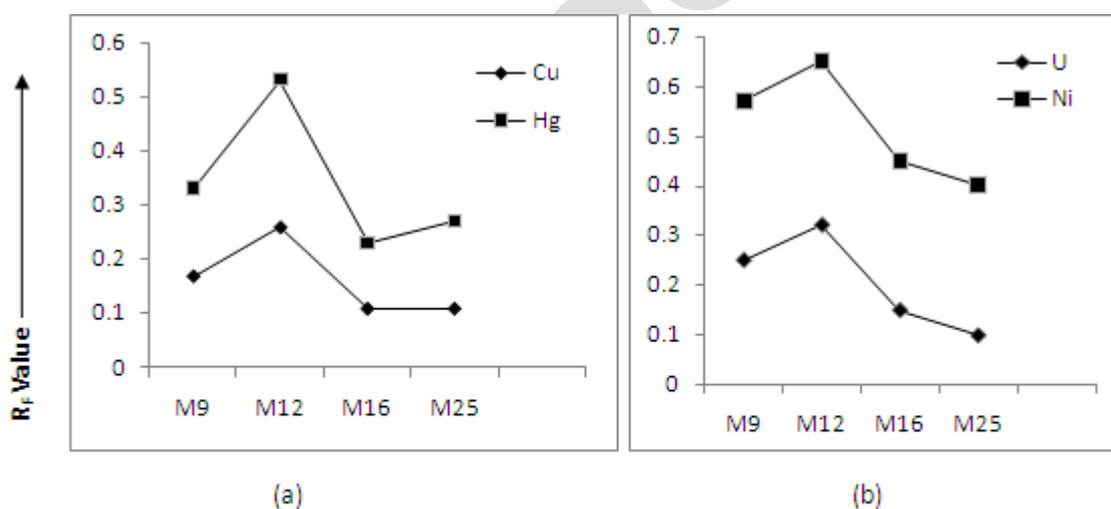


Table 3: R_f value of the metal cations obtained on stannous silicate layer developed with strong and weak electrolyte added in 1% BAC mobile phase systems.

Metal	NaCl		CH ₃ COOH	
	M22	M23	M24	M25
Cu ²⁺	0.12	0.12	0.34	0.45
Zn ²⁺	0.09	0.12	0.29	0.38
Pb ²⁺	0	0	0	0
Fe ³⁺	0.13	0.11	0.3	0.35
Ni ²⁺	0.2	0.19	0.45	0.65
Sb ³⁺	0.15	0.14	0.55	0.75
As ³⁺	0	0	0	0
UO ₂ ²⁺	0.11	0.09	0.18	0.28
Th ⁴⁺	0	0	0	0
Co ²⁺	0.18	0.19	0.45	0.65
Hg ²⁺	0.21	0.22	0.56	0.65
Ag ⁺	0	0	0	0
Zr ⁴⁺	0.07	0.07	0.57	0.67
VO ²⁺	0.07	0.07	0.57	0.65
Cd ²⁺	0.08	0.09	0.12	0.28
Bi ³⁺	0.11	0.13	0.14	0.3
W ⁶⁺	0	0	0	0
Mo ⁶⁺	0	0	0	0



M9- 1% Aqueous BAC in buffer solution of pH 5.7,

M12- 1% Aq. BAC: Methanol (9:1) (V/V)

M16- 1% Aq. BAC: Ethanol (8:2) (V/V)

M25- 1% aqueous BAC containing 3ml acetic acid per 100ml

Figure 3: Separation of cations from their binary mixtures.

3.5 Binary mixture separation

From all above conclusions, by using some mobile phase we were able to separate metal cations from their binary mixtures. In this section, we had taken two binary mixtures, Cu²⁺ - Hg²⁺ and UO₂²⁺ - Ni²⁺. Mobile systems M9, M12, M16 and M25 were used for separation of this binary mixture. Results are shown in Figure 3 (a) and (b).

3.6 Semi-quantitative estimation of Ni²⁺

An attempt has been made to determine the recovery of Ni²⁺ spiked into water using spot area measurement method by using 1% aqueous BAC:ethanol (8:2, v/v) 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 Ni²⁺ has been shown in Figure 3 respectively. The linearity is maintained up to 300 $\mu\text{g}/\text{spot}$. At higher concentration, a positive deviation from linear law was observed. The accuracy and precision was around Ni²⁺ = $\pm 55\%$.

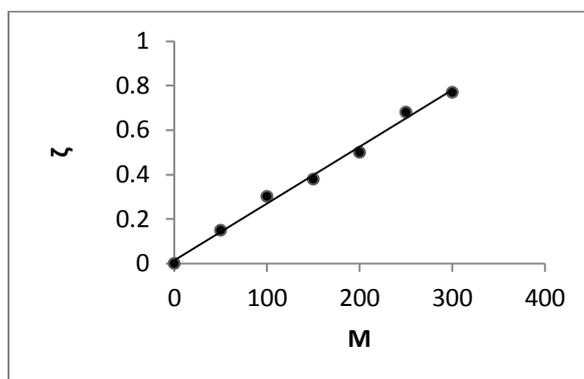


Figure 4: Calibration curve for semi-quantitative determination of Ni²⁺.

4. Application

The proposed method was applied for identification of various heavy metal cations in industrial wastewater and river water sample. Results are presented in Figure 3, which clearly demonstrate that Cu, Hg, Ni and U from their binary mixture can be identified and separated on stannous silicate thin layer plates developed with aqueous BAC surfactant containing organic-inorganic modifier at specific pH.

5. Conclusion

Macromolecular structure and consequently the polarity and absorptivity of stannous silicate are different from other sorbents. The ion exchanger stannous silicate is so selective than in many cases one metal ion can be separated from numerous cations. Normal phase TLC of heavy metal cations has been examined. The surfactant concentration from 1% to 7% resulted in minor changes in the mobility of individual metal ions. In order to achieve effective separations, the surfactant must be used in buffer solutions. The optimum experimental conditions for separating various metal ions include the use of a 1% BAC buffered surfactant solution (pH-5.7) as the mobile phase and stannous silicate as the stationary phase. Aqueous 1% BAC with added alcohols, NaCl or acetic acid resulted in minor changes in mobility of most of the metal ions.

Competing Interests

None declared.

Authors' Contributions

All authors contributed more or less equally to this work.

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