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Inducement of a New Micellar Mobile Phase for Thin-Layer Separation and Quantitative Estimation of Aluminum(III) in Bauxite with Preliminary Separation from Iron(III) and Titanium(IV)

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ABSTRACT

Silica gel has been used as a stationary phase in combination with surfactant-mediated acidic eluents for thin-layer chromatography (TLC) of 14 metal cations. Several combinations of mobile-phase systems comprising different surfactants (anionic, cationic, and nonionic) and carboxylic or mineral acids have been tested for rapid and reliable separation of metal cations. The results obtained on plain silica gel were compared with those obtained on plain alumina, cellulose, and keiselguhr, as well as on mixed

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adsorbents. The TLC system constituting silica gel as a stationary phase and 0.001 M aqueous sodium *bis*(2-ethyl hexyl) sulfosuccinate plus 1.0 M aqueous formic acid (1 : 1, v/v) as a mobile phase was identified as the most favorable system for the separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+} in the presence of common organic and inorganic impurities. The proposed method is rapid and is suitable for identification and separation of Al^{3+}, Fe^{3+}, and Ti^{4+} from sea, river, tap water, and bauxite ores. The separation of microgram quantities of Al^{3+} from milligram quantities of Fe^{3+} or vice versa and parameters such as limits of detection, reproducibility, and repeatability were studied. Quantitative determination of Al^{3+} in bauxite ores was done by TLC spectrophotometer.

Key Words: TLC; Separation; Cations; Spectrophotometric determination.

INTRODUCTION

Several interesting features, such as the possibility of direct observation, use of specific and colorful reactions, cost-effectiveness, reasonable sensitivity, rapidity, excellent resolution power, capability of handling a large number of samples simultaneously, and the applicability of two-dimensional separation, have maintained the continuing popularity of thin-layer chromatography (TLC) as a separation technique. The separation of heavy metal cations has attracted considerable attention in recent years, because of the environmental, technological, and metallurgical importance of these metals. Although many investigations have been made and reported[1–9] of the use of planar chromatographic techniques for the analysis of specific inorganic ions, there have been few studies on the simultaneous analysis of inorganic cations. Yoshinaga et al.[10] have used two-dimensional TLC for the simultaneous detection of 20 inorganic cations, including Al^{3+} and Fe^{3+} on cellulose layer when using two mobile phases, i.e., butanol saturated with a mixture of 3.0 M HNO_3 and 1.0 M HCl (1 : 1), and methanol–36% HCl (10 : 3). Mutual separation of Al^{3+}, La^{3+}, CO^{2+}, and Ni^{2+} by solvent extraction by using *bis*(2-ethyl hexyl) phosphinic acid also has been reported.[11] TLC in combination with scanning densitometry, has been used for the simultaneous determination of Cu^{2+}, Fe^{2+}, and Fe^{3+} in serum[12] as their complexes with 2-[(5-bromo-2 pyridinyl) azo] 5-(diethyl amino) phenol.

A TLC method involving the use of alumina layers and mixed aqueous organic solvent systems as a mobile phase has been used for the analysis of minerals consisting of Mo^{6+}, Au^{3+}, Pb^{2+}, Cr^{3+}, Ti^{4+}, Hg^{2+}, Bi^{3+}, and Mn^{2+}.[13] Copper, iron, and manganese ions in cotton materials have been detected with preliminary separation on microcrystalline cellulose plates developed with acetone–HCl–H_2O (8 : 1 : 2) by using rubeanic acid as a detector.[14] Both Al^{3+} and Fe^{3+} were strongly retained from aqueous solutions at $pH = 4$ by silica gel impregnated with a mixture of aliquot 336 and Alizarin Red S, and, hence, they could not be separated.[15]

Efforts of using silica gel "G" impregnated with mono(2-ethyl hexyl) acid phosphate[16] or high molecular weight amines[17] failed to resolve Ti^{4+} and Fe^{3+}. Similarly, Li^{+}-impregnated silica gel layers with formate ion containing eluents were found to be ineffective to separate Al^{3+} from Fe^{3+}.[18] Our earlier efforts to separate coexisting and Fe^{3+} by using tributylamine as an impregnant of silica layer[19] or as a component of the eluent[20] did not bear fruit. Although binary separation of Fe^{3+}, either from Ti^{4+} or from Al^{3+}, was always possible, separation from its ternary mixture was impossible.

Reversed-phase extraction TLC of inorganic ions performed with H_2SO_4 and $(NH_4)_2SO_4{-}H_2SO_4$ mobile phases on silica gel impregnated with tri-*n*-octylamine was very effective for selective separation of Cr^{3+} from associated metal ions, but Al^{3+}, Fe^{3+}, and Ti^{4+} were found to demonstrate the identical mobility trends.[21]

The TLC methods reported to date record good separation of Fe^{3+}, Ti^{4+}, and Al^{3+} from their binary mixtures, but none of these procedures claim the simultaneous separation of these metal cations from their ternary mixtures. However, paper electrophoresis has been used for quantitative separation of Al^{3+}, Ti^{4+}, and Fe^{3+} from a sample of bauxite[22] by using lactic acid as a carrier electrolyte. Ti^{4+} migrates toward the cathode during electrophoresis. This procedure suffers from the following limitations:

a. It lacks rapidity as the time of run was 5½ hr.
b. Interference of inorganic and organic species on the mutual separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+} ions has not been examined.
c. The effect of sample pH on the separation has not been investigated.
d. The influence of a large quantity of one component on the separation of another component in the mixture has not been studied.
e. Repeatability and reproducibility of the method has not been examined.

Aerosol OT; sodium bis(2-ethythexyl) sulfosuccinate (AOT) is one of the most widely studied anionic surfactants by physical scientists and biochemists,[23] because it is capable of forming cosurfactant free microemulsions and it exhibits remarkably rich aqueous-phase behavior. However, its use by analytical chemists in chemical analysis is lacking. An effort has been made to use reversed micelles of AOT formed in hexane as a mobile phase in normal-phase chromatographic analysis of phenol, naphthol, and 2,4-dinitro toluene by using both silica and bonded-phase columns.[24] As far as we are aware, no work has been reported on the use of an AOT–water–formic acid system as an eluent in TLC analysis of metal cations.

After a careful survey of the recent literature on planar chromatographic analysis of metal cations,[25–27] we reached the conclusion that the analytical potential of formic acid containing eluents has not been fully realized. It, therefore, was decided to use normal micelles of AOT with added aqueous formic acid solution as a mobile phase in TLC analysis of heavy metal cations. The literature data also show that simultaneous separation of Al^{3+}, Fe^{3+}, and Ti^{4+} is very interesting and analytically difficult. It, therefore, was decided to obtain full separation of the ternary mixture composed of Al^{3+}, Fe^{3+}, and Ti^{4+} by TLC. The proposed method has been successfully applied for the analysis of bauxite ore. Although inductively coupled plasma- atomic emission spectroscopy (ICP-AES) or intuctively coupled plasma-mass spectroscopy (ICP-MS) are more sensitive and reliable techniques for the analysis of Al, Fe, and Ti, TLC, being inexpensive, is more suitable for routine analysis. Furthermore, this is the first report that describes the applicability of micellar mobile phase system in TLC separation of coexisting aluminum, iron, and titanium ions.

EXPERIMENTAL

All experiments were performed at 30 ± 5°C.

Apparatus

A TLC apparatus (Toshniwal, Mumbai, Maherachtra, India). A $20 \times 3.5\text{-cm}^2$ glass plates and $24 \times 6\text{-cm}^2$ glass jar, spectrophotometer (ELICO, SL, 171, Hydrabad, Andhra Pradesh, India), and pH meter (ELICO 181E, Hydrabad, Andhra Pradesh, India) were used.

Reagents

Silica gel "G," formic acid, citric acid, tartaric acid, acetic acid, oxalic acid, hydrochloric acid, sulfuric acid, and nitric acid (E. Merck. India); cellulose microcrystalline, kieselguhr, alumina, cetyl-trimethyl ammonium bromide (CTAB) (CDH, India); sodium dodecyl sulfate (SDS) (Qualigens, India); Brij 35, Triton-l00 (Loba chemie, India); and AOT (BDH, England) were used without further purification.

Test Solutions

Standard aqueous test solutions, 1%, were nitrate, sulfate, and chloride of Al^{3+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+} Mo^{6+}, VO^{2+}, Cr^{6+}, and

Zn^{2+}. For Fe^{3+}, 1% ferric chloride solution was prepared in 1% aqueous HCl, whereas, 1% titanium tetrachloride solution was prepared in 0.5% aqueous HCl. The titanium solution was stable for 3–4 weeks.

Detectors

Mo^{6+} with 1% aqueous ferric chloride; Fe^{3+}, Cu^{2+}, Ti^{4+}, and VO^{2+} with 1% aqueous potassium ferrocyanide; Ni^{2+} and Co^{2+} with 1% alcoholic dimethyl glyoxime in ammonia; Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} with 0.5% dithizone in carbon tetrachloride; Al^{3+} with 0.1% aqueous aluminon solution; Mn^{2+} with 2 M aqueous NaOH in 30% H_2O_2 in 1 : 1 (v/v) and Cr^{6+} with saturated solution of $AgNO_3$ in methanol were detected.

The following stationary mobile phase were used.

Symbol	Composition
Stationary phase	
S_1	Silica gel "G"
S_2	Alumina
S_3	Alumina + silica gel "G" (1 : 9; w/w)
S_4	Alumina + silica gel "G" (1 : 1; w/w)
S_5	Aluminia + silica gel "G" (9 : 1; w/w)
S_6	Cellulose
S_7	Cellulose + silica gel "G"(1 : 9; w/w)
S_8	Cellulose + silica gel "G"(1 : 1; w/w)
S_9	Cellulose + silica gel "G"(9 : 1; w/w)
S_{10}	Kieselguhr
S_{11}	Kieselguhr + silica gel "G"(1 : 9; w/w)
S_{12}	Kieselghur + silica gel "G" (1 : 1; w/w)
S_{13}	Kieselghur + silica gel "G" (9 : 1; w/w)
Mobile phase	
Aqueous surfactant solutions	
M_1	0.0001 M AOT
M_2	0.001 M AOT
M_3	0.01 M AOT
Aqueous surfactant solution with carboxylic,[a] and mineral acids[a]	
M_4	M_2 + formic acid (1 : 1; v/v)
M_5	M_2 + formic acid (1 : 1; v/v)
M_6	M_2 + formic acid (1 : 1; v/v)
M_7	M_2 + acetic acid (1 : 1; v/v)
M_8	M_2 + oxalic acid (1 : 1; v/v)

(*continued*)

Symbol	Composition
M_9	M_2 + tartaric acid (: 1; v/v)
M_{10}	M_2 + citric acid (1 : 1; v/v)
M_{11}	M_2 + hydrochloric acid (1 : 1; v/v)
M_{12}	M_2 + sulfuric acid (1 : 1; v/v)
M_{13}	M_2 + nitric acid (1 : 1; v/v)
Aqueous surfactant solution with mononcarboxylic acid[a] (formic acid)	
M_{14}	0.001 M CTAB + formic acid (1 : 1; v/v)
M_{15}	0.001 M SDS + formic acid (1 : 1; v/v)
M_{16}	0.001 M Triton-100 + formic acid (1 : 1; v/v)
M_{17}	0.001 M Brij 35 + formic acid (1 : 1; v/v)

[a] Acids were taken as 1.0 M aqueous solution.

Preparation of TLC Plates

Plain Silica Gel, Cellulose, Alumina, and Kieselguhr

Plain silica gel plates were prepared by mixing silica gel with double-distilled water in 1 : 3 ratio with constant shaking until a homogeneous slurry was obtained. The resultant slurry was applied to the glass plates with the help of an applicator to give a 0.25-mm-thick layer. The plates were dried at room temperature and then activated at $100 \pm 5°C$ by heating for 1 hr. The activated plates were stored in a closed chamber at room temperature. Similarly, TLC plates of plain cellulose, alumina, and kieselguhr were prepared following the above mentioned process.

Mixed Silica Gel–Cellulose, Alumina, or Kieselguhr Plates

The mixtures containing cellulose, alumina, or kieselguhr, and silica gel "G" in different ratios (9 : 1, 1 : 1, 1 : 9 w/w) were slurried with double-distilled water in 1 : 3 ratio by shaking until a homogeneous slurry was obtained. Thin layers of resultant slurry were prepared by following the method as described above.

Preparation of Analyte Samples

Preparation of Spiked Seawater, Tap Water, and River Water

A total of 5 mL each of sea water (pH 8.47, collected from Anjana beach of the Arabian Sea, Goa, India), river water (pH 7.50 collected from Ganga

River at Naraura, India), and tap water (pH 7.23) was spiked with a 1-mL solution each of Al^{3+}, Fe^{3+}, and Ti^{4+} salts, and the resultant pH of the spiked samples were 1.83, 1.34, and 1.23, respectively. Aliquots, 0.01 mL of resultant samples were applied separately on three activated TLC plates (S_1), and chromatography was performed.

Preparation of Bauxite Solution

Sample solutions (1%) of bauxite was prepared by adding 10-mL concentrate HCl in 1-g bauxite ore sample followed by adding 5-mL concentrate HNO_3 and 15-mL (1 : 1) dilute H_2SO_4. The contents were heated at 100°C for 1 hr. The SiO_2 present in the sample was separated by filtration. Filtrate was completely dried, and the residue was dissolved in 1% HCl. The total volume was increased to 100 mL by adding 1% HCl.

Preparation of Spiked Bauxite Solution

Bauxite ore solution (5 mL), as prepared above, was spiked only with 1 mL of 1% solution of titanium tetrachloride and 0.01 mL of resultant spiked sample was applied on activated TLC plate (S_1), and chromatography was performed. The samples were spiked because we could not detect Ti^{4+} in real bauxite sample solutions, as described above on TLC plates.

Procedure

About 0.01 mL of test solutions, spiked ore solution or unspiked ore solutions was spotted separately on activated TLC plates (S_1). The spots were air dried and were developed with solvent systems (M_1–M_{17}) by the ascending technique up to 10 cm from the point of application in glass jars. After the development, the plates were withdrawn from glass jars, air dried, and sprayed with suitable detectors to locate the position of the analyte as a colorful spot. The R_L and R_T values for detected spots were determined, and the R_F value was calculated.

For separation, equal volumes of metal cations were mixed and 0.01 mL of the resultant mixture was loaded on the activated TLC (S_1–S_{13}) plates. The plates were developed with selected mobile phase M_5, the spots were detected, and R_F values of the separated metal cations were calculated.

To study the effect of the presence of organic and inorganic species as impurities on the separation of metal cations, 0.01 mL each of Al^{3+}, Fe^{3+}, and Ti^{4+} metal cations standard test solutions was spotted onto the TLC plates (S_1) followed by the 0.01 mL spotting of organic or inorganic species (which were considered impurities). The plates were developed with M_5, detected, and R_F values of the separated metal cations were calculated.

The limits of detection of the metal cations were determined by spotting 0.01 mL of metal salt solutions onto the TLC plates (S_1), which were developed with M_5, and the spots were visualized by using the appropriate detector. This process was repeated with successive reduction of the concentration of the metal salts by adding demineralized double-distilled water, except Ti^{4+} for which 1% aqueous HCl was used for dilution, until no detection was possible. The amount of metal just detectable was taken as the detection limit.

To achieve the separation and detection of metal cations at different pH values, the pH of the test samples were brought to the required value by adding borate phosphate buffer solutions of different pH.

For microgram separation of Fe^{3+} from milligram quantities of Al^{3+}, a TLC plate (S_1) was spotted with 0.01 mL of iron salt solution containing 3.43 μg Fe^{3+}, followed by spotting of 0.01 mL of aluminum salt solution containing 1.27–2.53 mg Al^{3+} at the same place. The spots were dried; the plates developed with M_5, visualized, and R_L and R_T values determined for both the metal cations. The same procedure was followed for microgram separation of Al^{3+} from milligram quantities of Fe^{3+} for which S_1 was spotted with 1.26 μg Al^{3+} and 0.17–0.51 mg Fe^{3+}.

Spectrophotometric Determination of Aluminum

Spectrophotometry of aluminum after TLC separation from iron and titanium was carried out as follows. A sample of aluminum nitrate solution containing 3.16–38.01 μg of aluminum was treated with 1 mL of 0.1% aqueous aluminon, and the volume was made up to 10 mL with demineralized double-distilled water. After thorough mixing, the solution was left for 10 min for complete color development. The absorption spectrum of this solution against reagent blank over 400–680 nm gave a maximum absorbance peak at 540 nm (λ_{max}) by using 1 cm cells, and a standard curve was constructed (Fig. 1a). The color produced with aluminum was stable and proportional to aluminum concentration.

This spectrophotometric method was used to determine aluminum. The recovery of aluminum after separation from iron and titanium was determined as follows.

Different volumes (0.01–0.12 mL) of aluminum nitrate solution containing 3.16–38.01 μg aluminum were spotted on the TLC (S_1) plates. After the spots were completely dried, 0.1 mg of iron and titanium salt solutions were spotted on the same spot on the TLC (S_1) plates, and the plates were redried at room temperature. The dried plates were developed in M_5. A pilot plate also was run simultaneously to locate the position of aluminum. After development, the region containing the aluminum spot on the pilot plate was detected the corresponding region on the working plates (undetected spot) was marked and this area of adsorbent was scraped into a clean beaker and followed by adding 25 mL of demineralized double-distilled water. The beaker was kept in an oven at 60°C for 1 hr. The adsorbent was separated from the solvent by filtration process and followed by washing of the adsorbent with demineralized double-distilled water to ensure complete extraction of aluminum. The filtrate was kept on a water bath for complete removal of formic acid (it would be present in scraped adsorbent due to the mobile phase M_5 used). The residue was dissolved in demineralized double-distilled water (2 mL) and 1 mL chromogenic reagent (0.1% aqueous aluminon) was added to it. The total volume in each case was maintained to 10 mL by using demineralized double-distilled water. The solution was left for complete color development for 10 min. The absorbance spectra of this solution was measured against reagent blank at 540 nm; λ_{max} by using 1-cm cells and a recovery curve was constructed [Fig. 1(b)].

The percentage recovery of aluminum after its chromatographic separation from iron and titanium, and the relative error were obtained. The constructed standard curve was used to estimate the aluminum present in different bauxite ores collected from Madhya Pradesh, central India, and east coastal region.

For checking repeatability of R_F values, equal volumes of 1% metal salt solutions of Ti^{4+}, Fe^{3+}, and Al^{3+} were mixed and 0.01 mL of the resultant mixture was loaded on the activated TLC plates (S_1). The plate was developed with M_5, and spots were detected. The same process was repeated five times by the same analyst within a day (short interval of time), and the R_F value of separated metal cations were calculated.

For reproducibility, the same process as mentioned above, was repeated by different analysts in the same laboratory for 7 days.

RESULTS AND DISCUSSION

The result of this study has been summarized in Tables 1–3 and Figs. 2–3. The mobility of 14 metal cations were examined on silica gel G layer by using aqueous solution of AOT. The interesting unique features of this study are:

1. Selection of micellar systems composed of anionic surfactant, AOT as a mobile phase. The AOT bears a fraction of a negative charge and tends to attract positively charged species, including metal cations.

Table 1. R_F of metal cations with different surfactant (AOT) concentrations.

Metal cations	M_1	M_2	M_3
Fe^{3+}	0.08	0.11	0.09
Cu^{2+}	0.08	0.10	0.06
Ni^{2+}	0.78T	0.82T	0.65T
Co^{2+}	0.62	0.63	0.66
Ti^{4+}	0.0	0.0	0.0
Pb^{2+}	0.0	0.0	0.0
Zn^{2+}	0.08	0.11	0.09
Hg^{2+}	0.20 T	0.15	0.22 T
Cd^{2+}	0.30	0.28	0.35T
Al^{3+}	0.05	0.09	0.10
Mn^{2+}	0.44	0.54	0.50
Mo^{6+}	0.98	0.98	0.97
Cr^{6+}	0.50 T	0.86	0.91
VO^{2+}	0.08	0.13	0.09

Note: T, tailed spot ($R_L - R_T > 0.3$).

2. Utilization of formic acid as an additive in the mobile phase. Formic acid being a carboxylic acid is capable of forming complexes with certain metal ions[28] and is sufficiently acidic [Ka(H_2O) at 25°C = 1.77×10^{-4}] to check the hydrolysis of salts. Its reducing properties do not permit the oxidation of metal cations during analysis. The acidic developers containing formic acid are less affected by silica gel properties and provide excellent resolution of aflatoxins[29] and cations.[30]
3. Realization of mutual separation of Al^{3+}, Fe^{3+}, and Ti^{4+} from their mixtures and examination of effect of various factors on the separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+} ions.

Table 2. R_F of metal cations on silica gel "G" layers developed with different mobile-phase systems.

Mobile phase	Separation
M_3	Cr^{6+} (0.92)–Mn^{2+} (0.51)–Cu^{2+} (0.05)/VO^{2+} or Fe^{3+} (0.07)/ Ti^{4+} (0.0)/Zn^{2+} or Al^{3+} (0.09).
M_4	Co^{2+} (0.77)–Al^{3+} (0.52)–Fe^{3+} (0.18)/Pb^{2+} or Ti^{4+} (0.07)
M_5	Ni^{2+} (0.86)/Mn^{2+} (0.84)/Co^{2+} (0.90)/Zn^{2+} (0.80)/Cd^{2+} (0.85)/ Hg^{2+} (0.76)/Al^{3+} (0.81)–Fe^{3+} (0.51)–Pb^{2+} or Ti^{4+} (0.0)

Table 3. R_F of Al^{3+}, Fe^{3+}, and Ti^{4+} cations from spiked and bauxite ore samples.

	Separations (R_F)		
Samples	Al^{3+}	Fe^{3+}	Ti^{4+}
Mobile phase: M_5			
Seawater	0.77	0.30	0.0
River water	0.81	0.52	0.0
Tap water	0.83	0.51	0.0
Central India bauxite	0.80	.043	ND
Spiked central India bauxite	0.81	0.43	0.0
East coastal bauxite	0.81	0.44	ND
Spiked east coastal bauxite	0.80	0.45	0.0
Madhya Pradesh bauxite	0.83	0.52	ND
Spiked Madhya Pradesh bauxite	0.83	0.51	0.0

Note: ND, not detected.

4. Quantitative determination of Al^{3+} by spectrophotometry with preliminary separation from other metal cations.
5. Application of proposed method to the analysis of several real and synthetic samples containing Al^{3+}, Fe^{3+}, and Ti^{4+}.

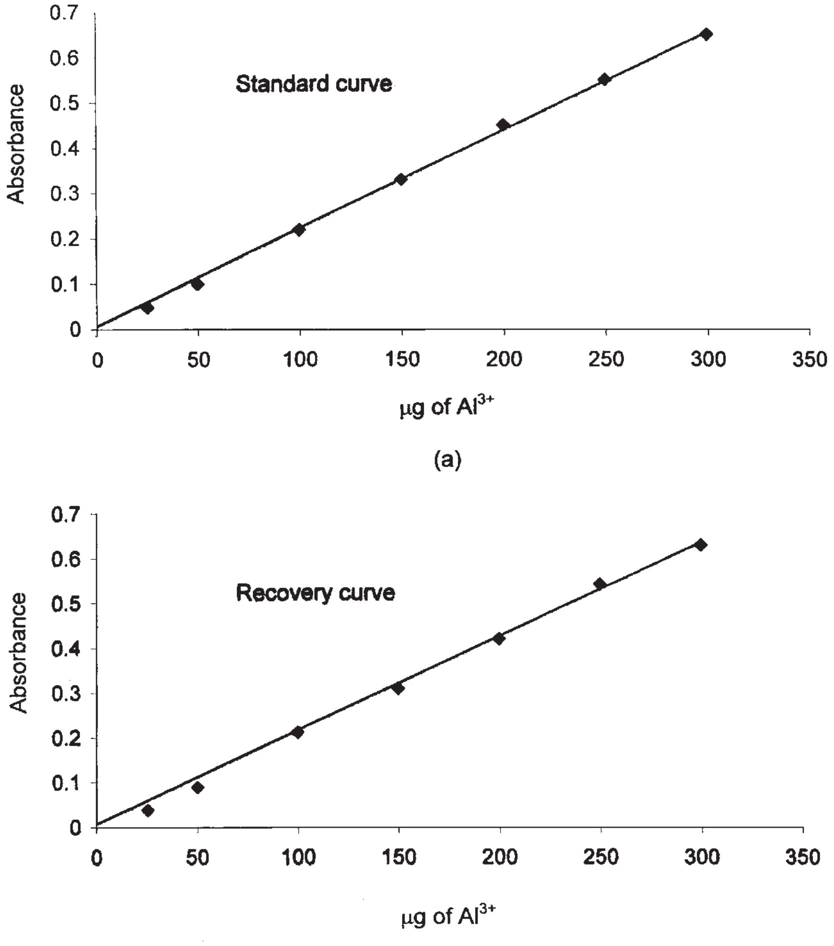
Optimization of Mobile Phase System

Effect of Concentration of Surfactant on Mobility of Metal Cations

To examine the effect of concentration levels of surfactant on the mobility of metal cations, chromatography was performed on silica gel layers by using different concentrations of surfactant in a mobile phase (M_1–M_3). This concentration range of AOT was selected to perform the chromatography with mobile phase systems, which have the surfactant concentration (a) below its critical micelle concentration (cmc) value; (b) near cmc; and (c) above cmc.

The R_F values of metal cations obtained in aqueous solutions of AOT (M_1–M_3) at various concentration levels have been presented in Table 1. From the data of Table 1 the following conclusions are drawn:

i. Metal cations such as Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, and VO^{2+} show very little mobility ($R_F \simeq 0.08$), whereas, Ti^{4+} and Pb^{2+} show no mobility ($R_F = 0.0$) at all concentration levels of aqueous AOT.



(a)

(b)

Figure 1. Standard (a) and recovery curves (b) for spectrophotometric determination of Al^{3+}.

ii. Ni^{2+} produces badly tailed spots at all concentrations of AOT. Hg^{2+} shows tailed spots at AOT concentration levels of 0.0001 and 0.01 M, whereas, it produces a well-formed compact spot at 0.001 M AOT. This observation indicates that tailed spots for Hg^{2+} occur when the surfactant concentration is either below or above its cmc value. The cmc of AOT is 0.00064 M. Cd^{2+} shows tailed spots only with a M_3 (AOT = 0.01 M) mobile phase.

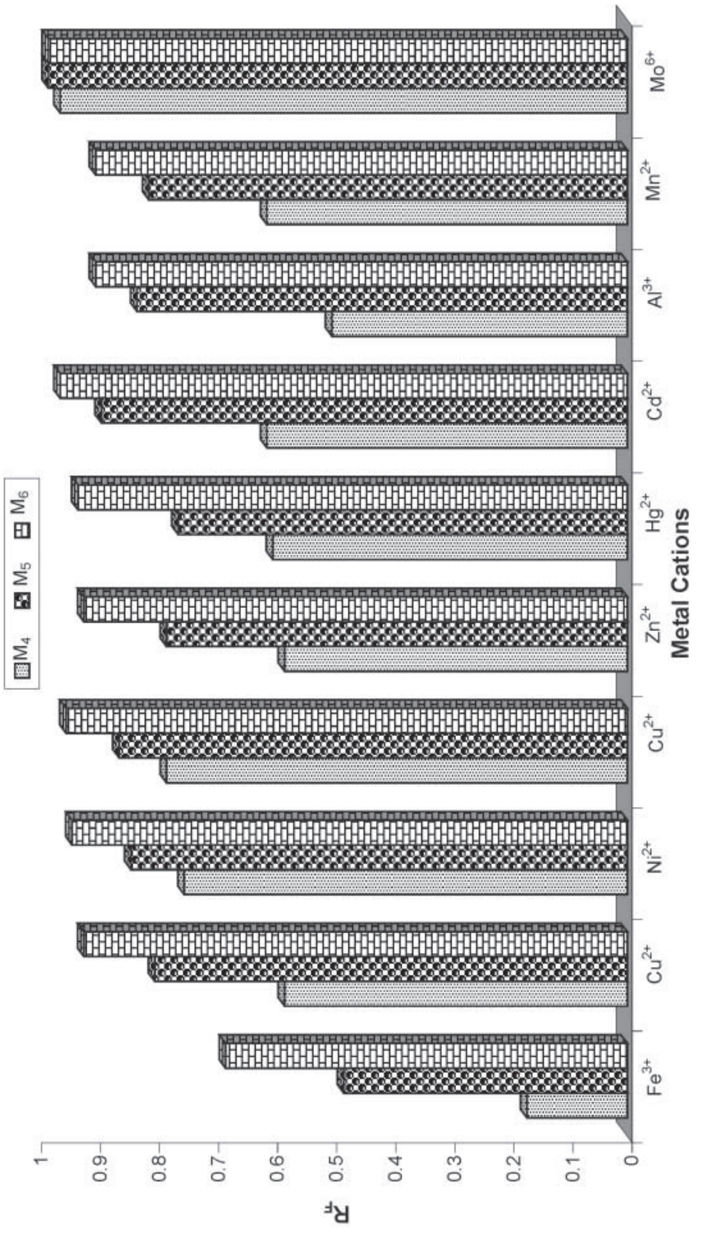


Figure 2. Effect of formic acid concentration of mobility of metal cations Ti^{4+} and Pb^{2+} show zero R_F.

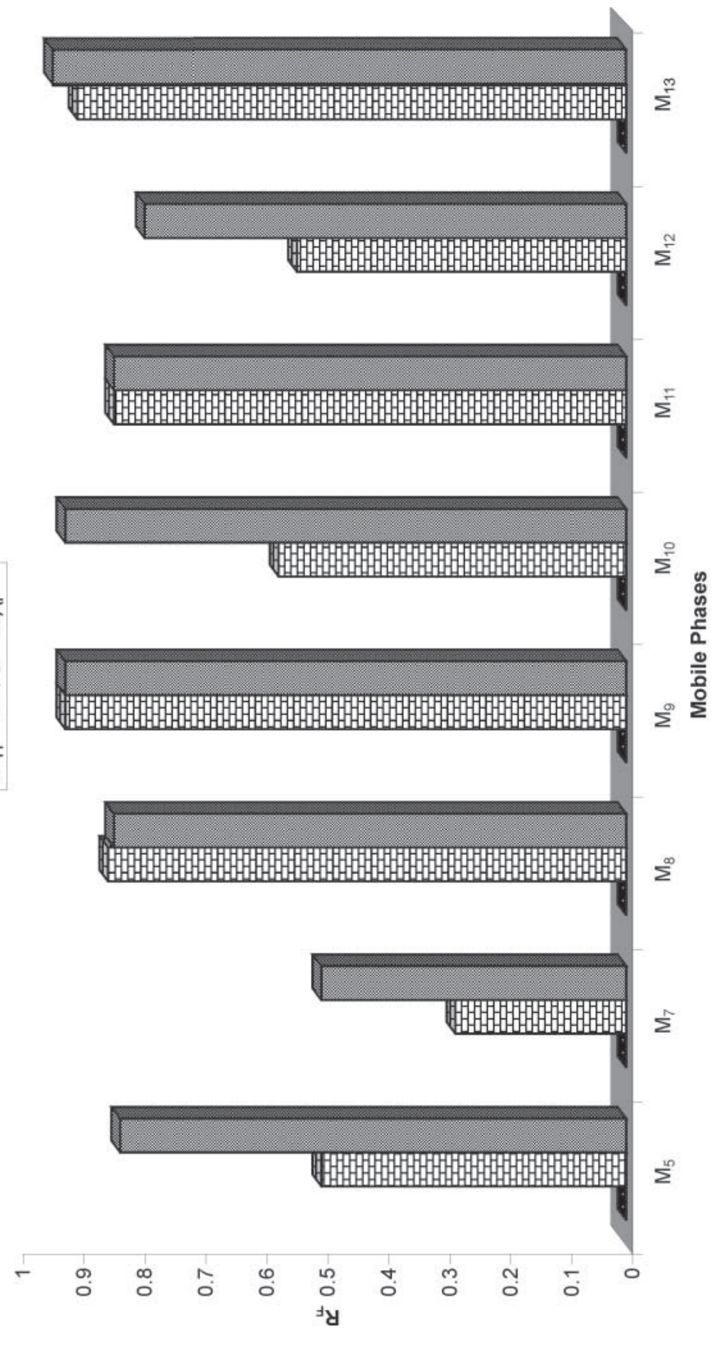


Figure 3. Effect of added carboxylic and mineral acid in M_2 (0.001 M AOT) Al^{3+} with M_7 and Fe^{3+} with M_7 and M_{10} show tailed spots.

iii. Co^{2+} and Mn^{2+} show intermediate R_F values that fluctuate between 0.62–0.66 and 0.44–0.54 for Co^{2+} and Mn^{2+} respectively.
iv. Mo^{6+} shows constant and high mobility ($R_F = 0.98$) and forms well-formed compact spots at all concentration levels.
v. Mobility of Cr^{6+} increases with the increase in concentration of AOT. However, badly tailed spots at concentration level below the cmc of AOT (M_1) were observed.

As more compact spots for cations were realized at 0.001 M AOT, this mobile phase (M_2) was selected for further studies.

Synergistic Effect of Formic Acid on Mobility of Metal Cations

The effect of formic acid, a monocarboxylic acid, on the mobility of metal cations was studied, using a mobile phase consisting of 0.001 M AOT and formic acid in different volume ratios (M_4–M_6). The R_F values of metal cations observed with these mobile phases are presented in Fig. 1. From this figure, the following trends about the mobility of metal ions are noticeable.

i. Mobility of most of the metal cations, such as Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Al^{3+}, and Mn^{2+}, was found to increase with an increase in the volume ratio of formic acid with 0.001 M AOT in mobile phase systems (M_4–M_6)
ii. VO^{2+} shows badly tailed spots at all volume ratios of formic acid.
iii. Ti^{4+} and Pb^{2+} remain at the point of application, regardless the concentration level of formic acid.
iv. Cr^{6+} forms double spots; the first spot appears near the solvent front ($R_F = 0.93$) on a TLC plate, whereas, the second spot appears in the middle of the plate. The R_F value of second spot depends on the forming acid concentration and varies from $R_F = 0.52$ to 0.64 with the increase in volume ratio of formic acid in the mobile phase systems (M_4–M_6) containing 0.001 M AOT.

It was observed that formic acid acts as a promoter of mobility, it is probably due to the higher density of H^+ ions in formic acid containing mobile phase systems, which compete with the cation for the exchange on silica gel layer, with enhanced compactness of spots for most of metal cations with exception of VO^{2+}.

From the above studies, a TLC system constituting of silica gel as a stationary phase (S_1) and 0.001 M aqueous AOT plus 1 M aqueous HCOOH in a 1 : 1 ratio as a mobile phase (M_5) was identified as the most favorable system for the separation of Ti^{4+}, Fe^{3+}, and Al^{3+} from their mixtures.

The order of mobility (R_F, given in parenthesis) was Al^{3+} (0.83) > Fe^{3+} (0.48) > Ti^{4+} (0), which is analogous to the mobility trend reported by Lacourt et al.,[31] who separated these cations by paper chromatography when using formic acid containing eluents.

To search out the most favorable experimental conditions for mutual separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+} ions, the following factors were examined.

Effect of Carboxylic and Mineral Acid on Mobile Phase

To understand the effect of carboxylic and mineral acids on the separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+}, formic acid (1.0 M) in M_2 was replaced by 1.0 M of other acids, and the resultant mobile phase systems were used for chromatography. The obtained results, as shown in Fig. 2, indicate the following trends.

i. Mineral (HCl and HNO_3) and carboxylic (citric, tartaric, acetic, and oxalic) acids have serious influence on the mobility of Al^{3+} and Fe^{3+} and, hence, hamper the separation.
ii. Ti^{4+} could not be detected in the presence of citric, tartaric, oxalic, hydrochloric, and nitric acids.
iii. The simultaneous separation of Al^{3+}, Fe^{3+}, and Ti^{4+} is possible only with mobile phase system containing either formic (M_5) or sulfuric (M_{12}) acid in combination with AOT.
iv. Compared with H_2SO_4, better separation was with formic acid containing eluent because of the formation of more compact spots of analytes.

Effect of Added Surfactants in the Mobile Phase

The effect of the nature of surfactants (anionic, cationic, and nonionic) of the same molarity (0.001 M) added to 1.0 M formic acid in a 1 : 1 ratio (M_{14}–M_{17}), on separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+}, was studied. It was found that the mobility of Ti^{4+} ($R_F = 0.0$) remains unaltered, irrespective of the nature of surfactant in the mobile phase (M_{14}–M_{17}). However, a little change in R_F values for Fe^{3+} and $A1^{3+}$ was observed. The cationic surfactant (CTAB) containing a mobile phase (M_{14}) promotes the mobility of both Fe^{3+} ($R_F = 0.67$) and Al^{3+} ($R_F = 0.90$) from their standard R_F values 0.48 and 0.83, respectively, in M_5, without hampering the possibilities of simultaneous separation of Al^{3+}, Fe^{3+}, and Ti^{4+}.

Effect of Nature of Sorbent Layers

To establish the effectiveness of silica gel “G”, the mutual separation of Al^{3+}, Fe^{3+}, and Ti^{4+} was examined by using different sorbent layers.

Thin layers of pure cellulose, alumina, and kieselguhr G fail to resolve the three-component mixture of Al^{3+}, Fe^{3+}, and Ti^{4+}. Separation of coexisting Al^{3+}, Fe^{3+}, and Ti^{4+} is possible only if silica gel "G" is kept $\geq$50% (w/w) in mixed adsorbent thin layers. Low-weight ratios of silica gel G with alumina, cellulose, and keiselguhr G causes tailing in Fe^{3+}.

Effect of Impurities

The presence of heavy-metal cations, pesticides, phenols, alcohols, ketones, and urea in the sample as impurities does not influence the mutual separation of Al^{3+}, Fe^{3+}, and Ti^{4+}, although the R_F value of Fe^{3+} is slightly modified (R_F varies between 0.62 and 0.39) from its standard value ($R_F = 0.48$) in the presence of impurities. Amines (dimethyl, triethyl, and tributyl) and anions (PO_4^{3-} and SCN^-) were found to hamper the separation. These impurities converted the compact spot of Fe^{3+} into a badly diffused spot.

Effect of pH of Test Sample

It was found that Al^{3+}, Fe^{3+}, and Ti^{4+} can be easily separated from each other up to pH 2.3. At higher sample pH, Ti^{4+} and Fe^{3+} are precipitated. Thus, separation of coexisting Fe^{3+}, Al^{3+}, and Ti^{4+} is possible, only up to pH 2.30 of the sample solution.

Effect of Loading Amount of Analyte

It was observed that 3.43 μg of Fe^{3+} can easily be separated from 1.78 mg of Al^{3+}. Similarly, 1.26 μg of Al^{3+} can be separated from 0.40 mg of Fe^{3+}. Thus, milligram quantities of one metal cations can be separated successfully from microgram amounts of other cation by using the proposed TLC system.

Limit of Detection

The lowest possible detectable nanogram amounts (given in parenthesis) of heavy-metal cations obtained on silica gel "G" layers (S_1) developed with M_5 were Fe^{3+} (42.5), Al^{3+} (0.5), and Ti^{4+} (200.8). These data show that the proposed method is very efficient at identifying these metal cations at trace level.

Quantitative Determination of Al^{3+}

The calibration curve for Al^{3+} was constructed [Fig. 3(a) and (b)]. The absorbance gives a linear relationship in the concentration range 3.16–38.01 μg of Al^{3+}. The maximum recovery of Al^{3+} after the TLC separation from Fe^{3+} and Ti^{4+} is 94%.

It was observed that the percentage amounts of Al^{3+} present in Madhya Pradesh, central India, and east coastal bauxites are 37.75, 62.5, and 57.5, respectively, which fall within the range of percentage content of Al^{3+} actually present in the bauxite ores.

Validation Parameters

The RSD of reproducibility and repeatability of our proposed method were not more than ±4.47% and ±7.085%, respectively.

Applications

Some important separations of metal ions obtained experimentally on silica gel "G" layer (S_1) with mobile phase systems M_3, M_4, and M_5 have been listed in Table 2. The M_3 and M_4 mobile phase are found useful for the separations of coexisting Cr^{6+} (0.92)–Mn^{2+} (0.51)–Cu^{2+}, VO^{2+}, Fe^{3+}, Ti^{4+}, Zn^{2+}, or Al^{3+} (0.05) and Co^{2+} (0.77)–Al^{3+} (0.52)–Fe^{3+}, Pb^{2+}, or Ti^{4+} (0.07), respectively, where as M_5 mobile phase is considered as one of the most favorable mobile phase for the separation of coexisting Ni^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, or Al^{3+}–Fe^{3+}–Pb^{2+} or Ti^{4+} (0.0). The results related to the separation and identification of Al^{3+}, Fe^{3+}, and Ti^{4+} in various spiked matrices and bauxite ore samples are listed in Table 3. From the data listed in Table 3, it is cleared that R_F of Al^{3+} and Fe^{3+} fluctuate from 0.77 to 0.83 and 0.52 to 0.30, respectively; whereas the seawater sample shows the lowest R_F values of Al^{3+} (0.77) and Fe^{3+} (0.3). In the case of the bauxite samples, the R_F value of Fe^{3+} (0.43) is slightly lowered in the case of central India and east coastal bauxite. The Ti^{4+} shows no mobility and remains at the point of application. Whereas, in bauxite samples Ti^{4+} is not detectable because of lower amount than limit of detection. These data clearly demonstrate the applicability of the proposed method for simultaneous separation of Al^{3+}, Fe^{3+}, and Ti^{4+} from a variety of samples.

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