USE OF MICELLAR ANIONIC SURFACTANT SOLUTIONS WITH ADDED CARBOHYDRATES AS MOBILE PHASES IN THIN-LAYER CHROMATOGRAPHY OF HEAVY METAL CATIONS. SEPARATION OF MIXTURES OF ALUMINIUM(III), MANGANESE(II), AND CHROMIUM(VI)

*A. Mohammad** and *H. Shahab*

Analytical Research Laboratory, Department of Applied Chemistry, Z.H. College of Engineering and Technology, Aligarh Muslim University, Aligarh-202002, India

SUMMARY

A new thin-layer chromatographic system comprising silica gel 'G' as stationary phase and a micellar solution of sodium dodecyl sulphate (0.01 M) with added maltose (0.5 M) in 7:3 (*v/v*) ratio has been identified as most favourable for identification and separation of mixtures of aluminium(III), manganese(II), and chromium(VI). The presence of the carbohydrate enhances the separation efficiency of micellar solution of anionic surfactant (i.e. SDS). The experimental conditions were optimized to achieve separation of aluminium, manganese, and hexavalent chromium under different experimental conditions of sample pH, layer material composition, presence of foreign substances in the sample, nature of the polar head group of the surfactant, and the nature of the carbohydrate in the micellar mobile phase. The limits of detection and semiquantitative determination of the separated metal cations were also determined.

INTRODUCTION

Micellar solutions with appropriate additives have found numerous practical applications in many areas of separation science. Organic solvents, ionic salts, cyclodextrins, ion-pairing, and complexing agents have been widely used as additives. Nishi et al. [1] resolved nine closely related antibiotics by micellar electrokinetic capillary chromatography using a micellar solution of an anionic surfactant (sodium dodecyl sulphate) with added tetraalkyl ammonium salts as mobile phase. Organic additives such as al-

cohols, diols, dipolar aprotic solvents (DMSO, dioxane), and alkyl nitriles have been found to affect the order of migration of solutes in micellar liquid chromatography [2,3]. Organic modifiers increase the chromatographic efficiency by reducing the amount of adsorbed surfactant on the stationary phase and by reducing the permittivity and increasing the hydrophilicity of the mobile phase [4]. In addition, higher levels of modifier may also lead to increased fluidity of the organic additive-modified, surfactant-coated, stationary phase. Simultaneous enhancement of separation selectivity and solvent strength in micellar chromatography with hybrid micelle–water–organic solvent mobile phases has been observed for different groups of ionic and non-ionic compounds with a variety of functional groups for both anionic and cationic micelles [5]. Publications on micellar liquid chromatography reveal that electrolytes and short-chain alcohols have been generally used as additives [6–8]. These additives have been found to modify the micro-environment of micellar solutions causing salting-in or salting-out effects [9,10]. As far as we are aware, no report is available on the use of micellar solutions with added carbohydrates as mobile phases in chromatography. The work reported from our laboratory [11] has demonstrated the enhanced chromatographic performance of micellar solutions with added inorganic electrolytes, organic molecular compounds, and alcohols in resolving closely related test substances. In continuation of previous studies, we have used anionic micellar solutions with added carbohydrates as mobile phases in thin-layer chromatographic analysis of heavy metal cations. As a result, an aqueous micellar solution of sodium dodecyl sulphate (SDS) with added maltose has been found very useful for selective separation of Mn(II) from all other metal ions studied.

Among the chromatographic techniques available, thin-layer chromatography (TLC) is currently enjoying popularity because of distinct advantages such as low cost, the disposable nature of TLC plates, ease of implementation, the possibility of separating many samples in parallel, the wide choice of detection reagents, reduced need for modern laboratory facilities, and continuous observation of the separation process because of the open nature of the layer. TLC of metal cations on immobilized chondroitin sulphate plates prepared by plasma polymerization techniques [12] and stripping voltammetry for quantitative analysis of heavy metals (Cd^{2+}, Cu^{2+}, and Pb^{2+}) after separation by TLC [13] have generated renewed interest in TLC. Work performed on TLC of inorganic species has been well documented in several reviews [14–18], book chapters [19,20], and research papers [21–23]. In micellar thin-layer chromatography (MLTC) of inorganic

species [24–26], mobile phases comprising SDS plus NaCl or thiourea have been found most suitable for identification and separation of Ag^+ from several other metal cations [11].

This communication reports the use of a new micellar mobile phase with added organic molecular compounds (e.g. carbohydrates) for analysis of heavy metal cations. The TLC system proposed enables very reliable rapid separation of mixtures of Al(III), Mn(II), and Cr(VI) in addition to highly selective separation of Mn(II) from all other metal cations studied.

EXPERIMENTAL

All experiments were performed at $20 \pm 5°C$.

Reagents

Silica gel 'G' was obtained from E. Merck (India), glucose, fructose, maltose, sucrose, lactose, cellulose, kieselguhr, and alumina from CDH (India), sodium dodecyl sulphate (SDS) from Qualigens (India), and so-dium bis(2-ethyl-1-hexyl)sulphosuccinate (Aerosol OT) from BDH (UK). All reagents were of analytical reagent grade.

Test Solutions

Standard aqueous test solutions (1.0%) of the nitrates, sulphates, and chlorides of Al^{3+}, Pb^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Cr^{6+}, Zn^{2+}, Ag^+, Tl^+, Bi^{3+}, VO^{2+} and UO_2^{2+} were used. For Fe^{3+} 1% ferric chloride solution was prepared in 1% aqueous HCl.

Detection Reagents

Fe^{3+}, Cu^{2+}, VO^{2+}, and UO_2^{2+} were detected with 1% aqueous potassium ferrocyanide, Ni^{2+} and Co^{2+} with 1% alcoholic dimethyl glyoxime in ammonia, Zn^{2+}, Bi^{3+}, Ag^+, Tl^+, Hg^{2+}, and Pb^{2+} with 0.5% dithizone in carbon tetrachloride, Al^{3+} with 0.1% aqueous aluminon solution, Mn^{2+} with 2 M aqueous NaOH–30% H_2O_2, 1:1 (v/v), and Cr^{6+} with a saturated solution of $AgNO_3$ in methanol.

Stationary and Mobile Phases

The stationary and mobile phases used are listed in Tables I and II, respectively.

Table I

The stationary phases investigated

Code	Composition
S_1	Silica gel 'G'
S_2	S_1 + kieselguhr, 9:1 (*m/m*)
S_3	S_1 + kieselguhr, 1:1 (*m/m*)
S_4	S_1 + kieselguhr, 1:9 (*m/m*)
S_5	S_1 + cellulose, 9:1 (*m/m*)
S_6	S_1 + cellulose, 1:1 (*m/m*)
S_7	S_1 + cellulose, 1:9 (*m/m*)
S_8	S_1 + alumina, 9:1 (*m/m*)
S_9	S_1 + alumina, 1:1 (*m/m*)
S_{10}	S_1 + alumina, 1:9 (*m/m*)

Preparation of TLC Plates

Plain Silica Gel Plates

A 1:3 mixture of silica gel and double-distilled water was shaken until a homogeneous slurry was obtained. The slurry was applied to 20 cm × 3.5 cm glass plates as 0.25-mm layers by means of a Toshniwal (India) applicator. The plates were dried at room temperature (20°C) and then activated by heating at 100 ± 5°C for 1 h. The activated plates were stored in a closed chamber at room temperature until used.

Procedure

Test solutions (spiked or unspiked metal solutions, approx. 0.01 mL) were spotted separately on activated TLC plates (S_1), by use of a micro-pipette, approximately 2.0 cm from the lower edge of the layer. The spots were dried in air and the plates were developed to a distance of 10 cm from the point of application, by the ascending technique, in 24 cm × 6 cm glass jars with selected mobile phases (M_1–M_{30}; Table II). After development the plates were withdrawn from the jars, dried in air and sprayed with appropriate detection reagents to locate the positions of the analytes as coloured spots. R_L (R_F of leading front) and R_T (R_F of trailing front) values were measured for the detected spots and R_F values were calculated from $R_F = (R_L + R_T)/2$.

For separation of mixtures, equal volumes of metal cations were mixed and 0.01 mL of the resulting mixture was applied to the TLC plate

Table II

The mobile phases investigated

Code	Composition
M_1	0.0005 M SDS
M_2	0.0001 M SDS
M_3	0.001 M SDS
M_4	0.005 M SDS
M_5	0.01 M SDS
M_6	0.1 M SDS
M_7	0.5 M Glucose–M_5, 9:1 (*v/v*)
M_8	0.5 M Glucose–M_5, 7:3 (*v/v*)
M_9	0.5 M Glucose–M_5, 3:7 (*v/v*)
M_{10}	0.5 M Glucose–M_5, 1:9 (*v/v*)
M_{11}	0.5 M Fructose–M_5, 9:1 (*v/v*)
M_{12}	0.5 M Fructose–M_5, 7:3 (*v/v*)
M_{13}	0.5 M Fructose–M_5, 3:7 (*v/v*)
M_{14}	0.5 M Fructose–M_5, 1:9 (*v/v*)
M_{15}	0.1 M Lactose–M_5, 9:1 (*v/v*)
M_{16}	0.1 M Lactose–M_5, 7:3 (*v/v*)
M_{17}	0.1 M Lactose–M_5, 3:7 (*v/v*)
M_{18}	0.1 M Lactose–M_5, 1:9 (*v/v*)
M_{19}	0.5 M Sucrose–M_5, 9:1 (*v/v*)
M_{20}	0.5 M Sucrose–M_5, 7:3 (*v/v*)
M_{21}	0.5 M Sucrose–M_5, 3:7 (*v/v*)
M_{22}	0.5 M Sucrose–M_5, 1:9 (*v/v*)
M_{23}	0.5 M Maltose–M_5, 9:1 (*v/v*)
M_{24}	0.5 M Maltose–M_5, 7:3 (*v/v*)
M_{25}	0.5 M Maltose–M_5, 3:7 (*v/v*)
M_{26}	0.5 M Maltose–M_5, 1:9 (*v/v*)
M_{27}	0.01 M CTAB–0.5 M maltose, 7:3 (*v/v*)
M_{28}	0.01 M AOT–0.5 M maltose, 7:3 (*v/v*)
M_{29}	0.01 M Triton–0.5 M maltose, 7:3 (*v/v*)
M_{30}	0.01 M Brij 35–0.5 M maltose, 7:3 (*v/v*)

(S_1). The plate was developed with mobile phase M_{24}, the spots were detected, and R_F values of the spots of the separated metal cations were calculated.

To study the effect of the presence of anions and amine species as impurities on the separation of metal cations, 0.01 mL each of standard test

solutions of the metal cations Al^{3+}, Mn^{2+} and Cr^{6+} were spotted on TLC plates (S_1) followed by 0.01 mL of the anions and amine species being considered as impurities. The plates were developed with M_{24}, 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 on the TLC plates (S_1), developing with M_{24}, and visualizing the spots with the appropriate detection reagent. This process was repeated with successive reduction of the concentration of metal salts by adding demineralized double-distilled water. The amount of metal just detectable was taken as the detection limit.

To achieve separation and detection of the metal cations at different pH, the pH of the test samples was adjusted to the required values by addition of borate–phosphate buffer solutions of different pH. pH was measured with an Elico (India) 181E pH meter.

For separation of microgram quantities of Mn^{2+} from milligram quantities of Al^{3+} a TLC plate (S_1) was spotted with 0.01 mL salt solution containing 10 µg Mn^{2+} then, at the same place, with 0.01 mL of aluminium salt solution containing from 0.05 to 0.35 mg Al^{3+}. The spots were dried, the plates developed with M_{24}, the metal cations were visualized, and R_L and R_T values were determined for both metal cations. The same procedure was followed for separation of microgram quantities of Al^{3+} from milligram quantities of Mn^{2+}, i.e. S_1 plates were spotted with 10 µg Al^{3+} and 0.1 to 0.35 mg Mn^{2+}

Chromatography of Spiked Waste Water

An industrial waste-water sample (pH 2.98) containing Cr^{6+}, collected from lock factories in Aligarh, India, was spiked with aqueous solutions of Mn^{2+} (1%) and Al^{3+} (1%) in 1:1:1 (*v/v*) ratio. Approximately 0.01 mL of the resulting spiked sample was chromatographed on silica layers using M_{24} as mobile phase and R_F values were determined for the resolved spots of Cr^{6+}, Mn^{2+} and Al^{3+}.

Preparation of Heavy Metal Hydroxide Sludge

A synthetic heavy metal sludge containing Al^{3+}, Mn^{2+}, and Cr^{6+} was prepared by adding a sufficient volume of 1% NaOH solution to a mixture of equal volumes of 1% solutions of these metal salts. The metal hydroxide precipitate obtained was isolated by filtration, dried, and dissolved in a minimum volume of conc. hydrochloric acid. The acid was completely eva-

porated, the residue was dissolved in 5 mL distilled water, and TLC was performed on 5 μL of this sample.

RESULTS AND DISCUSSION

Optimization of the Mobile Phase

To examine the effect of the concentration of surfactant on the mobility of metal cations, chromatography was performed on silica gel layers with mobile phases M_1–M_6 containing different concentrations (0.0005–0.1 M) of SDS. Because SDS (critical micelle concentration (CMC) = 8×10^{-3} M) behaves as an electrolyte at concentrations below its CMC and forms micelles when the concentration in the mobile phase exceeds the CMC (e.g. 0.0001 M SDS behaves as electrolyte but at 0.01 M it forms micellar solution), the concentration of surfactant in the mobile phases was kept (a) below the CMC, (b) near the CMC, and (c) above the CMC to examine the behaviour of the surfactant, both as an electrolyte and in the form of micelles, on the mobility of metal cations.

R_F values of the metal cations chromatographed with aqueous solutions of SDS at different concentration (M_1–M_6) are listed in Table III.

Table III

Effect of surfactant concentration on the mobility (or R_F value) of metal cations chromatographed on S_1 layer

Metal cation	Mobile phase					
	M_1	M_2	M_3	M_4	M_5	M_6
Ni^{2+}	0.82 (T)[a]	0.87	0.63	0.62	0.85	0.95
Co^{2+}	0.80 (T)	0.87	0.54	0.54	0.72	0.89
Hg^{2+}	0.20 (T)	0.15	0.15	0.16	0.10	0.20 (T)
Cr^{6+}	0.72 (T)	0.99	(a) 0.90 Ds[b] (b) 0.0	(a) 0.91 Ds (b) 0.0	0.94	0.71(T)
Ag^+	0.16 (T)	0.20 (T)	0.22	0.23	0.26	0.21 (T)
Tl^+	0.16 (T)	0.21	0.23	0.24	0.27	0.35 (T)
Mn^{2+}	0.30	0.50 (T)	0.50	0.52	0.80	0.85

The metal ions Fe^{3+}, Cu^{2+}, Bi^{3+}, Pb^{2+}, Zn^{2+}, VO^{2+}, UO_2^{2+}, and Al^{3+} always remain very close to the point of application ($R_F \approx 0.0$–0.1)
[a]Tailing spot
[b]Double spot

From the data in Table III it is apparent that the metal cations Fe^{3+}, Cu^{2+}, Zn^{2+}, Hg^{2+} Bi^{3+}, VO^{2+}, UO_2^{2+}, Al^{3+}, and Pb^{2+} are strongly retained by the adsorbent (S_1), irrespective the concentration of SDS and thus have little mobility (R_F values in the range 0.0–0.1). Ag^+, Tl^+, Hg^{2+}, and Ni^{2+} give badly tailed spots ($R_L - R_T > 0.3$) with most of the mobile phases. The behaviour of Cr^{6+} is peculiar – tailing spots are obtained with M_1 and M_6 and double spots with M_3 and M_4. With M_2 and M_5 Cr^{6+} moves with the mobile front giving high R_F values. The mobility of Mn^{2+} was found to increase with increasing SDS concentration. The best chromatographic performance, i.e. better detection and more compact spots, was obtained with M_5 (0.01 M SDS). This mobile phase was therefore selected for further studies.

Effect of Carbohydrates on the Mobility of the Metal Cations

The effect of added carbohydrates such as monosaccharides (glucose and fructose) and disaccharides (sucrose, lactose, and maltose) in M_5 on the mobility of the metal cations was examined to obtain a better mobile phase for separation of the cations. The results obtained on S_1 by use of mobile phases comprising mixtures of 0.01 M SDS (M_5) with 0.5 M glucose, fructose, sucrose, or maltose or 0.1 M lactose, in different volume ratios (M_7–M_{26}), are summarized in Table IV.

It is evident from Table IV that Co^{2+}, Ag^+, and Tl^+ usually give tailing spots whereas Cr^{6+} gives double spots with some mobile phases (M_{11}, M_{15}, M_{16}, M_{18}, M_{20}, and M_{21}). Mn^{2+} gives compact spots with most of the mobile phases, although tailing spots were occasionally obtained. Of all the mobile phases M_{24} was found most favourable for mutual separation of Al^{3+}, Mn^{2+}, and Cr^{6+} on silica layers (S_1), as is evident from Fig. 1. Thus, the TLC system comprising silica gel (S_1) as stationary phase and 0.5 M maltose–0.01 M SDS, 7:3 (v/v) (M_5) as mobile phase was found most suitable for selective separation of Mn^{2+} from other metal cations. Mn^{2+} (R_F 0.31) can be easily separated from all metal cations with higher or lower mobility on the silica layer.

Effect of Mixed Adsorbent Layers

To assess the effectiveness of silica gel 'G' mixed with other adsorbents for mutual separation of Al^{3+}, Mn^{2+}, and Cr^{6+} mixed adsorbent layers were prepared by blending silica gel with cellulose, alumina, or kieselguhr G in different ratios (9:1, 1:1, and 1:9 w/w). The results (not shown) clearly indicated that separation of Mn^{2+} from Al^{3+} and Cr^{6+} was hampered by the presence of added adsorbents (cellulose, alumina or kieselguhr) in silica gel 'G'.

Table IV

Effect of carbohydrates on the mobility (or R_F value) of metal cations chromatographed on S_1 with different mobile phases

Mobile phase	Metal cation				
	Co^{2+}	Ag^+	Tl^+	Cr^{6+}	Mn^{2+}
M_7	0.75 (T)[a]	0.20 (T)	0.23 (T)	0.84 (T)	0.54
M_8	0.49 (T)	0.26 (T)	0.15 (T)	0.92	0.24
M_9	0.56 (T)	0.24 (T)	0.25 (T)	0.97	0.37
M_{10}	0.75 (T)	0.22 (T)	0.23 (T)	0.95	0.44
M_{11}	0.70 (T)	0.15 (T)	0.15	(a) 0.91 (b) 0.0	0.45
M_{12}	0.72 (T)	0.20 (T)	0.15	0.95	0.83
M_{13}	0.71 (T)	0.23 (T)	0.19 (T)	0.90	0.50
M_{14}	0.75 (T)	0.16 (T)	0.15	0.90	0.30
M_{15}	0.75	0.17 (T)	0.20 (T)	(a) 0.87 (b) 0.0	0.52
M_{16}	0.67 (T)	0.16 (T)	0.20	(a) 0.95 (b) 0.0	0.48 (T)
M_{17}	0.63 (T)	0.15 (T)	0.31 (T)	0.95	0.33 (T)
M_{18}	0.39 (T)	0.22 (T)	0.22 (T)	(a) 0.95 (b) 0.0	0.59 (T)
M_{19}	0.79 (T)	0.16 (T)	0.18 (T)	0.97	0.72
M_{20}	0.64 (T)	0.17 (T)	0.21 (T)	(a) 0.95 (b) 0.0	0.55
M_{21}	0.70	0.15	0.15 (T)	(a) 0.97 (b) 0.0	0.49 (T)
M_{22}	0.77	0.11	0.12 (T)	0.77 (T)	0.41
M_{23}	0.64	0.15 (T)	0.20 (T)	0.73 (T)	0.57
M_{24}	0.62	0.16 (T)	0.31 (T)	0.95	0.31
M_{25}	0.61	0.17	0.32 (T)	0.78 (T)	0.59
M_{26}	0.60	0.18 (T)	0.33 (T)	0.79 (T)	0.47

The metal ions Fe^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, VO^{2+}, UO_2^{2+}, Bi^{3+}, and Al^{3+} always remain very close to the point of application (R_F values between 0.0 and 0.2)
[a]Tailing spot; Ni^{2+} produces tailing spots ($R_L - R_T > 0.3$) irrespective of the concentration and type of carbohydrate in the mobile phase

Effect of Impurities

The effect of the presence of foreign substances (iodide, bromide, and aniline) in the sample was also examined to optimize the conditions for separation of mixtures of Al^{3+}, Mn^{2+}, and Cr^{6+}. The R_F of Al^{3+} fluctuated between 0.01 and 0.03 in the presence of impurities, i.e. there was little effect on its value in the absence of the impurities (R_F 0.03). In the presence of iodide, bromide, and aniline the respective R_F values of Mn^{2+} (0.41, 0.36, and 0.46) and Cr^{6+} (0.85, 0.98, and 0.95) were also found to deviate slightly from those obtained in the absence of the impurities (Mn^{2+}, R_F 0.31; Cr^{6+}, R_F 0.95).
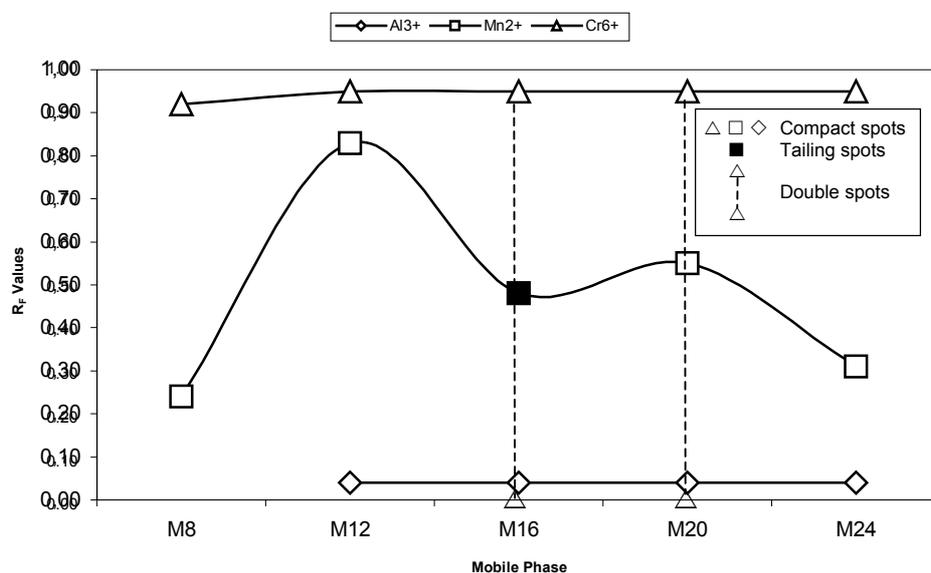
Fig. 1

Separation of a mixture of Al^{3+}, Mn^{2+}, and Cr^{6+} on S_1 with M_5 (0.01 M SDS) containing glucose (M_8), fructose (M_{12}), lactose (M_{16}), sucrose (M_{20}) or maltose (M_{24})

Effect of Test Sample pH

It was found that Al^{3+}, Mn^{2+}, and Cr^{6+} can be easily separated from each other up to pH 2.35. At higher pH precipitation occurred in sample solutions containing Al^{3+}, Mn^{2+} and Cr^{6+}.

Limits of Detection

The smallest amounts of Cr^{6+}, Mn^{2+}, and Al^{3+} detectable were 0.01, 0.1, and 0.2 μg, respectively. These values are indicative of the highly sensitive detection of these metal cations on silica gel layers developed with aqueous media.

Effect of the Amount of Analyte Loaded

It was possible to separate 10 μg Mn^{2+} from 0.05 mg Al^{3+}. Similarly, 10 μg Al^{3+} is readily separated from 0.1 mg Mn^{2+}. Thus, milligram quantities of one metal cation can be successfully separated from microgram amounts of other cations using the proposed TLC system.

Effect of Addition of Surfactants to the Mobile Phase

After examining the effect of substitution of silica gel (S_1) by mixed adsorbent layers (S_2–S_{10}) on the separation of mixtures of Al^{3+}, Mn^{2+}, and Cr^{6+}, as discussed above, we changed the nature of mobile phase M_5 by substituting SDS with CTAB (M_{27}), AOT (M_{28}), Triton (M_{29}), and Brij 35 (M_{30}) to investigate the effect of the nature of the surfactant on the mutual separation of Al^{3+}, Mn^{2+}, and Cr^{6+} on S_1. Detection of Al^{3+} was difficult when TLC plates were developed with M_{27}–M_{30}. With these mobile phases no changes in R_F values were observed for Mn^{2+} and Cr^{6+} and hence separation of Mn^{2+} from Cr^{6+} was always possible.

Semiquantitative Determination

When the possibility of semiquantitative determination of metal cations was assessed by measurement of spot area, a linear relationship was obtained when the amount of the sample spotted was plotted against spot area (Fig. 2). The empirical equation of the line was $\xi^2 = km$, where ξ is the area of the spot, m is the amount of solute, and k is constant. The linearity is maintained up to 0.2 mg/spot Al^{3+} (aluminium nitrate) and Mn^{2+} (manganese acetate). At higher concentrations negative deviation from the linear law was observed for both cations.

Application

The proposed method was successfully used for identification and separation of metal cations in spiked industrial waste water samples. The results shown in Fig. 3 demonstrate the applicability of the method for identification of Cr^{6+} and mutual separation of mixtures of Cr^{6+}, Mn^{2+}, and Al^{3+} from industrial waste water.

CONCLUSION

Mutual separation of Al^{3+}, Mn^{2+}, and Cr^{6+} was achieved experimentally on silica gel layers developed with 0.5 M maltose–0.01 M SDS, 7:3 (*v/v*) as mobile phase. The proposed method was used successfully for identification and separation of these metal cations in industrial waste water samples.
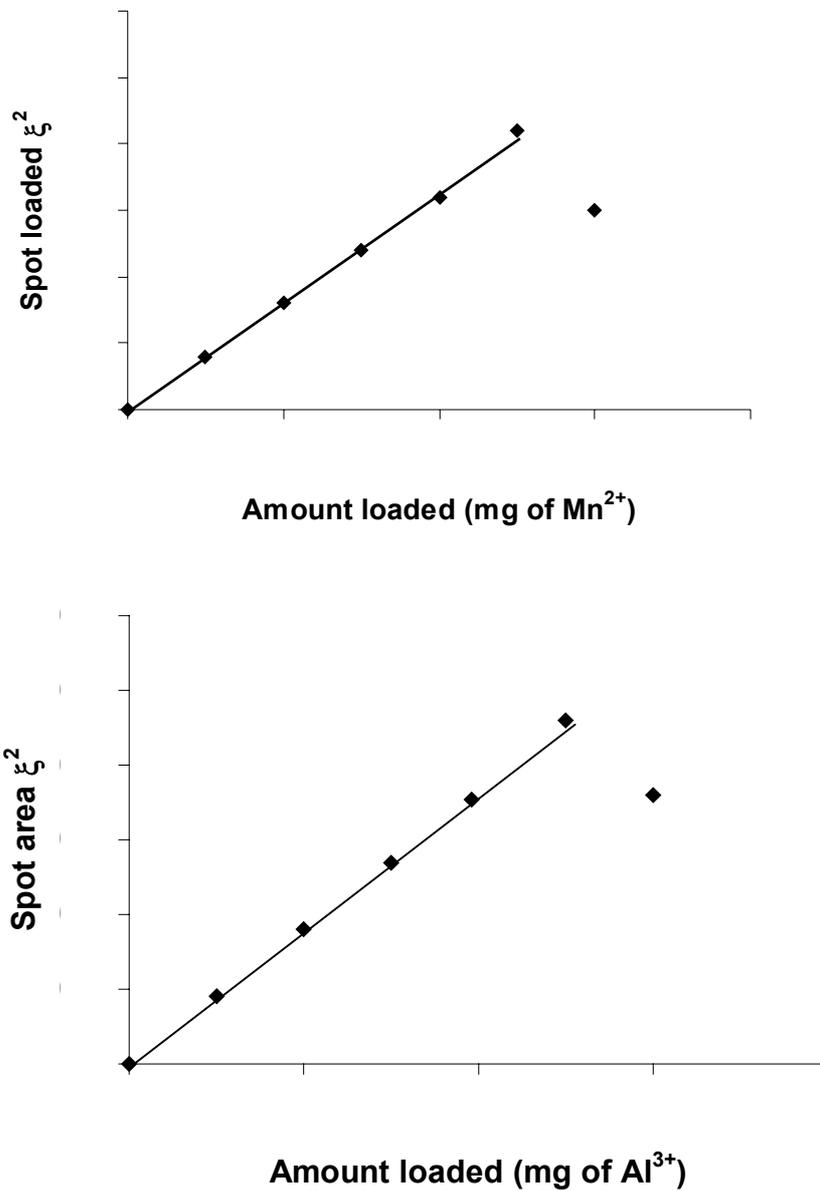
Fig. 2

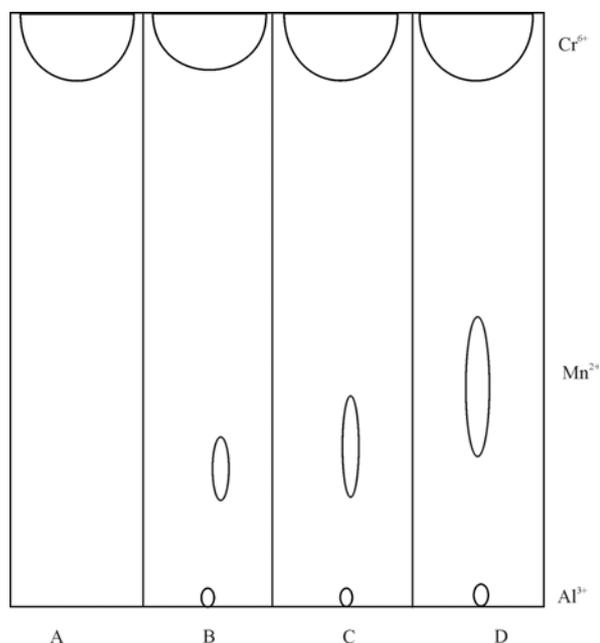Calibration plots for semiquantitative determination of (a) Mn^{2+} and (b) Al^{3+}

Fig. 3

Separation of mixtures of Al^{3+}, Mn^{2+}, and Cr^{6+} on stationary phase S_1 developed with mobile phase M_{24}. A. Electroplating waste water (Cr^{6+} only detected). B. $Cr^{6+} + Mn^{2+} + Al^{3+}$ standard. C. Electroplating waste waster spiked with Al^{3+} and Mn^{2+}. D. Hydroxide sludge sample containing Cr^{6+}, Al^{3+}, and Mn^{2+}

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