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Thin-Layer Chromatography of Certain Metal Cations with Anionic Micellar Mobile Phase Systems: Simultaneous Separation of Co-existing Gold (III), Copper (II) and Silver (I) and Quantitative Spectrophotometric Measurement of Copper (II)

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SUMMARY

Silica gel in combination with surfactant-mediated eluents has been used for thin-layer chromatography of sixteen metal cations. Several combinations of mobile phase systems comprising of sodium dodecyl sulfate (SDS) plus organic non-electrolytes and inorganic electrolytes have been tested for rapid and reliable separation of metal cations. TLC system constituting silica gel as a stationary phase and 0.3% SDS (pH 2.3) plus 5% aqueous NaCl (9:1, v/v) as mobile phase was identified most favorable system for the separation and identification of co-existing gold, copper and silver in alloys. Semiquantitative determination of Cu^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} by spot-area measurement method has been attempted. TLC-spectrophotometry technique has been used for quantitative determination of Cu^{2+} in synthetically prepared ores and alloys with preliminary separation from Au^{3+} and Ag^+ .

Key words: Micellar TLC, Separation, Metal cations, Gold, Copper, Silver, Spectrophotometry

INTRODUCTION

Because of poor toxicity, low cost, enhanced separation selectivity, non-flammability, capability of simultaneously separating hydrophilic and hydrophobic solutes and non-volatility, micellar mobile phases (i.e. solutions containing a surfactant at a concentration above its critical micellar concentration (CMC) have found interesting applications in liquid chromatography [1–8]. The use of micellar mobile phases (MMP) in thin-layer chromatography (TLC) was first proposed by Armstrong and co-workers [9–10]. MMP have been successfully utilized to separate pesticides and biphenyls [10], polynuclear aromatic hydrocarbons and vitamins [11], phenols [12], amino acids [13–14], alkaloids [15], dyes [16] and drugs [17]. Despite evident advantageous features, the use of MMP in chromatographic analysis of metal cations [18–20] has been less extensive compared with their use in the analysis of organic compounds.

In addition to simplifying chromatographic procedure, MMP result in improved separations as a result of electrostatic, hydrophobic and donor-acceptor interactions, or any combination of these [9, 11, 12, 16]. Secondary interactions arising from partitioning of solute within the mobile phase (between aqueous and micellar phases) also play a decisive role in the separation of solutes by micellar liquid chromatography. According to literature [2, 3, 20, 21], chromatographic performance of MMP can be further improved by using them in the presence of salts and organic additives which affect the size of micelles. Several analytical techniques [22–26] have been used to separate Au (III), Cu (II) or Ag (I) from associated metal ions but the work on simultaneous separation of these metal cations from their three component mixtures by TLC is lacking. This communication reports a simplest and convenient micellar TLC procedure for the separation of co-existing Au (III), Cu (II) and Ag (I) ions. The mutual separation of Au (III), Ag (I) and

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Cu (II) is very important from practical point of view as these metals are generally associated with each other in natural ores of silver or copper. Furthermore, after the separation, Cu (II), has been determined quantitatively by spectrophotometry using 1-(2-pyridylazo)-2-naphthol (PAN) solution in methanol as chromogenic reagent. The TLC-spectrophotometric method was applied to recovery of Cu (II) from synthetic alloy and ore samples.

EXPERIMENTAL

Apparatus: A TLC applicator (Toshniwal, India) was used for coating silica gel on 20×3.5 cm glass plates. The chromatography was performed in 24×6 cm glass jars. A glass sprayer was used to spray reagents on the plates to locate the position of the spot of analyte. Digital pH meter (Elico, India, Model 181 E of type PC-22) and spectrophotometer (Elico, India, SL-171) were used for pH measurements and spectrophotometric determination, respectively.

Chemicals and Reagents: Sodium dodecyl sulfate (BDH, India) and aerosol-OT (BDH, England); sodium chloride or nitrate and urea (G.S.C, India); Silica gel 'G' and thiourea (E. Merck, India); Brij-35 and Triton X-100 (Loba-chemie, India), cetyl trimethyl ammonium bromide (CTAB), phenols, amines, aminophenols and anions (CDH, India) were used. All reagents were of Analar Reagent grade.

Metal Cations Studied: Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , UO_2^{2+} , VO^{2+} , Cd^{2+} , Zn^{2+} , Ag^+ , Pb^{2+} , Ti^+ , Bi^{3+} , Hg^{2+} , Al^{3+} , Ti^{4+} , and Au^{3+} .

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

- Nitrates of Cd^{2+} , Zn^{2+} , Pb^{2+} , Ti^+ , Bi^{3+} , Al^{3+} , and Ag^+ .
- Chlorides of Ni^{2+} , Co^{2+} , Fe^{3+} , Hg^{2+} , Ti^{4+} , and Au^{3+} .
- Sulfates of Cu^{2+} , VO^{2+} , and UO_2^{2+} .

All the solutions were prepared in demineralized water with a specific conductivity ($K = 2 \times 10^{-6} \text{ ohm}^{-1}$ at 25 °C). The solutions of nitrates of lead, silver and bismuth, and the chloride of mercury also contained small quantities of corresponding acid to limit the extent of hydrolysis.

The solutions (1%) of various anions and surfactants were prepared in demineralized water. The solutions (1%) of various amines, phenols and aminophenols were prepared in methanol.

Test Materials Used

- Gold-plated printed-circuit board (GPCB) {Au, Ni and Cu} from Toyama Electric, Bangalore
- Silver mirror scrap (SMS) {Ag, Cu} and Silver mirror spent solution (SMSS) {Ag and Cu}, both from Ship Mirror Industries, Bangalore
- High-copper dental amalgam (HCDA) {Ag, Hg, Cu, Zn and Sn} from Dental College, A. M. U., Aligarh
- Electroplating gold waste from Anand Jewellers, Aligarh

- Sterling silver scrap (SS) {Ag, Cu}
- Gun metal (90% Cu + 10% Sn)
- Ornamental silver (80% Ag + 20% Cu)
- Copper pyrites (CuFeS_2 ; 4% Cu + 96% Fe)
- Copper glance (CuS)

Buffer Solutions

| S. No. | Composition | Volume ratio | pH |
|--------|--|--------------|------|
| 1 | 0.04 M Boric acid-0.04 M phosphoric acid | 50:50 | 2.3 |
| 2 | 0.04 M Boric acid-0.04 M phosphoric acid -0.24 M NaOH | 50:50:8 | 3.4 |
| 3 | 0.04 M Boric acid-0.04 M phosphoric acid -0.24 M NaOH | 50:50:10 | 5.7 |
| 4 | 0.04 M Boric acid-0.04 M phosphoric acid -0.24 M NaOH | 50:50:14 | 7.0 |
| 5 | 0.04 M Boric acid-0.04 M phosphoric acid -0.24 M NaOH | 50:50:60 | 11.9 |

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

- $8 \times 10^{-3}\%$ (w/v) Dithizone in carbon tetrachloride for Cd^{2+} , Zn^{2+} , Ag^+ , Pb^{2+} , Ti^+ , Bi^{3+} , and Hg^{2+} .
- 1% Aqueous potassium ferrocyanide for Fe^{3+} , Cu^{2+} , UO_2^{2+} , VO^{2+} , and Ti^{4+} .
- 1% Alcoholic dimethylglyoxime for Ni^{2+} , and Co^{2+} .
- 0.1% Aluminon for Al^{3+} .
- 1% (v/v) Yellow ammonium sulphide for Au^{3+} .

Stationary Phase: Silica gel 'G'

Mobile Phase: The following solvent systems were used as mobile phase

| Symbol | Composition |
|-----------------|---|
| M ₁ | 0.03, 0.144, 0.3 and 1.44% aqueous SDS |
| M ₂ | 0.03, 0.144, 0.3 and 1.44% buffered SDS (pH 2.3) |
| M ₃ | 0.03, 0.144, 0.3 and 1.44% buffered SDS (pH 3.4, 5.7, 7.0 and 11.9) |
| M ₄ | 0.03% SDS (pH 2.3)+1% urea (9:1, 1:1 and 1:9) |
| M ₅ | 0.3% SDS (pH 2.3)+5% urea (9:1, 1:1 and 1:9) |
| M ₆ | 0.3% SDS (pH 2.3)+10% urea (9:1, 1:1 and 1:9) |
| M ₇ | 0.3% SDS (pH 2.3)+15% urea (9:1, 1:1 and 1:9) |
| M ₈ | 0.3% SDS (pH 2.3)+1% thiourea (9: 1, 1:1 and 1: 9) |
| M ₉ | 0.3% SDS (pH 2.3)+5% thiourea (9: 1, 1:1 and 1: 9) |
| M ₁₀ | 0.3% SDS (pH 2.3)+10% thiourea (9: 1, 1: 1 and 1: 9) |
| M ₁₁ | 0.3% SDS (pH 2.3)+15% thiourea (9: 1, 1: 1 and 1: 9) |
| M ₁₂ | 0.3% SDS (pH 2.3)+1% NaNO ₃ (9: 1, 1: 1 and 1: 9) |
| M ₁₃ | 0.3% SDS (pH 2.3)+5% NaNO ₃ (9: 1, 1: 1 and 1: 9) |
| M ₁₄ | 0.3% SDS (pH 2.3)+10% NaNO ₃ (9: 1, 1: 1 and 1: 9) |
| M ₁₅ | 0.3% SDS (pH 2.3)+15% NaNO ₃ (9: 1, 1: 1 and 1: 9) |
| M ₁₆ | 0.3% SDS (pH 2.3)+1% NaCl (9: 1, 1: 1 and 1: 9) |
| M ₁₇ | 0.3% SDS (pH 2.3)+5% NaCl (9: 1, 1: 1 and 1: 9) |
| M ₁₈ | 0.3% SDS (pH 2.3)+10% NaCl (9: 1, 1: 1 and 1: 9) |
| M ₁₉ | 0.3% SDS (pH 2.3)+15% NaCl (9: 1 and 1: 1) |

CHROMATOGRAPHY

(a) Preparation of TLC Plates: Silica gel plates were prepared by mixing the adsorbent with double distilled water in 1: 3 ratio by weight. The resultant slurry was mechanically shaken for 10 min, after which it was applied to well-cleaned glass plates with the help of TLC applicator to give a layer of approximately 0.25 mm thickness. The plates were air dried at room temperature and then activated by heating at 100 ± 5 for 1 h. After activation, the plates were stored in a desiccator.

(b) Preparation of Test Materials

Peeling: Peeling of silver mirror scrap (specimen surface area 19 cm^2) was performed with concentrated formic acid (90%, w/w) in a glass beaker. The acid was heated at 110 and the material was added into it. On completion of peeling (within 1 min), the solution was separated and the peeled material was used as the 'source material' for silver.

Leaching: Leaching of silver mirror scrap (specimen surface area 19 cm^2) was performed with 50% nitric acid in a glass beaker. On completion of leaching (within 1 min), the solution was separated from the leached residue and used for silver separation. Similar leaching procedure was applied on other silver-containing material (0.153 g sterling silver scrap and 0.25 g high-copper dental amalgam).

Leaching of gold-plated printed-circuit board (specimen surface area 72.42 cm^2 containing 16 large pins and 14 small pins) was performed with aqua-regia in a glass beaker. On completion of leaching, the solution was separated from the residue and used for gold separation.

(c) Preparation of Synthetic Alloy and Ores: For the synthesis of gun metal (90% Cu + 10% Sn), 9 mL of 1% CuSO_4 solution was added into 1 mL of 1% aqueous $\text{SnCl}_4 \cdot 5 \text{ H}_2\text{O}$ solution and for the synthesis of ornamental silver (80% Ag + 20% Cu), 8 mL of 1% aqueous AgNO_3 solution was added into 2 mL of 1% aqueous CuSO_4 solution. The resultant solutions of synthetic gun metal and ornamental silver were transparent.

For the synthesis of copper pyrites (CuFeS_2), 0.2 mL of 1% aqueous CuSO_4 solution was added into 4.8 mL of 1% aqueous FeCl_3 solution and for the synthesis of copper glance (CuS), 5 mL of 1% CuSO_4 were taken in two different beakers. About 8 mL of 0.5% thioacetamide solution was added in both the beakers, as a result precipitates of CuFeS_2 and CuS are formed. Precipitates were dissolved in minimum possible amount/ volume of concentrated HNO_3 . The solutions were heated for complete removal of acid. The residues were dissolved in 5 mL of 1 M HCl and 5 mL of double distilled water, respectively. Clear solutions of synthetic ores were obtained.

Procedure: About 10 μL of test solution was applied using a micropipette about 2.0 cm above the lower edge of TLC plates. The

spots were dried, and the plates were developed in glass jars by ascending technique. The glass jars containing the mobile phase were covered with a lid for about 20 min so that the glass jars would get pre-saturated with the mobile phase vapors. The mobile phase (solvent) was allowed to migrate up to 10 cm from the starting line in all cases. After development, the plates were dried again and the cations were visualized as colored spots by spraying with appropriate detection reagents. The cations were identified on the basis of their R_F values, which was calculated from R_L (R_F of leading front) and R_T (R_F of trailing front) for each spot, whereas

$$R_F = (R_L + R_T) / 2$$

Separation: The test solution 10 μL of copper, silver and gold mixture was spotted on TLC plate coated with silica gel 'G' and the chromatography was performed with mobile phase M_{17} [0.3% SDS (pH 2.3) + 5% NaCl (9:1)]. The resolved spots for these metal cations were observed on TLC plates after spraying chromogenic reagents. The R_F values of Au^{3+} , Cu^{2+} and Ag^+ in their mixture were found to vary marginally from their individual R_F values.

Interference: For investigating the interference of inorganic anions, amines, phenols, aminophenols and surfactants on the separation of co-existing Au^{3+} , Cu^{2+} , and Ag^+ , an aliquot (10 μL) of additives was spotted along with the mixture (10 μL) of Au^{3+} , Cu^{2+} , and Ag^+ and chromatography was performed as described above with M_{17} (9:1). The spots were detected and the R_F values of separated metal ions were determined.

Limit of Detection: The identification limits of various cations including Cu^{2+} and Ag^+ were determined by spotting different amounts of cationic solutions on the TLC plates. The plates were developed in M_{17} (9:1) and the spots were detected as described above. The method was repeated with successive lowering of the amount of cation until spots could no longer be detected. The minimum amount of cation that could be detected was taken as the limit of detection.

Semiquantitative Determination by Spot-Area Measurement:

For semiquantitative determination by spot-area measurement method, 10 μL of a series of various standard solutions (0.5–2.0%) of Cu^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} were spotted on silica gel layers. The plates were developed with M_{17} (9:1). After detection the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated.

Quantitative Determination: Spectrophotometry of copper after TLC separation from gold and silver was carried out as follow:

A sample of copper salt $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ solution containing 5.08–25.45 μg of Cu^{2+} was treated with 0.1 mL of 0.1% 1-(2-pyridylazo)-2-naphthol (PAN) in methanol 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 spectra of this solution against

blank over 400–580 nm gave a maximum absorbance peak at 460 nm (λ_{max}). The color produced with copper was stable and proportional to copper concentration. The absorbance of developed color was measured against the blank at 460 nm using 1 cm cells and a calibration curve was obtained.

This spectrophotometric method was used to determine recovery of copper after separation from gold and silver as follows.

Different volumes (0.01–0.05 mL) of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ solution containing 5.08–25.45 μg Cu were spotted on the TLC plates. After the spots were completely dried, 0.1 mg of silver salt solution was spotted on the same spot and the plates were re-dried at room temperature. The dried plates were developed in M_{17} (9:1). A pilot plate was also run simultaneously to locate the position of copper. After development, the region containing the copper spot on the pilot plates were detected, the corresponding region on the working plates (undetected spot) was marked and this area of adsorbent was scraped into a clean beaker and the copper was extracted with approximately 15 mL of 1.0 M aqueous HCl, and followed by washing of the adsorbent to ensure complete removal of copper. The filtrate was kept on water bath for complete removal of HCl and the residue so obtained was dissolved in demineralized double distilled water and followed by addition of 0.1 mL of chromogenic reagent solution (0.1% PAN in methanol) and the total volume in each case was maintained to 10 mL 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 blank at 460 nm using 1 cm cells and a recovery curve was constructed. The copper was spectrophotometrically determined after its separation from other samples listed in the percentage recovery, % error and relative standard deviation (RSD) were calculated, using the formulae:

(a) Percentage recovery =

$$100 - \frac{\text{Amount recovered} - \text{Amount loaded}}{\text{Amount loaded}} \times 100$$

(b) Relative standard deviation (RSD) =

$$\frac{S}{\bar{X}}, \text{ where } S \text{ is standard deviation and } \bar{X} \text{ is mean of measurements.}$$

Application

Chromatography of Unspiked Materials: Chromatography of unspiked dental amalgam and printed circuit board was done using M_{17} (9:1) as mobile phase and the spots of Ag^+ , Hg^{2+} , Zn^{2+} , Cu^{2+} and Au^{3+} were detected and the R_F value of each cation was determined.

Chromatography of Spiked Materials: The spiked samples of PCB, dental amalgam, silver mirror scrap, silver mirror spent solutions, and sterling silver were prepared as follows:

(a) One mL of GPCB/ electroplating gold waste was mixed with

1 mL of silver test solution (1%). The chromatography was done using 10 μL solution of this mixture for spotting.

(b) One mL of gold solution was added to 1 mL of each SMS, SMSS or SS solution and HCDA solution and 10 μL of the mixture was used for chromatography and resolved spots of Au^{3+} , Cu^{2+} and Ag^+ from their mixtures were identified by their respective R_F values.

RESULTS AND DISCUSSION

(a) Effect of Concentration and pH of SDS Solution

Chromatography of sixteen metal cations was performed using various mobile phase systems (M_1 – M_3). The mobility pattern of metal cations was found to depend on the composition of mobile phase. Results obtained with different concentrations of unbuffered aqueous SDS (M_1) and buffered SDS (M_2 and M_3) solutions reveal the following trends:

- (i) Metal ions such as Al^{3+} , Ti^{4+} , VO^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Bi^{3+} and UO_2^{2+} show either no mobility ($R_F = 0.0$) or very little mobility ($R_F \approx 0.05$) at all concentration levels as well as over entire pH range of SDS solutions. A slightly higher mobility ($R_F = 0.30$) in the case of Zn^{2+} was observed when 1.44% SDS solution (pH 2.3) was used as mobile phase.
- (ii) Ni^{2+} , Co^{2+} and Tl^+ produce badly tailed spots ($R_L - R_T > 0.30$) almost with all the mobile phases (M_1 – M_3) used with the exception of 0.3% SDS (pH 2.3). Compared to buffered SDS solutions M_3 , higher mobility for these cations (R_F of Ni^{2+} or $\text{Co}^{2+} = 0.85$ and $\text{Tl}^+ = 0.34$) was observed with 0.3% SDS solution (pH 2.3).
- (iii) Au^{3+} as well-formed spot, always migrates near to solvent front ($R_F \approx 0.90$) regardless the concentration or pH of SDS solution and hence it can be selectively separated from binary mixtures containing other metal ions.
- (iv) The mobility of certain metal cations (Cu^{2+} , Zn^{2+} , Ag^+ , Bi^{3+} and Al^{3+}) was found to increase marginally on substitution of 0.03% or 0.144% buffered SDS (pH 2.3) with 0.3% or 1.44% SDS (pH 2.3).
- (v) The development time for 10 cm ascent was typically short i.e. 10–12 min for all mobile phase systems used.

The R_F data of metal ions obtained with buffered SDS (pH 2.3) at different concentrations (M_2) levels are compared and presented in Figure 1. It is clear from this figure that the mobility of metal ions is slightly influenced by the concentration of SDS in the mobile phase.

Keeping all the necessary conditions of being selected as better mobile phase e.g. compactness of spot and mobility of metal cations, M_2 (0.3% buffered SDS, pH 2.3) was selected for further study.

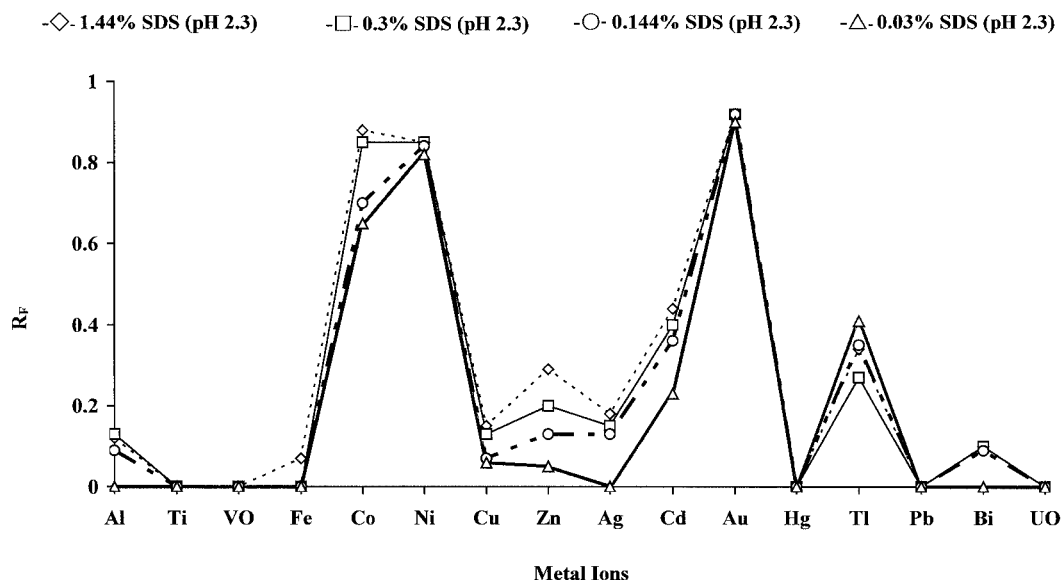


Figure 1. Effect of SDS concentration at fixed pH on the mobility of metal cations

(b) Effect of Added Urea and Thiourea

The effect of addition of organic non-electrolytes (e.g. urea and thiourea) at different concentration levels in M_2 (0.3% SDS, pH 2.3) on the mobility of metal cations was examined as described in Tables 1 and 2. On the basis of R_F values obtained with the resultant mobile phase systems (M_4 – M_{11}), the mobility trends of metal cations are summarized below:

- Metal cations such as Ti^{4+} , VO^{2+} , UO_2^{2+} , Fe^{3+} , Pb^{2+} and Zn^{2+} show little mobility ($R_F \approx 0.08$), whereas Au^{3+} shows high mobility ($R_F \approx 0.90$) at all concentrations of urea and thiourea.
- Ni^{2+} , Co^{2+} , Cd^{2+} , Hg^{2+} , Tl^+ and Bi^{3+} show tailed spots in the presence of urea, whereas in thiourea only Ni^{2+} , Co^{2+} and Tl^+ show tailed spots at all concentration levels.

- The mobility of Al^{3+} was found to decrease with the increase in concentration of thiourea (1%–15%) at all volume ratio with 0.3% SDS [Figure 2 (a)]. Conversely the mobility of Al^{3+} increases with the increase in concentration of urea (5–15%). However, its mobility decreases with the increase in volume ratio of urea in 0.3% SDS [Figure 2 (b)]. With 1% urea, Al^{3+} shows very little mobility ($R_F = 0.05$) at all volume ratio of urea and SDS.
- The mobility of Hg^{2+} was found to increase as the concentration of thiourea increases in 0.3% SDS whereas a reversal trend i.e. decrease in the mobility with increase in concentration of thiourea was observed in the case of Cd^{2+} .
- The mobility of Cu^{2+} was found to increase with the increase

Table 1. Mobility trends of metal ions on silica gel 'G' developed with 0.3% SDS (pH 2.3) plus different concentrations of urea

| Metal ions | 0.3% SDS + 1% urea | | | 0.3% SDS + 5% urea | | | 0.3% SDS + 10% urea | | | 0.3% SDS + 15% urea | | |
|------------|--------------------|--------|--------|--------------------|--------|--------|---------------------|--------|--------|---------------------|--------|--------|
| | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 |
| Al^{3+} | 0.05 | 0.05 | 0.05 | 0.30 | 0.05 | 0.20 | 0.35 | 0.05 | 0.30 | 0.38 | 0.05 | 0.30 |
| Co^{2+} | 0.75 T | 0.50 T | 0.65 T | 0.65 T | 0.60 T | 0.65 T | 0.60 T | 0.70 T | 0.60 T | 0.25 T | 0.75 T | 0.55 T |
| Ni^{2+} | 0.75 T | 0.50 T | 0.65 T | 0.65 T | 0.60 T | 0.65 T | 0.60 T | 0.65 T | 0.60 T | 0.29 T | 0.75 T | 0.55 T |
| Cu^{2+} | 0.49 | 0.00 | 0.19 | 0.40 | 0.14 | 0.35 | 0.40 | 0.17 T | 0.20 | 0.25 | 0.20 T | 0.20 |
| Ag^+ | 0.33 T | 0.15 | 0.23 T | 0.30 T | 0.28 T | 0.28 T | 0.30 T | 0.33 T | 0.30 T | 0.25 T | 0.35 T | 0.30 T |
| Cd^{2+} | 0.45 T | 0.27 T | 0.32 T | 0.45 T | 0.67 T | 0.63 T | 0.45 | 0.79 | 0.75 | 0.23 | 0.84 | 0.75 |
| Au^{3+} | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |
| Hg^{2+} | 0.50 T | 0.50 T | 0.50 T | 0.70 T | 0.75 T | 0.70 T | 0.70 T | 0.80 | 0.75 T | 0.70 T | 0.85 | 0.75 |
| Tl^+ | 0.40 T | 0.25 T | 0.27 T | 0.35 T | 0.25 T | 0.30 T | 0.35 T | 0.28 T | 0.33 T | 0.28 T | 0.31 T | 0.33 T |
| Bi^{3+} | 0.20 T | 0.15 | 0.16 T | 0.20 T | 0.30 T | 0.20 T | 0.20 T | 0.30 T | 0.27 T | 0.14 | 0.29 T | 0.28 T |

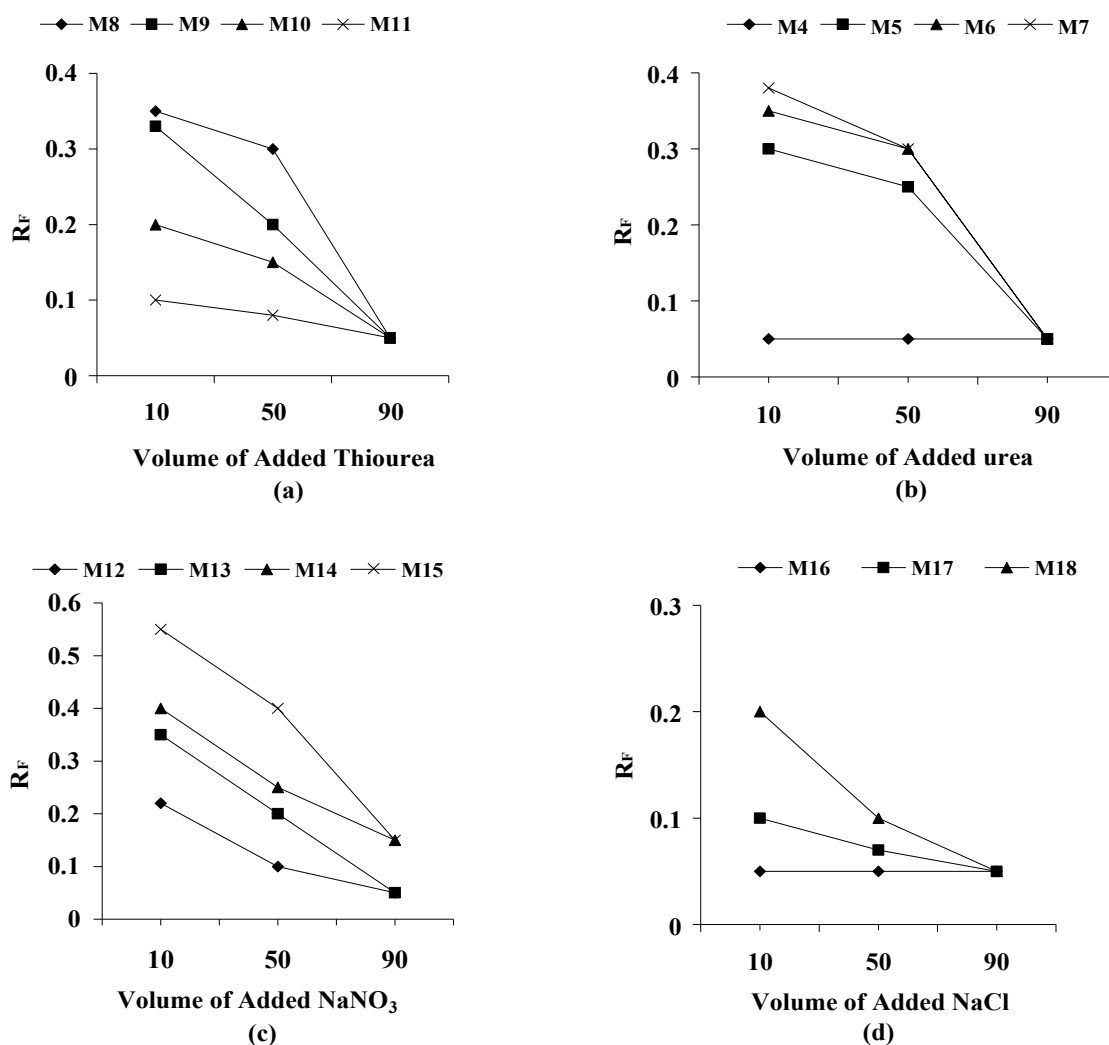
Ti^{4+} , VO^{2+} , Fe^{3+} , UO_2^{2+} , Zn^{2+} and Pb^{2+} show little mobility $R_F \approx 0.08$.

T = Tailed Spot ($R_L - R_T > 0.30$)

Table 2. Mobility trends of metal ions on silica gel 'G' developed with 0.3% SDS (pH 2.3) plus different concentrations of thiourea

| Metal ions | 0.3% SDS + 1% thiourea | | | 0.3% SDS + 5% thiourea | | | 0.3% SDS + 10% thiourea | | | 0.3% SDS + 15% thiourea | | |
|------------------|------------------------|---------------|---------------|------------------------|--------|--------|-------------------------|--------|--------|-------------------------|--------|--------|
| | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 |
| Al ³⁺ | 0.35 | 0.05 | 0.30 | 0.33 | 0.05 | 0.20 | 0.20 | 0.05 | 0.15 | 0.10 | 0.05 | 0.08 |
| Co ²⁺ | 0.80 T | 0.85 T | 0.80 T | 0.74 T | 0.60 T | 0.65 T | 0.65 T | 0.45 T | 0.65 T | 0.65 T | 0.33 T | 0.65 T |
| Ni ²⁺ | 0.80 T | 0.82 T | 0.80 T | 0.74 T | 0.70 T | 0.70 T | 0.65 T | 0.45 T | 0.65 T | 0.65 T | 0.40 T | 0.65 T |
| Cu ²⁺ | 0.66 | 0.85 | 0.80 | 0.68 | 0.85 | 0.83 | 0.75 | 0.86 | 0.83 | 0.89 | 0.87 | 0.87 |
| Ag ⁺ | 0.15 | 0.56, 0.0* | 0.32, 0.0* | 0.39, 0.0* | 0.77 | 0.73 | 0.80 | 0.78 | 0.78 | 0.83 | 0.83 | 0.83 |
| Cd ²⁺ | 0.54 | 0.44 | 0.47 | 0.56 | 0.47 | 0.51 | 0.60 | 0.50 T | 0.52 T | 0.60 T | 0.71 T | 0.61 T |
| Au ³⁺ | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |
| Hg ²⁺ | 0.33 T | 0.57 | 0.47 | 0.58 | 0.64 | 0.62 | 0.65 | 0.71 | 0.69 | 0.65 T | 0.85 | 0.82 T |
| Tl ⁺ | 0.20 T | 0.20 T | 0.17 T | 0.22 T | 0.20 T | 0.20 T | 0.25 T | 0.20 T | 0.22 T | 0.25 T | 0.20 T | 0.23 T |
| Bi ³⁺ | 0.07 | 0.10 | 0.10 | 0.15 | 0.10 | 0.14 | 0.15 | 0.10 | 0.15 | 0.20 T | 0.14 | 0.18 T |

T = Tailed Spot ($R_L - R_T > 0.30$); *Double Spot; Ti^{4+} , VO^{2+} , Fe^{3+} , UO_2^{2+} , Zn^{2+} and Pb^{2+} show little mobility $R_F \approx 0.08$

**Figure 2.** Plot of R_F of Al^{3+} Vs volume of added thiourea (a), urea (b), $NaNO_3$ (c) and NaCl (d) in M_2 (0.3% aqueous SDS in pH 2.3).

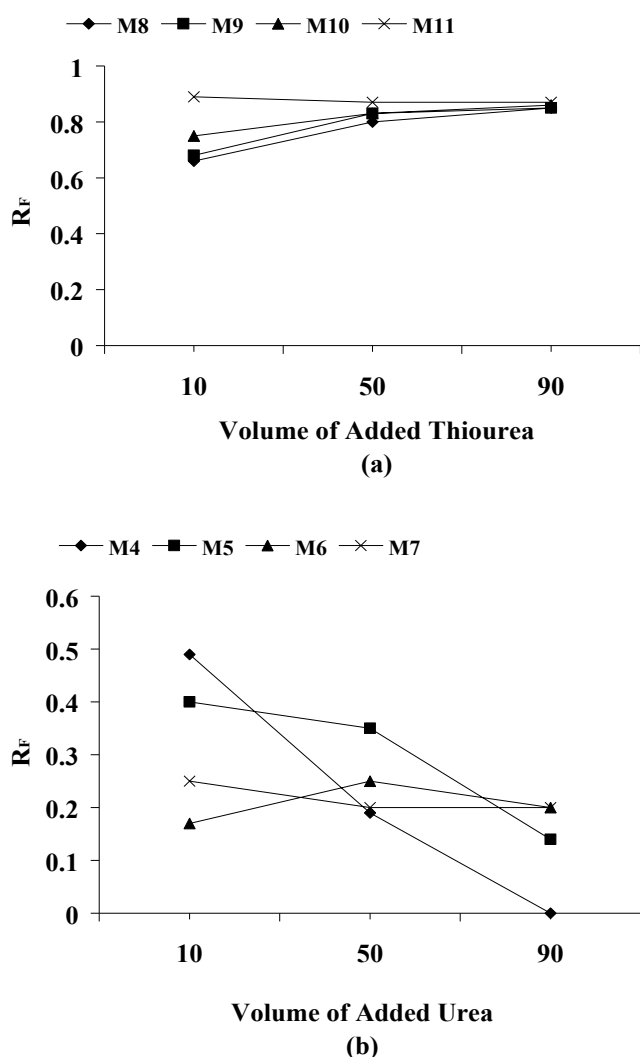


Figure 3. Plot of R_F of Cu^{2+} Vs volume of added thiourea (a), urea (b) in M_2 (0.3% aqueous SDS in pH 2.3)

in concentration of thiourea at all volume ratio with 0.3% SDS [Figure 3 (a)]. However, the mobility of Cu^{2+} increases with the increase in concentration of urea (1–15%), though its mobility decreases with the increase in volume ratio of urea at its particular concentration in 0.3% SDS [Figure 3 (b)].

- (vi) Ag^+ forms double spots at certain concentration of thiourea (2–10 g/L) in the mobile phase. The lower spot appearing near the point of application ($R_F = 0.04$) may be attributed to silver thiosulfate ($\text{Ag}_2\text{S}_2\text{O}_3$) which being sparingly soluble shows little mobility. The upper spot is probably due to the formation of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, and its mobility increases with the increase in concentration (2–10 g/L) of thiourea in the mobile phase. Being negatively charged species, it is not exchanged with silanol group of silica gel and hence move with the mobile phase giving higher mobility. At very low concentration of thiourea (1 g/L), only single spot is formed which remain

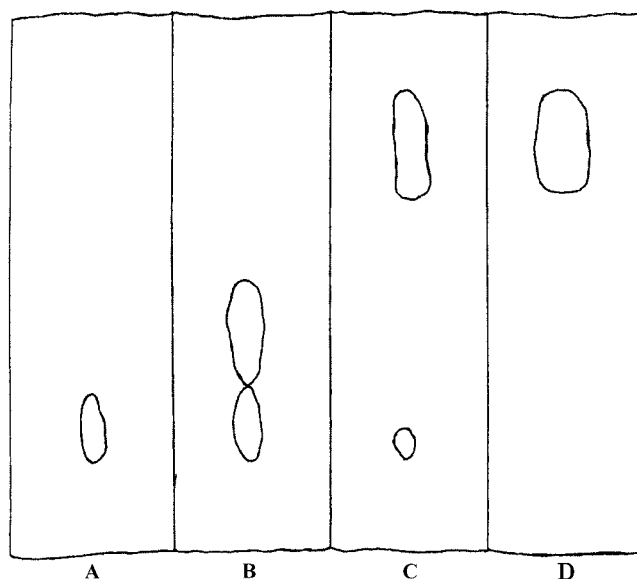


Figure 4. Detected spots of Ag^+ on silica gel 'G' plates developed with following mobile phases:

- A: 0.1% (1.0 g/L) aqueous thiourea plus 0.3% aqueous SDS (pH 2.3)
 B: 0.2% (2.0 g/L) aqueous thiourea plus 0.3% aqueous SDS (pH 2.3)
 C: 1.0% (10 g/L) aqueous thiourea plus 0.3% aqueous SDS (pH 2.3)
 D: 1.2% (12 g/L) aqueous thiourea plus 0.3% aqueous SDS (pH 2.3)

near the point of application. Conversely, at much higher concentration of thiourea (12–135 g/L), the single spot produced by Ag^+ appeared near the solvent front ($R_F = 0.83$). The positions of spots appeared on chromatoplates are depicted in Figure 4.

Thus, the higher concentration of thiourea in mobile phase is favorable for the formation of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ complex and checks the formation of $\text{Ag}_2\text{S}_2\text{O}_3$. Interestingly, badly tailed spots ($R_F = 0.33$) for Ag^+ were observed at concentration levels (1–15%) of urea containing mobile phase (M_4 – M_7). It is probably due to the fact that Ag^+ has relatively lower affinity towards oxygen donors (e.g. urea) compared to sulphur donors (e.g. thiourea). The formation of thio-complexes such as $\text{Ag}_2\text{S}_2\text{O}_3$, sparingly soluble and $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, soluble in water have been reported to be quite stable [27].

(c) Effect of Added NaNO_3 and NaCl

The effect of inorganic electrolyte additives (NaNO_3 and NaCl) on the mobility of metal cations was examined at their different concentration levels in 0.3% SDS (pH 2.3). The results are summarized in Tables 3 and 4. From these data following trends are noticeable.

- (i) Metal cations such as Ti^{4+} , VO^{2+} , Fe^{3+} , Cu^{2+} , UO_2^{2+} , Bi^{3+} and Pb^{2+}

Table 3. Mobility trends of metal ions on silica gel 'G' developed with 0.3% SDS (pH 2.3) plus different concentrations of NaNO₃

| Metal ions | 0.3% SDS + 1% NaNO ₃ | | | 0.3% SDS + 5% NaNO ₃ | | | 0.3% SDS + 10% NaNO ₃ | | | 0.3% SDS + 15% NaNO ₃ | | |
|------------------|---------------------------------|--------|--------|---------------------------------|--------|--------|----------------------------------|--------|--------|----------------------------------|--------|--------|
| | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 |
| Al ³⁺ | 0.22 | 0.05 | 0.10 | 0.35 | 0.05 | 0.20 | 0.40 | 0.15 | 0.25 | 0.55 | 0.15 | 0.40 T |
| Co ²⁺ | 0.70 T | 0.70 T | 0.60 T | 0.70 T | 0.70 T | 0.60 T | 0.87 | 0.80 T | 0.82 T | 0.85 | 0.80 T | 0.83 T |
| Ni ²⁺ | 0.60 T | 0.50 T | 0.60 T | 0.70 T | 0.50 T | 0.60 T | 0.85 | 0.70 T | 0.80 T | 0.85 | 0.80 T | 0.83 T |
| Zn ²⁺ | 0.14 | 0.25 T | 0.20 T | 0.15 | 0.26 T | 0.20 T | 0.25 T | 0.30 T | 0.27 T | 0.82 T | 0.34 T | 0.30 T |
| Ag ⁺ | 0.26 T | 0.25 | 0.26 T | 0.34 T | 0.30 T | 0.32 | 0.37 T | 0.35 | 0.37 T | 0.40 T | 0.38 T | 0.40 T |
| Cd ²⁺ | 0.83 | 0.69 | 0.73 | 0.90 | 0.83 | 0.85 | 0.90 | 0.86 | 0.87 | 0.90 | 0.85 | 0.87 |
| Au ³⁺ | 0.85 | 0.80 | 0.90 | 0.88 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |
| Hg ²⁺ | 0.70 T | 0.70 T | 0.70 T | 0.80 T | 0.80 T | 0.80 T | 0.85 | 0.86 | 0.85 | 0.85 | 0.85 | 0.85 |
| Tl ⁺ | 0.36 T | 0.35 T | 0.30 T | 0.47 | 0.64 T | 0.48 T | 0.66 | 0.68 T | 0.67 T | 0.65 | 0.70 T | 0.70 T |

Ti⁴⁺, VO²⁺, Fe³⁺, UO₂²⁺, Bi³⁺ and Pb²⁺ show little mobility $R_F \approx 0.07$.

T = Tailed Spot ($R_L - R_T > 0.30$)

Table 4. Mobility trends of metal ions on silica gel 'G' developed with 0.3% SDS (pH 2.3) plus different concentrations of NaCl

| Metal ion | 0.3% SDS + 1% NaCl | | | 0.3% SDS + 5% NaCl | | | 0.3% SDS + 10% NaCl | | | 0.3% SDS + 15% NaCl | |
|------------------|--------------------|--------|--------|--------------------|--------|--------|---------------------|--------|--------|---------------------|--------|
| | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:9 | 1:1 | 9:1 | 1:1 |
| Al ³⁺ | 0.05 | 0.05 | 0.05 | 0.10 | 0.05 | 0.07 | 0.20 T | 0.05 | 0.10 | 0.31 | 0.23 |
| Ti ⁴⁺ | 0.00 | 0.35 T | 0.35 T | 0.00 | 0.40 T | 0.40 T | 0.05 | 0.40 T | 0.40 T | 0.05 | 0.40 T |
| Co ²⁺ | 0.15 | 0.75 T | 0.40 T | 0.40 T | 0.85 | 0.60 T | 0.40 T | 0.89 | 0.70 T | 0.80 T | 0.84 T |
| Ni ²⁺ | 0.25 T | 0.50 T | 0.50 T | 0.60 T | 0.50 T | 0.55 T | 0.78 T | 0.78 T | 0.70 T | 0.80 T | 0.80 T |
| Cu ²⁺ | 0.21 | 0.00 | 0.10 | 0.28 | 0.10 | 0.12 | 0.30 T | 0.13 | 0.12 | 0.30 T | 0.13 |
| Zn ²⁺ | 0.25 | 0.20 | 0.22 | 0.30 | 0.25 | 0.30 | 0.41 | 0.30 | 0.30 | 0.43 | 0.38 |
| Cd ²⁺ | 0.30 T | 0.80 T | 0.55 T | 0.50 T | 0.89 | 0.80 T | 0.70 T | 0.90 | 0.90 | 0.89 | 0.89 |
| Au ³⁺ | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |
| Hg ²⁺ | 0.50 T | 0.70 T | 0.60 T | 0.60 T | 0.85 | 0.70 T | 0.70 T | 0.85 | 0.80 T | 0.86 | 0.85 |
| Tl ⁺ | 0.20 T | 0.27 T | 0.25 T | 0.33 T | 0.35 T | 0.30 T | 0.40 T | 0.40 T | 0.40 T | 0.62 T | 0.43 T |
| Bi ³⁺ | 0.10 | 0.20 T | 0.20 T | 0.17 T | 0.25 T | 0.25 T | 0.20 T | 0.40 T | 0.30 T | 0.23 T | 0.45 |

Fe³⁺, UO₂²⁺, Pb²⁺, Ag⁺ and VO²⁺ show little mobility $R_F \approx 0.06$.

T = Tailed Spot ($R_L - R_T > 0.30$)

show little mobility ($R_F \approx 0.07$) in presence of NaNO₃ as additive in 0.3% SDS (M₁₂–M₁₅).

- (ii) Mobility of Ag⁺, Ni²⁺, Co²⁺, Hg²⁺, Zn²⁺ and Tl⁺ was found to increase with the increase of NaNO₃ concentration levels. The increase in mobility is associated with the formation of tailed spot.
- (iii) The mobility of Al³⁺ increases with the increase in concentration of NaNO₃ and NaCl, although its mobility decreases with the increase in volume ratio of NaNO₃ and NaCl at their particular concentration in 0.3% SDS [Figures 2 (c) and (d)]. Like Al³⁺, Zn²⁺ and Cu²⁺ show the same trend in presence of NaCl.
- (iv) Au³⁺ shows a constant and high ($R_F = 0.90$) mobility, whereas

R_F value of Cd²⁺ fluctuates within the range $R_F = 0.70$ – 0.90 at all concentrations of NaNO₃.

- (v) The mobility of Ti⁴⁺, Co²⁺, Ni²⁺, Cd²⁺, Hg²⁺, Tl⁺ and Bi³⁺ was found to increase with the increase in NaCl concentration along with the formation of tailed spot, while Ni²⁺, Tl⁺ and Bi³⁺ produce tailed spots at all concentration levels, Hg²⁺ and Co²⁺ show tailed spots at low volume ratio of NaCl. Ti⁴⁺ and Cd²⁺ produce tailed spots at 1–5% NaCl in 0.3% SDS.
- (vi) In the presence of NaCl, UO₂²⁺, Pb²⁺, Ag⁺, VO²⁺ and Fe³⁺ show little mobility ($R_F \approx 0.06$).

On the basis of above studies, a TLC system comprising of silica gel as stationary phase and 0.3% buffered SDS (pH 2.3) plus 5% NaCl in 9:1 ratio by volume as mobile phase was selected for

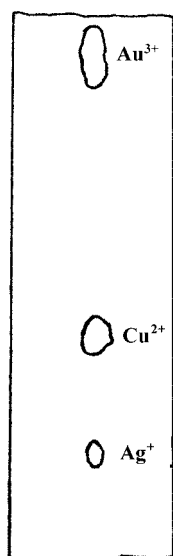


Figure 5. Separation pattern of coexisting Au^{3+} , Cu^{2+} and Ag^+ with 0.3% SDS (pH 2.3) + 5% NaCl (9:1)

Table 5. Effect of inorganic and organic impurities on the separation of co-existing Au^{3+} , Cu^{2+} , and Ag^+ on silica gel 'G' layers developed with 0.3% SDS (pH 2.3) + 5% NaCl (9:1)

| 1% aqueous solution of different impurities | Separation (R_F) | | |
|---|----------------------|------------------|---------------|
| | Au^{3+} | Cu^{2+} | Ag^+ |
| NO_2^- | 0.90 | 0.22 | 0.03 |
| Br^- | 0.89 | 0.17 | 0.00 |
| IO_3^- | 0.90 | 0.22 | 0.00 |
| SCN^- | 0.90 | 0.17 | 0.00 |
| PO_4^{3-} | 0.90 | 0.20 | 0.00 |
| <i>o</i> -Nitrophenol | 0.88 | 0.13 | 0.02 |
| <i>m</i> -Nitrophenol | 0.90 | 0.21 | 0.02 |
| <i>p</i> -Nitrophenol | 0.90 | 0.19 | 0.02 |
| <i>o</i> -Aminophenol | 0.89 | 0.14 | 0.03 |
| <i>m</i> -Aminophenol | 0.90 | 0.55 | 0.05 |
| <i>p</i> -Aminophenol | 0.90 | 0.22 | 0.02 |
| Methylamine | 0.89 | 0.17 | 0.00 |
| Dimethylamine | 0.89 | 0.13 | 0.00 |
| Trimethylamine | 0.90 | 0.25 | 0.00 |
| <i>o</i> -Chloroaniline | 0.90 | 0.22 | 0.02 |
| <i>m</i> -Chloroaniline | 0.90 | 0.23 | 0.02 |
| <i>p</i> -Chloroaniline | 0.90 | 0.21 | 0.02 |
| Brij-35 | 0.90 | 0.21 | 0.03 |
| Triton X-100 | 0.90 | 0.22 | 0.02 |
| CTAB | 0.88 | 0.14 | 0.00 |
| AOT | 0.88 | 0.13 | 0.03 |
| 10% Aqueous CTAB | 0.88 | 0.12 | 0.00 |
| 0.1% Aqueous AOT | 0.90 | 0.17 | 0.03 |

* R_F values of Au^{3+} , Cu^{2+} and Ag^+ in the absence of impurities are 0.90, 0.28 and 0.03, respectively.

T = Tailed Spot ($R_L - R_T > 0.3$)

detailed studies. This TLC system was found most favorable for analytically important separation of gold, copper and silver (Figure 5). These metals known as 'coinage metals', have been used for production of coins. Copper with gold and silver causes hardness and hence used for jewellery.

From the data listed in Table 5, it is evident that the R_F value of Cu^{2+} is decreased considerably in the presence of certain impurities. However, the R_F of Ag^+ and Au^{3+} remained almost unchanged. Although the separation of Ag^+ , Au^{3+} and Cu^{2+} from their mixture is possible in the presence of most of the impurities but the separation efficiency is adversely affected by the presence of *o*-nitrophenol, *o*-aminophenol, methylamine and dimethylamine. These compounds were found responsible to bring the Cu^{2+} spot very close to the spot of Ag^+ and hence the separation of Cu^{2+} from Ag^+ was very poor. In the case of surfactants as impurities, simultaneous separation of Au^{3+} , Cu^{2+} and Ag^+ is possible up to (10% CTAB) 1 mg per spot of cationic surfactant (CTAB) but in the presence of anionic surfactant (AOT) it is possible only up to 0.01 mg per spot (0.1%) as impurities.

The lowest possible detectable microgram amounts along with dilution limits of some heavy metal cations (given in parenthesis) obtained on silica gel layer with appropriate detectors were Fe^{3+}

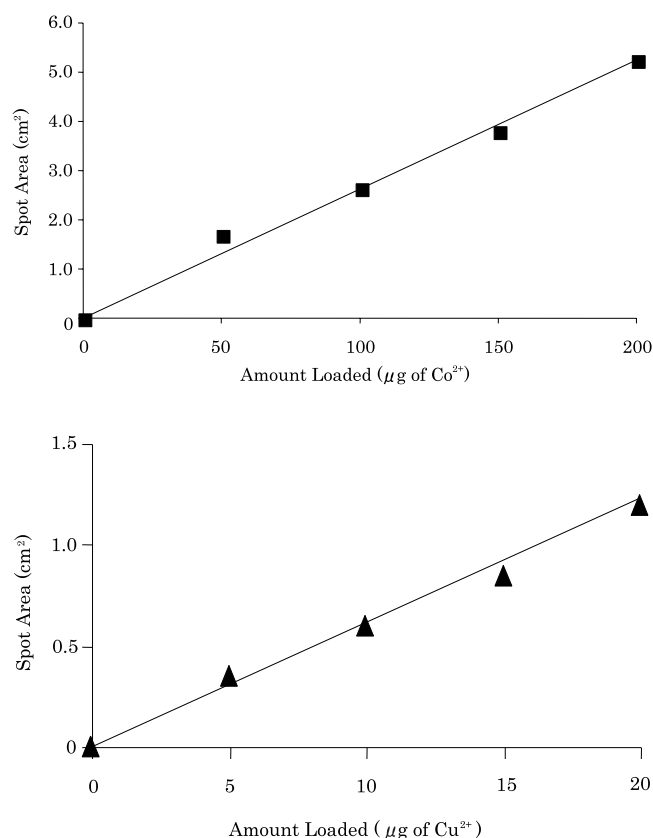


Figure 6. Calibration curves for semiquantitative determination of Co^{2+} and Cu^{2+}

(0.125, 1: 8×10^4); Cu^{2+} (0.25, 1: 4×10^4); Ag^+ (8.0, 1: 1.2×10^3); Ni^{2+} (0.1, 1: 1×10^5) and Co^{2+} (0.1, 1: 1×10^5). The present method is superior being more sensitive than reported methods [28, 29].

An attempt has been made for semiquantitative determination of metal cations by spot-area measurement method. The spots obtained were copied on tracing paper from the chromatoplates and the spot-area was measured. A relationship between the spot-area and microgram quantities of metal cations follows the equation $\zeta = km$, where ζ is the spot area, m is the spotted amount and k is constant. Representative plots of Cu^{2+} and Co^{2+} are shown in Figure 6. A linear relationship was obtained for Ni^{2+} , Co^{2+} , Cu^{2+} and Cd^{2+} when the area of spot was plotted against the amount of the sample spotted. At higher concentration, a negative deviation from linear law in all cases was observed. The accuracy and precision were below $\pm 15\%$.

Quantitative Studies

Cu^{2+} (up to 25.45 μg) was spectrophotometrically determined using 0.1% PAN as chromogenic reagent. Optical densities were measured at 460 nm and plotted against μg amounts of Cu^{2+} to obtain the standard calibration curve. This curve was used to study

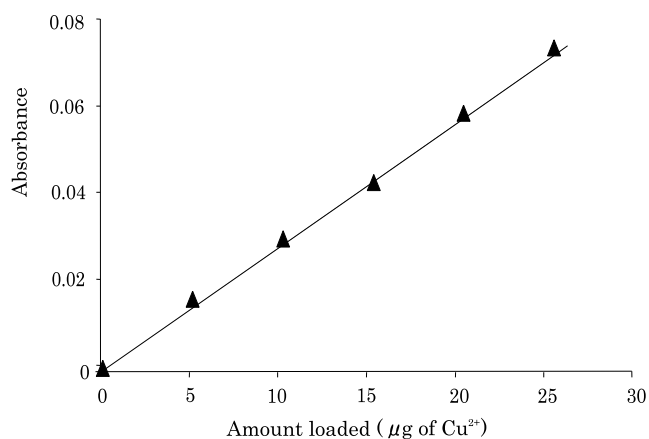


Figure 7. Calibration curve for quantitative determination of Cu^{2+}

the recovery (Figure 7) of Cu^{2+} from synthetic alloy and ore samples. It was observed that copper up to 97% can be recovered. The RSD remained below 3.16 and percent error was not more than 18.35 as listed in Table 6.

Application

Table 6. Spectrophotometric determination of Cu^{2+} after its separation from Ag^+ and Au^{3+}

| Samples | Amount loaded (μg) | Amount recovered (μg) | % Error | Percentage recovery | Relative standard deviation (pph) |
|-------------------------------------|---------------------------------|------------------------------------|---------|---------------------|-----------------------------------|
| Gun metal | 22.86 | 22.26 | 2.62 | 97.37 | 1.75 |
| Ornamental silver | 5.08 | 4.65 | 8.46 | 91.53 | 3.16 |
| Copper sulfide (CuS) | 25.45 | 23.45 | 7.85 | 92.14 | 2.56 |
| Copper pyrites (CuFeS_2) | 5.08 | 4.14 | 18.35 | 81.49 | 2.78 |

Table 7. Experimentally achieved separations on silica gel 'G' layers developed with different mobile phases

| Mobile phases | Separations (R_F) ^{a)} |
|---------------------------------------|---|
| 1.44% SDS (pH 2.3) | Co^{2+} (0.88), Ni^{2+} (0.85), Au^{3+} (0.90) – Al^{3+} (0.12), Fe^{3+} (0.05), Hg^{2+} , VO^{2+} , Ti^{4+} , UO_2^{2+} or Pb^{2+} (0.00) |
| 0.3% SDS (pH 2.3) | Co^{2+} (0.89), Ni^{2+} (0.87) – Al^{3+} (0.11) Co^{2+} (0.89), Ni^{2+} (0.87) – Cu^{2+} (0.14) Au^{3+} (0.90) – Ag^+ (0.12) Au^{3+} (0.90) – Cu^{2+} (0.15) Ni^{2+} (0.87) – Cd^{2+} (0.39) – VO^{2+} , Ti^{4+} , UO_2^{2+} , Fe^{3+} or Pb^{2+} (0.00) |
| 0.3% SDS (pH 2.3) + 1% urea (9:1) | Au^{3+} (0.91) – Cu^{2+} (0.47) – VO^{2+} , UO_2^{2+} (0.00) Au^{3+} (0.91) – Cu^{2+} (0.49) – Ti^{4+} (0.06) |
| 0.3% SDS (pH 2.3) + 5% urea (9:1) | Au^{3+} (0.90) – Cu^{2+} (0.42) – Ti^{4+} (0.07) |
| 0.3% SDS (pH 2.3) + 1% thiourea (9:1) | Au^{3+} (0.89) – Cd^{2+} (0.52) – Ti^{4+} , Pb^{2+} or Fe^{3+} (0.05) Au^{3+} (0.90) – Al^{3+} (0.32) – VO^{2+} or UO_2^{2+} (0.00) |
| 0.3% SDS (pH 2.3) + 5% NaCl (9:1) | Au^{3+} (0.90) – Cu^{2+} (0.32) – Ag^+ (0.02) Au^{3+} (0.92) – Cu^{2+} (0.30) – Pb^{2+} , VO^{2+} or UO_2^{2+} (0.05) Au^{3+} (0.90) – Cu^{2+} (0.28) – Ti^{4+} (0.00) |

^{a)} The R_F values of metal ions in their mixtures are slightly changed from their individual R_F values because of mutual interactions.

Table 8. Simultaneous separation of co-existing Au^{3+} , Cu^{2+} and Ag^+ from real and spiked samples on silica layers developed with M_{17} (9:1)

| Real samples (unspiked) | Separation (R_F) | Spiked samples | Separation (R_F) | | |
|-------------------------------------|--|-------------------------------------|----------------------|------------------|---------------|
| | | | Au^{3+} | Cu^{2+} | Ag^+ |
| High-copper dental amalgam (HCDA) | Ag^+ (0.04) – Cu^{2+} (0.30) Ag^+ (0.04) – Hg^{2+} (0.60 T) | High-copper dental amalgam (HCDA) | 0.90 | 0.32 | 0.03 |
| Printed-circuit board (PCB) | Cu^{2+} (0.32) – Au^{3+} (0.90) | Printed-circuit board (PCB) | 0.91 | 0.31 | 0.04 |
| Silver mirror scrap (SMS) | Ag^+ (0.03) – Cu^{2+} (0.30) | Silver mirror scrap (SMS) | 0.92 | 0.32 | 0.02 |
| Silver mirror spent solution (SMSS) | Ag^+ (0.03) – Cu^{2+} (0.30) | Silver mirror spent solution (SMSS) | 0.90 | 0.30 | 0.03 |
| Sterling silver (SS) | Ag^+ (0.02) – Cu^{2+} (0.31) | Sterling silver (SS) | 0.90 | 0.29 | 0.03 |
| Electroplating gold waste | Au^{3+} (0.89) – Cu^{2+} (0.30) | Electroplating gold waste | 0.92 | 0.30 | 0.04 |

Several important separations of metal cations were experimentally achieved on silica gel layers developed with a variety of mobile phase systems. These separations have been listed in Table 7. The most favorable TLC system comprising of silica gel as stationary phase and 0.3% aqueous SDS plus 5% NaCl (9:1) as mobile phase has been tested for identification and separation of Ag^+ , Cu^{2+} and Au^{3+} from a variety of matrices. The results presented in Table 8 indicate the versatility of the proposed TLC systems which has wider applications.

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