

Heavy Metal Ions Separation on Thin Layer of Impregnated Carbamide-Formaldehyde Polymer

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Abstract

Various heavy metal ions such as Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Fe³⁺, UO₂²⁺, VO²⁺ and Bi³⁺ have been chromatographed on thin layer of carbamide-formaldehyde polymer impregnated with sodium diethyl- dithiocarbamate and its admixture with Na₂CO₃, NaCl, EDTA, H₃PO₄ and NaOH. Common solvent namely acetone, benzene, carbon tetrachloride, methanol and ethanol have been used as mobile phases. Semiquantitative determination of Hg²⁺, Bi³⁺ and Ni²⁺ by visual comparison of color intensities on the TLC plates as well as by measurement of spot area was attempted.

Keywords: Carbamide; EDTA; TLC; Cu²⁺; Dithiocarbamate

Introduction

Thin layer chromatography (TLC) is a very convenient and rapid method for the separation and identification of inorganic ions. Therefore, any attempts to improve TLC for this application seem to be of interest for chromatographers. There are several ways to improve the TLC method. One of them is use of support possessing different characteristics than those commonly used in TLC. For that reason a number of metal ions were systematically chromatographed on thin layer of a synthesized carbamide-formaldehyde polymer, and already used for the separation of amino acid [1] and various metal ions were also chromatographed [2] using various organic solvents as a mobile phases. Sodium diethyl-dithiocarbamate [(C₂H₅)₂NCS₂]⁻Na⁺, (NaDDC) is an effective extraction reagent for over twenty metal ions into various organic solvents such as chloroform, carbon tetrachloride, methanol and ethanol [3]. Espinola et al. [4] have used immobilized dithiocarbamate on silica gel for extraction of cobalt, nickel, copper and zinc cations in ethanolic solution. Web et al. [5] have reported the simultaneous preconcentration of beryllium, bismuth, cobalt, gallium, silver, lead, cadmium, copper, manganese and indium in sea water by using poly(acrylamino phosphonic dithiocarbamate), chelating fibre, as an adsorbent. Various heavy metal ions and several binary mixtures were separated on thin layer cellulose plates and paper chromatographic strips impregnated with sodium diethyldithiocarbamate [6], and chromatographic behavior of various dithiocarbamate fungicides [7] were studied on cellulose plates. The aim of our work was to obtain a general feeling on the chromatographic behavior of a number of heavy metal cations on impregnated carbamide-formaldehyde polymer layer.

Experimental Procedure

Apparatus

Glass jars (25 × 5cm), glass capillary, watch glass and temperature controlled electric oven were used.

Reagents and chemicals

Urea, formalin solution, was obtained from Merk, dimethylglyoxime, dithizone, potassium ferrocyanide, carbon tetrachloride, NaCl, EDTA, NaOH, Na₂CO₃, H₃PO₄ methanol and ethanol were obtained from SD Fine India. Sodium diethyldithiocarbamate was obtained from CDH, India. All other chemicals were of analytical reagent grade.

Preparation of Solutions

Solutions (1%) of metal salts, sodium sulphide and

diethyldithiocarbamate (NaDDC) (0.01M) was prepared in distilled water. Aqueous solutions of metal salts were stabilized by adding the corresponding mineral acids (0.5ml of 4M) and ethanol (0.5ml).

Metal ions studied

Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Cu²⁺, Fe³⁺, UO₂²⁺, VO²⁺, Ni²⁺, Co²⁺ and Bi³⁺.

Detection

- 1% aqueous potassium ferrocyanide- Fe³⁺, Cu²⁺, UO₂²⁺ and VO²⁺
- 0.5% Dithiozone in CCl₄ – Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺ and Bi³⁺
- 1% alcoholic solution of DMG – Ni²⁺ and Co²⁺

Thin layer chromatography

Preparations of Carbamide-formaldehyde polymer plates: The carbamide- formaldehyde thin layer were prepared by suspending 10 gram of carbamide formaldehyde powder [1] in 60ml of distilled water, and the suspension was then coated onto glass plate using by dipping method. The plates were allowed to dry over night at room temperature and were used to next day for TLC.

Preparation of Carbamide- formaldehyde plates: Solutions with desired concentration of impregnants with various additives [(ICF₁)- NaDDC(20%), (ICF₂)- NaDDC (20%) + Na₂CO₃ (4%), (ICF₃)- NaDDC (20%) + NaCl (4%), (ICF₄)- NaDDC (20%) + EDTA (4%), (ICF₅)- NaDDC (20%) + NaOH (4%) and (ICF₆)- NaDDC (20%) + H₃PO₄ (4%)] were prepared in distilled water. After that plain carbamide – formaldehyde plates are dipped in above prepared solutions. The developed plates were then activated by heating at 60±1°C for 1hr. (ICF- Impregnated carbamide- formaldehyde)

Spotting of test solution: Thin layer chromatography was performed on impregnated carbamide-formaldehyde layer plates. Test

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solutions (1 µl) were applied on plates with the help of micropipettes at about 2cm above the lower edge of the plates. The solvent ascent was fixed to 10cm in all cases for the determination of R_F values of all individual metal ions. Linear ascending development was carried out in a TLC chamber.

Limit of detection: The limits of detection of the metal cations were determined by spotting different amounts of metal ion onto the TLC plates, developing the plates using the method describe above, and then detecting the spots. This method was repeated with a successive decrease in the amount of metal ion used until spots were not detected. The minimum detectable amount on the TLC plates was taken as the limit of detection.

Semiquantitative determination of Hg^{2+} , Bi^{3+} and Ni^{2+} : To determine recovery of Hg^{2+} , Bi^{3+} and Ni^{2+} by spot area measurement method, 0.01mL from series of standard solution of Hg^{2+} , Bi^{3+} and Ni^{2+} were spotted on ICF₅ plates. The plates were developed with carbon tetrachloride mobile phase. After detection, the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated. The recovery of Hg^{2+} , Bi^{3+} and Ni^{2+} were studied by analyzing various samples. For this purpose, experiments were performed by spotting 0.01mL of sample of solution containing 100 µg Hg^{2+} , Bi^{3+} and Ni^{2+} . The recovery of Hg^{2+} was $28 \pm 3\%$.

Result and Discussion

This study includes chromatography of eleven metal ions (Pb^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} , UO_2^{2+} , VO^{2+} , Ni^{2+} , Co^{2+} and Bi^{3+}) on thin layer of carbamide-formaldehyde polymer impregnated with six adsorbent and six mobile phase (water, acetone, benzene, carbon

tetrachloride, ethanol and methanol). The practically achieved separations of metal ions are given in the table 1.

The effect of impregnation material

The R_F values of all the metal ions were found to be zero on carbamide- formaldehyde layer impregnated with acidic admixture, ICF₆ [NaDDC (20%) + H_3PO_4 (4%)], in the mobile phases. These observations support the fact that metal dithiocarbamate complexes are unstable in acidic mixtures. The alkaline impregnation material, ICF₅ [NaDDC (20%) + NaOH (4%)] was found to be the best as it gives compact spots for all the metal ions. Hence, it seems that NaDDC act as a complexing agent as well as adsorbent. The role of water soluble salts is suppressed due to the excess of NaDDC (20%).

The effect of mobile phase

The R_F values were found to be zero for the metal ions on thin layer of carbamide – formaldehyde impregnated with any of the six impregnation materials in the mobile phase of highest dielectric constant ($\epsilon = 78.54$) such as water. It is on line with the fact that the dithiocarbamates of metal ions of atomic number more than 20 are water insoluble. The differential R_F values have been obtained for the metal ions in low dielectric constant mobile phase such as carbon tetrachloride ($\epsilon = 2.24$), benzene ($\epsilon = 2.27$), acetone ($\epsilon = 20.7$), ethanol ($\epsilon = 24.5$) and methanol ($\epsilon = 32.7$). Hence it is clear that the R_F values of metal dithiocarbamates depend on its solubility in the mobile phase, the adsorption affinity and pH of the impregnation materials. Therefore, the maximum numbers of separations have been achieved in lowest dielectric constant mobile phase that is carbon tetrachloride. Hence carbon tetrachloride seems to be better mobile phases for metal

Stationary phase	Separations R_F or (R_L-R_T)
	Mobile phase – Acetone
ICF ₁	Cd ²⁺ (0.80) from Co ²⁺ (0 - 7.0 cm) or Fe ³⁺ (0 - 3.0 cm)
ICF ₂	Zn ²⁺ (0.87) from Co ²⁺ (0 - 6.9 cm) or Fe ³⁺ (0 - 6.2 cm) or Hg ²⁺ (0-5.0 cm)
ICF ₃	Hg ²⁺ (0.90) from Fe ³⁺ (0.00)
ICF ₅	Hg ²⁺ (0.90) from Pb ²⁺ (0.75)
	Mobile phase – Methanol
ICF ₁	Hg ²⁺ (0.95) from Cd ²⁺ (0.00), Hg ²⁺ (0.93) from Cd ²⁺ (0.00)
ICF ₃	Fe ³⁺ (0.98) from Pb ²⁺ (6.6 - 8.8 cm)
ICF ₄	Hg ²⁺ (0.95) from Cd ²⁺ (0.00)
	Mobile phase – Ethanol
ICF ₁	Cu ²⁺ (0.00) from Cd ²⁺ (4.4 - 9.0 cm), Fe ³⁺ (0.00) from Cd ²⁺ (3.1 - 8.8 cm)
ICF ₂	Fe ³⁺ (0.13) from Cd ²⁺ (4.8 - 8.1 cm), Ni ²⁺ (0.19) from Zn ²⁺ (5.9- 9.8 cm)
ICF ₃	Hg ²⁺ (0.00) from Cd ²⁺ (6.1 – 9.4 cm) , Co ²⁺ (0.00) from Cd ²⁺ (6.5 - 9.4 cm)
ICF ₄	Hg ²⁺ (0.00) from Cd ²⁺ (6.5 – 8.6 cm) , Pb ²⁺ (0.00) from Cd ²⁺ (6.5 – 9.7 cm)
ICF ₅	Pb ²⁺ (0.00) from Cd ²⁺ (8.0 – 9.8 cm)
	Mobile phase – Carbon tetrachloride
ICF ₁	Hg ²⁺ (0.96) from Co ²⁺ (0 – 7.5 cm)
ICF ₂	Hg ²⁺ (0.98) from Cd ²⁺ (0.00), Cd ²⁺ (0.00) from Bi ³⁺ (5.7 – 10.0 cm)
ICF ₃	Cd ²⁺ (0.00) from Hg ²⁺ (5.7 – 10.0 cm), Cd ²⁺ (0.00) from Zn ²⁺ (4.6 – 10.0cm)
ICF ₄	Hg ²⁺ (0.95) from Ni ²⁺ (0.00), Hg ²⁺ (0.94) from Cd ²⁺ (0.00)
ICF ₅	Ni ²⁺ (0.00) from Hg ²⁺ (7.5 – 10.0 cm), Ni ²⁺ (0.00) from Zn ²⁺ (3.5 - 10.0 cm)
	Mobile phase – Benzene
ICF ₁	Cd ²⁺ (0.00) from Bi ³⁺ (7 – 9.8 cm), Cd ²⁺ (0.00) from Pb ²⁺ (2.1 – 9.6 cm)
ICF ₂	Hg ²⁺ (0.86) from Cd ²⁺ (0.00)
ICF ₄	Hg ²⁺ (0.97) from Cd ²⁺ (0.00)

ICF (Impregnated carbamide- formaldehyde) - Impregnations materials listed in experimental section.

R_L (tailing) = distance (cm) travelled by the lower edge of a tailing spot.

R_T (tailing) = distance (cm) travelled by the upper edge of a tailing spot.

Table 1: Separation achieved

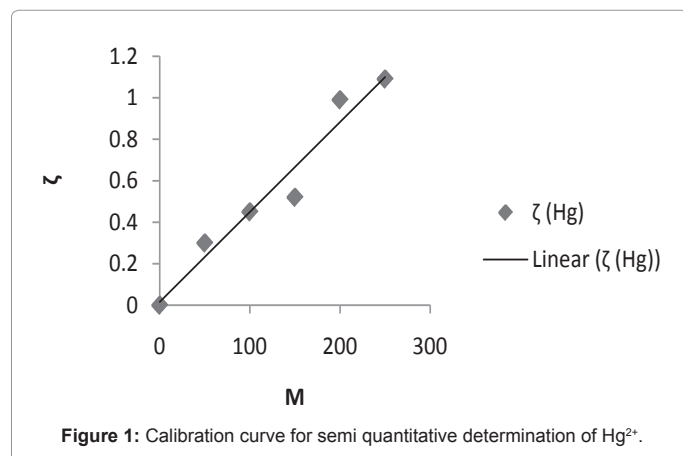


Figure 1: Calibration curve for semi quantitative determination of Hg^{2+} .

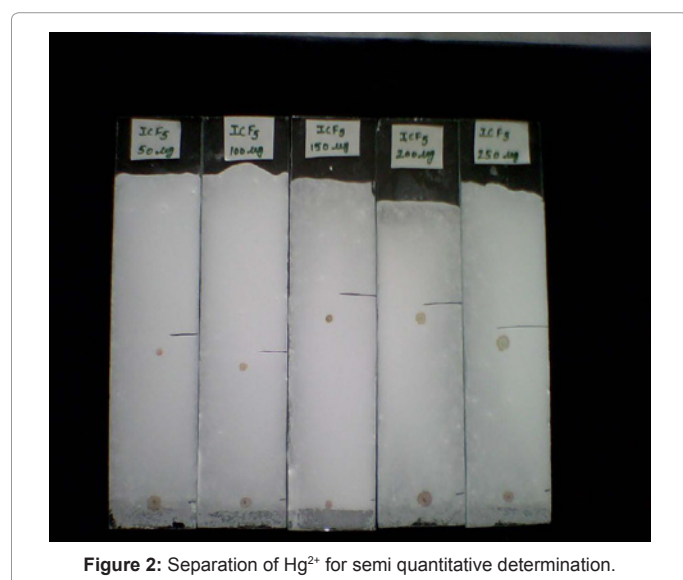


Figure 2: Separation of Hg^{2+} for semi quantitative determination.

ions chromatography on NaDDC using carbamide- formaldehyde polymer layer.

Quantitative analysis by spot area measurement method

An attempt has been made to determine the recovery of Hg^{2+} , Bi^{3+} and Ni^{2+} spiked into water using spot area measurement method by

using ICF_5 plates and carbon tetrachloride as a mobile phase. A linear relationship obtained when the amount of sample spotted was plotted against area of the spot follows the empirical equation $\zeta=km$, where ζ is the area of the spot, m is the amount of solute and k is a constant. Representative plot for Hg^{2+} has been shown in Figure 1 and 2. The linearity is maintained up to 250 μg /spot. At higher concentration a positive deviation from linear law was observed. The accuracy and precision was around $Hg^{2+} = \pm 28\%$.

Conclusion

Sodium diethyldithiocarbamate and carbamide - formaldehyde polymer is a promising chromatographic material for the separation of metal ions in organic mobile phases such as acetone, ethanol, methanol, carbon tetrachloride. However aqueous solutions and acidic solutions may not be useful as mobile phase in chromatography on sodium diethyldithiocarbamate. The thin layer plate of carbamide - formaldehyde with NaOH and carbon tetrachloride contains mobile phase was identified as the most useful for the analysis of heavy metal ions.

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