



Research Article

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## Rapid Separation of Some Toxic Heavy Metal ions by Thin Layer Chromatography

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### ABSTRACT

Thin layer chromatographic method has been developed for the separation of metal ions such as Cr (vi), Cr (iii), As (iii), Cd (ii), Tl (iii) and Hg (ii) from their two three and four component mixtures. The separations were performed on thin layer of silica gel 'G' using Glycine as mobile phase. The effect of concentration and pH of mobile phase on the  $R_f$  values of individual metal ions were studied and the optimum conditions for separation of metal ions from their mixture were determined.

**Key words:** Thin layer chromatography, Separation, Silica gel-G, Glycine, Toxic Heavy Metal Ions.

### INTRODUCTION

Thin layer chromatography is a versatile technique for the identification and separation of organic and in-organic compounds [1,2]. The coordination properties of solvent are one of the main factor which influence TLC separations. Success in thin layer chromatography depends to great extent upon the selection of proper mobile phase to achieve desired separations.

Heavy metals have received considerable attention from analysts, because of their physical and environmental importance [3, 4]. Metals such as As, Cr, Hg, Tl, Cd, Ni, Tl, Cu, Fe, Zn, Pb, Co, Mn is toxic and harmful to human health. These metal ions can form complexes with bio-ligands containing Oxygen, Nitrogen and Sulphur atoms [5], which causes many problems by their redox processes in living organisms.

In the past few decades, there is substantial increase in the use of heavy metal, due to the industrialization. Industrial waste is the major source of different kinds of metal pollution in aquatic systems. The major sources of pollution of Chromium in the aquatic environment are electroplating stainless steel industry, metal finishing industrial effluents, sewage and waste-water treatment plants discharge and chromates from cooling water; chromium occurs in several oxidation states such as di, tri, penta and hexavalent, but only Cr (iii) and Cr (vi) are biologically important. Chromium in the aquatic tends to speciate into Cr (iii) & Cr (vi), with the trivalent ion being oxidized to the hexavalent form or precipitating from solution.

There are different analytical techniques of detection and separation of chromium including graphite furnace atomic-absorption spectroscopy [6,7], atomic emission spectroscopy [8], normal phase and reverse phase thin layer chromatography [9-11], ion exchange chromatography [12, 13], precipitation floatation [14].

Out of these different separation procedures, thin layer chromatography is probably the most versatile, because it can be used for the selective separation of metal cations on the micro and as well as macro scales.

A. Mohammad and N. Fatima [15] used Formic acid because it form complex with many metal ions. K. N. Johri and R. K. Bajaj used MHNAMT [16] and MAMT. [17] For the separation of Ru (iii); Rh (iii); Pb (ii); Pt (v) and Au (iii) as complexing agent. Similarly many amino acids can form complex with metal ions [18].

In this paper we were going to discuss the separating possibility of Glycine. The dissociation constant of Glycine is [K<sub>a</sub> (H<sub>2</sub>O) at 25<sup>0</sup>C = 1.6 x 10<sup>-10</sup> and K<sub>b</sub> (H<sub>2</sub>O) at 25<sup>0</sup>C = 2.5 x 10<sup>-12</sup>]. Glycine in neutral compound and act as a dipolar ion [19] as [ <sup>+</sup>H<sub>3</sub>N-CH<sub>2</sub>-COO<sup>-</sup> ]. This dipolar ions form complex with metal ion.

All studies with Glycine as mobile phase has been performed using conventional, laboratory made TLC plates. It was observed in literature survey, the use of amino acids for the separation of metal ions was very less, therefore decided to find out and to use the analytical potential of glycine as mobile phase using silica gel-G as stationary phase for analysis of heavy metal ions. As a result several analytically important separations of heavy metals were realized. Separation of the chromium is industrially important, because Cr (iii) is converted to Cr (vi) in alkaline peroxide medium, which is very toxic for aquatic as well as terrestrial life.

This paper deals with the rapid separation of heavy metal ions present in three, as well as four component mixtures on non - impregnated silica gel 'G' coated plates, using aqueous solution of glycine as a mobile phase.

## EXPERIMENTAL SECTION

### Chemicals and Reagents: Chemicals and Reagents:

Glycine (E. Merck; India), Silica gel - G (E. Merck; India); Hydrochloric acid and Sodium hydroxide. All chemicals were of analytical reagent grade.

**Metal ion Studied:** Cr (vi); Cr (iii); Tl (iii); Cd (ii); Hg (ii); and As (iii).

**Test Solution:** TLC was performed using a standard aqueous solution (0.05 M) of potassium, chloride, sulphate and trioxide salts of the metal ions listed.

**Detection:** The metal ions [20] were detected using 0.05 % Dithiozone in Carbon tetra chloride for Cd (ii); Tl (iii); As (iii) and Hg (ii). Saturated Alcoholic AgNO<sub>3</sub> for Cr (vi) and Saturated Alcoholic Alizarin red for Cr (iii).

**Stationary Phase:** Silica gel -G.

**Mobile Phase:** The aqueous solution of Glycine as the mobile phases.

### Thin - layer chromatography:

**A. Preparation of Plates:** The TLC plates were prepared by mixing silica gel-G with demineralised water in 1:2 ratio by weight with constant stirring to obtain homogeneous slurry. It was then immediately applied on the glass plates by dipping method [21]. The plates were allowed to dry over night at room temperature and were used next day for TLC.

**B. Procedure:** Test solutions were spotted onto thin- layer plates with the help of a micropipette positioned about 1.0 cm above the lower edge of the TLC plates. The spots were air dried and the plates were then developed with the given mobile phase using by the one dimensional ascending technique in glass jars. The development distance was fixed at 10 cm in all cases. Following development, the plates were again air dried and the spots of the cations were visualized as coloring spots using the appropriate spraying reagent. R<sub>F</sub> values were then calculated.

**C. Separation:** For the separation, the metal ions to be separated were mixed in equal amounts. A test solution of the resultant mixture was spotted onto the activated TLC plate, and was then air dried. The plates were developed to a distance of 10 cm. The spots were detected and the separated metal cations were identified by their R<sub>F</sub> values.

## RESULTS AND DISCUSSION

**Effect of Concentration:** - This section deals with the separation of Cr (vi); Cr (iii); As (iii); Cd (ii); Tl (iii) and Hg (ii). Various experiments were carried out at different pH and at different concentration of Glycine for determining optimum separation concentration for the metal ions.

The results dealing with the effect of concentration of mobile phase, i.e. Glycine on the R<sub>F</sub> values of different metal ions such as Cr (vi); Cr (iii); As (iii); Cd (ii); Tl (iii) and Hg (ii) are tabulated in table 1. The variations in the R<sub>F</sub> values with concentration in the range of 0.005 to 0.1 M were studied in pH range of 1 to 7.

**Table 1:- Effect of Concentration on the  $R_f$  values of metal ions**

Conc. (M)	Metal Ions					
	Cr (vi)	Cr (iii)	As (iii)	Cd (ii)	Tl (iii)	Hg (ii)
0.005	0.95	0.07	0.80	0.31	0.81	0.75
0.01	0.93	0.10	0.80	0.37	0.18	0.78
0.05	0.94	0.11	0.81	0.48	0.25	0.89
0.1	0.97	0.35	0.72	0.56	0.49	0.90

It was observed that, at low concentration 0.005 M Cr (vi); Cd (ii); and Tl (iii) shows tailing, at 0.01 M concentration all metal ions shows little tailing. As the concentration of glycine was increased to 0.05 M, clear and distinct spots were seen. It was also observed that, there is an increase in the  $R_f$  values with increase in the concentration, but at 0.1 M glycine spots are not compact and shows little spreading, specially Cr (vi); Cd (ii); Hg (ii). However 0.05 M concentration was selected as the optimum concentration for further studies.

Effect of pH: - This section deals with effect of pH on  $R_f$  values of metal ions. The effect of pH on the  $R_f$  values of different metal ions was carefully studied by conducting several sets experiments. The plates were run near about to 10 cm above from the base line. The results are tabulated in table 2 which reveal variations in the  $R_f$  values with pH of Glycine. The  $R_f$  value measurements were done in the pH range of 1.0 to 7.0 at 0.05 M concentration.

**Table 2: Effect of pH on the  $R_f$  Values of metal ions at conc. 0.05M Glycine.**

Metal ions	pH of Mobile Phase								
	1.5	2	2.5	3	3.5	4	5	6	7
Cr (vi)	0.91	0.85	0.94	0.94	0.95	0.97	0.97 T	0.97 T	0.97 T
Cr (iii)	0.72	0.59	0.40	0.17	0.10	0.06	0.07 T	0.06 T	0.1 T
As (iii)	0.85	0.82	0.80	0.80	0.81	0.84	0.85	0.86	0.88
Cd (ii)	0.90	0.67	0.61	0.52	0.48	0.39 T	0.34 T	0.30 T	0.25 T
Tl (iii)	0.80	0.53	0.53	0.32	0.24	0.19 T	0.20 T	0.19 T	0.17 T
Hg (ii)	0.95	0.94	0.88	0.87	0.89	0.89	0.9 spr	0.91spr	0.87spr

Notation: - T- Tailing; Spr- Spreading; N.D. - Not Detected

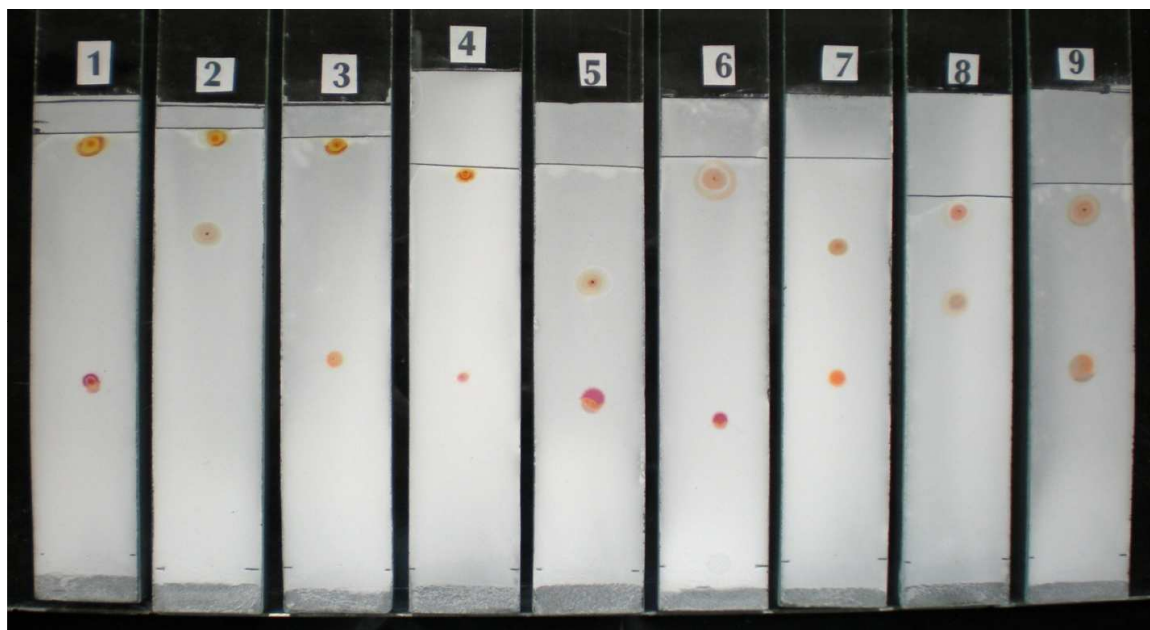
**Table No 3:- Binary separations**

Sr. No	Components of Binary mixture	Metal ions with there $R_f$ Values
1.	Cr (vi); Cr (iii)	Cr (vi) - 0.95; Cr (iii) - 0.42.
2.	Cr (vi); As (iii)	Cr (vi) - 0.97; As (iii) - 0.69.
3.	Cr (vi); Cd (ii)	Cr (vi) - 0.97; Cd (ii) - 0.53.
4.	Cr (vi); Tl (iii)	Cr (vi) - 0.98; Tl (iii) - 0.50.
5.	As (iii); Cr (iii)	As (ii) - 0.72; Cr (iii) - 0.45
6.	Hg (ii); Cr (iii)	Hg (ii) - 0.92; Cr (iii) - 0.44.
7.	As (iii); Cd (ii)	As (iii) - 0.75; Cd (ii) - 0.34.
8.	Hg (ii); As (iii)	Hg (ii) - 0.92; As (iii) - 0.69.
9.	Hg (ii); Cd (ii)	Hg (ii) - 0.87; Cd (ii) - 0.46

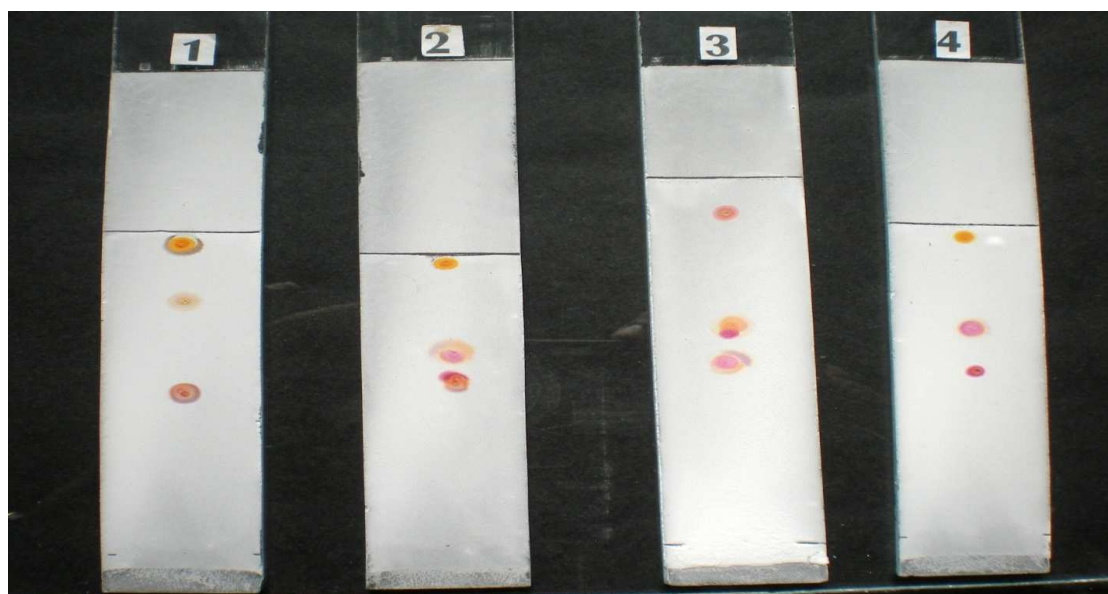
**Table No 4:- Ternary separations**

Sr. No	Component of Ternary Mixture	Metal ions with there $R_f$ Values
1.	Cr (vi); As (iii); Cr (iii).	Cr (iii) - 0.95; As (iii) - 0.78; Cr (iii) - 0.44.
2.	Cr (vi); Cd (ii); Cr (iii).	Cr (vi) - 0.98; Cd (ii) - 0.64; Cr (iii) - 0.53.
3.	Hg (ii); Cd (ii); Tl (iii)	Hg (ii) - 0.91; Cd (ii) - 0.61; Tl (iii) - 0.48.
4.	Cr (vi); Cd (ii); Tl (iii).	Cr (vi) - 0.96; Cd (ii) - 0.66; Tl (iii) - 0.53.
5.	Hg (ii); As (iii); Cr (iii).	Hg (ii) - 0.92; As (iii) - 0.69; Cr (iii) - 0.48.
6.	Hg (ii); As (iii); Cd (ii)	Hg (ii) - 0.82; As (iii) - 0.62; Cd (ii) - 0.48
7.	Cr (IV); As (iii); Cd (iii).	Cr (IV) - 0.92; As (iii) - 0.65; Cd (iii) - 0.44.
8.	Hg (ii); Cd (ii); Cr (iii).	Hg (ii) - 0.80; Cd (ii) - 0.58; Cr (iii) - 0.46.

Pictures for the achieved separations using above mention optimum separating conditions.

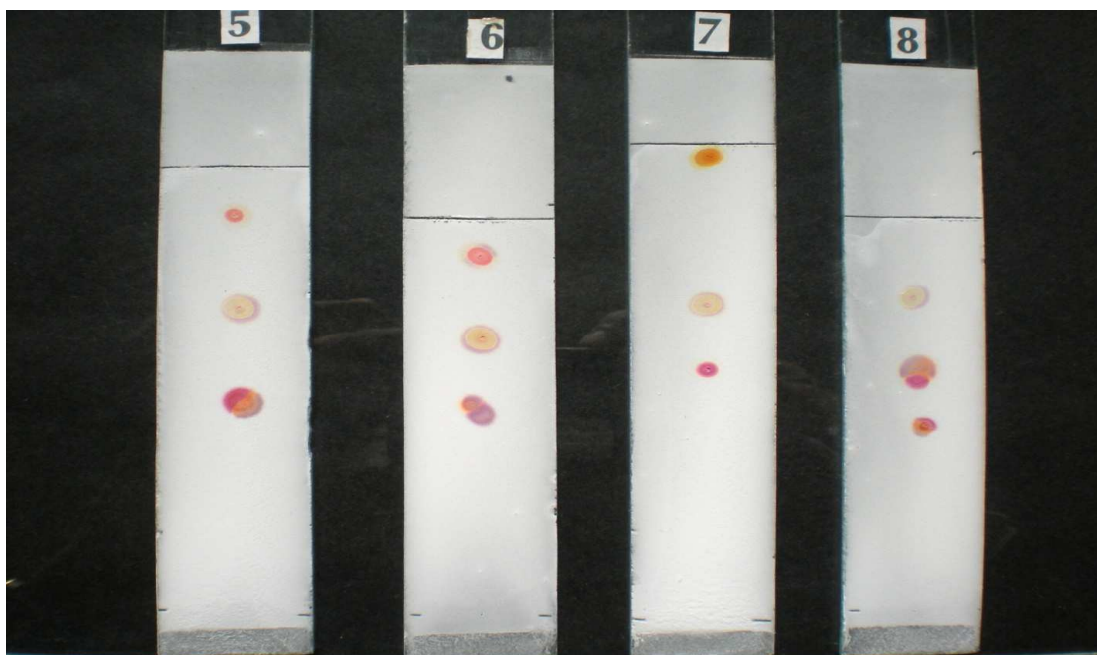


Picture No 1 Binary Separations.



Picture No 2:- Ternary Separations.

It was observed from table no 2, at low pH, all the six metal ions move with the solvent front. It is noted that all metal ions showed very little difference in the  $R_f$  values at pH 3.0, but as we increase the pH to 3.5, maximum difference in the  $R_f$  values of different metal ions could be achieved, which was required for better separation. However, the behavior of cations changed after the increase above pH 4.0 and especially at pH 5.0 and above and the metal ions Cr (vi) shows double spotting due to formation of hetero poly acid ; Cr (iii); Cd (ii); & Tl (iii) show tailing whereas Hg (ii) shows spreading. But As (iii) shows compact spot at all pH except pH 1 & pH 2. From the observed values, pH 3.5 has been found out to be ideal for bringing out maximum separation.  $R_f$  of all mention metal ions was not possible to measure above pH 7. Hence, separation measurements have not been carried beyond pH 7.0 and pH 3.5 fixed for further  $R_f$  measurement in glycine media.



Picture No 3:- Ternary Separations

Table No 5:- Quaternary separations

Sr. No.	Components of quaternary mixture	Metal ions with there $R_f$ Values
1.	Cr (vi); As (iii); Cr (iii); Tl (iii).	Cr (vi) – 0.97; As (iii) – 0.75; Cr (iii) – 0.50; Tl (iii) – 0.59.
2.	Hg (ii); As (iii); Cd (ii); Tl (iii).	Hg (ii) – 0.91; As (iii) 0.68; Cd (ii) – 0.58; Tl (iii) – 0.44.
3.	Hg (ii); Cd (ii); Cr (iii); Tl (iii).	Hg (ii) – 0.91; Cd (ii) – 0.65; Cr (iii) – 0.51; Tl (iii) 0.57.
4.	Cr (vi); As (iii); Cd (ii); Cr (iii).	Cr (vi) – 0.96; As (iii) – 0.71; Cd (ii) – 0.55; Cr (iii) – 0.44.
5.	Hg (ii); As (iii) ; Cd (ii); Cr (iii) ;	Hg (ii) – 0.89 As (iii) – 0.69; Cd (ii) – 0.54; Cr (iii) – 0.44;

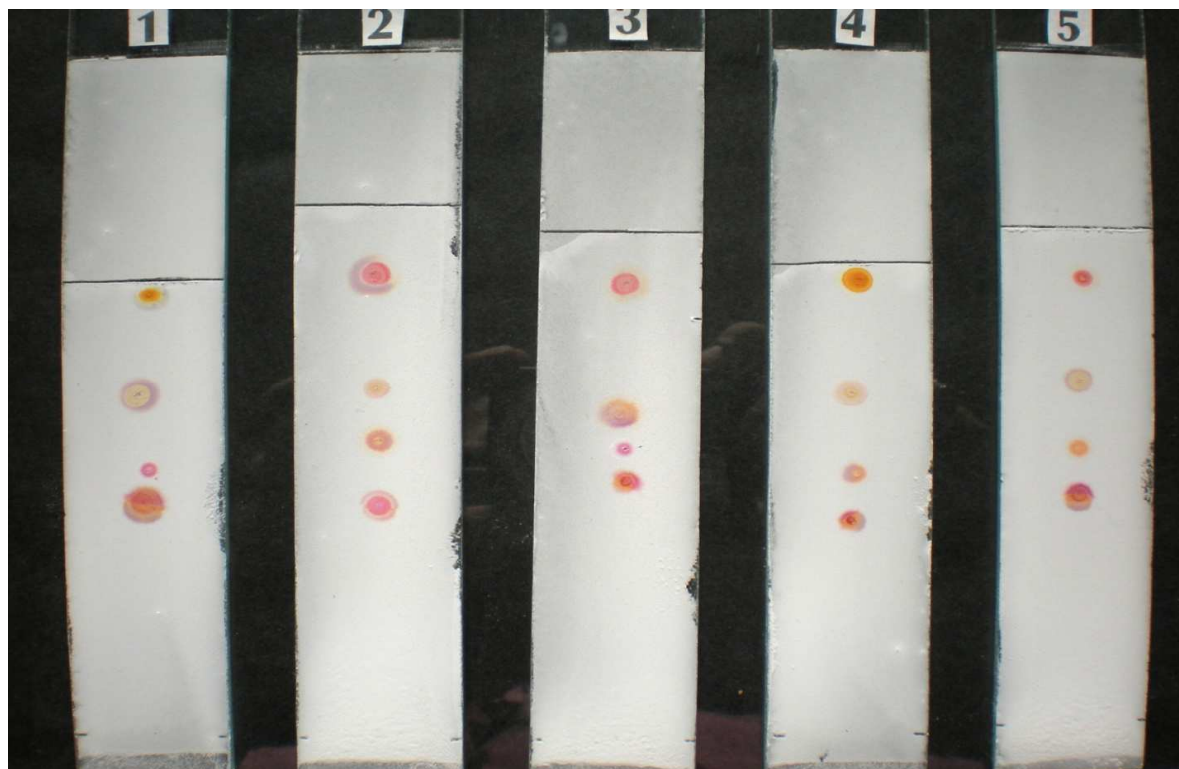
*There is slight difference in the  $R_f$  values of metal ions during the separations from their mixtures, due to the mutual interaction of metal ions.*

## CONCLUSION

Using the above mentioned optimum separating conditions, that is 0.05 M L Glycine at pH 3.5, qualitative separation of nine binary mixtures; eight ternary mixtures; and five quaternary mixtures of metal ions have been carried out. The  $R_f$  values of various binary, ternary and quaternary separations have been listed in Table no 3, 4, and 5 respectively. The  $R_f$  values of metal cations are given in top to bottom format, as they appear on the chromatographic plate. Photograph of achieved binary separations were given in picture no 1, for ternary separations in picture no 2 and quaternary separations in picture no 3.

$R_f$  values of experimentally achieved separations on silica gel 'G' layers developed with aqueous Glycine as mobile phase





Picture No 4:- Quaternary Separations.

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