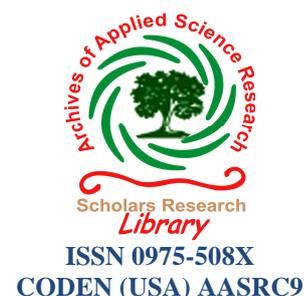




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# Thin Layer Chromatographic Separation of Toxic Heavy Metal Ions

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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 aqueous L - Valine as mobile phase. The effect of concentration and pH of mobile phase on the R<sub>f</sub> 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, L - Valine, Toxic Heavy Metal Ions.

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## INTRODUCTION

Heavy metals have received considerable attention from analysts, because of their physical and environmental importance [1, 2]. Metal such as As, Cr, Hg, Tl, Cd, Ni, Tl, Cu, Fe, Zn, Pb are toxic and harmful to human health. These metal ions can form complexes with bio-ligands containing Oxygen, Nitrogen and Sulphur atoms [3], 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 metals, due to the industrialization; this resulted in an increased flux of metallic substances. 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 industries, 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 separation and detection of chromium including graphite furnace atomic-absorption spectroscopy [4, 5], neutron activation analysis [6, 7], atomic emission spectroscopy [8], normal phase and reverse phase thin layer chromatography [9, 11], ion chromatography [12,13], precipitation floatation [14], titrimetry [15, 16], and hyphenated techniques such as ion-exchange chromatography - flame atomic absorption spectroscopy [17], solid - phase extraction - flame atomic emission spectroscopy [18].

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. Exhaustive survey off the literature published in the last thirty years [19] shows that much progress has been made in developing rapid and selective thin layer chromatographic method for separation of toxic heavy metals from interfering elements, by use of a variety of acidic developer containing mineral or carboxylic acid as one of the component.

Using of amino acid as mobile phase is not common for chromatographic separations using conventional laboratory made TLC plates. Therefore it was decided to use the analytical potential of amino acid that is aqueous L - Valine as mobile phase and 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  $\text{Cr}^{+3}$  are converted to  $\text{Cr}^{+6}$  in alkaline peroxide medium.

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 L - Valine as a mobile phase.

## MATERIALS AND METHODS

### Apparatus:

Glass plates of 4 x 20 cm size (coated with silica gel 'G'), 20 x 25 cm glass jars for the development of glass plates, glass sprayer for spraying reagents & EI pH meter.

### Chemicals and Reagents:

L - Valine (E. Merck; India), Silica gel- G (E. Merck; India); Hydrochloric acid and Sodium hydroxide.

### Stock Solutions:

The stock solutions of 0.05 M of following salts were prepared in the 0.1 M Hydrochloric acid.

- 1) Potassium salt of Cr(VI),
- 2) Chloride of Cd(II) and Hg(II),
- 3) Sulphate of Cr(III),
- 4) Trioxide of As(III) and Tl(III).

The mobile phase was prepared in double distilled water.

### Detection Reagents:

For the detection of various cations, the following reagents [20] were used

- 1) 0.05 % Dithiozone in Carbon tetra chloride.
- 2) Saturated Alcoholic  $\text{AgNO}_3$ .
- 3) Saturated Alcoholic Alizarin red.

**Procedure:****1) Preparation of plates:**

Slurry was prepared by mixing silica gel 'G' in double distilled water in the ratio of 1:2 with constant steering for about 10 minutes. It was then immediately applied to the glass plate by the dipping method [21] and dried over night at room temperature.

**2) Running of TLC plates:**

The test solutions were spotted on the silica gel – G plates using fine glass capillaries and they were blow-dried with hot air. The L - Valine of varying concentration was adjusted to the desired pH using sodium hydroxide and hydrochloride acid solution. The plates were developed for about 15 min in the glass jar containing 15 ml L - Valine solution. Approximately 2 -3 ml of solvent was required to run the sample per plate.

**3) Development of TLC plates:**

Plates were dried and different cations were detected by spraying various spot test reagent, which are saturated alcoholic silver nitrate, saturated alcoholic alizarin red and dithiozone in carbon tetra chloride, for Cr(IV), Cr(III), and other metal ions i.e. As(III), Cd(II), Tl(III), & Hg(II) respectively.

All experiments were carried out at room temperature. The  $R_f$  values were measured in triplicate for each set of determinations. Various experiments were carried out to study the mobile phase (0.005M - 0.1 M); pH (1.0 -7.0) and time (5 - 20 min) for the  $R_f$  values of the individual cations.

**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 run time, different pH and at different concentration of L -Valine for determining optimum condition for separation of the metal ions.

The results dealing with the effect of concentration of mobile phase, i.e. on the  $R_f$  values of different metal ions such as Cr (VI); Cr (III); As (III); Cd (II); Tl (III) and Hg (II) are represented graphically in **fig. 1** and tabulated in **table 1**. The variations in the  $R_f$  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	0.94	0.32	0.92	0.68	0.46	0.77
0.01	0.95	0.15	0.90	0.46	0.25	0.70
0.05	0.93	0.26	0.85	0.57	0.43	0.77
0.1	0.95	0.46	0.97	0.63	0.50	0.91

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. At 0.05 M concentration of L -Valine, clear and distinct spots were seen. At 0.1 M L -Valine spots were not compact and shows little spreading, especially Cr (VI); Cd (II); Hg (II). However 0.05 M concentration was selected as the optimum concentration for further studies.

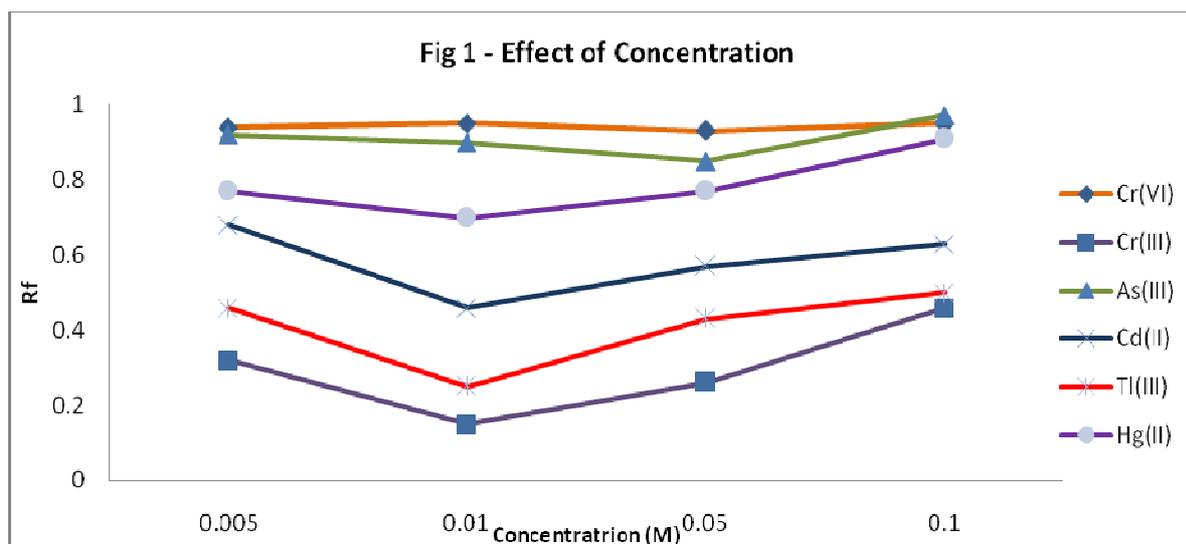


Fig No 1:- Effect of Concentration

**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 graphically represented in **fig. 2** and tabulated in **table 2** which reveal variations in the  $R_f$  values with pH of L -Valine. 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 L-Valine

Metal ions	pH of Mobile Phase								
	1	2	2.5	3	3.5	4	5	6	7
Cr (VI)	0.95	0.95	0.95	0.95	0.96	0.93	0.92 D.S	0.94 D.S	0.94 D.S
Cr (III)	0.70	0.76	0.54	0.27	0.20	0.15	0.06 T	0.07 T	0.08 T
As (III)	0.83	0.85	0.84	0.86	0.89	0.88	0.84	0.87	0.79
Cd (II)	0.90	0.83	0.69	0.57	0.46	0.37 T	0.35 T	0.33 T	0.37 T
Tl (III)	0.80	0.85	0.61	0.43	0.32	0.22 T	0.18 T	0.22 T	0.16 T
Hg (II)	0.95	0.93	0.91	0.79	0.71	0.72	0.67spr	0.69 spr	0.66 spr

Notation: - T- Tailing; Spr- Spreading; D.S – Double Spot

It can be observed from fig. 2 (combined graph of all metal ions) that, at low pH, all the six metal ions move with the solvent. It is noted that all metal ions showed very little difference in the  $R_f$  values at pH 2.0, but as we increase the pH to 2.5 up to pH 3, 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 in pH 4.0 and above, especially at pH 5.0, Cr (VI) shows double spotting due to formation of hetero poly acid ; Cr (III); Cd n(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 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 fixed for further  $R_f$  measurement in aqueous media of L –Valine.

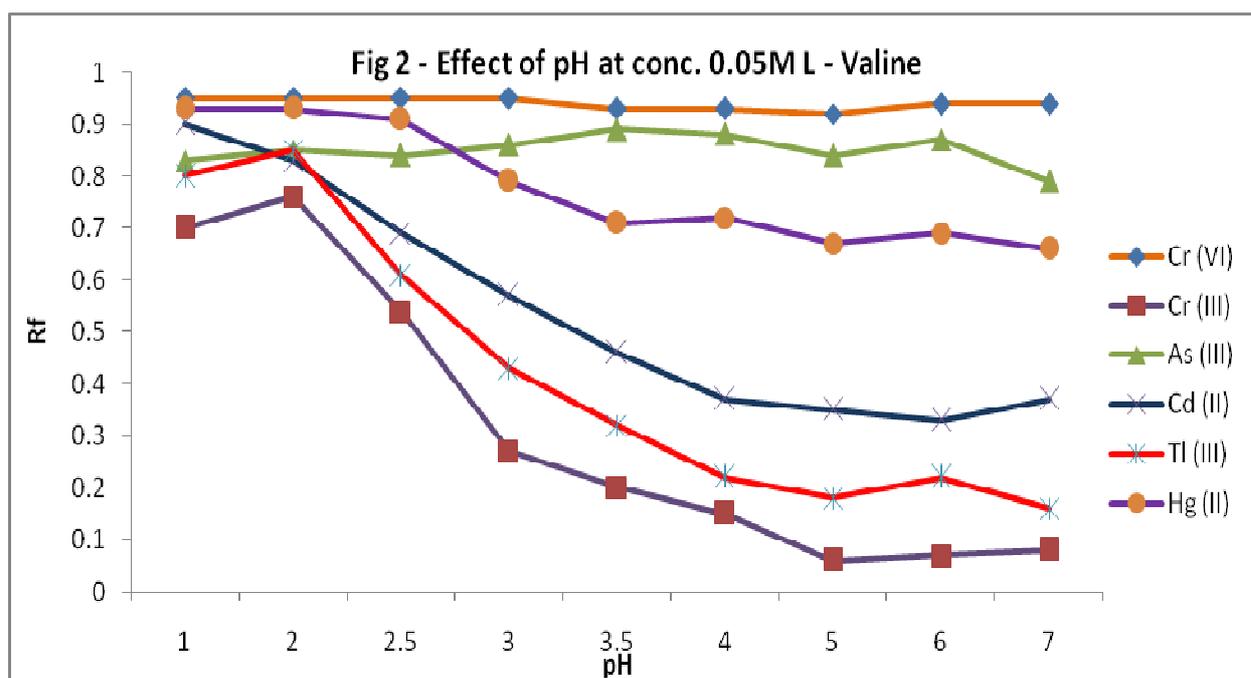


Fig No 2:- Effect of pH at Conc. 0.05 M L-Valine

*Effect of runtime:* -The variation in the  $R_f$  values of metal ions with run time was studied in this section. The data was tabulated in **table 3** and graphically represented in **fig.3**. The  $R_f$  values have been measured at pH 3 having 0.05 M concentration of L -Valine.

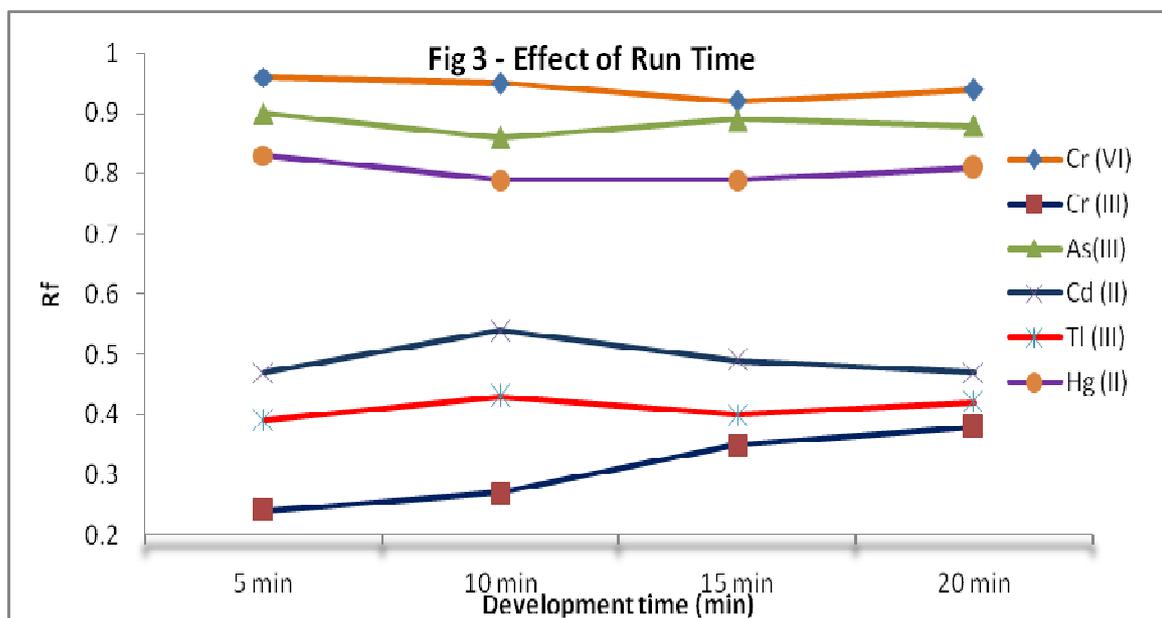


Fig No 3:- Effect of Runtime

From obtained data it revealed that, when the migration runtime was kept at 10 minutes, the metal ion shows remarkable difference in their  $R_f$  values which is required for the separation of binary, ternary and quaternary mixtures of metal ions. The  $R_f$  of metal ions were also studied at 15 and 20 min as run time, but separation of metals has been found out to be good at only 10 min. Further increase in the run time did not affect the separation, and hence, the run time of 10 minutes was considered for further  $R_f$  measurement.

**Table 3: Effect of development time at pH 3.5**

Metal Ions	Development time in minutes			
	5 min	10 min	15 min	20 min
Cr (VI)	0.96	0.95	0.92	0.94
Cr (III)	0.25	0.27	0.35	0.38
As (III)	0.90	0.86	0.89	0.88
Cd (II)	0.47	0.54	0.49	0.47
Tl (III)	0.39	0.43	0.40	0.42
Hg (II)	0.83	0.79	0.79	0.81

*Adsorbent: Silica gel 'G', Mobile phase: - 0.05M L-Valine, pH - 3*

## CONCLUSION

Using the above mentioned optimum separating conditions, that is 0.05 M L -Valine at pH 3, and 10 minutes as run time, qualitative separation of eight binary mixtures; seven 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 4, 5, and 6 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.

Table No: 4 Experimentally achieved separations on silica gel 'G' layers developed with aqueous L-Valine as mobile phase

**Table No: 4 Binary separations**

Sr. No	Components of Binary mixture	Metal ions with there $R_f$ Values
1.	Cr (VI);Cr (III)	Cr (VI) - 0.97; Cr (III) - 0.38.
2.	Cr (VI);As (III)	Cr (VI) - 0.97; As (III) - 0.80.
3.	Cr (VI);Cd (II)	Cr (VI) - 0.97; Cd (II) - 0.44.
4.	Cr (VI);Tl (III)	Cr (VI) - 0.98; Tl (III) - 0.18.
5.	Hg (II); Cr (III)	Hg (II) - 0.71; Cr (III) - 0.35
6.	As (III);Cd (II)	As (III) - 0.85; Cd (II) - 0.44.
7.	Hg (II);Cd (II)	Hg (II) - 0.74; Cd (II) - 0.53.
8.	Cr (VI);Hg (II)	Cr (VI) - 0.97;Hg (II) - 0.76

**Table No: 5 Ternary separations**

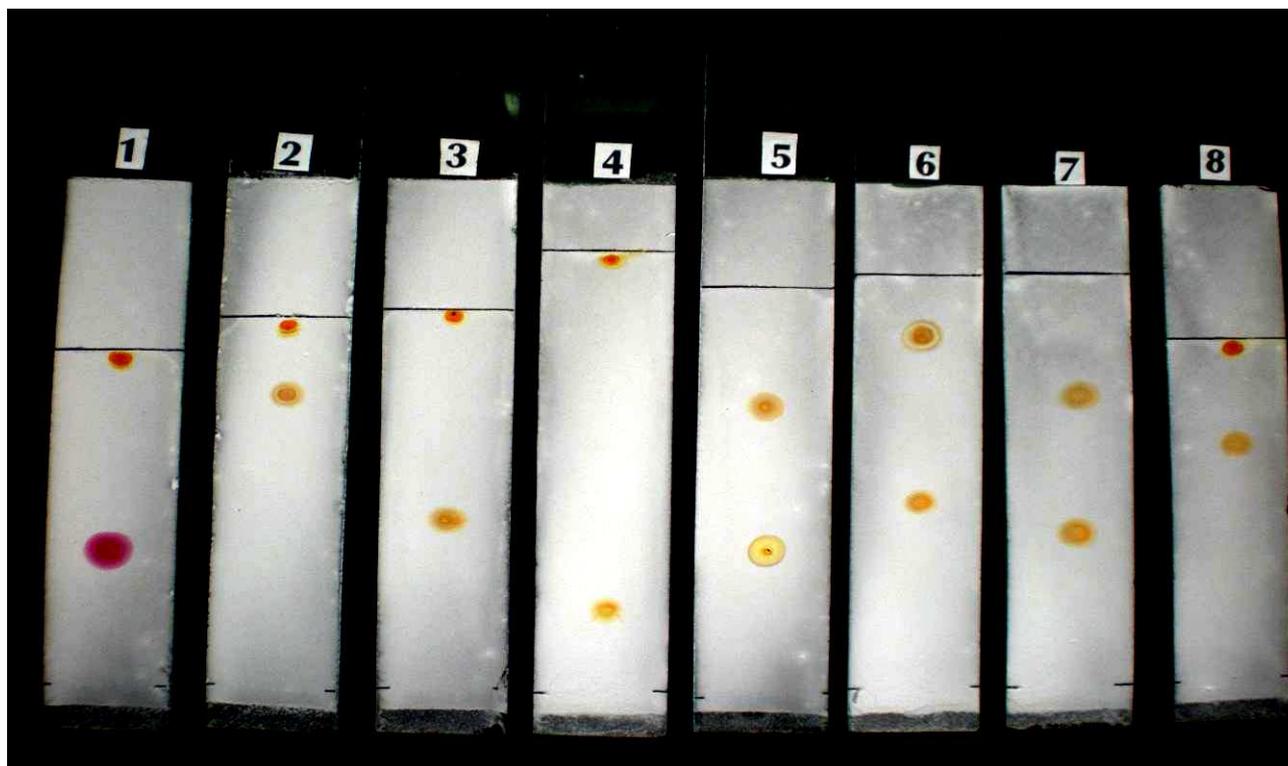
Sr. No	Component of Ternary Mixture	Metal ions with there $R_f$ Values
1.	Cr (VI); As (III); Cr (III).	Cr (III) - 0.96; As (III) - 0.29; Cr (III) - 0.37.
2.	Cr (VI); Cd (II); Cr (III).	Cr (VI) - 0.98; Cd (II) - 0.59; Cr (III) - 0.64.
3.	Hg (II);Cd (II); Tl (III)	Hg (II) - 0.85; Cd (II) - 0.34; Tl (III) - 0.23.
4.	Cr (VI); Cd (II); Tl (III).	Cr (VI) - 0.97; Cd (II) - 0.39; Tl (III) - 0.25.
5.	As (III); Hg (II); Cd (II)	As (III) - 0.83;Hg (II) - 0.62; Cd (II) - 0.36
6.	Cr (IV); As (III); Cd (III).	Cr (IV) - 0.98; As (III) - 0.80; Cd (III) - 0.50.
7.	As (III); Cd (II); Cr (III).	As (III) - 0.81; Cd (II) - 0.50; Cr (III) - 0.31.

**Table No: 6 Quaternary separations**

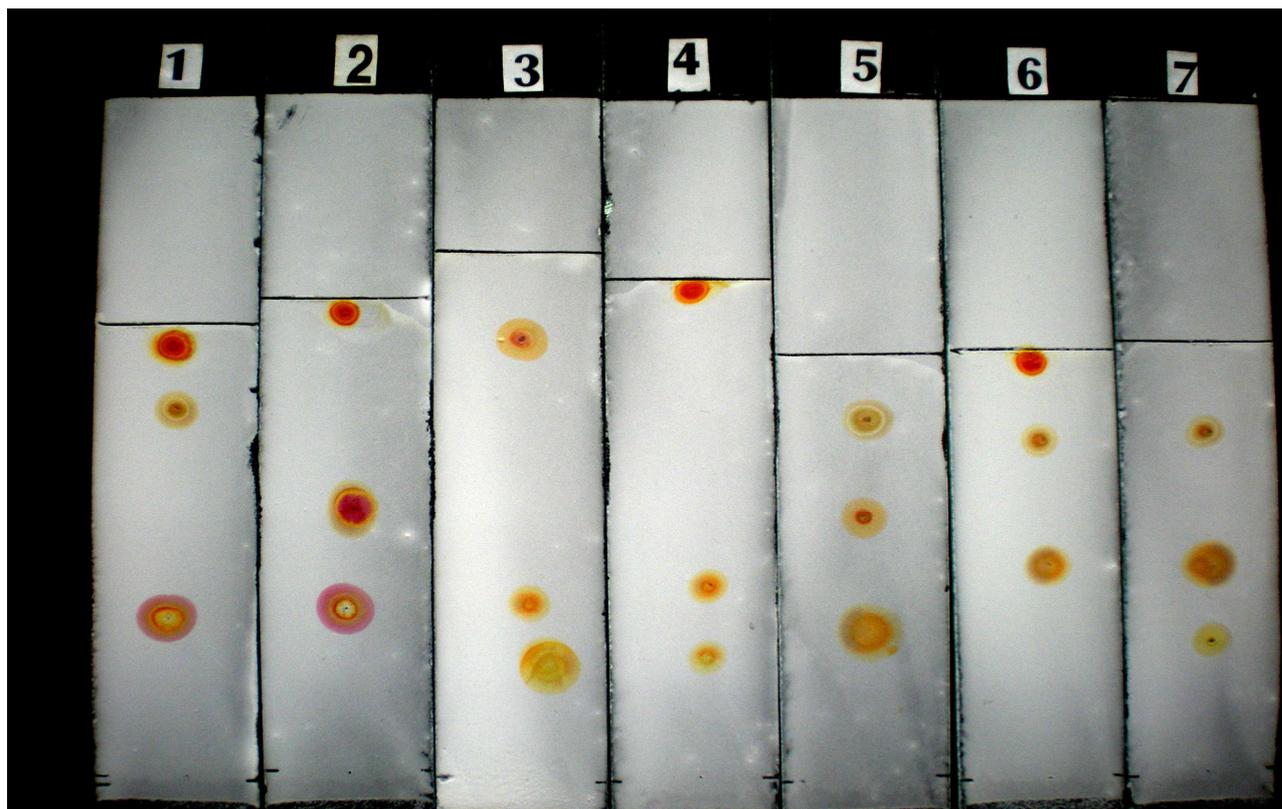
Sr. No.	Components of quaternary mixture	Metal ions with there Rf Values
1.	Cr (VI); As (III); Cr (III); Tl (III).	Cr (VI) – 0.97; As (III) – 0.23; Cr (III) – 0.22; Tl (III) – 0.30.
2.	Hg (II); As (III); Cd (II); Tl (III).	Hg (II) – 0.67; As (III) 0.83; Cd (II) – 0.46; Tl (III) – 0.32.
3.	Hg (II); Cd (II); Cr (III); Tl (III).	Hg (II) – 0.73; Cd (II) – 0.40; Cr (III) – 0.22; Tl (III) 0.26.
4.	Cr (VI); As (III); Cd (II); Cr (III).	Cr (VI) – 0.96; As (III) – 0.81; Cd (II) – 0.45; Cr (III) – 0.33.
5.	Hg (II); As (III) ; Cd (II); Cr (III) ;	Hg (II) – 0.70 As (III) – 0.86; Cd (II) – 0.49; Cr (III) – 0.23;

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

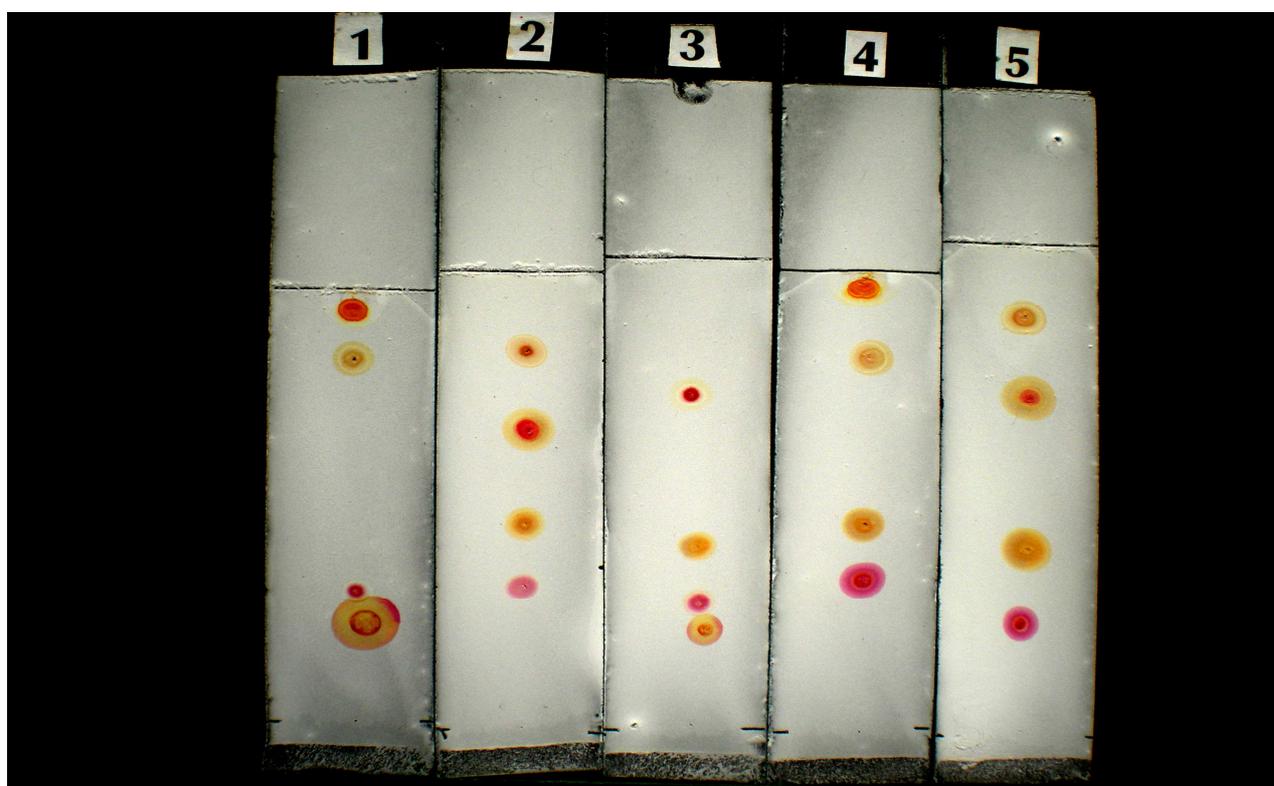
**Picture No 1 Pictures for the achieved separations using above mention optimum separating conditions.**



**Picture No 1: For Binary Separations**



Picture No 2: For Ternary Separations



Picture No 3: For Quaternary Separations

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**REFERENCES**

- [1] H Siegel; *Metal Ions in Biological System*, Vols. I and II, Marcel Dekker, New York, USA, **1986**.
- [2] V Venngopal and T Luckey; *Metal Toxicity of Metals and Metalloids*, Plenum, New York, USA, **1987**.
- [3] M Bukowska – Strzyzewska; W Maniukewicz; G Bazylak; and J Maslowska; *J Crystallogr. Spectrosc. Res.*, 21, 157 (**1991**)
- [4] ST Sauerhoff; ZA Grosser; and GR Carnrick; *At. Spectrosc*, 17, 225 (**1996**)
- [5] TW Lin and SD Huang; *Anal. Chem.*, 73, 4319 (**2001**)
- [6] TM Bahrainwala and ZR Tural; *J. Radioanal. Nucl. Chem.*, 214, 199 (**1996**)
- [7] H Rausch and T Braun; *Fullerene Sci. Technol.*, 5, 407 (**1997**)
- [8] ES Zolotovitskaya; LV Glushkova, ZV Shititelman, and AB Blank, *Khim. Tekhnol. Vody*, 15, 255 (**1993**)
- [9] G Schubert; V Alan; J Zirko – Babic; and S Turina; *J. Planar Chromatogr.* 11, 460 (**1998**)
- [10] S Przeszlakowski and M Maliszewska, *Chem. Anal.* 37, 547 (**1992**)
- [11] SD Sharma and SC Sharma, *J. Chromatogr.*, A 841, 263 (**1999**)
- [12] M Mizobuchi; Y Horie; and K Saito; *Nara-ken Eisei Kenkyusho Nenpo*, 26, 56 (**1991**)
- [13] Y Zhou; G. Shao; and S Mu; *Huanjing Huaxue*’ 15, 446 (**1996**); *Chem Abstr.*, 126, 36660z (**1997**)
- [14] KS Lee; HS Choi; and YS Kim, *Anal. Sci. Technol.*, 3, 419 (**1990**)
- [15] L Zheng and S wang; Yejin Fenxi, 16, 49 (1996); *Chem Abstr.*, 126, 165878a (**1997**)
- [16] KK Paliwal; DK Gorji; S. Kumar; N Naulakha, AK Goswami; and DN Purohit, *Asian J. Chem.*, 13, 299 (**2001**)
- [17] B Demirata; I Tar; H Filik; and H Afsar; Fresenius, *J. Anal Chem.*, 356, 375 (**1996**)
- [18] V Ostruba; J Pivnicka; and V Kanicky; *Proc. – Semin. At. Spectrochem.* 14 247 (**1998**)
- [19] A Mohammad; M Ajmal; S Anwar; and E Iraqi; *J. Planar Chromatogr*, 9, 318 (**1996**)
- [20] F Feigl, ‘Spot Test Inorganic Applications’ Elsevier Pub. Co., Amsterdam 4<sup>th</sup> Ed. (**1954**)
- [21] JJ Piefer, *Microchim Acta.*, 529 (**1962**)