RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.4, No.3 (2011), 630-635
ISSN: 0974-1496
CODEN: RJCABP

RAPID SEPARATION OF SOME TOXIC HEAVY METAL IONS BY THIN LAYER CHROMATOGRAPHY

L. J. Paliwal*[1], S. M. Wanjari[2] and Lata Deshmukh[2]

[1]Post Graduate Department of Chemistry, Mahatma Jotiba Phule Campus, RTM Nagpur University, Nagpur-440033 (M.S.) India.

[2]Dr. Mrs. Ira N. Nimdewkar P.G. & Research Centre for Chemistry, Hislop College, Nagpur-440001 (M.S.) India.

*E-mail: ljpaliwal@yahoo.co.uk

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 Oxalic acid 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, Oxalic acid, Toxic Heavy Metal ions.

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.

All studies with oxalic acid as mobile phase has been performed using conventional, laboratory made TLC plates. It was therefore decided to use the analytical potential of aqueous oxalic acid 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 Cr^{+3} are converted to 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 oxalic acid as a mobile phase.

EXPERIMENTAL

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
Oxalic acid (E. Merck; India), Silica gel- G (E. Merck; India); Hydrochloric acid and Sodium hydroxide.
Stock Solutions
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 regents[20] were used
1) 0.05 % Dithiozone in Carbon tetra chloride.
2) Saturated Alcoholic $AgNO_3$.
3) Saturated Alcoholic Alizarin red.

(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 oxalic acid 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 oxalic acid 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

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 oxalic acid for determining optimum conditions for separation of the metal ions.
The variation in the R_f values of metal ions with run time are shown in table 1 and graphically represented in Fig. 1. The R_f values have been measured at pH 4.0 and 0.1 M concentration of oxalic acid. From the data obtained it revealed that, when the migration time was kept at 10 minutes, the metal ion shows remarkable difference in there R_f values which was found out to be good for the binary separation, but for the ternary and quaternary mixtures of metal ions it was not effective. When the development time was

increased to 15 minutes, separation of metals has been found out to be good. Further increase in the run time did not affect the separation, and hence, the run time of 15 minutes was considered for further R_f measurements.

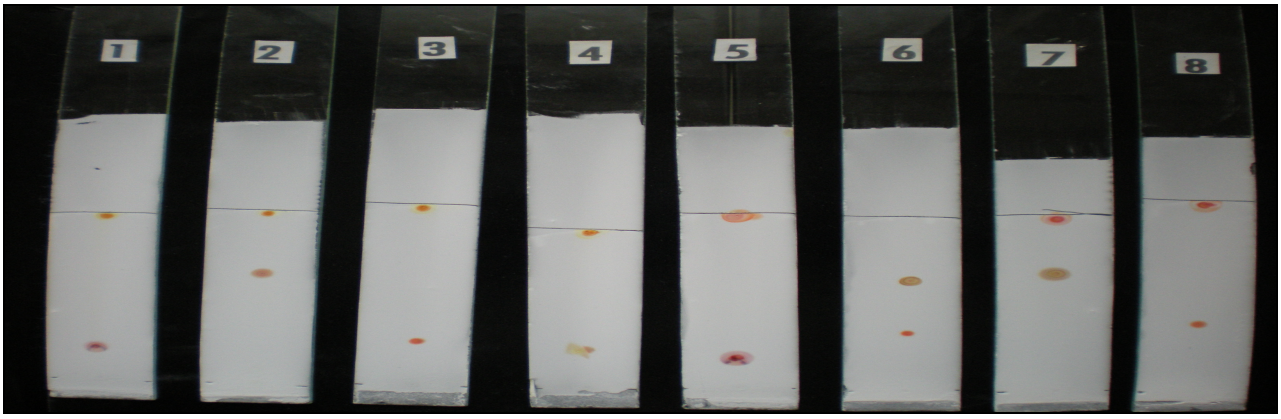

Fig.-1: Binary Separations

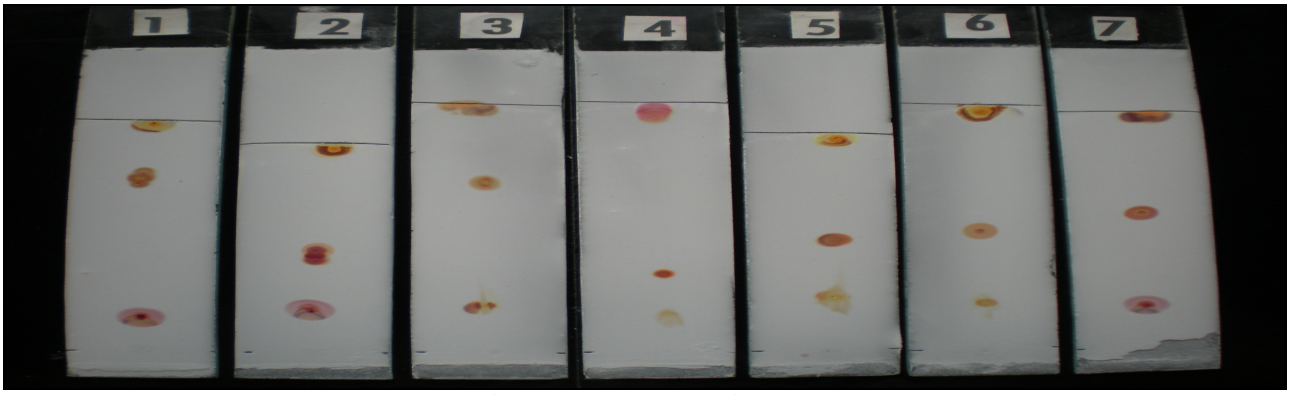

Fig.-2: Ternary Separations

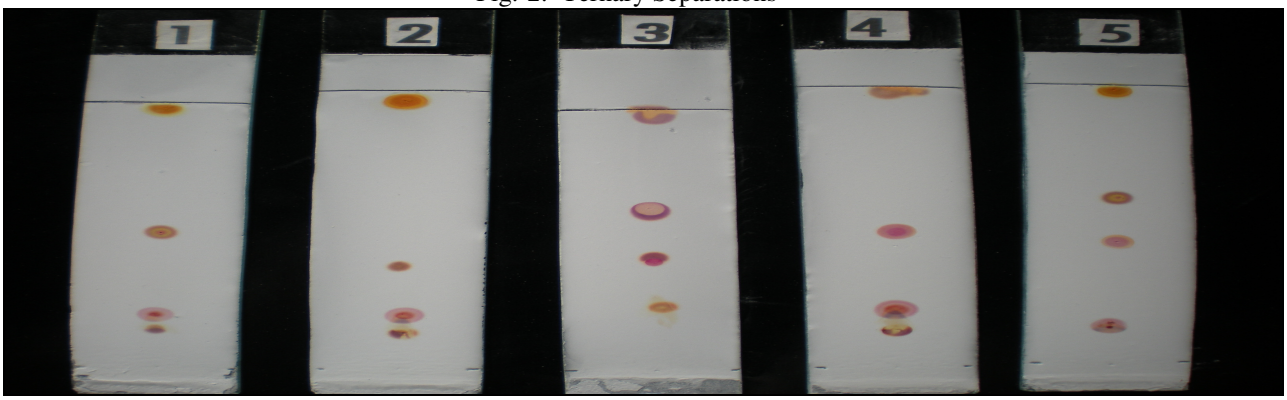

Fig.-3: Quaternary Separations

Table-1: Effect of development time at pH 4.0

Metal Ions	Rf Values at different development time			
	5 min	10 min	15 min	20 min
Cr(VI)	0.92	0.95	0.96	0.96
Cr(III)	0.45	0.44	0.47	0.48
As(III)	0.78	0.84	0.85	0.86
Cd(II)	0.67	0.68	0.69	0.69
Tl(III)	0.50	0.55	0.58	0.59
Hg(II)	0.93	0.96	0.97	0.97

Adsorbent: Silica gel 'G', Mobile phase: - 0.1M Oxalic acid, pH – 4.0

Table-2: Effect of pH on the R_f Values of metal ions at conc. 0.05M Oxalic acid

Metal ions	2	2.5	3	3.5	4	4.5	5	6	7
Cr (VI)	0.95	0.93	0.96	0.95	0.90	0.93	0.93 T	0.94 T	0.94 T
Cr (III)	0.65	0.52	0.49	0.48	0.43	0.30	0.15	0.12 T	0.18 T
As (III)	0.80	0.80	0.78	0.78	0.78	0.73	0.84	0.84	0.81
Cd (II)	0.63	0.69	0.70	0.68	0.63	0.61	0.66 T	0.67 T	0.70 T
Tl (III)	0.85	0.70	0.56	0.54	0.52	0.35 T	0.24 T	0.18 T	N .D
Hg (II)	0.93	0.96	0.98	0.96	0.93	0.95	0.96	0.96 spr	0.91 spr

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

The effect of pH on the R_f values of different metal ions was carefully studied by carring repeated experiments. The results are graphically represented in Fig. 2, and tabulated in table 2 which reveal variations in the R_f values with pH of oxalic acid. The R_f value measurements were done in the pH range of 1.0 to 7.0 at 0.05 M concentration and 15 minutes of run time.

Table- 3: Values showing effect of Concentration of Oxalic acid in mobile phase on the R_f values of metal ions at pH 4.0 in 15 min

Concentration of Mobile Phase	Cr (VI)	Cr (III)	As (III)	Cd (II)	Tl (III)	Hg (II)
0.005	0.97	0.18 T	0.83	0.48 T	0.46 T	0.96 spr
0.01	0.82 T	0.13 T	0.76	0.65 T	0.25 T	0.82 spr
0.05	0.90	0.25	0.76	0.63	0.33	0.93
0.1	0.97	0.48	0.89	0.71	0.50	0.97

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

It can be observed from fig. 2 & 3 (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 3.5, but as we increase the pH to 4.0, 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); Cr(III); Cd(II); & Tl(III) show tailing whereas Hg(II) shows spreading and As(III) could not be detected. From the observed values, pH 4.0 has been found out to be ideal for bringing about maximum separation. Hence, separation measurements have not been carried beyond pH 7.0. Therefore, pH 4.0 has been fixed for further R_f measurements in oxalic acid media.

Table-4: Binary Separations

S. No	Components of Binary mixture	Metal ions with there Rf Values
1.	Cr (VI);Cr (III)	Cr (VI) - 0.97; Cr (III) - 0.21.
2.	Cr (VI);As (III)	Cr (VI) - 0.97; As (III) - 0.64.
3.	Cr (VI);Cd (II)	Cr (VI) - 0.98; Cd (II) - 0.25.
4.	Cr (VI);Tl (III)	Cr (VI) - 0.97; Tl (III) - 0.23.
5.	Hg (II);Cr (III)	Hg (II) - 0.98; Cr (III) - 0.18.
6.	As (III);Cd (II)	As (III) - 0.62; Cd (II) - 0.32.
7.	Hg (II);As (III)	Hg (II) - 0.97; As (III) - 0.66.
8.	Hg (II);Cd (II)	Hg (II) - 0.98; Cd (II)- 0.36

The results dealing with the effect of concentration of mobile phase, i.e. Oxalic acid on the Rf 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. 4 and tabulated in table 3. The variations in the Rf values with concentration in the range of 0.1 to 0.005 M were studied at their respective optimum pH values.
It can be observed from table 3 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 short tailing. As the concentration at oxalic acid was increased to 0.05 M, clear and distinct spot was seen. It was also observed, there is an increase in the R_f values with increase in the concentration, but at 0.1 M oxalic acid spots are not compact and shows little spreading. However 0.05 M concentration was selected as the optimum concentration for further studies.
Further remaining separations are done at 0.05 M Oxalic acid, pH 4.0 with 15 minutes as run time.

Table-5: Ternary Separations

S. No	Component of Ternary Mixture	Metal ions with there Rf Values
1.	Cr (VI); As (III); Cr (III)	Cr (III) – 0.99; As (III) – 0.77; Cr (III) – 0.27.
2.	Cr (VI); Cd (II); Cr (III)	Cr (VI) – 0.97; Cd (II) – 0.48; Cr (III) – 0.20.
3.	Hg (II);Cd (II); Tl (III)	Hg (II) – 0.98; Cd (II) - 0.32; Tl (III) - 0.14.
4.	Cr (VI); Cd (II); Tl (III)	Cr (VI) – 0.97; Cd (II) – 0.51; Tl (III) – 0.22.
5.	Hg (II); As (III); Tl (III)	Hg (II) – 0.98; As (III) – 0.48; Tl (III) – 0.18.
6.	Cr(IV); As(III); Tl(III)	Cr(IV) - 0.98; As(III) - 0.48; Tl(III) - 0.18.
7.	Hg (II); As (III); Cr (III)	Hg (II) - 0.97; As (III) – 0.55; Cr (III) – 0.19.

Table-6: Quaternary Separations

S. No.	Components of quaternary mixture	Metal ions with there Rf Values
1.	Cr (VI); As (III); Cr (III); Tl (III)	Cr (VI) – 0.98; As (III) – 0.51; Cr (III) – 0.20; Tl (III) – 0.13.
2.	Cr (VI); Cd (II); Cr (III); Tl (III)	Cr (VI) – 0.98; Cd (II) – 0.37; Cr (III) – 0.20; Tl (III) – 0.13.
3.	Hg (II); As (III); Cd (II); Tl (III)	Hg (II) – 0.97; As (III) - 0.62; Cd (II) – 0.41; Tl (III) – 0.23.
4.	Hg (II); Cd (II); Cr (III); Tl (III)	Hg (II) – 0.98; Cd (II) – 0.49; Cr (III) – 0.21; Tl (III) 0.13.
5.	Cr (VI); As (III); Cd (II); Cr (III)	Cr (VI) – 0.98; As (III) – 0.60; Cd (II) – 0.44; Cr (III) – 0.14.

The R_f values of metal ions in their mixture are slightly change form their individual Rf values because of mutual interactions.

Using the above mentioned conditions qualitative separation of eight binary mixtures; six ternary mixtures; and five quaternary mixtures of metal ions have been carried out. The R_f values of metal cations are given in top to bottom format, as they appear on the chromatographic plate.
Experimentally achieved separations on silica gel 'G' layers developed with Oxalic acid as mobile phase
The Rf values of metal ions in their mixture are slightly change form their individual Rf values because of mutual interactions.
Several important separations of metal cations have been experimentally achieved using above experimental conditions on silica gel layers developed with oxalic acid as a mobile phase systems. Various binary, ternary and quaternary separations have been listed in Table 4, 5, and 6 respectively and photographs of achieved separations are given in picture no 1 for binary separations, Picture no 2 for ternary separations and Picture no 3 for quaternary separations.

ACKNOWLEDGEMENTS

The authors are thankful to The Principal, Dr. Dipti Christian, and Dr. R. M. Uttarwar, Head, Department of Chemistry, Hislop College, Nagpur, for providing research facilities.

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. S. T. Sauerhoff, Z.A. Grosser, and G.R. Carnrick, *At. Spectrosc.*, **17**, 225 (1996)
5. T. W. Lin and S. D. Huang, *Anal. Chem.*, **73**, 4319 (2001)
6. T. M. Bahrainwala and Z.R. Tural, *J. Radioanal. Nucl. Chem.*, **214**, 199 (1996)
7. H. Rausch and T. Braun, *Fullerene Sci. Technol.*, **5**, 407 (1997)
8. E. S. Zolotovitskaya, L. V. Glushkova, Z. V. Shititelman, and A. B. 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. S. D Sharma and S. C. 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. K. S. Lee, H. S. Choi, and Y. S. Kim, *Anal. Sci. Technol.*, **3,** 419 (1990)
15. L. Zheng and S. wang, Yejin Fenxi, 16, 49 (1996); *Chem Abstr.*, 126, 165878a (1997)
16. K. K. Paliwal, D. K. Gorji, S. Kumar, N. Naulakha, A.K. Goswami, and D. N. 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 4th Ed. (1954)
21. J. J. Piefer, *Microchim Acta.*, 529 (1962)

[RJC-825/2011]