Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2011, 3 (6):425-431
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Chromatographic Separation of Heavy Metal Cations on a Silica gel-G

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

[1]*Dr. Mrs. Ira N. Nimdewkar P.G. & Research Centre for Chemistry, Hislop College, Nagpur (M.S.) India*
[2]*Post Graduate Department of Chemistry, Mahatma Jotiba Phule Campus, RTM Nagpur University, Nagpur(M.S.) India*

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 Picolinic 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, α- Picolinic acid, Toxic Heavy Metal Ions.

INTRODUCTION

Thin layer chromatography (TLC) is considered to be superior to other chromatographic techniques, because of its simplicity and relatively low cost. Success in TLC depends to great extent upon the proper selection of the mobile phase. The separation possibilities in TLC are greatly enhanced when chromatoplates are developed with mixed solvent systems. TLC has been successfully utilized for various purposes, such as the separation of metal ions from a water sample [1], the characterization of the mobility of metal [2], and the estimation of concentration of toxic metal in industrial waste [3].The use of aqueous solution as a mobile phase in TLC was pioneered by Armstrong and Terrill [4]. Using a surfactant as the mobile phase gained popularity and became more widely applied due to its operational simplicity, cost effectiveness, relative non-toxicity and enhanced separation efficiency [5-8]. The use of silica gel and an alumina layer with surfactant –mediated mobile phase systems [9-15] has been used to separate various inorganic species. Number of metal ions was systematically chromatographed on thin layer of urea formaldehyde polymer which is already used for the separation of amino acid [16].

In this paper chromatographic separation was carried out on silica gel –G using aqueous solution of α Picolinic acid as mobile phase.

MATERIALS AND METHODS

Chemicals and Reagents: **Chemicals and Reagents:**
α- Picolinic acid (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^{+6}; Cr^{+3}; Tl^{+3}; Cd^{2+}; Hg^{2+}; and As^{3+}.

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 [17] were detected using 0.05 % Dithiozone in Carbon tetra chloride for Cd^{+2}; Tl^{+2}; As^{+3} and Hg^{+2}, saturated Alcoholic $AgNO_3$ for Cr^{+6} and saturated alcoholic alizarin red for Cr^{+3}.

Stationary Phase: Silica gel –G.

Mobile Phase: The aqueous solution of α- Picolinic acid as the mobile phases.

Thin - layer chromatography

A. Preparation of Plates: The TLC plates were prepared by mixing silica gel-G with deminerlised 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 [18]. 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_F 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_F 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 run time, different pH and at different concentration of α- Picolinic acid 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 **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 to7.

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	0.83	0.23	0.88	0.46	0.68	0.96
0.01	0.83	0.19	0.86	0.45	0.64	0.71
0.05	0.97	0.23	0.88	0.49	0.59	0.67
0.1	0.94	0.25	0.87	0.48	0.56	0.64

It was observed that, at concentration 0.1 M, Cr (VI) was not detected except pH 2, Cr (III) and Tl (II) shows long tailing while Hg (II) shows spreading. At 0.01 and 0.005 M α- Picolinic acid spots were not compact and shows little spreading, especially Cr (VI); Cd (II); Hg (II). However at 0.05 M concentration show compact spot were observed, hence this concentration was selected as the optimum separating concentration for further studies.

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

Metal Ions	pH of α- Picolinic acid at 0.05M Concentration								
	1	2	2.5	3	3.5	4	5	6	7
Cr (VI)	0.93	0.92	0.93	0.97	0.96	0.94	0.92 DS	0.95 DS	0.94 DS
Cr (III)	0.45	0.4	0.38	0.23	0.23	0.3 ST	0.38 ST	0.41 ST	0.39 ST
As (III)	0.89	0.89	0.87	0.88	0.92	0.9	0.88	0.89	0.86
Cd (II)	0.9	0.64	0.53	0.49	0.5	0.52	0.57	0.61	0.66
Tl (III)	0.73	0.7	0.63	0.59	0.52	0.46	0.47 LT	0.52 LT	0.36 LT
Hg (II)	0.87	0.78	0.74	0.67	0.63	0.65 spr	0.68 spr	0.72 spr	0.68 spr

Notation: - ST- Tailing; Spr- Spreading; DS – Double Spot.

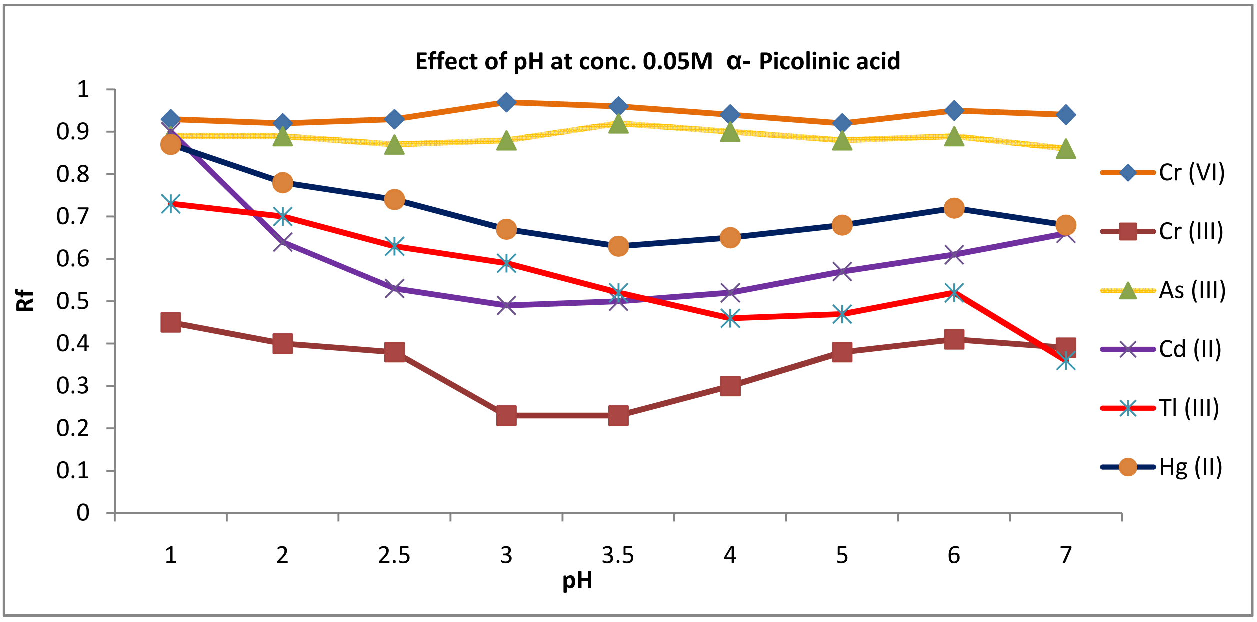


Fig No 1:- Effect of pH at Conc. 0.05M α Picolinic acid.

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. 1** and tabulated in **table 2** which reveal variations in the R_f values with pH of α Picolinic acid. The R_f value measurements were done in the pH range of 1.0 to 7.0 at 0.005 M concentration.

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 4. Maximum difference in the R_f values of different metal ions were seen at pH 3.5. This 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. From these 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 aqueous media of α- Picolinic acid.

Table No 3:- Binary separations

Sr. No	Components of Binary mixture	Metal ions with there Rf Values
1.	Cr (VI);Cr (III)	Cr (VI) - 0.96; Cr (III) - 0.51.
2.	Cr (VI);As (III)	Cr (VI) - 0.96; As (III) - 0.76.
3.	Cr (VI);Cd (II)	Cr (VI) - 0.96; Cd (II) - 0.48.
4.	Cr (VI);Tl (III)	Cr (VI) - 0.94; Tl (III) - 0.58.
5	As (III); Cr (III)	As (III) -0.72; Cr (III) -0.58.
6	Cr (III); Tl (III);	Cr (III) -0.56; Tl (III) -0.27/
7.	Hg (II); Cr (III)	Hg (II) – 0.46; Cr (III) - 0.60.
8.	As (III);Cd (II)	As (III) - 0.69; Cd (II) - 0.49.
9	Hg (II); As (III)	Hg (II) -0.49; As (III) -0.71.
10.	Hg (II);Cd (II)	Hg (II) - 0.37; Cd (II) - 0.53.
11.	As (III);Tl (III)	As (III) -0.74; Tl (III) -0.26.
12.	Cr (VI:)Hg (II)	\Cr (VI) – 0.95: Hg (II) – 0.45.

Table No 4:- Ternary separations.

Sr. No	Component of Ternary Mixture	Metal ions with there Rf Values
1.	Cr (VI); As (III); Cr (III).	Cr (III) – 0.97; As (III) – 0.74; Cr (III) – 0.55.
2.	Cr (VI); Cd (II); Cr (III).	Cr (VI) – 0.95; Cd (II) – 0.66; Cr (III) – 0.58.
3.	Cr (VI); Cr (III); Tl (III).	Cr (VI) -0.95; Cr (III) -0.60; Tl (III) -0.30.
4.	As (III); Hg (II); Tl (III).	As (III) -0.81; Hg (II) -0.41; Tl (III) -0.28.
5.	Cd (II); Hg (II); Tl (III).	Cd (II) - 0.61; Hg (II) – 0.44; Tl (III) - 0.27.
6.	Cr (VI); Cd (II); Tl (III).	Cr (VI) – 0.97; Cd (II) – 0.64; Tl (III) – 0.28.
7	Cr (IV); As (III); Tl (III).	Cr (IV) -0.97; As (III) -0.78; Tl (III) -0.35.
8.	As (III); Cr (III); Hg (II).	As (III) – 0.79; Cr (III) -0.65; Hg (II) – 0.44.
9.	Cr (III); Hg (II); Tl (III).	Cr (III) - 0.68; Hg (II) - 0.47; Tl (III) - 0.32.
10.	Cr (IV); Cr (III); Hg (II).	Cr (IV) -0.96; Cr (III) – 0.62. Hg (II) -0.55.

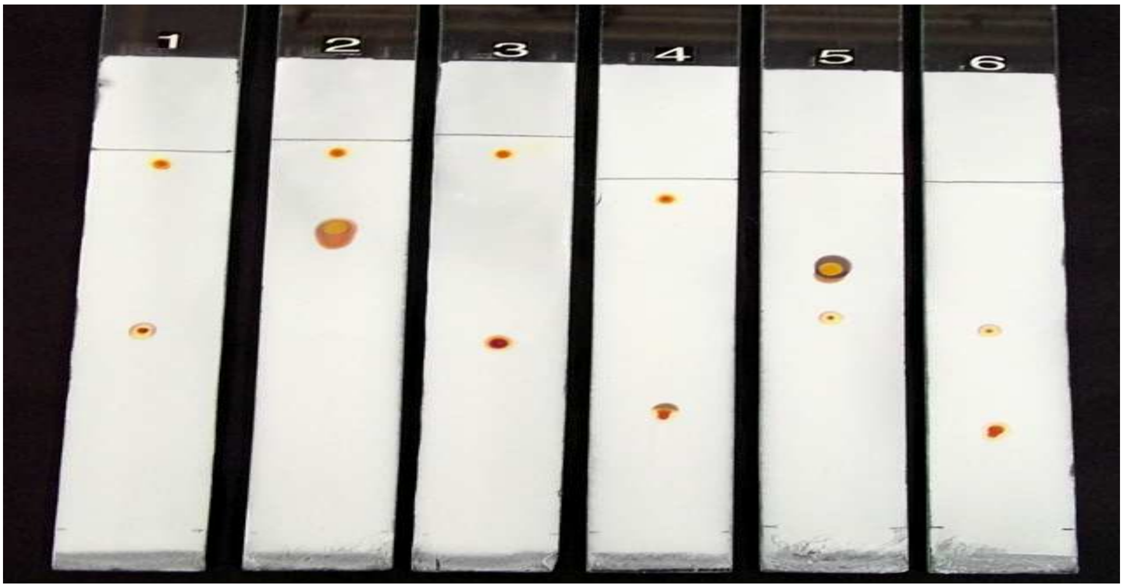
Table No 5:- Quaternary separations.

Sr. No.	Components of quaternary mixture	Metal ions with there Rf Values
1.	Cr (VI); As (III); Cr (III); Tl (III).	Cr (VI) – 0.95; As (III) – 0.71; Cr (III) – 0.55; Tl (III) – 0.22.
2.	Cr (VI); Cd (II); Cr (III); Tl (III).	Cr (VI) -0.96; Cd (II) -0.70; Cr (III) -0.59; Tl (III) -0.21.
3.	Cd (II);Cr (III); Hg (II); Tl (III).	; Cd (II) – 0.64; Cr (III) – 0.58; Hg (II) – 0.40; Tl (III) 0.30.
4.	Cr (VI); Cd (II); Cr (III); Hg (II).	Cr (VI) – 0.95; Cd (II) – 0.66; Cr (III) – 0.55 Hg (II) – 0.35.
5.	Cr (VI); Cr (III); Hg (II); Tl (II).	Cr (VI) -0.95; Cr (III) -0.65; Hg (II) -0.36; Tl (II) -0.21.
6.	Cr (VI); Cd (II); Hg (II), Tl (III).	Cr (VI) -0.97; Cd (II) -0.72; Hg (II) -0.33; Tl (III) -0.25.

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.

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

Picture No 1: Binary Separations.

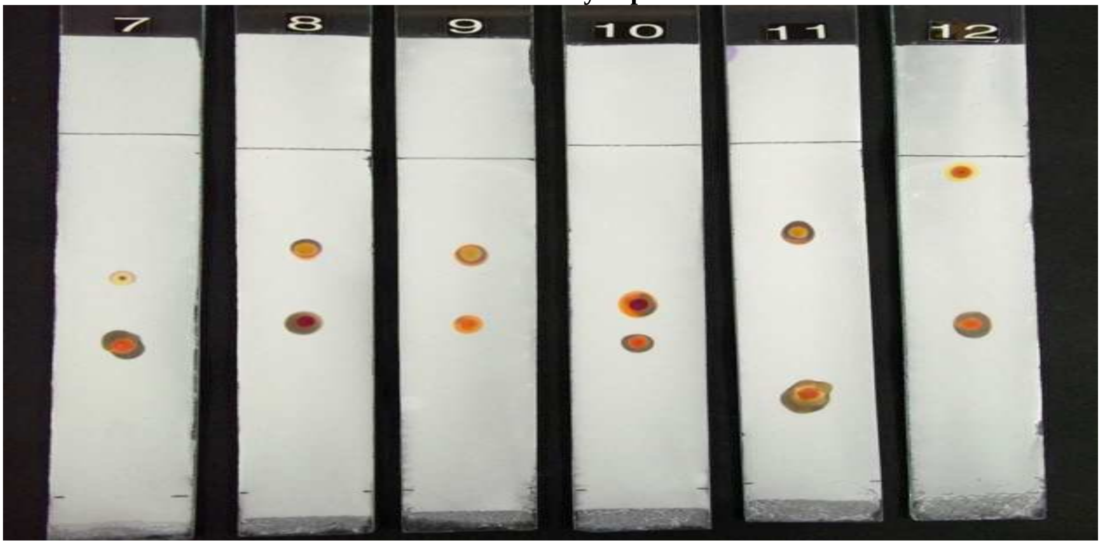


CONCLUSION

Using the above mentioned optimum separating conditions, that is 0.05 M α- Picolinic acid at pH 3.5, qualitative separation of eleven binary mixtures; twelve ternary mixtures; and four quaternary mixtures of metal ions have been carried out. 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 & 2, for ternary separations in picture no 3 and quaternary separations in picture no 4.

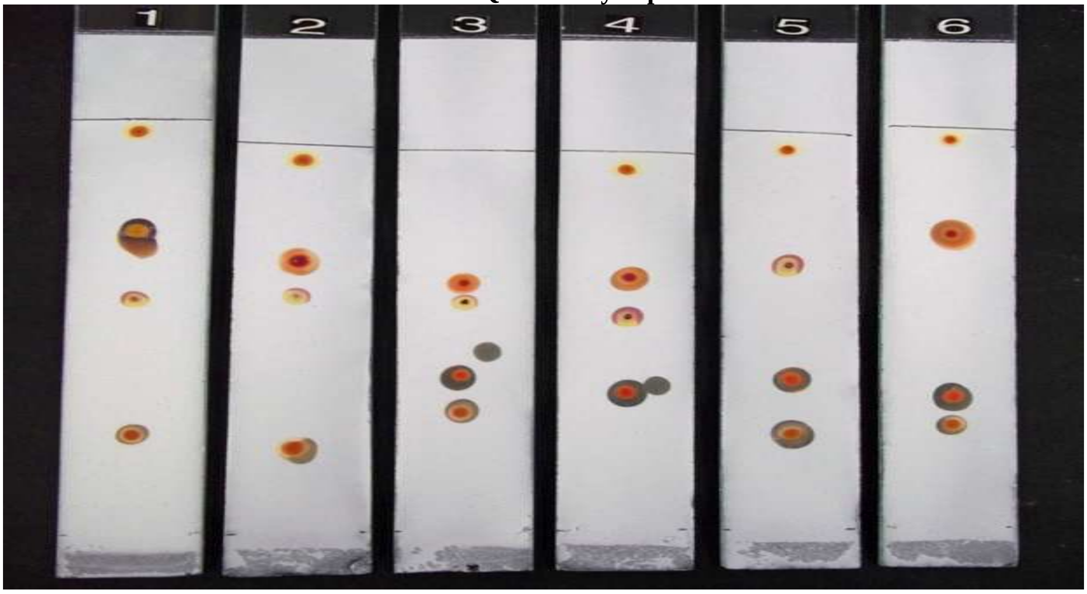
Experimentally achieved separations on silica gel ‘G’ layers developed with aqueous α Picolinic acid as mobile phase.

Picture No 2: Binary Separations



Picture No 3: Ternary Separations.

Picture No 4: Quaternary Separations.



Acknowledgement:-
The authors would like to thank the principal and head of the Department of Chemistry, Hislop College Nagpur, and M.S. India for the providing of the research facilities used in our study.

REFERENCES

[1] L Deshmukh ;.R B Kharat; *Intern J. Environ. Anal Chem.*; Vol.36, 1-6, **1988**.
[2] L Deshmukh;. R B Kharat; *Journal of Liquid Chromatography* 12(6), 937-947, **1989**.
[3] H Thielemann. *Acta Hydrochem. Hydrobio*. **1977**, 5, 191-193.
[4] D W Armstrong; R Q Terrill. *Anal. Chem.***1979**, 51, 2160-2163.
[5] M F Borgerding; R L Williams (Jr); W L Hinze; Quina, *J. Liq. Chromatography*.; **1989**, 12, 1367-1406.
[6] A S Kord; M G Khaledi; *Anal, Chem*. **1992**, 64, **1901-1907**.
[7] A Szymanski; W Szczepaniak, *Chem. Anal. Warsaw*, **1998**, 43, 346-349.
[8] M G Khaledi; J K Strasters; A H Rodgers; E D Breyer. *Anal. Chem*., **1990**, 62,130-136.
[9] A Mohammad; V J Agrawal; *Planar Chromatography. Mod.-TLC*, **2000**, 13, 210-216.
[10] [10] A Mohammad; Y H Sirwal, *J. Planar Chromatography-Mod.TLC*, **2001**, 15, 107-115.
[11] S Dingmi; L Suya; L Taohui. *Fenxi Huaxue*, **1984**, 12, 934; C.A. **1985**, 102,7195V.
[12] A Mohammad; Eram Iraqi, and Iftkhar Alam Khan; *J. of Surfactant and Detergent*, **1999**, Vol.2;No.4,523-529.
[13] A Mohammad; V Agrawal, Nahed Jabeen.; *Chromatography*, **2003**, 24, 2 1-7.
[14] C G Yeole; V M Shinde, *Analyst*.**1983**, 104, 1102-1107.
[15] J G Dorsey; M T De Etchegaray; J S Landy. *Anal. Cham*. **1983**, 55, 924-928.
[16] N U Perisic - Janjic; S M Petrovic; T L Djakovic; presented at Budapest Chromatography conference, 24-17 August (**1990**), Budapest.
[17] F Feigl, ‘Spot Test Inorganic Applications’ Elsevier Pub. Co., Amsterdam 4th Ed. (**1954**)
[18] J J Piefer, *Microchim Acta*., 529 (**1962**)