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Research Article

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Separation and identification of heavy metal ions by thin layer chromatography on silica gel-G

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ABSTRACT

Thin layer chromatographic method has been developed for the separation of metal ions such as Cr (VI), Cr (III), Ni (II), Co (II), Cu(II), Fe(III), Zn(II) and Mo(VI) from their two, three and four component mixtures. The separations were performed on thin layer of silica gel 'G' using aqueous Humic acid as mobile phase. Thin layer of Silica Gel-G was used to study the chromatographic behavior of metal ions in surfactant mixed solvents. Effect of presence of humic acid at various concentrations, presence of strong and weak electrolytes, and effect of concentration of surfactant, effect of acidity and basicity of aqueous surfactant on mobility of metal cations were also studied. By using surfactant and with various additives mixed in mobile phase, metal ions such as Cu^{2+}, Hg^{2+}, W^{6+} and Ni^{2+} were separated from their binary mixture. Semi-quantitative determination of Ni^{2+} by measurement of spot area was attempted.

Key words: Thin layer chromatography, separation, silica Gel –G, DMSO, toxic heavy metal ion

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INTRODUCTION

Thin layer chromatography is a versatile technique for the identification and separation of organic and inorganic compounds [1-2]. 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, Mo are toxic and harmful to human health. These metal ions can form complexes with bioligands containing oxygen, nitrogen and sulphur atoms, which causes many problems by their redox processes in living organisms [5]. The use of aqueous solution as a mobile phase in TLC was pioneered by Armstrong and Terrill [6]. 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 [7-10].

The use of silica gel and an alumina layer with surfactant –mediated mobile phase systems [11-16] has been used to separate various inorganic species. Organic matter soil amendments have been known by farmers to be beneficial to plant growth for longer than recorded history [17]. However, the chemistry and function of the organic matter has been a subject of controversy since humans began their postulating about it in the 18th century. Until the time of Liebig, it was supposed that humus was used directly by plants but after Liebig had shown that plant growth depends upon inorganic compounds, many soil scientists held the view that organic matter was useful for fertility only as it was broken down with the release of its constituent nutrient elements into inorganic forms. At the present time, soil scientists hold a more holistic view and at least recognize that humus influences soil fertility through its effect on the water-holding capacity of the soil. Also, since plants have been shown to absorb and translocate the complex organic molecules of systemic insecticides, they can no longer discredit the idea that plants may be able to absorb the soluble forms of humus[18] this may in fact be an essential process for the uptake of otherwise insoluble iron oxides. A study on the effects of humic acid on plant growth was conducted at Ohio state university which said in part humic acids increased plant growthand that here were relatively large responses at low application rates[19].

In Ancient Egypt, according to archeology, straw was mixed with mud in order to produce building bricks. Straw produces stronger bricks that are less likely to break or lose their shape. Modern investigations have found that humic acid is released from straw when mixed with mud, basically a mixture of sand and clay. Humic acid increases clay's plasticity[20]. Humic acid is a principal component of humic substances, which is produced by biodegradation of dead organic matter. By definition, humic acids are brownish-black, alkali-soluble solids which can either be recovered from naturally weathered coals or alternatively, be prepared by controlled oxidation 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 Humic acid and DMSO(dimethyl sulphoxide) as a mobile phase.

EXPERIMENTAL SECTION

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 and EI pH meter.

Chemicals and Reagents

Humic acid (Merck, India), DMSO (dimethyl sulphoxide), silica gel- G (Merck, India), hydrochloric acid and sodium hydroxide.

Metal ion studied : Cr (VI), Cr (III), Ni (II), Co (II), Cu (II), Fe(III), Zn (II) and Mo (VI)

Stock Solutions: Stock solutions of 1% of following salts were prepared in the 0.1 M hydrochloric acid.
1. Potassium salt of Cr(VI),
2. Chloride of Cr(III), Ni(II), Zn(II) and Fe(III),
3. Sulphate of Cu(II).
4. Trioxide of Mo(VI).
5. Nitrate of Co(II).

The mobile phase was prepared in double distilled water.

Detection Reagents:

For the detection of various cations, the following regents were used
1) 0.05 % Dithiozone in carbon tetrachloride.
2) Saturated alcoholic $AgNO_3$.
3) Saturated alcoholic alizarin red.
4) 1% Alcoholic solution of DMG ie. Dimethylglyoxime.
5) 1% Aqueous potassium ferrocyanide

Stationary phase : Silica gel –G.
Mobile phase: The aqueous solution of humic acid and DMSO(dimethyl sulphoxide) as the mobile phases.

Thin - layer chromatography (TLC)

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 humic acid and DMSO 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 humic acid and DMSO 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 , dithiozone in carbon tetra chloride, dimethylglyoxime and potassium ferrocyanide for Cr(IV), Cr(III), and other metal ions i.e. Mo(VI), Zn(II), Ni(II), Co(II), Cu(II) and Fe(III) 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 Rf values of the individual cations.

RESULTS AND DISCUSSION

Effect of Concentration

This section deals with the separation of Cr(VI), Cr(III), Ni(II), Co(II), Fe(III), Cu(II), Zn(II) and Mo(VI). Various experiments were carried out at different pH and at different concentration of humic acid and DMSO (dimethyl sulphoxide) for determining optimum separation concentration for the metal ions. The results dealing with the effect of concentration of mobile phase i.e. humic acid and DMSO on the R_f values of different metal ions such as Cr(VI), Cr(III), Ni(II), Co(II), Fe(III), Cu(II), Zn(II) and Mo(VI) are tabulated in Table 1. The variations in the R_f values with concentration in the range of 0.005 to 0.1M were studied in pH range of 1 to7.

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Table 1. Effect of Concentration on the R_f values of metal ions

Concentration	Metal ion							
	Cr(VI)	Cr(III)	Co(II)	Ni(II)	Zn(II)	Cu(II)	Fe(III)	Mo(VI)
0.1%Humic acid +2% DMSO	0.90	0.45	0.56	0.66	0.40	0.11	0.16	0.32
0.01%Humic acid +1% DMSO	0.94	0.37	0.56	0.67	0.23	0.08	0.11	0.28
0.02%Humic acid +1% DMSO	0.94	0.39	0.55	0.67	0.22	0.08	0.12	0.26
0.005%Humic acid +0.5% DMSO	0.95	0.38	0.52	0.68	0.20	0.06	0.06	0.26

It was observed that, at low concentration 0.005 M Cr(VI), Zn(II) and Ni(II) shows tailing, at 0.01 M concentration all metal ions shows little tailing. As the concentration of humic acid and DMSO was increased to 0.05 M, clear and distinct spots were seen[18]. It was also observed that, there is an increase in the Rf values with increase in the concentration, but at 0.1% humic acid +2% DMSO spots are not compact and shows little spreading, specially Cr(VI), Mo(VI). However 0.01 M concentration was selected as the optimum concentration for further studies.

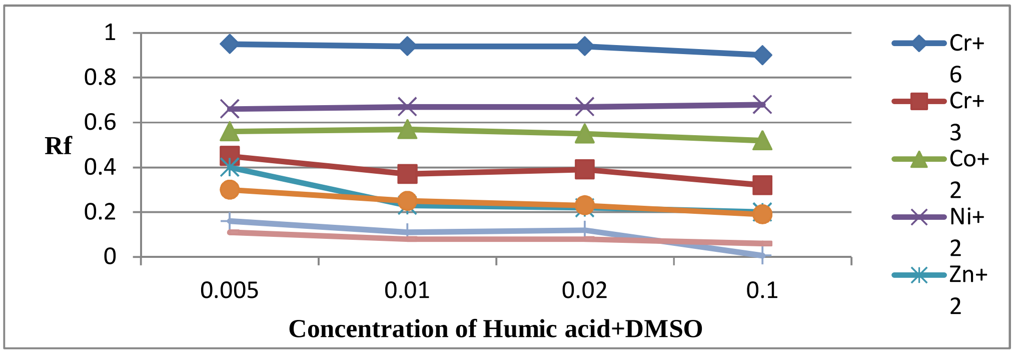

Fig.1 Effect of concentration on the R_f value of metal ion

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 to10 cm above from the base line. The results are tabulated in Table 2 which reveal variations in the R_f values with pH of humic acid + DMSO with the time of 15 minutes[19].

Table 2:- Effect of pH on the R_f values of metal ions

Metal Ion	pH of humic acid + DMSO									
	2	2.5	3	3.5	4	4.5	5	5.5	6	7
Cr(VI)	0.94	0.94	0.96	0.94	0.95	0.97	0.96 T	0.96 T	0.97 T	0.97 T
Cr(III)	0.70	0.66	0.63	0.50	0.39	0.38	0.37	0.35	0.34	0.35
Co(II)	0.72	0.50	0.45	0.46	0.42spr	0.34	0.35spr	0.35spr	0.36	0.36
Ni(II)	0.88	0.60	0.55	0.52spr	0.53spr	0.53spr	0.50spr	0.52spr	0.54	0.54
Zn(II)	0.70	0.61	0.32	0.31 T	0.32 T	0.31 T	0.30 T	0.30 T	0.16 T	0.15 T
Cu(II)	0.50spr	0.32spr	0.21	0.15	0.15	0.11	0.08	0.06	0.06	0.05
Fe(III)	0.30spr	0.15spr	0.15	0.12	0.12	0.11	0.12	0.11	0.10	0.10
Mo(V)	0.88	0.85	0.84	0.50T	0.43	0.44 T	0.43T	0.43T	0.40	0.40

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

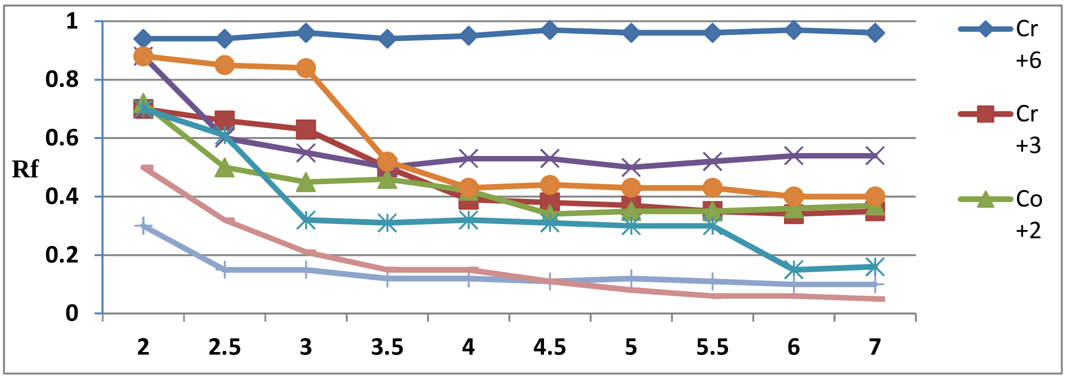

Fig. 2. Effect of pH on the R_f value of metal ion

Table 3. Binary separations

Sr. No	Components of Binary mixture	Metal ions with their R_f Values
1	Cr(VI), Co(II)	Cr(VI) - 0.95; Co(II) - 0.44
2	Ni(II), Zn(II)	Ni(II) – 0.60; Zn(II) – 0.11
3	Ni(II), Mo(VI)	Ni(II) – 0.71; Mo(VI) – 0.17
4	Ni(II), Cr(III)	Ni(II) – 0.54; Cr(III) – 0.19
5	Co(II), Zn(II)	Co(II) - 0.67; Zn(II) – 0.13
6	Cr(VI), Cr(III)	Cr(VI) – 0.92;Cr(III) – 0.20
7	Ni(II), Co(II)	Ni(II) – 068; Co(II) – 0.60
8	Ni(II), Cu(II)	Ni(II) – 0.65; Cu(II) – 0.11
9	Ni(II), Zn(II)	Ni(II) - 064; Zn(II) – 0.13
10	Cr(VI), Ni(II)	Cr(VI) - 093; Ni(II) - 0.70

Table 4. Ternary separations

Sr.No.	Components of Ternary mixture	Metal ions with their R_f Values
1	Ni(II), Co(II), Cr(III)	Ni(II) – 0.55; Co(II) – 0.36; Cr(III) – 0.24
2	Ni(II), Co(II), Zn(II)	Ni(II) – 0.53; Co(II) - 0.44; Zn(II) – 0.14
3	Ni(II), Cr(VI), Cu(II)	Ni(II) - 0.53; Cr(VI) – 0.93; Cu(II) – 0.10
4	Ni(II), Cr(VI), Co(II)	Ni(II) – 0.54; Cr(VI) – 0.93; Co(II) – 0.41
5	Ni(II), Cr(VI), Mo(VI)	Ni(II) – 0.51; Cr(VI) – 0.93; Mo(VI) – 0.11
6	Ni(II), Cr(VI), Zn(II)	Ni(II) – 0.53; Cr(VI) – 0.89; Zn(II) – 0.15

Table 5. Quaternary separations

Sr. No	Components of Quaternary mixture	Metal ions with their R_f Values
1	Cr(VI), Ni(II), Co(II), Zn(II)	Cr(VI) – 0.95; Ni(II) – 0.84; Co(II) – 0.73; Zn(II) – 0.15
2	Cr(VI), Ni(II), Co(II), Cu(II)	Cr(VI) – 0.95; Ni(II) – 0.83; Co(II) – 0.74; Cu(II) – 0.14
3	Cr(VI), Ni(II), Co(II), Cr(III)	Cr(VI) -0.95; Ni(II) – 0.82; Co(II) – 0.72; Cr(III) -0.32
4	Cr(VI), Ni(II), Co(II), Zn(II)	Cr(VI) – 0.94; Ni(II) – 0.82; Co(II) – 0.72; Zn(II) – 0.21
5	Cr(III), Ni(II), Co(II), Zn(II)	Cr(III) – 0.41; Ni(II) – 0.79; Co(II) – 0.69; Zn(II) – 0.13

Time = 20 minutes, Adsorbent = silica gel-G, pH = 4

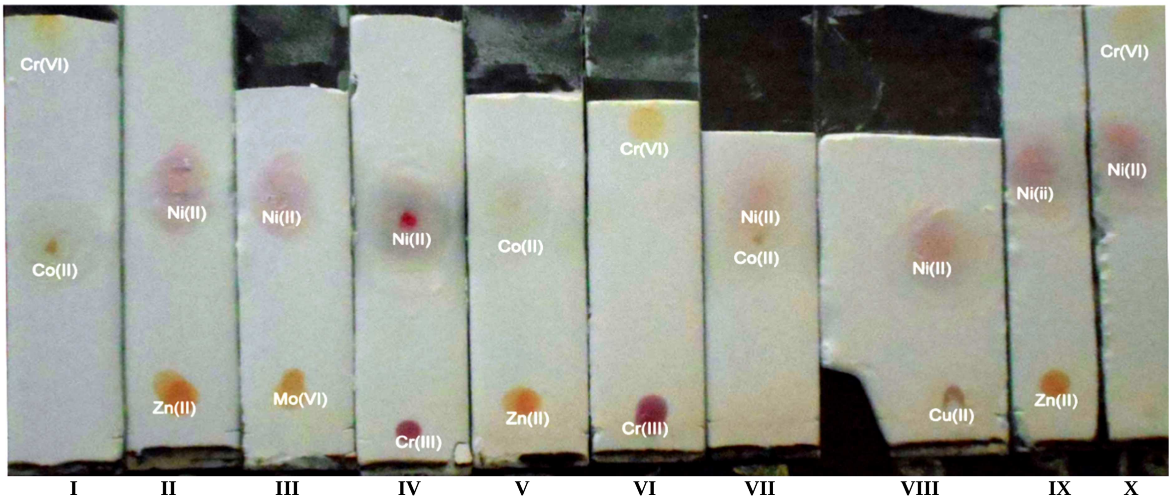

Fig.3. Binary Separations

Fig. 4. Ternary Separations
Time = 20 minutes, Adsorbent = silica gel-G, pH = 4

It was observed that from Table 2 at low pH all the metal ions moves with different solvent front. It is noted that all the metal ion showed very little difference in the R_f value at pH 3.0, but as we increase the pH to 3.5, maximum difference in the R_f value of different metal ion could be achieved, which was required for better separation. However, the behavior of cations changed after the increase above pH 4.0 and above pH 4 they have same values and above pH 5 the metal ions Cr(VI) shows double spotting due to formation of heteropoly acid Cr(III), Zn(II), Mo(VI) show tailing whereas Ni (II) shows spreading. But Co(II) and Cu(II) shows compact spot at all pH except pH 1 and pH 2 observed values, pH 3.5 and pH 4 has been found out to be ideal for bringing out maximum separation[20-21]. 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 4 fixed for further R_f measurement in humic acid + DMSO media.

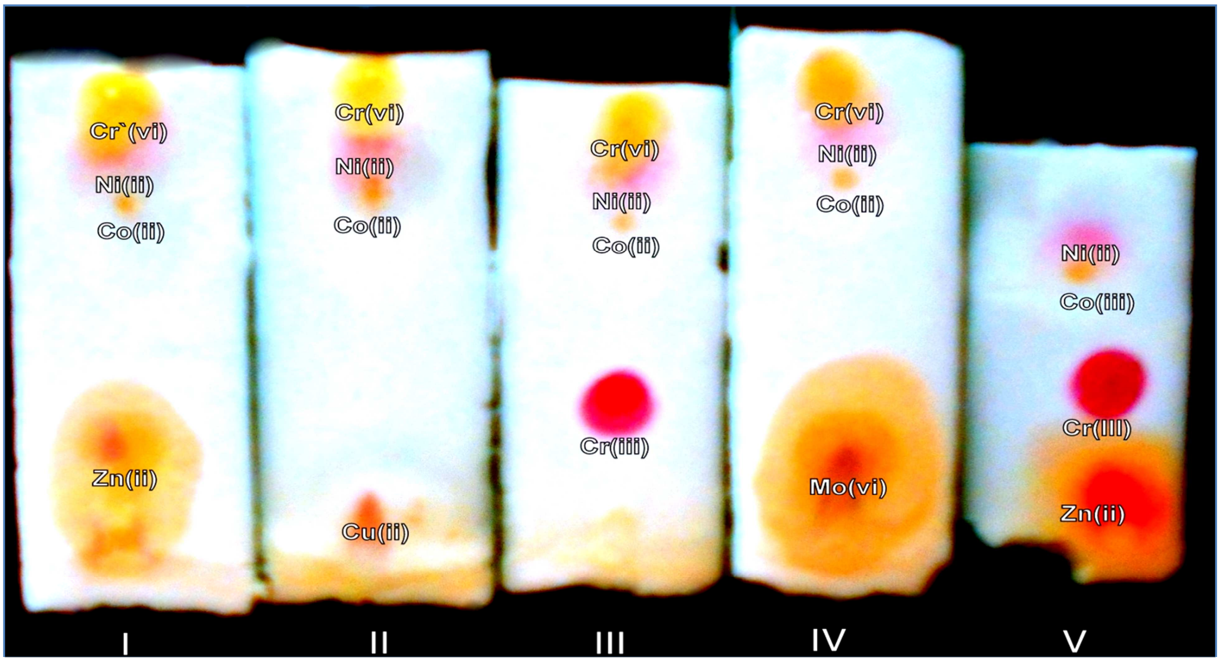

Fig. 5. Quaternary separation

CONCLUSION

Using the above mentioned optimum separating conditions, that is 0.01% humic acid +1% DMSO at pH 4, qualitative separation of ten binary mixtures, six 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 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 Fig. 1, for ternary separations in Fig. 2 and quaternary separations in Fig. 3. Rf values of experimentally achieved separations on silica gel 'G' layers developed with aqueous humic acid in DMSO as mobile phase.

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