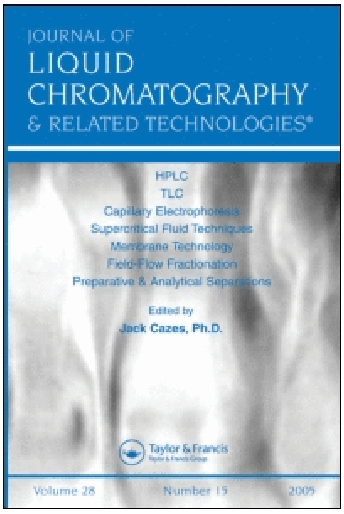

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Separation Studies of Metal Ions in Sodium Thioglycolate Medium by Thin Layer Partition Chromatography

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SEPARATION STUDIES OF METAL IONS IN SODIUM THIOGLYCOLATE MEDIUM BY THIN LAYER PARTITION CHROMATOGRAPHY

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ABSTRACT

A thin layer partition chromatographic method has been developed for separation of Fe(III), Ni(II), Zn(II), Cu(II), Pb(II) and Mn(II) on thin layers of silica gel-G as an adsorbent. The R_f values were determined using 0.01-0.2 aqueous solution of sodium thioglycolate as a mobile phase. The dependence of R_f values on the migration time, pH and concentration of mobile phase has been studied. The optimum conditions for possible 3-component separation have been determined. Metal ions have been separated, detected, eluted and quantitatively determined by atomic absorption spectroscopy. The present method was applied to the separation and determination of zinc in forensic samples.

INTRODUCTION

In all chromatographic procedures, the optimum conditions for separation yielded through mutual harmonisation of stationary phase and mobile phase. Specially for thin layer chromatography (TLC) the thin layers can be prepared from silica gel G(1), Calcium sulphate (2), Zirconium phosphate (3), Alumina, Magnesium silicate (4), Calcium silicate (5) and Cellulose (6). The use of silica gel G (SGG) impregnated with inorganic salts such as Barium nitrate or Ammonium chloride (7), high molecular weight amihes, substituted quaternary ammonium salts, heterocyclic amines and tetrasubstituted pyrazole (8,9) has become a powerful method of analysis. Literature reveals the use of various solvent systems like 1M HCl, 1M HNO_3, 0.5M H_2SO_4 , 0.1M Oxalic acid and 0.1M Citric acid (10). Similarly organic acids and their salts have also been used as mobile phases (11,12) for separation of metal ions. 4-Component separation of metal ions in tube well water samples within 10 min time has been reported (13) on unimpregnated SGG and sodium acetate as a mobile phase. Sodium salts of malic and malonic acid have been used in the 3-component separation of metal ions in industrial waste water samples (14). The use of trichloro acetic acid and glycolic acid in the mobile phases has also been reported for TLC separation of cations in flyash (15) and mineral samples (16). The present work is a simple convenient and economical method for separation, detection and quantitative determination of metal ions on unimpregnated thin layers of SGG as an adsorbent.

MATERIALS

Ordinary glass plates (4x10 cm) were used for coating SGG. An Elico pH meter model L 1 10T (Elico Pvt. Ltd.) was used for adjusting the pH of the solutions. The chromatoplates were developed in 18x13 cm glass jars. Metal ions were quantitativel determined on Chemico Atomic Absorption/Emission Spectrophotometer 200. The thin layers were prepared from SGG (E. Merck). Sodium thioglycolate was procured from B.D.H. Ltd. The stock solutions of 0.05M metal ions were prepared by dissolving their chlorides, nitrates and sulphates in 0.1M hydrochloric acid. Deionised water was used for preparation of all the solutions.

METHODS

Preparation of Thin Layer Plates

A slurry was prepared by mixing SGG and deionised water in the ratio 1:3 with constant stirring for five minutes. It was immidiately applied to the glass plates by dipping method (17). The plates were allowed to dry over night at room temperature and were used next day for TLC.

Procedure

The test solutions were spotted on the chromatoplates with the help of a Lambda pipette and dried. The sodium thioglycolate solution of a particular concentration was adjusted to desired pH with sodium hydroxide and hydrochloric acid. The plates were developed for 15 min in 20 ml sodium thioglycolate solution. Approximately 2 ml of solvent was required per plate. The plates were dried and different cations were detected by spraying various spot test reagents (13,18). R_f value measurements were done in triplicate for each set of determination. All the experiments were carried out at room temperature.

Elution of Metal Ions

The separated metal ions from the chromatograms were eluted and quantitatively determined by atomic absorption spectroscopy (AAS). Two chromatoplates were spotted with the same sample containing mixture of different metal ions, with the help of a lambda pipette. The separated metal ions on the developed plates were located by spraying with respective colour forming reagents. The positions of different metal ions were marked on the unsprayed plate. The SGG containing the different metal ions was scrapped with a blade and individual metals were collected in different beakers. The scrapped SGG containing the metal was digested with 5 ml of 2N HNO_3 and 10 ml of deionised water for about an hour on a hot plate and HNO_3 was completely boiled off. The residue was then extracted with HCl and volume was made up to 25 ml. Quantitative determination of eluted metal ions was done in these solutions by AAS.

Application to Forensic Samples

The human viscera samples containing Zn(II) were obtained from Regional Forensic Laboratory, Nagpur (India). The samples were subjected to wet digestion (19). 2-5 gms of the tissue was kept overnight with 20-25 ml concentrated HNO_3 , 4 ml concentrated H_2SO_4 and 3 ml $HClO_4$ (60-70%), preferably at the edge of a steam bath. Mixture was digested next day on a hot plate until digestion was complete. The solution was then filtered and filtrate was boiled off to remove SO_3 fumes, nitric acid and perchloric acid. The extract was cooled, 5 ml water was added and again it was evoporated to dryness

TABLE I

Variation in R_f values with Development Time
Adsorbent : SGG, Mobile phase : 0.01M Sodium thioglycolate, pH : 2.0.

Metal Ions	Development Time in Minutes			
	5	10	15	20
	R_f values			
Fe(III)	0.31	0.28	0.28	0.28
Ni(II)	0.78	0.74	0.75	0.75
Cu(II)	0.38	0.31	0.32	0.32
Zn(II)	0.24	0.16	0.17	0.17
Pb(II)	0.25	0.21	0.25	0.24
Mn(II)	0.74	0.64	0.65	0.65

on a low flame. Then the residue was extracted with 0.05 M HCl. TLC plates were spotted with the extract and chromatograms were run using sodium thioglycolate solution as a mobile phase. Separated Zn(II) metal was scrapped and eluted. Quantitative determination of Zn(II) was done by AAS method.

RESULTS AND DISCUSSION

Various experiments were carried out at different development time, pH and thioglycolate concentration for determining optimum conditions for separation of metal ions.

TABLE II

Separation of Metal Ions in Synthetic Mixtures

Adsorbent : SGG, Mobile Phase : 0.01 M Sodium thioglycolate, Development time : 10 min., pH : 2.0

Composition of Mixtures	Metal Ions Detected with R_f values		
Fe(II)-Ni(II)-Zn(II)	Fe(0.28),	Ni(0.74),	Zn(0.16)
Fe(III)-Mn(II)-Zn(II)	Fe(0.28),	Mn(0.64),	Zn(0.17)
Ni(II)-Cu(II)-Zn(II)	Ni(0.74),	Cu(0.30),	Zn(0.16)
Ni(II)-Cu(II)-Pb(II)	Ni(0.73),	Cu(0.29),	Pb(0.20)
Mn(II)-Cu(II)-Zn(II)	Mn(0.64),	Cu(0.29),	Zn(0.17)
Mn(II)-Cu(II)-Pb(II)	Mn(0.65),	Cu(0.30),	Pb(0.21)

The results are tabulated in Table 1-3 and are graphically shown in Fig. 1 and 2.

The variations in the R_f values of metal ions with development time are shown in Table 1. The R_f values were measured at pH 2.0 and 0.01 M thioglycolate concentration. It is revealed from the Table 1 that when the migration time was kept at 5 min., only binary separations of Fe(III)-Ni(II), Fe(III)-Mn(II), Ni(II)-Zn(II), Ni(II)-Pb(II), Mn(II)-Zn(II) and Mn(II)-Pb(II) were possible but when the time was increased to 10 min. The difference between the R_f values of different cations increased and many ternary separations were possible.

TABLE III

Quantitative Analysis of Separated Metal Ions in the Synthetic Mixtures and Forensic Samples by AAS

Composition	Metal Ions analysed	Metal Ions present in the mixture (μg/ml)	Metal Ions detected by AAS (μg/ml)
1) Synthetic Mixtures			
Fe(III)-Ni(II)-Zn(II)	Ni(II) Zn(II)	0.53 0.27	0.48 0.22
Fe(III)-Mn(II)-Zn(II)	Mn(II) Zn(II)	2.45 0.27	2.33 0.22
Fe(III)-Cu(II)-Zn(II)	Cu(II) Zn(II)	0.23 0.27	0.20 0.23
Ni(II)-Cu(II)-Zn(II)	Cu(II) Zn(II)	0.23 0.27	0.20 0.23
Ni(II)-Cu(II)-Pb(II)	Ni(II) Cu(II) Pb(II)	0.53 0.23 0.33	0.47 0.18 ND
Mn(II)-Cu(II)-Zn(II)	Mn(II) Cu(II) Zn(II)	2.45 0.23 0.27	2.34 0.19 0.23
Mn(II)-Cu(II)-Pb(II)	Mn(II) Cu(II) Pb(II)	2.45 0.23 0.33	2.33 0.18 ND
2) Forensic samples			
1	Zn(II)	-	1.99
2	Zn(II)	-	2.00
3	Zn(II)	-	1.97

ND = Not Detected

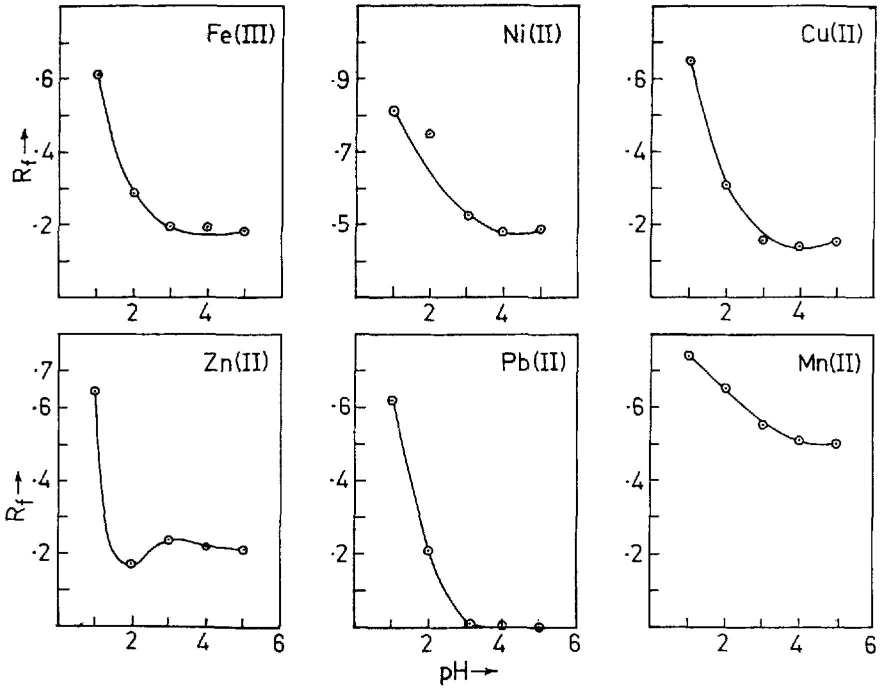

Figure 1. Variation in R_f with pH at 0.01M Sodium thioglycolate concentration.

The, still more increase in time did not much affect the separation conditions and hence the development time was fixed to 10 min for further R_f measurements.

Fig. 1 depicts the dependence of R_f values of cations on the pH of the thioglycolate solution. The R_f values in the pH range of 1.0-5.0 were studied. It is revealed from Fig. 1 that at pH 1.0 all the six cations i.e. Fe(III), Ni(II), Cu(II), Pb(II), Zn(II) and Mn(II) showed R_f between 0.6-0.8, and the differences in the R_f values started appearing from

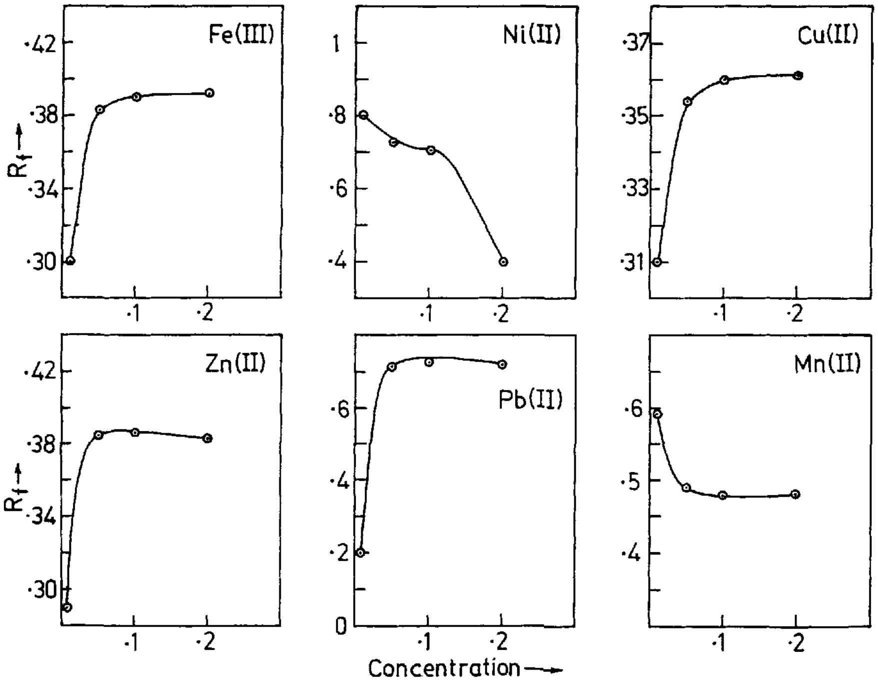

Figure 2. Variation in R_f with Sodium thioglycolate concentration at pH 2.

pH 1.5. The maximum difference in the R_f values of metal ions has been found to be at pH 2.0, Mn(II) started tailing. The Pb(II) precipitated at pH 3.0, did not remain as a compact spot and started migrating to the base line. When the pH was increased from 3.0 to 5.0, rest of the cations such as Fe(III), Ni(II), Cu(II) and Zn(II) started tailing, hence the R_f measurements were not continued beyond pH 5.0. Thus, it can be concluded from the above observations that pH 2.0 is the proper pH for the separation of metal ions in sodium thioglycolate medium and hence this pH was fixed as the optimum pH for rest of the R_f measurements.

Fig. 2 shows the effect of change in thioglycolate concentration on the R_f values of various metal ions at pH 2.0. It is revealed from Fig. 2 that as the thioglycolate concentration in the mobile phase increases from 0.01 to 0.1 M there is an increase in the R_f values of Fe(III), Cu(II), Zn(II) and Pb(II) ions. But after 0.1M, the R_f of all these four cations became steady. The Ni(II) behaved differently and travelled down after 0.1M concentration and showed the R_f value of 0.4 at 0.2M thioglycolate concentration. Mn(II) behaved similarly but at 0.05M it showed a steady R_f of 0.47. It can be observed from Fig. 2 that much better separations are possible at 0.01M concentration of sodium thioglycolate in the mobile phase, hence higher concentrations were avoided. Thus, the rest of the R_f measurements were made at 0.01 M thioglycolate concentration.

The different 3-component separations achieved are mentioned in Table 2, as Fe(III)-Ni(II)-Zn(II), Fe(III)-Mn(II)-Zn(II), Ni(II)-Cu(II)-Zn(II), Mn(II)-Cu(II)-Zn(II) and Mn(II)-Cu(II)-Pb(II). Present method gives faster separation than the methods suggested by earlier workers (20) as it requires only 10 min for the separation of a 3-component mixture. It was possible to separate some of the interesting combinations such as Cu(II)-Zn(II), Cu(II)-Pb(II), Mn(II)-Zn(II) and Mn(II)-Pb(II) by present method.

The quantitative determinations of the separated metal ions (Cu(II), Zn(II), Ni(II), Mn(II) and Pb(II)) in synthetic mixtures and that of Zn(II) present in human viscera are depicted in Table 3. It is revealed from the Table 3 that the results show a satisfactory trend, hence the method was applied to the forensic samples for determination of Zn(II). The amount of zinc determined in viscera samples by AAS can be presumed to be within experimental error, since the results obtained in synthetic mixtues are satisfactory. Experimental conditions for synthetic mixtures and forensic samples were identical.

The present method is economical as commercially available SGG was used for preparation of thin layer plates. A 3-component separation requires only 10 min as development time, which is very little for a ternary separation. The result show excellent reproducibility and variation does not exceed 5% of average R_f values for all metal ions detected. The quantitative determination of Fe(III) was not done as it present in SGG.

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