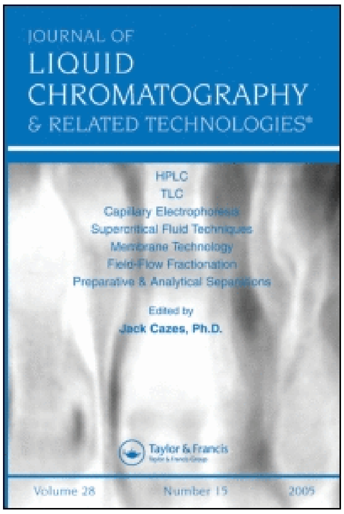

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New Inexpensive and Selective Sorbent Phases for Rapid Thin Layer Chromatographic Analysis of Metal Ions

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NEW INEXPENSIVE AND SELECTIVE SORBENT PHASES FOR RAPID THIN LAYER CHROMATOGRAPHIC ANALYSIS OF METAL IONS

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ABSTRACT

New sorbent phases have been developed by impregnating silica gel G with different inorganic salts for the analysis of metal ions by thin layer chromatography in carboxylic acids media. Thin layers prepared from silica gel G impregnated with ammonium chloride or barium nitrate show the unusual selectivity towards metal ions in comparison to the thin layers prepared from plain silica gel G or silica gel impregnated with silver nitrate or aluminium nitrate. Many qualitative separations

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of important metal ions and semiquantitative determination of Ag^+, Pb^{2+}, Cd^{2+}, Al^{3+}, Se^{4+} and Th^{4+} have been successfully achieved on impregnated silica gel. A novel feature of this study is the quantitative separation of uranium from numerous metal ions on silica gel impregnated with ammonium chloride.

INTRODUCTION

Thin layer chromatography (TLC) is one of the more commonly used separation techniques in analytical chemistry because it permits finer and sharper separations, easier manipulation of the plates and simpler dectection. It is suitable for submicrogram analysis as well as for preparative separations.

A larger number of sorbents are available which can be used in TLC but the need for a perfect sorbent has been always felt. In the absence of an ideal sorbent the predominent problem of TLC involved the search of inexpensive, reproducible and readily available stable sorbent phases to achieve improved chromatographic performance in terms of selectivity, resolution and reproducibility. The recent literature (1-6) on TLC points out that silica gel G (SG) impregnated with organic substances has been generally used for the analysis of organic and inorganic compounds while the SG impregnated with inorganic materials has been used for the analysis of organic compounds. A few studies have also been reported (7-10) on the use of inorganic ion-exchange materials. However, the use of inorganic ion-exchange materials as thin layers is expensive, more time consuming and suffers from the lack of reproducibility and stability in solvent systems. Surprisingly, no work has been reported on the use of SG impregnated with inorganic compounds for the analysis of metal ions.

In order to simplify the time consuming earlier investigations, it was decided to develop new inexpensive, selective and stable sorbent phases by impregnating SG with various inorganic salts for rapid qualitative as well as quantitative analysis of metal ions.

EXPERIMENTAL

Apparatus: A thin-layer chromatography apparatus (Toshniwal, India) for the preparation of thin layers on 20 x 3.5 cm glass plates was used. The chromatography was performed in 24 x 6 cm glass jars.

Reagents: SG of E. Merck and all other reagents of BDH analar grade were used.

Test solutions and Detectors: Test solutions were generally 0.1 M in the metal chloride, nitrate or sulphate. Conventional spot test reagents were used for detection purposes (11).

Preparation of thin-layer plates:

(a) Preparation of plain SG thin layer plates: To prepare plain SG thin layer plates, the slurry was first obtained by mixing the SG in demineralized water (DMW) in the ratio of 1:3 with constant shaking for five minutes. The resultant slurry was used immediately to coat the clean glass plates with the help of an applicator to get a layer of 250 μm thickness. The plates were first air dried in a protected area and then activated in an electrically controlled oven at 100 ± 5°C for 2 hours, before use.

(b) Preparation of impregnated SG thin layer plates: Two methods were adopted for the preparation of impregnated SG plates (i) In the precoating method an aqueous solution of the impregnant was substituted for DMW in the slurry employed to coat the plates. For example, the slurry was made by mixing aqueous solution of 0.2 M $AgNO_3$, or 0.5 M NH_4Cl or saturated solution of $Ba(NO_3)_2$ or 1.5 M $Al(NO_3)_3$ with SG in the ratio of 3:1. TLC plates were prepared by using the resultant slurry under the same experimental conditions as cited for plain SG plates followed by activation at 100°C for 2 hours, (ii) In post coating or immersion method SG plates were dipped in an aqueous solution of impregnant for a specific time period.

Solvent systems

The following solvent systems were used as mobile phases.

1. DMW
2. 1.0 M HCOOH
3. 1.0 M HCOONa
4. 1.0 M HCOOH + 1.0 M HCOONa
5. 1.0 M CH_3COOH
6. 1.0 M CH_3COONa
7. 1.0 M CH_3COOH + 1.0 M CH_3COONa

Procedure: Approximately 5 µl of the test solutions (0.1 M) were applied on each SG (impregnated or plain) plate with the help of a micropipette. The plates were developed by the ascending technique with a solvent ascent of 10 cm in all cases. After the development was over, the plates were dried in an air oven and the cations were detected with the usual reagents (11).

Semiquantitative determination of metal ions: For semiquantitative determination, various known volumes of 0.1 M metal salt solution were spotted with the help of a lambda pipette at the line of application, and the development was performed in the chosen solvent systems. After detecting the spots the planetary spots were traced on a tracing paper directly and the areas of spots were calculated.

Quantitative separation of uranium on impregnated SG TLC plates: A stock solution of uranium (10^5 ppm) was prepared by dissolving uranyl nitrate in DMW, and the standard spectrophotometric method was set up using potassium ferrocyanide as colouring reagent (12). Known amounts of uranium along with the other metal ions were spotted on NH_4Cl impregnated SG thin layer plates by using a lambda pipette and the development was performed in the chosen solvent systems. A pilot plate was employed simultaneously in order to locate the exact position of the spot on the working plate. The area covering uranium was scratched, and uranium was eluted with 0.1 N H_2SO_4. The adsorbent was separated from the solution and washed with 0.1 N H_2SO_4 to ensure complete elution of uranium. The filtrate was evaporated to dryness and the residue dissolved in DMW. The uranium was then determined spectrophotometrically.

RESULTS AND DISCUSSION

The main interesting features of this study are:

1) The proposed thin layer chromatographic method provides highly selective sorbent phases for quicker separations of metal ions compared to earlier reported methods (7-10).

2) The time required for the development of chromatographic plates is surprisingly little, i.e. 12 to 15 min.

3) The method is very inexpensive for it is based on the use of larger quantity of commercially available SG impregnated with small quantities of inorganic salts.

4) Thin layers prepared by precoating method were found better in providing reproducible R_f values.

5) Impregnated SG thin layers were found to be more selective (strongly sorbing) for metal ions than plain SG thin layers in all solvent systems. The appropriate concentration of various impregnants was found to be 0.5 M NH_4Cl, 0.2 M $AgNO_3$, 1.5 M $Al(NO_3)_3$ and saturated aqueous solution of $Ba(NO_3)_2$. Amongst these **impregnants**, NH_4Cl and $Ba(NO_3)_2$ impregnated thin layers gave excellent reproducible results and compact spots. The order of selectivity of different impregnated sorbents was found as follows: SG impregnated with $Ba(NO_3)_2 >$ SG impregnated with $NH_4Cl >$ SG impregnated with $AgNO_3 >$ SG impregnated with $Al(NO_3)_3$.

6) The semiquantitative determination of Ag^+, Pb^{2+}, Cd^{2+}, Al^{3+}, Th^{4+} and Se^{4+} on impregnated SG chromatoplates.

7) The quantitative separation of uranium on NH_4Cl impregnated SG chromatoplates.

8) Silver ion impregnated TLC which has been extensively used for the analysis of higher fatty acid esters (13), triglyceride (14), sterols (15), phospholipids and carbonyl compounds (16) was not found useful for the analysis of metal ions.

In the light of above facts attention was focussed on to exploring the analytical potential of SG impregnated with NH_4Cl and $Ba(NO_3)_2$ by TLC using thin layer plates prepared by precoating method.

The results obtained have been recounted in figures 1-5 and tables 1-4. Figures 1-3 show the relative selectivity of impregnated SG sorbents while the figure 4 shows the dependence of R_f values on the charge of the metal ions. Results for semiquantitative determination have been recounted in figure 5. Tables 1A and 1B tabulate the values of capacity factors (k') of some metal ions . The capacity factor is calculated by using the equation:

$$K' = \frac{1 - R_f}{R_f}$$

Tables 2 and 3 reflect the separations achieved on impregnated SG thin layers. The results for quantitative separation of uranium have been tabulated in table 4. Tables 1A and 1B illustrate clearly how the nature of stationary phase and mobile phase influence capacity factor (K' values) which is the measure of the degree

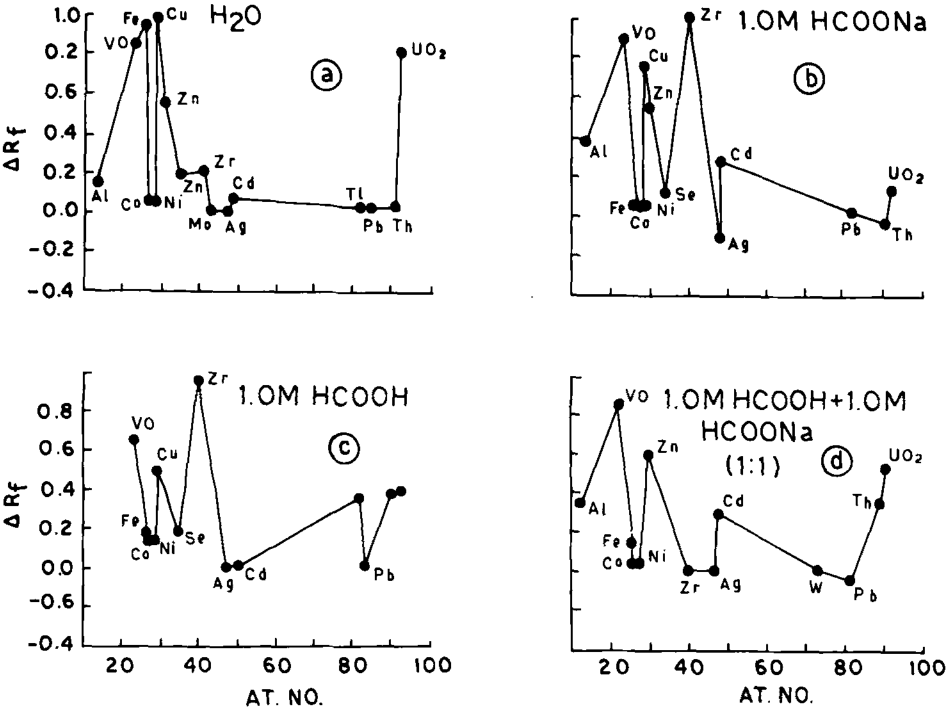

FIGURE 1 Plot of ΔR_f(R_f on plain SG - R_f on SG impregnated with $Ba(NO_3)_2$ vs. atomic number.

of retention of solute compared to the solvent front. K' values for metal ions varied with the change in both stationary and mobile phase systems. The initial selection of a phase system for chromatographic separation of metal ions often can be made on the basis of K' values. It is evident from tables 1A and 1B that Co^{2+} and Ni^{2+} show almost identical behaviour on all sorbent phases and move with the solvent front as indicated by low K' values. Cu^{2+} is strongly sorbed (K' = 99) on SG impregnated with $Ba(NO_3)$ in DMW leading to its separation from Co^{2+} and Ni^{2+}. Similarly, a good separation of Fe^{3+} (K' = 2.1) from Ni^{2+}, Co^{2+} and Cd^{2+} is possible on SG impregnated with $Ba(NO_3)_2$ in 1.0 M HCOOH. On the basis of difference in K' values, conclusions regarding many possible separations can be drawn from tables 1A and 1B.

The enhancement in selectivity of SG on impregnation opens a new door for achieving many analytically important difficult separations of metal ions. Thus a large number of important separations (binary, ternary and one from numerous metal ions) of metal ions were actually achieved on SG impregnated with NH_4Cl or $Ba(NO_3)_2$. These separations have been tabulated in tables 2 - 3. The separations such as: Fe^{3+} - Zn^{2+} - Cu^{2+}, Fe^{3+} - Zn^{2} - Cd^{2+}, Th^{4+} - Zr^{4+}, Ag^{+} - Cu^{2+} - Cd^{2+}, Cu^{2+} - Ni^{2+}, Fe^{3+} - Ni^{2+}, Pb^{2+} - Cu^{2+} - Cd^{2+}, Al^{3+} - Co^{2+}, Al^{3+} - Cu^{2+}- Ag^{+} and Zr^{4+} - Fe^{3+} - Cd^{2+} are interesting and show the advantage of impregnated phases.

The main factors which influence the separation on TLC are considered to be the ion exchange of the adsorbent and the coordinative property of the solvents. To understand the effect of these two factors on the migration of the metal ions, results on impregnated SG and plain SG have been compared and the difference in R_f

TABLE 1A

Capacity Factor (K') Values of Some Ions on Different Sorbents in H_2O, 1.0 M HCOOH, 1.0 M HCOONa, 1:1 Molar Mixture of HCOOH and HCOONa Solvent Systems.

Solvent System	DMW			1.0 M HCOOH			1.0 M HCOONa			HCOOH+HCOONa (1:1 Molar ratio)		
Impregnants / Metal ions	Plain SG	NH_4Cl	$Ba(NO_3)_2$	Plain SG	NH_4Cl	$Ba(NO_3)_2$	Plain SG	NH_4Cl	$Ba(NO_3)_2$	Plain SG	NH_4Cl	$Ba(NO_3)_2$
Al^{3+}	5.66	0.33		-	0.25	1.5	1.6	0.33		0.33	1.5	1.5
VO^{2+}	0.17	5.66		0.05	0.15	2.3	0.05			0.0		5.66
Fe^{3+}	0.00	0.15	19.0	1.0	0.05	2.1	5.66	7.5	7.5	1.5	3.0	4.0
Co^{2+}	0.00	0.05	0.05	0.0	0.05	0.17	0.04	0.17	0.05	0.0	0.05	0.05
Ni^{2+}	0.00	0.05	0.05	0.0	0.05	0.17	0.04	0.17	0.05	0.0	0.06	0.05
Cu^{2+}	0.00	0.05	99.0	0.05	0.05	1.2	0.1	0.15	5.66	0.0	1.1	0.33
Zn^{2+}	0.66	19.00		0.05	-	-	0.1	4.0		0.65	1.3	1.9
Se^{4+}	-	1.10	1.9	0.38	0.25	1.0	1.0	0.05	0.4	-	0.03	0.40
Zr^{4+}	4.00	19.00		0.0	0.11	19.0	0.0	49.0			99.0	
Mo^{6+}				-	0.11	-	-	-		-	-	1.9
Ag^{+}									7.5		19.0	49.0
Cd^{2+}	0.00	0.05	0.05	0.05	0.05	0.05	0.0	0.05	0.37	0.0	0.05	0.4
W^{6}			99.0	0.0	-	-			19.0	0.4	-	0.4
Tl^{+}				0.0	0.33	0.5	0.0	1.8	1.0	-	-	1.9
Pb^{2+}		-			1.0			19.0	49.0		19.0	49.0
Th^{4+}		19.0	99	0.27	0.5	1.5		9.0	13.0	0.66	2.0	3.0
UO_2^{2+}	0.2	-	19	0.2	0.15	1.5	5.66	-	19.0	0.17	0.8	1.9

TABLE 1B

Capacity Factor (K') Values of Some Metal Ions on Different Sorbents in 1.0 M CH_3COOH, 1.0 M CH_3COONa and CH_3COOH + CH_3COONa (1:1) Solvent Systems.

Solvent Systems	1.0 M CH_3COOH			1.0 M CH_3COONa			CH_3COOH+CH_3COONa (1:1 Molar Ratio)	
Impregnants	Plain SG	NH_4Cl	$Ba(NO_3)_2$	Plain SG	NH_4Cl	$Ba(NO_3)_2$	NH_4Cl	$Ba(NO_3)_2$
Metal ions								
Al^{3+}	4.9	0.33	2.33	0.11	0.05		5.66	19.0
VO^{2+}	5.36	0.33	5.66	19.0			2.3	
Fe^{3+}	-	0.38	0.17	15.7	19.0	19.0	5.64	9.0
Co^{2+}	0.67	0.05	0.09	0.17	0.06	0.17	1.1	0.17
Ni^{2+}	0.40	0.05	0.09	0.11	0.05	0.17	1.1	0.33
Cu^{2+}	0.5	0.56	1.9	0.43	0.11	9.0	0.33	2.0
Zn^{2+}	-	0.05	0.17	-			0.03	1.9
Se^{4+}	-	0.25	1.9	-	0.38	-	0.06	-
Zr^{4+}	11.5	19.0	19.0	-	19.0	99.0	99.0	-
Mo^{6+}	-	1.5		-			-	-
Ag^{+}	-			-				
Cd^{2+}	0.11	0.17	0.17	0.11	0.17	0.17	0.17	0.17
W^{6}	-		-	-	-	-	-	-
Tl^{+}	0.16	-	0.33	-	5.0	0.48		-
Pb^{2+}		19.0	19.0	6.5	19.0	19.0	18.0	19.0
Th^{4+}		1.9	4.0	-	-		9.0	19.0
UO_2^{2+}	0.11	4.3	1.9	-	13.0	19.0	0.33	1.5

TABLE 2

Separations achieved on SG impregnated with 0.5 M NH_4Cl

Solvent systems	Separations achieved
1.0 M HCOOH	Ag^+(0.0)-Al^{3+}(0.8), Ag^+(0.0)-Cu^{2+}(0.95), Ag^+(0.0)-Zr^{4+}(0.9), Ag^+(0.0)-Th^{4+}(0.65)-Mo^{4+}(0.9)
1.0 M HCOONa	Fe^{3+}(0.12)-Ni(0.85), Zn^{2+}(0.21)-Cd^{2+}(0.95) Zn^{2+}(0.21)-Cu^{2+}(0.38), Pb^{2+}(0.05)-Se^{4+}(0.94).
1.0 M CH_3COOH	Zr^{4+}(0.05)-Mo^{6+}(0.4)-Ni^{2+}(0.95), Zr^{4+}(0.05)-Th^{4+}(0.35), Mo^{4+}(0.4)-W^{6+}(0.0).
1.0 M CH_3COONa	Zn^{2+}(0.0)-Cd^{2+}(0.85), Zn^{2+}(0.0)-Cu^{2+}(0.9), Zn^{2+}(0.0)-Al^{3+}(0.95).
1.0 M CH_3COOH + 1.0 M CH_3COONa (1:1)	Zr^{4+}(0.01)-Uo_2^{2+}(0.74), Al^{3+}(0.15)-Cu^{2+}(0.75), Al^{3+}(0.15)-Zn^{2+}(0.9), Ag^+(0.0)-Vo^{2+}(0.3), Pb^{2+}(0.06)-Co^{2+}(0.4)-Cu^{2+}(0.75), Fe^{3+}(0.16)-Cu^{2+}(0.75)- Pb^{2+}(0.06).
1.0 M HCOOH + 1.0 M HCOONa (1:1)	Fe^{3+}(0.25)-Zn^{2+}(0.43)-Cu^{2+}(0.89), Fe^{3+}(0.25)-Zn^{2+}(0.43)-Cd^{2+}(0.95), Al^{3+}(0.41)-Ag^+(0.05)-Co^{2+}(0.94), Al^{3+}(0.41)-Ag^+(0.05)-Cu^{2+}(0.89), Fe^{3+}(0.25)-Cu^{2+}(0.39)-UO_2^{2+}(0.55), Fe^{3+}(0.25)-Ni^{2+}(0.93), Fe^{3+} (0.25)-UO_2^{2+}(0.55) Vo^{2+}(0.0)-Th^{4+}(0.94)-Co^{2+}(0.94), Ag^+(0.05)-Cd^{2+}(0.95)-UO_2^{2+}(0.55), Pb^{2+}(0.05)-Cu^{2+}(0.39)-UO_2^{2+}(0.55), Pb^{2+}(0.05) from mixture of Cd^{2+}, UO_2^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Th^{4+}, and Cd^{2+}. Vo^{2+}(0.0) from mixture of Cd^{2+}, UO_2^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Al^{3+} and Th^{4+}.

values i.e., ΔR_f values (R_f on plain SG - R_f on impregnated SG) have been plotted (Figures 1,2). It is evident from these figures that impregnation generally enhances the selectivity of plain SG in all solvent systems. SG impregnated with $Ba(NO_3)_2$ shows an unusual selectivity towards most of the metal ions in all solvent systems, as indicated by positive ΔR_f values (Figs. 1,a-d). However, the selectivity of the sorbent phase is drasti-

TABLE 3

Separations achieved on SG impregnated with $Ba(No_3)_2$

Solvent systems	Separations achieved
1.0 M HCOOH	Pb^{2+}(0.0)-Fe^{3+}(0.32), Pb^{2+}(0.0)-Co^{2+}(0.85) Pb^{2+}(0.0)-Uo_2^{2+}(0.44), Pb^{2+}(0.0)-Al^{3+}(0.44) Fe^{3+}(0.32)-Ni(0.85), Cu^{2+}(0.45)-Ni^{2+}(0.85) Zr^{4+}(0.05)-Th^{4+}(0.41), Zr^{4+}(0.05)-Al^{3+}(0.44) Pb^{2+}(0.0)-Cu^{2+}(0.45)-Cd^{2+}(0.95) Zr^{4+}(0.05)-Fe^{3+}(0.32)-Cd^{2+}(0.95) Zr^{4+}(0.05)-Al^{3+}(0.44)-Co^{2+}(0.85) Zr^{4+}(0.05)-Fe^{3+}(0.32)-Ni^{2+}(0.85) Zr^{4+}(0.05)-Tl^{+}(0.66)-Cd^{2+}(0.95) Pb^{2+}(0.0)_Cu^{2+}(0.45)-Ni^{2+}(0.85) Ag^{+}(0.0)-Fe^{3+}(0.32)-Co^{2+}(0.85) Ag^{+}(0.0)-Cu^{2+}(0.45)-Cd^{2+}(0.95)
1.0 M HCOONa	Cd^{2+}(0.73) from mixture of Pb^{2+}, Fe^{3+}, Uo_2^{2+}, Vo^{2+}, Zn^{2+}, Th^{4+}, Al^{3+}, W^{6+}, Mo^{6+} and Zr^{4+} Ni^{2+}(0.95) from mixture of Pb^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Th^{4+}, Al^{3+}, Mo^{6+}, Zr^{4+} and Vo^{2+} Co^{2+}(0.95) from mixture of Fe^{3+}, Uo_2^{2+}, Zn^{2+}, Th^{4+}, Al^{3+} and W^{6+}
1.0 M HCOOH + 1.0 M HCOONa (1:1)	Vo^{2+}(0.35)-Pb^{2+}(0.0)-Se^{4+}(0.7) Fe^{3+}(0.2)-Mo^{6+}(0.72), Fe^{3+}(0.2)-Cd^{2+}(0.72) Cu^{2+}(0.76)-Th^{4+}(0.24), Zn(0.35)-Ni^{2+}(0.95)
1.0 M CH_3COOH	Al^{3+}(0.3)-Ni^{2+}(0.92)-Ag^{+}(0.0) Vo^{2+}(0.15)-Tl^{+}(0.74), Se^{4+}(0.35)-Cd^{2+}(0.85) Uo_2^{2+}(0.35)-Fe^{3+}(0.85)-Pb^{2+}(0.05)
1.0 M CH_3COOH + 1.0 M CH_3COONa (1:1)	Zn^{2+}(0.35)-Ni^{2+}(0.75)-Th^{4+}(0.05) Cu^{2+}(0.32)-Co^{2+}(0.85)-Ag^{+}(0.0) Fe^{3+}(0.1)-Cd^{2+}(0.87), Fe^{3+}(0.1)-Ni^{2+}(0.75) Th^{4+}(0.05)-Se^{4+}(0.8), Pb^{2+}(0.05)-Cd^{2+}(0.85).

TABLE 4

Quantitative separation of Uranium in binary mixtures on NH_4Cl impregnated SG thin layers

Solvent systems	Synthetic mixtures	Amount of uranium applied (µg)	Amount of uranium found (µg)	% Error
1.0 M CH_3COONa	UO_2^{2+}-Al^{3+}	350	355	+1.4
	UO_2^{2+}-Co^{2+}	350	358	+2.3
	UO_2^{2+}-Ni^{2+}	350	332	-5.1
	UO_2^{2+}-Cu^{2+}	350	358	+2.3
	UO_2^{2+}-Se^{4+}	350	347	-0.85
	UO_2^{2+}-Cd^{2+}	350	349	-0.3
1.0 M HCOOH + 1.0 M HCOONa (1:1)	UO_2^{2+}-Fe^{3+}	350	352	+0.6
	UO_2^{2+}-Ag^{+}	350	356	+1.7
	UO_2^{2+}-Pb^{2+}	350	327	-6.5

cally influenced by the nature of solvent system. In DMW (Fig. 1a) Fe^{3+}, VO^{2+} and Cu^{2+} show high positive ΔR_f values (strong adsorption) which are significantly reduced when DMW is replaced by 1.0M HCOOH (Fig. 1c). Similarly, UO_2^{2+} shows more positive ΔR_f value in DMW compared to all other solvent systems. It is evident from Fig. 2 that most of the metal ions in almost all solvent systems have either positive or zero values for ΔR_f showing that SG impregnated with NH_4Cl is more selective than plain SG. The impregnated SG is highly selective for Zn^{2+} in HCOOH and for VO^{2+} in all other solvent systems as indicated by high positive ΔR_f values. However, in DMW Al^{3+} and Se^{4+} are strongly adsorbed on plain SG. An identical behaviour is noticed for Fe^{3+} and Se^{4+} in 1.0 M HCOOH.

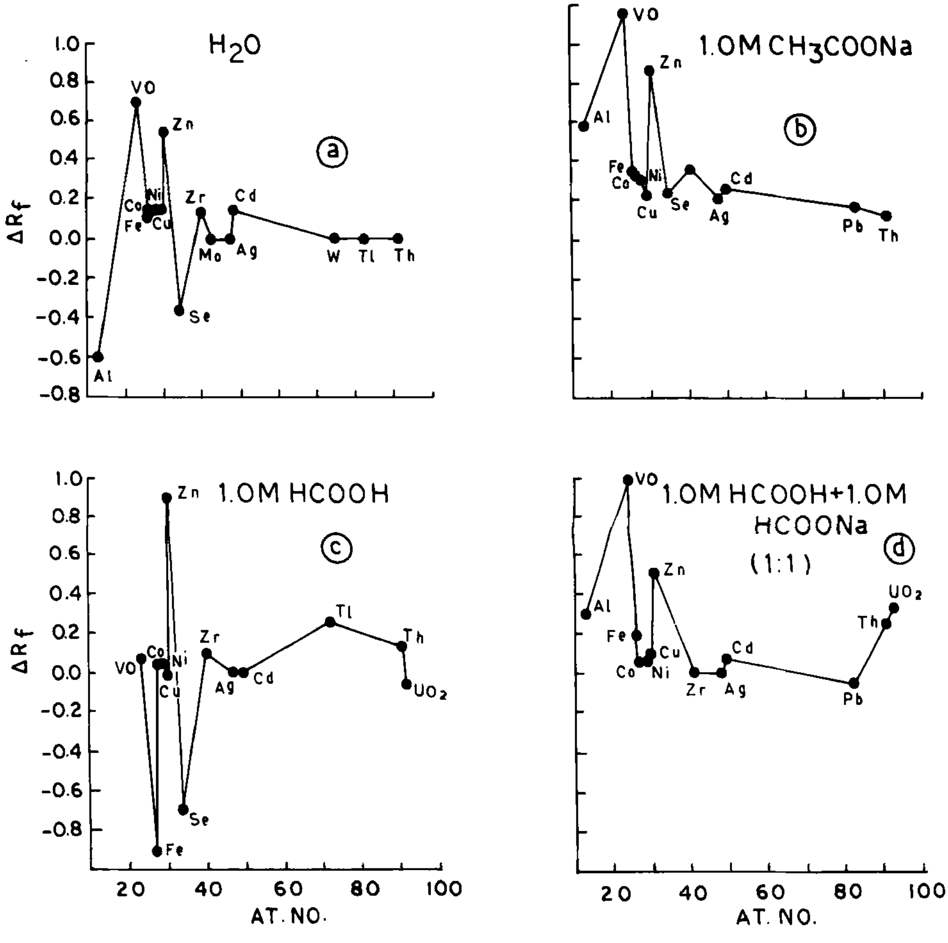

FIGURE 2 Plot of ΔR_f(R_f on plain SG - R_f on SG impregnated with NH_4Cl) vs. atomic number

It is pertinent to draw a comparison between the selectivities of SG impregnated with NH_4Cl and SG impregnated with $Ba(NO_3)_2$ thin layers. This comparison leads to the preferable choice of better sorbent phase when highly selective separations are desired. For this purpose, ΔR_f values $[R_f$ on SG impregnated with NH_4Cl - R_f on SG impregnated with $Ba(NO_3)_2]$ in different solvent systems have been evaluated and plotted in Fig. 3.

It is interesting to note in the light of the Fig.3 that SG impregnated with $Ba(NO_3)_2$ is more selective as compared to the SG impregnated with NH_4Cl in almost all solvent systems as indicated by positive ΔR_f value for most of the cations. However, the selectivity decreases with increase in pH of the solvent system. For example, ΔR_f value for Ag^+, Cd^{2+}, W^{6+}, Tl^+ and Th^{4+} in 1.0 M HCOONa (pH = 6.2) is negative (Fig. 3a), while it is either positive or zero (Fig. 3g) in 1.0 M HCOOH (pH = 1.3). Furthermore, in HCOONa or CH_3COONa (Fig.3a and 3d) SG impregnated with $Ba(NO_3)_2$ is highly selective for Cu^{2+} (maximum positive value of ΔR_f) while SG impregnated with NH_4Cl is more selective for Tl^+(maximum negative value of ΔR_f). Similarly, in CH_3COOH + CH_3COONa (1:1) SG impregnated with $Ba(NO_3)_2$ is highly selective for Zr^{4+} while SG impregnated with NH_4Cl is very selective for Ni^{2+} and Co^{2+} (Fig. 3f). In DMW, SG impregnated with $Ba(NO_3)_2$ is more selective for all

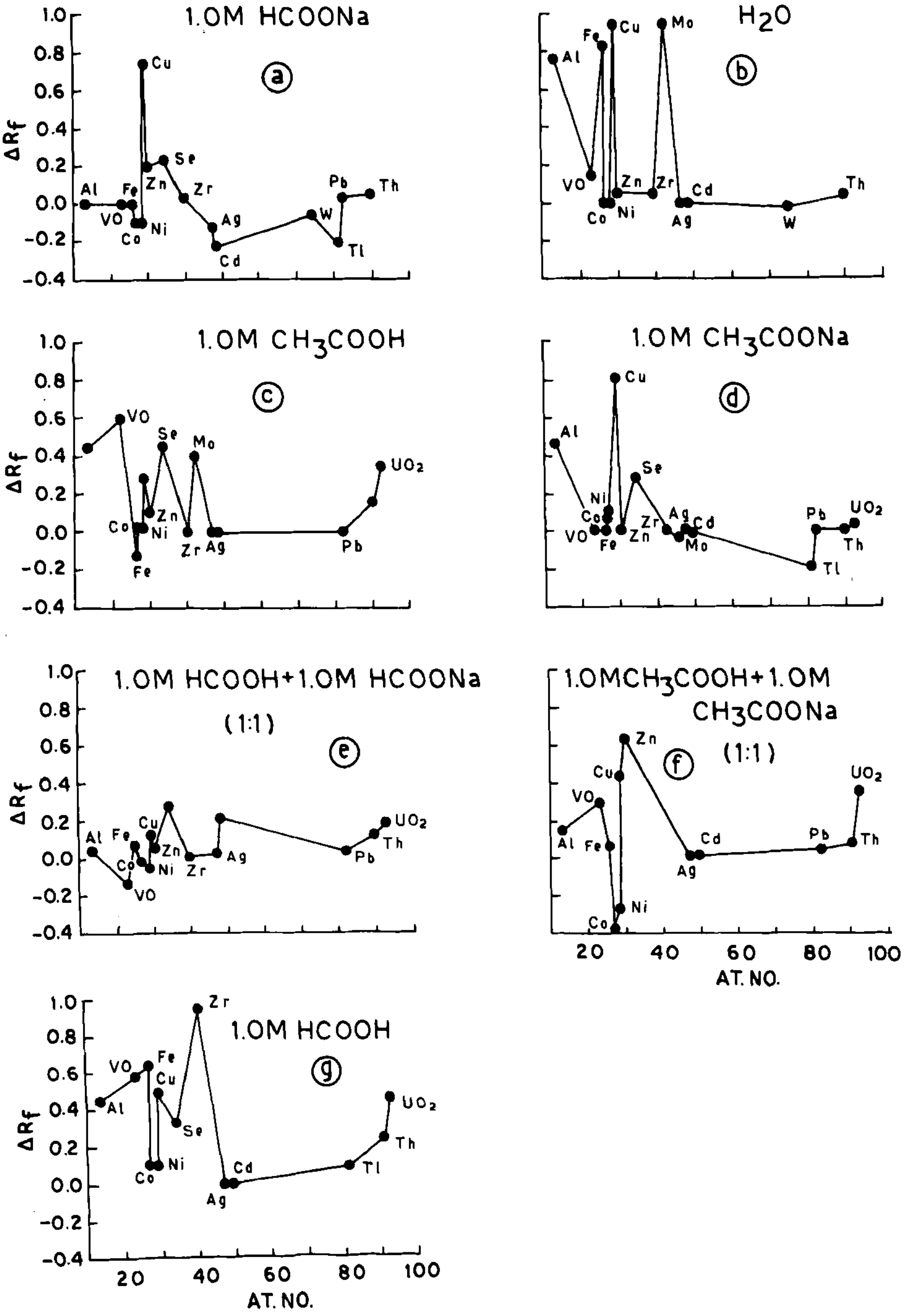

FIGURE 3 Plot of ΔR_f(R_f on SG impregnated with NH_4Cl – R_f on SG impregnated with $Ba(NO_3)_2$) vs. atomic number.

cations studied than that of SG impregnated with NH_4Cl (Fig. 3b).

In order to bring out some significant features of these studies, R_f values obtained in HCOONa solvent system have been plotted vs. atomic numbers (Fig. 4). A comparison of these figures 4a,b,c,d,e revealed some interesting points.

i) Figure 4a shows that Cu^{2+}(R_f=0.15) is strongly adsorbed on thin layers of SG impregnated with $Ba(NO_3)_2$. The unique feature of this new sorbent phase leads one to achieve some difficult separations of Cu^{2+} from Ni^{2+}, Co^{2+}, Se^{4+}, Cd^{2+} and Tl^+ within 15 minutes.

ii) It is worthwhile to compare the results obtained on SG impregnated with barium nitrate (Fig. 4a) with those obtained on SG impregnated with sodium molybdate (17)(Fig. 4b). It is clear from these figures that both the sorbents are copper selective. However, R_f for Cu^{2+} on the former sorbent (R_f = 0.15) is lower than that on the latter sorbent (Rf=0.35). This is because Cu^{2+} is more strongly adsorbed on $Ba(NO_3)_2$ impregnated SG thin layers. The behaviour of both sorbents towards Zn^{2+} is quite interesting. It moves with solvent showing R_f value 0.77 on SG impregnated with Na_2MoO_4 imposing a restriction on its separation from Ni^{2+}, Co^{2+} and Cd^{2+}. However,

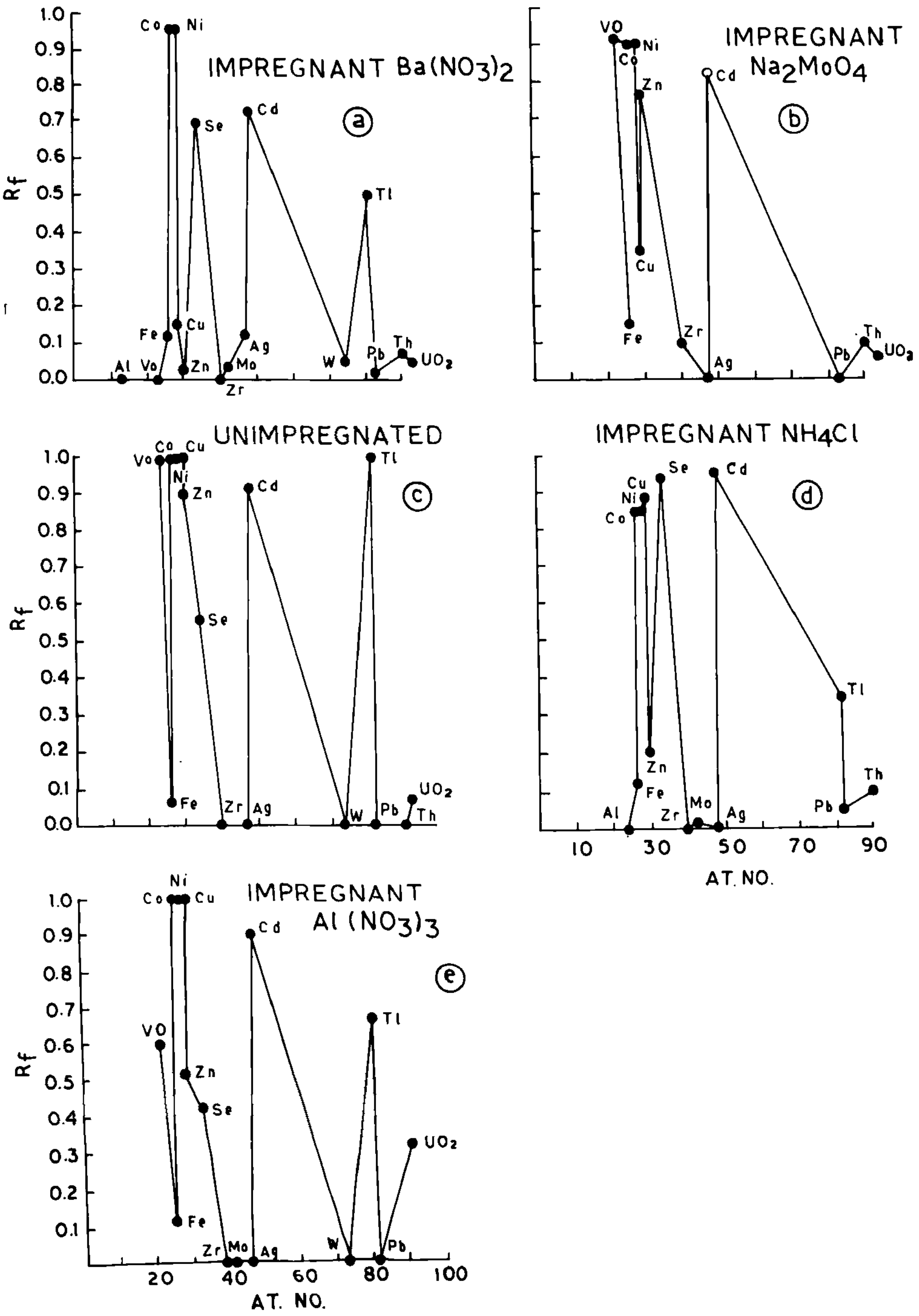

FIGURE 4 Plot of R_f vs. atomic number in 1.0 M HCOONa.

this restriction is removed in case of $Ba(NO_3)_2$ impregnated SG thin layers on which Zn^{2+} is strongly adsorbed (R_f = 0.02). Thus, $Ba(NO_3)_2$ can be profitably used as impregnant for the quick separation of Ni^{2+}, Co^{2+} and Cd^{2+} from Zn^{2+}.

iii) On plain SG thin layers (Fig. 4c) Ni^{2+}, Co^{2+}, Cu^{2+}, VO^{2+}, Zn^{2+}, Cd^{2+} and Tl^{+} show high value of R_f (0.9-1.0) while the other metal ions show R_f value less than 0.1 except for Se^{4+} (R_f = 0.55).

iv) On NH_4Cl impregnated SG thin layers Se^{4+}(R_f=0.49), Tl^{+}(R_f = 0.35), Zn^{2+}(R_f = 0.21) and VO^{2+}(R_f=0.00) show entirely different behaviour (Fig. 4d), when compared with plain SG. Thus, this new sorbent phase leads to achieve very important and useful separation of Zn^{2+} from Ni^{2+}, Co^{2+}, Cu^{2+}, Tl^{+} and Se^{4+} in general, and from Cd^{2+} in particular. The selective separation of Cd^{2+} from Zn^{2+} is a happy consequence as Zn^{2+} and Cd^{2+} both have a similar chromatographic behaviour.

v) On $Al(NO_3)_3$ impregnated SG thin layers Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} show no variation in R_f values (Fig. 4e). However, UO_2^{2+}(R_f = 0.32) shows an increase in R_f value while Se^{4+} (R_f = 0.43), Zn^{2+} (R_f = 0.52), VO^{2+}(R_f = 0.60) and Tl^{+}(R_f = 0.65) show lower value of R_f than those obtained on plain SG.

In addition to the qualitative analysis, quantitative evaluation of the metal ions is often required. There are two usual methods for quantitation. One is to elute or extract the isolated material from the spot and apply colorimetry. Another approach is to measure the area of the spots either planimetrically or by drawing the outline of the spot on a piece of paper, cutting it out and weighing it. The relationship between the area of the spot and the logarithm of the amount of the substance in the spot is usually linear. But some other quantitative relationships have also been reported(18,19).

Planimetric methods are simpler, though less accurate, than physico-chemical methods and can be sucessfully applied for semiquantitative evaluations with reasonable accuracy. This method has been used for semiquantitative determination of metal ions on paper chromatogram (20-23), but its use on thin layers is very limited. In TLC a linear relationship between the square root of the spot area and the logarithm of the compound concentration has been reported by Purdy and Truter (24). An attempt was made to determine the metal ions semiquantitatively by measuring the spot area planimetrically on impregnated SG. But this method was found successful only for Pb^{2+}, Ag^{+} and Se^{4+} on SG impregnated with NH_4Cl and for Cd^{2+}, Al^{3+} and Th^{4+} on SG impregnated with

$Ba(NO_3)_2$. In both the cases HCOOH was used as solvent system. A linear relationship was obtained when the spot area was plotted against the amount of the sample spotted (Fig.5). The upper limit of linear concentration was found to be 150 ug for Se^{4+}, 200 µg for Ag^+, 250 µg for Pb^{2+}, 350 µg for Al^{3+}, 600 µg for Cd^{2+} and 750 µg for Th^{4+}. For higher concentration a positive deviation from linear law is observed for all metal ions determined except Al^{3+} which shows negative deviation. The accuracy and precision falls within the range of ± 7-8% for all metal ions determined. Table 4 shows the results obtained for the quantitative separation of uranium from Co^{2+}, Ni^{2+}, Cu^{2+}, Al^{3+}, Cd^{2+}, Se^{4+}, Ag^+, Pb^{2+} and Fe^{3+} on NH_4Cl impregnated SG thin layers. The maximum error was always below ±6.50%.

The proposed method permits the rapid, reproducible, selective separation of metal ions and is amenable of both microanalytical and preparative studies. The availability of an improved series of inexpensive chromatographic supports, and further development of phase modifying reagents, will considerably broaden the capabilities of TLC. It is hoped that in future the emphasis will be on automated systems for optimization of the elution system with these new emerging sorbents in order to achieve greater selectivity and higher resolution. Thus the inherent versatility of TLC will

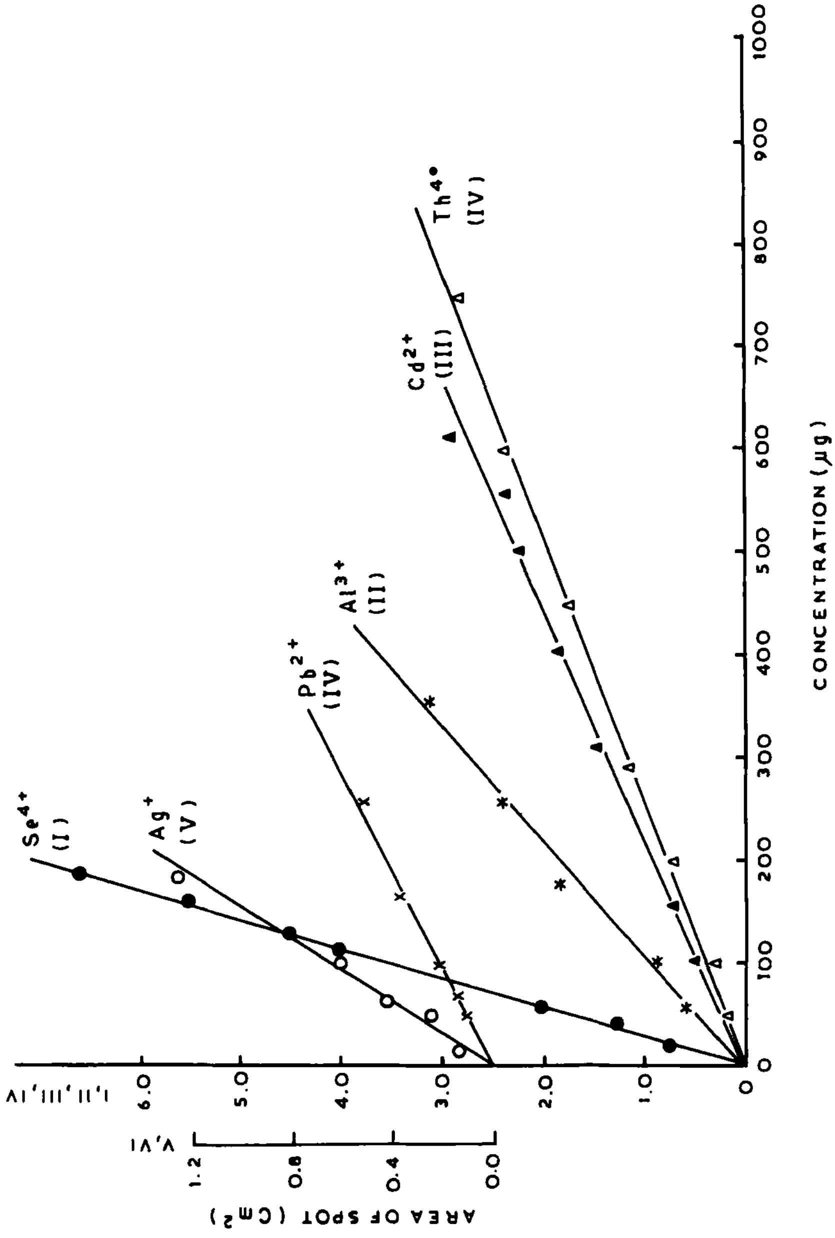

FIGURE 5 Plot of spot area vs. concentration of metal ions on impregnated SG.

become increasingly important for the chromatographic separation of the constituents of biological samples.

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