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Thin-Layer Chromatography of Metal Ions on Stannic Arsenate: Quantitative Separation of Hg(II) from Cd(II), Zn(II), and Cu(II)

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NOTE

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Abstract

Stannic arsenate thin layers (0.25 mm) have been applied for the chromatographic studies of 42 metal ions without using any binder. As a result, some important binary separations, such as Cd-Sb, V-Nb, V-Ta, Ni-Fe, Pd-Nb, Hg-Pb, and Pb-Mo, have been performed. Quantitative separation of Hg from Cd, Zn, and Cu has also been made by this technique. The study has been found to give reproducible results on refluxed and nonrefluxed samples of stannic arsenate used simultaneously.

INTRODUCTION

There has been considerable interest in the thin-layer chromatography (*1*) of metal ions. However, these studies have been mainly on silica gel. Zabin and Rollins (*2*) used, probably for the first time, zirconium phosphate and zirconium oxide for the separation of Ni, Co, Pb, Fe, Ag, Hg, Cd, and Cu. Other workers (*3–13*) have also used inorganic ion exchange materials in thin-layer chromatography. These studies suffer from two limitations: (a) In most cases a binder has been used which clouds the interpretation of the mechanism, and (b) quantitative aspects of these studies have usually been ignored.

We have, therefore, developed a technique for the preparation of thin layers of stannic arsenate without the use of binders. This technique may prove useful for the preparation of other thin layers. We have also found that Hg can be quantitatively separated from Cd, Zn, and Cu on stannic arsenate thin layers. Stannic arsenate (*14*) was selected as an adsorbant because it is highly stable in mineral acids and has good ion-exchange capacity.

EXPERIMENTAL

Reagents

All reagents and chemicals used were of Analar grade. Stannic chloride pentahydrate was a Poland product while sodium dihydrogen arsenate was obtained from Reidel Germany.

Test Solutions

The ions for the test solution, unless otherwise stated, were taken in the following valence states:

Monovalent:	Ag, Tl
Divalent:	Co, Ni, Cu, Zn, Pd, Cd, Pb, Hg
Trivalent:	Cr, Fe, Sb, La, Ce, Au, Bi, Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu
Tetravalent:	Se, Zr, Th, Pt, Ti
Pentavalent:	V, Ta, Nb
Hexavalent:	Mo, W, U

The test solutions were taken as nitrates as far as possible. Antimony, gold, bismuth, and titanium were taken as chlorides. Tantalum and niobium were dissolved by fusing their pentoxides with sodium carbonate and potassium nitrate and dissolving the solid mass in concentrated sulfuric acid. Vanadium pentoxide, sodium molybdate, and sodium tungstate were dissolved in distilled water.

Detectors

Hydrogen sulfide, Alizarine Red S, dimethylglyoxime stannous chloride, pyrogallol, potassium ferrocyanide, chrotopic acid, and diphenyl carbazide were used to detect the various ions by their usual color reactions.

Apparatus

The thin-layer chromatography applicator of Toshniwal (India) was used to prepare thin layers on 20 × 3.5 cm glass plates, and 24 × 6 cm glass jars were used for development.

Preparation of Thin Layer Plates

Without Refluxing the Exchanger. Stannic arsenate gel was prepared by mixing 0.05 M solutions of stannic chloride and sodium arsenate in a volume ratio of 3:2. The precipitate was allowed to stand at room temperature for 24 hr. After filtering and drying, the precipitate was washed thoroughly with demineralized water to remove any unreacted stannic chloride or sodium arsenate. The granules thus obtained were placed in 2 M HNO_3 to convert the material into the H^+ form. The acid was replaced at regular intervals and the exchanger finally washed with demineralized water and dried in air. Approximately 50 g of this material were mixed with 100 ml distilled water and the slurry was made by grinding the mixture vigorously in a glass mortar for a long time. This step proved to be very important for proper adhesion. The slurry was in the form of a fine uniform paste. It was spread by the applicator to give layers of 0.25 mm thickness. The plates were then dried at room temperature and used as such.

After Refluxing the Ion Exchanger. The gel of stannic arsenate produced by mixing stannic chloride and sodium arsenate was refluxed in the mother liquor for 40 hr followed by the treatment described above to prepare thin layers.

Solvent Systems Used

The following solvent systems were used in these studies:

1. 0.5 M HNO_3
2. 1 M HNO_3
3. 0.5 M HCl
4. 1 M HCl
5. 1 M HNO_3 + 1 M $NaNO_3$ (1:1)
6. 0.1 M Arsenic acid
7. 10% Tartaric acid

The reproducibility of the results was checked in the following additional solvent systems: 0.1, 0.2, 0.3, 0.5, 1, and 1.5 *M* $HClO_4$, and *n*-butanol + 1 *M* $HClO_4$ (1:9, 9:1, and 1:1).

Procedure

Qualitative chromatography was performed as usual by the ascending technique with a solvent ascent of 10 cm in all cases. The quantitative separation of Hg from Cd, Zn, and Cu was done as follows.

The known amount of synthetic mixture containing Hg was applied with the help of a lambda pipette on the line of application. The plates were developed in suitable solvent systems. A pilot plate was run simultaneously to locate the position of Hg by detecting it with a coloring reagent. The area corresponding to Hg was scratched out from the working plate. This material was treated several times with small portions of 1 *M* H_2SO_4. The suspended particles of the exchanger, if any, were filtered out and the solution was diluted to 20 ml with 1 *M* H_2SO_4. Two milliliters of 6 *N* acetic

TABLE 1

Some Binary Separations Achieved on Nonrefluxed Samples

Solvent system	Separations achieved	Time (min)
0.5 *M* HCl	Cd (0.78)–Sb (0.02)	60
	V (1.00)–Nb (0.10)	
	V (1.00)–Ta (0.06)	
1 *M* HCl	Co (0.30)–Fe(II) (0.00)	60
	Ni (0.24)–Fe(II) (0.00)	
	Cd (0.75)–Cu (0.10)	
0.5 *M* HNO_3	Pd (0.83)–Nb (0.00)	60
	Au (0.90)–Tl (0.00)	
1 *M* HNO_3	Pt (0.80)–Tl (0.00)	
0.1 *M* Arsenic acid	Hg (0.85)–Pb (0.00)	30
	Hg (0.85)–Ag (0.00)	
	Hg (0.85)–Cd (0.00)	
	Hg (0.85)–Bi (0.10)	
	Hg (0.85)–Cu (0.15)	
	Hg (0.85)–Fe(II) (0.07)	
	Hg (0.85)–Ni (0.15)	
1 *M* $NaNO_3$ + 1 *M* HNO_3 (1:1)	Pd (0.90)–Mo (0.00)	120
10% Tartaric acid	Cd (0.70)–Fe(II) (0.00)	60
	Cd (0.70)–Hg(I) (0.00)	
	Cd (0.70)–Ag (0.00)	

acid were then added followed by a few milliliters of chloroform. The mixture was shaken for 1 min to saturate the aqueous solution with the chloroform layer. The latter was drawn out and 2 ml dithiozone (0.001 % in chloroform) solution were added, shaking the mixture vigorously for 1 min. The mixture was transferred into a 10-ml standard flask and diluted to the mark with chloroform. The absorbance was measured at 610 mμ against dithiozone solution as the blank (*15*) and the amount of Hg was determined with the help of a calibration curve drawn separately.

RESULTS

Tables 1 and 2 summarize some binary separations achieved on nonrefluxed and refluxed samples. The quantitative results are reported in Table 3.

TABLE 2

Some Binary Separations Achieved on Refluxed Samples

Solvent systems	Separations achieved	Time (min)
1 *M* HNO_3	Co (0.40)-Cu (0.00) Ni (0.44)-Cu (0.00) Pd (0.99)-Tl (0.00)	60
0.5 *M* HCl	Hg (1.00)-Hg(I) (0.00)	60
1 *M* $NaNO_3$ + 1 *M* HNO_3 (1:1)	Tl (1.00)-W (0.00)	120

TABLE 3

Quantitative Separation of Hg from Cd, Cu, and Zn

Amount of Hg loaded (μg)	Amount of the other metal ion loaded (μg)	Amount of Hg found (μg)	% Error
20	Cd (56)	20.2	+1.00
40	Cd (33.6)	40.3	+0.75
60	Cd (22.4)	60.2	+0.33
20	Zn (800)	18.8	−1.00
40	Zn (28)	40.8	+1.60
60	Zn (56)	60.2	+0.33
20	Cu (300)	18.5	−0.75
40	Cu (28)	40.5	+1.20
60	Cu (56)	60.2	+0.33

DISCUSSION

The main features of this study are (a) the use of stannic arsenate as thin layers without any binder, and (b) the quantitative separation of metal ions on these layers. The use of pure stannic arsenate as thin layers enabled us to predict the behavior of metal ions on these layers purely on the basis of the ion-exchange properties of the adsorbant. The movement of the metal ions was noticed to be affected on refluxing the material. In general the R_F values on refluxed stannic arsenate layers are less than on the nonrefluxed ones. This means that the selectivity is increased by refluxing. In certain cases a reversal of this trend was noticed. Thus in 0.5 M HNO_3 Cr and Pd; in 1 M HNO_3 Pd, Cd, and Au; in 1 M $NaNO_3$ + 1 M HNO_3 (1:1) Co and Nb; in 0.1 M arsenic acid Eu; and in 10% tartaric acid Zr, Pd, Ce, W, and Pt are the cations for which the selectivity of stannic arsenate decreases on refluxing. The results obtained in 0.5 M HCl and 1 M HCl as developers (Figs. 1 and 2) are quite interesting. While 0.5 M HCl shows no appreciable change in R_F values ($\Delta R_F = 0$) for most cations, a remarkable total reversal in the behavior of stannic arsenate is observed in 1 M HCl. This may be due to the large tendency of the metal ions to form chlorocomplexes.

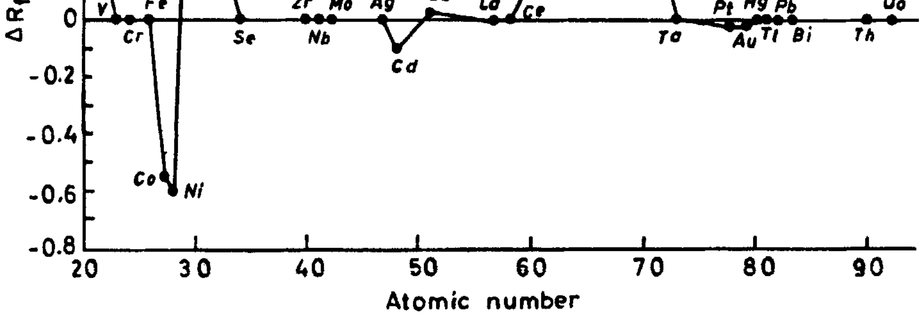

FIG. 1. Plot of ΔR_F vs atomic number in 0.5 M HCl system.

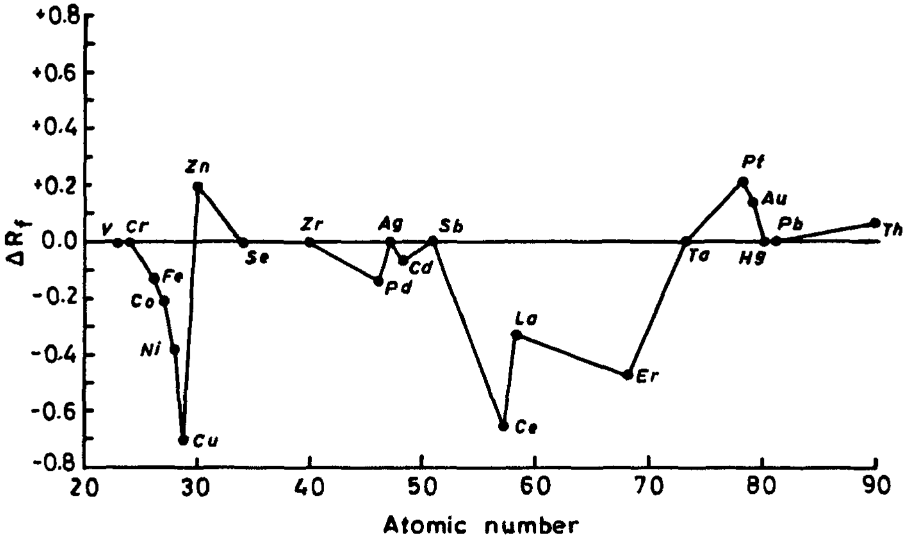

FIG. 2. Plot of ΔR_F vs atomic number in 1 M HCl system.

Tables 1 and 2 give the binary separations achieved on stannic arsenate thin layers based on the R_F values in different solvent systems. The examples worth mentioning are Cd–Sb, V–Nb, V–Ta, Ni–Fe, Pd–Nb, Hg–Pb, and Pd–Mo which are very important from the industrial point of view. Table 3 shows the quantitative aspect of the study. Thus Hg has been successfully separated from Cd, Zn, and Cu in microamounts, and the results are quite accurate and precised. The maximum error reported in these separations is +1.60%. The reproducibility of results on these thin layers was checked in some solvent systems such as $HClO_4$ of different concentrations and n-butanol + 1 M $HClO_4$ (1:9, 9:1, and 1:1). It was observed that the R_F values obtained were nearly the same on repeating the same experiment several times. This is an important criterion of this study because inorganic ion exchangers, in general, show a lack of reproducibility. Hence this study singles out stannic arsenate as one of the most suitable ion exchangers for thin-layer chromatography because of its reproducible characteristics.

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