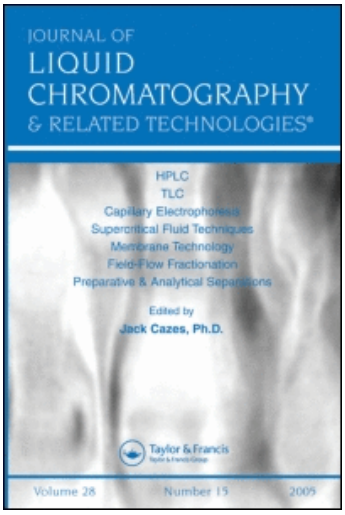

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EFFECT OF SILICA GEL 'G' ON THE ION EXCHANGE BEHAVIOUR OF ANTIMONIC ACID THIN LAYERS IN THE CHROMATOGRAPHIC STUDY OF ANIONS IN SOME AQUEOUS ORGANIC ACID SYSTEMS: DETERMINATION OF FERRICYANIDE AND DICHROMATE IONS

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ABSTRACT

The ion exchange potential of antimonic acid and silica gel 'G' has been explored in thin layer chromatographic studies for the separation of anions. Several important and difficult binary separations of anions have been achieved as a result of these studies. IO_3^- - BrO_3^-, I^- - IO_3^-, IO_4^- - IO_3^-, IO_4^- - PO_4^{---}, Br^- - BrO_3^-, AsO_4^{---} - CrO_4^{--}, $S_2O_3^{--}$ - PO_4^{--}, CNS^- - $S_2O_3^{--}$, IO_4^- - CrO_4^{--}, BrO_3^- - CrO_4^{--}, IO_3^- -

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$Cr_2O_7^{--}$ and S_2O_3 - CrO_4^{--} etc. are separations of analytical interest. Besides, a rapid microgram determination of $[Fe(CN)_6]^{3-}$ (1-10 μg) and $Cr_2O_7^{2-}$ (2-10 μg) ions have been made.

INTRODUCTION

Chromatographic behaviour of metal ions has been extensively studied on several ion exchange materials by different chromatographic techniques. Numerous separations of metal ions have been achieved as a result of such studies. Procedure of determining the cations has also received great attention in analytical chemistry, reported methods include atomic adsorption or emission spectroscopy, polarography, spectrophotometery and others.

On the other hand the situation is different where the separation and determination of small amount of anions is concerned. There exist various methods including ion selective electrode or polarographic method but these fail when anions are to be determined in mixture with various organic compounds. In such a case only separation method based on chromatographic principles may help. Only a scarce attention has been made in this direction as evidenced by the reviews of Brinkman *et al*[1] and Sherma *et al*[2,3] which cover the papers upto 1985. Similar problems were solved by column chromatography[4], electrophoresis[5,6], isotachophoresis[7] and even by gel chromatography on sephadex[8]. Most of the work describes only the separation and identification of anions and not their determination. Very few studies deal with the determination of phosphate[9-11], nitrate and nitrite[12,13].

Synthetic inorganic ion exchangers have been widely used for the chromatographic studies of cations. Zirconium molybdate[14] and Zirconium tellurite[4] were also used as anion exchanger. Krause et al.[15], Amphelett[16] and Clearfield[17] have shown that the hydrous oxides of polyvalent metals behave both as cation as well as anion exchangers. Hyderated zirconium oxide and hydrous stannic oxide have also been used both as cation[18,19] and as anion[20-22] exchanger.

In the present work we have selected hydrous antimony (V) oxide (antimonic acid) as anion exchanger for thin-layer chromatographic studies. Antimonic acid was also mixed with silica gel 'G' in 1:1 ratio and used for preparing thin layers. Detection limits for some anions were achieved. Numerous separation of anions from one another have been achieved both on antimonic acid thin layers and on mixtures of antimonic acid and silica gel 'G' thin-layers in aqueous organic acids. A comparison of results was done on the two types of thin layers. Besides, microgram determination of ferricyanide and dichromate has also been achieved by densitometery. The method has proved to be useful for the separation of some anions from sugar industry, fertilizer and chemical industry waste water.

EXPERIMENTAL

Materials and Methods

All the chemicals and solvents used in the work were of G.R. grade. Thin-layers of anti-

TABLE 1

Stain-colour intensities of anions

Anions	A	B	C	D	E	F	G	H	I
NO_2^-	b	v	y	-	b	-	-	slbr	-
NO_3^-	b	slv	-	-	rs	-	-	slbr	-
ClO^-	b	v	-	bl	rs	-	-	-	-
ClO_3^-	b	-	-	-	rs	-	-	-	-
ClO_4^-	-	-	-	w	rs	-	-	-	-
I^-	b	-	-	-	-	-	-	slbr	-
IO_3^-	b	-	-	-	-	-	-	slbr	-
IO_4^-	b	v	b	w	-	-	-	slbr	-
Br^-	-	-	-	bl	-	-	-	slbr	rs
BrO_3^-	b	v	-	w	slrs	-	-	slbr	-
MnO_4^-	b	b	-	br	-	-	-	-	-
VO_3^-	b	y	y	y	rs	-	-	-	-

Anions	A	B	C	D	E	F	G	H	I
CNS^-	-	-	rs	bl	-	-	-	-	-
CrO_4^{--}	b	v	y	yrbl	-	-	-	-	-
CrO_7^{--}	b	v	-	ybr	-	-	-	-	-
$S_2O_3^{--}$	-	-	-	bl	-	-	-	-	rs
$S_2O_5^{--}$	-	-	-	w	-	-	-	-	rs
$S_2O_8^{--}$	b	v	-	br	rs	-	-	-	rs
WO_4^{--}	b**	slv	-	ly	-	-	-	-	-
SeO_3^{--}	slb	v	ly	w	rs	-	-	-	-
SeO_4^{--}	slb	v	ly	w	rs	-	-	-	-
PO_4^{3-}	-	-	-	-	-	-	y	-	-
$[Fe(CN)_6]^{3-}$	b	v	bg	y	yg	b	-	-	-
$[Fe(CN)_6]^{4-}$	slb**	-	b	w	-	-	-	-	-

A= diphenylamine; B = KI; C=$FeCl_3$; D=$AgNO_3$; E=2,6 dichlorophenolindophenol;F= Ferrous sulphate solution; G=ammon. molybdate followed by $SnCl_2$; H= silver nitrate (ammonical); I=sodium nitropruside. Key to detection : b=blue; Sl.= slight; y=yellow; g=green; bl=black; w=white; r=red; br=brown; rs=rose; v= violet; l=light. **After a prolonged period. (-)=No detection.

monic acid and antimonic acid & silica gel 'G' (1:1) were prepared on glass plates of 15 cm X 2.9 cm size and subsequently developed in several solvent systems in 20 cm x 5 cm glass jars. For quantitative work Biochem M-71 densitometer (Biochem, India) has been used.

Preparation of Antimonic Acid and Thin-layer plates

Antimonic acid was prepared as per literature method[23]. For preparing thin-layers, antimonic acid and antimonic acid + silica gel 'G' (1:1) mixture was slurried separately with a little deionised water in a glass mortar and then spread over the glass plates with the help of an applicator. Almost uniforn thin layers (0.1 mm thickness) were obtained which were ready for use after drying in air. The plates gave reproducible R_f values.

Test Solutions and Detection Reagents

Test solutions were 0.1M sodium and potassium salts. The anions were detected using several agents : (a) 1% KI solution in 1 M HCl, (b) 2 M fresh ammonical silver nitrate solution, (c) sodium nitroproside, (d) silver nitrate, (e) 1% aqueous ferric chloride, (f) freshly prepared 1% aqueous ferrous sulphate, (g) Aqueous ammonium molybdate followed by stannic chloride, (h) aqueous solution of 2,6-dichlorophenolindophenol (a freshly prepared saturated solution), (i) diphenylamine (0.2% solution in concentrate sulfuric acid). The stain colour intensities of anions has been shown in the Table 1.

Procedure

For the quanlitative work, one or two spots of the test solutions were spotted with the fine glass capillaries and the plates were dipped in suitable solvent systems after drying in air for 15 min. the solvent ascent was always 11 cm.

For quantitative work, a known amount of potassium ferricyanide and potassium dicromate (1 μg to 10 μg) was applied on the plates. After developing in the appropriate solvent systems, the spots were detected by 0.2% diphenylamine in concentrate sulphuric acid and the absorbance was taken within 2-4 minutes by Biochem M-71 densitometer using green filter (520 nm) against blank spot (same amount of test solution without development). Because the colour intensity varies with time, it was necessary to carry out densitometric measurements within 2-4 minutes after sprinkling with diphenylamine.

RESULTS AND DISCUSSION

In many cases it was possible to separate one anion for nemerous ions. The qualitative separations given in the Tables 2 and 3 and quantitative separations of $[Fe(CN)_6]^{3-}$ and $Cr_2O_7^{2-}$ actually achieved as a result of these studies are given in Tables 4, 5, 6 and 7.

Antimonic acid has so far been used exclusively as cation exchanger[23-26]. Silica gel 'G' can also act both as a cation exchanger and anion exchanger[14,27-29]. The present study has been undertaken to explore the ion exchange potential of antimonic

TABLE 2

Separations achieved on antimonic acid thin layers

Solvent system	Anions separation (R_T - R_L)
0.1M Acetic acid	IO_3^-(0.00-0.32)/IO_4^-(0.00-0.07) - BrO_3^-(0.63-0.72)/ $Fe(CN)_6^{4-}$(0.60-0.70)
	S_2O_3(0.00-0.00)/NO_2^-(0.00-0.00)/NO_3^-(0.00-0.00) - $Fe(CN)_6^{3-}$(0.33-0.62)/$Cr_2O_7^{2-}$(0.30-0.48)/CrO_4^{2-}(0.44-0.62)
0.1M Tartaric acid	Br^-(0.00-0.16)/I^-(0.00-0.00)/IO_4^-(0.00-0.08)/ S^-(0.00-0.00) - BrO_3^-(0.63-0.71)/$Fe(CN)_6^{3-}$(0.45-0.78)/ $Fe(CN)_6^{4-}$(0.50-0.68)
0.1M Formic acid	Br^-(0.00-0.15)/BrO_3^-(0.00-0.08)/$S_2O_3^{2-}$(0.00-0.00)/ IO_3^-(0.00-0.28) - CrO_4^{2-}(0.50-0.68)/$Cr_2O_7^{2-}$(0.52-0.68)/ PO_4^{3-}(0.27-0.51)

Solvent system	Anions separation (R_T - R_L)
0.1M Succinic acid	I^-(0.00-0.00)/IO_4^-(0.00-0.07)/CNS^-(0.00-0.00) -$S_2O_3^{2-}$ (0.23-0.64)/CrO_4^{2-}(0.37-0.57)/$Fe(CN)_6^{3-}$(0.60-0.90)
0.1M Oxalic acid	NO_2^-(0.00-0.00)/IO_3^-(0.00-0.15)/IO_4^-(0.00-0.09)/$S_2O_3^{2-}$ (0.00-0.00)/AsO_4^{3-}(0.00-0.17) - CrO_4^{2-}(0.34-0.65)/ CrO_7^{2-}(0.51-0.80)/$Fe(CN)_6^{3-}$(0.65-0.89)
0.1M Citric acid	I^-(0.00-0.10)/IO_4^-(0.00-0.12)/IO_4^{3-}(0.00-0.28) - $Cr_2O_7^{2-}$(0.52-0.73)/$Fe(CN)_6^{3-}$(0.63-0.90)/$Fe(CN)_6^{4-}$ (0.30-0.81)

TABLE 3

Separation achieved on antimonic acid and silica gel 'G' (1:1) thin layers

Solvent system	Anions separation (R_T-R_L)
0.1M Acetic acid	CNS^-(0.00-0.00)/IO_3^-(0.00-0.25)/$S_2O_3^{2-}$(0.00-0.00) - CrO_4^{2-}(0.50-0.68)/$Cr_2O_7^{2-}$(0.57-0.68)/PO_4^{3-}(0.56-0.85)/ $Fe(CN)_6^{4-}$(0.67-0.82)
0.1M Tartaric acid	CNS^-(0.00-0.00)/IO_4^-(0.00-0.41)/$S_2O_3^{2-}$(0.00-0.00) - IO_3^-(0.68-0.77)/CrO_4^{2-}(0.67-0.84)/$Cr_2O_7^{2-}$(0.75-0.87)/ $Fe(CN)_6^{3-}$(0.59-0.76)
0.1M Formic acid	BrO_3^-(0.00-0.00)/IO_4^-(0.00-0.12)/$S_2O_3^{2-}$(0.00-0.00) - PO_4^{3-}(0.47-0.73)/CrO_4^{2-}(0.47-0.60)/$Cr_2O_7^{2-}$(0.48-0.57)

Solvent system	Anions separation (R_T-R_I)
0.1N Succinic acid	Br^-(0.00-0.00)/I^-(0.00-0.00)/IO_4^-(0.00-0.48)/CNS^- (0.00-0.00)/NO_2^-(0.00-0.05)/$S_2O_3^-$(0.00-0.00) - BrO_3^-(0.64-0.80)/IO_3^-(0.62-0.72)/$Cr_2O_7^{2-}$(0.73-0.89)/ PO_4^{3-}(0.55-0.84)
0.1M Oxalic acid	I^-(0.00-0.00)/Br^-(0.00-0.00)/BrO_3^-(0.00-0.00)NO_2^- (0.00-0.00) - CrO_4^-(0.45-0.55)/$Cr_2O_7^{2-}$(0.42-0.56)/ PO_4^{3-}(0.43-0.68)/$Fe(CN)_6^{3-}$(0.55-0.70)/$Fe(CN)_6^{4-}$ (0.35-0.55)
0.1M citric acid	Br^-(0.00-0.00)/IO_4^-(0.00-0.11) - PO_4^{3-}(0.52-0.87)/ $Fe(CN)_6^{3-}$(0.43-0.60)/$Fe(CN)_6^{4-}$(0.57-0.70)

TABLE 4

Quantitative separation of ferricyanide ion from binary mixtures on antimonic acid and silica gel 'G' (1:1) thin layers. (Amount of $[Fe(CN)_6]^{3-}$ applied = 5 μg)

Anions mixture	Amount of $[Fe(CN)_6]^{3-}$ found*	% Error
1. IO_3^- - $[Fe(CN)_6]^{3-}$	4.8	-4.0
2. CNS^- - $[Fe(CN)_6]^{3-}$	4.7	-6.0
3. $S_2O_3^{2-}$-$[Fe(CN)_6]^{3-}$	4.9	-2.0
4. NO_2^- - $[Fe(CN)_6]^{3-}$	4.9	-2.0
5. Br^- - $[Fe(CN)_6]^{3-}$	4.9	-2.0
6. AsO_4^{3-}-$[Fe(CN)_6]^{3-}$	4.6	-8.0

*Average value of three sets

TABLE 5

Quantitative separation of ferricyanide ion from synthetic mixture on antimonic acid and silica gel 'G' (1:1) thin layers

Anion mixture	Amount of ferricyanide applied (μg)	Amount of ferricyanide found (μg)	% Error
10 μg of each of the following anions alongwith 10 μg ferricyanide anion	1	0.95	-5.00
	2	1.98	-1.00
	4	3.95	-1.25
	5	4.95	-1.00
IO_3^-, IO_4^-, CNS^-,	6	5.94	-1.00
$S_2O_3^-$, NO_3^-, NO_2^-,	8	7.90	-1.25
AsO_4^{3-}	10	9.70	-3.00

TABLE 6

Quantitative separation of dichromate from binary mixture on antimonit acid and silica gel 'G' (1:1) thin layers. (Amount of dichromate applied = 5 μg)

Mixture applied	Amount found	% Error
1. I^- - $Cr_2O_7^{2-}$	4.90	-2.0
2. IO_3^- - $Cr_2O_7^{2-}$	4.80	-4.0
3. IO_4^- - $Cr_2O_7^{2-}$	4.90	-2.0
4. CNS^- - $Cr_2O_7^{2-}$	4.90	-2.0
5. $S_2O_3^-$ - $Cr_2O_7^{2-}$	4.70	-6.0
6. NO_3^- - $Cr_2O_7^{2-}$	4.94	-1.2
7. NO_2^- - $Cr_2O_7^{2-}$	4.90	-0.2
8. Br^- - $Cr_2O_7^{2-}$	4.95	-1.0
9. AsO_4^{3-} - $Cr_2O_7^{2-}$	4.80	-4.0

TABLE 7

Quantitative separation of dichromate from synthetic mixture on antimonic acid and silica gel 'G' (1:1) thin layers

Anion mixture	Amount of dichromate applied (μg)	Amount of dichromate found* (μg)	% Error
10 μg of each of the	2	1.90	-5.00
following anions	4	3.90	-2.50
along with 10 μg of	6	5.80	-3.33
dichromate anion	8	7.85	-1.87
IO_3^-, IO_4^-, CNS^-,	10	9.90	-1.00
$S_2O_3^-$, NO_3^-, Br^-, I^-,			
NO_2^-, AsO_4^{3-}			

*Average value of three sets

acid and silica gel 'G' as anion exchangers. A careful examination of results of these studies indicates that CrO_4^{--} is transformed into $Cr_2O_7^{--}$ in the acid solvent systems and so the two anions correspond approximately to the same R_f values on antimonic acid and 1:1 mixtures of antimonic acid and silica gel 'G' thin layers. CO_3^{--} is probably decomposed in the solvent systems studied and so it escapes detection. It is obvious from the results (Table 2 and 3) that different pairs of anions can be separated from one another by thin layer chromatography on antimonic acid and 1:1 mixture of silica gel 'G' and antimonic acid. Some of the important and difficult separations of the anions may be given as IO_3^- - BrO_3^-, IO_4^- - BrO_3^-, IO_3^- - $Cr_2O_7^{--}$, I^- - IO_3^-, IO_4^- - IO_3^-, IO_4^- - PO_4^{---}, Br^- - BrO_3^-, BrO_3^- - CrO_4^{--}, IO_4^- - CrO_4^{--}, IO_4^- - CrO_4^{--}, AsO_4^{---} - CrO_4^{--}, PO_4^{---} - $Cr_2O_7^{--}$, $S_2O_3^{--}$ - PO_4^{--}, $S_2O_3^{--}$ - CrO_7^{--}, CNS^- - $S_2O_3^{--}$ which are also the separation of practical interest.

On comparing the results of thin layer chromatographic studies of anions on antimonic acid and 1:1 mixture of antimonic acid and silica gel 'G', it is obvious that most of the anions do not move on antimonic acid thin layers in any of the solvent systems used in these studies. Only a few anions namely $Cr_2O_7^{--}$, $Fe(CN)_6^{---}$ and BrO_3^- show a little tendency of moving up in same solvent system. However, on mixing antimonic acid with silica gel 'G', the R_f values of anions are found to increase to a considerable extent in all the solvent systems which clearly indicate that antimonic acid is a strong anion exchanger than silica gel 'G'. The same fact is revealed on comparing the results of these stu-

dies with our earlier studies of TLC of anions on pure silica gel 'G' thin layers[14]. This has enabled us to effect numerous binary separations of anions from one another which have been summarised herein. The detection limit for $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{3-}$ is 1 μg on antimonic acid thin layers.

The unique feature of these studies has been the quantitative separation of ferricyanide (5 μg) and dichromate (2-10 μg) on the thin layer of mixture of antimonic acid and silica gel 'G' in 0.1M acetic acid solvent system. It has been observed that in 0.1M acetic acid system only $[Fe(CN)_6]^{3-}$ and $Cr_2O_7^{2-}$ have appreciable R_f values while most of the anions are retained on the point of application. The method can be used for determining the anions listed when present in the concentrations down to hundredths of one percent in various organic mixtures. The determination method is applicable to all anions that give blue colour with diphenylamine. The method has proved to be applicable in determining the concentration of anions from fertilizer waste passing into the soil and plants from these into further products and from sugar industries, chemical industry waste water. Unfortunately the separation results are poorer than other chromatographic methods.

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