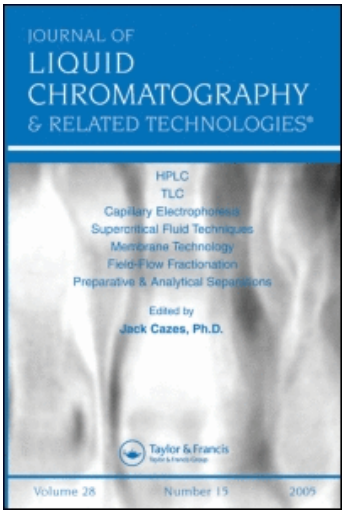

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CHROMATOGRAPHIC SEPARATION OF SOME PHENOLS BY NEW ADSORBENT

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ABSTRACT

Papers impregnated with iron(III) hexamine have been used to chromatograph various phenols in ethanol, varying concentrations of ammonia and mixture of ethanol and ammonia. A large difference in R_F values was taken as a criterian for satisfactory separation. Various analytically important qualitative separations on impregnated papers and quantitative separations on iron(III) hexamine columns have been developed.

INTRODUCTION

Recently, interest in chromatographic adsorbents for efficient separation of phenols has been increased. Clark suggested use of ion excnange papers for the separation of phenols (1). Most of the earlier reported sorbents either interferced in the detection of phenols, or lacked adequate resolution. Stannic molybdate (2) and zinc silicate (3) in paper chromatography and iron(III) diethanolamine (4) both in

paper and column chromatography have been employed as adsorbents for the separation of phenols. Our previous study showed that iron(III) hexamine gel (IHA) (5) is readily reproducible and fairly stable in water, acids upto 1 M and ammonia upto 4M. The high sorption capacity and selective behaviour of IHA for phenols suggested its use as a new chromatographic adsorbent for their separation. On the basis of differences in R_F values some phenols were separated on these papers and on columns of iron(III) hexamine adsorbent. After separation, the phenols, eluted successfully from the adsorbent column, were determined spectrophotometrically using Follins reagent (6).

EXPERIMENTAL

Apparatus

Chromatography was performed on impregnated Whatman No.3 paper strips 15x2.5 cm using 20x5 cm glass jars.

Reagents

Chemicals and solvents were of analytical grade. Phenol solutions were prepared in water or ethanol.

Preparation of Impregnated Papers

Whatman No.3 paper strips of required size were dipped in 0.1 M iron(III) nitrate for 15-20 sec and dried at room temperature. They were then dipped in 0.4 M hexamine for 40-45 sec, the excess of the reagent was drained off and finally the strips were dried at room temperature (4).

Detectors

All the phenols gave coloured spot. Phenolphthalein was detected with ammonia in alcoholic system only.

TABLE 1

Sorption Capacity of Iron(III) Hexamine

Sl.No.	Phenols	Sorption capacity (mg g^{-1})
1	Resorcinol	20.68
2	Quinol	22.82
3	Phloroglucinol	42.24
4	Salicyclic acid	67.20
5	Pyrocatechol	76.00
6	Pyrogallol	92.10

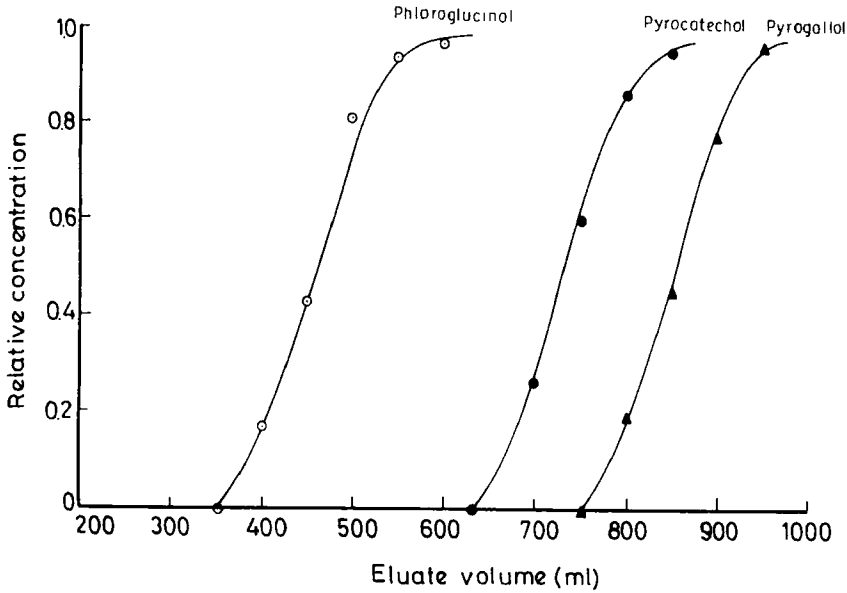

FIGURE 1 Breakthrough curves of phloroglucinol, pyrocatechol and pyrogallol.

TABLE 2

R_F values of Phenols on Iron(III) Hexamine impregnated Papers

Phenols	Concentrations of Ammonia(M)				Ethanol - NH_3(0.1 M) (1:1)
	Ethanol	0.01	0.1	1.0	
Pyrogallol	0.0	0.0	0.0	0.06	0.0
Pyrocatechol	0.10	0.10	0.12	0.24	0.14
Phloroglucinol	0.64	0.36	0.41	0.50	0.52
Resorcinol	0.90	0.42	0.53	0.67	0.65
Quinol	0.81	0.30	0.46	0.66	0.75
2-Methyl resorcinol	0.72	0.40	0.46	0.54	0.68
Phenol	0.90	0.44	0.50	0.74	0.82
m-Nitrophenol	0.63	0.42	0.49	0.62	0.50
p-Nitrophenol	0.80	0.48	0.50	0.68	0.68
2,5-Dinitrophenol	0.56	0.52	0.58	0.65	0.60
2,4-Dinitrophenol	0.66	0.60	0.62	0.68	0.62
Picric acid	0.50	0.42	0.56	0.62	0.60
α-Naphthol	0.80	0.0	0.06	0.08	0.45
β-Naphthol	0.86	0.38	0.49	0.56	0.72
2,4-Dinitro-1-naphthol	0.22	0.28	0.30	0.54	0.50
Vanillin	0.78	0.52	0.72	0.82	0.80
Orcinol	0.90	0.30	0.42	0.68	0.60
p-tert-amylphenol	0.56	0.22	0.34	0.42	0.49
p-Bromophenol	0.70	0.26	0.38	0.44	0.56

O-Cresol	0.80	0.0	0.02	0.24	0.68
m-Cresol	0.90	0.28	0.40	0.55	0.72
3,4-Xylene-1-ol	0.80	-	0.72	0.78	0.75
Salicylic acid	0.18	0.42	0.48	0.52	0.50
3,5-Dinitro-salicylic acid	0.08	0.38	0.52	0.68	0.44
Gallic acid	0.18	0.12	0.20	0.34	0.20
Tannic acid	0.0	0.0	0.04	0.10	0.02
Xylenol orange	0.0	0.15	0.26	0.40	0.20
Bromocresol green	0.40	0.42	0.52	0.90	0.68
Bromothymol blue	0.78	0.46	0.58	0.70	0.68
Phenolphthalein	0.82	0.36	0.46	0.62	0.78
3-Aminophenol	0.40	0.0	0.08	0.28	0.24

PROCEDURE

One or two spots of phenol solution were placed with the help of a fine glass capillary on the impregnated strip. After 5 min conditioning of the strip, the solvent was allowed to ascend. The R_F values were calculated as usual.

Synthesis of Iron(III) Hexamine

Iron(III) hexamine (5) was synthesized by mixing 0.1 M aqueous solution of iron(III) nitrate to 0.4 M aqueous solution of hexamine (2:1). After aging for 24 h at room temperature the resultant gel was filtered by suction, thoroughly washed with deionized water and then dried at 60°C in an oven. Grinding the gel followed by sieving to 100-150 mesh size, gave the adsorbent.

TABLE 3

Separation achieved on Iron(III) hexamine impregnated papers

Sl No.	Separation	Solvent
1	Pyrogallol(0.0)-Resorcinol(0.90)	Ethanol
2	Pyrogallol(0.0)-2-Methyl resorcinol(0.72)	,,
3	Pyrogallol(0.0)-Phloroglucinol(0.62)	,,
4	Pyrogallol(0.0)-Phenol(0.88)	,,
5	Pyrogallol(0.0)-Vanillin(0.76)	,,
6	Xylenol orange(0.0)-Phenolphthalein(0.80)	,,
7	Xylenol orange(0.0)-Bromothymol blue(0.75)	,,
8	3,5-Dinitrosalicylic acid (0.08) - 2,4-Dinitrophenol (0.64)	,,
9	Pyrogallol(0.0) - Bromocresol green(0.40) - Resorcinol (0.90)	,,
10	Pyrocatecnol(0.10) - 3-Aminophenol(0.40) - Phenol (0.89)	,,
11	Salicylic acid(0.15) - Picric acid (0.50) - Phenol (0.90).	,,
12	α-Naphthol(0.05) - β-Naphthol(0.56)	1 M NH_3
13	α-Naphthol(0.05) - Phenol(0.72)	,,
14	Tannic acid(0.0) - Picric acid (0.60)	,,
15	Tannic acid(0.0) - Salicylic acid (0.50)	,,
16	3-Aminophenol(0.20)-2,4,6-Trinitrophenol(0.61)	,,
17	3-Aminophenol(0.20)-4-Bromophenol (0.46)	,,
18	Pyrogallol(0.0) - Picric acid (0.60) - Bromocresol green (0.92)	,,
19	Aminophenol (0.20) - Picric acid (0.60) - Bromocresol green (0.92)	,,

20	o-Cresol(0.0) - m-Cresol(0.40)	0.1 M NH_3
21	o-Cresol(0.0) - Phenol (0.78)	,,
22	o-Cresol(0.0) - Resorcinol (0.53)	,,
23	3-Aminophenol(0.01) - Quinol(0.46) - Vanillin (0.72)	,,
24	Pyrogallol(0.0) - Quinol(0.72)	Ethanol + 0.1 M NH_3 (1:1)
25	Pyrogallol(0.0) - p-Nitropnenol(0.78)	,,
26	Pyrogallol(0.01) - m-Nitrophenol(0.60)	,,
27	Pyrocatechol(0.12) - Resorcinol(0.50)	,,
28	Pyrocatechol(0.12) - Quinol (0.72)	,,
29	Pyrocatechol(0.11) - Phenol (0.80)	,,
30	Pyrocatecnol(0.12) - 2-Methyl resorcinol(0.65)	,,
31	Pyrocatechol(0.11) - Phloroglucinol(0.52)	,,
32	Pyrogallol(0.0) - Salicylic acid (0.48) Phenol(0.80)	,,
33	Pyrogallol(0.0) - Orcinol(0.56) - Vanillin(0.80)	,,

Separations

A glass column 30 x 0.39 cm^2 was packed with 2 g of IHA. The flow rate of effluent was maintained about 0.5 ml $min.^{-1}$ The effluent was collected in 10 ml fractions and was analyzed spectrophotometrically (6).

RESULTS AND DISCUSSION

Sorption capacity

To determine sorption capacity 1 g IHA was packed in a column with glass wool support. 10 ml fractions of predeter-

mined amounts of phenols were passed through the column and the phenol collected in the effluent was determined. The amount initially taken minus the amount found after the passage through the column gave the amount of phenol retained by the adsorbent. The process was continued until the amount of phenol in the fraction remained same before and after passing through the adsorbent (4). The results are shown in Table 1. Sorption capacity of various phenols varied from 20.68 to 92.10 mg g^{-1}. This variation in sorption capacity for phenols may be due to the iron-phenol complex formation of varying stability.

Break-through capacity

The breakthrough behaviour was studied by passing 1 mg 10 ml^{-1} solution of each phenol through a glass column 30x0.39 cm^2 packed with 1 g IHA. The flow rate was maintained 0.5 ml $min.^{-1}$ The breakthrough curves are given in Fig.1. The order of breakthrough obtained for phloroglucinol, pyrocatechol and pyrogallol is also supported by R_F values (Table 2).

The R_F values of 31 phenols in ethanol, various concentrations of aqueous ammonia (0.01 - 1.00 M) and in 0.1 M ammonia - ethanol (1:1) are presented in Table 2. The R_F values show an increasing trend on increased concentration of ammonia. This may be attributed due to high solubility of phenols in higher concentration of ammonia, or the complex iron(III) - hydroxide becomes more stable than the complex iron(III) - phenol. Ternary amines act as good electron donors towards phenol in forming strong hydrogen bonds (7). Hence, hydrogen bond formation between the H atom of OH group of phenol and N atom of amine may also be held responsible for the chromatography of phenols. Srivastava et al.(8) have also discussed

TABLE 4

Separations on Iron(III) Hexamine Columns

Sl. No.	Mixture	Eluent	Eluate (ml)	Amount loaded (μg)	Amount recovered (μg)	% Error
1	Resorcinol-	Ethanol	20	400	400	0.0
	Pyrogallol	2 M NH_3 in ethanol	50	500	492	-1.6
2	Resorcinol-	Ethanol	20	400	400	0.0
	Pyrocatechol	2 M NH_3	40	500	495	-1.0
3	Quinol	Ethanol	20	400	402	+0.5
	Pyrogallol	2M NH_3 in ethanol	50	500	493	-1.4
4	Phloroglucinol	Ethanol	30	400	398	-0.5
	Pyrogallol	2M NH_3 in ethanol	50	500	494	-1.2
5	Resorcinol -	Ethanol	20	400	401	+0.2
	Salicylic acid	1 M NH_3	30	400	398	-0.5
6	Quinol -	Ethanol	20	400	401	+0.2
	Pyrocatechol	2 M NH_3	40	500	494	-1.2
7	Resorcinol -	0.1 M NH_3	20	400	400	0.0
	α-Naphthol -	Ethanol	20	400	398	-0.5
	Pyrocatechol	2 M NH_3	40	400	396	-1.0
8	Quinol -	0.1 M NH_3	40	400	402	+0.5
	3-Aminophenol-	Ethanol	40	400	398	-0.5
	Pyrogallol	2M NH_3 in ethanol	50	500	492	-1.6

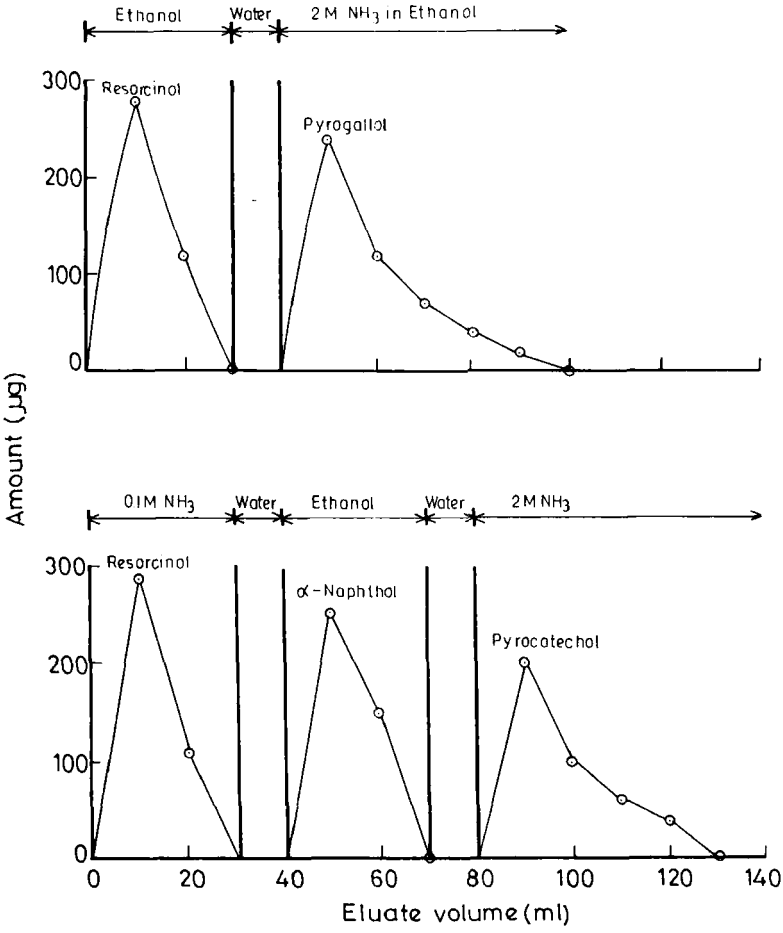

FIGURE 2 Separations of resorcinol-pyrogallol, and resorcinol-α-naphthol-pyrocatechol.

the chromatographic behaviour of aliphatic amines on phenol - impregnated thin layers due to hydrogen bond formation between the amine and silica gel as well as phenols.

Phenol mixtures having large differences in R_F values were tried for separation. Qualitative and quantitative separations

achieved experimentally on impregnated papers and IHA columns are presented in Tables 3 and 4 respectively. The results of this study indicate that chromatography on impregnated papers can be used to predict the separations on columns of the impregnating material. The separations are distinct and quantitative (Table 4) and the results are within experimental error range. The elution curves (Fig.2) given for illustration show that no significant tailing is obtained during the elution of various phenols and only small volumes of eluents are required. The phenol having higher R_F value (Table 2) is eluted first and that having lower R_F value is eluted later. This is because the phenol having lower R_F value has greater affinity towards IHA.

It, therefore, seems that chromatographic behaviour of phenols on iron(III) hexamine impregnated papers and IHA columns is due to the complex iron(III) - phenol as well as hydrogen bond formation between amine and phenols.

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