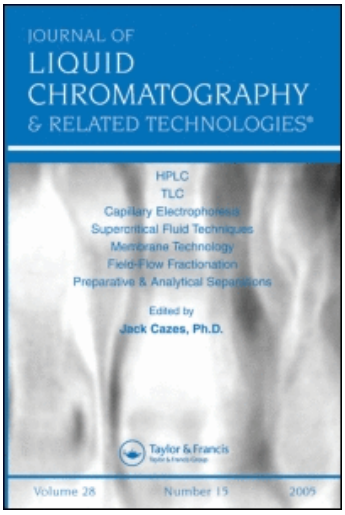

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THE BEHAVIOR OF SOME CARBOXY AND HYDROXY BENZENE DERIVATIVES ON THIN LAYERS OF PLAIN AND Fe(III)-IMPREGNATED SILICA-GEL

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ABSTRACT

The behaviour of some carboxy and hydroxy benzene derivatives related to lignin and humic materials was examined by thin layer chromatography on plain and Fe(III)-impregnated silica-gel plates, in three solvent systems. The mobility differences on impregnated and plain plates, expressed as R_i values, were calculated and can be used as one of the parameters for identification of the compounds tested.

INTRODUCTION

It appears that the complexation of metals in soils and sediments takes place via functional groups of humic substances (Fig. 1), mainly hydroxyl and carboxyl (1-4) and it is considered that this complexation is the main factor governing the mobility of metals through soils. Earlier we examined the chromatographic

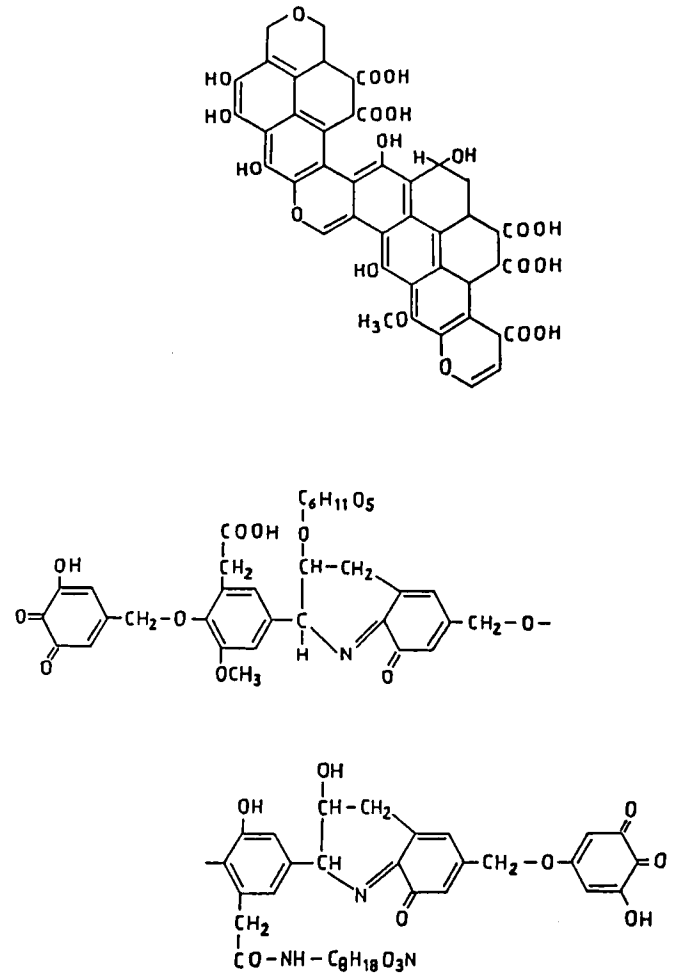

Fig. 1 Some of the presumed structures of humic acids.

behaviour of some phenolic acids and aldehydes, commonly found as degradation products of humic materials (5-7) on thin layers of plain and Fe(III)-impregnated silica-gel, in different organic solvent systems (8) and waters (9).

Now we extend this investigation to some hydroxy- and carboxy-benzene derivatives, in order to get more information on chromatographic behaviour, separation and the affinity of hydroxyl and carboxyl functional groups against Fe(III) of these types of compounds under the experimental conditions investigated.

MATERIALS AND METHODS

Chemicals

The compounds tested and all the other chemicals used were of analytical grade, purchased from Fluka A.G., Switzerland, Merck, FR Germany and B.D.H., England.

Sorbent layers

Precoated plates of silica-gel 60 F_{254} (Merck), plain and impregnated with $Fe(NO_3)_3$ (1%, by spraying) were used.

Solvent systems

1. Ethyl acetate
2. Ethyl acetate - benzene (9:11) v/v (10)
3. Ethyl acetate - benzene (5:15) v/v

Detection

The detection was performed by sprying with bromocresol green indicator reagent, with methanolic 1% $FeCl_3$ and by inspection under UV light.

	1	2	3	4	5
I	COOH	-	-	-	-
II	COOH	COOH	-	-	-
III	COOH	-	COOH	-	-
IV	COOH	OCH_3	-	-	-
V	COOH	-	OCH_3	OCH_3	OCH_3
VI	OH	-	-	-	-
VII	OH	OH	-	-	-
VIII	OH	-	OH	-	-
IX	OH	-	-	-	-
X	COOH	OH	-	-	-
XI	COOH	-	OH	-	-
XII	COOH	-	-	OH	-
XIII	COOH	-	OCH_3	OH	-
XIV	COOH	-	OCH_3	OH	OCH_3

(8)

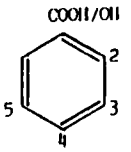

Fig. 2 Types of compounds tested.

Procedure

The procedure was the same as described earlier (8) using the ascending technique with the solvent front reaching approximately 8 cm. R_i values stand for $R_{f\,impr.} - R_{f\,plain}$.

RESULTS AND DISCUSSION

The types of compounds tested are shown in Fig. 2. The results of their chromatographic behaviour on plain and Fe(III)-impregnated silica-gel plates are presented in Table 1.

The solvent systems were chosen on the basis of published data (10) with some modifications regarding the component ratio

Table 1

R_f and R_i Values of Carboxy and Hydroxy Substituted Benzenes on Fe(III)-Impregnated and Plain Silica-Gel Plates

No	Compound	R_f x 100 Plain*			R_f x 100 Impregnated*			R_i x 100**		
		1	2	3	1	2	3	1	2	3
I	Benzoic acid	80	69	55	89	78	66	+ 9	+ 9	+11
II	1,2-Benzenedicarboxylic acid (o-Phthalic acid)	11	5	0	29	9	4	+18	+ 4	+ 4
III	1,3-Benzenedicarboxylic acid (m-Phthalic acid)	49	5	0	56	11	7	+ 7	+ 6	+ 7
IV	2-Methoxybenzoic acid	58	45	30	79	63	46	+21	+18	+16
V	3,4,5-Trimethoxybenzoic acid	56	37	17	84	65	39	+28	+28	+22
VI	Hydroxy benzene (Phenol)	89	82	78	92	85	76	-	-	-
VII	1,2-Dihydroxy benzene (Catehol)	87	75	52	85	73	53	-	-	-
VIII	1,3-Dihydroxy benzene (Resorcinol)	87	74	45	88	74	46	-	-	-
IX	1,4-Dihydroxy benzene (Quinolinol)	89	70	41	88	68	41	-	-	-
X	2-Hydroxybenzoic acid (8)	42	23	25	79	72	42	+37	+49	+17
XI	3-Hydroxybenzoic acid (8)	65	29	16	89	62	28	+14	+33	+12
XII	4-Hydroxybenzoic acid (8)	79	43	24	86	62	31	+ 7	+19	+ 7
XIII	4-Hydroxy-3-methoxybenzoic acid (Vanillic acid) (8)	67	35	16	85	59	26	+18	+24	+10
XIV	4-Hydroxy-3,5-dimethoxybnezoic acid (Syringic acid) (8)	60	40	39	79	67	46	+19	+27	+ 7

* Solvents: **1** Ethyl acetate; P'=4.30 ; **2** Ethyl acetate-benzene (9:11) v/v; P'=3.58; (10);
3 Ethyl acetate-benzene (5:15) v/v; P'=3.32

** Only greater than 3 were considered

(their polarity index P' (11) is marked in the foot-note of the Table 1). All the compounds tested exhibit retardation in mobility on plain and impregnated plates when the amount of benzene in the solvent increases, what indicates that the solubility of the compounds themselves as well as their Fe(III)--complexes is diminishing. By using the suitable solvent, all the substances can be separated on either plain or impregnated layers.

With regard to impregnation, one can see that all the phenolic acids with either free or substituted phenolic groups and benzene carboxylic acids move faster on impregnated than on plain silica-gel ($R_i > 0$), while compounds without the carboxylic group - hydroxy or dihydroxy benzenes - have similar R_f values on both layers ($R_i \cong 0$).

In addition, the dependency of phenolic acids, i.e. compounds with carboxyl and hydroxyl groups in the benzene ring, on the polarity of the solvent system, can be observed, showing the greatest R_i values in the solvent system with the polarity index 3.58.

We believe that the behaviour of the compounds tested may be the consequence of formation of different complexes with the ferric-ion with different solubility and stability in the solvents applied. Also, the support of impregnated layers itself, consisting of an aged Fe(III)--hydroxyde precipitate (12) has to be taken into consideration.

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