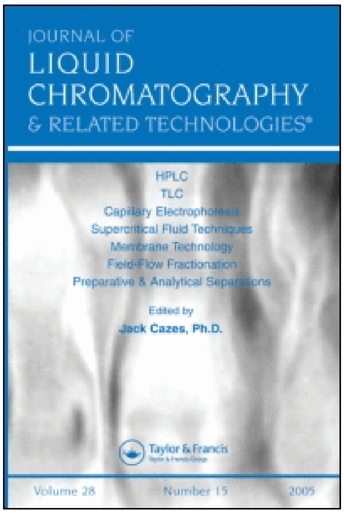

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BEHAVIOR OF SOME BENZENE DERIVATIVES ON PROGRESSIVELY DRIED Fe(III)-IMPREGNATED SILICA GEL PLATES

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ABSTRACT

The influence of progressive drying of Fe(III)-hydroxy oxide support on the behaviour of hydroxy and carboxy benzene derivatives in thin layer chromatography was investigated. The results show that different complexes are formed depending on the kind of substances and/or condition applied.

INTRODUCTION

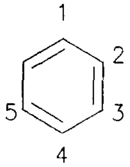
It is known that the surface of rocks, sediments and soils have active functional groups, in particular OH, derived from metal hydrous oxides or organic materials. The hydroxy groups of metal hydroxy/oxides are the active factors for the interaction with organic ligands i.e. for the formation of inner sphere surface complexes (1). In the transformation of iron in soils and sediments, and also in biochemical systems, great importance has been attributed to the dissolution of iron hydrous oxides (2). In natural systems this process is affected by biogenic ligands such as organic acids, dicarboxilic or hydroxy carboxilic. Iron hydrous oxides may differ widely with regard to chemical composition and structure and consequently may have different chemical reactivity (1-5). In our work we examined the dependence of the level of hydratation of iron hydrous oxides on the behaviour of some benzene derivatives which could simulate the active parts of humic material. As the technique thin-layer chromatography on silica gel impregnated with Fe(III)-ions and dried for different time intervals was applied.

EXPERIMENTAL

All chemicals used were of analytical grade (purchased from Fluka A.G. Switzerland, Merck, F.R. Germany and B.D.H. England). Pre-coated plates of silica gel 60 F_{254} (Merck) were impregnated with $Fe(NO_3)_3$ (1%, ethanolic, by spraying) and dried at 75°C for 5 min., as well as for 24 and 72 hours, respectively. Tap water was used as the developer for ascending technique with solvent ascent cca 8 cm. Detection was performed by visual inspection and by spraying with bromocresol green indicator solution. R_f values were determined using the arithmetic means of 2-5 runs. In the case of pyrogallol and gallic acid the "R_f" denotes the upper border of the spot (see later).

RESULTS AND DISCUSSION

In Fig. 1. the structures of the compounds tested are shown. It can be seen that the benzene derivatives with hydroxy and carboxy groups respectively, in different positions in the benzene ring were considered. The results of the experiments are presented



	1	2	3	4	5
I	OH	OH	-	-	-
II	OH	-	OH	-	-
III	-	-	OH	OH	OH
IV	COOH	-	-	-	-
V	COOH	COOH	-	-	-
VI	COOH	OH	-	-	-
VII	COOH	-	-	OH	-
VIII	COOH	-	OH	OH	OH

Figure 1. Benzene derivatives tested

in Table 1. If one assumes that the migration of the compounds on plain plates is mostly governed by their solubilities in water (6,7) and by comparing these mobilities with those observed on the impregnated plates the importance of the functional groups as well as of their position in the benzene ring becomes obvious. A different behaviour on impregnated plates versus nonimpregnated ones and the influence of the duration of heating of the support should point to the formation of complexes. The formation of complexes by carboxyl groups only (benzoic and o-phthalic acid) could not be verified by this method. On the other side, the compounds bearing phenolic groups only or both phenolic and carboxy groups show clearly the formation of complexes the mobility of

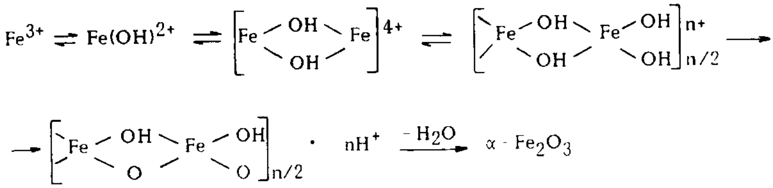
TABLE 1.

R_fx100 values of some hydroxy and carboxy benzene derivatives on progressively dried (75°C) Fe(III)-impregnated silica gel
Developper: tap water

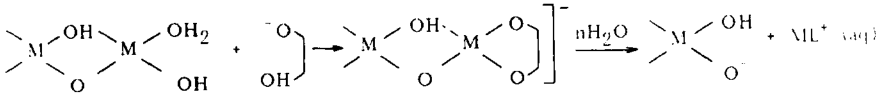
No	Compound	R_f x 100			
		5 min	24h	72h	Plain
I	Catechol	78	84	91	100
II	Resorcinol	86	89	96	100
III	Pyrogallol	0-71	0-96	0-100	100
IV	Benzoic acid	16	14	17	17
V	o-Phthalic acid	23	22	27	12
VI	Salicylic acid	82	90	100	17
VII	4-Hydroxybenzoic acid	80	85	88	3
VIII	Gallic acid	0-37	0-52	0-91	100

*Results published earlier (6,7).

which was also influenced by the duration of heating of the impregnated plates. Thus, both diphenols (catechol and resorcinol) and both monohydroxybenzoic acids (salicylic and 4-OH-benzoic) respectively, although of completely opposite solubility in water, gave complexes of almost identical and considerable migration. The mobilities of these complexes were also moderately increased by the duration of the heating of the support. The introduction of the third hydroxy group in the molecule (pyrogallol and gallic acid) enhanced further the complexation, and from the compounds very soluble in water the complexes of lower solubilities were formed. However, in this instance, the spots on impregnated plates were very elongated, from the start toward the front, and these elongations were considerably increasing with the duration of heating of the support. The influence of heating regime of Fe(III)-hydroxy oxide support on the migration of the compounds used is shematically presented in Fig. 2. Thus, it is obvious that prolonged heating causes modifications of the Fe(III)-hydroxyoxide what reflects in the behaviour of the compounds tested. Namely, investigating the precipitates of hydrolysed and for different time intervals aged $Fe(NO_3)_3$ solution by Mössbauer spectroscopy the following equation was suggested (5)



presenting the formation of Fe(III)-hydroxy polymer. It can be presumed that on impregnated plates similar precipitates are formed. By attaching of organic molecules with their active functional groups to the surface of the metal hydroxy/oxide, inner sphere surface complexes can be formed leading to the detachment of the metal from the support. Such a process was observed by investigating the reaction of δ-Al_2O_3 with different ligands (1), and the following reaction scheme was proposed:



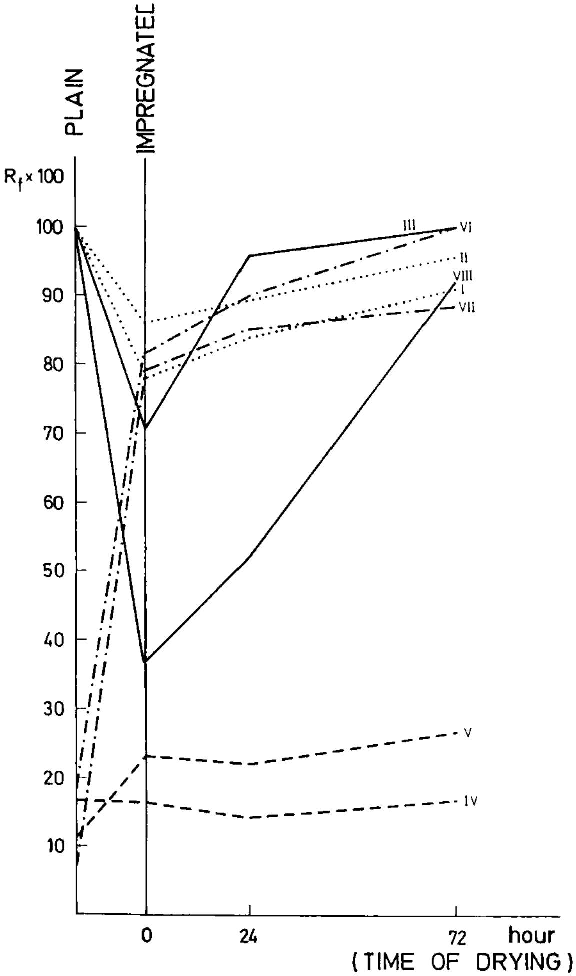


Figure 2. Dependence of R_f values of hydroxy- and carboxybenzene derivatives on progressively dried Fe(III)-impregnated silica gel and comparison with TLC on plain silica gel

It seems likely to apply this model for the chromatography of the benzene derivatives in water media on the support consisting of Fe(III)-hydroxy/oxide. It can be presumed that the complexation between iron and the active ligands may occur with all kinds of Fe(III)-hydroxy/oxide formed. From the behaviour of the compounds during the chromatography it could be drawn some conclusions how the complexation process may occur. Looking at the Fig. 2 it can be seen that all compounds tested exhibit similar behaviour on impregnated plates, with respect to the time of heating of the support. Namely, the mobility of the complexes formed is increasing to the more or less extent proportionally with the time of heating. This is the fact, but the explanation of the behaviour may be different for different groups of compounds. Benzene carboxilic acids show very small differences in mobilities on plain and impregnated plates, as well as on impregnated plates with regard to duration of heating. For this reason it is not possible to conclude that either complexes are not formed at all, or complexes of small solubility in water are formed. It can be supposed that the last presumption is more probable because the investigations on preparation and characterization of this kind of complexes revealed that they are formed and built on Fe(III)-hydroxy/oxide as well as on Fe_3O units as cores for complexation (8,9). Regardless to different solubility in water of the parent compounds, the complexes formed from diphenols and phenolic acids behaved very similarly showing moderate rising of the mobility proportionally to the drying time of Fe(III)-hydroxy/oxide support. For phenolic acids this behaviour can be attributed to changing the characteristics of the complexes with the changing of characteristics of the support. Transformation of the composition of the support is reflected in the loosing of hydroxy groups from the surface. In the case of diphenols this progressive loosing of hydroxy groups from the surface of impregnant may cause diminishing in complexation and on longly dried layers complexes behaved as their parent compounds. The behaviour of gallic acid and pyrogallol expresses special characteristics. Beginning on short drying supports the complexes show low mobility which rises considerably on heating but with tailing all the way from the start. It is known that this kind of compounds form complexes where two hydroxy groups are included in primary complexation (10) while the third is available for polymerization. It can be presumed that a similar process occurs during the chromatography retarding the movability. On the other side loosing of the hydroxy groups by progressive drying of the support make it less active for complexation and the compounds partially behaved as the parent compounds what results in the tailing.

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