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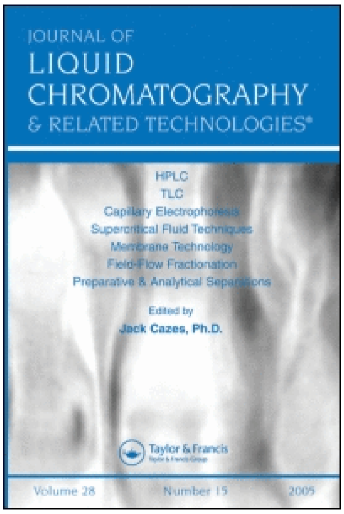

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BEHAVIOUR OF HUMIC ACIDS ON Fe(III)-IMPREGNATED SILICA GEL COMPARED WITH MODEL SUBSTANCES

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ABSTRACT

Behaviour of humic acids under the conditions of thin layer chromatography on Fe(III)-impregnated silica gel with tap water as developer was investigated. Compounds having similar functional groups as the humic material were compared and conclusions extended to natural conditions were drawn.

INTRODUCTION

In our previous papers we presented the study of the behaviour of some benzene derivatives related to humic material in conditions simulating the natural ones (1-3). These were: thin layer chromatography on silica gel impregnated with Fe(III)-hydroxy/oxide (4) as the support and water as the developer. The model compounds were benzene derivatives with hydroxy and/or carboxy groups representing types of structures that might occur in humic acids. The R_f-values of the compounds investigated served us as a lead for their solubility i.e. movability of the Fe(III)-complexes formed. By using this simple system we could follow the conduct of compounds with various functional groups and deduce on their abilities to detach Fe-ion from the support to the solution (5). Summarizing the results obtained with

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model substances, the differences in activities of carboxy and hydroxy groups in the benzene ring became evident.

In the present work we now examined the behaviour of commercially isolated humic acids as the natural occuring molecules under the same conditions.

EXPERIMENTAL

The chemicals and the procedures were the same as described previously (1-3). For TLC precoated plates of silica gel G_{254} (Merck) were used. Humic acids, as Na- or NH_4-salts, were commercially products purchased by: "EGA" Germany, "FLUKA" Switzerland and "GMS" Chechoslovakia.

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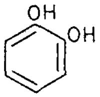
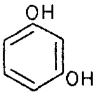
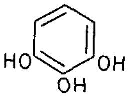
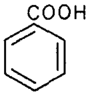
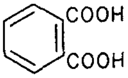
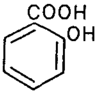
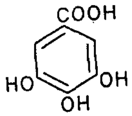
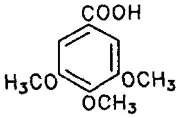
RESULTS AND DISCUSSION

In Table 1 the behaviour of model compounds, simulating humic acid structure on Fe(III)-impregnated plates, taken from earlier publications, is presented. They are representative compounds having characteristic numbers and positions of carboxy and hydroxy groups. One can see that differences in the mobilites of the compounds exist with respect to the kind of functional groups. Looking at that one of presumed structures of humic acids (Fig. 1) it can be seen the similarities of the composition of the functional groups in the compounds tested with that of humic structure. From the behaviour of the hydroxy benzenes (Table 1: I, II, III and IV) on Fe(III)-impregnated plates it can been concluded that the related functional groups make iron and possibly also other metals under natural conditions movable by turning them to water soluble complexes. On the other hand, benzene carboxilic acids (Table 1: V, VI and IX) behave differently indicating retardation of the metal. Salicylic acid, as well as other phenolic acids (2), having the carboxilic- and hydroxy- groups, also form soluble complexes with Fe-ion and consequently moved considerably. An addditional prove would be the compounds with blocked hydroxy-groups (like: trimethoxy benzoic acid, Table 1:IX) with small Rf's.

In Table 2 the R_f values of three humic acid preparations in the salt and H^+-forms, respectively, together with their chemical characteristics, are presented. By

Table 1. R_f x 100 values of hydroxy and carboxy benzene derivatives on Fe(III)-impregnated silica gel.
Developer: tap water

No	Compound	Structures	R_f x 100	Ref
I	Catechol		78	3
II	Resorcinol		91	2
III	Quinol		88	2
IV	Pyrogallol		0 - 7	3
V	Benzoic acid		16	3
VI	o-Phthalic acid		23	3
VII	Salicylic acid		90	1
VIII	Gallic acid		0 - 37	3
IX	3,4,5-Trimethoxy-benzoic acid		6	1

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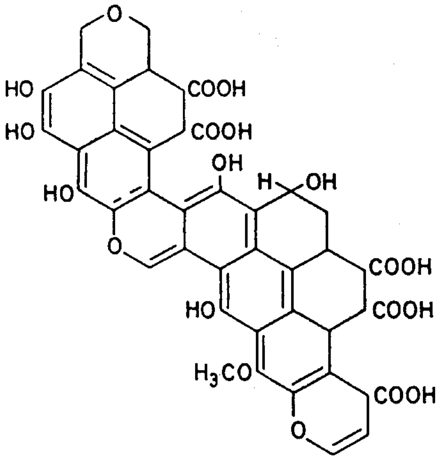

Figure 1.

One of the presumed structures of humic acid

Table 2.

R_fx100 values of humic acids on Fe(III)-impregnated silica gel and their COOH content

Developer: tap water

Humic Acid	R_fx100		COOH* (meq/g)	
	Original	H+ form**	Original	H+ form**
"EGA"	0 - 88	11	1.3	4.4
"FLUKA"	0 - 88	11	0.5	4.4
"GMS"	0 - 60	3	6.5	5.8

*Determined by $Ca(OAc)_2$ method (7)

**Transformation into H^+ form was performed by repeated shaking with 0.1N HCl and centrifugating followed by washing with distilled water till the negative reaction to chloride

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comparing the R_f - values of the model substances with those of humic acids under the same conditions (Table 1 and 2), one can conclude that humic acids (in the original forms) as well as compounds like catechol, quinol, resorcinol and salicylic acid move considerably on Fe(III)-impregnated plates. Due to the exchange capacity of the Na^+ or NH_4^+ ion of humic acid with Fe-ion from the support, depending on the stability and solubility of the formed complexes, the tailing effect can be explained. Looking to the behaviour of humic acids in the H^+-form (Table 2) one can recognize similar small mobilities as with model carboxilic acids.

Summarizing the above results it can be presumed that during the chromatographic process complexes between Fe(III) from the support and the active functional groups from humic acids were formed, causing successive attaching and detaching of Fe(III) from the support of Fe(III)-hydroxy/oxide. The result is the moving by tailing of the so formed more or less soluble complexes. All these results so far could partially give the answer how the process of metal migration in soils and sediments is progressing.

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