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Short Communication

Thin-layer chromatographic behaviour of substituted phenolic compounds on silica gel layers impregnated with Al(III) and Cu(II)

M. Petrović, M. Kaštelan-Macan and A. J. M. Horvat

Faculty of Chemical Engineering and Technology, Institute of Analytical Chemistry, Marulićev trg 20, 41000 Zagreb (Croatia)

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ABSTRACT

The chromatographic behaviour of some substituted phenolic compounds on silica gel layers impregnated with Al(III) and Cu(II) was studied. Addition of metal ions gives very good separations of some structural isomers. In order to establish whether any improvment in the separation could be achieved by varying the concentration of impregnant, three different concentrations of $CuSO_4 \cdot 5H_2O$ and $AlCl_3 \cdot 6H_2O$ (1, 2 and 4%, w/w) were used. A very good separation of hydroquinone and resorcinol on silica gel layers impregnated with $CuSO_4$ was achieved. Aminophenols can be successfully separated using silica gel layers modified by $CuSO_4$ addition. The optimum resolution of *meta* and *para* isomers was achieved on silica gel containing 0.51% Cu(II) ions (2% $CuSO_4 \cdot 5H_2O$).

INTRODUCTION

Thin-layer chromatography (TLC) is commonly used for the identification of phenolic compounds. The separation of substituted phenols using various chromatographic systems has been reported. Silica gel [1-4] is the material preferred by most workers, but examinations showed that structural isomers cannot be succesfully separated, although a certain separation by variation of the solvent system can be achieved. Therefore, difficulties in obtaining adequate resolution of closely related structural isomers have led to the application of modified sorbents.

Improved resolution has been achieved by impregnating silica gel with some inorganic or organic substances. Thielmann [5] obtained good results in the resolution of a mixture of naphthols and some polyphenols using silica gel layers impregnated with amonium molybdate. Hadžija and co-workers [6,7] studied the chromatographic behaviour of phenolic acids and aldehydes on precoated silica gel plates impregnated with iron(III) nitrate and while some other researchers [8-11] suggested the use of different impregnants such as silver nitrate, sodium nitrite, aniline chloride and oxalic, tartaric and citric acid. The improved resolution and changed mobility on the modified silica gel plates is a result of complex interactions between phenolic compounds and impregnants.

In this work we studied the chromatographic behaviour of some structural isomers of phenolic

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Correspondence to: Dr. M. Kaštelan-Macan, Faculty of Chemical Engineering and Technology, Institute of Analytical Chemistry, Marulićev trg 20, 41000 Zagreb, Croatia.

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TABLE I

SOLVENT SYSTEMS USED

Solvent system	Components	Ratio of components (v/v)
S_1	Chloroform	
S_2	Chloroform–acetone	65:35
S_3	Chloroform–ethyl acetate	95: 5
S_4	Chloroform–ethyl acetate	95:10
S_5	Toluene–chloroform–acetone	40:25:15
S_6	Toluene–chloroform–acetone	40:25:25
S_7	Hexane–acetone	80:20
S_8	Hexane–acetone	80:40
S_9	Benzene	
S_{10}	Benzene–acetone	70:30

compounds on silica gel thin layers modified with copper and aluminium.

EXPERIMENTAL

Chromatographic plates were prepared by spreading a slurry of silica gel GF_{254} (Merck) and an aqueous solution of $CuSO_4 \cdot 5H_2O$ or $AlCl_3 \cdot 6H_2O$, by means of a Camag applicator on to 20 × 20 cm glass plates. The layer thickness was 300 μm. The plates were dried in air and activated for 1 h at 105°C.

Stock standard solutions containing 1 mg/ml of phenol, *o* -, *m*- and *p*-cresol, *o*-, *m*- and *p*-nitrophenol, *o*- and *p*-chlorophenol, *o*-, *m*- and *p*-aminophenol, salicylic acid, hydroquinone, resorcinol and pyrogallol in acetone were prepared. Samples of 5 μl were applied to the activated plates with a Camag micropipette.

The chromatograms were developed with the solvent systems listed in Table I in saturated chambers to a distance of 12 cm.

Phenolic compounds were detected by spraying with a 5% (w/v) aqueous solution of $FeCl_3 + K_3Fe(CN)_6$ to obtain blue spots on a white background or by UV irradiation at 254 nm.

RESULTS AND DISCUSSION

The chromatographic separation of sixteen substituted phenols was carried out on silica gel layers modified with various concentrations of $CuSO_4$ and $AlCl_3$. R_F-values of the compounds examined on impregnated plates were compared with those ob-

TABLE II

R_F VALUES ON SILICA GEL LAYERS

Compounds examined	R_F values					
	S_1	S_2	S_3	S_4	S_5	S_6
Phenol	0.24	0.63	0.73	0.38	0.22	0.91
o-Cresol	0.42	0.74	0.80	0.49	0.33	0.91
m-Cresol	0.27	0.63	0.73	0.39	0.23	0.90
p-Cresol	0.27	0.65	0.72	0.37	0.24	0.90
o-Nitrophenol	0.94	0.94	0.92	0.70	0.82	1
m-Nitrophenol	0.16	0.57	0.65	0.25	0.11	0.85
p-Nitrophenol	0.14	0.52	0.61	0.22	0.09	0.82
o-Chlorophenol	0.68	0.83	0.75	0.41	0.51	0.93
p-Chlorophenol	0.25	0.61	0.70	0.37	0.22	0.90
o-Aminophenol	0.22	0.27	0.45	0.21	0.05	0.68
m-Aminophenol	0	0.15	0.26	0.10	0	0.57
p-Aminophenol	0	0.13	0.23	0.09	0	0.52
Salicylic acid	0	0	0	0	0	0.05
Hydroquinone	0	0.12	0.34	0.08	0	0.58
Resorcinol	0	0.12	0.34	0.09	0	0.62
Pyrogallol	0	0.10	0.17	0.06	0	0.40

tained on plain silica gel plates. The influence of different solvent systems, chosen on the basis of published data, was studied.

The introduction of functional groups into a phenol molecule generally raises its adsorption affinity on the silica gel layers, but the position of functional groups, and especially steric effects, have to be taken into acount. The R_F values obtained for phenolic compounds using different solvent systems are listed in Table II. The R_F values of *m*- and *p*-cresol show little difference from those of phenol, whereas a methyl group in the *ortho* position increases the R_F value. This decreased adsorption of *ortho* isomers is attributed to steric effects, which are particularly marked in the case of *o*-nitrophenol. Adsorption of phenols on silica gel layers is a result of hydrogen bonding with silica surface, but in the *ortho*-substituted compounds the formation of intramolecular hydrogen bonds between the hydroxyl group and the *ortho* substituent is possible. The consequence of this chelation is a reduced adsorption affinity of *ortho* isomers.

Aminophenols are more weakly acidic than phenol, owing to the inhibited resonance of the hydroxyl group with the benzene ring caused by the amino group. An amino group in the *ortho* or *para* position has a much greater inductive effect than one in the *meta* position. The R_F values of aminophenols obtained on silica gel layers show that *m*- and *p*-aminophenol cannot be succesfully separated, although some resolution by variation of the solvent system can be achieved. Examining the chromatographic separation of aminophenols using modified layers, it can be concluded that addition of metal ions to the silica gel during the layer preparation gives an opportunity for very good separations of *meta*- and *para*-isomers.

In order to establish whether any improvment in the separation of aminophenols could be made by varying the concentration of impregnants, three different concentrations of $CuSO_4 \cdot 5H_2O$ and $AlCl_3 \cdot 6H_2O$ (1, 2 and 4%, w/w) were used. The addition of $CuSO_4$ leads to a significant increase in adsorption of *p*-aminophenol, which is shown by a rapid decrease in R_F values (Fig. 1), whereas adsorption of *m*-aminophenol is gradually increased.

On Cu(II)-impregnated plates pyrogallol has smaller R_F values than on plain plates. On the other hand, the mobility of resorcinol is almost the same on the impregnated and plain silica gel plates (Fig. 2).

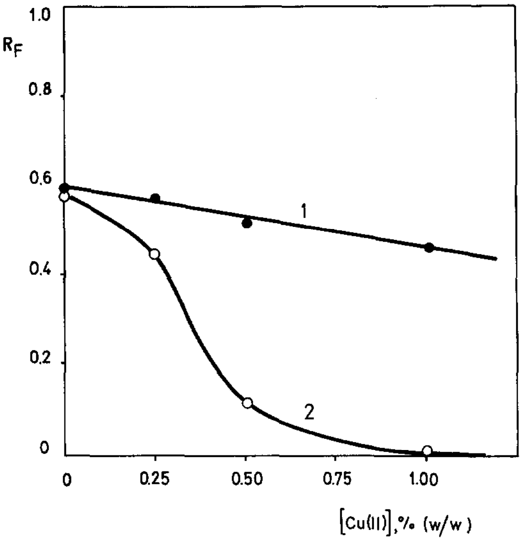

Fig. 1. R_F values of aminophenols as a function of Cu(II) mass fraction in the layer; solvent system S_2. 1 = *m*-aminophenol; 2 = *p*-aminophenol.

This increased adsorption of pyrogallol can be considered to be a result of a copper(II) complex, which is expected to be formed during the chro-

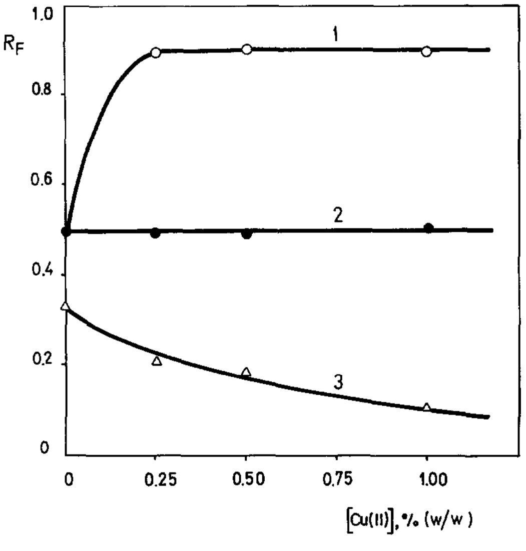

Fig. 2. R_F values of polyphenols as a function of Cu(II) mass fraction in the layer; solvent system S_6. 1 = Hydroquinone; 2 = resorcinol; 3 = pyrogallol.

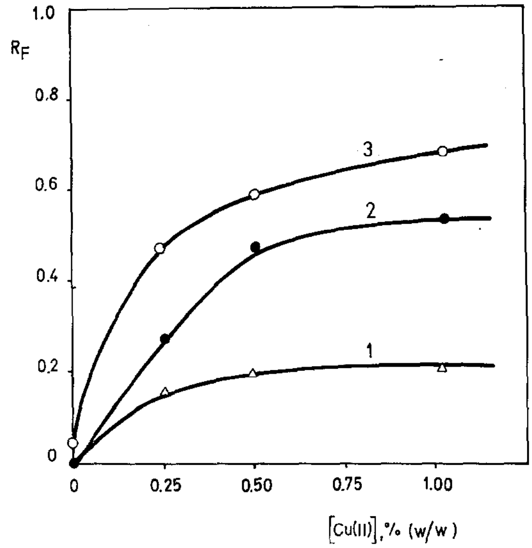

Fig. 3. R_F values of salicylic acid as a function of Cu(II) mass fraction in the layer. Solvent system: 1 = S_3; 2 = S_5; 3 = S_{10}.

matographic process on the copper-impregnated plates.

An interesting phenomenon is observed on examining hydroquinone. The addition of copper to the silica gel layer leads to a rapid decrease in the adsorption of hydroquinone. As copper(II) is an oxidizing agent, the significant increase in R_F values using different solvent systems can be explained as a consequence of oxidation of hydroquinone to the *p*-benzoquinone. The high R_F values of hydroquinone obtained on copper-impregnated plates correspond to those obtained by testing a genuine reference sample of *p* -benzoquinone on silica gel layers. On the other hand, hydroquinone cannot be oxidized by Al(III) ions. Therefore, the chromatographic behaviour of hydroquinone on the Al(III) impregnated plates is identical with that on plain silica gel layers.

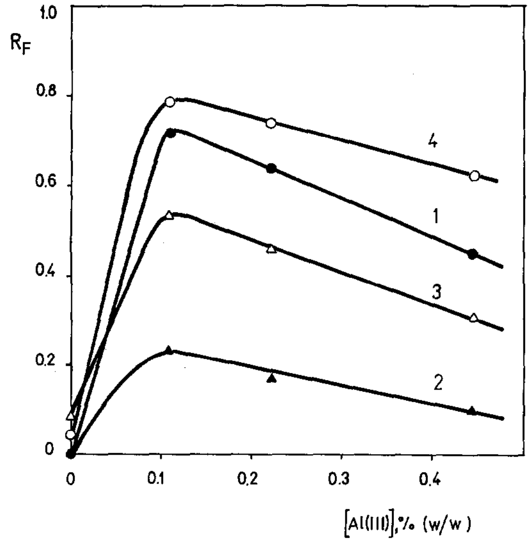

Fig. 4. R_F values of salicylic acid as a function of Al(III) mass fraction in the layer. Solvent system: 1 = S_2; 2 = S_4; 3 = S_5; 4 = S_{10}.

We also examined the chromatographic behaviour of salicylic acid on copper- and aluminium-impregnated plates. On the impregnated plates salicylic acid has higher R_F values than on plain plates (Figs. 3 and 4).

Adsorption of phenolic compounds is a result of hydrogen bonding between the oxygen atom of the phenolic group and hydrogen atoms of the hydroxyl groups on the silica gel surface. As salicylic acid forms stable complexes with Cu(II) and Al(III) ions [12], in which the metal ions are coordinated between the oxygen atom of the phenolic group and the oxygen atom of the carboxyl group, which is present in an *ortho* position, adsorption of salicylic acid on metal impregnated plates is reduced.

On examining the behaviour of other phenolic compounds (cresols, nitrophenols and chlorophenols) on Cu(II)- and Al(III)-impregnated plates, no improvement in resolution was observed.; the $R_F$values obtained on impregnated plates were similar to those obtained on plain silica gel plates.

It can be concluded that the formation of phenol–metal interaction products, different solubilities of the phenol and the interaction product in the solvent system used and the changed adsorption properties of impregnated silica gel play prominent roles in the TLC separation of phenols.

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