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Note

High-performance thin-layer chromatography of chloro-, bromo- and alkylphenols on ready-for-use plates of silanized silica gel alone and impregnated with anionic detergents

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Many phenols have been studied on home-made layers of silanized silica gel (C_2) with good results[1]. Ready-for-use plates of silanized silica gel, on the other hand, have been little used for the systematic investigation of these compounds, except for studies on food additives[2,3], the homologues of *p*-hydroxybenzoic acid[4] and some stereoisomers of phenolic acids[5]. We have therefore studied the chromatographic behaviour of chloro-, bromo- and alkylphenols on commercially available RP-18, Sil C_{18}-50 and OPTI-UP C_{12} plates, alone and impregnated with anionic detergents, in order to establish the best conditions for their separation and to compare the results with those achieved on home-made layers.

EXPERIMENTAL

RP-18 (Merck), Sil C_{18}-50 (Machery, Nagel & Co.) and OPTI-UP C_{12} (Anteg) plates were impregnated as described previously[8]. The anionic detergents used were dodecylbenzensulphonic acid (HDBS) and triethanolamine dodecylbenzenesulphonate (DBS). The migration distance was 6 cm unless stated otherwise. The measurements were carried out at 25°C.

Standard solutions (0.5–1 mg/ml) were obtained by dissolving the phenols in 95% ethanol. For polyhalogenated phenols more concentrated solutions (2–3 mg/ml) were used. A 0.5-μl volume of each solution was deposited on the layer. The phenols were detected by the Boute reaction[6] by exposure of the layer to nitrogen dioxide and subsequently ammonia vapour.

RESULTS AND DISCUSSION

RP-18 plates cannot be used alone, because owing to their hydrophobicity, phenols cannot be detected by the Boute reaction. However, impregnation with anionic detergents (HDBS and DBS) removes this disadvantage.

The elution time depends on the kind of detergent used; for instance, with acetic acid–methanol–water (5.7:40:54.3), the elution time is about 6 h on layers impregnated with 4% DBS and 50 min on layers impregnated with 4% HDBS.

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Halogenated phenols

Table I lists the chromatographic characteristics of 22 halogenated phenols on layers or RP-18 + 4%HDBS, Sil C_{18}-50 + 4%HDBS and OPTI-UP C_{12}, eluting with solutions at different pH values.

As columns of results 1–3 in Table I show, on RP-18 + 4%HDBS plates the retention of the phenols is more marked with acidic solutions (apparent pH = 5.55), where the compounds are in the undissociated form, than with alkaline eluents, where their retention decreases along with increase in the percentage of the deprotonated form. The degree of deprotonation can be calculated by adding to the pK_a values in Table I at least 2 units to account for the presence of 60% methanol[7].

Similarly to what is observed on home-made layers, compounds with one or two halogen groups in the *ortho* position are less retained. The bromophenols, furthermore, are more retained than the corresponding chlorophenols. The best conditions for the separation of the trichlorophenols on RP-18 + 4%HDBS are achieved eluting with 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 60% methanol; the separations of the dichlorophenols and, overall, of the monohalogenated compounds

TABLE I

R_F VALUES OF HALOGENATED PHENOLS ON RP-18 + 4%HDBS, Sil C_{18}-50 + 4% HDBS AND OPTI-UP C_{12} PLATES WITH DIFFERENT ELUENTS

(a) 0.1 *M* acetic acid + 0.1 *M* sodium acetate in 60% methanol; (b) 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 60% methanol; (c) 1 *M* ammonia in 40% methanol; (d) 1 *M* ammonia + 0.1 *M* ammonium chloride in 40% methanol; (e) 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 20% methanol.

No.	*Compound*	*RP-18 + 4%HDBS*			*Sil C_{18} + 4%HDBS*		*OPTI-UP C_{12}*	*pK_a (25°C)*
		a	*b*	*c*	*d*	*c*	*e*	
1	*o*-Chlorophenol	0.48	0.48	0.77	0.50	0.71	0.25	8.48
2	*m*-Chlorophenol	0.36	0.34	0.50	0.26	0.49	0.16	9.02
3	*p*-Chlorophenol	0.37	0.34	0.37	0.19	0.40	0.16	9.38
4	2,6-Dichlorophenol	0.32	0.59	0.86	0.57	0.76	0.40	6.79*
5	2,5-Dichlorophenol	0.21	0.41	0.81	0.46	0.68	0.26	7.35*
6	2,3-Dichlorophenol	0.25	0.35	0.78	0.42	0.66	0.21	7.45*
7	2,4-Dichlorophenol	0.20	0.27	0.69	0.33	0.59	0.16	7.75*
8	3,5-Dichlorophenol	0.13	0.16	0.55	0.22	0.50	0.12	7.93*
9	3,4-Dichlorophenol	0.19	0.18	0.48	0.19	0.43	0.10	8.39*
10	2,3,6-Trichlorophenol	0.15	0.52	0.74	0.34	0.57	0.28	6.12
11	2,4,6-Trichlorophenol	0.10	0.43	0.63	0.24	0.48	0.22	6.42
12	2,3,5-Trichlorophenol	0.07	0.36	0.63	0.24	0.46	0.16	7.23
13	2,4,5-Trichlorophenol	0.11	0.42	0.63	0.24	0.48	0.22	7.33
14	2,3,4-Trichlorophenol	0.11	0.29	0.66	0.24	0.49	0.16	7.59
15	3,4,5-Trichlorophenol	0.08	0.16	0.50	0.16	0.39	0.10	7.74
16	2,3,5,6-Tetrachlorophenol	0.08	0.38	0.43	0.14	0.35	0.11	5.44
17	2,3,4,5-Tetrachlorophenol	0.05	0.35	0.44	0.13	0.32	0.08	6.96
18	*o*-Bromophenol	0.43	0.43	0.75	0.45	0.68	0.23	8.44
19	*m*-Bromophenol	0.28	0.31	0.48	0.24	0.47	0.15	9.03
20	*p*-Bromophenol	0.29	0.29	0.35	0.16	0.36	0.15	9.36
21	2,6-Dibromophenol	0.21	0.55	0.78	0.44	0.68	0.38	6.6
22	2,4-Dibromophenol	0.13	0.22	0.53	0.24	0.49	0.15	7.8

* pK_a values at 29°C.

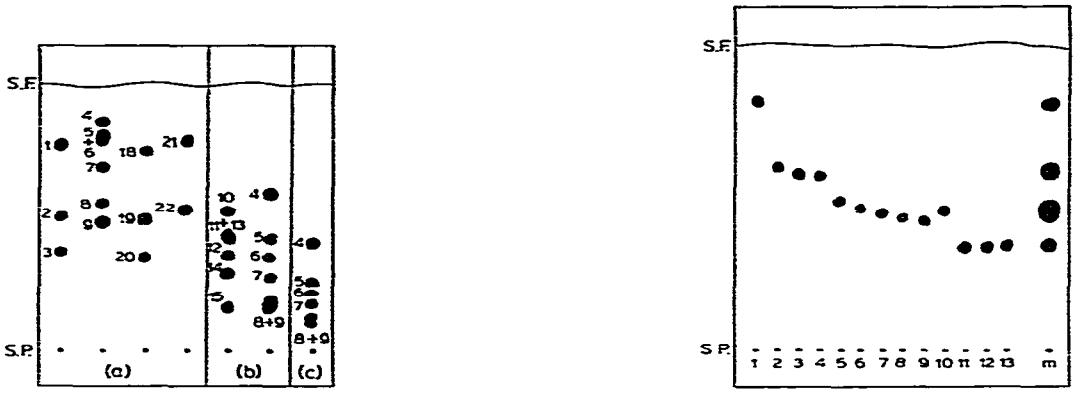

Fig. 1. Thin-layer chromatograms of halogenated phenols under different experimental conditions. Migration distance = 7 cm. The numbers refer to the compounds in Table I. (a) RP-18 + 4%HDBS plate with 1 *M* ammonia in 40% methanol as eluent; (b) RP-18 + 4%HDBS plate with 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 60% methanol as eluent; (c) OPTI-UP C_{12} plate with 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 20% methanol as eluent. S.P. = Starting point; S.F. = solvent front.

Fig. 2. Thin-layer chromatogram of phenol and alkylphenols on OPTI-UP C_{12}. Eluent: 7 *M* ammonia in 40% methanol. Elution time = 20 min. Migration distance = 8 cm. (1) = phenol; (2) = *m*-cresol; (3) = *p*-cresol; (4) = *o*-cresol; (5) = 3,5-dimethylphenol; (6) = 3,4-dimethylphenol; (7) = 2,5-dimethylphenol; (8) = 2,3-dimethylphenol; (9) = 2,4-dimethylphenol; (10) = 2,6-dimethylphenol; (11) = 2,3,5-trimethylphenol; (12) = 2,4,6-trimethylphenol; (13) = 2,3,6-trimethylphenol; (m) = mixture of 1–13.

are obtained with more basic eluents (see Fig. 1). The two tetrachlorophenols can be separated with 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 40% methanol (2,3,4,5-tetrachlorophenol, R_F 0.00; 2,3,5,6-tetrachlorophenol, R_F 0.07).

The affinity sequences of dichloro and trichlorophenols on RP-18 + 4%HDBS plates (see column 2 in Table I) is different from that found on home-made layers of C_2 + 4%HDBS on eluting with 0.1 *M* ammonia + 0.1 *M* ammonium chloride in 30% methanol[1] and do not agree with the sequence of the pK_a values in Table I; 3,4-dichloro- and 2,4,5-trichlorophenol, in fact, are less retained than 3,5-dichloro- and 2,3,5-trichlorophenol, respectively. The strong adsorption of the undissociated forms of these last compounds accounts for the above-mentioned sequence reversals.

On plates with 50% C_{18} silanization (Sil C_{18}-50) the phenols exhibit a behaviour similar to that observed on RP-18 + 4%HDBS (see columns 4 and 5 in Table I). On these layers, the presence of HDBS gives the best resolution of some compounds.

The OPTI-UP C_{12} plates must be used without detergents, as the presence of HDBS causes the formation of a double solvent front. These layers can be eluted with water–methanol mixtures containing low alcohol percentages (see column 6 in Table I) and exhibit very short elution times (10 min for a migration distance of 7 cm).

Alkylphenols

On the three plates examined, the behaviour of the methylphenols is determined by the number of substituent groups in the molecule. The chromatogram in Fig. 2, obtained on OPTI-UP C_{12} plates when eluting with 7 *M* ammonia in 40% methanol, refers to phenol, methylphenols and their mixtures and illustrates the

possibility of the determination of the number of methyl groups in the molecule from the R_F value. A straight line is obtained if the R_M values calculated from the spots of the mixture in Fig. 2 are plotted against the number of methyl groups in the molecule.

On RP-18 + 4%HDBS and Sil C_{18}-50 alone and impregnated with 4% HDBS, similar behaviour is observed, even if the separation of the different groups of isomers is not so sharp. The position of the substituent groups, on the other hand, hardly affects the chromatographic behaviour on OPTI-UP C_{12} plates, in contrast to the results on home-made layers of C_2 + 4%DBS[1].

A decrease in the percentage of methanol in the eluent to 20% does not result in a better resolution of isomers on OPTI-UP C_{12} plates. Better results are achieved on the more hydrophobic RP-18 + 4%HDBS plates, where the separation of 2,3,6-trimethylphenol (R_F 0.27) and 2,4,6-trimethylphenol (R_F 0.22) (which cannot be affected on home-made layers) when eluting with 3 *M* ammonia in 60% methanol and that of the three isomers of ethylphenol on eluting with 3 *M* ammonia in 40% methanol (migration distance = 7 cm) can be achieved.

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