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EVALUATION OF POROCHROM I AS A SUPPORT IN THE GAS–LIQUID CHROMATOGRAPHY OF PESTICIDES

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SUMMARY

The influence of geometry and chemistry of the surface on the gas chromatographic separation of pesticides was studied using different liquid stationary phases. It is shown that a support with an easily wettable surface should be used, a hydrophilic surface for polar stationary phases and a hydrophobic (*e.g.*, treated with hexamethyldisilazane) surface for non-polar and slightly polar liquids.

INTRODUCTION

The gas–liquid chromatography of reactive compounds, which are strongly adsorbed, requires the use of macroporous supports with a small surface area and a surface that is sufficiently inert but easily wettable by the stationary liquid surface. Pesticides usually have a low volatility and are unstable compounds, able to be adsorbed on the support surface.

EXPERIMENTAL AND RESULTS

We tested Chromosorb W (Johns-Manville, Denver, Colo., U.S.A.) and Porochrom I (U.S.S.R.) as liquid phase supports. The integral and differential curves of the pore size distribution are presented in Fig. 1. Chromosorb W and Porochrom I have very similar homogeneous macroporous structures. Chromatograms of the separation of some pesticides are given in Fig. 2. When Spherochrom, a support with a geometrically heterogeneous surface, is employed, the chromatographic peaks broaden and the separation becomes less satisfactory. Only homogeneous macroporous supports can be used for this purpose.

The chemical nature of the support surface is of great importance for the separation of compounds that contain halogens. In order to reduce the adsorption on the support surface, chemical modification of the surface is carried out by replacing the surface hydroxyl groups with inert trimethylsilyl groups[1]. Usually, this modification leads to a shortening of retention times and to an improvement in the shape of the chromatographic peaks, particularly for molecules that are capable of specific intermolecular interaction with hydroxyl groups and other active centres of the support surface.

The Porochrom I support (sample A) and the same support treated with hexamethyldisilazane (sample B) were used for the separation of halogenated compounds,

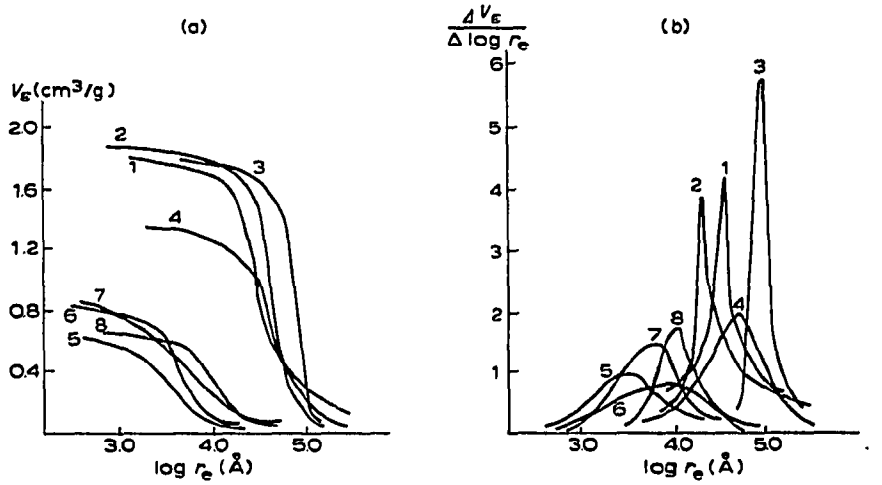

Fig. 1. Integral (a) and differential (b) curves of the pore distribution of the supports. 1 = Chromosorb W; 2 = Celite-545; 3 = Porochrom I; 4 = Chromaton N-AW; 5 = Chezasorb AW; 6 = Sterchamol; 7 = Celite C-22; 8 = Spherochrom.

using squalane, dinonyl phthalate (DNP) and polyethylene glycol (PEG-300) as stationary liquid phases.

With squalane, smaller V_g values were observed on the hexamethyldisilazane-treated Porochrom I (sample B) for chloroalkanes. For PEG-300, on the contrary, the V_g values were smaller on the unmodified Porochrom I (sample A). For other substances, the V_g values vary in the same manner on passing from a non-polar to a strongly polar stationary phase (Table I).

The difference in the variation of V_g with the polarity of the liquid phase deposited on the Porochrom samples is apparently connected with differences in the spreading of the liquid phase on the unmodified and modified surfaces of the macroporous support. The macroporous support is effective if the stationary phase spreads

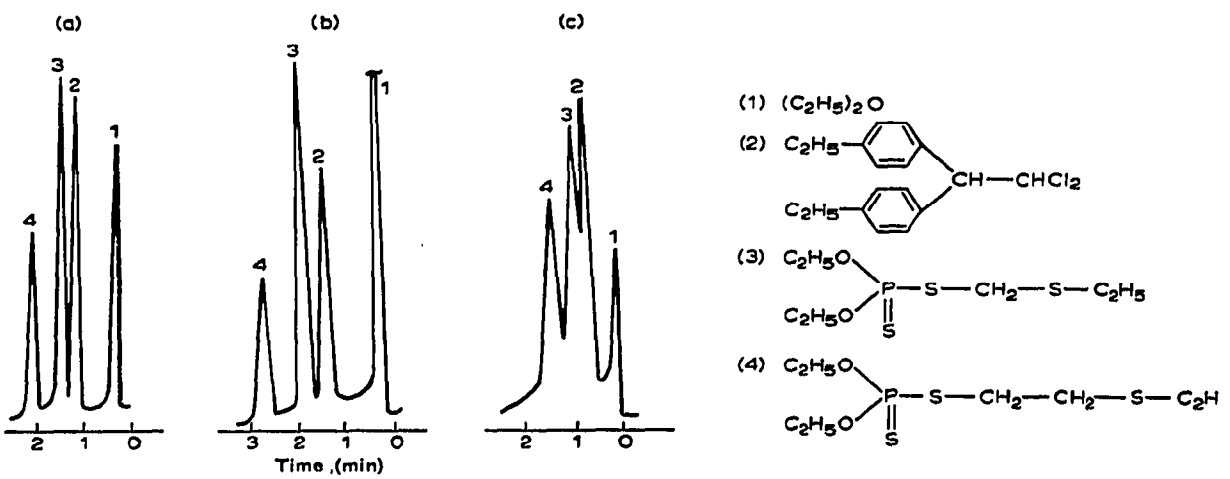

Fig. 2. Chromatograms on SE-30, deposited on: (a) Porochrom I, (b) Chromosorb W and (c) Spherochrom.

TABLE I

SPECIFIC RETENTION VOLUMES, V_g, ON POROCHROM I (SAMPLE A) AND MODIFIED POROCHROM I (SAMPLE B)

Stationary phase	*Support*	*Temperature of column (°C)*	V_g *(ml/g)*					
			$(CH_3)_2CO$	C_6H_5Cl	$p\text{-}Cl\cdot C_6H_4\cdot CH_3$	$CCl_2=CCl_2$	CCl_4	$CCl_2=CHCl$
Squalane	A	110	44.7	427	959	376	122.0	352
	B	110	14.6	402	820	306	86.5	112
DNP	A	110	38.6	412	930	227	76.6	122
	B	110	36.5	385	631	214	70.8	96
PEG-300	A	80	40.8	335	628	98	40.5	79
	B	80	53.0	442	804	112	48.9	91

over its surface so as to form a thin film, that is, if the stationary phase wets the surface well.

In order to characterize the wettability, we used the comparative method of impregnation of supports and the direct determination of contact angle on clean glass plates treated with hexamethyldisilazane. The results of these measurements are presented in Table II.

TABLE II

WETTABILITY OF THE SUPPORTS AND GLASS PLATES

Support	*Stationary phase*		
	Squalane	*DNP*	*PEG-300*
	Cosines of contact angle		
A	0.14	0.24	0.94
B	1.00	0.63	0.16
	Contact angle (degrees)		
Glass plates	2.0	8.0	12.0
Modified glass plates	12.0	12.0	25.0

Non-polar and slightly polar liquid phases wet the modified support surface well. The hydrophobic surface obtained by treatment with hexamethyldisilazane is wetted most by squalane (a saturated hydrocarbon). Dinonylphthalate also wets this surface well, as its molecules contain large alkyl groups. The surface of unmodified Porochrom is hydrophilic, and consequently it is wetted by polyethylene glycol containing many polar ether and hydroxyl groups.

Evidently, for chromatographic separations on non-polar or slightly polar liquid phases, it is expedient to use homogeneous macroporous diatomaceous supports treated with hexamethyldisilazane. For chromatographic separation on polar liquid phases, a support with weakly adsorbing but hydrophilic surface should be utilized. We used 2-aminopropyltriethoxysilane as a modifying agent[2]. A sufficiently chemically homogeneous hydrophilic surface of the support is formed as a result.

Our investigations have shown that such a surface is wetted well by both squalane and PEG-300. The relative cosine of the contact angle (impregnation meth-

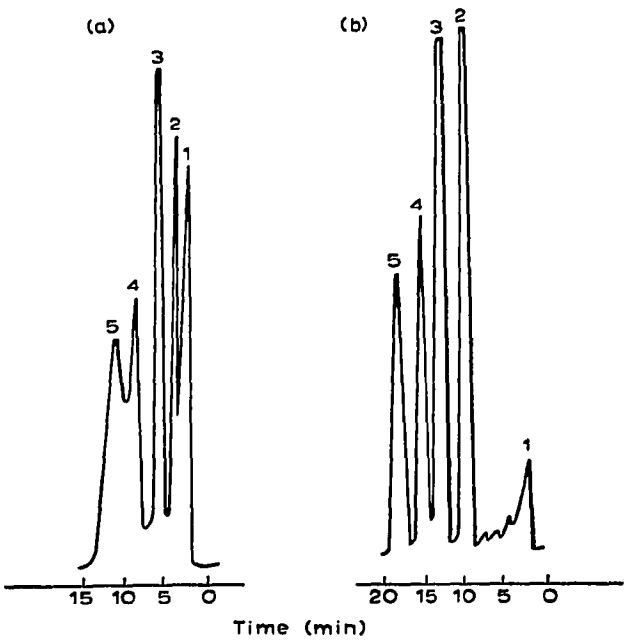

Fig. 3. Chromatograms of pesticides (isomeric hexachlorocyclohexanes) on SE-30 and OV-17 deposited on (a) Porochrom I and (b) Porochrom I treated with 2-aminopropyltriethoxysilane. 1 = hexane; 2 = α-hexachlorocyclohexane; 3 = γ-hexachlorocyclohexane; 4 = β-hexachlorocyclohexane; 5 = δ-hexachlorocyclohexane.

od) on the unmodified sample A is 0.14 for squalane, 0.24 for DNP and 0.94 for PEG-300, while on sample B, treated with 2-aminopropyltriethoxysilane, it is 0.9, 0.8 and 0.8, respectively. The contact angle on a clean glass surface is 2 for squalane, 8 for DNP and 12 for PEG-300, while on the amine-modified surface it is 9, 8 and 10, respectively. Therefore, all of the liquid phases, independent of their polarity, wet such a surface well.

Chromatograms of the separation of some pesticides on samples A and B with stationary phases of different polarity (SE-30 and OV-17) are given in Fig. 3. A comparison of the chromatograms shows that hexachlorocyclohexane isomers are separated well on the polar phase when using a support treated with 2-aminopropyltriethoxysilane, which creates a hydrophilic surface.

CONCLUSIONS

For chromatographic separations on non-polar and slightly polar liquid phases, it is expedient to utilize supports with a hydrophobic surface, which are wetted well by these stationary phases. For polar liquid phases, the use of a hydrophilic support surface is necessary. Porochrom I has very similar properties to those of Chromosorb W.

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