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GAS AND LIQUID CHROMATOGRAPHY ON SILOCHROM MODIFIED WITH A SURFACE FILM OF MELONE*

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SUMMARY

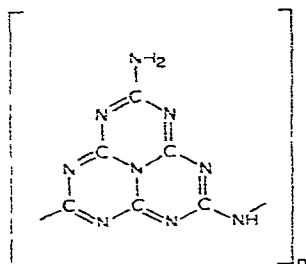
The chromatographic properties of the adsorbent obtained by polymerization of melamine previously adsorbed on the surface of a homogeneous macroporous adsorbent, Silochrom C-80, have been investigated. The product of polymerization is melone, which forms a film on the silica surface. The chromatographic properties of melone-Silochrom adsorbent were compared with the properties of pure Silochrom and the polymer Porapak-T. The melone-Silochrom adsorbent has a comparatively greater specificity. Melone film has an extremely high thermal stability (up to 600°) and is insoluble in common solvents. This makes melone-silica adsorbents suitable not only for gas chromatography but also for liquid chromatography. Examples of chromatographic separations on melone-Silochrom adsorbents of various mixtures (from gases to polynuclear aromatic compounds) are given.

INTRODUCTION

Of the silica adsorbents used in chromatography, arosilogels¹ (commercial name: Silochroms²) possess the most geometrical homogeneity. In particular, Silochrom C-80, with a high specific surface area ($s = 80 \text{ m}^2/\text{g}$), has a narrow distribution of pore volumes, the mean effective pore diameter being *ca.* 500 Å. Consequently, Silochrom can be used not only as the adsorbent itself but also as an adsorbent-support for thin films of different organic substances. This permits us to obtain geometrically homogeneous adsorbents with chemically different surfaces. Silochrom has been used as an adsorbent-support of monolayers of molecules and macromolecules^{3,4}, and the chemical binding of polymer liquids with silica gel surfaces has also been described⁵⁻⁸. In this paper, a new adsorbent was studied, consisting of a melone polymer film synthesized from melamine directly on the surface of a macroporous adsorbent-support, Silochrom C-80. Melone is thermally stable up to 600°

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and is insoluble in water, acids and organic solvents. Therefore, adsorbents modified with a surface melone film can be used in both gas chromatography and liquid chromatography. Melone has the following structural unit:



It was assumed that a positive charge is localized on the central nitrogen atom⁹. Therefore, an adsorbent with a melone film on its surface is a specific adsorbent¹⁰, but this specificity is influenced by interactions with the hydroxyl groups of the Silochrom surface.

EXPERIMENTAL

Melamine (20%, w/w, of Silochrom) is dissolved in boiling water and the required amount of Silochrom is added to the solution while vigorously stirring the mixture. Water is removed by evaporation, then the adsorbent is placed in a muffle furnace at 470° where the polymerization of adsorbed melamine into melone takes place immediately.

RESULTS AND DISCUSSION

Fig. 1 shows that Silochrom with the melone surface film was more effective than pure Silochrom. For melone-Silochrom adsorbent, the curve is not only lower but at high u values it is flatter than the corresponding curve for pure Silochrom. This indicates that the mass exchange proceeds considerably more easily with the modified adsorbent. Probably, pores of smaller sizes being present to a small extent

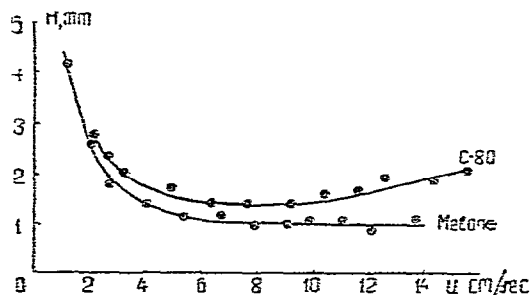


Fig. 1. Dependence of HETP (H) on gas flow-rate (u) for benzene at 150°. 1-m column with Silochrom C-80 covered with melone film, granule size 0.20-0.25 mm.

on the adsorbent-support were filled with melone and the adsorbent surface became geometrically more homogeneous. The decrease in specific surface area from 80 to 63 m²/g supports this explanation.

In order to compare the chromatographic properties of melone-Silochrom adsorbent with those of pure Silochrom, the retention indices of a standard set of substances were measured and the relative polarity of the adsorbent was calculated in accordance with the Rohrschneider method¹¹. It is clear from Table I that the relative polarity of the melone-Silochrom adsorbent is rather high, for benzene and ethanol being even higher than the relative polarity of pure Silochrom. Table II gives the values of retained volumes per unit surface area of melone-Silochrom adsorbent, $V_{A,1}$, at 150° for substances whose molecules belong to *A* and *B* groups in terms of their ability to undergo non-specific and specific intermolecular interactions, respectively¹⁰.

TABLE I

KOVÁTS RETENTION INDICES AT 100° (I^{100}) OF SUBSTANCES ON SQUALANE, SILOCHROM C-80 AND MELONE FILM ON SILOCHROM C-80

Relative adsorbent polarity, $\Delta I = (I_{\text{adsorbent}} - I_{\text{Squalane}})/100$.

Substance	I^{100}			ΔI	
	Squalane	Silochrom	Melone-Silochrom	Silochrom	Melone-Silochrom
Benzene	649	663	680	0.14	0.31
Ethanol	384	918	948	5.34	5.64
Methyl ethyl ketone	531	1081	996	5.50	4.65
Nitromethane	457	780	797	3.23	3.40
Pyridine	695	1374	1158	6.79	4.63

TABLE II

RETENTION VOLUMES ($V_{A,1}$) PER UNIT SURFACE AREA OF SUBSTANCES AT 150° ON A COLUMN WITH MELONE FILM ON SILOCHROM C-80 ADSORBENT

Adsorbate	$V_{A,1}$ (μm)	Adsorbate	$V_{A,1}$ (μm)
<i>n</i> -Pentane	0.032	<i>n</i> -Propylbenzene*	0.690
<i>n</i> -Hexane	0.063	<i>n</i> -Butylbenzene*	1.425
<i>n</i> -Heptane	0.120	<i>o</i> -Xylene*	0.542
<i>n</i> -Octane	0.242	<i>m</i> -Xylene*	0.449
<i>n</i> -Nonane	0.411	<i>p</i> -Xylene*	0.457
<i>n</i> -Decane	0.792	Mesitylene*	0.887
Heptene-1*	0.157	Durene*	2.195
Cyclopentane	0.043	Acetonitrile*	0.284
Cyclohexene*	0.089	Thiophene*	0.104
Cyclohexane	0.066	Methyl propionate*	0.782
Benzene*	0.108	Methyl ethyl ketone*	0.938
Toluene*	0.241	Perfluorooctane	0.136
Ethylbenzene*	0.442	Perfluorobenzene*	0.120

* Belonging to *B* group (see text).

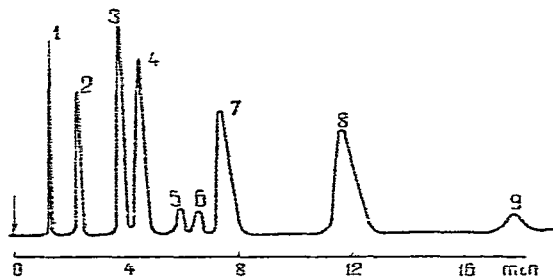


Fig 2. Chromatogram of monoalkyl- and polymethylbenzenes on a 1.125-m column with melone-Silochrom adsorbent at 150°. Carrier gas: helium, flow-rate 24 ml/min. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *o*-xylene; 5 = isopropylbenzene; 6 = *n*-propylbenzene; 7 = mesitylene; 8 = *n*-butylbenzene; 9 = *c*urene.

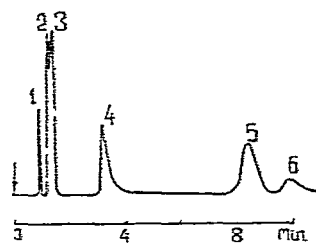


Fig 3. Chromatogram of separation of different classes of substances with similar boiling points on a 1.125-m column with melone-Silochrom adsorbent at 150°. Carrier gas: helium, flow-rate 30 ml/min. 1 = Cyclohexane, 2 = thiophene; 3 = benzene; 4 = acetonitrile; 5 = methyl propionate; 6 = methyl ethyl ketone.

$V_{A,1}^{150^\circ}$ values for the molecules of these groups are not high and unsaturated compounds are retained more strongly than saturated compounds and fluorinated compounds more strongly than non-fluorinated compounds. These values illustrate the considerable contribution of specific interactions to the total energy of the adsorbate-melone-Silochrom interaction.

Fig. 2 shows the chromatogram of polymethylbenzenes and monoalkylbenzenes. Monoalkylbenzenes are retained much more weakly than the polymethylbenzenes, as occurs also on graphitized carbon black¹².

When separating mixtures of different classes of substances that have similar boiling points (Fig. 3), substances with an ether-oxygen and especially those with keto-groups are retained more strongly.

Table III gives a comparison of the differential molar changes of internal energy (heats of adsorption). $-\Delta U_1 = q_{v,1}$ (ref. 13), at small (zero) sample size (surface coverage) for several inorganic and hydrocarbon gases on the melone-Silochrom adsorbent and on Porapak-T. The results obtained show that the chromatographic properties of the melone-Silochrom adsorbent have considerable advantages over those of Porapak-T, *i.e.*, at substantially lower total energy values of adsorbate-adsorbent intermolecular interaction, stronger specific interactions take place with melone-Silochrom.

Melone-Silochrom adsorbent can be recommended for use in the separation and analysis of *A* and *B* group substances. Figs. 4 and 5 give the examples of chromatograms. Fig. 4 shows the chromatogram for the separation of C_1 - C_4 hydrocarbons, including isomers. Fig. 5 shows the chromatogram of halothane, a new narcotic substance used in medicine. The percentage of impurity in it should not exceed 0.01%. The asymmetric isomer of halothane is the most difficult to separate and to determine. The isomers and other impurities were well separated on a 2.5-m column with melone-Silochrom adsorbent at 80°.

In principle, it is possible to produce melone-Silochrom adsorbents with specific surface areas from several to several hundred square metres per gram, because their specific surface areas are largely defined by the adsorbent-support surface,

TABLE III

ΔU_1 VALUES FOR SOME INORGANIC AND HYDROCARBON GASES ON MELONE FILM ON SILOCHROM C-80 AND PORAPAK-T

Adsorbate	ΔU_1 (kJ/mole)	
	Melone (21%, w/w) on Silochrom C-80 ($s = 63 \text{ m}^2/\text{g}$; $d = 500 \text{ \AA}$)	Porapak-T ($s \approx 250 \text{ m}^2/\text{g}$; $d \approx 90 \text{ \AA}$)
CO ₂	23.1	25.1
H ₂ S	20.6	28.4
SO ₂	27.6	38.0
N ₂ O	20.8	24.3
CH ₄	9.6	17.7
C ₂ H ₂	22.9	30.5
C ₂ H ₄	16.7	24.7
C ₂ H ₆	13.6	25.1
C ₃ H ₆	25.2	32.6
C ₃ H ₈	22.3	32.2
<i>n</i> -C ₄ H ₈	31.5	36.4
<i>i</i> -C ₄ H ₈	31.8	37.6
<i>n</i> -C ₄ H ₁₀	28.8	36.4
<i>i</i> -C ₄ H ₁₀	27.7	34.7

which is easy to change over a large range. Owing to their thermal stability up to 600° they can be used for the separation of the substances that have *A* and *B* group molecules, and from gases to high-boiling liquids and solids. Figs. 6 and 7 give examples of applications of melone-Silochrom adsorbent at high column temperatures.

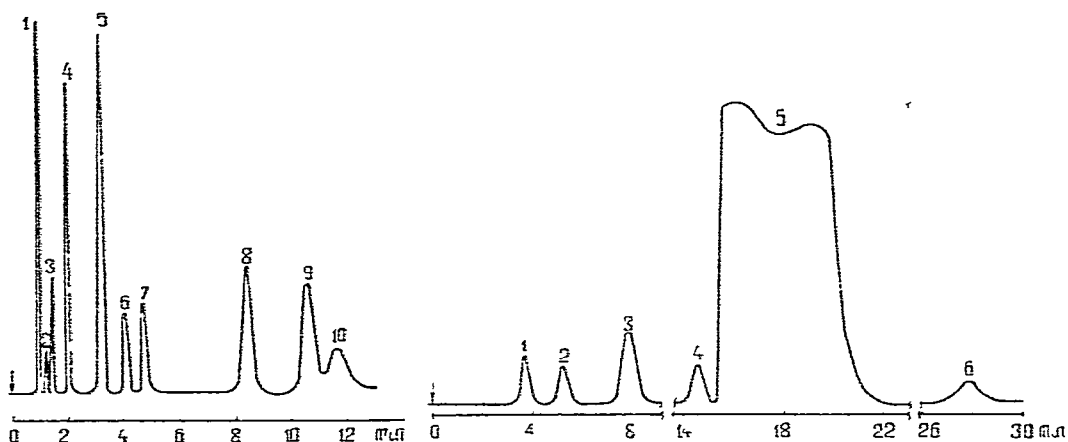


Fig. 4. Chromatogram of C₁-C₄ hydrocarbon gases on a 2-m column with melone-Silochrom adsorbent at 25°. Carrier gas: helium, flow-rate 35 ml/min. 1 = methane; 2 = ethane; 3 = ethylene; 4 = propane; 5 = propylene; 6 = isobutane; 7 = *n*-butane; 8 = isobutene; 9 = butene-1 + *trans*-butene-2; 10 = *cis*-butene-2.

Fig. 5. Chromatogram of halothane and its impurities on a 2.5-m column with melone-Silochrom adsorbent at 80°. Carrier gas: nitrogen, flow-rate 16 ml/min. 1 = 1,2,2-Trifluoro-1,1,2-trichloroethane; 2 = 1,2-dibromotetrafluoroethane; 3 = chlorallylene (internal standard); 4 = 1,1,2-trifluoro-2-chloro-1-bromoethane; 5 = 1,1,1-trifluoro-2-chloro-2-bromoethane (halothane); 6 = 1,1,1-trifluoro-1,2-dibromochloroethane.

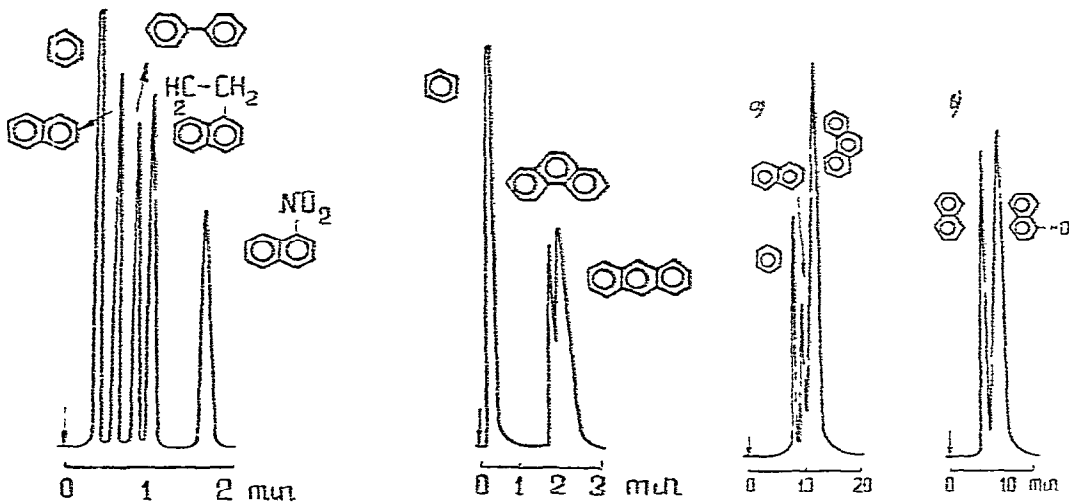


Fig. 6. Chromatogram of separation of benzene, naphthalene, diphenyl, acenaphthene and α -nitronaphthalene on a 1.125-m column with melone-Silochrom adsorbent at 320°. Carrier gas: helium, flow-rate 45 ml/min.

Fig. 7. Chromatogram of phenanthrene and anthracene on a 1.125-m column with melone-Silochrom adsorbent at 340°. Carrier gas: helium, flow-rate 45 cm/min.

Fig. 8. Example of application of melone-Silochrom adsorbent in liquid chromatography. Column, 0.5 m, temperature, 25°. (a) *n*-Hexane eluent, flow-rate 0.5 ml/min; (b) chloroform eluent, flow-rate 0.5 ml/min.

Fig. 8 shows that the melone-Silochrom adsorbent is also effective in liquid chromatography.

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