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SILOCHROMS AS ADSORBENTS AND SUPPORTS IN LIQUID CHROMATOGRAPHY*

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SUMMARY

The use of macroporous silica gels, silochroms, with homogeneous geometrical structure as adsorbents and supports for liquid stationary phases in liquid chromatography is described.

The selectivity of separation and retention volumes of silochroms depend strongly on the degree of hydroxylation of the surface and on the nature of the mobile phase. In optimizing the parameters, rapid and complete separation of strongly polar isomers and biological active substances and drugs is obtained.

The dependence of retention volumes and column efficiency on the amount of liquid phase, covered on silochrom, has been investigated.

INTRODUCTION

It is known that rapid and complete separation in liquid chromatography can be obtained on macroporous[1] and surface porous[2,3] or porous-layer[4,5] sorbents. On such sorbents, mass transfer is more rapid, which allows the use of high speeds in the mobile phase and so reduces the time required for analysis. From this point of view, adsorbents such as commercial macroporous silica, aerosilogels prepared from aerosil, are preferable. These adsorbents are known as silochroms[6], and their impurity content is less than 0.1%. Their geometrical homogeneity is high, with a rather large pore volume. A study of silochroms as adsorbents and liquid-phase supports in liquid chromatography is of great interest. The use of silochroms as adsorbents and supports for inorganic salts has been partially investigated earlier[2].

EXPERIMENTAL

Some measurements were made on a laboratory chromatograph equipped with a UV detector and a liquid plunger pump. The separation of steroids and drugs was carried out on a DuPont 820 liquid chromatograph. Samples of steroids and drugs were obtained from Botkin's Hospital, Moscow.

Silochroms were used as adsorbents; their structural properties are given in Table I.

* This paper completes the series of papers which were presented at the 4th Russian–Italian Symp. in Memory of M. S. Tswett and were published in *J. Chromatogr.*, 77 (1973).

TABLE I

STRUCTURAL PROPERTIES OF SILOCHROMS

Type	*Specific surface area, S (m^2/g)*	*Pore diameter (Å)*
Silochrom-1	15–20	1000–1500
Silochrom-2	40–60	650–900
Silochrom-3	80–115	400–600
Silochrom C-80	80	500

Hydroxylation of silochroms was carried out by boiling them in water for two days, and dehydroxylation by heating them at 800–900° for 6–8 h.

Commercial solvents were used as eluents without preliminary treatment.

Columns were packed in the usual manner with small amounts of sorbent by tapping and vibrating them.

The silochrom was covered with the liquid stationary phase (β,β'-oxydipropionitrile) by mixing known amounts of adsorbent with calculated amounts of liquid stationary phase dissolved in methanol, followed by evaporation of the alcohol and mixing and drying for 1 h at 60°.

RESULTS AND DISCUSSION

The adsorption properties of hydroxylated and dehydroxylated surfaces of silica gels differ greatly, especially with strongly polar substances. This effect is also observed in liquid chromatography when non-polar and weakly polar phases are used.

Fig. 1 shows the differences in the chromatograms of α-naphthylamine obtained on hydroxylated and dehydroxylated silochroms. The retention volume and the selectivity of separation (relative to impurities) are greater on hydroxylated than on dehydroxylated silochrom. However, highly polar multifunctional compounds have considerably greater retentions on hydroxylated silochrom, so that in some instances partially or completely hydroxylated silochrom proved to be useful in reducing the time required for analysis.

Fig. 2 shows the separation of dihydroxybenzene isomers on dehydroxylated (about 80%) silochrom-1.

In liquid chromatography retention volumes may vary with changes in the elution ability of the mobile phase. To shorten considerably the time required for analysis when separating polar compounds of high molecular weight on silochrom, polar mobile phases should be used.

Fig. 3 shows the separation of steroids over a relatively short period. Elution is carried out with a mixture of chloroform and ethanol as the mobile phase. The separation of such steroids in gas chromatography presents some difficulties. Usually, they are separated as derivatives. In this case, the time required for analysis is comparable with that in gas chromatography. In some instances, separation can be achieved in liquid chromatography in a shorter time than in gas chromatography. For example, the liquid chromatographic separation of drugs (papaverine and

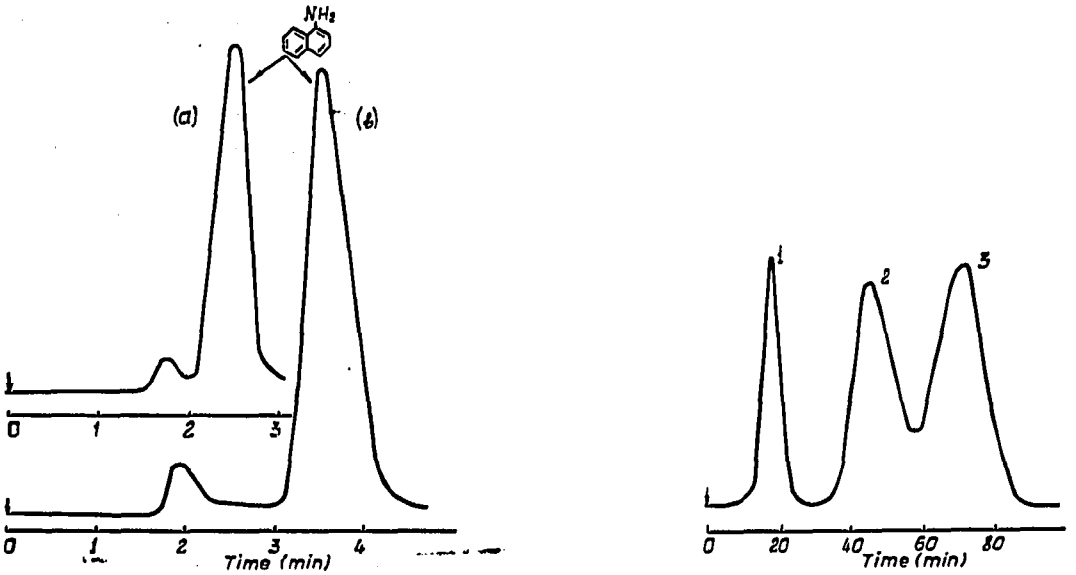


Fig. 1. Chromatogram of α-naphthylamine on (a) dehydroxylated and (b) hydroxylated silochrom C-80. Column, 100 × 0.21 cm; eluent, benzene, 1.3 ml/min.

Fig. 2. Chromatogram of dihydroxybenzene isomers on dehydroxylated silochrom-1. Column, 15 × 0.6 cm; eluent, carbon tetrachloride, 0.5 ml/min. (1) *ortho*-; (2) *meta*-; (3) *para*-dihydroxybenzene.

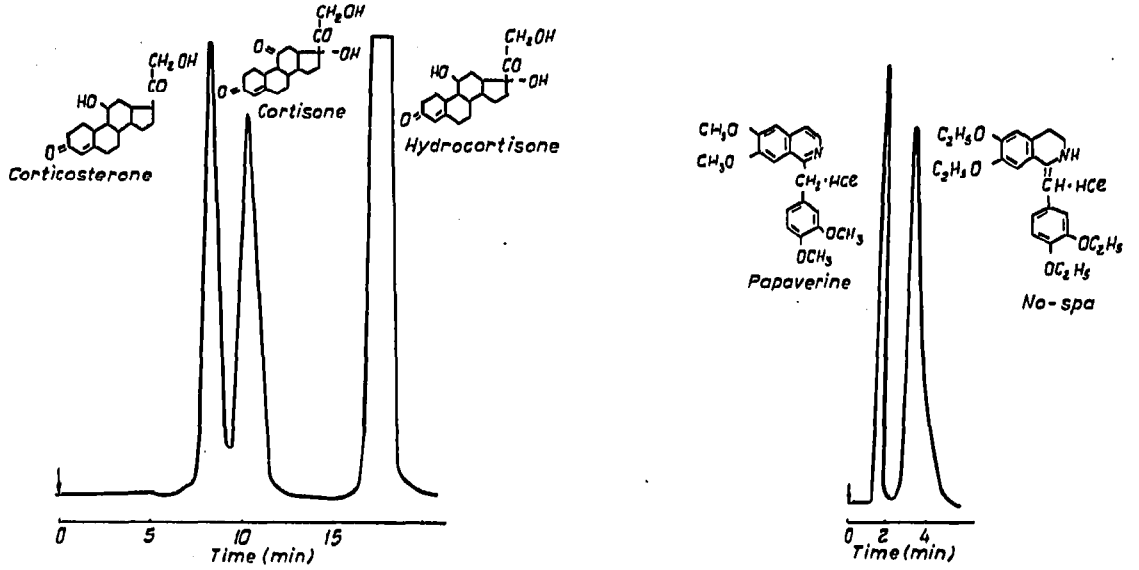
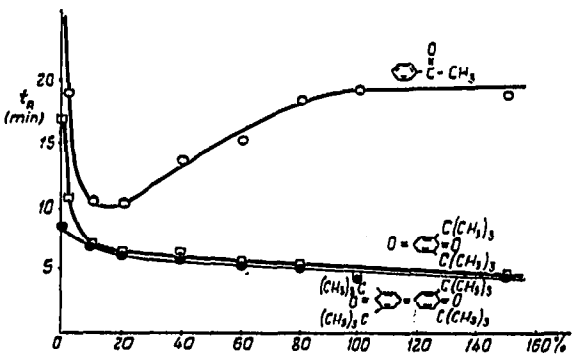


Fig. 3. Chromatogram of steroids on silochrom C-80. Column, 100 × 0.21 cm; eluent, chloroform + 3% ethanol, 0.33 ml/min, 22°.

Fig. 4. Chromatogram of papaverin and no-spa on silochrom C-80. Column, 100 × 0.21 cm; eluent, chloroform + 5% ethanol, 1.5 ml/min, 22°.

no-spa) can be carried out in 5 min (Fig. 4), while by gas chromatography it takes 30–40 min.

Various types of active sites are possible on the surface of partially hydroxylated silochrom, due to free, bound and geminal hydroxyl groups and also to siloxane groups[7]. In some instances, in order to increase chemical homogeneity it is useful to deposit stationary liquid phase on the silochrom surface. Fig. 5 shows the dependence of retention time for three compounds on the amount of β,β'-oxydipropio-



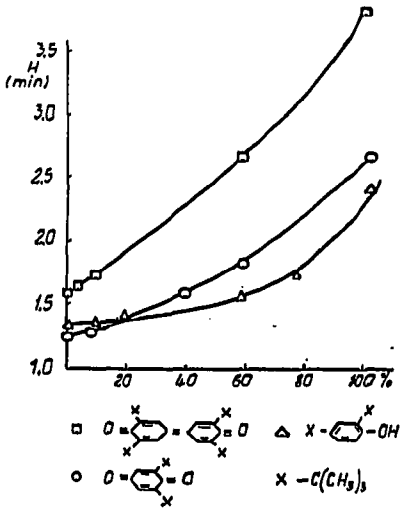


Fig. 5. Dependence of retention times of the compounds on the amount of stationary liquid phase. Column, 50 × 0.3 cm; eluent, hexane, 22°.

Fig. 6. Dependence of HETP on the amount of stationary liquid phase. Conditions as in Fig. 5.

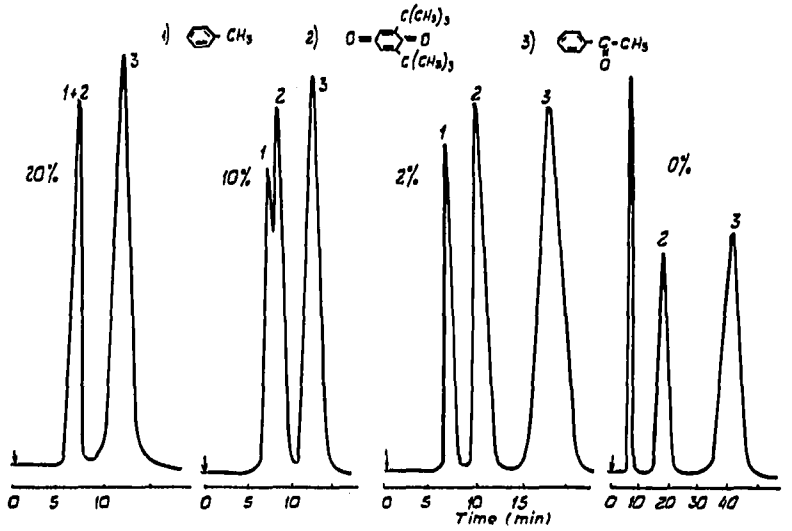


Fig. 7. Comparative chromatograms of compounds on silochrom C-80 with different amounts (0, 2, 10 and 20%) of stationary liquid phase.

nitrile covering the silochrom surface. A minimum in this dependence curve is observed for acetophenone in the range of 10–20 % of β,β'-oxydipropionitrile relative the weight of silochrom. This minimum corresponds approximately to the capacity of the monolayer. For the two other compounds, an increase in retention time with increase in the amount of liquid phase is not observed, probably because these compounds are weakly dissolved in β,β'-oxydipropionitrile and adsorption occurs mainly on the surface of the liquid film. Fig. 6 shows the variation of the HETP obtained on a column filled with various amounts of liquid phase. In all instances, with an increase in the amount of the liquid, the efficiency of the column decreases owing to slower inner mass transfer. The selectivity of separation increases with a decrease in the amount of the liquid phase. However, this results in an increase in the time required for analysis. In order to shorten the time required for separation, it is therefore useful to use silochrom with 2 % of liquid phase (Fig. 7). Molecules of the polar stationary liquid phase are strongly adsorbed on the most active sites of the surface and thus block them. The addition of small amounts of liquid phase on to the surface of silochrom (less than monolayer capacity) improves the energetic homogeneity. Such amounts of liquid phase are strongly retained by the surface, so that columns with such adsorbents are stable in relation to time.

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