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Note

Selective monomolecular layers for improved wettability of glass capillary columns for gas–liquid chromatography

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The potential of high-resolution glass capillary columns in biochemical analysis is now widely recognized. In spite of advances obtained recently in the analysis of complex mixtures of labile compounds, the experimental difficulties associated with the preparation of such columns, together with their limited commercial availability at present, prevent their wider use.

The poor wettability of glass surfaces with organic liquids has been recognized for many years as a key problem in the preparation of highly efficient and stable glass capillary columns. Surface phenomena associated with the wettability of glass had been the subject of fundamental studies[1,2] long before becoming topical in the preparation of chromatographic columns. With the exception of liquid paraffins and polydimethylsiloxanes, which spread freely on the high-energy glass surface, no stable homogeneous films of other organic liquids of chromatographic interest could be obtained. As an increase in the specific surface area of solids is a general method of decreasing the contact angles of wetting liquids, carbonization of the inner capillary wall[3] and gas-phase etching[4,5] have achieved a certain measure of success with many stationary phases and diverse analytical problems. From experimental evidence[4–6], we have postulated[7] that chemical similarities between the wall of a glass capillary and the stationary phase are also important for homogeneous spreading. Therefore, suitable chemical modifications of surface silanol groups may lead to improved properties of glass capillary columns. Furthermore, two additional reasons for the importance of a chemical compatibility between the surface and the stationary phase may be quoted:

(1) Although low values of contact angles of liquids on the glass surface are essential for the spreading effect, a rearrangement of the coated film may nevertheless take place during use of the column, thus resulting in loss of efficiency. This effect is less marked with suitably modified surfaces, as verified by the recent experiments of Bartle[8].

(2) Recent (non-chromatographic) work by Shafrin and Zisman[9] can be interpreted to show that for low-energy surfaces (including chemically treated glass)

the temperature dependence of *surface* critical surface tension (γ_c) and of *liquid* surface tension (γ) are comparable, only if surface and liquid are chemically similar. A decrease in γ_c for the surface with increasing temperature is matched by a corresponding decrease in γ for the liquid. This is of particular concern here, as high-temperature operation and temperature programming are common in high-resolution gas–liquid chromatography.

The basic modification methods for the silanol groups of glass were discussed by one of us in review article[7]. The model of a monomolecular layer compatible with the stationary phase is shown in Fig. 1. In order to comply with the requirements for stability of such monomolecular layers, the use of silane compounds seems to be the only realistic approach. For instance, the formation of a hydrophobic monolayer is easily accomplished through trialkylsilylation of the glass surface. However, only moderate chromatographic efficiencies with commercially available mono- and disubstituted chlorosilanes can be obtained[6,10], even though the contact angles of stationary phases are reduced[8]. This is presumably due to the polymerization of these compounds on the glass surface and the formation of films of resinous consistency[11]. We have, consequently, chosen monochlorosilanes for further studies of surface modification, as only monomolecular surface coverage is likely in this case.

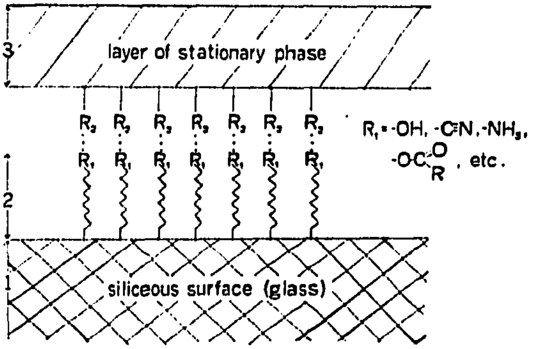
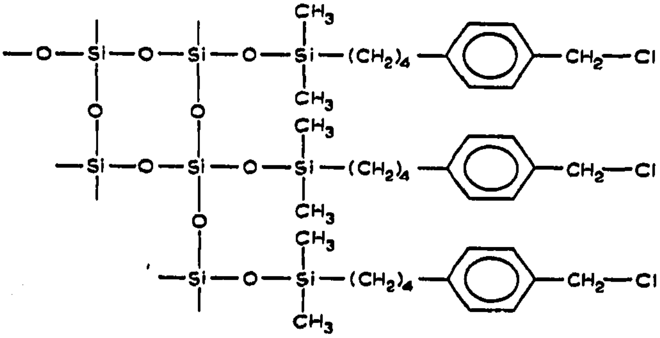


Fig. 1. Model of chemically compatible surface structures. 1 = Part of the glass silica framework, 2 = monolayer possessing a selective group R_1, 3 = layer of stationary phase possessing R_2, which is chemically compatible with R_1.

Monochlorodimethyl-[3-(4-chloromethylphenyl)butyl]silane, synthesized recently by one of us[12], proved to be the most versatile reagent owing to a large number of possibilities for chemical modification of the terminal $-CH_2-Cl$ group.



Hence, hydroxy groups can easily be generated by hydrolysis with a slightly alkaline solution, cyano groups can be introduced into the surface structures by reaction with potassium cyanide, while esters can be prepared from the hydroxy monolayers by further action of an acyl chloride, etc. Many further selective modifications based on this and similar silanes seem worth exploring. The reaction between glass and allyldimethylchlorosilane followed by the oxidation of the double bond in the side chain is another route to the preparation of selective monolayers.

Different combinations of selective treatments and stationary phases studied in this work proved the validity of our compatibility concept. High chromatographic efficiencies (1500 to 4000 theoretical plates per meter) have been obtained with a number of systems of different polarities using both previously etched[4,5] and untreated glass capillaries. Stationary phases such as polyethylene and polypropylene glycols as well as various polyesters yielded regular and efficient films on a surface provided with hydroxy and ester groups. An example of the results from such a column can be seen in Fig. 2. In a similar fashion, stationary phases that possess cyano groups in their molecules (*e.g.*, cyanoethyl silicone or 2-cyanoethyl ether) showed the increased wettability of the glass capillary walls which were modified with a cyano monolayer, thus forming stable and homogeneous films instead of commonly observed droplets. While in some cases thin films of stationary phases can be spread uniformly on the monolayers formed on unetched surfaces, the combination of increased specific surface area and the selective chemical modification is mostly desirable. More rigorous correlations between the surface monolayer chemistry of glass capillaries and contact angles of organic liquids are under investigation[13] in order to prepare efficient columns of a controlled film thickness and capacity.

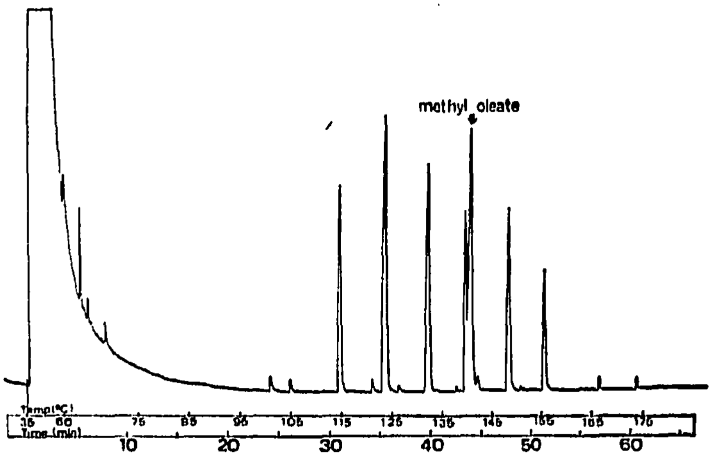


Fig. 2. Chromatogram of C_{15}–C_{20} fatty acid methyl esters (major constituents) on a glass capillary column provided with a hydroxy monolayer on unetched glass and coated with 3% STAP (a modified Carbowax obtained from Supelco, Bellefonte, Pa., U.S.A.). Column: 12 m × 0.3 mm I.D.; sample injected without splitting.

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