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SURFACE MODIFICATION OF GLASS CAPILLARIES BY HIGH-TEMPERATURE SILYLATION

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SUMMARY

High-temperature silylation (HTS) on leached glass capillaries is a highly effective deactivation method for preparing neutral and inert surfaces. Several silylating agents such as disilazanes and disiloxanes containing different alkyl groups and phenyl groups were prepared and investigated for their usefulness in HTS. The conditions of the procedure, especially the influence of the amount of silylating agent, were examined. It was found that most of the reagents are suitable for use in HTS in achieving very low adsorption activities of the treated glass surface. With increasing chain-length or number of phenyl groups in the reagent, not only was a change of critical surface energy of the treated glass capillaries effected but also a better wettability for numerous stationary phases was observed.

INTRODUCTION

In 1977 a method for the silylation of glass capillary columns by the use of pure hexamethyldisilazane (HMDS) at temperatures around 300°C was introduced[1], giving capillaries of very low surface activity. The method was further developed by Grob *et al.*[2,3]. It was shown that silylation at 400°C applied after prior leaching of the glass surface for the removal of metal ions yields truly neutral, highly inert glass capillary columns. Thus the chromatographic separation of practically all volatile substances, independent of their chemical nature, became possible. This silylation procedure, called "persilylation" by Grob *et al.*[2] and "high temperature silylation (HTS)" by Verzele's group[4], respectively, was studied and modified by other authors[5–7].

After HTS with HMDS the surface energy is too low to be able to use other than methylsilicone stationary phases. Further experiments showed that application of silylating agents other than HMDS yielded inactive surfaces with better wettability for medium-polar stationary phases[1,8–10].

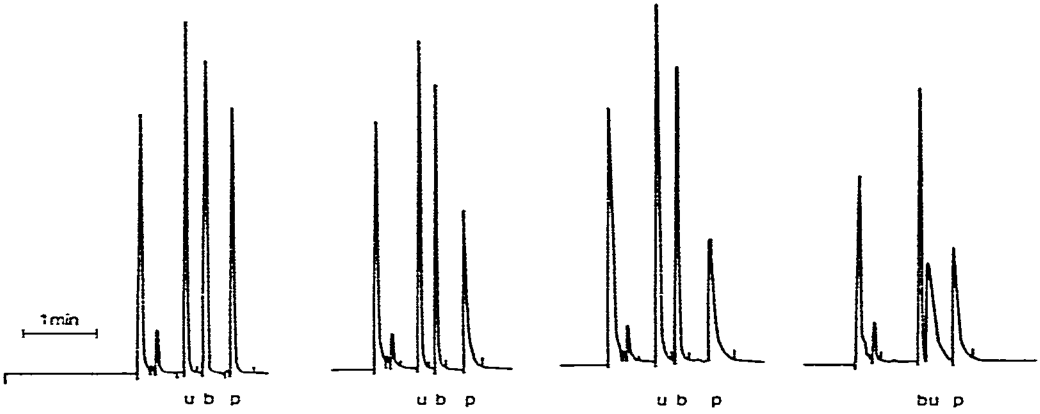
In this paper some investigations of the influence of alkyl and phenyl substituents in silylating agents on the deactivation and surface energy of soda-glass capillaries are reported.

TEST CRITERIA FOR GLASS CAPILLARIES

The glass capillaries modified in these experiments were distinguished by their adsorption activity and critical surface energy.

The adsorption activity was determined using the arrangement of a separation and test capillary proposed by Schomburg *et al.*[11]. The activity was evaluated by comparing the peak shapes and areas for three compounds of different polarity.

After an appropriate split injection, 5–11 ng of *n*-undecane, 1-butanol and pyridine entered the test capillary. On the basis of the peak shapes and areas four types of chromatograms can be distinguished; these are shown in Fig. 1. The relationships between the areas in the different types of chromatograms also given in Fig. 1 indicate the extent of irreversible adsorption. For instance for type B a loss of 0.1 ng of butanol and 0.25 ng of pyridine may be recognized. During the experiments it was found that relatively long (>5 m) test pieces should be used as even a very low bleeding of the primary column may produce additional deactivation of the test capillary giving misleading results.



Type	A	B	C	D
A_r:	u 1.00	u 1.00	u 1.00	u 10
	b 1.00±0.01	b 1.00±0.02	b 0.90±0.05	
	p 1.00±0.02	p 0.90±0.05	p 0.75±0.10	

Fig. 1. Test chromatograms indicating different degrees of adsorption activity of uncoated capillaries. u = *n*-undecane, b = 1-butanol, p = pyridine. A_r = ratio of areas (relative to *n*-undecane) after the test column and after the pre-column. Columns: pre-column, soda glass (20 m × 0.26 mm); $BaCO_3$ pretreated; C 20 M deactivated; C 20 M coated. Uncoated test capillaries: soda glass (7 m × 0.26 mm), pretreated by HTS with (A) DDTLMDS, (B) DHTLMDO, (C) TPSA, (D) TPSO + NH_3 (in this case the amount of *n*-undecane in the test mixture was 10 times higher than in A, B and C). Conditions: oven temperature, 90°C; FID temperature, 180°C; carrier gas, nitrogen.

For the determination of critical surface energies, the contact angles of various liquids (Fig. 2) were measured using the capillary-rise method[12,13]. Pretreated capillary coils, sealed under vacuum, were broken and dipped into the liquid at 20°C in a position such that the "chord" between both capillary ends was perpendicular to the surface of the liquid. After 30 min in the liquid, the height of the meniscus above the liquid surface was measured with a cathetometer. The error resulting from coiled capillaries is low provided that the meniscus height is less than 20% of the circum-

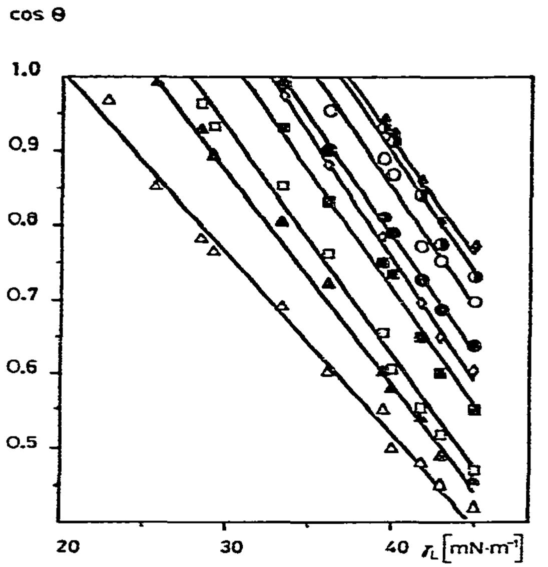


Fig. 2. Zisman plots for glass capillary surfaces modified by the following organosilyl groups: trimethyl- (△), butyldimethyl- (▲), hexyldimethyl- (□), decyldimethyl- (■), octadecyldimethyl- (◇), phenyldimethyl- (●), diphenylmethyl- (○), triphenyl- (◑), and octadecyldiphenyl- (◆). Liquids used for measurements [surface tension (mN/m) and density (g/cm) at 20°C, respectively, in parentheses]: ethanol (22.8, 0.803), tetrachloromethane (25.8, 1.594), toluene (28.4, 0.871), ethylbenzene (29.2, 0.867), chlorobenzene (33.3, 1.104), bromobenzene (36.2, 1.493), iodobenzene (39.3, 1.820), benzaldehyde (39.9, 1.048), nitrobenzene (41.8, 1.205), aniline (43.0, 1.026), quinoline (45.0, 1.096).

ference of the coil. The inner diameter of the capillaries was determined by a measuring microscope.

The critical surface energy was determined in spite of the fact that it is difficult to draw direct correlations to the wettability for liquids (stationary phases) having widely differing structures. On the other hand, the values are well suited for the classification of glass capillary surfaces which have been HTS-modified by different organosilyl groups and can be used to rule out stationary phases which will definitely not exhibit any wetting characteristics.

SURFACE MODIFICATION

It was shown that, besides HMDS, reagents with considerably lower vapour pressures containing phenyl groups or other larger substituents can be used for HTS[1,8-10]. The investigation of further reagents of this type seemed promising.

Several disilazanes and disiloxanes, triphenylsilylamine and triphenylsilanol (listed in Table I) were prepared from dimethyldichlorosilane or diphenyldichlorosilane by Grignard reaction followed by ammonolysis or hydrolysis[14]. These compounds were investigated for their usefulness in HTS. Prior to this, the conditions for leaching and dehydration of glass capillaries, as well as the conditions for HTS given in the literature[3,4,15], were critically examined. The influence of the amount of silylating agent on the degree of deactivation was especially studied.

TABLE I

DEGREE OF ADSORPTION ACTIVITY AND CRITICAL SURFACE ENERGY OF SODA GLASS CAPILLARIES AFTER HTS-TREATMENT WITH DIFFERENT REAGENTS

Reagent	*Abbrevation/ additionally applied reagent*	*Adsorption activity (type in Fig. 1)*	*Critical surface energy (mN/m)*
Hexamethyldisilazane	HMDS	A...B	20.2
Di-*n*-butyltetramethyldisilazane	DBTMDS	A	25.8
Di-*n*-hexyltetramethyldisilazane	DHTMDS	A	27.7
Di-*n*-decyltetramethyldisilazane	DDTMDS	A	30.8
Di-*n*-octadecyltetramethyldisilazane	DOTMDS	A	32.7
Diphenyltetramethyldisilazane	DPTMDS	A	33.1
Tetraphenyldimethyldisilazane	TPDMDS	A	35.3
Triphenylsilylamine	TPSA	C...B	36.6
n-Octadecyldiphenylsilylamine	ODPSA	B	36.8
Di-*n*-hexyltetramethyldisiloxane	DHTMDO	B	27.9
Di-*n*-decyltetramethyldisiloxane	DDTMDO	B...A	
Triphenylsilanol	TPSO	C	
	DHTMDS + NH_3*	D...C	
	TPSO + NH_3*	D	

* After introducing the reagent, the capillary is flushed with a stream of nitrogen containing 10% (v/v) of ammonia.

Leaching, dehydration and HTS

For the soft glass used we can confirm the optimum leaching conditions suggested by Grob *et al.*[3,15]. Use of temperatures higher than those recommended (140–160°C) resulted in very active surfaces.

For dehydration, a static drying procedure, similar to that described by Grob *et al.*[3,15], was employed. This was found (at least for soda glasses) to be superior to drying in a stream of nitrogen at 300°C, as reported in ref. 4.

To achieve a high degree of deactivation by HTS the silylation has been performed at temperatures near 300°C for 20 h[1]. Other authors increased the reaction temperature to 400°C and were able to shorten the time to 4–10 h[2–4,10,15]. Because of the observed thermal decomposition of some of the compounds from Table I at 400°C we found a reaction temperature of 340°C for 13–14 h sufficient for complete deactivation (type A).

Amount of silylating agent

For introducing low-boiling reagents such as HMDS or DPTMDS into the capillaries a dynamic method was used[2,3]. Unfortunately in this case the exact amount of the introduced reagent is not known and is difficult to determine. Therefore introduction of a small amount of a high-boiling reagent was attempted by the static coating procedure[16], which offers the possibility of calculating the amount of introduced material in the capillary. Assuming five silanol groups per nm^2 on a leached and dehydrated glass surface, as has been reported for silica surfaces[17], the necessary concentration of reagent in the solution used for filling can, for complete reaction, be calculated from eqn. 1:

$$c_{\min} = \frac{\mathrm{MW}}{3dn} \cdot 10^{-4} \tag{1}$$

where $c_{\min}$ is the minimum concentration of the solution (mg/ml), MW the molecular weight of the reagent, d the inner diameter of the capillary and n the stoichiometric coefficient of the silylation reaction. This minimum concentration corresponds to a concentration of reagent of $8.3 \cdot 10^{-10}$ mol/cm^2.

To determine the concentration necessary for optimum deactivation, solutions of DDTMDS and TPDMDS in dried pentane with 2-, 5-, 10-, 20- or 100-fold minimum concentrations of the reagent were prepared and used for filling the capillaries by the static procedure. The adsorption tests showed no great differences in the activity of capillaries silylated at 2- to 20-fold minimum concentrations. All test chromatograms belonged to type A or B of Fig. 1. Repeated investigations showed a 10-fold excess to give the best deactivation (type A) with the highest reproducibility. This means that for the high-boiling reagents investigated such a large quantity as that described for HMDS in ref. 4 is not necessary.

Influence of the silylating agent on the properties of the capillaries

The capillaries were prepared and tested according to the principles described above.

The critical surface energies were obtained from the Zisman plots shown in Fig. 2. Table I includes the resulting critical surface energies and the degrees of adsorption activity. The dependence of the critical surface energy on the number of carbon atoms of the surface-bonded organosilyl group (n_C) is shown in Fig. 3. For organosilyl groups containing alkyl or phenyl substituents two separate curves are obtained. These show the possibilities and limitations of changing the critical surface

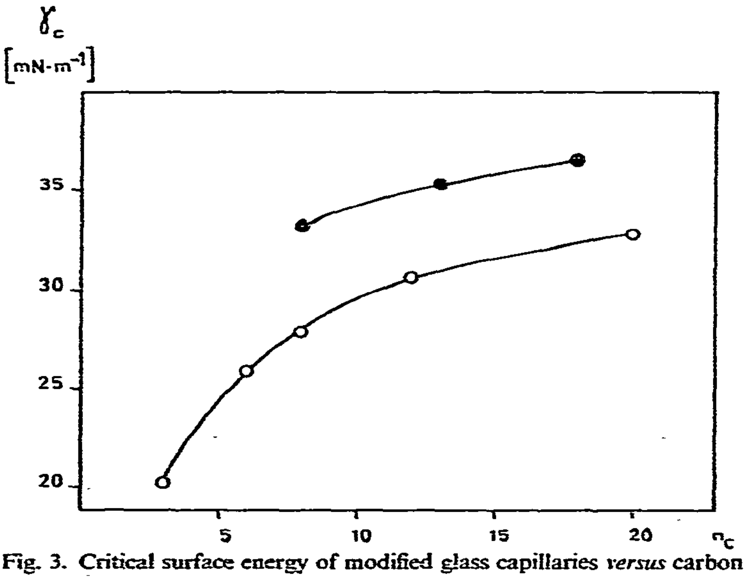


Fig. 3. Critical surface energy of modified glass capillaries *versus* carbon number (n_C) of the organosilyl groups, containing only alkyl (○) and phenyl (●) groups, respectively.

energy of a smooth, silylated glass surface by replacing alkyl or phenyl substituents in the reagent. It is easy to understand that a homologation starting from HMDS will first result in a steep slope, which becomes less steep with increasing chain length. The surface energy is not so strongly affected if, in reagents that already contain a phenyl group, a second or third phenyl group is introduced.

By homologation of the alkyl groups in reagents no marked improvement in wettability for medium-polar phases may be expected. However it was found that as the critical surface energy increases, there is a corresponding improvement in the wettability for the methylsilicone phases and very efficient capillaries have been produced. In addition to OV-1 and SE-52, Dexsil 300 forms uniform, stable films on DDTMDS modified glass capillaries, as illustrated in Fig. 4 which also demonstrates the degree of inertness achieved for very polar solutes. Our results on the wettability of capillaries modified with reagents containing phenyl groups agree well with the results of Grob *et al.*[9].

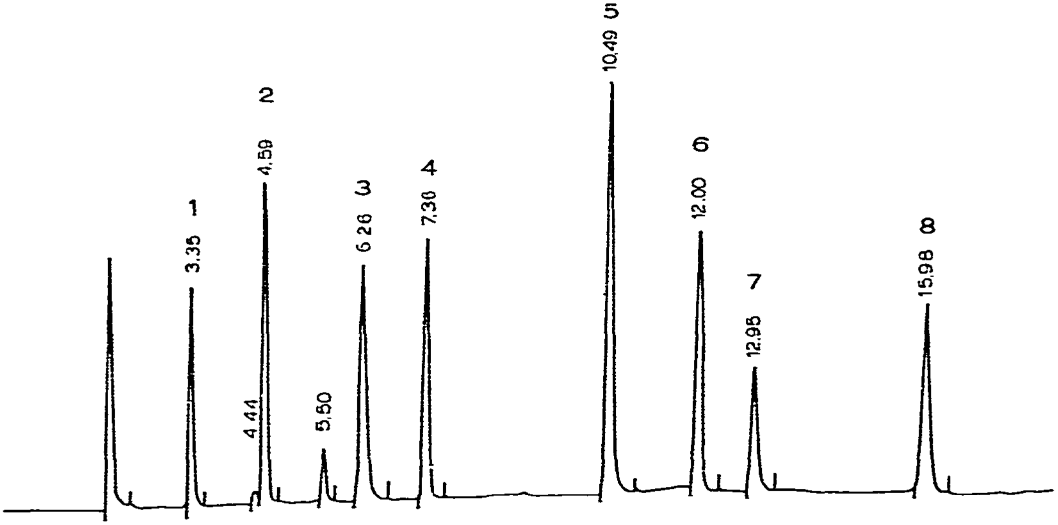


Fig. 4. Gas chromatogram of a text mixture. Column: soda-glass capillary (18 m × 0.26 mm), pretreated by HTS using DDTMDS, coated with Dexsil 300; film thickness, 0.23 μm; HETP, 0.29 mm measured at k' = 6.25. Initial oven temperature, 110°C; after 2 min programmed at 4°C/min. Carrier gas, nitrogen. Peaks: 1 = 1,4-butanediol, 2 = di-*n*-butylamine, 3 = 1-octanal + impurity, 4 = 1-octanol, 5 = naphthalene + methyl salicylate, 6 = *n*-tridecane, 7 = 2,6-dimethylphenol, 8 = *n*-tetradecane.

In accordance with them having the highest critical surface energy values, TPSA- or ODPSA-treated glass capillaries show good wettability for, for instance, squalane, Ucon HB, OV 25 and Dexsil 400. Unfortunately the advantages of applying TPSA or ODPSA are reduced by the treated glass having too high a degree of adsorption activity.

Progress in HTS with respect to increased wettability is to be expected by application of silylating agents having polar groups. Further investigations are necessary to examine their thermal stability. For coating glass capillaries with silicone phases an optimum adaptation is probably easier to achieve by the "baking" procedure desribed by Schomburg *et al.*[18].

The results of the activity test in Table I show that bifunctional disilazanes produce the highest degree of deactivation (type A). With DHTDMS and DDTDMS, in contrast to HMDS, this is possible with such good reproducibility, in addition to the previously mentioned better wettability, that we recommend these reagents for preparing OV-1 or SE-52 capillaries.

When disiloxanes were used for HTS a somewhat lower inertness was observed. It is not clear whether this is caused by the reagent or by the conditions, which could have different optima for disiloxanes and disilazanes.

With the monofunctional reagents TPSA, ODPSA and TPSA, a satisfactory deactivation could not be achieved. Very often tailing of hydrocarbons appeared in the test chromatogram. Experiments to catalyse HTS by addition of ammonia were not successful, the ammonia-treated capillaries showing also a strong adsorption for hydrocarbons. Ammonia obviously attacks the silica network during HTS, thus leading to the formation of adsorption centres. The same effect of hydrocarbon adsorption was observed by Grob *et al.*[2] when using a large excess of silylating agent ("excessive silylation").

Some ideas on the mechanism of HTS

For further progress in the preparation of HTS-pretreated capillary columns it would be helpful to know more about the mechanism of HTS. For a discussion, the following observations and facts have to be taken into consideration:

(1) The critical optimum amount of reagent seems to be influenced by the vapour pressure of the reagent. For HMDS (high vapour pressure) a much higher excess with respect to the stoichiometric amount is necessary than for reagents with lower vapour pressure.

(2) According to our experimental results multifunctional basic reagents produce a higher degree of deactivation than monofunctional reagents of the same concentration.

(3) Addition of gaseous ammonia as a catalyst results in poorer deactivation and a strong adsorption for hydrocarbons.

(4) A change in the chain-lengths of the alkyl groups or in the number of phenyl groups in the reagent effects a definite change of the critical surface energy. The surface energies agree well with the results for polymers having similar groups on the surface[12].

(5) HTS-treated surfaces are less active than fused silica surfaces, as discussed by Grob[15].

(6) First results of HTS using a silica material and DDTMDS show that the treated surfaces are likewise completely inactive[19]. The surface concentration of the chemically bonded layer does not differ so much from the values obtained by Unger[17] for "normal" silylation using *n*-octyldimethylchlorosilane.

Considering the facts mentioned above (especially the last-mentioned) the mechanism for HTS proposed by Godefroot *et al.*[4] is probable. Some of the trialkylsilyl groups formed may react with neighbouring unchanged hydroxyl groups thus forming siloxane bonds with elimination of the corresponding silanol. This is assumed to be an equilibrium reaction which will become irreversible, because a new attack on the siloxane bonds formed will be complicated owing to shielding by the bulky organosilyl groups. We assume that as a result of the simultaneous reactions not only a bonded layer of high density is formed but also few unreacted hydroxyl groups and considerably less adsorption-active siloxane bonds exist between the organosilyl groups on the surface.

A similar reaction course may be taken into consideration in the procedure using organopolysiloxanes, described by Schomburg *et al.*[18].

EXPERIMENTAL

Glass capillaries (0.256 mm I.D.) were drawn from soda-glass tubes (type 940, VEB Technisches Glas Ilmenau, G.D.R.) cleaned by the method of Marshall and Parker[20]. The capillaries were leached as described by Grob *et al.*[2,3] and dried by the following method. The capillary still containing water droplets was connected at both ends to a vacuum line installed in an oven of a gas chromatograph. The oven was then heated at a rate of 4°C/min to 140°C where it was held for 45 min. The temperature was then increased to 180°C for 2 h. After opening the oven, the capillary was flame sealed immediately.

For introducing HMDS, DBTMDS, DHTMDS, DHTMDO and DPTMDS into the capillaries the dynamic procedure described by Grob *et al.*[3] was used. Introduction of a defined amount of DDTMDS, DOTMDS, TPDMDS, ODPSA, DDTMDO, TPSA and TPSO was performed by the static procedure of Bouche and Verzele[16]. Carefully dried pentane or ether was used as solvent. The capillary end was closed as described in ref. 21. After the reagent had been introduced the capillary was heated at a rate of 4°C/min to 340°C where it was held for 13–14 h. The capillary was then rapidly cooled to room temperature and one end was opened under toluene which moved into the capillary, filling *ca.* 80% of its length. The other end was then also opened and the capillary subsequently flushed with ether and dried with a stream of nitrogen at 250°C for 1 h. The capillary was now ready for testing or coating. For longer storage, the pretreated capillaries should be sealed.

For testing pretreated capillary pieces or coated capillary columns a Hewlett-Packard 5840 A gas chromatograph with a modified injection port was used. The conditions for the adsorption test are given in Fig. 1.

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