A study of some deactivation methods for fused silica capillary columns by CP-MAS NMR and capillary gas chromatography


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4 Conclusions

The model system shown here effectively generates linear breakthrough-gradients with volumes between 40-550 µl, suitable for 200-400 µm i.d. micro-HPLC columns. This work shows that gradient volumes can be readily changed. Decreasing gradient-generator column lengths, column cross-sectional areas, porous particle diameters or flush flow rates all decrease gradient volumes. Thus breakthrough-gradients may be the best approach for generating gradients with packed ultra-micro-HPLC systems [11] using 100-200 µm i.d. packed columns or open-tubular systems [12] using ca. 50 µm i.d. columns (both with flows ca. 1 µl/min). Conversely, 1 mm i.d. columns have employed gradient volumes ranging from 800-4,000 µl [1], and it may be possible that linear breakthrough-gradients can be extended to these larger columns. As Figure 9 shows, the possibility even exists for making nonlinear gradients by using fast flush flows with small porous particle gradient-generator columns.

Acknowledgments

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References


A Study of Some Deactivation Methods for Fused Silica Capillary Columns by CP-MAS NMR and Capillary Gas Chromatography

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Key Words:
Gas chromatography, GC
Fused silica capillary columns
CP-MAS NMR
Deactivation methods

Summary

The effect of deactivating a fused silica surface by silylation with 1,1,3,3-tetraphenyl-1,3-dimethylsilazane (TPDMDS), triphenylsilyleamine (TPSA), and octamethylcyclotetrasiloxane (D4) and by polydimethylsiloxane degradation (PSD) is studied. Rehydrated, dried, and deactivated Cab-O-Sil M5 samples are used as model materials for 29Si CP-MAS NMR analysis.

At about 350 °C, TPDMDS yields mainly diphenylmethylsiloxysilane, dimethylchlorosiloxylane, and triphenylsiloxysilane groups. TPSA yields phenyltrimethoxysilane, diphenyldimethoxysilane, and triphenylsiloxysilane groups. At 400 °C, the products formed initially are eventually replaced by methyltrimethoxysilane or phenyltrimethoxysilane groups, while a substantial number of silanol groups still remains. The possible consequences for wettability are discussed.

D4 reacts with Cab-O-Sil even at 200°C, but a large number of silanol groups remains. This number decreases gradually at higher temperatures and becomes negligible above 400°C. The formation of methyltrimethoxysilane groups, which starts at 425°C, is predominant at 490°C.
SE-30 forms surface-bound dimethyldisiloxysilane groups at 400°C, but dimethyldisiloxane polymer chains are also present. The silanol groups react partially. At temperatures of 425°C and above, the silanol groups disappear and methyltrisiloxysilane groups are formed. It is essentially this reaction that is responsible for shielding the remaining silanol groups and thus for the process of deactivation.

Some fused silica columns which were deactivated with D4 and PSD are tested with a dual column system. A new, simple, and dead volume-free coupling device is introduced. The difference in the quality of deactivation among the test columns is not significant. The amount of SE-30 bound to the surface ranges from 46% at 350°C to 5% at 450°C.

1 Introduction

Due to ever increasing demands for inertness in fused silica capillary gas chromatography further improvement of column deactivation is needed. Recently, we reported on the effects of some deactivation methods on column inertness [1]. In particular, the silylation of fused silica with hexamethyldisilazane (HMDS) and diphenyltetramethyldisilazane (DPTMDMS) was studied by means of $^{29}$Si CP-MAS NMR [1]. The silylation of fused silica with hexamethyldisilazane, $^{13}$C cross polarization – magic angle spinning (CP-MAS) NMR using Cab-O-Sil as a model material.

Here, again using Cab-O-Sil as a model material, we report the application of $^{29}$Si CP-MAS NMR to other deactivation methods. Moreover, for D4 treatment and PSD the NMR measurements are supplemented by chromatographic evaluation of the deactivation procedures: fused silica columns, treated as similarly as possible to the Cab-O-Sil samples, are examined during various stages of their preparation prior to coating. A new and simple device is presented for coupling the column to the perfectly deactivated precolumn employed for intermediate surface testing [4].

Four deactivation methods are studied. TPDMS and TPSA are evaluated because of interest in using reagents with two or more phenyl groups attached to the silicon to improve wettability [2,3]. D4 and PSD are studied because they are often applied to fused silica columns [5,6,7], and little is known about the temperature dependence of these reactions. Specifically, temperatures at and above 400°C, although often specified in GC literature, but hardly reported elsewhere [8-13], are impractical with the polyimide outer coating, and it is important to know whether this temperature is really needed.

2 Experimental

2.1 Materials

The Cab-O-Sil M5 (Cabot Corp., Tuscola, Ill., USA) was a gift from Heybroek & Co's Handel Maatschappij N.V., Amsterdam. The specific surface area of grade M5 is, according to the manufacturer, 200 ± 25 m$^2$/g. The Cab-O-Sil was ignited at 720°C, rehydrated as described before [1], and kept in a vacuum desiccator over P$_2$O$_5$. TPDMS and TPSA were from Fluka AG, Buchs, Switzerland*. D4 was a gift of R. Dandeneau, Hewlett Packard, Avondale PA, USA. The polydimethylsiloxane SE-30 was obtained through Chrompack, Middelburg, The Netherlands.

Solvents were all analytical grade from E. Merck, Darmstadt, FRG. The fused silica columns (0.25 mm i.d.) were a gift of Hewlett Packard, Avondale PA, USA.

2.2 Preparation of the Reaction Ampoules

TPDMDS and TPSA: The required amount of TPDMDS or TPSA was dissolved in toluene and the corresponding amount of Cab-O-Sil was added (0.860 g TPDMDS or 0.578 g TPSA per gram Cab-O-Sil). The toluene was evaporated under reduced pressure in a rotary evaporator. The resulting Cab-O-Sil coated with TPDMDS or TPSA was dried in a vacuum desiccator over P$_2$O$_5$ for several weeks. About 0.3 g of the coated Cab-O-Sil sample was placed in a test tube of vitreous quartz (length 20 cm, i.d. 1 cm, wall thickness 1 mm). A constriction was drawn in the middle of the tube and the tube was placed again in the vacuum desiccator over P$_2$O$_5$ for some days. Then the tube was evacuated and filled with nitrogen. This process was repeated twice. Finally, the tube was evacuated and sealed at the constriction.

D4: About 0.3 g Cab-O-Sil was placed in a test tube of vitreous quartz and weighed. The constriction was drawn and the tube was placed again in the vacuum desiccator over P$_2$O$_5$ for some days. Then the tube was evacuated and filled with nitrogen; this was repeated twice. The D4 was added with a syringe (0.633 g D4 per gram of Cab-O-Sil), while the tube was cooled in dry ice. The tube was evacuated and sealed at the constriction.

PSD: Cab-O-Sil was coated with 1.96 g SE-30 per gram which corresponds to a layer of 10 nm. The SE-30 was dissolved in pentane and the procedure described for TPDMDS and TPSA followed.

2.3 Reaction and Rinsing

The ampoules were wrapped in aluminium foil and heated at the required temperature for 16 h. Then the contents were washed twice with toluene (in the case of PSD with ultrasonication for 5 min) and twice with methanol. They were dried in an oven at 70°C and then overnight in a vacuum oven at 150°C. Table 1 lists the Cab-O-Sil samples.

2.4 NMR Measurements

The $^{29}$Si CP-MAS NMR spectra were obtained on a Bruker CXP 300 spectrometer at 59.63 MHz as described previously [1].

* We appreciate the gift of samples of both compounds from K. Grob,
ETH Zürich, Dübendorf, Switzerland
2.5 Preparation of Fused Silica Capillary Columns

Pretreatment. The columns (15 m) were rinsed with methanol, acetone, and pentane and dried in a stream of nitrogen. Then the columns were hydrated: at 100°C, high quality demineralized water was forced through the column at a rate of ca. 0.2 ml/min for 5 h, then at 110°C for 1 h. The water was forced out and the column connected to vacuum at both ends and dried at 110°C overnight, after which the ends were sealed.

Treatment with D4. Three columns were coated dynamically with pure D4 at a rate of 1.0-1.5 cmls. The columns were evacuated and sealed at both ends. Then the columns were heated overnight in a nitrogen atmosphere at the following temperatures: column 1 at 245°C, column 2 at 300°C, and column 3 at 400°C. After cooling the columns were rinsed copiously with pentane.

Table 1

<table>
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<tr>
<th>Sample no.</th>
<th>Reagent</th>
<th>Reaction temp. (°C)</th>
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<tr>
<td>1</td>
<td>TPDMDS</td>
<td>358</td>
</tr>
<tr>
<td>2</td>
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<td>400</td>
</tr>
<tr>
<td>3</td>
<td>TPSA</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>TPSA</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>D4</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
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<td>15</td>
<td>SE-30</td>
<td>500</td>
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Table 2

Composition of the "polarity" mixture (µg/ml).

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<td>10</td>
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<tr>
<td>11</td>
<td>1-Octanol</td>
<td>111.9</td>
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<tr>
<td>DMP</td>
<td>2,6-Dimethylphenol</td>
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<td>DMA</td>
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<tr>
<td>Am</td>
<td>1-Aminodecane</td>
<td>111.4</td>
</tr>
<tr>
<td>13</td>
<td>n-Tridecane</td>
<td>110.6</td>
</tr>
<tr>
<td>Nic</td>
<td>Nicotine</td>
<td>11.20</td>
</tr>
<tr>
<td>14</td>
<td>n-Tetradecane</td>
<td>106.5</td>
</tr>
<tr>
<td>Ace</td>
<td>Acenaphthene</td>
<td>137.6</td>
</tr>
</tbody>
</table>

Polysiloxane Degradation. Three columns were coated statically with a 0.0164% (v/v) solution of SE-30 in pentane corresponding to a film thickness of 10 nm. After coating, the film thickness was checked by determining k' of tetradecane at 120°C. Then the columns were sealed at both ends under helium, and heated under nitrogen at the next temperatures overnight: column 4 at 350°C, column 5 at 400°C, and column 6 at 450°C. After cooling the columns were rinsed with hexane, toluene, and pentane (30 ml each) and dried in a stream of nitrogen.

2.6 Testing of Noncoated Columns

Coupling Device. The two columns (typical i.d. 0.25 mm) were connected by a piece of fused silica of smaller diameter (o.d. 0.20 mm, i.d. 50 µm). To keep the components in place and to avoid leakage, the connection was secured in a transparent silicone septum as shown in Figure 1.

Figure 1

The coupling device. For explanation see text.

One of the columns was forced through the septum (Figure 1A). The connection capillary was inserted into this column (Figure 1B). Then the other column was slipped over the connection capillary (Figure 1C). Both columns and the connection piece inside them were then pushed halfway back into the septum (Figure 1D). Finally, the two columns were pulled apart so that the connection capillary became visible and was held in place by the septum (Figure 1E).

Precolumn. A precolumn showing as little adsorption as possible is needed. Therefore, a thick film column was selected: length 25 m, i.d. 0.32 mm, stationary phase CP-Sil 5 CB (a chemically bonded polydimethyl siloxane), film thickness 1.1 µm (Chrompack, Middelburg, The Netherlands). Figure 2 shows a chromatogram of the test mixture (Table 2) on this column under the test conditions.

Figure 2

Chromatogram of the test mixture on the precolumn. For conditions see text.
Chromatographic Test Conditions. The columns were tested at 120°C in a Varian 3400 gas chromatograph with FID using helium as a carrier gas. The inlet pressure was adjusted so that the elution time of methane was 170 s (giving a mean linear velocity in the second column of 34 cm/s), injector and detector temperatures were both 250°C, the split ratio 1:100, injection volume 1 μl. Kovats indices were calculated with respect to the dead time obtained from regression of n-alkanes, according to Guardino et al.,[14], the least squares criterion changed as described by Wainwright and Haken[15]. Peak areas were normalized to n-decane = 100%, but not corrected for FID response factors. Thus the maximum possible normalized peak area of most components except the alkanes is less than 100% (for 1-octanol the maximum response will be 85%[16]).

3 Results and Discussion

3.1 NMR Measurements

The rehydration and drying of the Cab-O-Sil and of the fused silica columns were based on the procedure of De Boer et al.[17], which "produces a silica surface completely covered with OH-groups, on which no water is physically adsorbed". As Cab-O-Sil contains no pores, contrary to the silicas used by De Boer et al., we reduced the drying temperature from 120° to 110°C and applied vacuum. Like Cab-O-Sil, the inner surface of a fused silica column contains no pores and, in addition, is flat and smooth. Although a fused silica column of some length cannot be dried over P₂O₅, drying overnight at 110°C and under vacuum produces a similar result due to its simple geometry. Therefore, we presume that the states of hydration of the Cab-O-Sil and the fused silica columns are very similar.

Reaction with TPDMDS. ²⁹Si CP-MAS NMR spectra of samples 1 and 2(Figure 3) were recorded. Four signals can be distinguished in both spectra at the following chemical shifts: -8.5 ± 0.5 ppm, -18.5 ± 0.5 ppm, -28 ± 1 ppm, and -110 ppm. The signals were assigned by comparison with the spectra of TPSA (see next section) and tabulated values[18]: the signal at -8.5 ± 0.5 ppm can be ascribed to -O(≡Si(C₆H₅)₂CH₃, the signal at -18.5 ± 0.5 ppm to* (-O)₂Si(CH₃)₂ or -O(≡Si(C₆H₅)₃ groups, the signal at -28 ± 1 ppm to (-O)₂Si(C₆H₅)CH₃ groups, and the signal at -110 ppm to the silica network (-O)₃Si(OH). (The shoulder at about -101 ppm is the signal of the silanol groups (-O)₃Si(OH).)

The signal at -8.5 ppm is in agreement with the expected reaction:

\[
\text{Si(C₆H₅)₂CH₃NH} + 2\text{SiOH} \rightarrow 2\text{SiOSi(C₆H₅)₂CH₃} + \text{NH₃.}
\]

The presence of (-O)₂Si(C₆H₅)CH₃ groups can be explained by the loss of a phenyl group from the -O(≡Si(C₆H₅)₂CH₃ group and the concomitant formation of a second siloxane link. The preferential loss of a phenyl group over a methyl group was observed earlier for the -O(≡Si(C₆H₅)₃ group[1]. The signal at -18.5 ppm can be ascribed to a -O(≡Si(C₆H₅)₃ group as well as to a (-O)₂Si(CH₃)₂ group. It is chemically unlikely, however, that a triphenylsilyl group is formed from TPDMDS. Because of the established tendency of a phenyl-containing silyl group to loose a phenyl group rather than a methyl group, it is more plausible that the signal at -18.5 ppm represents a (-O)₂Si(CH₃)₂ group. A possible reaction would be:

\[
(-O)Si(C₆H₅)₂CH₃ + (-O)₂Si(C₆H₅)CH₃ \rightarrow (-O)₂Si(C₆H₅)₃ + (-O)₂Si(CH₃)₂
\]

At 358°C, most surface silyl groups are still -O(≡Si(C₆H₅)₂CH₃ groups and few of these groups have reacted to (-O)₂Si(C₆H₅)CH₃ or (-O)₂Si(CH₃)₂ groups. The signal of the surface silanol groups has practically disappeared, indicating that the primary reactions are almost complete. At 400°C, the number of -O(≡Si(C₆H₅)₂CH₃ groups has decreased and (-O)₂SiR₁R₂ groups are in the majority.

Reactions with TPSA. ²⁹Si CP-MAS spectra were recorded of samples 3 and 4(Figure 4). After reaction at 350°C, roughly six signals can be distinguished: a signal at -18.5 ppm due to the -O(≡Si(C₆H₅)₂CH₃ groups; a signal at -44 ppm due to the (-O)₂Si(C₆H₅)₃ groups; a signal at -71 ppm; a signal at about -79 ppm due to the (-O)₂Si(C₆H₅)₂CH₃ groups; the usual signals in the -90/-110 ppm range due to Cab-O-Sil.

The interpretation of the NMR spectra of Figures 3 and Figures 4 is facilitated by bearing in mind that substitution of a methyl by a phenyl group shifts the signal by ca. -10 ppm.

Note: throughout this paper -O(≡Si(-O)²Si, etc. are abbreviations for -Si-O-Si, (=Si-O=)²Si, etc.

Figure 3

Reactivity of Cab-O-Sil with TPDMDS: ²⁹Si NMR spectra of samples 1 and 2 (see Table 1).

Figure 4

Reaction with TPSA. ²⁹Si CP-MAS spectra were recorded of samples 3 and 4 (Figure 4). After reaction at 350°C, roughly six signals can be distinguished: a signal at -18.5 ppm due to the -O(≡Si(C₆H₅)₂CH₃ groups; a signal at -44 ppm due to the (-O)₂Si(C₆H₅)₃ groups; a signal at -71 ppm; a signal at about -79 ppm due to the (-O)₂Si(C₆H₅)₂CH₃ groups; the usual signals in the -90/-110 ppm range due to Cab-O-Sil.

The interpretation of the NMR spectra of Figures 3 and Figures 4 is facilitated by bearing in mind that substitution of a methyl by a phenyl group shifts the signal by ca. -10 ppm.

Note: throughout this paper -O(≡Si(-O)²Si, etc. are abbreviations for -Si-O-Si, (=Si-O=)²Si, etc.
Deactivation Methods for Fused Silica Capillaries

From the ratio of the signal of the silanol groups to the signal of the silica network it can be concluded that reaction has taken place, but that a substantial number of silanol groups still remains on the surface.

At 400°C, the signal of the –OSi(C6H5)3 groups practically disappears, the signal at –44 ppm is still present, and the signals in the –70/–80 ppm region are increased. Silanol groups, however, are still present (shoulder in the hump at –90/–110 ppm).

**Reaction with D4.** 29Si NMR spectra were recorded of samples 5-11 (Figure 5). Four signals can be distinguished:
- the signal at –18.5 ± 1 ppm due to (–O)2Si(CH3)2 groups;
- the signal at –66 ± 1 ppm due to the (–O)3SiCH3 group;
- the usual signals in the –98/–110 ppm range.

These spectra indicate a gradual decrease of the number of (–O)3SiOH groups (at –98 ppm) as the reaction temperature is increased. Even at 200°C partial reaction takes place, at 400°C few silanol groups remain, and above 425°C the signal at –98 ppm is completely absent. In this connection the absence of a signal due to (–O)Si(CH3)2OH is noteworthy. This would be expected at –4.9 ppm [19], had the siloxane ring of D4 opened by proton transfer from a silanol group and attached itself at one end to the surface: \( \equiv Si-O-[Si(CH_3)_2O]_4-H \).

Unfortunately, the NMR spectra do not show unequivocally whether loops of four dimethylsiloxane units are formed on the surface or shorter ones (e.g. of two siloxane units as shown by Li [20]). The chemical shifts of a and b do not differ enough to resolve these signals:

From 425°C upwards (–O)3SiCH3 groups are formed and at 495°C these groups predominate. The reaction of Cab-O-Sil with D4 therefore proceeds easily and straightforwardly and does not lead to a variety of organic surface moieties.

**Polysiloxane Degradation.** 29Si NMR spectra of samples 12-15 are shown in Figure 6. The following signals can be distinguished:

![Figure 4](image1)

**Figure 4**
Reaction of Cab-O-Sil with TPSA: 29Si NMR spectra of samples 3 and 4 (see Table 1).

![Figure 5](image2)

**Figure 5**
Reaction of Cab-O-Sil with D4: 29Si NMR spectra of samples 5-11 (see Table 1).
Deactivation Methods for Fused Silica Capillaries

Table 3

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<tr>
<th>Dual Column Test</th>
<th>Column Treatment</th>
<th>k' C14,120°</th>
<th>Test substances</th>
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<th>Amino-decane</th>
<th>Nicotine</th>
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<tr>
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<td>After 'baking' + rinsing</td>
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<td>After</td>
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<td>Pre-column</td>
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<td>72 1320.4</td>
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<td>-</td>
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<td>114 1442.5</td>
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</tr>
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- a signal at -19.3 ppm due to the (-O)2Si(CH3)2 groups attached to the surface;
- a sharp signal at -22.9 ppm due to the (-O)2Si(CH3)2 units of the siloxane chain of SE-30;
- the usual signals in the -98/-110 range;
- at higher reaction temperatures, a signal at -66 ± 1 ppm due to the (-O)3SiCH3 groups.

From these results we conclude that at 400°C the long polysiloxane chain has reacted with the surface and is partly broken into smaller units. The sharp signal at -22.9 ppm indicates, however, that also longer, more mobile chain segments of unknown length remain. (One should keep in mind that the cross polarization technique should yield only very small signals from mobile molecular fragments.) After treatment at 425°C and above, the sharp signal at -22.9 ppm disappears and only surface bonded (-O)2Si(CH3)2 groups are present: the siloxane chains are now almost completely broken into smaller surface-bonded segments or have reacted in the following way:

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si} \rightarrow \\
\quad \text{CH}_3 \quad \text{CH}_3 \\
\text{O} \quad \text{OH} \\
\text{Si} /\backslash \quad \text{Si} /\backslash \\
\]

At 400°C silanol groups are still present on the surface (shoulder at approx. -101 ppm). Only at 425°C and above do they disappear.

3.2 Gas Chromatography

The Untreated Column. Column 4 was tested before deactivation (Figure 7). The Kovats indices and normalized peak areas (NA) are listed in Table 3.

Before hydration, octanol, aminodecane, and nicotine do not elute from the column and 2,6-dimethylaniline (DMA) and 2,6-dimethylphenol (DMP) show tailing. After hydration, a small, severely tailing octanol peak elutes, the peak shape of DMP is nearly perfect, DMA shows tailing, and aminodecane and nicotine still do not elute. This can be
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Figure 7
Dual column test (for conditions see text). A) Chromatogram of column 4 after hydration (see Table 3). B) Chromatogram of column 4 after rinsing (see Table 3). (For abbreviations see Table 2.)

Figure 9
Dual column test after PSD treatment (for conditions see text). A = 350°C, B = 400°C, C = 450°C. (For abbreviations see Table 2.)

These results cannot immediately be brought in line with the NMR spectra of similarly treated Cab-O-Sil. Sample 6 (Table 1) treated at 245°C still has a fairly large number of silanol groups (Figure 5). We must assume, however, that these are efficiently screened by the (-O)2Si(CH3)2 groups.

Polysiloxane Degradation. The chromatograms of columns 4-6 are shown in Figure 9. Differences in peak shape among these chromatograms are negligible: all peaks (except aminodecane) elute symmetrically, although the NMR spectrum of the Cab-O-Sil sample 12, treated similarly to column 5, shows a signal of silanol groups. However, the NMR spectrum also indicates the presence of siloxane chains of some length. Apparently, these siloxane chains attached to the surface screen the silanol groups even better than the D4 products do.

The presence of siloxane chains was also established by comparison of the k’ value of C14 at 120°C before and after “baking” and rinsing (Table 3). These figures show that the signal SE-30 layer was partly immobilized after “baking”. The higher the PSD temperature, however, the more the SE-30 breaks down into smaller (cyclo?) siloxane fragments, which are not immobilized and not retained on rinsing.

4 Conclusions

4.1 Surface Modification with Phenyl-Containing Silazanes

Surface modification of glass capillary columns by high temperature silylation (>400°C) with reagents containing phenyl groups is an attractive way to improve the wettability of the column wall: the phenyl group is thermally stable,
chemically inert, and could raise the critical surface tension to about 35 dyn/cm [21]. TPDMS and TPSA were used by Grob [3] and by Welisch et al. [22]. Although the reactions with Cab-O-Sil might not precisely duplicate the reactions that may occur on the surface of a fused silica column, our NMR findings for Cab-O-Sil with these reagents are in accordance with their results in GC experiments.

In the case of TPDMS, reaction with the silanol groups largely takes place at 358°C (cf. 340°C used by [22]), and raising the temperature to 400°C (optimum temperature according to [3]) hardly decreases the number of unreacted silanol groups.

The NMR spectra indicate that at 400°C, the \((-\text{O})-\text{Si(C}_3\text{H}_5)_2\text{CH}_3\) groups partially decompose. A semiquantitative interpretation of the spectra shows that the phenyl/methyl ratio of the whole surface decreases only slightly, even if we assume that the signal at -18.5 ppm originates solely from \((-\text{O})_2\text{Si(CH}_3)_2\) groups.

In the case of TPSA, reaction with the silanol groups is incomplete at 350°C, and at 400°C silanol groups still remain, which explains the insufficient deactivation. The small increase in critical surface tension of a TPSA-modified surface [22] can also be attributed to the insufficient density of phenyl moieties obtained.

Silazanes have been used for the deactivation of capillary columns because of their high reactivity towards silanol groups. To obtain complete conversion of the silanol groups, a temperature of about 400°C appears necessary. At this high temperature, however, chemical rearrangements in the reagent and/or surface silyl groups take place. While this may help to attain a high degree of conversion it also involves the risk, notably in the case of phenyl-containing silazanes, of losing the phenyl groups one would want to attach to the surface. Therefore, we do not think that the wettability of a fused silica capillary can be improved and at the same time deactivation maintained, by the route of reaction with silazanes. Perhaps cyclic siloxanes offer better prospects.

### 4.2 Surface Modification with D4 or PSD

Our results on D4 deactivation show that the number of unreacted silanol groups is still large at 200°C and 245°C, decreases considerably at 300°C, and it is practically zero at 400°C and higher. This is in agreement with Aristova [9].

The presence of unreacted silanol groups on the other hand has no deleterious effects on the chromatographic performance. This can be explained by the well-known fact that only 50% of the silanol groups are directly accessible for reaction by bulky molecules [23]. Likewise, these are hardly accessible to our test compounds; the dimethylsiloxane units screen the silanol groups effectively.

The results of the polysiloxane degradation are very similar to those of the D4 treatment. However, somewhat higher temperatures are advisable: at 400°C, the number of unreacted silanol groups is higher than it is after treatment with D4 at the same temperature. Also, \((-\text{O})_3\text{SiCH}_3\) groups are formed less readily. The k' value of the columns and the NMR spectra show that siloxane chains remain bonded to the surface (or are at least immobilized).

The screening effect of these siloxane chains depends on their fixation to the surface: short, chemically bonded siloxane units might be more effective than long, loosely adsorbed and/or crosslinked chains.

Schomburg [6] deactivated glass capillary columns by PSD at temperatures varying from 350°C to 450°C. The highest temperature was used for glass dealkalized by the action of gaseous HCl and HF and well dried, thus producing a surface with a close resemblance to fused silica. Our results support this: PSD treatment of well dried Cab-O-Sil needs temperatures of >425°C to remove all silanol groups.

Comparing both methods of deactivation, viz. PSD or D4 treatment, the latter is to be preferred judged by NMR data alone, because lower temperatures are necessary to remove the silanol groups: an advantage with respect to the polyimide coating. Chromatographically, however, much lower temperatures have already given a satisfactory result in the intermediate test for both PSD and D4. For conclusive results the range of temperatures must be further extended.

### References

Applications of a Miniaturized Fluorimetric Photodiode Array Detector for Capillary Liquid Chromatography

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Key Words:
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Summary
A high sensitivity, multichannel fluorescence detector with small volume has been developed for capillary column liquid chromatography. Using an intensified linear photodiode array to monitor fluorescence emission, several important mixtures exhibiting native fluorescence have been examined following high efficiency separation on a capillary column. By correlating mass spectral, fluorescence spectral, and retention time data, information of potential utility in the structural elucidation of aromatic molecules contained in complex mixtures can be obtained. Examples include the separation and spectral examination of the polyaromatic compounds in samples of both biological and environmental interest.

1 Introduction
Today's best analytical techniques are often challenged by the highly complex nature of certain technologically and biologically important samples, a knowledge of whose chemical composition is frequently needed to resolve the difficult problems of contemporary science and technology. Efficient separation methods are essential to facilitate the identification and quantitation of various substances in these materials. While capillary gas chromatography (GC) and its ancillary techniques have made substantial progress in this area over the last decade, they are limited by the volatility and thermal stability of some samples. Capillary column liquid chromatography (LC) or capillary supercritical fluid chromatography [1-4], on the other hand, have proven their ability to achieve separation efficiencies in excess of 200,000 theoretical plates [5], for nonvolatile and thermally labile compounds, within reasonable analysis times and with sample capacities of up to a few micrograms [6].

To fully realize the analytical potential of capillary columns, it is, however, important to couple them with equally effective detectors. Detection volumes on the order of nanoliters or below are required for most work in microcolumn chromatography. Among the several detector types which have been miniaturized [7,8], fluorimetric detectors are particularly attractive. Not only does fluorescence emission provide inherently high sensitivity and the potential for selective monitoring, but emission spectra can frequently yield valuable information on the structure of an unknown compound. As a complement to recent advances in the development of combined LC/mass spectrometric analytical techniques [9], on-line optical spectroscopy combined with capillary column LC can provide detailed structural information within the small detection volumes required by high resolution chromatography.