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DEACTIVATION WITH POLYMETHYLHYDROSILOXANE

A COMPARATIVE STUDY WITH CAPILLARY GAS CHROMATOGRAPHY AND SOLID-STATE ^{29}Si NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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SUMMARY

Deactivation of fused-silica capillary columns and vitreous silica surfaces with polymethylhydrosiloxanes (PMHS) at temperatures between 240 and 360°C was investigated by gas chromatography (GC) and solid-state ^{29}Si NMR spectroscopy. The influence of temperature, amount of water at the surface and film thickness on the stability and nature of the polymer deactivation layer was studied by solid-state ^{29}Si NMR of the model substrate Cab-O-Sil, a fumed silica. These NMR measurements match the GC results and offer additional information relating to the nature of the deactivating layer at surfaces silylated under various reaction conditions. Differences in the nature and structure of the deactivating film occur when the silica surface is coated with a different thickness. Optimum deactivation is achieved when a few monolayers of densely cross-linked polymers anchored to the silica surface are formed. On top of this thin, rigid layer, longer mobile polymer chains containing unreacted silicon hydride groups are present. After optimum deactivation, the fused-silica capillary column wall shows no interaction with various critical test components as used in GC practice. The deactivating films exhibit good thermal stability and solvent resistance.

INTRODUCTION

Substantial improvements in non-polar surface deactivation and modification of the inner wall of fused-silica capillary columns at lower temperatures have been made in recent years by the use of several kinds of methylhydrosiloxanes^{1,2}. Mostly, mixtures of linear and cyclic polymers are used. The advantages of the use of polymethylhydrosiloxanes (PMHS) for the modification of fused-silica capillary column walls are the lower silylation temperatures, the relatively short reaction times and the high degree of effective deactivation. Narrow-bore fused-silica columns modified with PMHS coated with non-polar stationary phases have shown excellent deactivation also in capillary liquid and supercritical fluid chromatography^{3,4}.

Although very effective deactivation of fused-silica capillary columns with PMHS was achieved with an optimum silylation time and temperature, the exact nature of the deactivating film inside fused-silica capillaries is not yet known. Some workers have explained the effective deactivation of methylhydrosiloxanes by the formation of a very thin film² (film thickness of a few monolayers), where all hydrogen groups have reacted with silanol groups into a dense network of cross-linked polymer bonded to the surface via siloxane linkages and with methyl groups protruding upwards from the surface. Although this explanation accounts for the character of the deactivated capillaries observed in gas chromatographic (GC) tests, in view of the high original hydrogen content it is bold to assume that the silylated film is devoid of hydrogen groups.

Here we describe deactivation with PMHS inside fused-silica capillaries and on Cab-O-Sil, a vitreous silica, as a model substrate for fused-silica material that allows spectrometric surface characterization. Fused-silica capillary columns deactivated with PMHS were tested for inertness, acidity and thermal and chemical stability after silylation between 260 and 320°C for various reaction times. Further, the influence of traces of water present on the inner wall before silylation was studied.

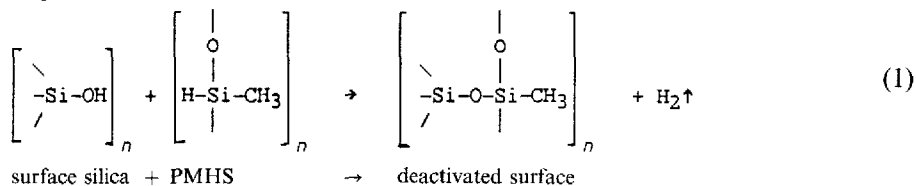
PMHS-modified fused-silica capillaries were subjected to a test for remaining silanol activity and acid or basic adsorption⁵⁻⁷. The deactivated uncoated fused-silica capillaries were tested by a double column method⁸, using a thick-film apolar precolumn as reference.

The use of fused vitreous silica for model experiments in combination with solid-state NMR spectroscopy has proved to be a powerful tool for the study of surface moieties after silylation^{5,9}. Solid-state ²⁹Si NMR provides information on the nature, amount and chemical properties of the groups formed at the surface of the silica. PMHS coated with different film thicknesses on both dried and wetted Cab-O-Sil was silylated between 240 and 360°C for various reaction times. In this study the relative amounts of organo-siliceous surface moieties not directly connected to the surface were determined by ²⁹Si magic-angle spinning (MAS) NMR. ²⁹Si cross-polarization magic-angle spinning (CP-MAS) NMR provided information about the mobility of the anchored and auto cross-linked PMHS chains by contact-time variation experiments. Also, the relative amounts of the siliceous moieties directly attached to the silica surface were determined by ²⁹Si CP-MAS NMR.

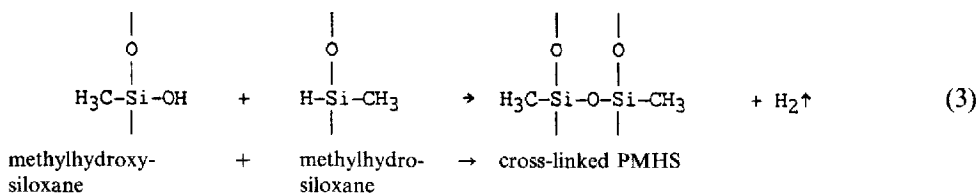
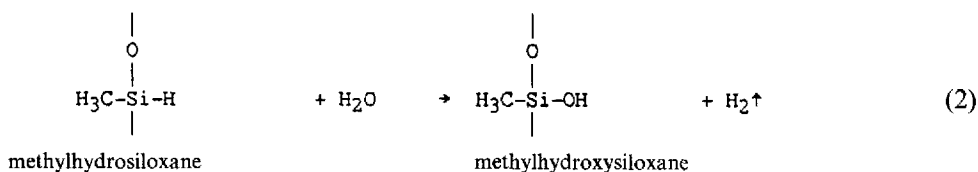
The results of the measurements on silylated Cab-O-Sil match the retention behaviour and peak shape of the test compounds on the likewise deactivated fused-silica capillaries very well.

THEORY

In contrast to polydimethylsiloxanes, in which siloxane bonds are broken at high temperatures to react with surface silanols¹⁰, the bonding of PMHS with surface silanols proceeds through condensation¹¹:



This reaction proceeds rapidly at moderate temperatures (around 290°C). If some physisorbed water is present on the surface, it interferes by hydrolysis of the silicon-hydrogen bond and intra- or intermolecular cross-linking of PMHS can occur according to the following successive reactions:



The presence of water also causes extra silanol activity, which should be reduced by the deactivation of the siliceous surface. Another problem can be the hydrogen content of the deactivating film. Unreacted hydrosiloxanes could exhibit hydrogen bonding with eluting compounds and interfere with the chromatographic process.

In this study, the effects of the reaction temperature, the film thickness and the water content of the surface are parameters which were considered.

EXPERIMENTAL

Materials

The PMHS material PS 122 (50% Si-H, $\eta = 85$ cS, liquid) was obtained from Petrarch Systems (Bristol, PA, U.S.A.). The amount of methylhydrodisiloxysilane groups, as determined by high-resolution (HR) ^{29}Si liquid NMR was $96 \pm 1\%$. The only other significant signal in the ^{29}Si NMR spectrum was assigned to trimethylsiloxy-silane (see below). The fused-silica capillary column material used was a gift from Chrompack (Middelburg, The Netherlands). Cab-O-Sil M5 (Cabot, Tuscola, IL, U.S.A.) was a gift from Heybroek & Co. Handelsmij (Amsterdam, The Netherlands). The specific surface area of grade M5, according to the manufacturer's specification, is 200 ± 25 m²/g; a value of 200 m²/g was used in this study. The solvents were all of analytical-reagent grade from Merck (Darmstadt, F.R.G.), except the demineralized, deionized water, which was obtained with a Milli-Q system (Millipore, Bedford, MA, U.S.A.).

Deactivation and evaluation of fused-silica capillaries

A piece of 85 m \times 0.25 mm I.D. fused-silica capillary column material was conditioned by flushing with helium at 290°C for 2 h. After drying, 90% of the fused-silica capillary was filled with 10% (w/w) hydrochloric acid and flame-sealed at

both ends. Hydrothermal treatment was performed by heating at 120°C for 90 min. After this treatment, the column was rinsed with deionized water until neutral and with methanol for 30 min. It was then dried again by flushing with helium at 140°C for 1 h and cut into five sections: four sections had lengths of *ca.* 18 m and the fifth section (*ca.* 12.5 m) was rinsed with deionized water and dried at room temperature by flushing with helium for 1 h.

These five capillaries were coated dynamically with a 1% (v/v) solution of PS 122 in *n*-pentane. A coating speed of approximately 25 cm min⁻¹ was applied. According to Bartle¹², this results in a film thickness of approximately 10 nm (assumed viscosity, $1.8 \cdot 10^{-3}$ kg m⁻¹ s⁻¹, and surface tension, $2.5 \cdot 10^{-2}$ N m⁻¹).

After coating with PMHS, the columns were flushed with helium for 15 min and flame-sealed. Silylation was carried out at different temperatures and reaction times (see Table I). Subsequently, the capillaries were carefully rinsed with 10 column volumes of dichloromethane to avoid plugging and conditioned by purging with helium at 290°C for 30 min.

For evaluation, the deactivated fused-silica capillary columns were connected via a zero-dead-volume connector (Valco Instruments, Houston, TX, U.S.A.), to a thick-film reference column (24 m × 0.32 mm I.D.) of CP-Sil 5 CB (Chrompack), a chemically bonded polydimethylsiloxane (film thickness, $d_f = 1.1$ μm; phase ratio = 72), showing as little adsorption as possible. In this way column evaluation can be performed with mixtures. It allows the observation of peak shapes, measurements of column polarity by means of retention indices and quantitative comparison of column activities for differently deactivated capillaries.

The connected columns were placed in a Carlo Erba (Milan, Italy) Model 5300 gas chromatograph equipped for split injection and flame ionization detection (FID). Helium was used as the carrier gas. The test runs were performed isothermally at 110°C and chromatograms were recorded with an SP 4290 integrator with a 256K data memory (Spectra-Physics, San Jose, CA, U.S.A.). The injector and detector temperature were each 250°C.

A test mixture consisting of activity markers for various active sites on the column wall before or after deactivation or coating is specified in Table II. It was used for the determination of column wall activity with respect to adsorption.

The solute test mixture contained ten components, five C₁₀–C₁₄ *n*-alkanes and

TABLE I
DEACTIVATED FUSED-SILICA CAPILLARIES

Column No.	Length (m) (I.D. 0.25 mm)	Silylation		Special treatment
		Temperature(°C)	Time (h)	
1	17.90	260	2	—
2	17.90	290	2	—
3	17.70	310	2	—
4	17.90	290	8	—
5	12.65	290	2	Rinsed with water before coating
6 ^a	17.90	—	—	Reconditioned at 290°C for 65 h

^a Column 2.

TABLE II
TEST MIXTURE FOR EVALUATION OF DEACTIVATED CAPILLARIES

Elution order on CP-Sil 5 CB	Compound	Symbol	Concentration ($\mu\text{g ml}^{-1}$ cyclohexane)	Activity marker for
1	Decane	10	119.0	—
2	1-Octanol	C ₈ -OH	112.4	Exposed siloxane bonds, weak
3	2,6-Dimethylphenol	DMP	118.3	Exposed basic sites, strong
4	Undecane	11	116.6	—
5	2,6-Dimethylaniline	DMA	114.7	Exposed acid silanol, strong
6	Dodecane	12	114.4	—
7	1-Aminodecane	Am	116.4	Shielded acid silanol, weak
8	Tridecane	13	107.8	—
9	Nicotine	Nic	121.0	Acid silanol, weak
10	Tetradecane	14	128.4	—

five compounds susceptible to various column wall activities. The mean linear velocity of the carrier gas in the deactivated capillaries was kept between 30 and 35 cm s⁻¹; the velocity in the reference column was typically about 25 cm s⁻¹. The splitting ratio varied between 1:50 and 1:100. The injection volume was 1 μl , corresponding to an amount on the column of typically 1–3 ng for each component.

After the first evaluation, column 2 was reconditioned for 65 h at 290°C under helium and tested again as column 6. The original fused-silica capillary column material was also tested and for comparison the test mixture was also injected on to the reference column.

Kováts retention indices were calculated taking the elution time of methane as the dead time. Peak areas were normalized to *n*-decane = 100% and corrected for relative weight, but were not corrected for FID response factors.

Silylation of Cab-O-Sil and ²⁹Si solid-state NMR measurements

Cab-O-Sil M5 was pretreated by ignition at 720°C and rehydrated as described previously⁹. Part of the Cab-O-Sil was dried further over phosphorus pentoxide in a vacuum desiccator for several weeks and will be referred to as “dry Cab-O-Sil”. Another part of the Cab-O-Sil was conditioned in air over a saturated solution of potassium bromide (84% relative humidity). This batch of Cab-O-Sil contained 5.5% (w/w) of water, which corresponds to 15.3 $\mu\text{mol m}^{-2}$ siliceous surface. This batch will be referred to as “wet Cab-O-Sil”.

The dry Cab-O-Sil was coated with the equivalent of 0.98 and 0.20 g of PMHS per gram, resulting in a “thick-film” coating of 5 nm and a “thin-film” coating of 1 nm thickness, respectively. For this purpose 10% (v/v) PMHS was dissolved in *n*-pentane and added to the required amount of Cab-O-Sil. The *n*-pentane was evaporated slowly under reduced pressure in a rotary evaporator at room temperature. The coated Cab-O-Sil was dried further in an oven at 100°C under atmospheric pressure.

The wet Cab-O-Sil was coated with 0.93 and 0.19 g of PMHS per gram, resulting in films of the same thickness as described above. After evaporation of the *n*-pentane,

the coated Cab-O-Sil was conditioned in a GC oven with temperature programming from 40 to 80°C at 5°C/min followed by 15 min at 80°C to prevent evaporation of adsorbed water.

About 0.4 g of coated Cab-O-Sil was placed in a quartz glass reaction ampoule (20 cm × 1 cm I.D., wall thickness 1 mm). A constriction was drawn in the middle of the tube. The tube was evacuated twice while cooled in dry-ice because of the volatility of some short linear and cyclic methylhydrosiloxane polymers and of the remaining water. It was filled with helium to atmospheric pressure both times. Finally, the ampoule was sealed to give a volume of about 8 ml.

After sealing, the ampoule was wrapped in aluminium foil, placed in a well ventilated oven and heated at the required temperature for several hours. After silylation the ampoule was opened and the contents were washed twice with dichloromethane and dried overnight in a vacuum oven at 110°C. Table III lists the silylated Cab-O-Sil samples. The carbon contents of a few silylated Cab-O-Sil samples were obtained with a Perkin-Elmer (Norwalk, CT, U.S.A.) Model 240 Analyzer.

With these samples, various solid-state ^{29}Si NMR measurements were carried out in order to gain information about the chemical properties, the nature and the mobility of the deactivating film at the silicious surface. Solid-state ^{29}Si NMR spectra were obtained on a Bruker CXP 300 spectrometer at 59.63 MHz. The samples were spun at *ca.* 3.5 kHz using aluminium oxide rotors of the standard Bruker double-bearing type.

From the 5-nm PMHS-coated Cab-O-Sil samples, ^{29}Si MAS NMR spectra were obtained with a pulse interval of 10 s, an acquisition time of 100 ms and an accumulation of typically 256 free induced decays (FIDs) in 4K data points. Prior to

TABLE III
PMHS MODIFIED CAB-O-SIL SAMPLES AND ^{29}Si SOLID-STATE NMR MEASUREMENTS

Sample	Film thickness (nm)	Silylation		Water content [% (w/w) with respect to PMHS]	^{29}Si NMR ^a measurements
		Temperature (°C)	Time (h)		
1	5	240	12	—	MAS
2	5	280	12	—	MAS, CT
3	5	320	12	—	MAS
4	5	360	12	—	MAS, CT
5	5	290	4	5.9 ^b	MAS, CT
6	5	290	4	—	MAS, CT
7	1	280	8	—	CP-MAS, CT
8	1	300	8	—	CP-MAS
9	1	320	8	—	CP-MAS
10	1	360	8	—	CP-MAS
11	1	280	8	29.6 ^b	CP-MAS
12	1	320	8	29.6	CP-MAS
13	1	360	8	29.6	CP-MAS

^a MAS = magic-angle spinning; CT = contact-time variation experiments; CP-MAS = cross-polarization magic-angle spinning.

^b 5.5% (w/w) water with respect to Cab-O-Sil.

Fourier transformation the data files were zero-filled to 16K data points. The spectral width was 20 kHz and no line broadening was applied.

From the 1-nm PMHS-coated Cab-O-Sil samples ^{29}Si CP-MAS NMR spectra were obtained using a contact time of 15 ms, a pulse interval of 5 s and an acquisition time of 25.6 ms. Typically 500 FIDs were accumulated in 1K data points, zero-filled to 8K prior to Fourier transformation. The spectral width was 20 kHz. A line broadening of 15 Hz was used prior to zero-filling and Fourier transformation.

For cross-polarization experiments with variable contact times, a series of nineteen contacts ranging from 0.1 to 40 ms were applied. Typically 6×50 FIDs were accumulated for each contact. The other spectral parameters were the same as above, except for a line broadening of 10 and 30 Hz prior to zero-filling and Fourier transformation for the 5- and 1-nm PMHS-coated Cab-O-Sil, respectively.

RESULTS AND DISCUSSION

Characterization of the PMHS used

An HR ^{29}Si NMR spectrum of the PMHS reagent used (PS 122) is given in Fig. 1. One sharp signal is detected at -34.7 ppm upfield from tetramethylsilane (TMS). This signal is assigned to the methylhydrodisiloxysilane groups (D_2H or methylhydrodisiloxanes) of the various polymers present in this reagent¹³. The relative amount of trimethylsiloxysilane end groups (M_1) (signal at $+9$ ppm) is less than 5% in this sample. This indicates that only a small amount of short linear polymers is present in PS 122. A gas chromatographic-mass spectrometric (GC-MS) analysis of PS 122 on

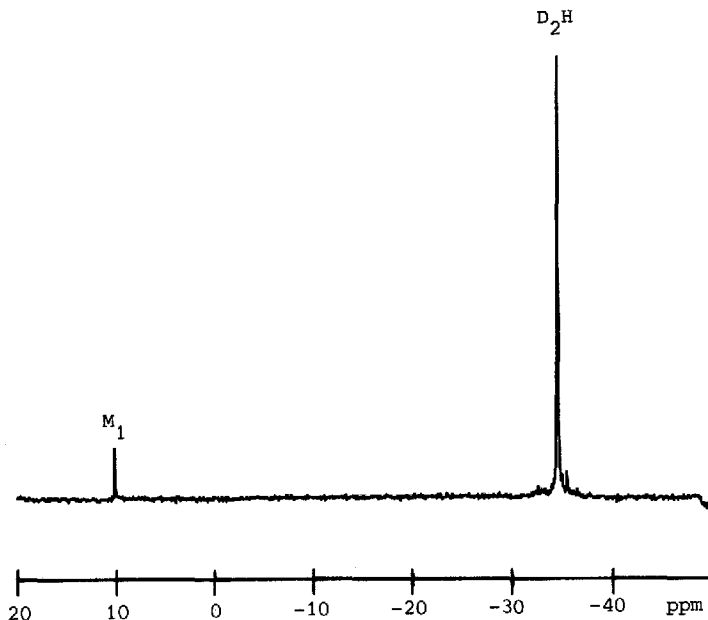


Fig. 1. HR ^{29}Si NMR spectrum of the PMHS reagent, PS 122, used for deactivation. $N_s = 23\,000$; pulse interval time, 10 s; acquisition time, 100 ms.

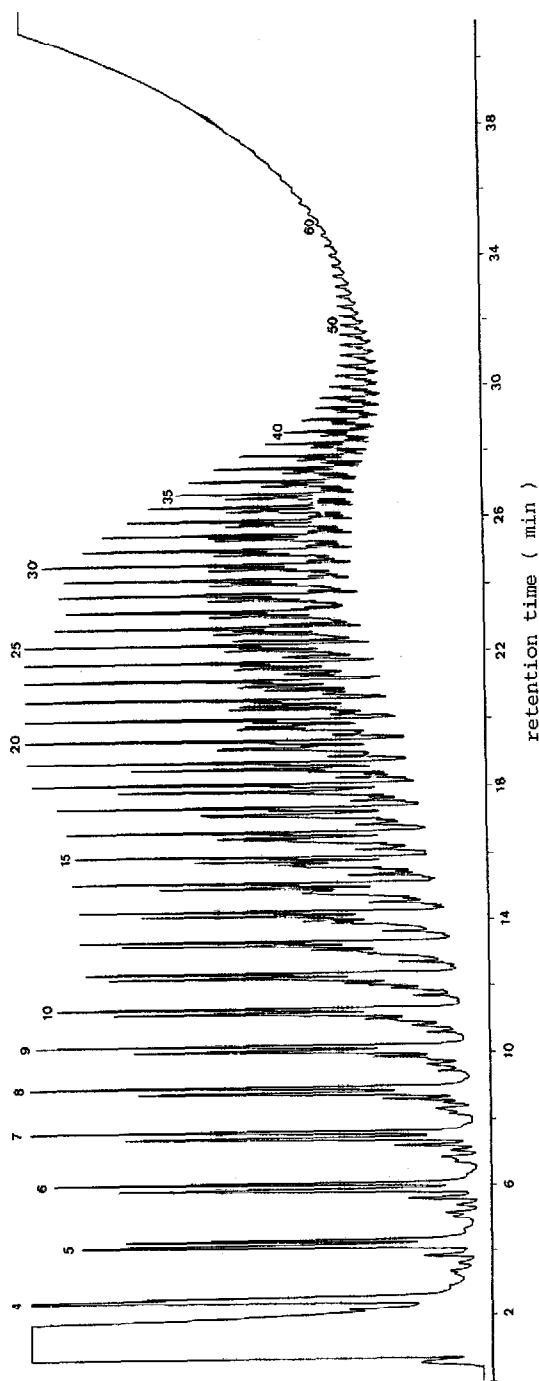


Fig. 2. Chromatogram of the PMHS reagent PS 122. Chromatographic conditions: OV-1 column ($25\text{ m} \times 0.32\text{ mm I.D.}$), $d_f = 0.1\ \mu\text{m}$; carrier gas, helium; temperature programme, initial temperature 80°C for 2 min, increased at $10^\circ\text{C min}^{-1}$ to 380°C , then at 5°C min^{-1} to 410°C . The peak numbers represent the methyl/hydrosiloxysilane units in the various polymers.

a thin-film apolar column showed an extremely large dispersion of both cyclic and linear polymethylhydrosiloxanes. The chromatogram of PS 122 recorded with FID (Fig. 2) starts with cyclic and linear tetramers and continues up to 66 methylhydrosiloxysilane units. Probably polymers containing over 70 units are present in this sample.

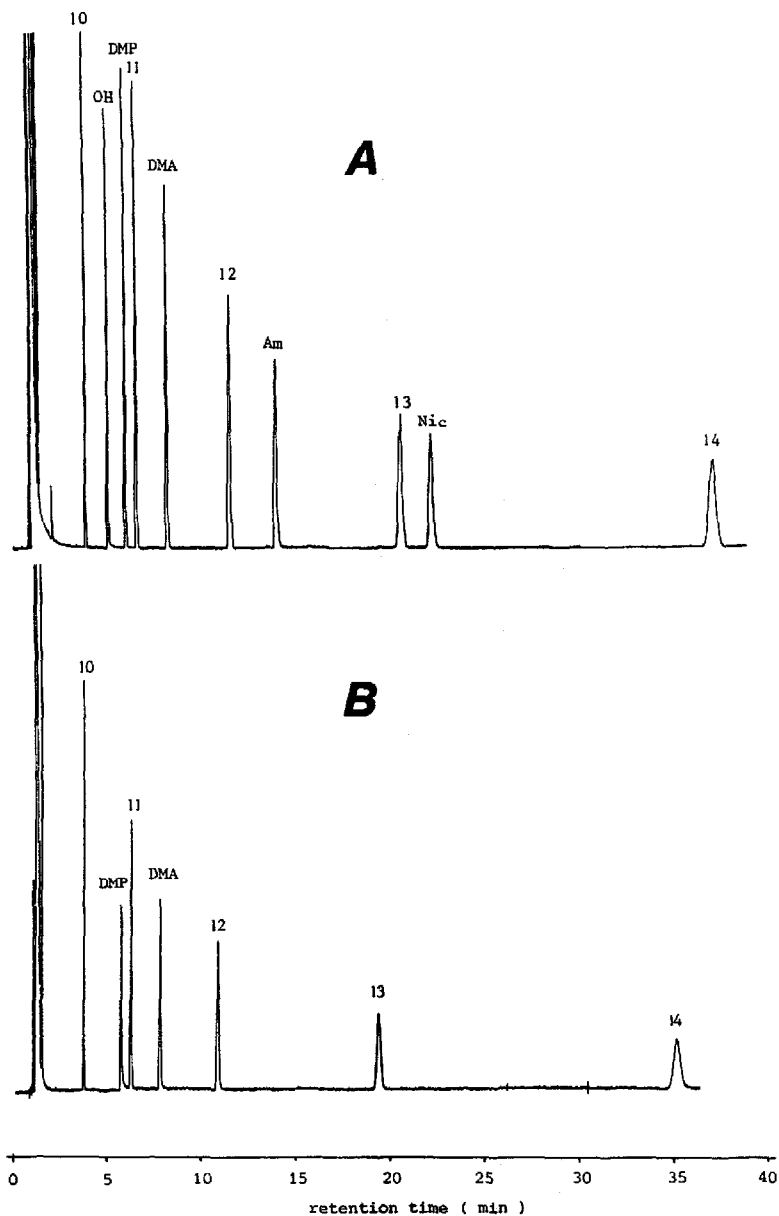


Fig. 3. Representative chromatograms of the thick-film reference column (A) and an untreated capillary (B) characterized with the double column system. Test conditions: helium carrier gas, isothermal operation at 110°C. For peak identifications of the test mixture, see Table II.

Evaluation of the PMHS-deactivated fused-silica capillaries

The recorded chromatograms of the reference column and the reference column connected to a piece of untreated fused-silica capillary column are shown in Fig. 3. Corresponding Kováts retention indices and normalized peak areas for all evaluated fused-silica capillaries and the reference column are given in Table IV.

The untreated piece of fused-silica capillary showed strong adsorption for all selective compounds in the test mixture. 1-Octanol (C₈-OH), 1-aminodecane (Am) and nicotine (Nic) did not elute at all, and 2,6-dimethylphenol (DMP) and 2,6-dimethylaniline (DMA) showed tailing and a decrease in the normalized peak areas, indicating strong acid silanol activity and the presence of basic sites.

Optimum deactivation was observed after silylation at 290°C for 2 h (column 2, Fig. 4), which is in agreement with results reported by Woolley *et al.*^{2,11}. The peak shapes of all components as eluted from the dual column system were similar to those on elution from the reference column alone. Deactivation at a lower temperature (260°C, column 1) resulted in a substantial increase in the wall activity, especially towards Am and Nic, which did not elute, and DMA, which partly eluted. This indicates that acid activity remained on the inner wall. Deactivation took place but was not yet completed, which is also evident from adsorption of C₈-OH; interaction with exposed siloxane bridges^{5,7} is responsible for this adsorption.

Deactivation at a higher temperature (310°C, column 3) or with a longer silylation time (8 h, column 4) demonstrated remaining, probably shielded, weak acid silanol activity. DMP and DMA showed no interactions with the column wall, but C₈-OH was adsorbed mildly, again indicating little activity of exposed siloxane bridges. A small amount of water on the inner surface prior to coating (column 5) is detrimental for the deactivating film formed during silylation (see Fig. 4). The selective compounds were all partly adsorbed and showed increased retention indices. This deactivated capillary demonstrated the largest adsorption of C₈-OH and DMP.

Reconditioning column 2 at 290°C for 65 h gave no increase in the activity of the column wall (column 6, Table IV). All components eluted in the same way as before

TABLE IV
NORMALIZED PEAK AREAS (*NA*) AND RETENTION INDICES (*I*) FOR MARKER COMPOUNDS IN THE TEST MIXTURE DETERMINED WITH A DUAL-COLUMN METHOD

Column No.	Marker compound									
	1-Octanol		DMP		DMA		Aminodecane		Nicotine	
	<i>NA</i>	<i>I</i>	<i>NA</i>	<i>I</i>	<i>NA</i>	<i>I</i>	<i>NA</i>	<i>I</i>	<i>NA</i>	<i>I</i>
Reference column	80	1050.2	94	1082.5	100	1139.2	96	1233.3	81	1312.6
1	66	1064.1	91	1076.3	74	1132.7	0	—	0	—
2	80	1050.3	94	1082.9	99	1139.8	95	1233.4	81	1313.0
3	65	1050.0	92	1080.4	96	1136.8	86	1235.5	75	1312.6
4	64	1049.2	93	1078.4	97	1134.8	88	1233.0	70	1309.2
5	43	1051.3	80	1083.3	84	1140.8	20	1239.4	26	1314.6
6 (ex. 2)	79	1049.7	93	1076.6	98	1137.1	93	1234.5	80	1313.0
7 ^a	0	—	76	1082.5	85	1139.6	0	—	0	—

^a Untreated fused-silica capillary (length 18.1 m).

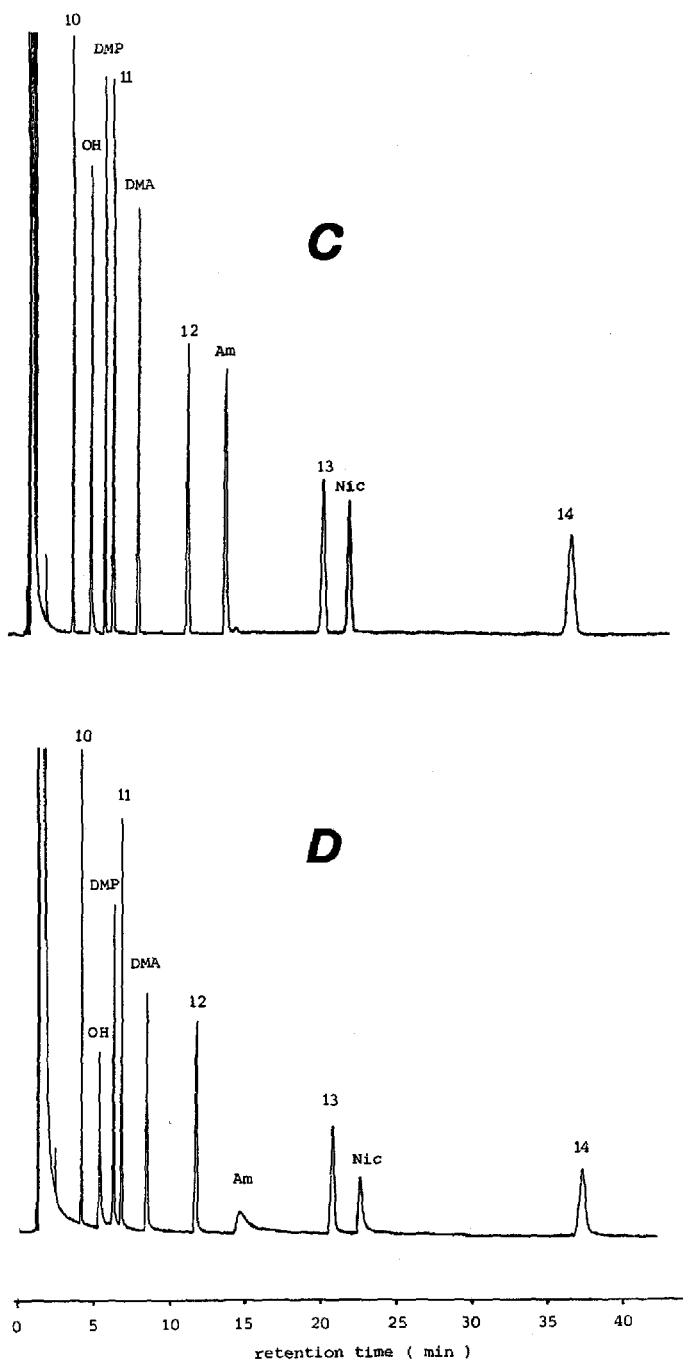


Fig. 4. Representative chromatograms of the optimum deactivated capillary (C) and the prewetted capillary, deactivated under optimum conditions (D). Test conditions: helium carrier gas, isothermal operation at 110°C. For peak identifications of the test mixture, see Table II.

conditioning. The column showed very good thermal stability, even after this long period of conditioning. The resistance towards solvents was evaluated by rinsing with *n*-pentane, dichloromethane and liquid carbon dioxide. No change in normalized peak areas or retention indices was noticed.

²⁹Si NMR measurements of PMHS-silylated Cab-O-Sils

The average carbon content determined after washing and drying of thick-film deactivated Cab-O-Sil was about 9.5% (w/w). Two exceptions were observed: the sample silylated at 240°C showed a lower content, *viz.*, 8.0% (w/w) carbon, probably caused by washing of unreacted PMHS from the surface, and the silylated wet Cab-O-Sil showed a 9.8% (w/w) carbon content, owing to slightly more cross-linking.

The formation of various siloxysilane surface moieties on Cab-O-Sil coated with a thick-film PMHS, silylated at temperatures ranging from 240 to 360°C for 12 h (Cab-O-Sil samples 1–6), was investigated by ²⁹Si MAS NMR. The spectra are presented in Fig. 5 and Table V lists chemical shifts most relevant to this paper. The relative ratios of the ²⁹Si MAS NMR signals, representing siliceous surface moieties, of Cab-O-Sil samples 1–6 are listed in Table VI.

From these spectra it can be concluded that the silylation products have chemical shifts mainly in the –35 ppm region, indicating that only methylhydroxiloxanes are anchored to the surface. The shape of the narrow signals at –35.3 and –36.1 ppm indicates that the methylhydroxiloxane units are still part of mobile polymer chains now anchored to the silica surface. This was confirmed by contact-time variation experiments (see below). The methylhydrodisiloxysilane group with a chemical shift at –35.3 ppm has two identical unreacted neighbouring groups, whereas the group with a chemical shift at –36.1 ppm has one methyltrisiloxysilane (T₃) on the α -position¹³ (see Fig. 6). This T₃ group is responsible for intra- and intermolecular cross-linking of the polymer chains (see reaction 3) or surface attachment at the silica (see reaction 1). Most of the T₃ groups on these silylated Cab-O-Sil samples were formed with the silica surface (see the appearance of a broad signal at –66.2 ppm). With increasing temperature the polymer chains degrade and react with the surface.

TABLE V
SILOXANE/SILANE FUNCTIONALITY NOTATION, TYPICAL ²⁹Si CHEMICAL AND SUBSTITUENT-INDUCED SHIFTS

<i>Compound</i>	<i>Chemical (spectral) functionality</i>	<i>Topological (network) functionality</i>	<i>Code</i>	<i>Chemical shift (ppm downfield from TMS)</i>
Trimethylsiloxysilane	M	1	M ₁	+9
Methylhydrodisiloxysilane ^a	D	2	D ₂ H	–36
Methylhydroxydisiloxysilane	T	2	T ₂	–55
Methyltrisiloxysilane	T	3	T ₃	–66
Hydroxysiloxane	Q	3	Q ₃	–101
Tetrasiloxysiloxane	Q	4	Q ₄	–110

^a Substituent-induced shift (ppm downfield from TMS) for methylhydrodisiloxysilane: D₂H · D₂H · D₂H – 35.3 ppm = D₂H; D₂H · D₂H · T₃ – 36.1 ppm = D₂H', one methyltrisiloxysilane on the α -position (see Fig. 6).

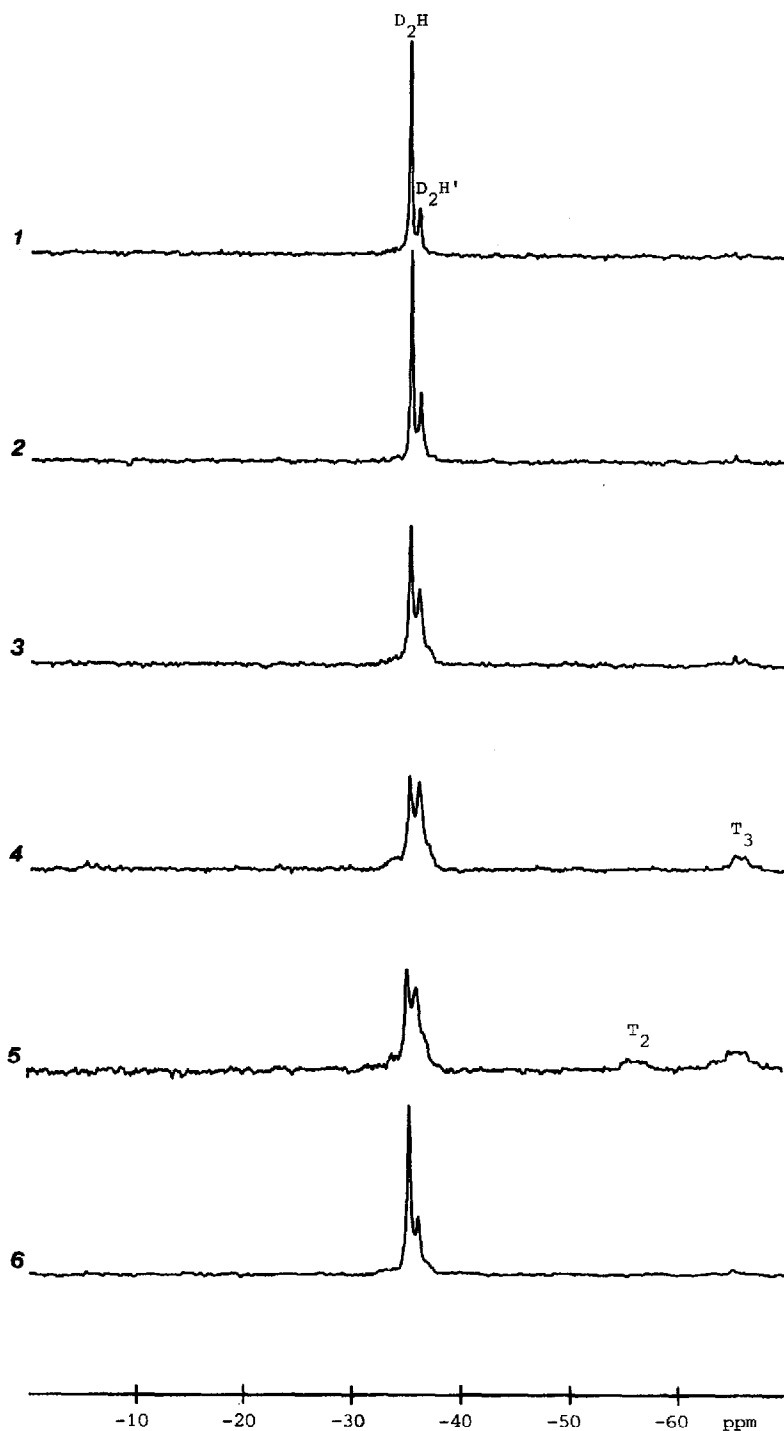


Fig. 5. ^{29}Si MAS NMR spectra of thick-film PMHS-silylated Cab-O-Sil samples 1-6. $N_s = 256$; pulse interval time, 10 s; acquisition time, 100 ms.

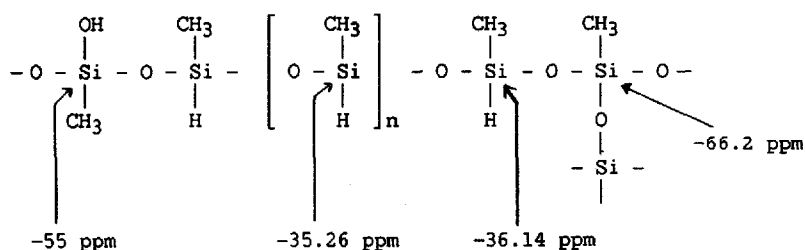


Fig. 6. Chemical shifts of possible surface siloxane moieties after silylation with PMHS.

Using contact-time variation experiments in ^{29}Si CP-MAS NMR, the mobilities of the methylhydrodisiloxysilane groups (D_2H and $\text{D}_2\text{H}'$) and, if present, of the methyltrisiloxysilane (T_3) groups were determined. Contact-time (CT) curves of Cab-O-Sil samples 2 ($280^\circ\text{C}/12\text{ h}$) and 4 ($360^\circ\text{C}/12\text{ h}$) are presented in Fig. 7.

Solid-state ^{13}C NMR contact-time variation experiments showed similar curves for the Cab-O-Sil samples to those obtained with octyl-modified reversed-phase high-performance liquid chromatographic (HPLC) silica in our laboratory¹⁴, as shown in Fig. 8. For the two methyl groups and C_1 the maxima in the CT curves were between 5 and 10 ms, caused by the close connection to the rigid silica surface of these groups, resulting in only slight mobility. For C_4 and C_5 the maxima were about 25 ms, indicating greater mobility than for methyl and C_1 groups. The maximum for C_8 was above 30 ms, indicating a high mobility owing to the large distance to the surface bond.

The CT curves for sample 2 indicate that mobile methylhydrodisiloxane chains are still present after silylation at 280°C . The maximum intensity for the signals in the -35 ppm region was observed for a contact time of *ca.* 27 ms. This equals the mobility of a C_6 group in the octyl chain in Fig. 8. The deactivating film can be conceived as two

TABLE VI

RELATIVE AMOUNTS OF ^{29}Si SOLID-STATE NMR SIGNALS OF SURFACE MOIETIES ON SILYLATED CAB-O-SIL SAMPLES

Cab-O-Sil sample No.	^{29}Si NMR measurement	Relative ratio of ^{29}Si NMR signals			
		D_2H	$\text{D}_2\text{H}'$	T_2	T_3
1	MAS	0.82	0.18	—	—
2	MAS	0.71	0.29	—	—
3	MAS	0.54	0.43	—	0.03
4	MAS	0.39	0.49	—	0.12
5	MAS	0.40	0.44	0.05	0.11
6	MAS	0.71	0.29	—	—
7	CP-MAS	—	0.55	—	0.45
8	CP-MAS	—	0.44	—	0.56
9	CP-MAS	—	0.37	—	0.63
10	CP-MAS	—	0.18	—	0.83
11	CP-MAS	—	0.31	0.05	0.64
12	CP-MAS	—	0.24	0.06	0.70
13	CP-MAS	—	0	0.10	0.90

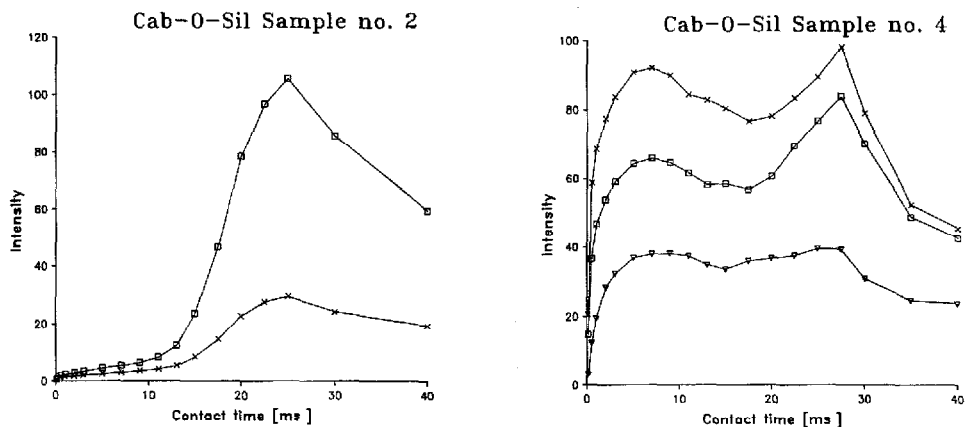


Fig. 7. Contact-time variation curves with observed chemical shifts for surface siloxane moieties of PMHS-silylated Cab-O-Sil samples 2 and 4. $N_s = 300$; pulse interval time, 10 s; acquisition time, 100 ms. Sample 2: □, -35.25 ; ×, -36.07 ppm. Sample 4: □, -35.45 ; ×, -36.27 ; ▽, -66.3 ppm.

layers: a dense cross-linked network near the surface anchored through methyl-trisiloxysilane, only a few monolayers thick and with longer mobile methylhydro-siloxane polymers attached to this rigid layer (see Fig. 9). The total number of methyltrisiloxysilane cross-linking groups is very small. After silylation of 360°C the CT curves demonstrated at least two distinct maxima at contact times of *ca.* 7 and 27 ms, indicating that two coherent methylhydro-siloxysilane systems are present in the deactivating film: a small amount of mobile, slightly cross-linked methylhydro-siloxane polymer, similar to silylation at 280°C , on top of a rigid layer with many immobile small-chain segments anchored to the surface and intensely cross-linked polymers. Cab-O-Sil sample 5 was originally a wet Cab-O-Sil coated with 5 nm of PMHS, silylated at 290°C for only 4 h. As a reference also a dry Cab-O-Sil was coated and silylated in the same way (Cab-O-Sil 6). Their ^{29}Si MAS spectra are shown in Fig. 5. The ratio between the signals at -35.3 and -36.1 ppm was influenced by the presence of water; more short-chain segments were present in the silylated film of sample 5. The amount of methyltrisiloxysilane (T_3) was increased by enhanced cross-linking and surface attachments and an extra signal at -55 ppm, corresponding to not yet cross-linked methylhydroxydisiloxysilanes (T_2), was detected (see reaction 2). These T_2 groups add extra silanol activity to the modified silica surface. CT curves were also recorded for Cab-O-Sil sample 5 and are presented in Fig. 10. The CT curves for Cab-O-Sil sample 6 were similar to those of sample 2 shown in Fig. 7. From the ^{29}Si MAS NMR spectrum one would expect that a more rigid extensively cross-linked layer

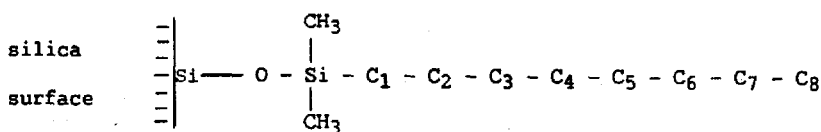


Fig. 8. Octyl-modified reversed-phase HPLC silica.

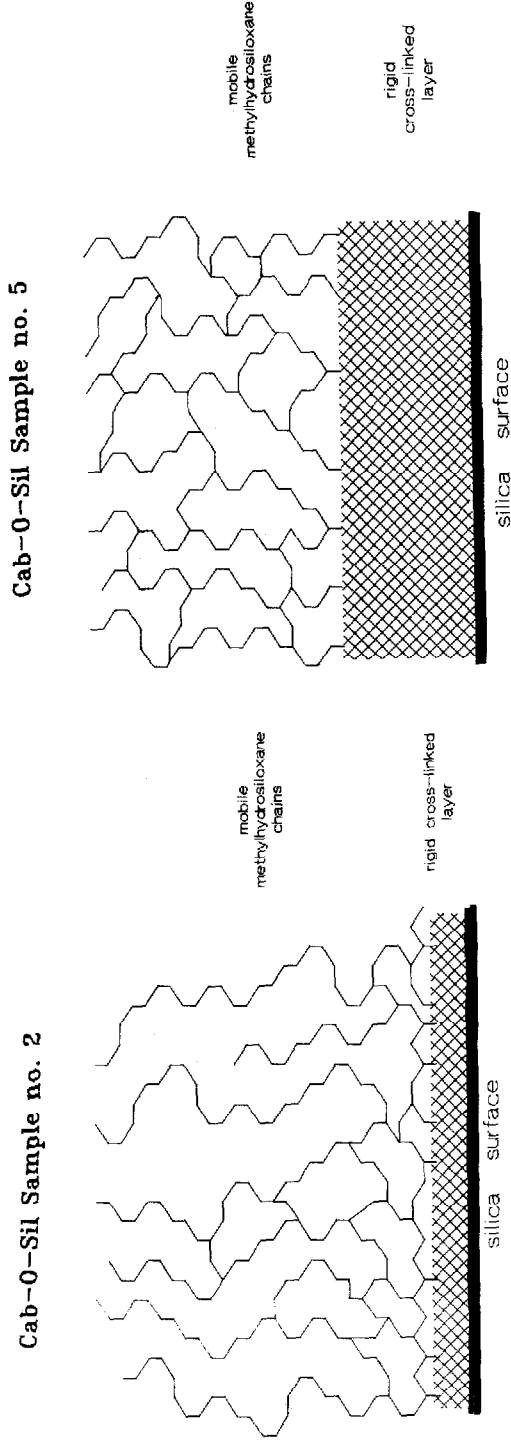


Fig. 9. Models of the structure of the deactivating film after silylation of Cab-O-Sil samples 2 and 5.

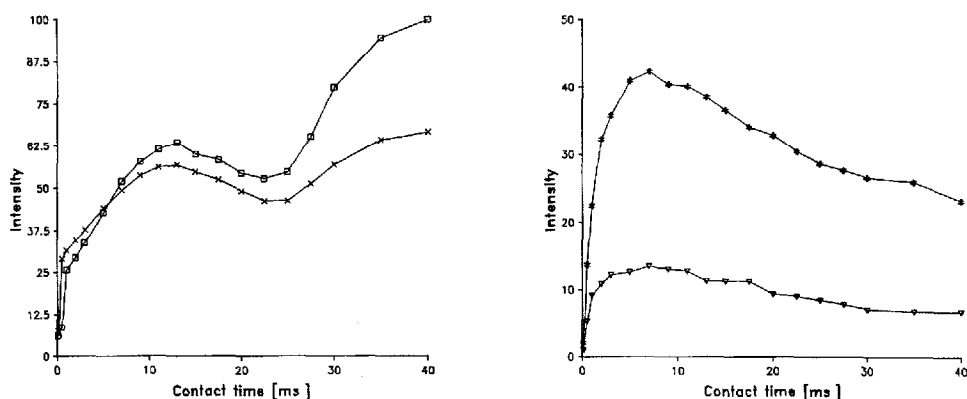


Fig. 10. Contact-time variation curves with observed chemical shifts for surface siloxane moieties of PMHS-silylated Cab-O-Sil sample 5. $N_s = 300$; pulse interval time, 10 s; acquisition time, 100 ms; line broadening, 10 Hz. □, -35.3 ; ×, -36.1 ; ▽, -56.8 ; +, -66.1 ppm.

was formed. This is shown by the CT curves for the T_2 and T_3 groups, but the CT curves for D_2H and D_2H' show a second maximum with an optimum contact time longer than 40 ms, again indicating long, flexible methylhydrosiloxane chains, probably on top of the rigid layer (see Fig. 9). In all thick-film deactivated Cab-O-Sil samples mobile methylhydrosiloxane chains were observed. This indicated the presence of exposed hydrogen groups as part of the deactivating film.

The carbon content of thin-film deactivated Cab-O-Sil silylated at 280°C was about 4.4% (w/w). This suggested that a deactivating film more than a few monolayers thick was formed. However, from the 1-nm coated Cab-O-Sil samples it was not possible to obtain ^{29}Si MAS NMR spectra within a reasonable time, because of the long relaxation times. This also confirms the more rigid structure of the deactivating film.

The ^{29}Si CP-MAS NMR spectra of silylated Cab-O-Sil samples 7–10 coated with a thin PMHS coating are shown in Fig. 11. These samples demonstrate a structure of the siloxane moieties different from the thick film; the methylhydrosiloxane chains were degraded. The remaining methylhydrodisiloxysilanes (mainly D_4H') were anchored to the surface via methyltrisiloxysilanes and formed a rigid, fairly thin film, as is demonstrated by the CT curves in Fig. 12. Pronounced maxima for D_2H' and T_3 groups are observed between 10 and 20 ms. These groups exhibit approximately the same mobility as C_3 (Fig. 8) in the octyl chain of a reversed-phase C_8 silica. The silylated films consisted of a densely cross-linked network of D_2H' and T_3 groups anchored to the surface via T_3 groups.

As the temperature increased from 280 to 300°C , the amount of D_2H and D_2H' groups decreased and the amount of T_3 groups increased. Above 300°C no significant changes in the amount of T_3 groups were observed. Deactivation of wet Cab-O-Sil with 1 nm of PMHS even caused a total loss of methylhydrodisiloxysilane moieties at a silylation temperature of 360°C owing to conversion into methyltrisiloxysilanes (T_3) and to a smaller extent into methylhydroxydisiloxysilanes (T_2) (see also Fig. 11). The total amount of T_2 groups did not change with increasing temperature. These

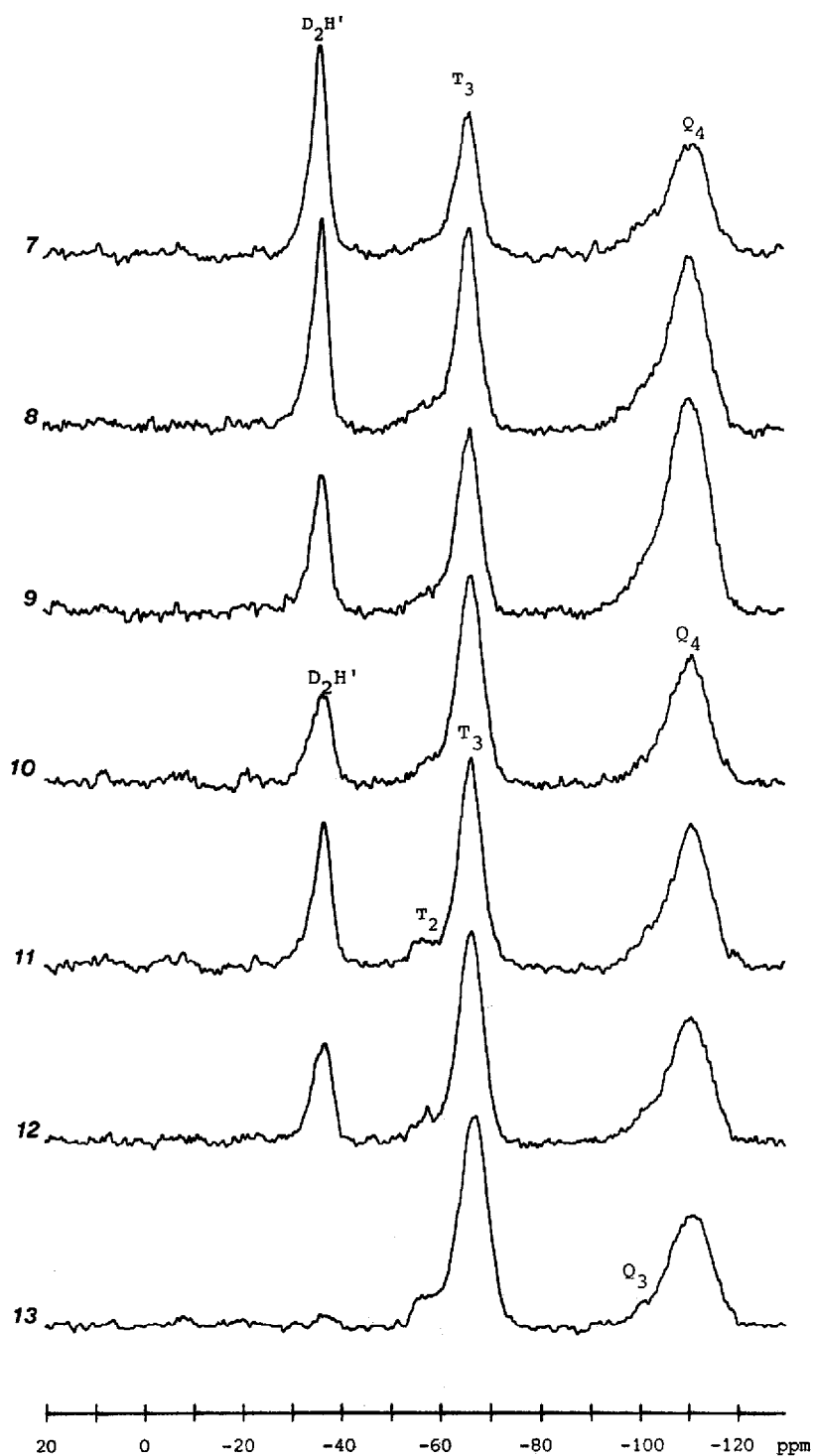


Fig. 11. ^{29}Si CP-MAS NMR spectra of thin-film PMHS-silylated Cab-O-Sil samples 7–13. $N_s = 500$; pulse interval time, 5 s; contact time, 15 ms; acquisition time, 25.6 ms; line broadening, 15 Hz.

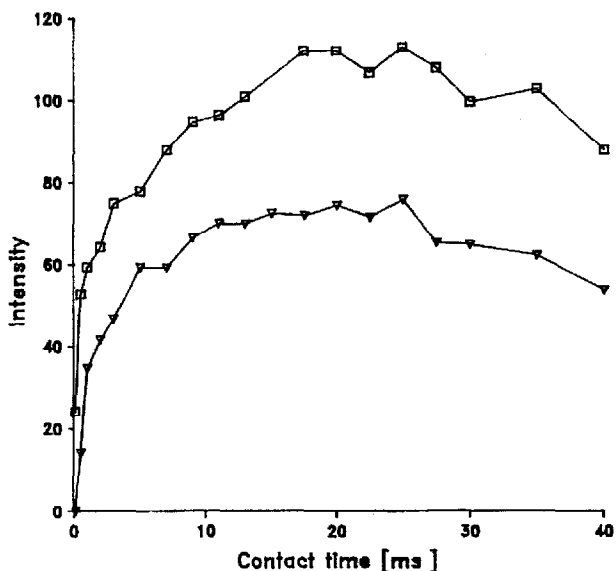


Fig. 12. Contact-time variation curves with observed chemical shifts for surface siloxane moieties of PMHS-silylated Cab-O-Sil sample 7. $N_s = 300$; pulse interval time, 5 s; acquisition time, 25.6 ms; line broadening, 30 Hz. □, -36.2 ; ▽, -66.1 ppm.

unconverted T_2 groups add extra silanol activity to the silylated surface, as mentioned above. At silylation temperatures around 290°C a remaining substantial amount of methylhydrodisiloxysilanes was still detected (see Table VI), although the broad signal at -36.5 ppm implied that most of these groups had converted neighbours and were part of a rigid and thus shielding film.

The 1-nm PMHS films showed different physical and chemical properties to deactivating films silylated after coating with 5 nm of PMHS. Relatively more T_3 groups were observed, causing a rigid and dense network. No long, flexible methylhydrodisiloxane polymer chains were detected. The amounts of silicon hydride groups in the network were relatively low in comparison with thick films, but not negligible. At silylation temperatures below 300°C over 50% of the surface siloxane groups contained hydrogen when dry Cab-O-Sil was deactivated. Only part of these hydrogen groups will be shielded by the rigid structure.

Silylation of Cab-O-Sil as a model for deactivation of fused silica

In any comparison between results obtained with model chemistry, as introduced in this and earlier papers^{5,9,10}, on the one hand, and actual deactivation of fused-silica columns as judged by GC, on the other, the thickness of the deactivating film plays a crucial role. It was shown above with solid-state ^{29}Si NMR that the natures of the films obtained on Cab-O-Sil on deactivation with PMHS layers of 1 and 5 nm differ considerably.

With fused-silica columns, according to equations for dynamic coating as applied by Bartle¹², the thickness was *ca.* 10 nm. Consequently, one should compare these fused-silica capillaries with thick-film silylated Cab-O-Sil samples as prepared in

this study. After silylation of Cab-O-Sil with PMHS for several hours at 280–290°C, with a stoichiometry corresponding to a film thickness of 5 nm, an anchored network was obtained close to the surface of Cab-O-Sil with only slight cross-linking (see above). Of the total methylhydrosiloxane units that were attached to the surface, only *ca.* 20% occupied α -positions with respect to surface attachment or cross-linking after silylation. It proved difficult to detect the methyltrisiloxanes (directly attached to the Cab-O-Sil surface) by ^{29}Si MAS NMR, mainly because of their relatively low concentration of *ca.* 5–10%. In spite of this apparent low conversion of methylhydrosiloxanes to methyltrisiloxysilanes which attached the polymer chain tightly to the silica surface, the surface was adequately covered and deactivated, as shown by the GC experiments (see Fig. 4).

In earlier reports, the high deactivation efficiency of various PMHS forms and other organosilicon hydride deactivating agents was attributed to the almost complete conversion of hydrogen–silicon bonds into siloxane bonds (reactions 1–3). In this study we observed that methylhydrosiloxanes show a high reactivity towards silanol groups, in particular to those which are Brønstedt acids. In order to achieve a more or less complete conversion of the silicon hydride groups, a temperature of *ca.* 360°C is required. In our opinion it seems that one of the main advantages of silylating agents containing silicon hydride moieties is connected with the small (Van der Waals) dimensions of these groups rather than with their allegedly high intrinsic reactivities^{1,11,15}. The lack of reaction propensity of the chains towards the surface silanol groups, however, does not prevent a tight attachment of the chain to the surface (the surface silanol groups have disappeared). Further, cross-linking of the chains near the surface, although of low overall concentration, provides additional surface screening. Remaining silicon hydride groups on the chains apparently do not interfere with the elution of the appropriate test components in GC experiments.

Deactivation under more severe conditions (higher temperatures and/or longer reaction periods) mainly caused an increase in the extent of cross-polymerization near the surface. However, the mobilities of the chains protruding upwards from this layer were not affected significantly, as was shown by variable-contact time ^{29}Si CP-MAS NMR (see above). An increase in the adsorption of 1-octanol by cross-linking products became noticeable in the GC experiments. Cross-linking serves to increase the total amount of siloxane bonds in the deactivating film. Intuitively, one would expect these siloxane moieties to be rather shielded (inaccessible), but this seems only partially true when coating a column wall with a thick film (*ca.* 10 nm) of PMHS. Woolley *et al.*² reported optimum silylation after 4 h at 300°C with PMHS, after which a very thin deactivating film was formed. In the determination of the capacity of these films, a film thickness of 1–4 monolayers was assumed. An exact experimental determination from the chromatographic retention of such a film thickness is hardly feasible. Therefore, we assume here that a cross-linked layer near the surface is formed with a thickness similar to that postulated by Woolley *et al.* Moreover, on top of these initial layers we observed long, mobile methylhydrosiloxane chains. These chains could play a role in the anchoring of phenyl-containing stationary phases during radical-induced cross-linking¹⁶. A complete rigid, densely cross-linked film exists only after silylation at optimum temperature of a thin-film coated silica.

The influence of water, present at the silica surface, on the silylation is evident; advanced cross-linking occurs and a relatively thick rigid layer is formed near the

surface containing methyltrisiloxysilanes, methylhydrodisiloxysilanes and a small amount of active, unreacted methylhydroxydisiloxysilanes. These hydroxyl groups caused strong adsorption of all critical components present in the test mixture in GC. When coated with a thick film again a top layer of mobile methylhydrosiloxane chains appears after silylation at 280°C. Very small amounts of water are necessary for cross-linking of a thin rigid layer near the surface and increase the surface anchoring of the methylhydrosiloxane network. The appropriate amount of water is present after severe leaching, extensive flushing with water and drying at a moderate temperature of 140°C. Remaining, probably physisorbed, water influences the structure and attachment of the deactivating film near the surface. Too high a content of water yields unreacted hydroxyl groups and increased activity of the surface. Further, the thickness of the densely cross-linked layer is increased proportionally with the amount of water present at the surface before silylation.

CONCLUSIONS

In conclusion, PS 122 is an efficient PMHS-deactivating reagent for fused-silica capillary column walls for the preparation of non-polar columns. The advantage of organosilicon hydride agents for deactivation of fused-silica capillary columns is the small (van der Waals) dimension of the silicon hydride and their selective reactivity towards the Brønsted acid silanol groups. The intrinsic reactivity of silicon hydride to form siloxane bonds is not sufficient to provide total conversion of the silicon hydride groups. Important differences in the nature and structure of the deactivating films on the silica surface have been established between coatings with a thickness of 5 or 1 nm. When coated with a 5-nm film, the remaining methylhydrosiloxane groups are part of anchored mobile longer polymer chains protruding upwards on top of a densely cross-linked network of polymers near the surface. Physisorbed water present at the surface before silylation provides a good deactivating film on the fused-silica capillary column wall under optimum silylation conditions of 290°C for 2 h. Too high a content of water present before silylation leads to increasing activity caused by exposed siloxane bonds and methylhydroxydisiloxysilanes in the polymer network.

The optimum deactivating film exhibits excellent thermal stability and solvent resistance. No decrease in either film thickness or deactivation was observed on the silylated Cab-O-Sil samples or inside the deactivated capillaries after the completed deactivation of these surfaces.

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