

Vinyl modification of fused-silica surfaces in polysiloxane-coated 10–50 μm I.D. capillaries for open-tubular liquid chromatography

Karin Göhlin

Department of Analytical and Marine Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg (Sweden)

Marita Larsson*

Bioanalytical Chemistry, Astra Hässle AB, S-431 83 Mölndal (Sweden)

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ABSTRACT

Attempts were made to improve the stability of narrow-bore open-tubular columns for liquid chromatography. In addition, the LC selectivity shift for thin stationary phase films was examined. Three different pretreatment methods based on vinyl-containing reagents were tested in 50 μm I.D. fused-silica capillaries. The modified capillaries were coated with the stationary phase PS 255, a polydimethylvinylsiloxane, and cross-linked. The columns were evaluated according to selectivity in LC and also to the degree of immobilization and column inertness in GC. Deactivating the capillaries with polydimethylvinylsiloxane was the preferred method. It was not possible to confirm bonding between the deactivation layer and the cross-linked polysiloxane stationary phase film. The proposal that the selectivity shift, for thin stationary phase films in open-tubular LC, originated from influence of the fused-silica surface on the stationary phase configuration could be excluded. The polydimethylvinylsiloxane method was also used in narrow-bore (10 μm I.D.) columns. Preliminary LC studies with anthracene derivatives as model substances indicated that deactivation has no influence on the efficiency.

INTRODUCTION

The need to improve the separation power in liquid chromatography (LC) has directed development towards miniaturization. One approach is to use extremely narrow open tubes as separation columns. In addition, small-diameter open columns are of current interest in gas chromatography (GC) and supercritical fluid chromatography (SFC), owing to their ability to perform high-resolution and high-speed separations. The main advantage of open-tubular columns (OTCs) is associated with the openness

of the column, which facilitates the use of longer columns and consequently provides a higher efficiency. In LC, OTCs with I.D. of 10 μm or less are able to out-perform conventional packed columns. Considering that the volume of a 5 μm I.D. column is 20 nl/m , it is obvious that the use of OTCs in LC places high demands on the column preparation method and on the chromatographic system. In our group, fused-silica capillaries are coated with immobilized polysiloxanes, using the static evaporative coating technique [1–3]. We use split injections and on-column laser-induced fluorescence detection to minimize extra-column band broadening. Recently, our group compared 5–15 μm I.D. OTCs and conventional packed columns in LC using

* Corresponding author.

the same type of polysiloxane stationary phase [4]. The experimental data support the chromatographic theories [5], which conclude that narrow OTCs are able to compete with conventional packed columns with respect to high-resolution and high-speed separations. Up to 2000 theoretical plates/s were reached for early-eluting solutes when 5 μm I.D. columns in reversed-phase (RP) LC were used [1,4].

Although the efficiency of non-polar polysiloxane-coated narrow open-tubular (OT) LC columns have been thoroughly investigated [1-4], there are still some questions concerning the selectivity characteristics. Folestad *et al.* [2] studied the chromatographic performance of immobilized polysiloxane stationary phase films coated on untreated 5-50 μm I.D. fused-silica capillaries. They showed that thin stationary phase films ($<0.25 \mu\text{m}$) caused a shift in selectivity for fluorene derivatives in RPLC. This has also been observed by us with polymethyloctadecylsiloxane-coated 50 μm I.D. columns [1]. An influence from the fused-silica surface on the stationary phase configuration at the glass-to-polymer interface was suggested [2]. This explanation was based on a model presented by Cohen-Addad *et al.* [6], illustrating a local orientation effect of the polymer chains close to the glass surface. Thus, the stationary phase at the surface could differ from the bulk phase. This observation called for further studies on the effect of pretreatment of the fused-silica surface prior to coating.

Also, it is well known that fused-silica capillaries have batch-to-batch variations. The silanol density on the capillary surface is one of the differences. In addition, it has been found that the background fluorescence from different capillaries varies [7]. Considering that the nature of the surface layer could influence the properties of the column, it would be desirable to control such parameters. A pretreatment of the capillaries before coating with stationary phase could possibly reduce the variation in silanol density on the glass surface.

Columns used in LC are continuously exposed to a liquid mobile phase. It is therefore important that the liquid-like polysiloxane stationary phase film in OTCs is non-extractable. To

stabilize the stationary phase layer it is cross-linked by a radical initiated reaction. It can also be assumed that an increase in the stability can be obtained through the incorporation of vinyl groups at the glass surface in a deactivation layer. These vinyl groups may form a covalent linkage with the stationary phase layer as indicated by Grob's finding, which was that a cross-linked silicone deposited on a methylvinyl-modified glass surface was less extractable in organic solvents than silicones deposited on methyl-modified surfaces [8].

In this work, the fused-silica surface of 50 μm I.D. capillaries was pretreated in three different ways prior to coating with PS 255. The primary aim was to study the influence of deactivation on LC selectivity and we also wanted to improve the immobilization through the possible binding of the stationary phase to the surface. The favoured method was deactivating the capillaries with polydimethylvinylsiloxane (PDMVS). This method was also applied in 10 μm I.D. columns. The columns were evaluated according to efficiency, selectivity, degree of immobilization and column inertness using LC and GC.

EXPERIMENTAL

Pretreatment

Fused-silica capillaries of 50 μm I.D. (Scientific Glass Engineering, North Melbourne, Australia) and 10 μm I.D. (Polymicro Technologies, Phoenix, AZ, USA) were used. All columns had an approximate length of 2 m. Before any other treatment, the polyimide coating was removed from a 1-cm length of the capillary by heat from a butane flame, to make on-column detection possible. The capillaries were then pretreated in three different ways, as described in Table I.

When the deactivation reagents 1,3-divinyltetramethyldisilazane (DVTMDS) and vinyltrimethoxysilane were used the capillaries were treated with acid, according to a method earlier used for fused-silica surfaces by Schutjes *et al.* [9]. First the capillaries were rinsed with a mixture of hydrofluoric and nitric acid [2% (v/v) each] for 30 min and then with 2% (v/v) hydrochloric acid for 10 min. All acids were of

TABLE I
DESCRIPTION OF THE PRETREATMENT METHODS USED

Parameter	Deactivation reagent		
	A 1,3-divinyltetramethyldisilazane (DVTMDS)	B polydimethylvinylsiloxane (PDMVS)	C vinyltrimethoxysilane
Acid treatment	Yes	No	Yes
Concentration (% v/v in n-pentane)	50	5	50
Temperature programme	20–350°C at 2°C/min	20–350°C at 2°C/min	20–200°C at 8°C/min
Time (h)	6-22	1-2	1-4

analytical-reagent grade and from Merck (Darmstadt, Germany). Finally, the capillaries were rinsed to neutrality with water obtained from a Milli-Q system (Millipore). The capillaries were dried under a nitrogen flow in 280°C for 3 h. A dynamic coating method was applied for the deactivation reagents (see Table I), all from Petrarch Systems (Bristol, PA, USA). The capillary was filled with the reagent dissolved in n-pentane (analytical-reagent grade; Merck) and emptied at an average speed of 2-3 cm/s. The helium-pressurized device used for filling was the same as that for the static coating technique [1–2]. The capillary ends were then flame sealed and the capillary was heated to the reaction temperature. The capillaries were allowed to cool slowly and then rinsed with 2-3 column volumes of n-pentane to remove the excess of reagent before testing and coating.

Column coating

After pretreatment, the capillaries were coated with the stationary phase PS 255, a dimethylsiloxane-1-3% methylvinylsiloxane gum phase (Fluka, Buchs, Switzerland). The static coating procedure used has been thoroughly described earlier [1,2]. Cross-linking of the stationary phase was performed by a free radical-initiated reaction. The concentration of the initiator dicumyl peroxide was 1% (w/w with respect to the stationary phase). Inside diameters of the coated columns were calculated from the measured electrical resistance of the mercury-filled capillary as described by Guthrie *et al.* [10].

The stationary phase film thickness, d_t , in static coating can be determined by the column radius, r , and the concentration of the stationary phase in the coating solution, c (% v/v). A density of 0.98 g/ml for the PS 255 was used to calculate the stationary phase film thickness according to

$$d_t = r \left[\frac{1}{(100/c) - 1} + 1 \right]^{1/2} - r \quad (1)$$

Equipment

GC measurements were performed at 80°C using a Carlo Erba Fractovap 2101 instrument equipped with a split injector and a flame ionization detector. Test solutes were a mixture of n-alkanes (C₁₀–C₁₃), n-octanol, dicyclohexylamine, naphthalene (Merck) and Testmischung II nach Grob (Fluka). The splitting ratio was 1:2500 and the injection volume 2 μl. The gas hold-up time was measured by a procedure developed for these short columns [11].

LC measurements were made using a conventional LDC Constametric I LC pump and a Valco six-port valve equipped with an external loop and a split. On-column detection with the 50 μm I.D. columns was performed with a modified Shimadzu RF-530 fluorescence detector. The excitation and emission wavelengths used for the fluorene derivatives [9-fluorenylmethanol (Fluka) and 9-phenylfluorene and fluorene (Sigma, St. Louis, MO, USA)] were 265 and 315 nm, respectively. Nitromethane was used as an unretained solute. With the 10 μm I.D. columns laser-induced on-column fluorescence detection was used [12]. Anthracene derivatives (synthes-

ized at the Department of Organic Chemistry, University of Göteborg) were used as test solutes. Chromatograms were recorded on a Perkin-Elmer Model 56 strip-chart recorder and all measurements of chromatographic parameters were made manually.

RESULTS AND DISCUSSION

Efficient deactivation methods are crucial in the production of open-tubular fused-silica columns, especially for the determination of trace amounts of substances that tend to interact with the glass surface. Until now our work on fused-silica columns in OT-LC has been done using columns with the polymeric stationary phase coated on the bare fused-silica surface. Fused silica has a lower metal content and a lower silanol density than other types of glass used in capillary chromatography, and its chemical reactivity is therefore lower. However, the fused-silica still has a slightly acidic character. The only pretreatment used was to purge the capillaries with helium at room temperature in order to remove acidic residues [13]. These columns have behaved well chromatographically [1,2,4], but they have not really been exposed to difficult test substances in LC, such as amine-containing solutes.

The pretreatment and deactivation of fused-silica surfaces in capillary chromatography has, to a great extent, been based on the well established methods for open-tubular glass columns in GC. The technology is essentially the same, but the smaller dimensions of OT-LC columns place higher demands on the technique, owing to the increased risk of plugging.

The first step in the surface modification is hydrothermal treatment with acid and water followed by drying at elevated temperatures. To examine the effect of this treatment, the chromatographic properties of untreated fused-silica capillaries were studied with GC measurements at 80°C. Both n-tridecane and dicyclohexylamine were retained on the crude capillaries showing a large difference in the k' values, especially for the amine, *viz.*, 7.4 and 24, for two different batches of fused silica. Acid treatment made the batches more similar, as indicated by the same k'

for the amine after the treatment. These data imply the need for a pretreatment of the surface to enable reproducible column performance to be achieved.

Two deactivation techniques were studied (Table I), (A) high-temperature silylation [14,15] and (B) polysiloxane degradation (PSD) [16,17]. They are both among the most commonly used deactivation methods in capillary GC. These methods have also been used previously with 50 μm I.D. columns for GC and SFC [18]. A third method (C), with vinyltrimethoxysilane, resulted in poor peak shapes in GC and was excluded early in this study.

With the PSD-type deactivation (B), a lower concentration of the deactivation reagent was used compared with the high-temperature silylation method (A). The reason for this was that in the initial attempts with PDMVS as a 1:1 solution in n-pentane resulted in plugging of the capillaries during the heat treatment.

Our choice of deactivation reagents was based on the fact that a deactivation layer containing vinyl groups amenable to covalent linkage to the stationary phase has previously been shown to reduce the extractable part of the stationary phase [8]. It was shown that the extractability decreased strongly when there were vinyl groups both at the surface of borosilicate glass capillary and in the stationary phase (5% of the stationary phase was extractable compared with 36% without vinyl groups). In this study the columns were coated with thin layers of stationary phase to enhance the influence of the underlying surface. The OTCs are presented in Table II. The nominal film thickness was varied between 26 and 280 nm in the 50 μm I.D. columns.

Immobilization and column efficiency

The degree of immobilization was investigated by measuring capacity factors in coated columns with GC before and after column rinsing with dichloromethane and n-pentane (see Table II). As can be seen, there is a large variation in the degree of cross-linking. However, the relative standard deviation for the k' values was less than 1%.

Folestad et al. [2] found a stationary phase loss of ca. 8–10% for 50 μm I.D. columns coated

TABLE II
CHARACTERISTICS OF THE OPEN-TUBULAR COLUMNS

The degree of immobilization of the cross-linked stationary phase was measured as the GC retention of *n*-alkanes before and after rinsing the columns with dichloromethane and *n*-pentane.

Column No.	Deactivation method ^a	Concentration of PS 255 (% v/v)	Film thickness (μm)	Decrease in retention (%)
1	A	2.0	0.26	17
2	A	1.0	0.13	11
3	A	1.0	0.13	21
4	A	0.5	0.067	21
5 ^b	B	2.0	0.060	Not measured
6	B	2.0	0.26	14
7	B	1.0	0.13	0
8	B	0.5	0.066	13
9	B	0.2	0.026	8
10 ^b	—	2.0	0.060	Not measured
11	—	2.0	0.28	12
12	—	1.0	0.13	4
13	—	1.0	0.13	8

^a See Table I.

^b 10 μm I.D. columns.

with PS 255 directly on the bare fused-silica surface, which agrees well with our data. Grob and Grob [8] suggested that the vinyl groups at the surface could consume peroxide and decrease the possibility of cross-linking occurring in the stationary phase. Despite this they obtained a higher degree of immobilization of the stationary phase with vinyl-containing reagents and stationary phases.

In our work some of the vinyl-modified columns showed a larger loss of stationary phase compared with the non-deactivated columns, despite the use of a similar reaction temperature and amount of peroxide to those used by Grob and Grob [8]. For example, columns deactivated with DVTMDS (A) lost up to 21% of the stationary phase. However, column 2 with a loss of 11% had the longest treatment time (22 h) during deactivation, while the columns with the higher loss were treated for 6-12 h. Also, the columns deactivated with PDMVS (B) in general showed a higher loss of stationary phase than columns coated without any pretreatment. Hence the possible covalent bonding between the deactivated surface and the stationary phase layer, which was meant to increase the immobili-

zation of the stationary phase, could not be confirmed.

In spite of the large differences in extractability between the columns there was no notable difference in efficiency, i.e., number of theoretical plates, *N*. A typical example is 24 000 and 29000 for dodecane and tridecane, respectively, in column 6 at a separation temperature of 80°C. An alternative GC test of column efficiency is shown in Fig. 1. Average Trennzahl (separation number) values for methyl decanoate (*E*_n) and methyl dodecanoate (*E*_n) (see eqn. 2) were measured before and after column rinsing at different temperature program rates.

$$TZ = \left[\frac{t_R(E_{12}) - t_R(E_{10})}{w_{1/2}(E_{12}) + w_{1/2}(E_{10})} - 1 \right] / 2 \quad (2)$$

where t_R is the retention time and $w_{1/2}$ is the peak width at half-height. The Trennzahl values increase after column rinsing. This can be explained by the reduced elution temperature, owing to the smaller stationary-to-mobile phase ratio in the column after removal of the non-cross-linked stationary phase, rather than an improved stationary phase quality.

Efficiency was also evaluated in LC. In Fig. 2

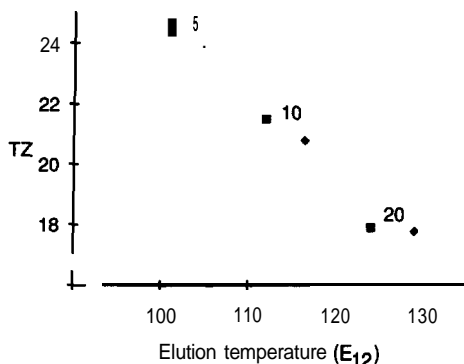


Fig. 1. Average Trennzahl (TZ) for the solute pair *n*-C₁₀ and *n*-C₁₂, methyl esters vs. elution temperature (◆) before and (■) after solvent rinsing. Column 8, deactivated with PDMVS. Numbers denote temperature programming rate (°C/min). Elution temperature is given for E₁₂ (methyl dodecanoate).

the reduced plate height, h , vs. the reduced velocity, ν , is presented for two 10 μm I.D. columns coated with a stationary phase solution of 2%. Column 5 was deactivated with PDMVS and in column 10 the stationary phase was coated on the bare fused-silica surface. There were some differences in the retention capacities of the columns, hence two solutes with the same k' values were chosen. The degree of cross-linking was not determined in these columns. There is good agreement between the two

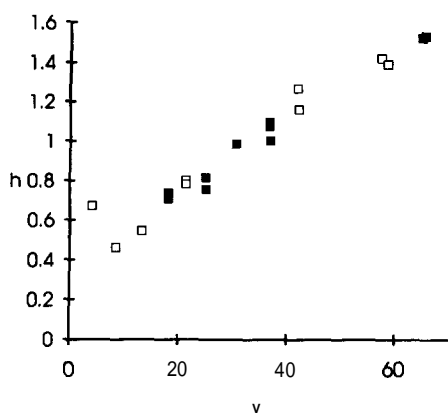


Fig. 2. Reduced plate height vs. reduced velocity for two 10 μm I.D. columns, (□) column 5 and (■) column 10, deactivated with PDMVS and non-deactivated, respectively. Solutes were propylenephenylanthracene column 5 and *n*-butylanthracene in column 10, both with $k' = 0.21$. Mobile phase: acetonitrile-water (1: 1).

columns, which indicates that the deactivation method has no influence on the efficiency obtained in LC.

Column inertness

Adsorption in fused-silica columns is generally considered to be a result of surface silanol interactions. Inertness determined in terms of adsorption due to hydrogen bonding is often viewed in GC by primary alcohols or amine-containing solutes, and is ascertained either by tailing or by an increase in retention. It can be evaluated by asymmetry factors, peak-height ratios or retention indices. The deactivation procedures used in this study were evaluated by GC measurements using the standardized comprehensive Grob test [19]. Catalytic activity was not considered in this study.

Figs. 3 and 4 show chromatograms of columns after rinsing with organic solvent. The columns were coated with stationary phase solutions of the same concentration (1%). The column in Fig. 3 was deactivated with PDMVS and for that in Fig. 4 the stationary phase was deposited on the bare untreated fused-silica surface. It can be seen that deactivating with PDMVS substantially improves the peak symmetry and reduces retention of am (dicyclohexylamine). Also, the peak shape of DMA (2,6-dimethylamine) and DMP (2,6-dimethylphenol) was improved. Peak-height ratios of am vs. *n*-dodecane in columns coated with a 1% solution of PS 255 were measured. In the deactivated columns (2 and 7) the peak-height ratio was 0.5, whereas in the untreated column (13) it was 0.07, which illustrates the acidic properties of the non-deactivated fused-silica surface.

The silanol effect is also illustrated by the Kováts retention index (Z) for 1-octanol, measured at 80°C. The deactivated column in Fig. 3 had an Z value of 1058, compared with 1094 for the column in Fig. 4, while the Z value for naphthalene was 1150 for both columns. Deactivating the columns with DVTMDS using a long treatment time (22 h) showed a column inertness similar to that of the columns deactivated with PDMVS. However, the columns treated at shorter times gave an excessive loss of stationary phase after column wash (see Table II) and

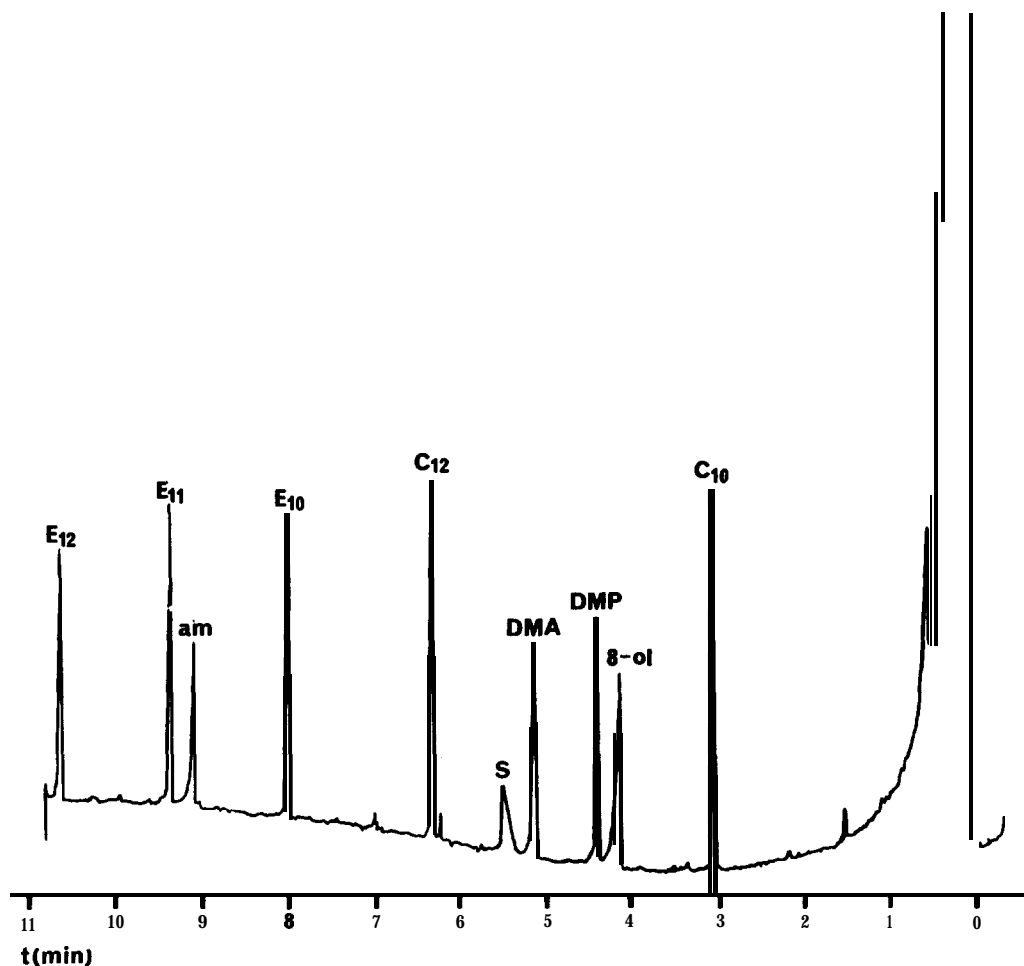


Fig. 3. GC separations of the standard Grob mixture on column 7. The column was deactivated with PDMVS (C). Temperature programmed at 10°C/min. Carrier gas: hydrogen at 50 cm/s. Solutes: C₁₀ = *n*-decane; ol = 1-octanol; DMP = 2,6-dimethylphenol; DMA = 2,6-dimethylaniline; S = 2-ethylhexanoic acid; C₁₂ = *n*-dodecane; E₁₀ = methyl decanoate; am = dicyclohexylamine; E₁₁ = methyl undecanoate; E₁₂ = methyl dodecanoate.

consequently these columns also exhibited increased column activity after rinsing.

For comparison, we examined a low temperature (6300°C) deactivation method developed for fused-silica GC columns, using poly-methylhydrosiloxane (no vinyl groups) according to Woolley et al. [20]. These columns showed a similar inertness to the columns deactivated with vinyl-containing reagents.

Taking different aspects into consideration, such as time, the number of manipulative steps and column inertness, the PDMVS deactivation method was our method of choice. Recently in

our laboratory 5-10 μm I.D. columns coated with polyorganosiloxane were used with indirect detection, using basic dyes as detection agents [21]. The stationary phase film thickness is relatively thin in these columns, 20-100 nm. The results indicate that there is a glass surface activity in untreated, coated fused-silica columns when used in LC. Deactivating the capillaries with PDMVS improved the chromatographic behaviour of the basic dyes. For example, the asymmetry factor (measured at 10% of the peak height) for 1,1',3,3',3'-hexamethylindotricarbocyanine iodide was 8-12 in the untreated column

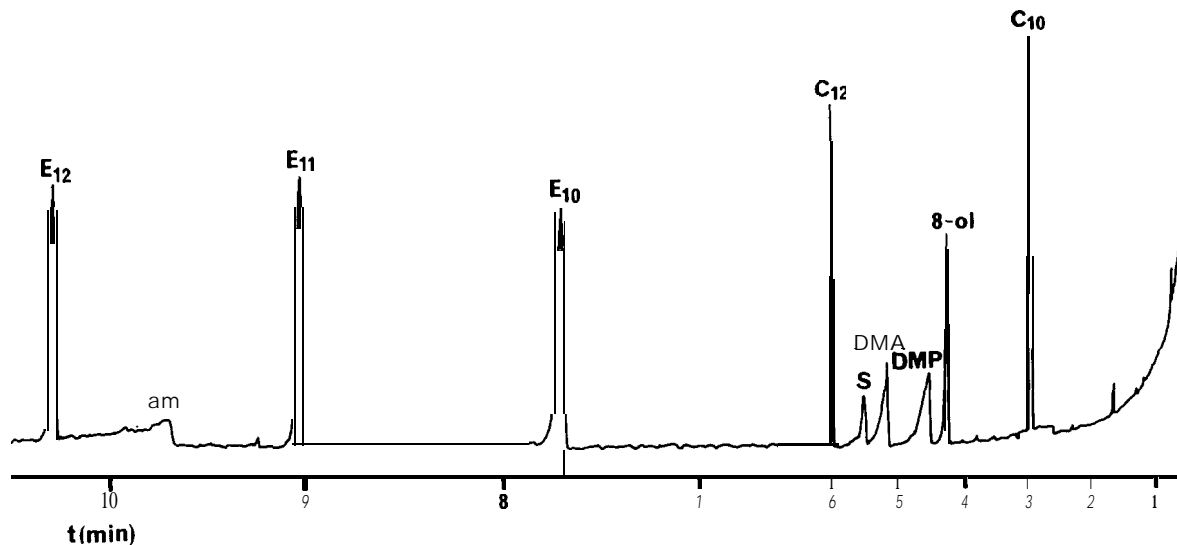


Fig. 4. GC separations of the standard Grob mixture on column 13. The column was coated on the bare fused-silica surface. GC conditions as in Fig. 3.

(10) and 1.8-2 in the deactivated column (5). In addition, the k' value was lower in column 5, 0.9 compared with 3.1 in column 10 [21].

LC selectivity

The earlier observed [2] shift in OT-LC selectivity for small stationary-to-mobile phase ratios initiated this study. The relative contribution from the bulk phase decreases with a decrease in the film thickness and consequently the **interfacial** effects would be more evident for thin films. The possible influence of the fused-silica surface on the polysiloxane configuration at the **glass-to-polymer** interface was studied using fluorene derivatives as test substances. In Table III selectivity factors for fluorene derivatives, for columns deactivated with PDMVS and coated with different stationary phase thicknesses, are summarized. It was found that the selectivity deviations for thin films appeared also when the stationary phase was coated on deactivated fused-silica capillaries. The selectivity factor was the same for these columns as for columns coated on the bare fused-silica surface. We can therefore exclude the selectivity effects from the fused-silica surface on the stationary phase configuration.

The cause of the selectivity shift for thin films

TABLE III

LC SELECTIVITY FACTORS, $\alpha = k'_{\text{phenylfluorene}}/k'_{\text{fluorene}}$, IN PDMVS-DEACTIVATED COLUMNS OF VARIOUS PHASE RATIOS

Mobile phase: acetonitrile-water (30: 70)

Column No.	Film thickness, nominal (μm)	Selectivity factor
6	0.26	3.2
7	0.13	3.1
8	0.066	3.2
9	0.026	3.7

remains unsolved. However, the reason could be a disturbance of the polymer structure at the stationary-to-mobile phase interface [22]. Further studies should be performed in order to examine the effects of the mobile phase **interface**.

CONCLUSIONS

A practical procedure with PDMVS is suggested for reducing the activity in narrow fused-silica columns in both LC and GC. Our choice of vinyl-containing deactivation reagents, unexpectedly, did not improve the immobilization of the

stationary phase in 50 μm I.D. fused-silica columns. The selectivity shift for thin stationary phase films in OT-LC columns was observed also after deactivation of the fused-silica surface.

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