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Column preparation for reversed-phase high-temperature open tubular column liquid chromatography

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Abstract

A method for the preparation of stable reversed-phase columns for high temperature open tubular column liquid chromatography (HT-OT-LC) has been developed and the effect of covalent bonding of the stationary phase to a covalently bonded deactivation layer, as well as, crosslinking of the polysiloxane stationary phase has been investigated. It was found that the column lifetime depended primarily on the extent of crosslinking of the stationary phase film with azo-*tert*.-butane and a dynamic crosslinking procedure was developed for this purpose. By extensive crosslinking of the polysiloxane stationary phase, column lifetimes of more than several hundreds of hours could be obtained at 150°C. Inadequate crosslinking, on the other hand, resulted in shorter column lifetimes most likely as a result of hydrolysis of the stationary phase polymer leading to its collapse in the centre of the column. No significant difference in column lifetime was seen between columns prepared with 50% *n*-octylpolymethylsiloxane or 49% *n*-octyl-, 1% *n*-octenylpolymethylsiloxane stationary phases, with cyano or octyl groups in the deactivation layer, or between columns with different stationary phase film thickness (in the range between 0.25 and 0.60 μm).

Keywords: Stationary phases, LC; Columns; Open tubular columns

1. Introduction

The use of high temperatures significantly improves the chromatographic efficiency and shortens the analysis time in open tubular column liquid chromatography (OT-LC), as discussed by several authors [1–3]. The hydrophilic mobile phases used in reversed-phase high temperature (HT) OT-LC, however, become very strong solvents at temperatures of 100–200°C. It has consequently been found [4] that the stability of the stationary phase is a severe problem under these conditions. As the limited stability of commercially available wall coated columns at elevated temperatures in fact is the main reason why high temperatures cannot be used in OT-LC at present, there is a strong need for a development of columns with improved stability.

The preparation of wall coated columns for HT-LC requires a number of considerations. When fused-silica columns are used (as a result of their inertness and high tensile strength [5] compared to other glass materials), the acidic silanol groups on the column surface first need to be efficiently covered by a covalently bonded deactivation layer [6,7]. A comparison of monomer, dimer and polymer deactivation reagents in gas chromatography (GC) has indicated that deactivation with polymers result in higher surface coverages and thus better deactivations [7,8].

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Deactivations with hydrosiloxane polymers have, for example, been shown to efficiently reduce the interaction of solutes with silanol groups in GC [7,9,10]. The deactivation layer must also be readily wetted by the stationary phase which must be tailor-made to be chemically and physically stable in aqueous solutions at high temperatures while a sufficiently fast diffusion of the analytes in the stationary phase is still maintained. The versatility, thermal stability and high diffusion rates of analytes in polysiloxanes have made these polymers popular for use as stationary phases in OT-GC and supercritical fluid chromatography (SFC). These properties also make polysiloxanes interesting as stationary phases in HT-OT-LC although the conditions employed here are more demanding.

One way to improve the stability of polysiloxane stationary phases could involve extensive crosslinking of the polymers by creating covalent bonds both between the polymeric chains of the stationary phase and between the stationary phase and the deactivation layer. Free radical reactions involving alkyl groups in the polymer are often used for this purpose. There are several types of initiators available which are active at varying temperatures and sometimes selective towards different chemical groups. To achieve a sufficient crosslinking while maintaining a smooth and intact polymeric film on the column wall, the right initiator needs to be found. Over the years, azo-*tert*-.butane (ATB) has become one of the most popular free radical initiators as it has little effect on the polarity of the stationary phase [11,12]. ATB, however, requires a rather high reaction temperature (220°C) [11] and is a volatile liquid that needs to be added after the coating of the column. Dicumyl peroxide (DCP) is a more efficient crosslinking reagent than ATB especially together with vinyl groups [12,13], but gives rise to polar decomposition products that may be incorporated in the stationary phase [14,15]. This reagent has also been shown to cause oxidation of functional groups, such as tolyl and cyanopropyl groups, during crosslinking [16]. Unlike ATB, DCP can be added to the stationary phase solution prior to the coating to generate radicals throughout the whole stationary phase film.

Several authors have presented procedures for column preparation for OT-LC at room temperature [17–23] but to our knowledge there is no published method for the preparation of sufficiently stable wall coated columns for HT-OT-LC. For the development of such a method, it is important to understand the processes associated with column degradation in aqueous media at high temperatures. Potential limiting factors include swelling of the stationary phase polymer, etching of the fused-silica column inlet and the silica surface underneath the polymers [24] by the mobile phase, as well as hydrolytic [25–27] or oxidative degradation [28–31] of the stationary phase. In the case of etching of the fused-silica, the column lifetime would be limited by the undermining of the support for the stationary phase film. Hydrolytic or oxidative attacks on the polymer can result in the scission of either siloxane (Si–O) or Si–C bonds. Thomas [27] found that the rate of network scission in crosslinked methylvinyl silicone rubbers was proportional to the water concentration at temperatures below 250°C and concluded that the scission was chiefly due to hydrolytic reactions in the main polymer chain. Significant oxidation of the polymer was found only at temperatures above 250°C.

In this study, a method for the preparation of highly crosslinked alkyl containing polysiloxane stationary phases of improved stability is presented. The method is based on a double layer design in which a deactivation layer minimises the influence of the fused-silica column material on the separation process, while the polysiloxane stationary phase layer provides retention according to hydrophobicity. While developing this method, a screening study was undertaken to investigate the influence of several parameters on the column lifetime. The effect of varying degrees of bonding and crosslinking of the stationary phases on the column stability was thus, for example, evaluated based on experiments involving an incorporation of cyano or octyl groups in the deactivation layer and octenyl and/or octyl groups in the stationary phase layer. The processes which may limit the column lifetime in HT-OT-LC are also discussed.

2. Experimental

2.1. Instrumentation

The instrumental set-up for HT-OT-LC, which has

been described in detail elsewhere [32], consisted of an LC pump, 2150, LKB (Sweden), a manual injection valve, C6W, (Valco Instruments, Houston, TX, USA) equipped with a 10-μl sample loop and a 30 cm×0.25 cm I.D. stainless steel preheating tube. A 1/32 in. tee, 0.01 in. bore from Valco and a ss-4R3 A-EP valve, (Nupro, Willoughby, OH, USA) was used to split the flow (1 in.=2.54 cm). A 1 m×15 μm I.D. fused-silica capillary restrictor (Polymicro Technologies, Phoenix, AZ, USA) was employed to keep the mobile phase as a liquid. A laboratory-made oven and a preheating device that could be heated separately were used for temperature control. The detector was a UV detector designed for use with optical fibres, (μ-Peak monitor, Pharmacia, Uppsala, Sweden). The on-column detector cell design is described in more detail elsewhere [32]. The wavelength used for detection was 254 nm unless stated otherwise.

2.2. Chemicals

Pro analysi quality of acetonitrile and dichloromethane, methanol of gradient grade and water of HPLC quality were supplied by Merck (Darmstadt, Germany). Phenanthrene and uracil were obtained from Sigma (St. Louis, MO, USA). For the deactivation of the capillaries, bis(50% cyanopropyl)-methylhydrosiloxane and 25% *n*-octyl-methylhydrosiloxane, both having 25% silicon-hydride groups, were used. Two stationary phases, 50% *n*-octyl-polymethylsiloxane and 49% *n*-octyl-, 1% *n*-octenylpolymethylsiloxane, were employed. The polycyclic aromatic test compounds and the deactivation polymers were a kind gift of Professor Milton Lee, Brigham Young University (UT, USA). The experimental polymeric stationary phases were gifts from Dionex (Sunnyvale, CA, USA) and Supelco (Bellefonte, PA, USA), respectively.

2.3. Column preparation

Columns of approximately 2 m length were prepared from 50 μm I.D.×190 μm O.D., fused-silica capillaries (Polymicro Technologies). To remove impurities and to create a uniform surface of silanol groups, the capillaries were washed with 1 ml of HPLC grade water, purged with nitrogen for 5 min, sealed and heated to 250°C overnight. The capillaries were then purged with dry nitrogen for 10 h at 250°C and deactivated by dynamic coating with 2% (w/v) of bis(50% cyanopropyl)methyl-hydrosiloxane in acetonitrile [7] or 25% octylmethylhydrosiloxane in dichloromethane. The acetonitrile was dried over P_2O_5 and distilled. The capillaries were next purged with dry nitrogen for 10 h, sealed and heated to 250°C or 350°C during 10 h for cyano and octyl deactivation, respectively, rinsed with 4 ml of dichloromethane and dried with nitrogen gas for 2 h.

The capillaries were statically coated with the stationary phase, 50% *n*-octyl polymethylsiloxane or 49% *n*-octyl-, 1% *n*-octenyl polymethylsiloxane diluted in dichloromethane, at 25°C. The film thickness was controlled by the concentration of the stationary phase solution [33], e.g., a concentration of 20 mg/ml was used to achieve a film thickness of 0.25 μm. Dicumyl peroxide was mixed with the stationary phase solution at the desired level, 0–5% (w/w). Prior to crosslinking by free radical polymerisation, the columns were purged with nitrogen for 2 h. Crosslinking was then performed either statically or dynamically. In the case of static crosslinking, the column ends were sealed and the column was heated to 170°C for 1 h to initiate the DCP crosslinking. The stationary phase was next crosslinked with azo-*tert*.-butane, two, four or six times. In each step, the column was purged with nitrogen saturated with ATB vapour (≤0.1 ml/min) at room temperature for 1 h, after which the ends were sealed and the column was heated to 220°C for 1 h. The ATB treatment was then repeated from the other end of the column. During the dynamic crosslinking, the column was also first purged with nitrogen saturated with ATB vapour at room temperature employing a low flow-rate (≤0.1 ml/min) for 1 h. While maintaining the flow of nitrogen saturated with ATB vapour (at room temperature) through the column, the column was next heated to 170°C for 30 min. The temperature of the column was subsequently raised to 220°C and kept there for the desired time, still with a continuous flow of ATB saturated nitrogen through the column. After both the static and dynamic crosslinking, the column was conditioned in a flow of nitrogen for 10 h at 250°C.

2.4. Column test procedure

A test mixture of phenanthrene and uracil (used to

determine the hold-up time, t_0) was repeatedly injected at 150°C using a mobile phase of methanol–acetate buffer, pH 5 (30:70). This test was employed to detect any loss of stationary phase by monitoring the change in the retention factor for phenanthrene. The flow-rate through the column was 1 μl/min. To monitor the efficiency, a mixture of uracil, 5,6-benzoquinoline, acridine and 7,8-benzoquinoline was injected at a flow-rate of 0.5 μl/min. The column lifetime was defined as the time the column could be used at 150°C with a mobile phase of methanol–acetate buffer, pH 5 (30:70) before the column became blocked. A split ratio of 1:2000 was used in all experiments and care was taken to remove oxygen from the mobile phase by continuous purging with helium.

2.5. Critical surface tension measurements

The deactivated fused-silica capillaries for the measurements of the critical surface tension according to the capillary rise method [34] were prepared from 200 μm I.D. fused-silica capillaries (Polymicro Technologies). The capillaries were pre-treated with water followed by deactivation with either cyano- or octyl-deactivation, as described above. The measurements were kindly performed by Professor Keith Bartle.

3. Results and discussion

The experience gained while preparing stable open tubular columns for GC and SFC can also be utilised in conjunction with column preparation for HT-LC. To enable use in HT-OT-LC, the fused-silica capillaries first need protection from the hot hydrophilic mobile phase, for instance, by a highly crosslinked carbon rich deactivation layer which also should minimise the access of solutes to the fused-silica silanol groups. In addition, the polysiloxane stationary phase most likely needs to be highly crosslinked to be stable in reversed-phase HT-OT-LC. As the crosslinked phase has to withstand the stress from the mobile phase while at the same time allowing a sufficiently fast diffusion of analytes in the stationary phase film, a proper crosslinking density needs to be generated in the crosslinking step. The presence of covalent bonds between the stationary phase and the deactivation layer may also affect the stability of the columns.

3.1. Stationary phase crosslinking

In this study, the influence of extensive stationary phase crosslinking on column stability has been investigated using columns statically or dynamically crosslinked with combinations of both DCP and ATB at varying levels. The results show that DCP concentrations in the stationary phase, between 0 and 5%, did not influence the column lifetime significantly while the lifetime of the columns increased with increasing number of treatments upon static crosslinking with ATB (see Fig. 1). Janák et al. [23] recommended the use of two, or at the most three, subsequent treatments with ATB for open tubular columns to be used in OT-LC at room temperature. In this study, not even six repeated treatments with ATB were found to be sufficient for HT-OT-LC at 150°C. Since more than six successive ATB treatments were impractical, a dynamic method for ATB treatment was developed to allow continuous crosslinking of the stationary phase with ATB for long periods of time. It was found that only columns crosslinked with the dynamic method could be used

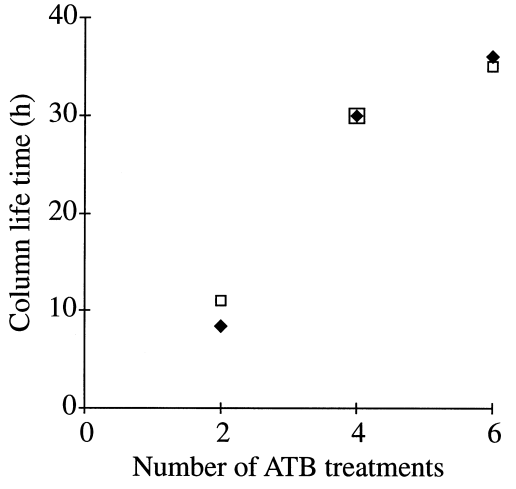

Fig. 1. Influence of the number of static ATB treatments on the column lifetime at 150°C for columns prepared with (♦) 50% *n*-octylpolymethylsiloxane and (□) 1% *n*-octenyl-, 49% *n*-octylpolymethylsiloxane stationary phases. 5% DCP.

for more than 50 h without plugging of the column. A dynamic crosslinking for 15 h produced columns that could be used for more than 100 h without plugging while still allowing a fast diffusion in the stationary phase. The diffusion coefficient of 7,8-benzoquinoline in the stationary phase was, for example, calculated to be approximately $2 \cdot 10^{-7}$ cm^2/s for a film thickness of 0.6 μm [35]. A column that was dynamically crosslinked with ATB for as long as 60 h was, on the other hand, not suited for chromatography since the efficiency of this column was very poor (i.e., the diffusion rate in this stationary phase was most likely too low). For this column, the retention factors for both phenanthrene, acridine and the benzoquinolines were observed to decrease with time indicating a gradual loss of the stationary phase. The cause for such a loss of the stationary phase is not fully understood. The fact that no plugging of the 15 μm I.D. restrictor occurred in this case, suggests that the polymer fragments formed must have been rather small. For the columns with the lowest crosslinking density, i.e., the columns exposed to a static crosslinking with ATB for two or four times, restrictor plugging was, on the other hand, frequently observed.

An introduction of double bonds in the side chains of the polysiloxanes is known to increase the crosslinking density and also direct the crosslinking when DCP is employed as the free radical initiator [12,13]. The vinyl selective property of DCP can then be used to further improve the stability of the stationary phase. Grob and Grob [13] and Wright et al. [12] consequently observed significant differences in the extractability of dimethylpolysiloxanes in the presence and absence of 1% of vinyl groups. The results obtained in the present study, however, show that no improvement in column lifetime was obtained with the stationary phase containing 1% octenyl groups compared to that for the phase lacking the octenyl groups. The two phases also gave rise to similar retention factors, indicating that the retention mechanism was practically identical for the two phases. The column lifetime did neither depend on the stationary phase film thickness, in the range of 0.25 to 0.6 μm, suggesting that relatively thick films with larger retention and sample capacity can be employed.

3.2. Column deactivation

Another factor that influences the stability of the stationary phase film on the column wall is its wettability with respect to the underlying deactivation layer. An incomplete wetting of the column wall by the stationary phase is, for example, known to reduce the column efficiency and stability in GC [34]. The fused-silica surface has a surface energy that is high enough (i.e., $>50 \cdot 10^{-3}$ N/m [34]) to ensure even coatings of most deactivation polymers but the surface energy of the deactivation layer also has to be sufficiently high to allow a complete wetting of the deactivation layer by the polysiloxane stationary phase. Two different polymers, bis(50% cyanopropyl)methyl-hydrosiloxane and 25% *n*-octylmethylhydrosiloxane, both containing 25% silicon-hydride groups, were employed as deactivation reagents in this study, based on the reaction [36] depicted in Fig. 2. In the case of cyano-deactivation, R_1 and R_2 in Fig. 2 correspond to cyanopropyl groups while R_1 and R_2 represent octyl and methyl groups, respectively, for the octyl deactivation. The cyano-deactivation is known to be an effective

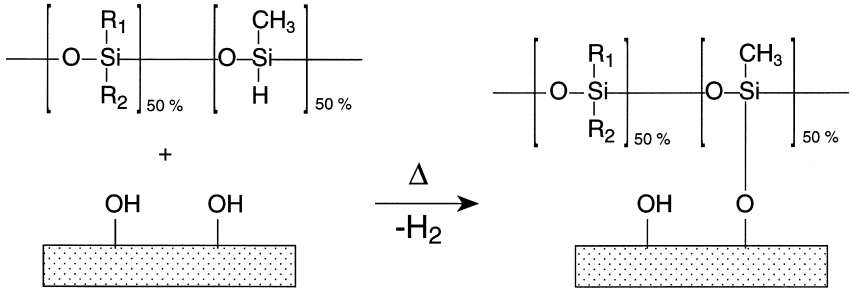

Fig. 2. Deactivation of a fused-silica surface.

deactivation method for fused-silica columns and generates a surface of high energy [7]. An incorporation of octyl groups in the deactivation polymer opens up the possibility of covalent bonding of the stationary phase to the deactivated surface, but also lowers the surface energy. The critical surface tensions of the deactivated surfaces were, in this case, found to be $37 \cdot 10^{-3}$ N/m and $32 \cdot 10^{-3}$ N/m after cyano- and octyl-deactivation, respectively. Both surfaces are therefore expected to be wetted by the employed stationary phases since the surface tension of the 49% *n*-octyl-, 1% *n*-octenylpolymethylsiloxane stationary phase was found to be approximately $25 \cdot 10^{-3}$ N/m and since the value for the 50% *n*-octylpolymethylsiloxane phase should be similar to that for the octenyl containing phase. As seen in Table 1, the results show no significant difference in column lifetime for columns deactivated with cyano- or octyl-deactivation reagent. The possibility of covalent bonding of the stationary phase to the deactivation layer introduced by the use of the octyl-containing deactivation polymer does hence not seem to have a profound effect on the column stability under these experimental conditions. A similar conclusion was reached by Göhlin and Larsson for OT-LC at room temperature [22].

3.3. Reasons for column plugging

The plugging of the columns in HT-OT-LC at 150°C could be due to either hydrolysis, oxidation or swelling of the stationary phase or etching of the fused-silica at the column inlet by the mobile phase, thus removing the support for the stationary phase film. As will be shown below, our data show that the blocking of the column is due to a physical collapse of the stationary phase, most likely as a result of a decreased strength of the polymer layer due to scissions of bonds by hydrolysis. Although an etching of the fused-silica inlet might occur, it is not likely to be the main cause for column plugging since the plugged columns were found to be blocked at several places throughout the whole column length, when cutting the blocked columns into approximately 10-cm long pieces which then were checked for flow. After static crosslinking, more than 50% of the pieces were found to be blocked and there was no apparent trend in the distribution of the plugs along the column length. For the dynamically crosslinked columns, on the other hand, the blocked pieces predominantly originated from the end of the column. For static crosslinking, the extent of crosslinking is expected to be the same throughout the whole column length while a smaller extent of crosslinking is expected at the end of the column after dynamic crosslinking since a longitudinal ATB concentration gradient then will be present in the column. No column plugging was seen in the absence of a stationary phase when an untreated fused-silica capillary was subjected to the mobile phase at 150°C for 65 h. Further indications that the plugging was caused by the stationary phase came from inspections of blocked columns under a light microscope which showed that the plugs had a spongy character, and examinations of plugged columns by scanning electron microscopy (SEM). A SEM micrograph of a section of a plugged statically crosslinked column is shown in Fig. 3. It is clearly seen that the blockage of the column was a result of a folding of the stationary phase film and that the stationary phase film had a smooth surface. The pieces of fused-silica that can be observed to the left in the figure resulted from the cutting of the capillary.

Swelling of the stationary phase is unlikely to be a reason for the blockage of the columns as the swelling of polydimethylsiloxane by methanol, acetonitrile or water has been found to be small [37,38]. The collapse of the polysiloxane stationary phase is therefore more likely to be a result of a degradation of the polymer film. Hydrolysis is believed to be the main cause for the degradation in reversed-phase HT-OT-LC due to the large concentration of water in the system and the relatively low temperatures used

Table 1
Influence of the deactivation method on column lifetime

		Column life time	
Deactivation	n[a]	Hours	s[b]
Cyano-	4	35	1
Octyl-	2	34	2

[a] No. of separately coated columns.
[b] Standard deviation.
Conditions: 49% *n*-octyl-, 1% *n*-octenylpolysiloxane stationary phase, 0.25–0.4 μm film thickness, static crosslinking 6×1 1 h ATB and 5% DCP, temperature 150°C.

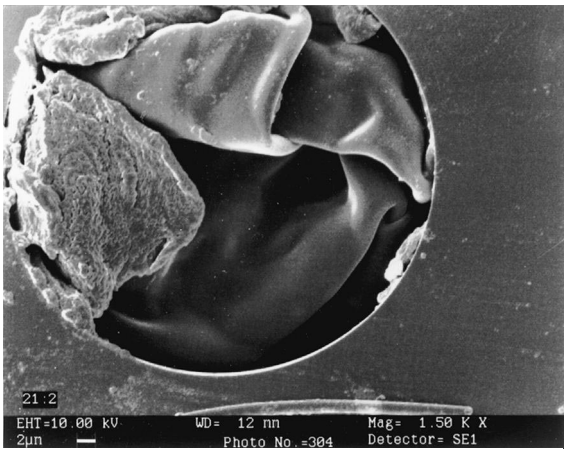

Fig. 3. SEM micrograph of a section of a blocked cyano-deactivated column coated with 0.6 μm 50% *n*-octylpolymethylsiloxane stationary phase and statically crosslinked with 5% DCP and 6×ATB.

(150–200°C). The oxidation of methylvinyl silicone polymers have been reported to become important only at temperatures above 250°C [27]. An increasing number of carbons in the alkyl side chain, has however been found to reduce the resistance towards oxidation [28,38] and grate care was therefore taken to remove oxygen from the mobile phase in this study. Extensive rinsing with the mobile phase prior to a slow increase of the temperature, to remove non-crosslinked fragments, was found to have little effect on the column lifetime. The performance of a statically crosslinked column that exhibited the typical behaviour associated with a stationary phase collapse is shown in Fig. 4. As seen in this figure, depicting test chromatograms recorded after 2, 14, 30 and 35 h of operation, the uracil peak became very broad as a first sign of the deterioration of a column. Right before plugging, the retention factors for all test compounds increased while the peak width of all peaks increased significantly. Large oscillations in the baseline were also seen for some columns immediately prior to plugging, probably as a result of light scattering due to, for instance, vibrations in the stationary phase layer or passing polymer fragments. The retention factor and the column efficiency as a function of the time of exposure to the mobile phase at 150°C for a statically crosslinked column are shown in Fig. 5. Although the decrease in the efficiency seen in this figure could partly be explained by the increased retention factor, it should be noted that the largest decrease in the efficiency is in fact seen for the unretained compound. This suggests adsorption on silanol groups, exposed either on the silica wall or in the polymer, or the presence of a dead volume in the column. For some columns

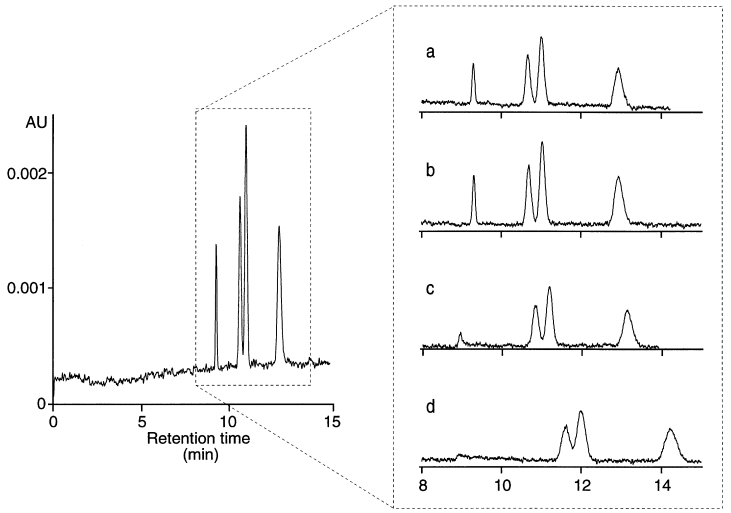

Fig. 4. Separations of uracil, 5,6-benzoquinoline, acridine and 7,8-benzoquinoline obtained after an exposure of an unstable statically crosslinked column to the mobile phase for (a) 2 h, (b) 14 h, (c) 30 h and (d) 35 h at 150°C. Cyano-deactivation, 0.4 μm film of 49% *n*-octyl- 1% *n*-octenyl-polysiloxane stationary phase, 5% DCP, 6×ATB.

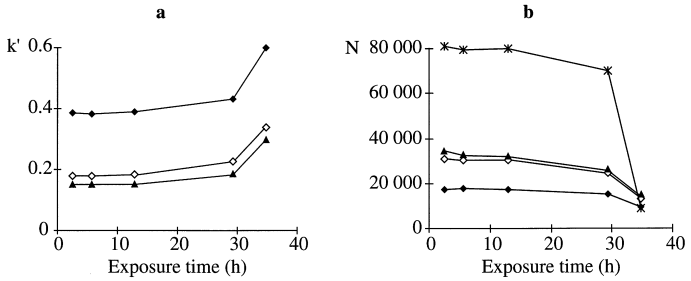

Fig. 5. Influence of the exposure time to the mobile phase at 150°C on (a) retention factor and (b) column efficiency, for an unstable column. Experimental conditions as in Fig. 3, (×) uracil, (▲) 5,6-benzoquinoline, (◇) acridine and (♦) 7,8-benzoquinoline.

the peak tailing for uracil increased to such an extent that this peak became almost undetectable.

Almost all columns that exhibited a lifetime longer than about 50 h (i.e., the dynamically crosslinked columns) went through an instability period after approximately 30 h of operation. During this stage, the flow-rate dramatically dropped in the column but then suddenly returned to its original value with no measurable change in retention factor or efficiency provided that the columns did not become plugged during this period. These columns could then be used for up to several hundreds of hours with more or less constant overall performance (see Fig. 6 and Table 2 for a comparison of the performance of a column before and after the instability period). The phenomenon responsible for the column instability period is still not fully understood but a possible explanation could involve an initial hydrolysis of the polymer giving rise to silanol groups that then give rise to new crosslinks by the formation of Si–O–Si bonds until an equilibrium is reached [39].

3.4. Recommended procedure

Although an instability period appeared after approximately 30 h of use, the experimental results clearly show that the columns that survive this stage (i.e., the majority of the dynamically crosslinked columns) can be used for up to several hundreds of hours at 150°C. The performance of such a dynamically crosslinked stable column is, as already indicated, presented in Table 2 and Fig. 6 which show that the retention and efficiency remained unaltered after more than one month of operation for this column. The difference in the peak height in the chromatograms in Fig. 6 was due to the use of different UV-detector wavelengths. From these results, it can be concluded that good columns for reversed-phase HT-OT-LC can be prepared by cyano deactivation, followed by the application of a 0.4 μm film of 49% *n*-octyl-, 1% *n*-octenylpolymethylsiloxane stationary phase and dynamic crosslinking with 5% DCP and ATB vapour for 15 h. Cyano-deactivation is preferred since it results in columns that are as

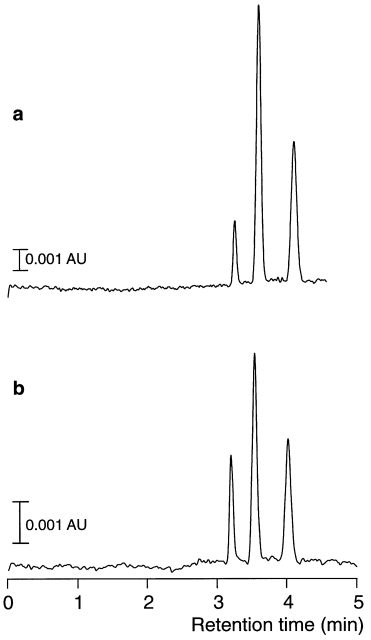

Fig. 6. Separations of uracil, 5,6-benzoquinoline and 7,8-benzoquinoline recorded with a 15 h dynamically crosslinked column (a) after a few hours and (b) after more than one month of use. Cyano deactivation, 0.4 μm 49% *n*-octyl-, 1% *n*-octenylpolymethylsiloxane stationary phase, 5% DCP. The detector wavelength was (a) 220 nm and (b) 254 nm.

Table 2
Performance of a 15 h dynamically crosslinked column at 150°C

	No. of plates			Retention factor	
	1	2	3	2	3
New column	24 500	14 800	12 900	0.104	0.253
After use for more than a month	24 400	14 900	13 000	0.103	0.253

Conditions: cyano deactivation, 49% *n*-octyl-, 1% *n*-octenylpolysiloxane stationary phase, 0.4 μm film thickness, 15 h dynamic crosslinking with ATB and 5% DCP. The R.S.D. values were smaller than 9% for three determinations, 1=uracil, 2=5,6-benzoquinoline and 3=7,8-benzoquinoline.

stable as the octyl deactivated ones and since the cyano-deactivated surface is known to be wetted by most stationary phases. Although no significant beneficial effect of the combination of DCP and octenyl groups in the stationary phase was detected in this screening study, this combination is still recommended since it has no major drawbacks. For the preparation of long columns it is recommended that the direction of flow is reversed after half the dynamic ATB crosslinking treatment.

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