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A Stationary Phase for Open Tubular Liquid Chromatography and Electrochromatography Using Sol–Gel Technology

Yong Guo and Luis A. Colón*

Department of Chemistry, Natural Science and Mathematics Complex, State University of New York at Buffalo, Buffalo, New York 14260-3000

An organic–inorganic hybrid material was fabricated by the sol–gel method and cast as a thin glass film onto the inner walls of fused silica capillary columns. The thin film in the capillaries functioned as the stationary phase for reversed phase open tubular liquid chromatography (OTLC) and open tubular electrochromatography (OTEC). The stationary phase provides high surface area and thus an improved phase ratio. Multiple preparation steps are avoided by attaching the stationary phase and increasing the surface area in a single procedure. By adjusting the ratio of the monomeric precursors in the original sol–gel solution, the retentive characteristics of the stationary phase are controlled. This new approach facilitates column preparation for OTLC and OTEC. Capillary columns prepared in this manner showed retention characteristics superior to conventionally prepared ones. Polycyclic aromatic hydrocarbons were used to evaluate the stationary phase; under the experimental conditions used, efficiencies of 204 000–285 000 and 280 000–500 000 plates/m were observed in OTLC and OTEC, respectively. The sol–gel-derived stationary phase was shown to be stable under acidic and basic conditions.

Open tubular liquid chromatography (OTLC) and open tubular electrochromatography (OTEC) have shown a great potential to reach high efficiencies for the analysis of complex sample mixtures.^{1–3} The preparation of the stationary phase is of key importance to achieve the high performance offered by these

techniques. It has been very difficult, however, to prepare capillary columns (<15 μm i.d.) with appropriate coating materials having sufficient retentive and mass loadability characteristics. This is one of the reasons why OTLC, for example, is being used in only a few research laboratories (as pointed out by Poppe and co-workers⁴), despite its many advantages^{1–4} over the more conventional high-performance liquid chromatography (HPLC).

Although in the past 15 years efforts have been made to prepare stationary phases for capillary columns,^{5–11} there are still some problems associated with the methods developed so far. Stationary phases that are chemically bonded directly onto the inner wall of capillary columns offer very low phase ratios, which lead to low retention and low sample capacity.^{5,6} Additionally, methods developed to increase surface area and phase ratio involve two major steps: (1) laying down a porous silica layer and (2) attaching functional groups onto the prepared layer through chemical bonding.^{7,8} These procedures are time consuming, and not all the prepared columns are suitable for use (success rate below 80%).⁸ Furthermore, the functional groups serving as the stationary phase are attached to the inner wall of the capillary columns (with or without the porous layer) through surface–O–Si–C bonds, limiting the pH range at which the column can be operated. The polymeric stationary phases, such as cross-linked

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polysiloxanes⁹⁻¹¹ and polyacrylates,^{12,13} usually give good column stability, high phase ratio, and sufficient retention. However, the drawback of these phases is their poor column efficiency, due to the slow diffusivity of solutes in the retentive layers.

We are exploring sol-gel technology to produce porous silica glass films that can be cast onto the inner walls of capillary columns for OTLC and OTEC applications. The sol-gel-derived materials used have varied from nonlinear optical composites to bioactive glasses and chemical sensing platforms.¹⁴⁻¹⁸ Generally, the sol-gel process consists of hydrolysis and polycondensation of metal alkoxide monomers; tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) is commonly used in silica glasses.¹⁴ During the process, a liquidlike colloidal suspension (the "sol") is transformed first into a gel, through gelation (polycondensation of the "sol" to form a wet network of porous material); then, a xerogel (i.e., the dried gel) is formed after the loss of solvent, through aging and drying. The initial hydrolysis can be either acid or base catalyzed, and the rates of hydrolysis and polycondensation are highly pH dependent. Control of the processing parameters (e.g., drying temperature, pressure, pH, molar ratio of water, alcohol solvent, and the structure of alkoxy groups, among others) during different stages of the process (polymerization, gelation, drying) has permitted the fabrication of sol-gel-derived materials with desired structural characteristics (e.g., pore size and surface area).^{14,15}

In this paper, we describe the preparation of a silica glass coating material, based on the sol-gel method, that contains a retentive layer (i.e., the stationary phase) for chromatographic applications. A porous glass film is fabricated in such a way that the stationary phase (octyl groups) is incorporated into the glass matrix during the glass formation process. In this fashion, the supporting glass matrix and the stationary phase are prepared in a single step. This, in turn, eliminates chemical attachment procedures to fix the stationary phase, which otherwise would have to be done after the porous layer was prepared. We have cast the material onto the inner walls of fused silica capillaries and used it for reversed phase OTLC and OTEC.

EXPERIMENTAL SECTION

Instrumentation. All the OTLC experiments were performed in a system constructed in our laboratory. The mobile phase was delivered by a syringe pump (Model 100DM, Isco, Lincoln, NE). Sample injection was achieved with a 60 nL loop Valco injection valve. The capillary column was situated at the exit of the injector, where the injected sample and the eluent were split to deliver appropriate amounts through the capillary column. On-column detection was carried out by using a UV detector (Model CV⁴, Isco) at 220 nm. The signal from the UV detector was fed into an A/D converter board (DT2804, Data Translation, Marlboro, MA) mounted on an IBM PC. Data acquisition was controlled by means of GRAMS 386 for Chromatography software (Galactic Industries Corp., Salem, NH).

The OTEC experiments were performed in a system constructed for capillary electrophoresis (CE). The electrical field was supplied with a Glassman (Whitehouse Station, NJ) high-voltage power supply (0–30 kV). The high voltage was housed in a plexiglass box for the operator's safety. On-column detection was made with the UV detector described above. Samples were introduced into the column by electrokinetic injection. The electroosmotic mobility in OTEC was measured by injecting a sample solution containing a small amount of ethanol, which served as the unretained neutral marker.

Chemicals. Tetraethoxysilane (TEOS), *n*-octyltriethoxysilane (C₈-TEOS), and *n*-octyldimethylchlorosilane were purchased from United Chemical Technologies (Horsham, PA). Polycyclic aromatic hydrocarbons (PAHs) were used as test compounds and obtained from Aldrich (Milwaukee, WI). Water was purified with an Ultra-Pure water purification system (Millipore, Bedford, MA). Stock solutions of the test compounds were prepared in HPLC grade methanol or ethanol (Fisher, Pittsburgh, PA) and diluted with the mobile phase prior to injection. The desired mobile phase was prepared by mixing appropriate amounts of methanol and water, for OTLC, and methanol and a sodium phosphate solution (~1 mM), for OTEC. The mobile phase was filtered through 0.45 μ m nylon membrane filters (Supelco, Bellefonte, PA) and degassed prior to use. Fused silica capillaries (13 μ m i.d., 350 μ m o.d.) were obtained from Polymicro Technologies (Phoenix, AZ).

Column Preparation. Preparation of a capillary column with the stationary phase involved the following: (1) pretreatment of the bare fused silica capillary, (2) preparation of the sol-gel solution, and (3) coating of the pretreated capillary. To expose the maximum number of silanol groups on the silica surface, the fused silica capillaries were first treated with 1 M KOH solution for 1 h and then washed with water for another hour. The columns were then dried in an oven at ~180 °C under nitrogen flow overnight. The sol-gel solution was prepared by mixing appropriate amounts of TEOS, C₈-TEOS, ethanol, and water. For example, to obtain a C₈-TEOS/TEOS ratio of 0.2, the following amounts were used: 0.14 mL of C₈-TEOS, 0.50 mL of TEOS, 0.18 mL of water, 0.30 mL of ethanol, and 6 μ L of 0.1 M HCl. HCl was added as the catalyst; the apparent pH of the solution was ~5, obtained by a short-range Alkacid test paper (Fisher Scientific). The solution was stirred for 6 h at room temperature and introduced into the pretreated capillary by a syringe. The sol-gel solution was allowed to stay inside the capillary for several minutes (~5 min) and then was forced out of the capillary by applying pressure, leaving a thin film on the inner wall of the capillary. A coated column was then dried overnight in an oven at a temperature of 120 °C, under nitrogen flow. The prepared column was washed with acetone and methanol and then equilibrated with the mobile phase before use.

A capillary column with a chemically bonded stationary phase, attached by conventional procedures, was prepared by filling the pretreated capillary with *n*-octyldimethylchlorosilane, or octyltriethoxysilane, capping both ends of the capillary with septa, and heating the capillary in the oven at 70 °C overnight. The excess of silane reagent was forced out of the column, and the column was washed with acetone and methanol for 2 h prior to equilibration with the mobile phase.

RESULTS AND DISCUSSION

Unlike the commonly used sol-gel process, in which only one metal alkoxide is used as the precursor to produce silica

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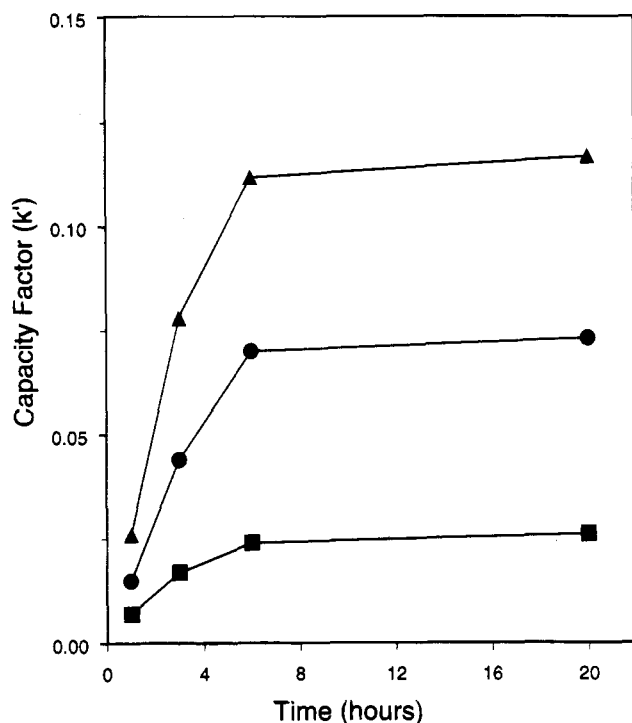


Figure 1. Effect of reaction time on capacity factors for three model compounds separated by OTEC. The original sol-gel solution contained a C_8 -TEOS/TEOS ratio of 0.3. Separation conditions: fused silica capillary, 13 μ m i.d. \times 50 cm long (injection to detection); mobile phase, methanol/1 mM phosphate (67:33); separation voltage, 30 kV; electrokinetic injection, 1 s at 30 kV; detection, UV at 220 nm. Test compounds were naphthalene (■), phenanthrene (●), and pyrene (▲).

glasses,^{14,15} our process involves the synthesis of thin films of silica glasses using two different silicon monomers as coprecursors. A commonly used precursor for a glass matrix, TEOS, was hydrolyzed in conjunction with a second monomeric unit that contains an alkyl substituent. We conveniently selected C_8 -TEOS as the coprecursor to impart an organic character to the silica glass; the organic moiety acts as the stationary phase for reversed phase OTLC and OTEC. The amount of water added corresponds to the stoichiometric quantity required to completely hydrolyze TEOS and C_8 -TEOS. The material was introduced into the capillary during its liquidlike stage after 6 h of stirring at room temperature. For our processing conditions, this stirring time was necessary to achieve a reproducible retention behavior, as shown in Figure 1. Retention is increased with reaction time, indicated by the increase in the capacity factors; however, only a small change in capacity factor is observed after 6 h of reaction. At this time, hydrolysis should be complete and the sol-gel material is mainly undergoing polycondensation reactions,^{14,19} involving the hydrolyzed TEOS and C_8 -TEOS precursors. The silanol groups at the surface of the silica capillary are incorporated into the polycondensation reactions, anchoring the material to the capillary walls. Since the octyl (C_8) groups of the organosilane precursor do not participate in the condensation reactions, they are exposed to serve as the stationary phase in the separation process. This can be seen in Figure 2, where the separation of three model compounds is shown for two columns, one coated with the C_8 -TEOS/TEOS material (A) and the other with TEOS only (B). The three test compounds were baseline separated in the C_8 -TEOS/

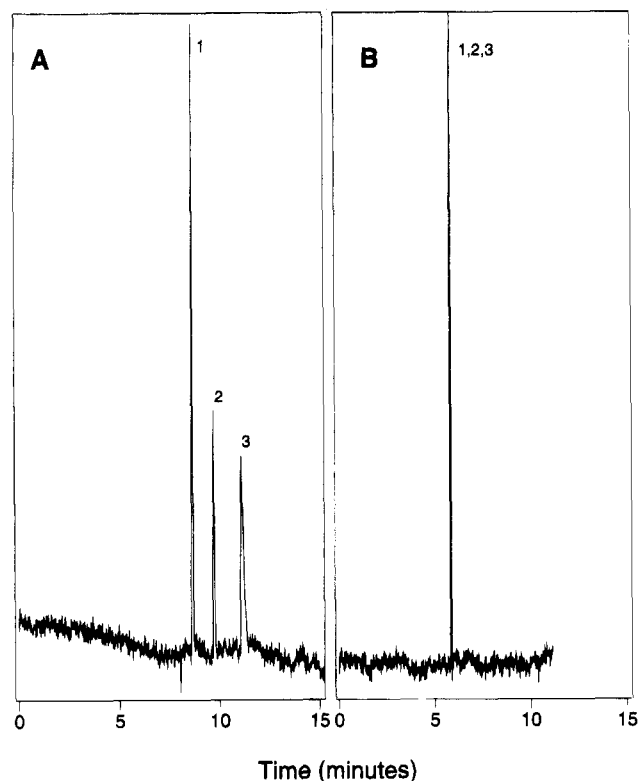


Figure 2. Separation of a test mixture containing three PAH compounds by OTEC in two different capillaries: (A) capillary coated with a C_8 -TEOS/TEOS ratio of 0.2; (B) capillary coated with TEOS only. Separation conditions: capillary column, 13 μ m i.d. \times 50 cm (injection to detection); mobile phase, methanol/1 mM phosphate (67:33); separation voltage, 30 kV; electrokinetic injection, 1 s at 30 kV; detection, UV at 220 nm. The test mixture contained (1) naphthalene, (2) phenanthrene, and (3) pyrene.

TEOS column. In contrast, no separation was achieved in a capillary column coated with a silica glass layer prepared with only TEOS. This indicates, chromatographically, that C_8 groups were exposed at the coating surface, serving as the stationary phase for the separation.

Column Performance. A group of PAH compounds was used as a probe mixture to test the capillary columns coated with the sol-gel material. The capillaries were used for OTLC and OTEC and compared with capillary columns containing a C_8 stationary phase that was prepared by reacting *n*-octyldimethylchlorosilane or *n*-octyltriethoxysilane with the capillary walls (conventional procedure). Figures 3A and 4A depict the separation of five model compounds by OTLC and OTEC in capillary columns with the stationary phase prepared by the sol-gel method (C_8 -TEOS/TEOS ratio of 0.4 and 0.5 for OTEC and OTLC, respectively). The compounds were also separated in columns prepared by the conventional procedure (see Figures 3B and 4B). The columns prepared by the sol-gel procedure offer superior separation characteristics (see capacity factors, resolution, and plates in figure captions); for example, efficiencies of 240 000 plates/m for biphenyl were observed in OTLC and 500 000 plates/m for biphenyl in OTEC, under our experimental conditions. In the OTLC experiments, using a column with the sol-gel-derived phase, the resolution between peaks 2 and 3 is 2.3, while it is 1.2 between peaks 4 and 5. Using a column prepared by the conventional method, the resolution between peaks 2 and 3 was calculated to be 0.7, while peaks 4 and 5 were not resolved at all. For OTEC, even when the separation conditions were

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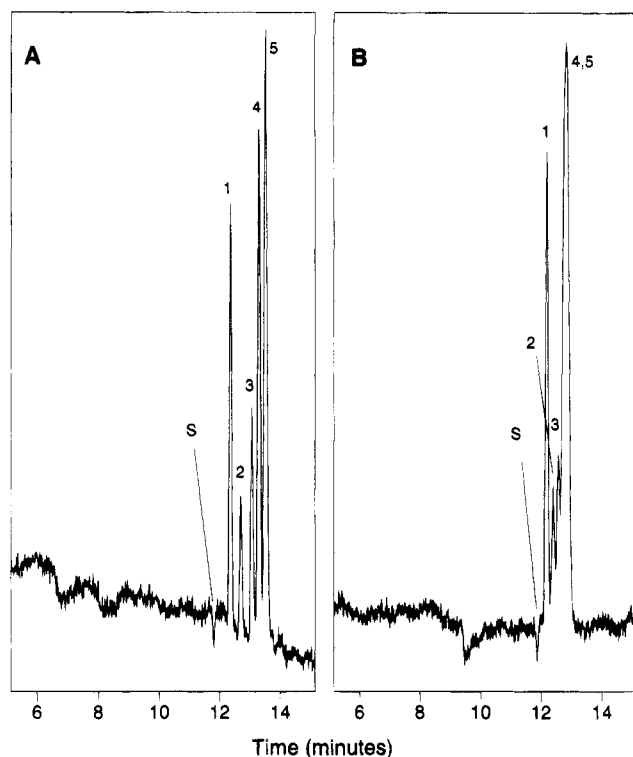


Figure 3. Chromatograms of a test mixture containing five PAH compounds separated by OTLC. The stationary phases were prepared by (A) the sol-gel method with a C_8 -TEOS/TEOS ratio of 0.5 and (B) attaching octyltriethoxysilane to the capillary walls. Separation conditions: capillary column, 10 μ m i.d. \times 50 cm long (injector to detector); mobile phase, methanol/water (70:30); flow rate, 3.3 nL/min; injection volume, 5 μ L; detection, UV at 220 nm. Solvent front is identified with S. (A) $R_{2,3} = 2.3$, $R_{4,5} = 1.2$, $\alpha_{2,3} = 1.40$, $\alpha_{4,5} = 1.14$; (1) naphthalene ($K' = 0.047$, $N = 285\,000/m$), (2) biphenyl ($K' = 0.076$, $N = 240\,000/m$), (3) fluorene ($K' = 0.106$, $N = 211\,000/m$), (4) 2-ethylnaphthalene ($K' = 0.126$, $N = 230\,000/m$), and (5) 2,6-dimethylnaphthalene ($K' = 0.144$, $N = 204\,000/m$). (B) $R_{2,3} = 0.7$, $R_{4,5} = 0$, $\alpha_{2,3} = 1.34$, $\alpha_{4,5} = 1.00$; (1) naphthalene ($K' = 0.026$, $N = 231\,000/m$), (2) biphenyl ($K' = 0.044$), (3) fluorene ($K' = 0.059$), (4) 2-ethylnaphthalene ($K' = 0.080$), and (5) 2,6-dimethylnaphthalene ($K' = 0.080$).

slightly adjusted to a more favorable retention in the conventionally prepared column (60% instead of 75% organic), insufficient retention and poor resolution were also observed. The α values indicate that the sol-gel-derived phase has a different selectivity than the conventionally prepared column. The increase in retention in the capillaries with the sol-gel material is indicative of a larger phase ratio. We attribute this to an increase in surface area, which is characteristic of glasses fabricated by the sol-gel procedure.^{14,15,18}

The retention of the solutes in the sol-gel material can be varied by changing the molar ratio of the two precursors (C_8 -TEOS/TEOS) in the initial sol-gel solution. The effect of C_8 -TEOS/TEOS ratio on the capacity factors of three test compounds is shown in Figure 5. The k' for each C_8 -TEOS/TEOS ratio was determined at least five times with reproducibilities between 2% and 3% (RSD). Such reproducibility in capacity factors was also attained for at least 30 runs using the same column (C_8 -TEOS/TEOS = 0.3). The capacity factors of all three test compounds increase with increasing C_8 -TEOS/TEOS ratio in the initial solution. This indicates that the surface coverage of the stationary phase prepared with the sol-gel method is increased by raising the C_8 -TEOS content in the sol solution. When the capacity factor

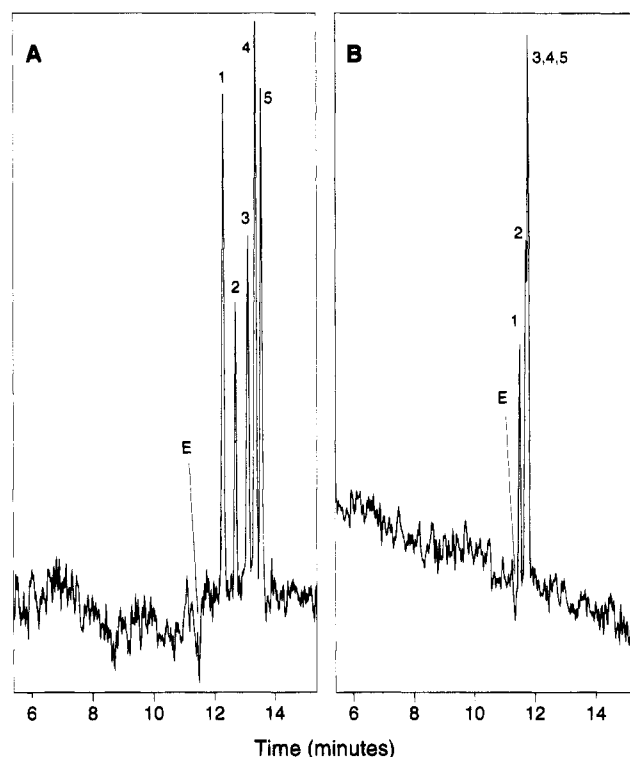


Figure 4. Electrochromatograms of a test mixture containing five PAH compounds. Stationary phases were prepared by (A) the sol-gel method (C_8 -TEOS/TEOS ratio of 0.4) and (B) the conventional procedure using *n*-octyldimethylchlorosilane. Separation conditions: capillary columns, 13 μ m i.d. \times 50 cm long (injection to detection); mobile phase, methanol/1 mM phosphate (75:30 and 60:40 for (A) and (B), respectively); separation voltage, 30 kV; electrokinetic injection, 2 s at 21 kV. Electroosmotic mobility indicated with E. (A) $R_{2,3} = 3.2$, $R_{4,5} = 1.5$, $\alpha_{2,3} = 1.35$, $\alpha_{4,5} = 1.11$; (1) naphthalene ($K' = 0.069$, $N = 280\,000/m$), (2) biphenyl ($K' = 0.104$, $N = 500\,000/m$), (3) fluorene ($K' = 0.140$, $N = 310\,000/m$), (4) 2-ethylnaphthalene ($K' = 0.162$, $N = 353\,000/m$), and (5) 2,6-dimethylnaphthalene ($K' = 0.179$, $N = 382\,000/m$). (B) $R_{2,3} = 0.4$, $R_{4,5} = 0$, $\alpha_{2,3} = 1.23$, $\alpha_{4,5} = 1.00$; (1) naphthalene ($K' = 0.014$), (2) biphenyl ($K' = 0.031$), (3) fluorene ($K' = 0.038$), (4) 2-ethylnaphthalene ($K' = 0.038$), and (5) 2,6-dimethylnaphthalene ($K' = 0.038$).

increases, the plate height (H) also increases under the same separation conditions, as predicted by theory. If the mobile phase is adjusted in such a way that similar k' are obtained from two columns containing different C_8 -TEOS/TEOS ratios, then the efficiencies are similar. For example, the efficiency for naphthalene having a $k' \sim 0.06$ was $\sim 430\,000$ theoretical plates/m for a column with either C_8 -TEOS/TEOS = 0.3 or C_8 -TEOS/TEOS = 1.

Five different columns containing a C_8 -TEOS/TEOS ratio of 0.3 were prepared and evaluated under similar experimental conditions. The capacity factors and theoretical plates for the test compounds are shown in Table 1. The average k' for naphthalene and phenanthrene in the columns was 0.049 (RSD = 17%) and 0.124 (RSD = 16%), respectively. The average plates/m were 334 000 (RSD = 12%) and 280 000 (RSD = 8%) for naphthalene and phenanthrene. The differences between the columns can be attributed to the capillary coating step. In our procedure, we flush the sol-gel solution through the capillary manually by means of a syringe. Although very simple and convenient, the procedure does not give us an accurate control of the flow through the capillary. Therefore, this operation can lead to different film thicknesses, which in turn can affect the retention characteristics

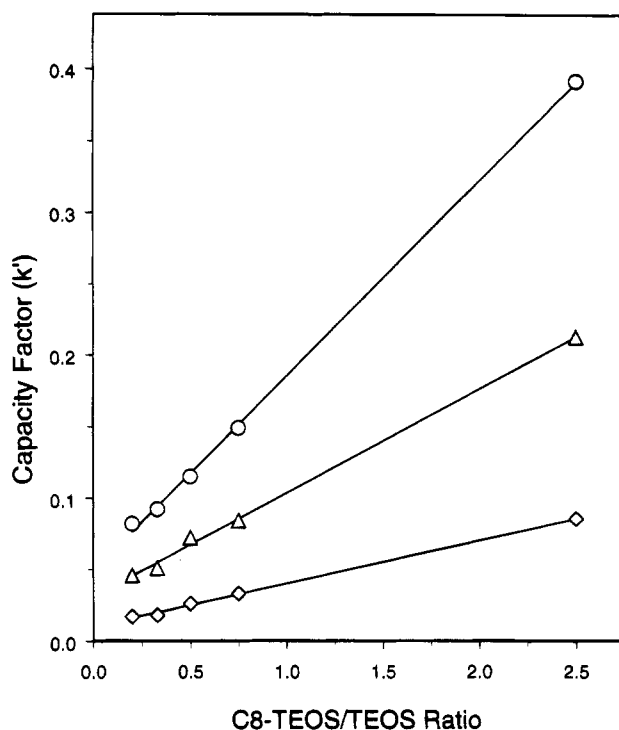


Figure 5. Effect of C₈-TEOS/TEOS ratio on capacity factors. Separations were performed by OTEC. Separation conditions are the same as in Figure 1. Test compounds: naphthalene (◇), phenanthrene (△), and pyrene (○).

Table 1. Performance of Five Different Columns^a

column no.	naphthalene		phenanthrene	
	k'	plates/m	k'	plates/m
1	0.054	293 000	0.144	264 000
2	0.036	334 000	0.091	293 000
3	0.046	344 000	0.129	277 000
4	0.058	304 000	0.135	256 000
5	0.049	395 000	0.122	310 000

^a Results for each column are based on at least three separate runs.

of the columns. Under more controlled coating conditions, a more reproducible film thickness is expected and thus the variability between columns should be minimized.

Stability. We also studied the stability of the stationary phase prepared by the sol-gel method under acidic and basic conditions. The test at low pH involved the washing of a capillary column (10 μ m i.d. and 37 cm long, injector to detector) with 1% trifluoroacetic acid (pH \sim 0.3) for a period of time, after which the acid was flushed out of the column. The capillary was filled with a mobile phase consisting of methanol/1 mM phosphate buffer (70:30) and equilibrated for 20 min. A sample mixture containing naphthalene and phenanthrene was injected into the column to evaluate its performance. The procedure was repeated several times until the column was exposed to 1% trifluoroacetic acid for a period of 32 h. The stability at high pH was tested by adjusting the pH of the mobile phase to 11.4 with Na₃PO₄, and the mobile phase was continuously run through the capillary column (10 μ m i.d. and 37 cm long, injector to detector) for a period of 48 h. Injections of the test mixture were made at certain intervals to examine column performance.

Figure 6 shows the capacity factor for the probe compounds

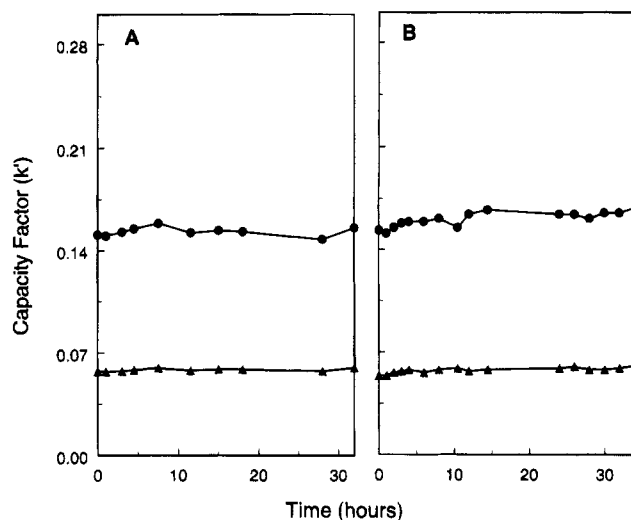


Figure 6. Retentive characteristics of capillary columns prepared by the sol-gel method after being exposed to (A) acidic conditions and (B) basic conditions for naphthalene (△) and phenanthrene (●).

during both tests, under acidic and basic conditions. The capacity factors remained unchanged throughout the test. This indicates that a retentive layer is still on the surface of the capillary to effect separation, even after exposition to high- or low-pH conditions. The hydrolytic stability of the stationary phase can be attributed to the fact that the phase is not prepared by modifying the silica surface through siloxane bonds, as in the conventional procedure; instead, the stationary phase is obtained through bulk modification of the silica glass prepared through the sol-gel process. The C₈ groups serving as the stationary phase on the sol-gel coating are linked to the silica support through Si-C bonds, which are more hydrolytically stable than O-Si bonds obtained during surface modification.²⁰ It has also been postulated that at high-pH values the degradation on performance of the stationary phase prepared by conventional means is more a result of hydrolytic dissolution of the silica surface than of siloxane bond cleavage.²¹ In our procedure, the C₈-TEOS precursor is incorporated into the sol-gel network, and the modification becomes an intrinsic property of the glass matrix. Therefore, if a layer of the material is removed from the surface by hydrolytic processes, the following layer would exhibit the corresponding characteristics of the glass material;²² this accounts for the performance at high-pH conditions.

Loadability. The mass loadability of the column was assessed by injecting different concentrations of naphthalene into a capillary column (C₈-TEOS/TEOS = 1) operated in the OTEC mode. Figure 7 shows the loadability of a column containing a C₈-TEOS/TEOS ratio of 1. It can be seen that the efficiency starts to degrade at a concentration of 100 mM, indicating overloading. In a conventional column, the efficiency was observed to deteriorate at concentrations below 10 mM. Since the column can be operated at concentrations in the millimolar range (<100 mM), demands for detection systems are less stringent. For example, on-column UV detection is facilitated in these very narrow tubes,

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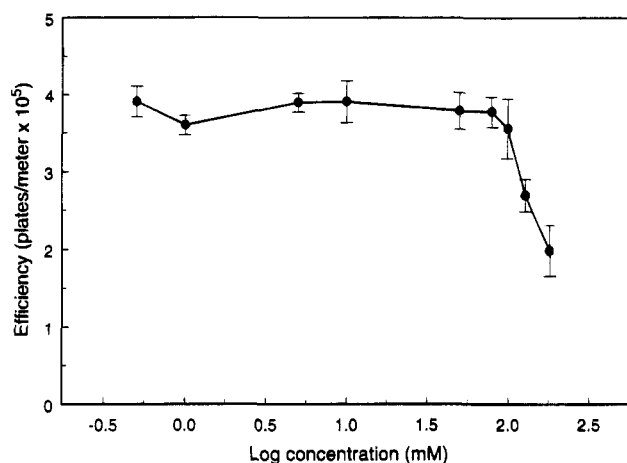


Figure 7. Effect of sample concentration on efficiency for a column prepared with the sol-gel-derived material (C_8 -TEOS/TEOS = 1). Separation conditions: capillary column, 10 μ m i.d. \times 50 cm long (injector to detector); mobile phase, methanol/1 mM phosphate (70:30); injection volume, \sim 15 μ L; detection, UV at 220 nm.

where the path length for detection is the inner diameter of the capillary column (\sim 10 μ m).

CONCLUSION

We have used an organic-inorganic hybrid glass material fabricated by the sol-gel process to prepare a stationary phase for OTLC and OTEC. The unique preparation procedure com-

bines the synthesis of a bonded phase and a supporting porous glass matrix in a single step. This approach increases the column surface area leading to a higher phase ratio and, at the same time, reduces the overall column preparation time (compared with other porous glass layer approaches^{7,8}). We can use the C_8 -TEOS/TEOS ratio as a tunable parameter to achieve a desired selectivity in a column; the percent carbon loading is controlled by the quantity of the monomeric precursor added to the initial solution. Moreover, using this sol-gel procedure, it is possible to prepare columns with mixed phases to attain a desired selectivity. All attempts to prepare a column by the described procedure have been successful. The chromatographic results shown above are very encouraging, and a more detailed chromatographic evaluation is being conducted to further understand the characteristics of the C_8 -TEOS/TEOS sol-gel hybrid material.

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