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Sol−Gel Column Technology for Single-Step Deactivation, Coating, and Stationary-Phase Immobilization in High-Resolution Capillary Gas Chromatography

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A sol−gel chemistry-based novel approach to column technology for high-resolution capillary gas chromatography is described that effectively combines surface treatment, deactivation, coating, and stationary phase immobilization into a single step. In the conventional approach, these operations are carried out in separate steps that make column fabrication a time-consuming job. In the new approach, a cleaned fused silica capillary is filled with a sol solution of appropriate composition, and sol−gel reactions are allowed to go on inside the capillary for a controlled period, typically 15−60 min. A wall-bonded coating results due to condensation of the surface silanol groups with the sol−gel network evolving in their vicinity. Because of the direct chemical bonding to fused silica substrates, sol−gel coatings possess significantly higher thermal stability than conventional coatings. This is especially important for thick and/or polar stationary phase coatings that are difficult to immobilize. Scanning electron microscopic studies revealed that sol−gel coatings were characterized by roughened surfaces, providing a number of chromatographic advantages, including higher surface area and faster mass transfer kinetics. Sol−gel column technology does not require any free radical cross-linking procedures for stationary phase immobilization and easily avoids any undesirable changes in the stationary phase properties that might be associated with the cross-linking reactions used in conventional technology. Sol−gel-coated poly(dimethylsiloxane) and Ucon columns provided efficient separations for analytes from a wide polarity range, including free fatty acids, phenolic compounds, amines, aldehydes, ketones, alcohols, and diols that are prone to peak tailing due to adsorptive interactions with the column walls. This suggests excellent quality of column deactivation. The new technology provided at least a 10-fold reduction in column preparation time. The sol−gel approach is universal in nature and can be effectively applied to a wide range of microcolumn separation techniques.

The introduction of open-tubular columns by Golay[1] about three decades ago revolutionized the analytical capability of gas chromatography (GC). Capillary GC is now a matured separation technique that is widely used in various fields of science and industry.[2−5] Contemporary technology for the preparation of open-tubular columns is, however, time-consuming. It consists of three major, individually executed steps:[6] capillary surface deactivation,[7] static coating,[8] and stationary phase immobilization.[9] Involvement of multiple steps in conventional column technology increases the fabrication time and is likely to result in greater column-to-column variation.

The column deactivation step is critically important for the GC separation of polar compounds that are prone to undergo adsorptive interactions with the silanol groups on fused silica capillary inner walls. In conventional column technology, deactivation is usually carried out as a separate step and involves chemical derivatization of the surface silanol groups. Various reagents have been used to chemically deactivate the surface silanol groups.[10−13] The effectiveness of these deactivation procedures greatly depends on the chemical structure and composition of the fused silica surface to which they are applied. Of special importance are the concentration and mode of distribution of surface silanol groups. Because the fused silica capillary drawing process involves the use of high temperatures (∼2000 °C), the silanol group concentration on the drawn capillary surface may initially be low due to the formation of siloxane bridges under high-temperature drawing conditions. During subsequent storage and handling, some of these siloxane bridges may undergo hydrolysis due to reaction with environmental moisture. Thus, depending on the postdraw-

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ing history, even the same batch of fused silica capillary may have different concentrations of the silanol groups that may also vary by the modes of their distribution on the surface. Moreover, different degrees of reaction and adsorption activities are shown by different types of surface silanol groups.[14] As a result, fused silica capillaries from different batches (or even from the same batch but stored and/or handled under different conditions) may not produce identical surface characteristics after being subjected to the same deactivation treatments. This makes surface deactivation a difficult-to-reproduce procedure. To overcome these difficulties, some researchers have used hydrothermal surface treatments to standardize silanol group concentrations and their distributions over the surface.[15] However, this additional step makes the lengthy column-making procedure even longer.

Static coating is another time-consuming step in conventional column technology. A typical 30-m-long column may require as much as 10 h or more for static coating. The duration of this step may vary depending on the length and diameter of the capillary and the volatility of the solvent used. To coat a column by the static coating technique, the fused silica capillary is filled with a stationary phase solution prepared in a low-boiling solvent. One end of the capillary is sealed (using a high-viscosity grease or by some other means[16]), and the other end is connected to a vacuum pump. Under these conditions, the solvent begins to evaporate from the capillary end connected to the vacuum pump, leaving behind the stationary phase that gets deposited on the capillary inner walls as a thin film. Stationary phase film of desired thickness can be obtained by using a coating solution of an appropriate concentration that can be easily calculated through simple equations.[17] In static coating, two major drawbacks are encountered. First, the technique is excessively time-consuming and not very suitable for automation. Second, the physically coated stationary phase film shows a pronounced tendency toward rearrangements that may ultimately result in droplet formation due to Rayleigh instability.[18] Such a structural change in the coated films may serve as a cause for the deterioration or even complete loss of the column's separation capability. To avoid these undesirable effects, static-coated stationary phase films need to be stabilized immediately after their coating. This is usually achieved by stationary phase immobilization through free radical cross-linking[19] that leads to the formation of chemical bridges between coated polymeric molecules of the stationary phase. In such an approach, the stability of the coated film is achieved not through chemical bonding of the stationary phase molecules to the capillary walls but mainly through an increase of their molecular size (and, consequently, through decrease of their solubility and vapor pressure). Such an immobilization process has a number of drawbacks. First, polar stationary phases are difficult to immobilize by this technique.[20] Second, free radical cross-linking reactions are difficult to control to ensure the same degree of cross-linking in different columns with the same stationary phase. Third, cross-linking reactions may lead to significant changes in the polymer structure, and chromatographic properties of the resulting immobilized polymer may significantly differ from those of the originally taken stationary phase.[9] All these drawbacks add up to make column preparation by conventional techniques a difficult-to-control and reproduce task.[21]

In this context, the goal of this research was to develop a rapid and simple method for simultaneous deactivation, coating, and stationary phase immobilization in GC. To achieve this goal, we developed a sol−gel chemistry-based approach to column preparation that has the potential to be a viable alternative to conventional GC column technology. As will be shown later in this paper, the sol−gel column technology eliminates the major drawbacks of conventional column technology through chemical bonding of the stationary phase molecules to an interfacial organic−inorganic polymer layer that evolves on the top of the original capillary surface. This provides a speedy fabrication of high-efficiency columns with enhanced thermal stability.

EXPERIMENTAL SECTION

Materials and Chemicals. Fused silica capillary (250-μm i.d.) was obtained from Polymicro Technologies Inc. (Phoenix, AZ). HPLC-grade tetrahydrofuran (THF), methylene chloride, and methanol were purchased from Fisher Scientific (Pittsburgh, PA). Tetramethoxysilane (TMOS, 99+%), poly(methylhydrosiloxane) (PMHS), and trifluoroacetic acid (TFA, containing 5% water) were purchased from Aldrich (Milwaukee, WI). Hydroxy-terminated poly(dimethylsiloxane) (PDMS), methyltrimethoxysilane (MTMS), and trimethylmethoxysilane (TMMS) were purchased from United Chemical Technologies, Inc. (Bristol, PA). Ucon 75-H-90,000 polymer was obtained from Alltech (Deerfield, IL).

Equipment. Gas chromatographic experiments were carried out on a Shimadzu Model 14A capillary GC system. A JEOL Model JSM-35 scanning electron microscope was used for the investigation of coated surfaces. A homemade capillary filling device[22] was used for filling the capillary with the coating sol solution using nitrogen pressure. A Microcentaur Model APO 5760 centrifuge was used to separate the sol solution from the precipitate. A Fisher Model G-560 Vortex Genie 2 system was used for thorough mixing of various solution ingredients. A Barnstead Model 04741 Nanopure deionized water system was used to obtain 17.8-MΩ water.

Column Preparation. *General Procedure.* To prepare an open-tubular sol−gel column, a fused silica capillary of appropriate length and diameter is first rinsed with 5 mL of methylene chloride to clean its inner surface, which is then dried by purging with an inert gas. A sol solution is prepared using an alkoxide-based precursor, a hydroxy-terminated stationary phase, a surface derivatizing reagent, and a catalyst dissolved in a suitable solvent system. The sol solution is then centrifuged to remove the precipitates (if any), and the capillary is filled with the clear sol solution, allowing the latter to stay inside the capillary for a controlled period. After that, a pressurized inert gas is used to expel the solution from the capillary. The surface-bonded coating, formed as a result of sol−gel reactions inside the capillary, is then dried by purging it with an inert gas flow. The coated capillary is conditioned at an appropriate temperature, determined by the upper temperature limit for the stationary phase. Prior to first-

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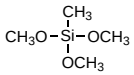
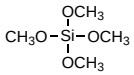
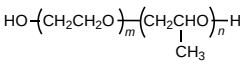
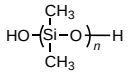
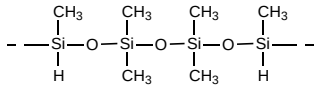
Table 1. Names and Chemical Structures of Sol−Gel Coating Solution Ingredients

ingredients	name	structure
precursors	methyltrimethoxysilane	
	tetramethoxysilane	
polymers	Ucon 75-H-90,000	
	poly(dimethylsiloxane), silanol terminated	
catalyst	trifluoroacetic acid/water 95:5 (v/v)	CF_3COOH
solvent	methylene chloride	CH_2Cl_2
deactivation reagent	poly(methylhydrosiloxane)	

time operation, the column is rinsed with 1 mL of methylene chloride and dried with helium purge. Sol−gel open-tubular columns were prepared using two different hydroxy-terminated stationary phases: (a) Ucon-75-H-90,000 and (b) (PDMS). The key ingredients of sol solutions used to prepare these columns are listed in Table 1.

Preparation of Sol−Gel Ucon Columns. The sol solution for the Ucon column was prepared as follows: 0.187 g of Ucon 75-H-90000 was dissolved in 500 μL of methylene chloride using a Vortex shaker. A 100-μL volume of TMOS and 45 μL of TFA containing 5% water were then sequentially added with thorough mixing. The resulting solution was centrifuged, and the clear liquid (sol) from the top was transferred to a clean vial. It was further used to fill a previously cleaned and dried fused silica capillary (10 m × 250-μm i.d.), using a nitrogen pressure of 100 psi. The solution was expelled from the column under the same nitrogen pressure, after allowing it to stay inside the capillary for 30 min. The capillary was then purged with nitrogen (100 psi) for 30 min, followed by temperature-programmed heating from 40 to 250 °C at a rate of 1 °C min^{-1} using continued purging with helium. The column was held at the final temperature for 5 h.

Preparation of Sol−Gel PDMS Columns. Sol−gel PDMS columns were prepared in an analogous way. In this case, 0.218 g of hydroxy-terminated PDMS and 50 mg of PMHS were dissolved in 100 μL of methylene chloride. A 100-μL volume of MTMS and 100 μL of TFA (containing 5% water) were added to this solution, and the mixture was thoroughly vortexed. The clear top portion of the resulting sol solution was used to coat a capillary of the same dimensions as those of the Ucon columns. For a PDMS column, the solution residence time inside the capillary was 20 min. The rest of the column preparation procedure was identical with that for the Ucon column, except that the PDMS column was conditioned at 330 °C.

RESULTS AND DISCUSSION

The goal of this research was to work out a new approach to column technology that will effectively overcome the shortcomings of conventional approaches and provide a rapid, simple, and reproducible way of preparing high-quality GC columns. To achieve this goal, we critically analyzed the drawbacks and limitations of current GC column technology to pinpoint the origins of such shortcomings. Four major drawbacks were identified: (a) strong dependence of fused silica surface properties on thermal conditions for their industrial manufacture and on postdrawing storage/handling environments, (b) multistep technology with difficult-to-reproduce processes and reactions, (c) lengthy and cumbersome individual steps that make the technology excessively time-consuming and are directly related to the cost of commercially manufactured columns, and (d) lack of stable chemical bonding between the stationary phase film and the column walls that limits the column thermal stability and lifetime.

The first of the above-mentioned drawbacks poses a serious obstacle to the effective column deactivation through derivatization of silanol groups on the *original* capillary inner surface. For such an approach to be consistent, the surface derivatization chemistry should be applied to fused silica capillary surfaces with identical or similar surface characteristics (e.g., concentration and distribution of surface silanol groups). As was mentioned before, these surface characteristics of fused silica capillaries may greatly vary from batch to batch and even within the same batch. Thus, the problem of consistent column deactivation now translates into the problem of preparing capillary surfaces with consistent silanol concentration and distribution. In our view, conventional deactivation procedures that are based on the derivatization of silanol groups on the *original* capillary surface are likely to be limited in their effectiveness and consistency. Here, the problems of surface derivatization chemistry combine with the challenges of consistent surface generation and turn into a difficult problem to solve.

In the sol−gel approach, we looked at the column deactivation problem from a different perspective. Instead of trying to achieve consistent deactivation through derivatization of capillary walls that often have widely different surface characteristics, we turned our efforts to creating a surface-bonded organic−inorganic sol−gel layer on the top of the original capillary surface. In this approach, the original surface serves just as an anchoring substrate for the newly evolving sol−gel top layer before the original surface gets "buried" to disappear in the background.

Here, deactivation takes place as an integral part of the top layer formation during its evolution from solution. Here, the concept of column deactivation finds a wider meaning, extending the silanol derivatization process from the surface into the bulk of the coating. Silanol concentration on the original surface is not likely to have any influence on the deactivation of the top sol−gel coating.

In the new approach, the inherent advantage of sol−gel processes to conduct chemical reactions in solution under extraordinarily mild thermal conditions was employed to achieve surface pretreatment, deactivation, coating, and stationary phase immobilization in a single step. For this, coating solutions were designed to contain sol−gel-active ingredients that can concurrently undergo liquid phase reactions inside the capillary and produce a well-deactivated, surface-bonded coating. An important aspect of the sol−gel column technology is that the stationary phase itself can serve as a deactivation reagent. In our research, we used hydroxy-terminated stationary phases that can chemically bind with the silanol groups of the growing 3-D network of the sol−gel polymer to form an organic−inorganic composite coating. Deactivation is spontaneously achieved as a consequence of the bonding of stationary phase molecules to the evolving sol−gel network. Such chemical bonding also provides strong immobilization of the stationary phase without requiring any free radical cross-linking reactions. Thus, the sol−gel chemistry-based new approach to column technology effectively combines column coating, deactivation, and immobilization procedures into a single step. Being a single-step procedure, the new column technology is fast, cost-effective, and easy to reproduce.

The choice of the solvent system, catalyst, and other sol solution ingredients plays an important role in sol−gel column technology. Table 1 lists the key ingredients used to prepare columns with two different stationary phases: (a) Ucon, a poly(alkylene glycol)-type polar material, and (b) hydroxy-terminated poly(dimethylsiloxane) (PDMS). For both types of columns, the sol−gel reactions were conducted in an organic-rich solvent system. Methylene chloride was used as the solvent, and trifluoroacetic acid (TFA, containing 5% water) served as the catalyst. Neither of these is a typical ingredient for sol−gel processes, since sol−gel reactions are frequently conducted in water-rich solvent systems and catalyzed by either a strong inorganic acid or a strong base. However, use of the above-mentioned chemicals allowed significant acceleration of the gelation process—a factor which is important for speedy fabrication of columns by the sol−gel technique.

In a recent paper, we have described sol−gel reactions involved in the formation of surface-bonded Ucon coatings on the inner walls of open-tubular columns for capillary electrophoresis.[22] The same technology was applied in this work for the preparation of open-tubular GC columns, with the exception that the capillary inner diameter for GC columns was 250 μm instead of 25 μm used in CE. Also, a different catalyst was used in our previous work instead of TFA.

Trifluoroacetic acid served multiple purposes: as a catalyst, a solvent, and a source of water. TFA is a strong organic acid with a pK_a value of 0.3.[23] Carboxylic acids with pK_a values smaller than 4, as was shown by Sharp,[24] can provide enhanced gelation speeds that are a few orders of magnitude higher than that provided by an acid with a pK_a value of greater than 4.0. The key sol−gel reactions involved in the coating procedure are (I) catalytic hydrolysis of the alkoxide precursor, (II) polycondensation of the hydrolyzed products into a three-dimensional sol−gel network, (III) chemical bonding of hydroxy-terminated PDMS to the evolving sol−gel network, and (IV) chemical anchoring of the evolving sol−gel polymer to the inner walls of the capillary. These reactions are represented in Scheme 1.

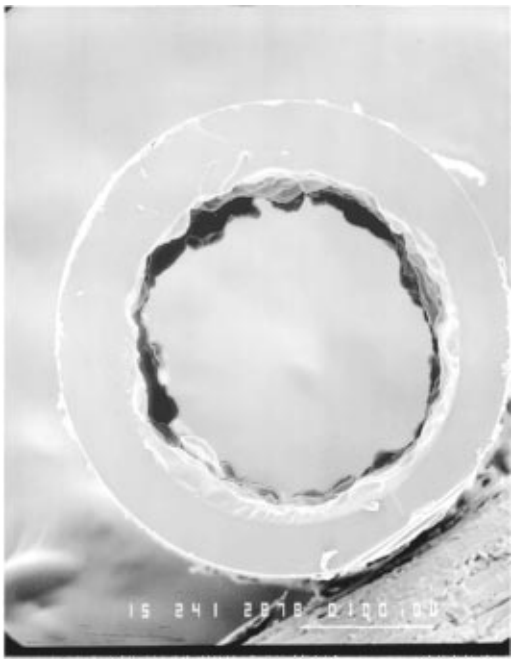


Figure 1. Cross-sectional view of a 250-μm-i.d. sol−gel-coated PDMS column obtained by scanning electron microscopy with a magnification of 240×.

As can be seen from this reaction scheme, the sol−gel procedure represents a dynamic process leading to the evolution of an organic−inorganic stationary phase coating chemically bonded to the original surface. This opens new possibilities to fine-tune the constitutional attributes of the stationary phase (from pure inorganic to pure organic) by controlling the organic−inorganic compositions in the coating sol solution.

Conventionally, tetraalkoxysilanes are used as the sol−gel precursors.[25] However, the use of alkyl or aryl derivatives of tetraalkoxysilanes as precursors may provide important advantages. Sol−gel polymers obtained by using these derivative precursors possess more open structures that provide them the flexibility to effectively release the capillary stress generated during drying of the coated surface (gel).[26] The absence of such a stress-relieving mechanism (e.g., in gels formed from tetraalkoxysilane precursors) may lead to cracking and shrinking of the coating. This, in turn, may have negative consequences on chromatographic performances of the prepared columns.

Figure 1 represents a cross-sectional view of a sol−gel-coated PDMS column obtained by scanning electron microscopy (SEM) with a magnification of 240×. The sol−gel coating is clearly visible as a thin layer on the inner surface of the capillary. Figure 1 also shows a surface roughening effect due to sol−gel processes

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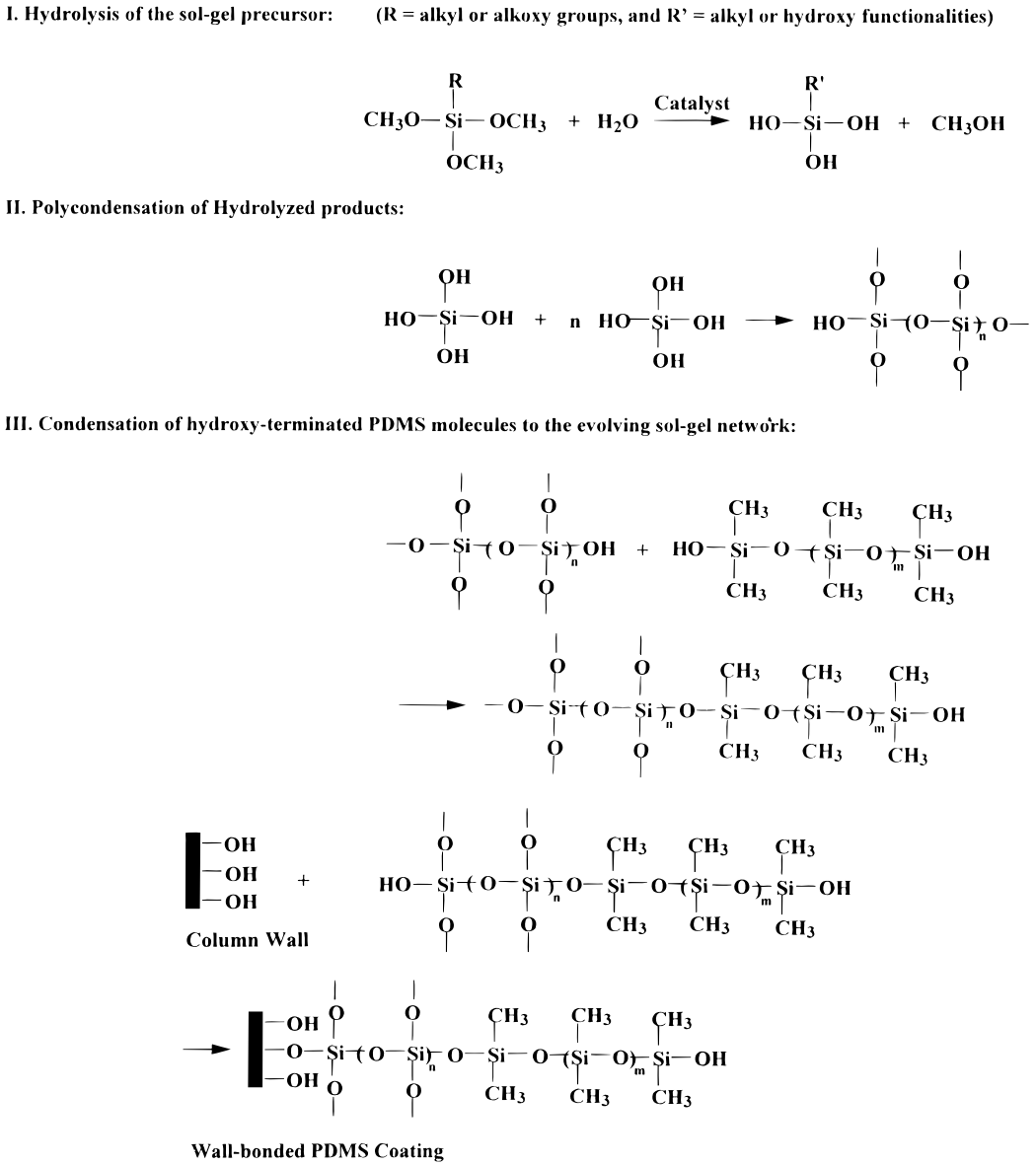
Scheme 1. Chemical Reactions Involved in Sol−Gel Coating with Hydroxy-Terminated PDMS Stationary Phase



on the capillary inner walls. An SEM surface view of the sol−gel coating is presented in Figure 2. Here, about 4 times higher magnification (1000×) was used. Figure 2 reveals some fine structural details of this roughened surface. Similar surface roughening effects were previously observed in our SEM experiments with sol−gel-coated solid phase microextraction fibers.[27]

From a column technology point of view, this surface roughening effect is important, since it should provide enhanced surface area for the solute/stationary phase interaction during chromatographic separations. It should also provide enhanced sample capacity for the sol−gel-coated columns compared with the conventional wall-coated columns. A thorough investigation into the structural details of sol−gel coatings and their effects on column performance in analytical microseparations is now underway.[28]

Figure 3 represents the van Deemter plot for a sol−gel-coated PDMS column obtained at 250 °C using fluoranthene as a test solute (k = 8.4). These efficiency data were used to estimate *utilization of theoretical efficiency* (UTE)[29] and the coefficient C in the mass transfer term of the van Deemter equation.[30] At the optimum flow rate, the minimum plate height for the 250-μm-i.d. column was 0.28 mm, which corresponded to 3400 theoretical plates/m and a UTE value of approximately 79%. Thus, the sol−gel-coated column easily exceeds the recommended performance level of 70% UTE for capillary columns of these dimensions and operating conditions.[31] It should be mentioned that these performance indicator values were obtained on a sol−gel column for which fabrication conditions were not optimized.

The ascending, right-hand part of this plot was used to estimate the value of the coefficient C that characterizes the mass transfer rates between the stationary and mobile phases. The estimated value was approximately 8.7×10^{-4} s. This value compares

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(31) Ettre, L. S.; Hinshaw, J. V. *Basic Relationship in Gas Chromatography*; Advanstar: Cleveland, OH, 1993; p 127.

Figure 2. Fine surface structures of a sol−gel PDMS coating on the inner walls of a 250-μm-i.d. fused silica column obtained by scanning electron microscopy with a magnification of 1000×.

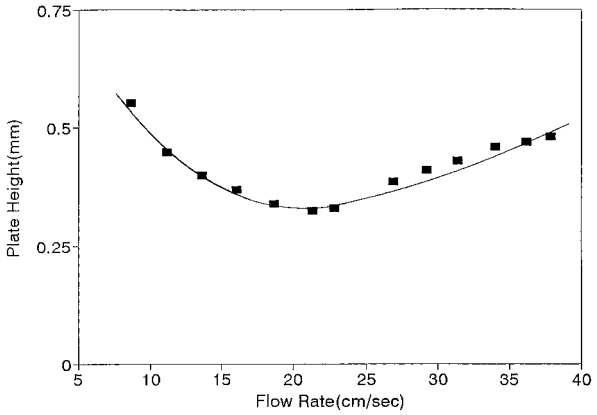

Figure 3. Van Deemter plot for a sol−gel-coated PDMS column. Conditions: 10-m × 250-μm-i.d. fused silica capillary column; split injection (100:1, 300 °C); helium carrier gas; FID, 350 °C; fluoranthene as the probe for efficiency measurements ($k = 8.4$); isothermal runs at 250 °C.

favorably with those typically obtained for static coated open-tubular columns[32] and reflects the fast kinetics of solute interchange between the two phases. Enhanced column surface area and the flexibility of polymeric chains in sol−gel coatings are likely to be positively contributing to this mass transfer process. It should be pointed out that, in conventional coating technology, free radical cross-linking reactions[33] are normally carried out to immobilize the stationary phase in the column. In such columns, stationary phase stability is often achieved at the expense of the polymeric chain flexibility, a determining factor in mass transfer kinetics. Sol−gel coating technology does not require such free radical cross-linking procedures, and the stationary phase molecules in a sol−gel column can be expected to possess a higher

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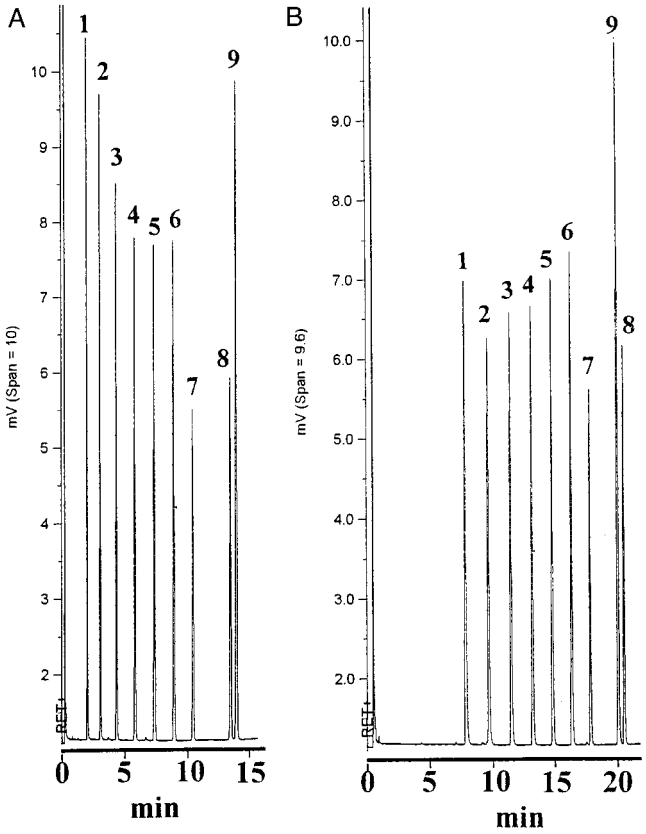

Figure 4. Gas chromatogram of fatty acid methyl esters on two sol−gel-coated columns: Ucon 75-H90,000 (A) and hydroxy-terminated PDMS (B). Conditions: columns, 10-m × 250-μm-i.d. fused silica capillary; carrier gas, helium; injection, split (100:1, 250 °C); detector, FID, 300 °C. Temperature programming: from 80 °C at 6 °C min^{-1}. Peaks: (1) methyl decanoate, (2) methyl undecanoate, (3) methyl dodecanoate, (4) methyl tridecanoate, (5) myristic acid methyl ester, (6) pentadecanoic acid methyl ester, (7) palmitic acid methyl ester, (8) stearic acid methyl ester, and (9) linoleic acid methyl ester.

degree of flexibility. A practical implication of fast mass transfer in sol−gel columns is that such columns will allow high flow rate operations in fast analyses with minimal efficiency loss.

Gas chromatographic performances of sol−gel-coated columns were investigated using polar, moderately polar, and nonpolar compounds. Mixtures of alkanes and polycyclic aromatic hydrocarbons (PAHs) were used as nonpolar samples. Fatty acid methyl esters represented moderately polar samples. Various mixtures of aniline derivatives, alcohols, diols, aldehydes, ketones, phenolic compounds, and free fatty acids were used as polar samples.

A conventionally coated Ucon column is more polar than a PDMS column. However, in a sol−gel-coated column, the stationary phase coating is not just an organic film (as in conventionally coated columns) but represents an organic−inorganic composite coating. Moreover, the PDMS stationary phase used is hydroxy-terminated, which makes it more polar than the conventionally used PDMS stationary phase. In this context, a mixture of saturated and unsaturated fatty acid methyl esters was used to probe the selectivity and polarity of sol−gel-coated Ucon and PDMS columns (Figure 4). The elution order of stearic acid (peak 8) and linoleic acid (peak 9) methyl esters was reversed on the two columns. These two solutes have identical ester functionality and the same number of carbon atoms in their

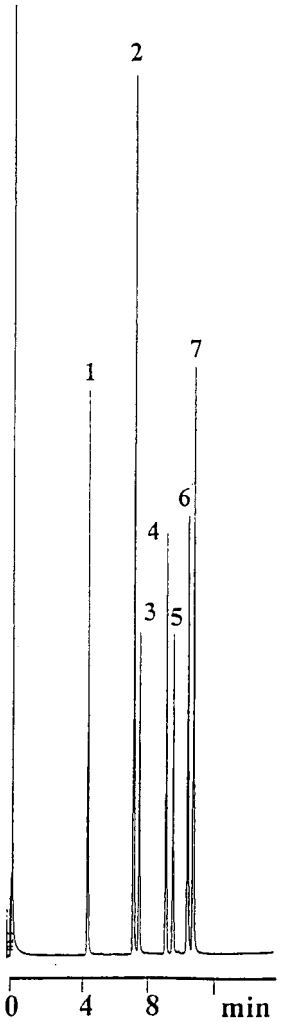

Figure 5. Gas chromatogram of aniline derivatives on a sol−gel-coated Ucon column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, Ucon 75-H-90,000; carrier gas, helium; injection, split (100:1, 250 °C); detector, FID, 300 °C. Temperature programming: from 40 °C at 6 °C min^{-1}. Peaks: (1) *N,N*-dimethylaniline, (2) *N*-methylaniline, (3) *N*-ethylaniline, (4) 2,6-dimethylaniline, (5) 2-ethylaniline, (6) 4-ethylaniline, and (7) 3-ethylaniline.

aliphatic chains. With two double bonds in the structure, linoleic acid methyl ester will interact more strongly with the stationary phase of higher polarity. On the sol−gel Ucon column, linoleic acid methyl ester showed longer retention time than the stearic acid methyl ester. This suggests that the sol−gel-coated Ucon column is still more polar than the sol−gel column with hydroxy-terminated PDMS as the stationary phase.

Basic compounds (e.g., amines) are especially prone to tailing on a poorly deactivated column. Acid−base interaction of such analytes with the acidic surface silanol groups is a key factor that leads to the tailing of their peaks on inadequately deactivated fused silica columns.[34] Figure 5 represents the GC separation of six aniline derivatives on a sol−gel-coated Ucon column. Perfectly symmetrical peak shapes for these basic compounds are an indication of excellent quality of deactivation in a sol−gel column. Mention should be made here that no special deactivation reagents were used for the preparation of the sol−gel-coated Ucon column.

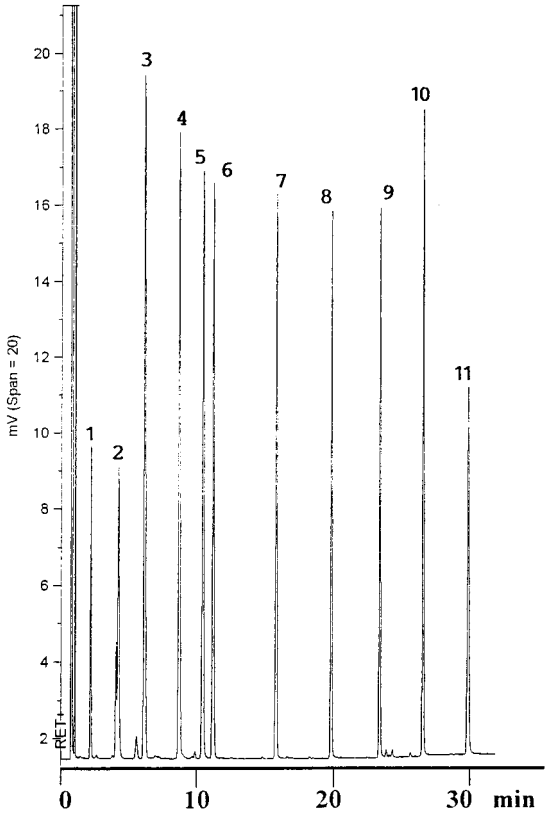

Figure 6. GC separation of alcohols and diols on a sol−gel-coated PDMS column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, hydroxy-terminated PDMS; carrier gas, helium; injection, split (100:1, 300 °C); detector, FID, 300 °C. Temperature programming: from 40 °C at 6 °C min^{-1}. Peaks: (1) 1-butanol, (2) 2,3-butanediol, (3) 1-hexanol, (4) 1-heptanol, (5) *trans*-1,2-cyclohexanediol, (6) 1-octanol, (7) 1-decanol, (8) 1-dodecanol, (9) 1-tetradecanol, (10) 1-hexadecanol, and (11) 1-octadecanol.

It is also impressive that these perfect peak shapes were obtained at relatively low temperatures. The starting temperature in the program used was only 40 °C, and the last peak eluted before the column temperature reached 110 °C. This is an inherent advantage of sol−gel-coated columns that also holds true for the separation of other types compounds, as will be evident from the examples that follow.

Alcohols and diols are two other classes of compounds that are prone to tailing due to hydrogen bonding and other polar interactions with silanol groups.[34,35] Figure 6 represents a chromatogram illustrating GC separation of a mixture of alcohols and diols on a sol−gel-coated PDMS column. As can be seen in Figure 6, perfectly symmetrical peaks were obtained for these adsorptive analytes. Excellent peak shapes were also obtained for aldehydes and ketones as can be seen in Figure 7. All these can be translated as evidences of excellent surface deactivation in the sol−gel-coated columns.

Figure 8 represents gas chromatographic separation of the polarity test mixture[36] on a sol−gel-coated Ucon column. The presented chromatogram shows symmetrical peaks for both polar and nonpolar components of the mixture, indicating excellent column performance and deactivation quality. Analogous conclusion can be drawn from the chromatogram of the Grob test

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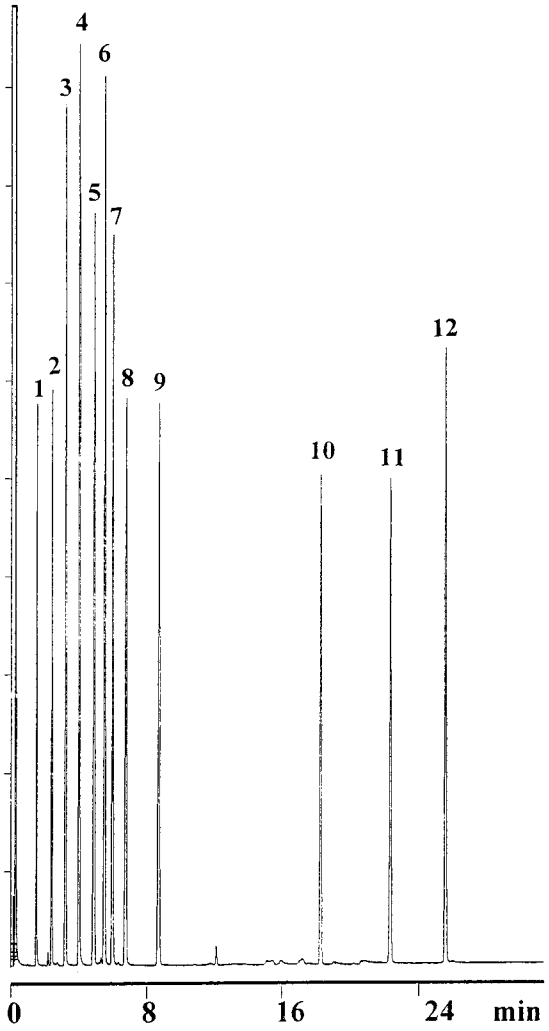

Figure 7. Gas chromatographic separation of aldehydes and ketones on a sol−gel-coated Ucon column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, Ucon 75-H-90,000; carrier gas, helium; injection, split (100:1, 300 °C); detector, FID, 300 °C. Temperature programming: from 40 °C at 6 °C min^{-1}. Peaks: (1) cyclohexanone, (2) 5-nonanone, (3) nonanal, (4) benzaldehyde, (5) *n*-decylaldehyde, (6) *o*-tolualdehyde, (7) *p*-tolualdehyde, (8) undecylic aldehyde, (9) dodecanal, (10) benzophenone, (11) 4′-phenylacetophenone, and (12) *trans*-chalcone.

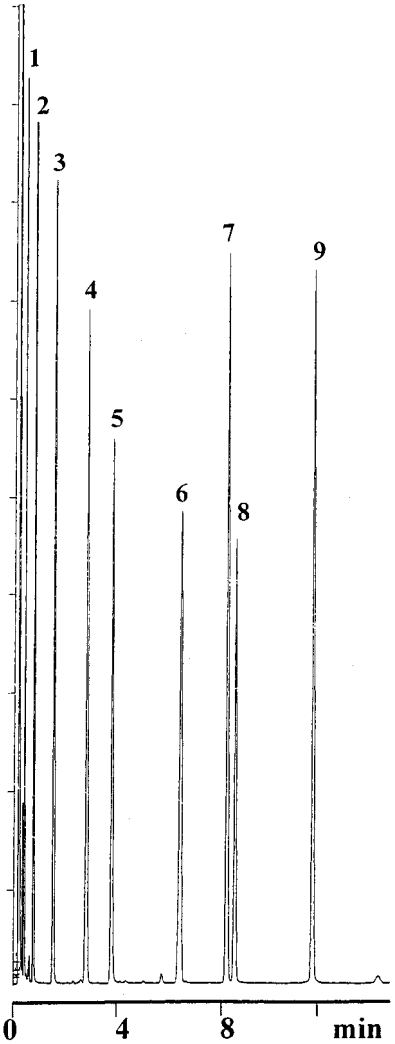

Figure 8. GC separation of polarity test mixture on a sol−gel-coated Ucon column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, Ucon 75-H-90,000; carrier gas, helium; injection, split (100:1, 250 °C); detector, FID, 300 °C; column temperature: programmed from 30 °C (hold for 1 min) at 6 °C min^{-1}. Peaks: (1) *n*-nonane, (2) *n*-decane, (3) *n*-undecane, (4) *n*-dodecane, (5) 5-nonanone, (6) *n*-tetradecane, (7) *cis*-2-*n*-propyl-1-cyclohexanol, (8) *trans*-2-*n*-propyl-1-cyclohexanol, and (9) 2,6-dimethylaniline.

mixture[37] presented in Figure 9. Retention time repeatability data for the components of the Grob test mixture is presented in Table 2. In 13 replicate measurements, the relative standard deviation in retention time was less than 0.3% for all the components, except for the two early-eluting *n*-alkanes.

As can be observed in Figure 9, symmetrical peak shapes were obtained for all the polar and nonpolar components, except for 2-ethylhexanoic acid, which showed slight tailing. It should be pointed out that free carboxylic acids often produce tailing peaks with reduced height on conventionally deactivated columns.[38]

Difficulties associated with the GC separation of free fatty acids are well-known.[39−41] Fatty acids are very polar compounds. For GC analysis, free fatty acids are frequently converted into volatile derivatives of lower polarity.[42] However, ensuring complete derivatization of these compounds, especially when present in small concentrations, is associated with practical difficulties. Incomplete derivatization may introduce significant error in their quantitation.

Specially designed stationary phases (e.g., FFAP,[43] which contains terminal carboxyl groups) are sometimes used to allow for direct separation of free fatty acids and other acidic compounds. However, as was cautioned by Rotzsche,[44] the stationary phase tends to undergo temporal changes in its chromatographic properties (possibly due to splitting of the terminal carboxyl groups at elevated temperatures) and may cause reproducibility problems. In this application, the sol−gel PDMS column provides a significant thermal stability advantage over a conventionally

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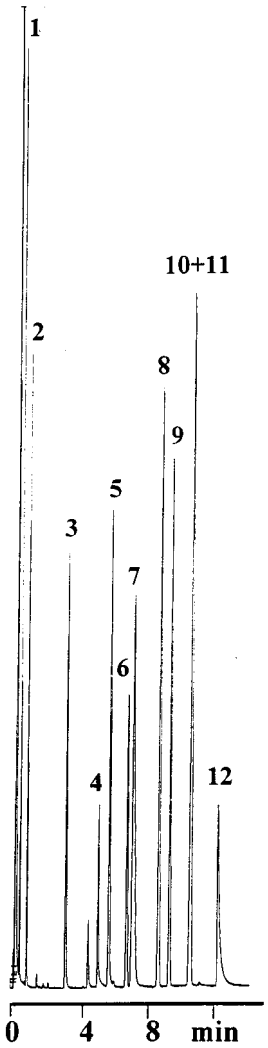

Figure 9. GC separation of Grob test mixture on a sol−gel-coated Ucon column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, Ucon 75-H-90,000; carrier gas, helium; injection, split (100:1, 250 °C); detector, FID, 300 °C; column temperature, 30 °C (hold for 1 min) at 6 °C min^{-1}. Peaks: (1) *n*-decane, (2) *n*-undecane, (3) 1-nonanal, (4) 2,3-butanediol, (5) 1-octanol, (6) methyl dodecanoate, (7) dicyclohexylamine, (8) methyl undecanoate, (9) 2,6-dimethylaniline, (10 + 11)-methyl dodecanoate and 2,6-dimethylphenol, and (12) 2-ethylhexanoic acid.

coated FFAP column. FFAP columns are thermally stable at best up to 260 °C,[44] whereas sol−gel-coated PDMS columns can provide stable performance up to 350 °C and higher. A comprehensive study on various aspects of free fatty acid separations on sol−gel-coated columns will be published elsewhere.[45]

Sol−gel column technology allows us to solve these and other difficult separation problems by using conventional stationary phases (e.g., PDMS) in combination with a deactivation reagent (e.g., poly(methylhydrosiloxane), PMHS) in the coating sol solution. PMHS are well-known surface deactivation reagents that contain chemically reactive hydrogen atoms for effective derivatization of silanol groups at elevated temperatures.[46] In contrast to conventional GC column technology, the sol−gel approach does not require any additional steps to deactivate the column using these reagents. It simply requires the addition of appropriate amounts of PMHS to the coating sol solution. After sol−gel coating, the newly created surface layer will contain physically bound molecules of PMHS that will perform the deactivation reaction during the column conditioning step, according to the reaction presented in Scheme 2.

Table 2. Retention Time Repeatability Data for the Components of Grob Test Mixture Obtained on a Sol−Gel-coated Ucon Column[a]

solutes	average retention time (min)	SD	RSD (%)
n-decane	0.56	4.08×10^{-3}	0.73
n-undecane	0.99	5.55×10^{-3}	0.56
1-nonanal	3.38	8.62×10^{-3}	0.26
2,3-butanediol	5.37	5.99×10^{-3}	0.11
1-octanol	6.04	3.76×10^{-3}	0.06
methyl decanoate	7.13	8.01×10^{-3}	0.11
dicyclohexylamine	7.48	5.55×10^{-3}	0.07
methyl undecanoate	9.10	8.77×10^{-3}	0.10
2,6-dimethylaniline	9.77	3.76×10^{-3}	0.04
methyl dodecanoate and 2,6-dimethylphenol	11.03	1.01×10^{-2}	0.09
2-ethylhexanoic acid	12.78	3.56×10^{-2}	0.28

[a] Experimental conditions are the same as those in Figure 9.

Addition of PMHS to the coating solution provided enhanced deactivation of the column, evidenced from the perfect peak shapes of free fatty acids presented in Figure 10. High-efficiency separation of isomeric phenol derivatives (that are also acidic in nature) on a sol−gel PDMS column with PMHS deactivation is illustrated in Figure 11. Excellent separation of these acidic compounds was achieved under mild thermal conditions using the sol−gel column with organic−inorganic composite coating.

Sol−gel coatings showed a significant thermal stability advantage over those conventionally obtained by the static coating technique. It should be pointed out that sol−gel technology provides high thermal stability not only to thin coatings (d_f < 1 μm), as are used in gas chromatography, but also to coatings that are a few orders of magnitude thicker. From this perspective, sol−gel technology has much to offer in creating thick, stable coatings (10−100 μm). Solid phase microextraction fiber technology is one such area that can take advantage of the sol−gel coating technique. Our preliminary results show reliable and consistent performance of thick sol−gel PDMS coatings on SPME fibers at temperatures up to 360 °C and higher. Detailed treatments of the thermal stability of sol−gel coatings in GC and SPME will be presented elsewhere.[47,48]

The enhanced thermal stability of sol−gel coatings may be attributed to the formation of strong chemical bonds between the hydroxy-terminated stationary phase and the surface-bonded silica substrate. Unlike conventional approaches to high-temperature use of OH-terminated stationary phases,[49−51] the sol−gel approach does not require the use of glass substrates,[49] extensive leaching of their surfaces,[50] or high-temperature immobilization[51] of the stationary phase.

In a recent publication, we demonstrated the applicability of sol−gel technology to the preparation of highly efficient columns

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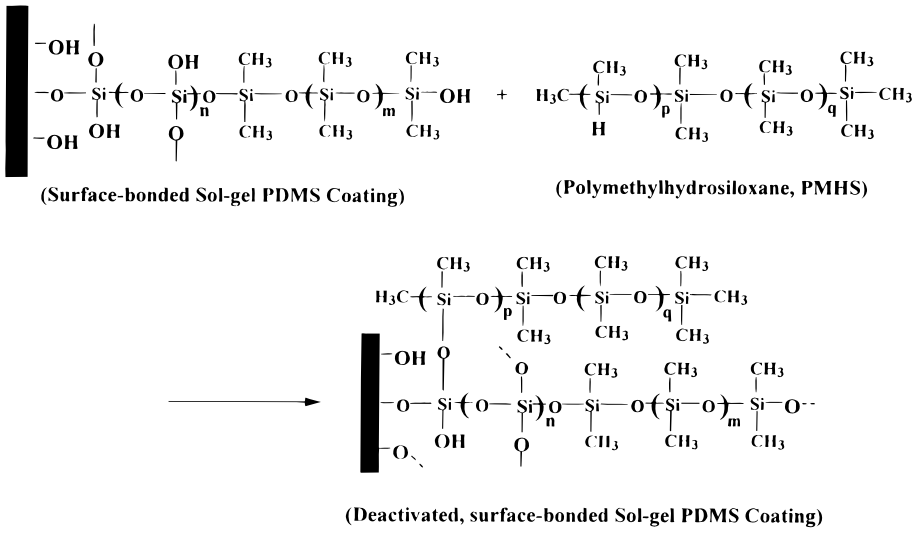
Scheme 2. Deactivation of Surface-Bonded Sol−Gel PDMS Coating with Poly(methylhydrosiloxane) (PMHS)



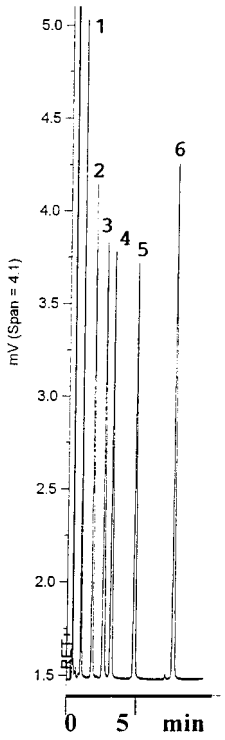


Figure 10. GC separation of free fatty acids on a sol−gel-coated PDMS column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, hydroxy-terminated PDMS; carrier gas, helium; injection, split (100:1, 300 °C); detector, FID, 300 °C. Temperature programming: from 40 °C at 6 °C min^{-1}. Peaks: (1) propanoic acid, (2) butyric acid, (3) isovaleric acid, (4) *n*-valeric acid, (5) *n*-caproic acid, and (6) ethylhexanoic acid.

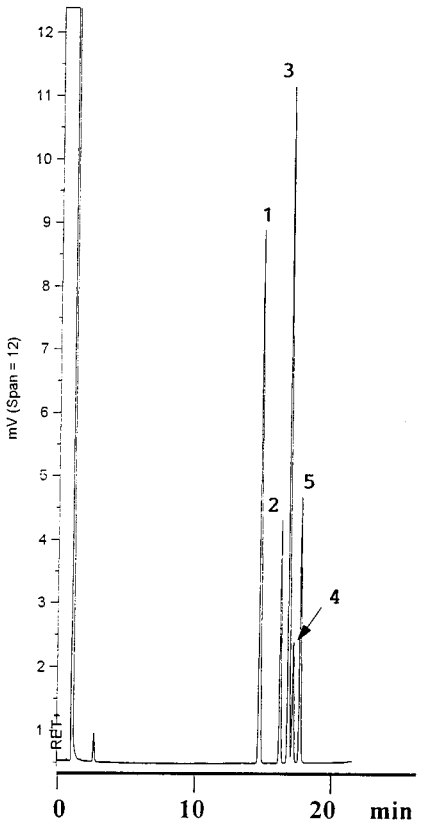


Figure 11. Gas chromatographic separation of dimethylphenol isomers on a sol−gel-coated PDMS column. Conditions: column, 10-m × 250-μm-i.d. fused silica capillary column; stationary phase, hydroxy-terminated PDMS; carrier gas, helium; injection, split (100:1, 300 °C); detector, FID, 300 °C. Temperature programming: from 40 °C at 6 °C min^{-1}. Peaks: (1) 2,6-dimethylphenol, (2) 2,5-dimethylphenol, (3) 3,5-dimethylphenol, (4) 2,3-dimethylphenol, and (5) 3,4-dimethylphenol.

for capillary electrophoresis.[22] We have applied sol−gel chemistry in combination with supercritical drying technology to prepare monolithic columns[52] that can be used in various condensed phase separation techniques, including capillary electrochromatography, high-performance liquid chromatography, and supercritical fluid chromatography. Thus, sol−gel technology appears to be universally applicable to a wide variety microseparation and sample preparation techniques.

In our view, the potential of sol−gel chemistry in analytical microseparations is enormous. It presents a universal approach to creating advanced material systems,[53] including those based on alumina, titania, and zirconia that have not been adequately evaluated in conventional separation column technology. Thus, the sol−gel chemistry-based column technology has the potential to effectively utilize advanced material properties to fill this gap.

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Although this prospective approach is just making its first steps[22,23,52,54−59] in analytical microseparations, it poses a bright prospect for being widely applied in a diverse range of analytical separation techniques.

CONCLUSION

A sol−gel chemistry-based novel approach to column technology is presented for high-resolution capillary GC that provides a speedy way of surface roughening, deactivation, coating, and stationary phase immobilization—all carried out in a single step. Unlike conventional column technology, in which these procedures are carried out as individual, time-consuming steps, the new technology can achieve all these just by filling a capillary with a sol solution of appropriate composition and allowing it to stay inside the capillary for a controlled period, followed by inert gas purging and conditioning of the capillary. The new technology greatly simplifies the methodology for the preparation of high-efficiency GC columns and offers an opportunity to reduce the column preparation time at least by a factor of 10. Being simple in technical execution, the new technology is very suitable for automation and mass production. Columns prepared by the new technology provide significantly superior thermal stability due to direct chemical bonding of the stationary phase coating to the capillary walls. Enhanced surface area of the columns, as evidenced by SEM results, should provide a sample capacity advantage to the sol−gel columns. The new methodology provides excellent surface deactivation quality, which is either comparable with or superior to that obtained by conventional techniques. This is supported by examples of high-efficiency separations obtained for polar compounds including free fatty acids, amines, alcohols, diols, aldehydes, and ketones. The new technology is universal in nature and is equally applicable to other microseparation and sample preparation techniques, including CE, SFC, LC, CEC, and SPME. The sol−gel column technology has the potential to offer a viable alternative to existing methods for column preparation in microseparation techniques.

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