Anal. Chem. **1998,** *70,* 5103−5107

Preparation and Characterization of Monolithic Porous Capillary Columns Loaded with Chromatographic Particles

Maria T. Dulay, Rajan P. Kulkarni, and Richard N. Zare*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Using sol−gel technology, a porous glass matrix (xerogel) is formed in a capillary column and acts as a support for a stationary phase of chromatographic particles used in capillary electrochromatography. Preparation of the sol−gel matrix and immobilization of the octadecylsilica (ODS) stationary phase occur in a single step. The presence of the particles in the column greatly reduces matrix cracking caused by internal pressure differentials within the pores of the sol−gel matrix. Good electroosmotic flow is achieved in part because of the inherent negative charge of both the particles and the sol−gel matrix. The performance of these sol−gel/ODS capillary columns was evaluated with a mixture of aromatic and nonaromatic organic compounds. Efficiencies of up to 80 000 plates/m were observed in columns with immobilized 3-μm ODS particles. The efficiency and resolution are enhanced when 3-μm ODS particles are used in place of the 5-μm particles.

Over the past decade, capillary zone electrophoresis (CZE),[1,2] with its high peak capacity (i.e., the number of peaks separated per unit time), has developed into a powerful and widely used technique for separating ionic species by their electrophoretic mobilities. The lack of selectivity for uncharged analytes in CZE, however, has remained more problematic. Several methods have been developed, such as micellar electrokinetic chromatography (MEKC),[3] to help overcome this problem by providing a pseudostationary phase in which uncharged compounds can be separated. The application of methods such as MEKC is limited because of the restricted number of pseudostationary phases that can be employed in this technique.

With the advent of capillary electrochromatography (CEC),[4,5] where both chromatographic and electrophoretic transport mechanisms are combined, separation and analysis of mixtures of uncharged analytes can be achieved using low sample volumes with high resolution and efficiency.[6−12] The increased interest in CEC for analytical applications arises from the large plate numbers and relatively high separation speeds achieved[12] and the wide range of stationary phases (those commonly used in high-performance liquid chromatography) that can be used.

Many groups have reported on the use of slurry or electrokinetic packing methods for the fabrication of electrochromatography capillary columns with typical inner diameters of 75 μm. Reversed-phase capillary columns have been prepared, typically with octadecylsilica (ODS) whose particle diameters are on the order of 1.5−5 μm. In both packing techniques, the use of retaining frits at both the inlet and the outlet of the capillary is required to prevent the chromatographic packing material from exiting the capillary. Although systematic studies regarding the effects of the frits on the performance of such capillaries have not been reported, it is thought that these frits may degrade the efficiencies of these capillary columns.

Alternative approaches have been reported for the preparation of capillary columns that avoid the technical problems of frit fabrication and column preparation associated with slurry and electrokinetic packing. One approach uses bonded stationary phases. Capillary columns prepared in this manner, however, suffer from low retention and low sample capacities as well as long preparation times.[13−20] An alternative method for the preparation of open tubular capillary columns uses monolithic packing technology.[21−24] Although this method avoids the techni-

(1) Jorgenson, J. W.; Lukas, K. D. *J. Chromatogr.* **1981**, *218*, 209.
(2) Weinberger, R. *Practical Capillary Electrophoresis*; Academic Press: San Diego, 1993.
(3) Terabe, S.; Otsuka, K.; Ichikawa, K.; Tsuchiya, A.; Ando, T. *Anal. Chem.* **1984**, *56*, 113.
(4) Pretorius, V.; Hopkins, B. J.; Schieke, J. D. *J. Chromatogr.* **1974**, *99*, 23.
(5) Knox, J. H.; Grant, I. H.*Chromatographia* **1991**, *32*, 317.
(6) Dulay, M. T.; Yan, C.; Rakestraw, D. J.; Zare, R. N. *J. Chromatogr., A* **1996**, *725*, 361.
(7) Smith, N. W.; Evans, M. B. *Chromatographia* **1994**, *38*, 649.
(8) Lelievre, F.; Yan, C.; Zare, R. N.; Gariel, P. *J. Chromatogr., A* **1996**, *723*, 145.
(9) Yan, C.; Dadoo, R.; Zhao, H.; Zare, R. N.; Rakestraw, D. J. *Anal. Chem.* **1995**, *67*, 2026.
(10) Engelhardt, H.; Lamotte, S.; Hafner, F. T. *Am. Lab.* **1998**, *30*, 40.
(11) Huber, C. G.; Choudhary, G.; Horváth, C. *Anal. Chem.* **1997**, *69*, 4429.
(12) Dadoo, R.; Zare, R. N.; Yan, C.; Anex, D. S.; Rakestraw, D. J. *Anal. Chem.*, submitted.
(13) Tsuda, T.; Hibi, K.; Nakanishi, T.; Takeuchi, T.; Ishii, D. *J. Chromatogr.* **1981**, *11*, 332.
(14) Jorgenson, J. W.; Guthrie, E. J. *J. Chromatogr.* **1983**, *255*, 335.
(15) Crego, A. L.; Diez-Masa, J. C.; Dabrio, M. V. *Anal. Chem.* **1993**, *65*, 1615.
(16) Bohlin, K.; Larsson, M. *J. Chromatogr.* **1993**, *645*, 41.
(17) Bruin, G. J. M.; Tock, P. P. H.; Kraak, J. C.; Poppe, H. *J. Chromatogr.* **1990**, *517*, 557.
(18) Tan, Z. J.; Remcho, V. T. *Anal. Chem.* **1997**, *69*, 581.
(19) Mayer, S.; Schurig, V. *Electrophoresis* **1994**, *15*, 835.
(20) Garner, F. W.; Yeung, E. S. *J. Chromatogr.* **1993**, *640*, 397.
(21) Fields, S. M. *Anal. Chem.* **1996**, *68*, 2709.
(22) Asiaie, R.; Huang, X.; Farnan, D.; Horváth, C. *J. Chromatogr., A* **1988**, *806*, 251.
(23) Minakuchi, H.; Nakanishi, K.; Soga, N.; Ishizuka, N.; Tanaka, N. *J. Chromatogr., A* **1997**, *762*, 135.
(24) Svec, F.; Fréchet, J. M. *Science* **1996**, *273*, 205.

10.1021/ac9806456 CCC: $15.00
Published on Web 10/24/1998

cal problems of frit fabrication, these monolithic structures are often restricted to the use of monomers with limited hydrophobicity. The use of molded rigid polymer monoliths as separation media for reversed-phase CEC resulted in monolithic capillary columns with high efficiencies.[25−27] Although these monolithic capillary columns are produced in "one step", this method appears to be limited in the range of compounds that can be separated.

A new column preparation method based on sol−gel chemistry is described here. Sol−gel technology has been used previously to cast porous silica glass films on the inner walls of capillary columns for use in open tubular electrochromatography applications[28,29] and for gas chromatography.[30] This method of preparing sol−gel capillaries for CEC, however, requires pretreatment of the capillary walls.

Because sol−gel glasses (xerogels) are formed from hydrolysis of water, alcohol, and a metal alkoxide source,[31] other molecules can be imbedded inside the pores or inside the cavities created.[32,33] Consequently, this monolithic packing method is utilized as a means to incorporate a separation phase in fused-silica capillary columns by embedding chromatographic particles in porous sol−gel glass cavities. It is this porosity that allows for the diffusion of protons and other neutral or ionic species through the channels. These pores are large enough to allow species diffusion but small enough so that the ODS particles cannot leave the sol−gel matrix.

The usefulness of this monolithic packing method arises from the specific advantage of a fritless design, which is in sharp contrast with the use of slurry or electrokinetic packing methods used previously. An additional advantage of this monolithic packing method is the ease in which capillary columns can be prepared with the appropriately selected chromatographic material (charged or uncharged) in a single step. In particular, we demonstrate the use of suspensions of ODS particles that are prepared in tetraethyl orthosilicate (TEOS), the sol−gel precursor. This suspension is introduced simply into a fused-silica capillary column by pressure, and preparation of the filled column is completed upon heating of the column overnight at a temperature above 373 K. We report here the use of reversed-phase CEC to separate a test mixture of neutral compounds. The sol−gel-filled capillary column displays properties similar to those of normal fused-silica capillary, including chemical resistance to most solvents and UV transparency that is characteristic of silica.

In what follows, we describe the packing procedure and present some typical separations we have obtained with such columns. We can achieve over 70 000 plates/m on a routine basis with these columns when they are loaded with 3-μm ODS particles. Our results suggest that such monolithic sol−gel columns might find many uses when further refinements are made.

(25) Peters, E. C.; Petro, M.; Svec, F.; Fréchet, J. M. *Anal. Chem.* **1998**, *70*, 2288.
(26) Peters, E. C.; Petro, M.; Svec, F.; Fréchet, J. M. *Anal. Chem.* **1997**, *69*, 3546.
(27) Peters, E. C.; Petro, M.; Svec, F.; Fréchet, J. M. *Anal. Chem.* **1998**, *70*, 2296.
(28) Guo, Y.; Colón, L. A. *Anal. Chem.* **1995**, *67*, 2511.
(29) Guo, Y.; Colón, L. A. *J. Microcolumn Sep.* **1995**, *7*, 485.
(30) Wang, R.-X.; Chong, S.-L.; Malik, A. *Anal. Chem.* **1997**, *69*, 3889.
(31) Brinker, C. J.; Scherer, R. W.; *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Aacademic Press: New York, 1990; Chapter 1.
(32) Bandini, G. E.; Grattan, K. T. V., Tseung, A. C. C. *Analyst* **1995**, *120*, 1025.
(33) Klein, L. *Sol−Gel Optics: Processing and Applications*; Kluwer Academic Publishers: Boston, 1994.

EXPERIMENTAL SECTION

Apparatus. All the CEC experiments were performed in a commercial capillary electrophoresis system (Beckman model 2000 P/ACE, Fullerton, CA) equipped with an UV detector set at 254 nm. The fused-silica capillary columns used in this study were purchased from Polymicro Technologies (Phoenix, AZ). Scanning electron microscopy (SEM) analyses were performed on a Hitachi S2500 scanning electron microscope.

Reagents. The 5- and 3-μm spherical ODS particles (porous, 120 Å pore size) were purchased from YMC Technologies (Burnt Hill, NC) and the 1-μm bare silica particles (nonporous) were purchased from Geltech, Inc. (Miami, FL). TEOS was purchased from Aldrich Chemicals (Milwaukee, WI) and used as received. Thiourea (T), benzyl alcohol (BA), toluene (To), naphthalene (N), phenanthrene (Ph), and pyrene (Py) were used as test compounds and were purchased from Aldrich Chemicals (Milwaukee, WI).

Stock solutions of the analytes were prepared in millimolar concentrations in the running buffer and degassed by sonication. Millipore water was used in the preparation of all samples and buffers. HPLC-grade acetonitrile was purchased from Aldrich Chemicals and used without further purification. The running buffer was made of 20% (v/v) 50 mM sodium phosphate buffer (pH 6.5) and 80% (v/v) acetonitrile.

Preparation of Sol−Gel-Filled Capillary Columns. The sol−gel glasses were prepared from a mixture of 0.2 mL of TEOS, 0.73 mL of ethanol, and 0.10 mL of 0.12 M hydrochloric acid that was added to acidify the solution and prevent instantaneous solidification. ODS, either 5 or 3 μm in diameter, was added at a concentration of 300 mg/mL to the TEOS solution to create a suspension. Bare silica was added to the solution at a concentration of 4% (w/w) to improve and stabilize the electroosmotic flow.[6] This solution was sonicated for several minutes and then introduced into 75-μm-inner diameter (i.d.) capillary columns of ∼40-cm lengths by applying vacuum pressure across the column. The filled columns were then observed under a microscope (at magnifications of 100× and 400×) to ensure that a relatively equal distribution of ODS particles occurred throughout the column. The column was then coiled into a loop and placed onto a hot plate to heat above 373 K for ∼24 h to facilitate ethanol evaporation.

As the ethanol evaporated, the TEOS began polymerizing into a long rodlike monolithic structure. Once the column was dry, the structure was integrally fixed to the walls of the capillary and could not be pushed out with moderate pressures (200 psi). The sol−gel matrix also trapped the silica particles in place, which prevented particle migration.

After heating, the capillary column was again inspected under a microscope (at 100× and 400× magnifications) to ensure that a good sol−gel had formed in the column as well as to ensure even coverage of ODS throughout the column and not just at the column walls. The column was then preconditioned (by pressurizing the column inlet to ∼200 psi with a syringe pressurized with a hand-held vise) with running buffer that had been degassed by sonication. Once droplets could be seen migrating at the outlet end of the capillary column, indicating that liquid could actually flow throughout the entire column, it was carefully removed from the vise. A window was created on each column by using a thermal wire stripper to burn the polyimide coating and expose

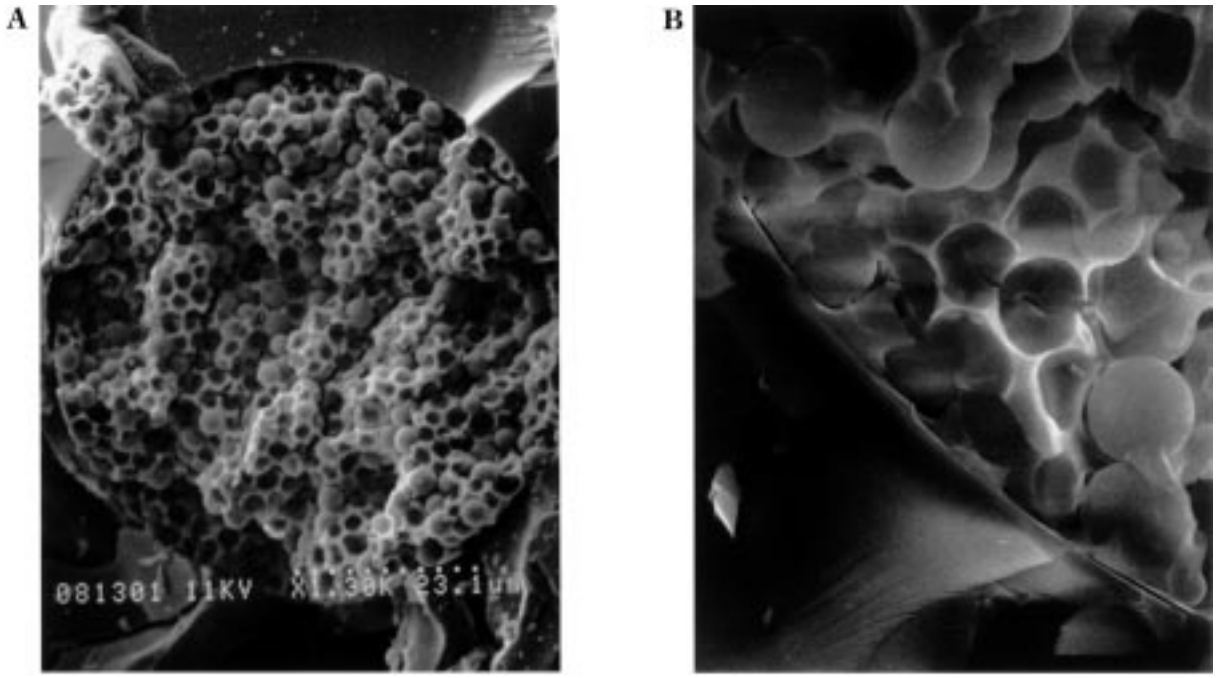

Figure 1. Scanning electron micrographs of a sol−gel/ODS- (3 μm) filled capillary column with an inner diameter of 75 μm (cross-sectional view) at (A) 1300× and (B) 4900× magnification. During the preparation of the capillary for scanning electron microscopy, ODS particles were dislodged from the sol−gel matrix, which causes the appearance in the electron micrographs of some empty cavities where these particles had been imbedded.

the glass. It was important that there be no ODS particles in the window, which was achieved by filling only 15−20 cm of the capillary column with the TEOS/ODS slurry solution. Next, the column was further conditioned electrokinetically in the CE instrument by driving the buffer mobile phase through the capillary at an applied voltage of 5 kV until a stable baseline was achieved, typically for 2−3 h. This equilibration time may correspond to a period for the alteration of the nature of the stationary phase by the application of a voltage (i.e., the saturation or release of adsorptive species from the surface of the particles). This behavior is consistent with observations previously made by Tsuda.[34] We found that, for capillary columns containing only the sol−gel matrix, preconditioning of the columns through pressure rinsing (85 psi) with the buffer for 1 min was required to achieve a stable baseline.

Capillary Electrochromatographic Separations. The test mixture was injected into the packed capillary columns electrokinetically at a temperature of 293 K. The applied voltage for each separation was variable, and the analytes were observed by monitoring their absorbance at 254 nm.

SEM Analyses. Short lengths of both sol−gel- and sol−gel/ODS-filled capillary columns were sectioned and vapor-deposited with gold for SEM analyses at 15 keV with a working distance of 15 mm.

RESULTS AND DISCUSSION

Sol−Gel-Filled Capillary Columns. As shown in the micrograph in Figure 1A, the sol−gel matrix is formed throughout the entire width of the capillary. Both Panels A and B provide physical information on the nature of the sol−gel matrix that forms in the presence of chromatographic particles. The micrographs show the "trapping" of the ODS particles within the sol−gel matrix. The micrograph shown in Figure 1B, which is an enlargement of a portion of Figure 1A, clearly shows a fracture in the sol−gel matrix surrounding the ODS particles. This cracking phenomenon has been attributed to pressure distribution (produced by modest drying rates) in the pores of the sol−gel matrix.[35] The sol−gel is more likely to fracture or crack as the pressure distribution becomes steeper. In contrast, less fractures are observed in the sol−gel matrix when ODS particles are imbedded within the matrix because the pressure gradients are smaller than in a capillary containing only the sol−gel matrix. It appears that the addition of ODS particles helps to reduce the cracking on the sol−gel matrix by decreasing the stress within the matrix. Chemical additives, such as surfactants, have been found to reduce cracking.[36,37] It has been reported that shrinkage of the sol−gel matrix by the addition of surfactants to the pore liquid will have a beneficial effect on the gel permeability, which contributes to the reduction of the stress in the matrix during the drying process.[37,38] Studies of particulate gels made from fumed silica demonstrated that large particles of Aerosil OX-50 (particle size ∼50 nm) allows drying without cracks.[39] Additionally, sol−gels prepared from a mixture of TEOS and Aerosil OX-50 resulted in gels with larger pores, and the gels could be dried

(34) Tsuda, T. *Anal. Chem.* **1987**, *59*, 521.

(35) Brinker, C. J.; Scherer, R. W.; *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing;* Aacademic Press: New York, 1990; p 478.
(36) Simpkins, P. G.; Johnson, D. W.; Fleming, D. A. *J. Am. Ceram. Soc.* **1989**, *72*, 1816.
(37) Zarzycki, J.; Prassas, M.; Phalippou, J. *J. Mater. Sci.* **1982**, *17*, 3371.
(38) Kingery, W. D.; Francl, J. *J. Am. Ceram. Soc.* **1954**, *37*, 596.
(39) Scherer, G. W.; Luong, J. C. *J. Non-Cryst. Solids* **1984**, *63*, 163.

much faster than gels not containing the particles.[40] Larger pores produce lower capillary pressure within the matrix because of the high permeability of the gel, thus preventing cracking of the matrix. An added benefit of the presence of particles in the sol−gel matrix is the contribution of the particles to the strength of the gel.[41] We conducted no studies, however, to address any degradation of the sol−gel/ODS phase over time. The SEM analyses further demonstrate that our packing method produces capillary columns that are completely filled with the sol−gel/ODS matrix (Figure 1A); i.e., the sol−gel matrix is not merely cast along the capillary wall.

Because the sol−gel packing method involves the use of a suspension of ODS particles; each column exhibited slightly different characteristics, such as retention time and efficiency. A good suspension of ODS in the sol−gel mixture is essential in the preparation of a capillary column with homogeneous distribution of the stationary phase within the capillary column. By varying the ODS concentration in the sol−gel mixture, an optimal concentration of 300 mg of ODS for each milliliter of TEOS solution results in sol−gel/ODS-filled capillary columns with good retentivity and selectivity. At lower concentrations of ODS (<200 mg/mL), the selectivity of the capillary column was poor. Baseline separation of thiourea, benzyl alcohol, and toluene was not achieved with capillaries prepared with low ODS concentrations. Capillary columns that were prepared with higher ODS concentrations (>350 mg/mL) resulted in significant inhomogeneity of the ODS packing density in the capillary (i.e., there were numerous sections of the capillary column that did not contain any ODS particles). This condition also resulted in poor selectivity for the components of our probe mixture. The use of vacuum pressure to fill small-bore capillary columns with the TEOS/ODS slurry suspension has greatly improved our column preparation over our earlier syringe-filling method. Efficiency, however, did increase as the particle size decreased, because the smaller particles allow for accelerated mass transport within the capillary.[42−44]

"Drying out" of the sol−gel/ODS-filled capillary columns appears to be less of a problem after column conditioning than what we have observed with columns that are packed by slurry or electrokinetic methods.[6] Drying out of the capillary column is brought about by formation of bubbles within the capillary and results in portions of the stationary phase not being in contact with the mobile phase. The charged nature of the sol−gel matrix may increase the pumping power of the column by increasing the electroosmotic flow.

One marked advantage of the sol−gel packing method is that frit fabrication is not required. Instead, the sol−gel monolith appeared to display uniform properties throughout the column and behaved quite similarly to the glass of the fused-silica column, thus not interfering with the detection of the analytes. Thus, our fabrication procedure avoids one problem of all packed capillary columns.

Column Performance. To demonstrate the performance of our sol−gel/ODS-filled capillary columns, we evaluated a mixture of uncharged organic compounds. Two different capillaries (Table 1) were prepared and tested under similar experimental conditions. The average k' values for all the test compounds are listed in Table 1 for the two capillary columns tested. The relative standard deviations (RSD) of k' and R_S in column 1 were better than 3% and 5%, respectively. In contrast, the RSD of k' and R_S for all compounds separated in column 2 were better than 2% and 15%. As predicted by theory,[45] when the capacity factor increases, the plate height (H) also increases under the same separation conditions. The differences observed between column 1 and column 2 markedly depend on the size of the particles that can be packed in the capillary column.[5,46]

Table 1. Performance of Two Different Packed Capillary Columns[a]

analyte	k'	N/m	R_S
	Column 1[b]		
thiourea (T)[c]		79 500	
benzyl alcohol (BA)	0.086	79 400	2.2 (BA/T)
toluene (To)	0.150	69 500	1.4 (To/BA)
naphthalene (N)	0.401	80 400	5.9 (N/To)
phenanthrene (Ph)	0.693	76 700	5.4 (Ph/N)
pyrene (Py)	1.050	72 000	5.4 (Py/Ph)
	Column 2[d]		
thiourea		41 900	
naphthalene	0.150	32 800	2.62 (N/T)
phenanthrene	0.263	27 500	1.82 (Ph/N)
pyrene	0.396	21 000	1.71 (Py/Ph)

[a] Results for each column is based on at least three separate runs. [b] Thiourea was used as an "unretained" marker. [c] 27-cm × 75-μm i.d. (~15-cm section packed with 3-μm ODS particles); mobile phase, acetonitrile/50 mM phosphate buffer (pH 6.5) (80:20, v/v). [d] 27-cm × 75-μm i.d. (~20-cm section packed with 5-μm ODS particles); mobile phase, acetonitrile/50 mM phosphate buffer (pH 6.5) (80:20, v/v).

Figure 2 demonstrates the separation of the probe mixture by CEC using these columns that were prepared by the sol−gel packing method. These compounds were also analyzed in columns containing only the sol−gel matrix; no separation of these compounds was achieved in these columns in the absence of chromatographic particles. In comparison, the sol−gel columns containing the ODS stationary phase offer good separation characteristics (see Table 1), such as capacity factors (k'), resolution (R_S), and theoretical plate counts (N/m), over columns containing only the sol−gel matrix. A decrease in the stationary-phase particle size resulted in improved separation characteristics. For example, efficiencies of greater than 80 000 plates/m (RSD = 5.8%) for naphthalene were observed when the ODS particle size was 3 μm (column 1) as compared to less than 33 000 plates/m (RSD = 5.6−8.1%) for columns with ODS particles of 5 μm in diameter (column 2). These modest column efficiencies may be attributed to two factors. First, there may be inhomogeneous packing of the ODS chromatographic phase within the capillary column. Second, some of the ODS particles may be "shielded" from the analytes because the particles are too deeply imbedded within the sol−gel network to play a role in the separation mechanism. (Refinements are being made to our packing method to ensure greater homogeneous packing.) The

(40) Toki, M.; Miyashita, S.; Takeuchi, T.; Kanbe, S.; Kochi, A. *J. Non-Cryst. Solids* **1988**, *100*, 479.
(41) Zarzycki, J. *J. Non-Cryst. Solids* **1988**, *100*, 359.
(42) Knox, J. H.; Grant, I. H. *Chromatographia* **1987**, *24*, 135.
(43) Smith, N. W.; Evans, M. B. *Chromatographia* **1994**, *38*, 649.
(44) Karger, B. L. In *Modern Practice of Liquid Chromatography*; Kirkland, J. J., Ed.; Wiley-Interscience: New York, 1971; Chapter 1.
(45) Snyder, L. R.; Kirkland, J. J.; Glajch, J. L. *Practical HPLC Method Development*; John Wiley & Sons: New York, 1997; pp 27−31.
(46) Colón, L.; Guo, Y.; Fermier, A. *Anal. Chem.* **1997**, *15*, 4461A.

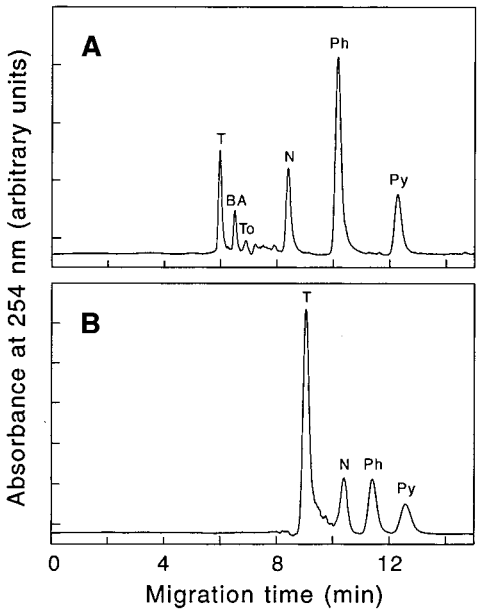

Figure 2. Separation of a test mixture containing six different uncharged organic analytes by capillary electrochromatography in two different capillaries. (A) Column 1: sol−gel-filled capillary with 3-μm ODS particles immobilized, 27-cm × 75-μm i.d., effective length of 15 cm; 10-kV applied voltage; 1-s injection at 3 kV. (B) Column 2: sol−gel-filled capillary with 5-μm ODS particles immobilized, 27-cm × 75-μm i.d., effective length of 20 cm; 5-kV applied voltage; 1-s injection at 3 kV. Running buffer of 20% 50 mM phosphate buffer (pH 6.5) and 80% acetonitrile (v/v) was used for each capillary. The analytes were detected at 254 nm. Key: T, thiourea; BA, benzyl alcohol; To, toluene; N, naphthalene; Ph, phenanthrene; Py, pyrene.

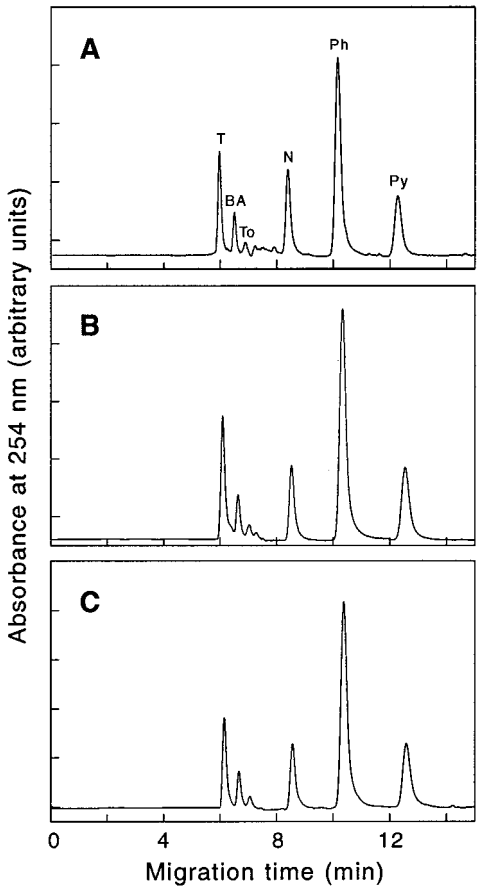

Figure 3. Typical daily electrochromatograms obtained using column 1: (A) day 1, (B) day 2, and (C) day 3. Running conditions are similar to Figure 2A. Key: T, thiourea; BA, benzyl alcohol; To, toluene; N, naphthalene; Ph, phenanthrene; Py, pyrene.

relative standard deviations for capacity factor and resolution for naphthalene in column 1 were 1.7% and 4.4%, respectively. The increase in the capacity factors of all the test compounds with a decrease in the ODS particle diameter indicates an increase in the amount of C_{18} phase per unit volume of the capillary column. For column 2, poor resolution was observed for thiourea, benzyl alcohol, and toluene, even under conditions of higher organic content in the running buffer.

Figure 3 illustrates the reproducibility of the separation of the analyte mixture using a single capillary column containing immobilized 3-μm ODS particles. All six of the test compounds were baseline separated. To determine the lifetime of the sol−gel matrix within the capillary column, we ran multiple samples of thiourea over a period of 2 months (~6 h/day) on a capillary column filled with only the sol−gel matrix. During this period, the sol−gel-filled capillary column gave consistent migration time and efficiency for thiourea. Capillary columns containing ODS particles imbedded within the sol−gel matrix were used only for a few days after preconditioning the columns. During this period, the columns showed consistent retentivity and selectivity for the probe mixture.

Future improvements in capillary column preparation are anticipated. Even so, the results obtained for a test mixture of uncharged organic compounds show the potential of sol−gel/ODS-filled capillary columns for resolving mixtures of related compounds present at millimolar concentrations. Furthermore, the presence of a sol−gel matrix in a capillary column as a supporting structure for chromatographic particles has led to the elimination of retaining frits in CEC columns. We have demonstrated that these packed capillary columns can be easily integrated into a fully automated commercial CZE instrument. The use of sol−gel columns in which chromatographic particles are embedded opens the possibility of utilizing the known power of HPLC separation in a capillary format.

ACKNOWLEDGMENT

We thank Kyle Baughman for the SEM data and Michael P. Henry and Chitra Ratnayake of Beckman-Coulter, Inc. for helpful discussions. Financial support provided by Beckman-Coulter, Inc. is gratefully acknowledged.

Received for review June 12, 1998. Accepted September 14, 1998.

AC9806456