Polyimide Polymer Glass-Free Capillary Columns for Gas Chromatography

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Abstract

Polymeric polyimide capillary tubing, both uncoated and coated with stationary phases of two polarities, is explored for use as capillary columns for gas chromatography (GC). These glass-free polyimide columns are flexible and their small winding diameter of less than a cm around a solid support makes them compatible for potential use in portable GC instruments. Polyimide columns with dimensions of 0.32 mm i.d. × 3 m are cleaned, annealed at 300°C, and coated using the static method with phenylmethylsilicone (PMS). Separations of volatile organics are investigated isothermally on duplicate sets of polyimide columns by GC with a flame ionization detector using split injection. Unlike the uncoated ones, the coated polyimide columns successfully separate Grob test mix classes of alkanes, amines, and fatty acid methyl esters. The relative standard deviations for retention time and peak area are 0.5% and 2.5%, respectively. With the 3 m PMS-coated column connected to a retention gap to permit operation at its optimum flow rate of 30 cm/s, a plate count of 3200 or plate height of 1 mm is possible. Lack of retention and tailing peaks are evident for the polyimide polymer capillary columns as compared to that of a 3 m commercial cross-linked PMS fused silica capillary. However, headspace analyses of an aromatic hydrocarbon mix and a Clearcoat automotive paint sample are viable applications on the PMS polyimide polymer column.

Introduction

The open-tubular GC capillary column consists of a fused-silica glass capillary core covered with a protective outer layer of polyimide polymer. This polyimide coating is responsible for the flexibility of the column and any compromise of the integrity of the coating can lead to column breakage (1). Temperature control is a critical factor in chromatographic analyses, and it must be reproducible from run to run to achieve quantitative results. These factors combine to make the oven of the typical lab-based instrument quite large. The standard winding diameter for most commercial GC capillary columns is about 25–30 cm. Bending stress of polyimide coated fused silica capillaries increases with their outer diameter (o.d.) and is commercially tested to 100 kPsi (2). This pressure limit occurs for GC capillaries of 0.3–0.8 mm o.d. in the range of 2.5–5 cm bend radius. Narrow bore 0.1–0.2 mm inner diameter (i.d.) GC capillary columns can be wound to about 5–6 cm in diameter to accommodate small ovens. Fused silica coated stainless steel columns can be fabricated to tighter dimensions for a particular instrument design (3).

Glass-free polyimide capillary tubing of very high purity and with a variety of inner diameter values is manufactured from Kapton (pyromellic acid anhydride-4,4'-diaminodiphenylether or PMDA-ODA) polyimide (4) for use by medical device manufacturers. The polyimide capillaries are manufactured with i.d. values < 0.5 mm with tolerances of ± .005 mm of nominal i.d., similar to tolerances for fused-silica capillary (1,2), and are available in lengths up to 3 m (5). The flexibility of the polyimide capillary allows it to be wound into a coil with a diameter of a cm or less, when held in place around a rigid rod.

The surface of the PMDA-ODA polyimide polymer has been extensively researched because of its ubiquity in the electronics industry. A characterization of the surface performed by ultraviolet photoemission spectroscopy (UPS) determined that the surface chemical bonds are dominated by the C π bonds associated with the aromatic rings, and the 2p non-bonding orbitals of the N and O lone pairs (6). This study also determined that the intrinsic polyimide surface could not be revealed by UPS until after water, which was entrained at the surface during polymerization, was removed by annealing the polyimide above 250°C.

Another study characterized the components of surface tension measured on a variety of polyimides using contact angle measurements (7). For polyimides with ether linkages, such as PMDA-ODA, the polar component of surface tension was much less than the other polyimides tested, and the dispersive component was much larger. The surface was characterized as hydrophobic and dispersive, or less polar, when compared to polyimides where no ether linkages were present. The contact angles measured for polar liquids such as water and glycerol were still below 90°, indicating that the surface was wetted by the liquids. The dispersive nature of the surface can be explained by the high level of conjugation of the bonds in the PMDA-ODA polyimide. This is one of the reasons that the PMDA-ODA polyimide demonstrates a desirable low dielectric constant and is relatively impervious to chemical attack (8).

Research has been published indicating that a variety of GC stationary phases were successfully wetted on the surface of PMDA-ODA polyimide films. Glass capillary columns, 20 m × 0.5 mm i.d., with polyimide deposited on the inside surface were

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coated with GC stationary phases such as methylsilicone and polyethylene glycol and used to separate various mixtures such as hydrocarbons and aliphatic alcohols (9). Based on the previously described surface studies and the glass capillary GC study, it is hypothesized that polymeric polyimide capillary columns should be able to be coated with GC stationary phases and be able to perform separations. To the best of our knowledge, the use of totally polymeric polyimide capillary columns for GC has not been reported. Our long term goal is to use such columns for a low cost portable gas chromatograph that we have envisioned using pumped air as the carrier gas, a septum based injector, and a photoionization detector.

This research project involved the pre-treatment, stationary phase coating, and GC characterization of totally polymeric polyimide capillary columns of the dimensions 0.32-mm i.d. × 3 m. Although longer columns are not available, a variety of GC column compatible i.d.s (0.1–0.5 mm) can be selected. After cleaning and annealing at 300°C, the polyimide columns were then coated using the static method with one of two phenylmethylsilicone (PMS) stationary phases: 50%-PMS or 5%-PMS. Film thickness was measured by scanning electron microscopy (SEM). Uncoated, polymeric polyimide columns were also prepared and tested as GC columns. Different test mix types representing Grob components such as aromatics with a variety of polarity and acid/base character as well as fatty acid methyl esters (FAMEs) were used as chromatographic probes on the polyimide columns. The sample mass load limit of the 50%-PMS column was assessed before column reproducibility and van Deemter studies were performed. Typical workplace samples such as a benzene, toluene, ethylbenzene, and xylenes (BTEX) mix and a clearcoat automotive paint sample were analyzed by static headspace.

Experimental

Chemicals and materials

The stationary phases, 5%-PMS, (SE-54) and 50%-PMS, (OV-17), were purchased from Sigma-Aldrich, St. Louis, MO. The individual Grob test components and various solvents were purchased from Fisher Scientific (Chicago, IL) and from Sigma-Aldrich. The Grob standards (63 ppm of each component in the mixture) were made using carbon tetrachloride as the solvent for the alkanes (*n*-decane, undecane) and methylene chloride for the aldehyde (nonanal), amines (2,6-dimethylaniline, dicyclohexylamine), and FAMEs (methyl decanoate, methyl undecanoate, and methyl dodecanoate). A BTEX standard solution was prepared from equal volume neat solvents using Acros Organics (at least 99% purity) benzene, ethylbenzene, and *o*-, *m*-, *p*-xylenes; the toluene used was Fisher brand (ACS reagent grade). A Sherwin-Williams Dupli-Color Lacquer Clear Topcoat Paint sample (NGSF125) was bought from Auto Zone.

The capillary column washer used to clean and coat the polyimide columns, as well as the digital flow check meter, were purchased from Alltech Associates. Standard column nuts and graphite ferrules, purchased from a variety of suppliers, were used as column installation supplies for the polyimide columns. A column hanger was fabricated from a standard hanger to accommodate the polyimide column in a coil of about a 6-cm diameter.

The polyimide columns used for the development of cleaning and bleed testing procedures were purchased in dimensions of 0.32 mm i.d. × 0.76 m in length (L) from Small Parts, Inc. (Miami Lakes, FL). Polyimide columns in dimensions of 0.32 mm i.d. × 3 m L, with o.d. ranging from 0.35–0.39 mm, were purchased from MicroLumen, Inc., (Tampa, FL) and from RiverTech Medical (Chattanooga, TN). Per discussions with both of these companies, which are manufacturers of the polyimide capillaries, 3 meters is the longest practical length of capillary polyimide tubing currently available.

The uncoated fused-silica retention gap in dimensions of 0.25 mm i.d. × 10 m L, deactivated for intermediate polarity solvents, was purchased from Restek (Bellefonte, PA). For comparison to the polyimide polymer column, a 3 m section was cut from a J&W Scientific (Agilent Technologies, Santa Clara, CA) fused silica column of dimensions 0.32-mm i.d. × 30-m L, coated with 1 µm of 5%-PMS, (DB-5), bonded and cross-linked by a proprietary process.

Instrumentation

A Hewlett-Packard (HP) 5890 Series II gas chromatograph equipped with an HP 7673 autosampler and an Agilent 3396 Series III integrator was used for all analyses. The helium carrier gas flow on this instrument was controlled by column head pressure. The lowest practical setting for column head pressure, 2 psi, was used for all analyses unless otherwise noted. Column flow on the 3-m polyimide columns averaged 8–10 mL/min as measured by the digital flow meter, with linear flow rates between 70–100 cm/s. All test mixture separations were performed isothermally with temperatures indicated in the figure legends. Unless otherwise noted, GC instrument parameters were: injector and the flame ionization detector temperatures, 250°C; attenuation, 2; and range, 3. Integrator attenuation was set as required to bring analyte peaks onto scale. The Agilent injection split liner (PN 19251-60540) was made of deactivated glass, with glass wool packing. The auto-sampler injection volume was 1 µL, and analyses were performed in split mode, with the split ratio approximately 35:1, unless otherwise noted. Using the auto-sampler, the injection size for headspace injection of the BTEX and paint samples was 5 µL. A Hewlett-Packard GCD instrument with a 30-m × 0.25-mm i.d., 0.25 µm film thickness column with a cross-linked HP-5MS (5%-phenyl) stationary phase permitted mass spectrometry identification of the peaks in the BTEX and the clearcoat automotive paint chromatograms.

Column cleaning and annealing

After trial runs with the shorter (0.76 m L) polyimide columns, a column cleaning and preparation sequence was developed and applied to all of the 3-m polyimide columns used for GC separations. The columns were washed with a series of solvents of increasing polarity: hexane, 2-propanol, and methanol. The Alltech column washer was connected to a helium carrier gas source, and pressure was controlled by a regulator. The top of the column washer was fitted with a 0.5-mm i.d. ferrule so that the column could pass through the top. The

column was hand-held with one end immersed in the solvent contained in the column washer tube. Pressure was applied above the solvent with He gas, pushing liquid through the column. The column washer was later used in a similar manner to coat the columns with stationary phase, followed by quiescent vacuum drying.

During the cleaning step, the 3-m columns were washed for several minutes with each solvent at a gas pressure of < 5 psi. The columns were dried for several minutes with a helium purge before being individually wound into glass crystallizing dishes and baked in a lab oven at 265°C for 60 min.

Column annealing tests were performed on each of the polyimide columns prior to coating with stationary phase or use as polymeric GC columns. The purpose of the tests was to determine polymer stability at separation temperatures near the upper limit of the stationary phases planned for use in this study, which was approximately 350°C. A temperature ramp program was run: initial temperature (T), 30°C; ramp rate, 5°C/min; final T, 300°C; hold time (at 300°C), 10 min. Plots of consecutive runs are shown in Figure 1.

Column coating and conditioning

The static method for column coating was used to coat the stationary phases on the inner surface of the cleaned and annealed polyimide columns (10). Actual stationary phase thickness was measured by scanning electron microscopy (SEM) after the columns had been coated, conditioned, and used in separations. SEM scans of both a coated and an uncoated polyimide column are shown in Figure 2 along with an SEM scan of a commercial fused-silica capillary column with a cross-linked and bonded 5%-PMS (DB-5) stationary phase. The concentrations of the solutions for stationary phase coating were calculated two ways. One method was to calculate the volume of the empty capillary tube ($\pi r^2 L$) as V_1. The volume of the capillary inside the coating, V_2, was then calculated using $(r - d_f)$ as the radius corrected for the coating thickness. The volume of the coating, V_3, is $(V_1 - V_2)$. The volume percent of the coating in solution is then (V_3/V_1). These calculations were verified using the equation $d_f = r/(2\beta) = dc/400$ where r is the radius of the capillary, β is the phase ratio, d is the capillary diameter (in µm) and c is the concentration of the stationary phase in volume percent. To make the stationary phase solution accurately, the density of the stationary phase must be known and taken into account (10). Methylene chloride was the solvent for the 50%-PMS, and toluene was the solvent for the 5%-PMS.

The column washer was used to force the stationary phase through the capillary. After allowing the solution to flow for several minutes to assure that the column had time to be wetted completely and to avoid entrained bubbles, the column was completely filled with the solution and one end was capped. The other

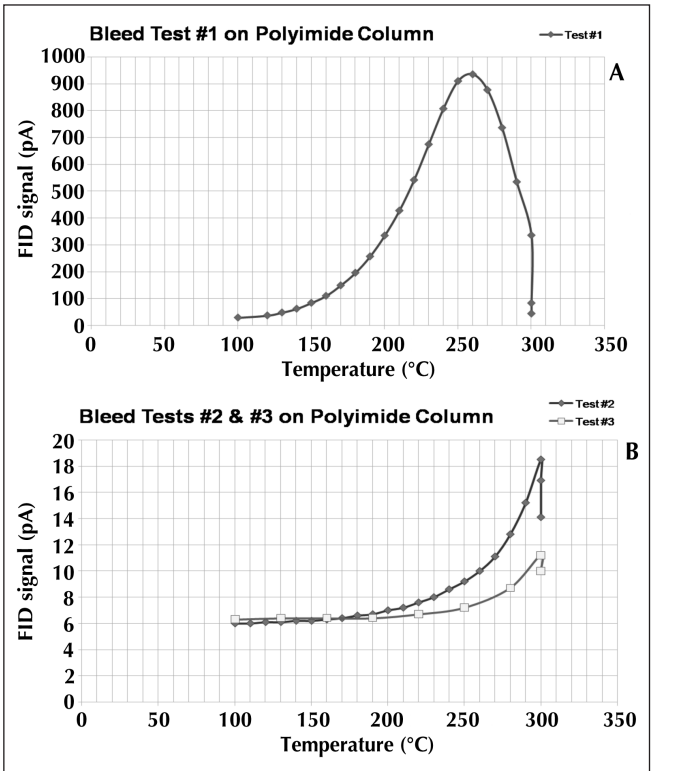

Figure 1. (A) Initial bleed test results on an uncoated polymeric polyimide column and (B) results of additional bleed tests on an uncoated polymeric polyimide column.

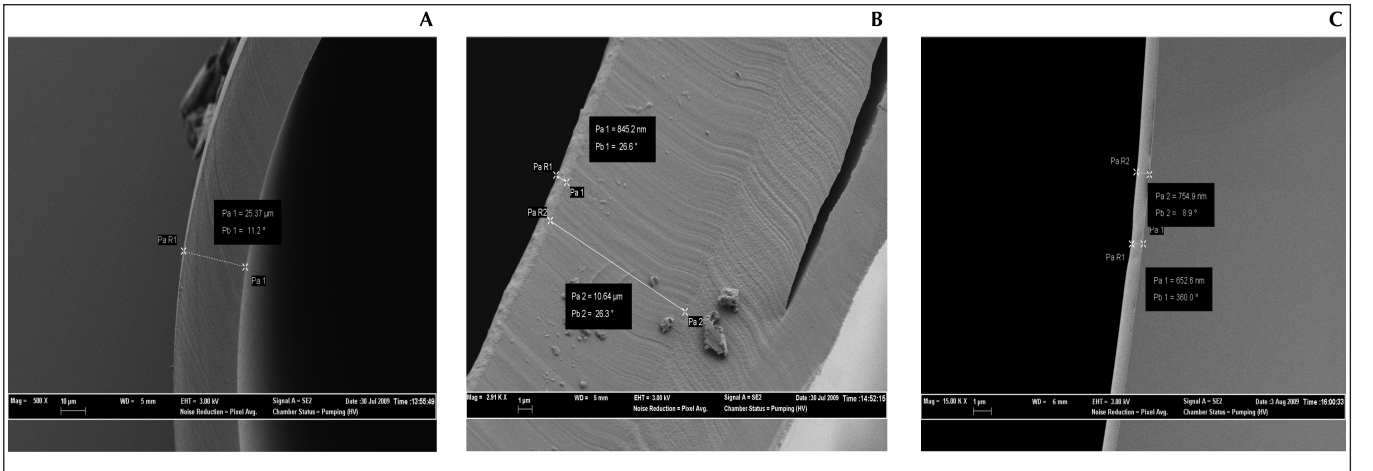

Figure 2. SEM Scans on capillary column cross sections: (A) Smooth inner surface of an uncoated polyimide column (10 micron scale); (B) Coating thickness of 50%-PMS on a polyimide column between Pa1 and PaR1 (thin layer next to black background, 1 micron scale); (C) Coating thickness of cross-linked and bonded DB-5 fused-silica column measured between Pa1 and Pb1 and Pa2 and Pb2 (1 micron scale).

end was installed in an open, ferruled Swagelok fitting and was attached to the vacuum drying apparatus. The round-bottom flask was evacuated to 25-in Hg several times. Finally, the column was opened to the vacuum and allowed to dry quiescently for several days.

The coated column was trimmed on both ends and was installed into the GC on the injector side to facilitate column conditioning. The unattached end of the column was immobilized on the floor of the GC oven. Carrier gas flow through the column was confirmed by bubbling it into a small beaker of methanol.

A conditioning program was run as follows: initial temperature, T, 30°C; ramp rate, 5°C/min; final T, 100°C; hold time, 120 min. The purpose of this procedure was to allow the column to completely dry without sending any evolved solvent through the detector. The column was then installed into the detector side of the instrument, and a high temperature conditioning program was run as follows: initial T, 40°C; ramp rate, 20°C/min; final T, 200°C; hold time, 15 min. This high temperature conditioning step was performed well above the operating temperature of the columns (100°C, typically) and well below the temperature limit of the stationary phases (about 350°C). FID signals ranged from about 4000–8000 pA at 200°C and then stabilized at around 5–6 pA at 40°C.

The columns were conditioned before daily use by raising the oven temperature to 130°C with a hold time of 30 min. The uncoated polyimide columns were cleaned, baked out, annealed, and conditioned in the same manner.

Chromatographic approach and calculations

The polyimide columns were robust enough to be installed in the GC oven with careful tightening using standard ferrules and column nuts. The columns were taken in and out of the instrument on several occasions and, after running the normal conditioning program, were found to perform reproducibly with previous determinations.

Grob test mix components were injected by class (alkanes, aldehyde, amines, and FAMEs) on both uncoated and coated columns. Two sets of polyimide columns were prepared and tested. These columns were from two different manufacturers and were prepared many months apart for a good test of the reproducibility of the process as well as the columns. Other samples such as BTEX and the clearcoat automotive paint sample, as well as the FAMEs mixture, were also separated using the retention gap and 5%-PMS column combination. The 3 m section of the commercial DB-5 fused-silica capillary column was coiled on a standard wire hanger, secured with heat-proof string, and installed into the GC. The column was conditioned with the daily conditioning program described above before use to separate Grob text mixtures.

The following parameters were calculated for each chromatogram if appropriate: the retention factor, k, the selectivity factor, α, the column plate number, N, calculated using the retention time corrected for the unretained component ($t'_R = t_R - t_0$), peak width at half height (w_h), the plate height, H, and resolution, R_S. Peak asymmetry was assessed at $w_{0.10}$, the peak width at 10% of peak height. This value for the peak width is used when the tailing factor, TF, of the peak is measured as TF = b/a where a is the peak width on the left side of a line drawn from the apex of the peak to the $w_{0.10}$ baseline, and b is the width to the right of the line (11).

Column reproducibility and mass load studies

A series of five sequential injections and separations was performed on a polyimide column coated with 5%-PMS. A standard containing 32 ppm each of the three FAME probes, methyl decanoate, methyl undecanoate, and methyl dodecanoate, was analyzed isothermally at 60°C. The split ratio was 35:1. The mean and standard deviations of the retention times and the peak areas were calculated.

A series of standards from a 680 mg/10 mL stock solution was prepared with n-undecane in a range from 0.15–2.0 µg mass injected in a 1 µL injection and then split at a ratio of 34:1. Additional standards were made with 1.0215 g/10 m and 0.8505 g/10 mL solutions to expand the range to 3.0 µg injected into the column. The standards were determined in random order on a 5%–PMS coated polyimide column. The plate number N was plotted versus sample mass load.

van Deemter study

The HP 5890 Series II GC used for this research project controlled column flow by column head pressure. Due to the short length of the column, flow rates could not be reduced to values low enough to perform the van Deemter study. To accomplish a reduced flow to the 5%-PMS polyimide column used in the study, it was connected with a zero dead volume connector on the injection side to an uncoated, deactivated fused-silica retention gap with dimensions of 0.25 mm i.d. × 10 m L. The retention gap was installed on the injection side of the GC, and the polyimide column was installed on the detector side. A 20-cm wire hanger was placed in the oven in front of the polyimide column hanger, and the retention gap was coiled around it and secured to it with heat-proof string. A 50 ppm standard of n-undecane was used in the study. Column head pressures ranging from 2–20 psi were used, with u values measured from 14–82 cm/s.

A program called FlowCalc 2.05 was downloaded from the Agilent Technologies web site (12). This program allows the analyst to enter various column dimensions, column flows or column head pressures and calculate the effect on the other parameters. This program was used to estimate the mobile phase linear velocities, u, and holdup times, t_M, for an unretained species on the 13 m combined column used in the van Deemter study. The FlowCalc values for flow rates and u have been compared in the text.

Results and Discussion

Column annealing tests

Commercial polyimide polymer (Kaptan) is used in flexible heating elements (13) and therefore temperature stability compatible to GC use was expected. A previously published study had focused on how to improve the durability of the polyimide outer coating of fused-silica capillary electrophoresis (CE) columns. It was determined that annealing the columns in a GC oven at 300°C for 240 h (not optimized) greatly improved the chemical

resistance of polyimide to common CE solvents. This improvement was documented in the study with SEM photographs (14). This temperature of 300°C was also chosen for the following annealing studies.

The column cleaning and annealing procedures were performed on polyimide columns of different lengths from three vendors. The results were consistent on all of the columns. A plot of the first temperature test performed on a short polyimide column is shown in Figure 1A. The FID signal increased from 14 pA at 40°C to over 900 pA at 260°C, then fell to 34 pA after holding the temperature at 300°C for 10 min. The results of a second and third test on the same column are graphed in Figure 1B. In the second test, the signal started at 5.4 pA, an acceptable baseline signal, and only increased to 18.5 pA at 300°C before falling to 14.1 pA after being held at 300°C for 10 min. A third test demonstrated that the column did not produce a signal above 12 pA over the entire temperature range of the test.

The column temperature tests performed for this study demonstrated that the polyimide annealed at about 265°C and, after annealing, did not contribute significantly to the FID signal in subsequent tests. The annealing process may involve the evolution of water molecules, which had been entrained near the polyimide surface during polymerization, as well as polymer outgassing.

Column coating and conditioning

The 50%-PMS (OV-17 in methylene chloride) flowed through the columns readily, and all solvent appeared to have dried under vacuum when the columns were conditioned after coating. The 5%-PMS (SE-54 in toluene) was more viscous than the 50%-PMS solution and required a higher gas pressure to push it through the capillary during coating. There was still solvent in both of the 5%-PMS columns when they were put into use, and they were dried with helium flow in the GC oven at ambient temperatures for about 30 min prior to conditioning.

The columns were first conditioned at the anticipated operating temperature, 100°C for 120 min, and then at a temperature exceeding analytical range, ramping from 40–200°C, with a final hold time 15 min. A daily conditioning program, 130°C held for 30 min, typically resulted in a signal of < 10 pA at 130°C, and a signal of < 6 pA after cooling back down to 30°C. These results were confirmed by the observation of a stable baseline in all chromatograms. Normal baseline signal for these columns was < 6 pA.

The actual coating thickness on both sets of the polyimide columns was measured by SEM. The thickness measurements ranged from 0.5–2 µm, with an observed mean value near 1 µm. The measurements may have varied within the observed range due to distortion caused by the cutting process, since the stationary phase is a viscous semi-liquid. Figure 2A is an SEM micrograph of an uncoated polyimide column. The regularity of the wall thickness and the smooth inner surface of the capillary can be observed. Figure 2B is an SEM micrograph of the 50%-PMS stationary phase coating as was seen around the entire surface of the polyimide capillary column in a smooth, continuous layer, and which appeared to be well-adhered to the polyimide surface. The presence of silicon in the observed stationary phase layer was confirmed by energy dispersive X-ray spectroscopy (EDS). EDS was performed to ensure that the layer observed in the SEM image was, in fact, the stationary phase layer on the inner diameter of the polyimide capillary. Figure 2C is an SEM scan of the cross-linked and bonded DB-5 coating on the fused-silica commercial column. This stationary phase appeared to be denser than the PMS phases coated on the polyimide columns, with a smooth, highly uniform surface. Coating thickness was determined to be near 0.8 µm.

The apparent loss of stationary phase coating thickness between the coating process and the SEM measurements on the polyimide columns may have occurred during the conditioning steps. Some of the stationary phase thickness may have been lost from the 5%-PMS columns when the excess solvent was dried with helium flowing through the columns.

Chromatography on the uncoated polyimide columns

The Grob test mix contains a diverse and instructive set of probes for observing and assessing the column – solute interactions in standard GC capillary columns (15), and these compounds were therefore chosen to characterize the polyimide columns. Since α is the ratio of the k values of a pair of eluting peaks, it should remain consistent from column to column with the same phase ratio, β, and the separation of the peaks can be

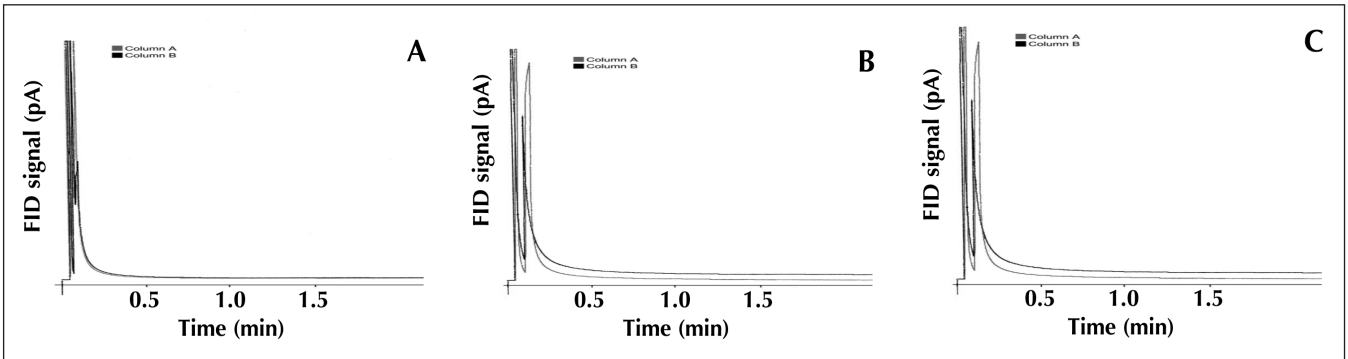

Figure 3. (A) Overlay of alkanes separation on uncoated polymeric polyimide columns. Probes: n-decane, n-undecane. Conditions: Isothermal 40°C. Flow rates: column a, 100 cm/s; column B, 94 cm/s.

(B) Overlay of aldehyde elution on uncoated polymeric polyimide columns. Probe: Nonanal. Conditions: Isothermal 40°C. Flow rates: column A, 102 cm/s; column B, 98 cm/s .

(C) Overlay of amines separation on uncoated polymeric polyimide columns. Probes: 2,6-dimethylaniline; dicyclohexylamine. Conditions: Isothermal 60°C. Flow rates: column A, 100 cm/s; column B, 94 cm/s .

considered to have a similar retention mechanism. All of the separations were performed on two different duplicate columns isothermally at temperatures determined experimentally to balance k, α, and resolution, R_S.

The uncoated polymeric polyimide columns demonstrated a minimal ability to separate and resolve most compound classes, as expected. Figure 3A shows a chromatogram of the alkanes, *n*-decane and *n*-undecane, run on two different uncoated columns. These neutral compounds lack a functional group and are retained primarily with dispersive forces. They were nearly unretained on the uncoated columns, with very low k values calculated at 0.5 and 1.0, respectively, although some resolution (0.8 and 1.3) did occur. Figure 3B shows the elution of the aldehyde, nonanal, on two different uncoated columns. This compound had a k value < 2 on the columns and the values of N, although very low at less than 100, were reasonably consistent. Since the polyimide structure is not considered to be conducive to dipole-dipole interactions, the retention is probably due to dispersive forces with the long hydrocarbon chain of the molecule.

Figure 3C shows the separation of the amines, 2,6-dimethylaniline (k = 1.2 and 1.4) and dicyclohexylamine (k = 3.2 and 3.9), on two different uncoated columns. The conformation of the peaks shown in the overlay was somewhat reproducible, and the values of α (2.7 and 2.9) were fairly consistent, with R_S (1.8 and 2.1) calculated above the baseline value of 1.5. The retention and separation of these compounds on the uncoated polyimide is surprising with N values between 100–200. Interaction between the *n*- and π-electrons of the polymer and those of the 2,6-dimethylaniline and with the *n*-electrons of the dicyclohexylamine, as well as dispersive effects, may explain the ability of the uncoated polyimide to retain the bases.

Chromatography on the coated polyimide columns

The sample mass load study, plotted in Figure 4, showed that the efficiency as plate number N of the coated 5%-PMS polyimide column was not degraded significantly until the sample mass load exceeded 1 µg. This broad mass load range is a benefit of using a medium-bore column with a relatively thick stationary phase of 1 µm. Considering a 1-µL injection and the average split ratio of 34:1, the sample mass injected in most of the determinations in the following chromatograms was below 100 ng, 2 ng for the Grob mix sample.

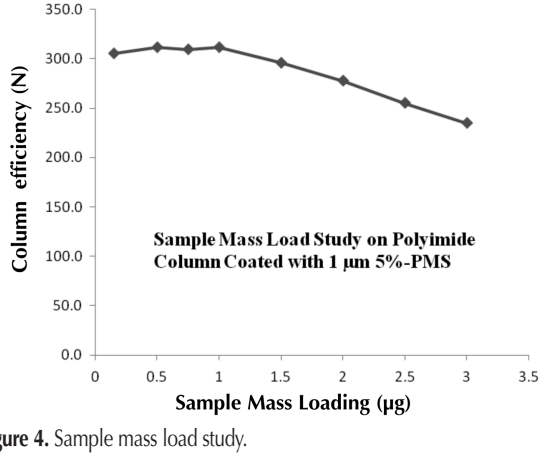

Figure 4. Sample mass load study.

Analogous mixtures to those in Figure 3 were injected on two different polyimide columns coated with 50%-PMS. Unlike for the uncoated polyimide columns, significant retention and separation of the analytes was noted. For the separation of *n*-decane and *n*-undecane (Figure 5A), quite symmetrical peaks were seen with w_h = 0.03 and 0.06 min, respectively. Retention on the columns was good, with k values of 3.4 and 4.6 for *n*-decane and 9.0 and 11.9 for *n*-undecane. The values for α of 2.6 and 2.7 were consistent between the columns, and the integrated peak areas for the alkanes were very close. Resolution was excellent on both columns, averaging above 5.0 and plate counts were in the 700–1100 range. Retention of nonanal (Figure 5B) was strong with k values of 21 and 29. The peaks were quite sharp (w_h = 0.14 min), with minimal tailing observed above the 10% point of the peak width, although some fronting was apparent in the peak

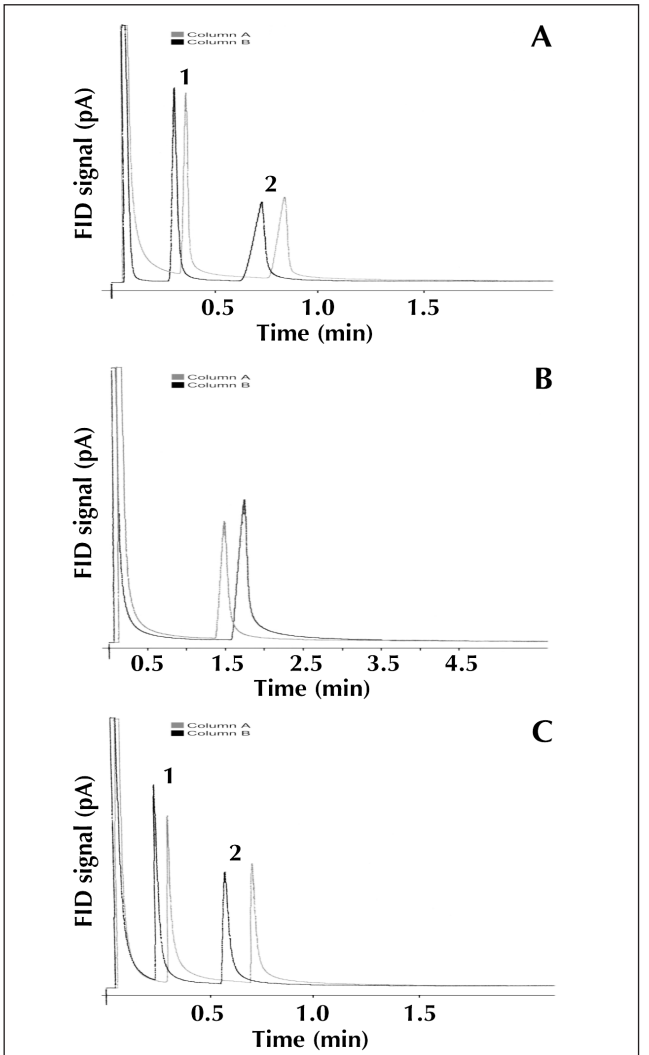

Figure 5. (A) Overlay of alkanes separation on 50%-PMS coated polyimide columns. Probes: *n*-decane, *n*-undecane. Conditions: Isothermal 40°C. Flow rates: column A, 77 cm/s; column B, 67 cm/s .

(B) Overlay of aldehyde elution on 50%-PMS coated polyimide columns. Probe: Nonanal. Conditions: Isothermal 40°C. Flow rates: column A, 82 cm/s; column B, 85 cm/s .

(C) Overlay of amines separation on 50%-PMS coated polyimide columns. Peaks: 1 = 2,6-dimethylaniline; 2 = dicyclohexylamine. Conditions: Isothermal 100°C. Flow rates: column A, 79 cm/s; column B, 91 cm/s.

shape. Figure 5C shows the separation of 2,6-dimethylamine (k = 3.6 and 4.0) and dicyclohexylamine (k = 9.8 and 10.5) on two different polyimide columns (A and B), both coated with 50%-PMS. Peak conformation on the two columns was very similar. The α values of 2.6 and 2.7 were very close between the columns, which was expected given the peak conformation. Resolution of the bases is excellent and consistent between the columns, averaging above 6.0. Retention order is the same as found previously for fused silica GC columns with PMS stationary phases (15).

Figure 6A shows the results of the separation of the FAMEs, methyl decanoate (average k = 6), methyl undecanoate (average k = 11.5), and methyl dodecanoate (average k = 22), on two different polyimide columns (A and B), both coated with 50%-PMS. Peak conformation is reproduced well for peaks 1 and 2, but peak 3 is larger and sharper on Column A. Tailing factors (TF) were estimated to be 2-3, well above the optimum. Values for α (1.9) were nearly identical for each peak pair on both columns, indicating that the separation processes were reproducible on each column. Slightly longer retention times and slightly narrower peak widths improved the values for N and H on Column A to about 1,400 and 2.1 mm, respectively. These values were lower than expected but due to the limitation of the instrument when used with short columns, the flow rate was significantly higher than the optimum. Resolution was consistent between the peak sets on each of the columns, averaging 5.6 on Column A and about 4.0 on Column B.

Figure 6B shows the separation of methyl decanoate, methyl undecanoate, and methyl dodecanoate, on the polyimide A and B columns coated with 5%-PMS exhibited similar average k values of about 7, 13, and 24. The α values (1.9) were identical among all of the columns, and resolution was reproducible at about 2.8 for all of the peak pairs. Considering the high flow rate of about 100 cm/s, N and H value were not high, about 460 and 6.5 at best.

Reproducibility results for five replicate FAME determinations on the 5% PMS polyimide column are shown in Table I. Average retention times and peak areas for each of the three FAME peaks were determined. The standard deviation (σ_{n-1}) was determined and % relative standard deviation (%RSD) was calculated. For the peak retention times, the %RSD ranged from 0.46–0.52. The %RSD of the peak areas were also consistent, ranging from 2.3–2.8. An accepted value for the %RSD of an optimized GC instrument is ± 1%, with repeatability of the GC method at ± 2% (16).

Figure 7A shows the separation of n-decane and n-undecane, on two different polyimide columns (A and B), both coated with 5%-PMS. This stationary phase is less polar than the 50%-PMS phase, and since the alkanes are also nonpolar, they were retained much longer on the 5%-PMS phase. The values for k of about 7.5 and 20 were essentially doubled on these columns due to the longer retention times. However, the values for α (2.6 for both 5%-PMS columns and both 50%-PMS columns) indicated that the mechanism of the separation of these compounds was reproducible in all cases. Peaks were symmetric, although the peaks for Column A showed some distortion. This also resulted in larger peak widths on Column A, lowering values for N to about 200-400 and raising values for H to about 9-14 mm. Resolution was above baseline values and was consistent between these columns, averaging 3.5.

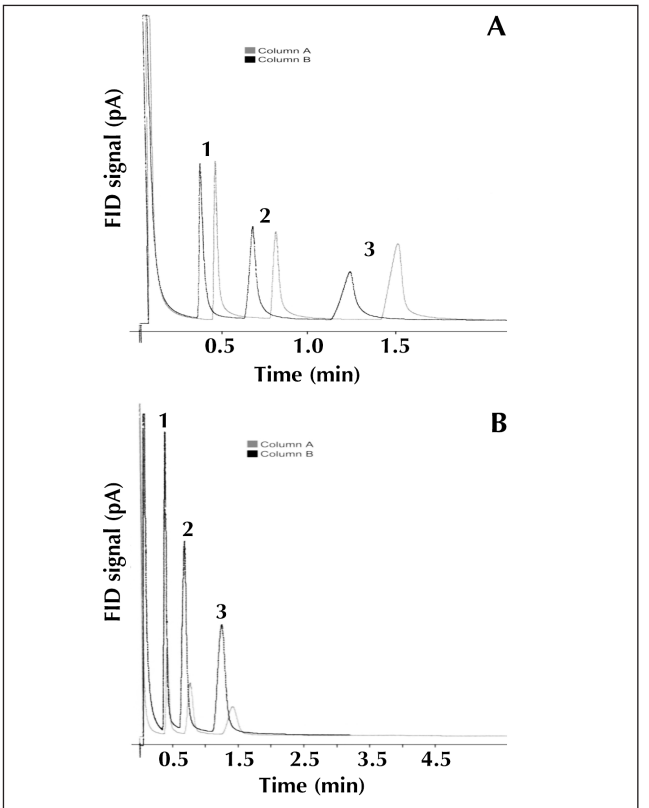

Figure 6. (A) Overlay of FAMEs separation on 50%-PMS coated polyimide columns. Peaks: 1 = methyl decanoate; 2 = methyl undecanoate; 3 = methyl dodecanoate. Conditions: Isothermal 100°C. Flow rates: column A, 81 cm/s; column B, 91 cm/s.

(B) Overlay of FAMEs Separation on 5%-PMS Coated Polyimide Columns. Peaks: 1 = methyl decanoate; 2 = methyl undecanoate; 3 = methyl dodecanoate. Conditions: Isothermal 100°C. Flow rates: column A, 98 cm/s; column B, 102 cm/s.

Table I. Reproducibility Study on 5%-PMS Polyimide Column*

Injection Number (n)	t_R 1 (min)	t_R 2 (min)	t_R 3 (min)	Area 1	Area 2	Area 3
1	0.375	0.665	1.210	1222916	1312577	1284983
2	0.374	0.664	1.206	1302418	1380348	1344171
3	0.372	0.661	1.203	1249913	1313812	1279812
4	0.373	0.660	1.204	1259576	1323858	1282598
5	0.370	0.657	1.195	1242371	1304234	1243119
Mean, x	0.373	0.661	1.204	1255439	1326966	1286937
SD†0.002	0.003	0.006	29509	30644	36294	
% RSD‡	0.52	0.49	0.46	2.4	2.3	2.8

* Probe retention order: methyl decanoate, methyl undecanoate, and methyl dodecanoate. Temp.: Isothermal 100°C.
† SD = Standard Deviation (σ_{n-1}).
‡ % RSD = % Relative Standard Deviation.

The chromatogram (not shown) of nonanal on the polyimide Column B, coated with 5%-PMS, indicated the peak shape, peak width, and retention time of the compound on this column were very similar to those of the 50%-PMS columns. The compound was well retained, and *k* values were comparable. The consistency of these values between the PMS stationary phases indicates that the aldehyde was most likely retained on the PMS columns by dispersive effects rather than by dipole-dipole interaction with the functional group.

The separation of 2,6-dimethylaniline (*k* = 2.7 and 2.9) and dicyclohexylamine (*k* = 10.8 and 12.2), on the polyimide columns coated with 5%-PMS, indicated they were not retained as long on this less polar column, but peaks were quite sharp and conformation was reproduced between the columns (data not shown). The *k* values were consistent between these columns and were lower than those on the 50%-PMS columns. The values for α (4.1 and 4.2) were consistent between the 5%-PMS columns and were observed to be higher than those for the 50%-PMS. This variance in α indicates that there is a difference in the separation mechanism for one or more of these compounds. The *k* value of the 2,6-dimethylaniline was higher on the 50%-PMS columns, indicating enhanced retention. This difference may be caused by the ability of the 50%-PMS phase to interact with the *n*- and π-electrons of the 2,6-dimethylaniline, resulting in a longer retention time on those columns.

The coated polyimide columns were not able to separate and resolve the alcohols 1-octanol and 2,3-butanediol. Injections of the individual components revealed that the 2,3-butanediol was not retained on the column. On nonpolar to moderately polar columns, this is the first compound to elute in the classical Grob test (15), so it was most likely unretained and came off with the solvent peak. The columns were also unable to separate and resolve the acids, 2,6-dimethylphenol and 2-ethylhexanoic acid. The 2,6-dimethylphenol peak was not seen when injected individually or in the acid group standards. Future work should address the interaction of alcohols and organic acids with both the coated as well as the uncoated polyimide polymer columns.

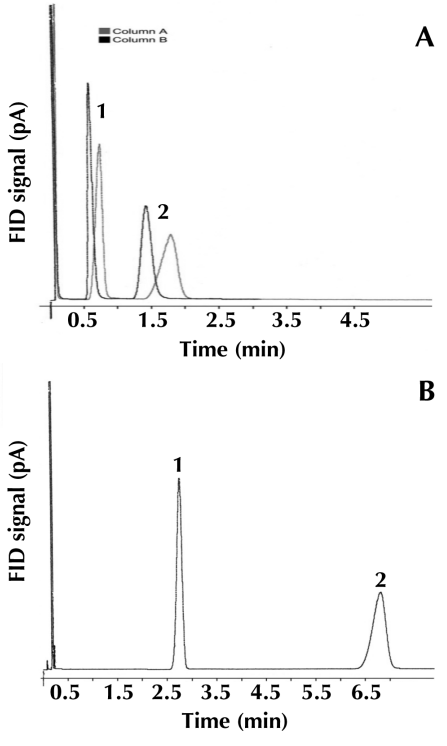

Figure 7. (A) Overlay of alkanes separation on 5%-PMS coated Polyimide Columns. Peaks: 1 = *n*-decane, 2 = *n*-undecane. Conditions: Isothermal 40°C. Flow rates: column A, 67 cm/s; column B, 69 cm/s.

(B) Alkanes separation on the DB-5 fused silica commercial column. Peaks: 1 = *n*-decane, 2 = *n*-undecane. Conditions: Isothermal 40°C. Flow rate: 65 cm/s.

Chromatography on the commercial DB-5 glass capillary column

Figure 7B shows the separation of the alkanes on the commercial 3 m fused-silica DB-5 column. At near the same flow rate, retention times were about 4 times longer on the DB-5 column when compared to the 5%-PMS polyimide column, with *k* values increased from about 8 to 33 and 20 to 84 for n-decane and undecane, respectively. However, the α value (2.6) for this column was identical to those of the polyimide polymer columns. The increase in retention time was not achieved at the expense of peak width, so calculated values of *N* and *H* were much improved over the polyimide columns, averaging 2540 and 1.2 mm, respectively. Resolution was improved by a factor of 2, to 7.5.

A summary of the chromatograms taken (data not shown) for the other analyte mixtures on the commercial DB-5 fused silica column follows. In general, retention factors were enhanced and the peaks were sharp and quite symmetric. The *k* value for the nonanal aldehyde peak was about three times greater and the values for *N* and *H* were much improved over the polyimide column and were comparable to those measured with the alkane separations. The amine values for *k* were larger, by about 3-4 times to about 9 and 40, respectively, for 2,6-dimethylaniline and dicyclohexylamine. The α values (4.1 & 4.2) were very close to those of the 5%-PMS polyimide columns, indicating reproducible selectivity of the stationary phases. The FAME average *k* values of about 24, 45, and 85 were about 3-4 times larger on the 3-m commercial DB-5 fused silica column. Again, the α values of 1.9 were identical to those with the polyimide polymer 5%-PMS column, indicating selectivity reproducibility for each of the phases. Average values of *N* and *H* of 3,300 and 1 mm were much improved in comparison to the polyimide polymer columns, due in part to the lower flow rate of 77 cm/s. Resolution was also higher on this commercial fused silica column at about 8.6, compared to about 2.8.

The consistently larger *k* values for the analytes separated on the commercial DB-5 column as compared to those on the 5%-PMS polyimide columns are likely the result of a well-engineered stationary phase which is bonded and cross-linked using a proprietary process. Comparison of the SEM scans (Figures 2B and 2C) of the 50%-PMS coated on the polyimide column and that of the cross-linked and bonded DB-5 phase on the fused-silica column seems to show an apparent difference in stationary phase density and surface uniformity. The improved plate count and H values may be in part due to the more uniform thickness of the stationary phase on the commercial DB-5 column than that for the coated polyimide columns.

van Deemter study

The van Deemter study required the use of the retention gap in front of the coated 0.32 mm polyimide column to slow the column flow down enough to run the study at low flow rates. This approach was effective, as shown in Figure 8A. The plotted values moved through a minimum of H = 1.0 mm and N = 2867. The minimum of the curve occurred at about 30 cm/s, which is consistent with that determined for longer capillary columns and He carrier gas. Efficiency, N, for the polyimide column was improved by almost one order of magnitude under optimal flow conditions. The flow rate profile from 10–40 cm/s was virtually the same as those previously reported for van Deemter plots of 7.5, 15, and 25 m fused silica columns generated on a similar GC instrument (17). However, our H value is still significantly larger than that (0.3 mm) reported for these SE-30 coated columns of 0.25 i.d. but unknown film thickness, even when the smaller diameter is taken into account (17).

Figure 8B shows the separation of the FAMEs on the retention gap-5%-PMS coated polyimide column combination used for the van Deemter study, at optimal flow conditions, near 30 cm/s. It is well known that the retention gap itself should not contribute significantly to column efficiency (18). Significant TF values of 2–3 are still evident, possibly due to some instrumental factors as well the nature of the coated stationary phase. The values for k of about 2.6, 4.9, and 9.3 were smaller than those for the 5%-PMS polyimide columns without the retention gap due to the larger measured retention time of the tailing solvent peak. The α values of 1.9 were identical to those of all of the other columns, including the commercial DB-5. However, the more optimal flow conditions improved the values of N and H to a maximum of 3254 and minimum of 0.9 mm, respectively. Resolution of about 7 was 2–3 times the values seen on the 5% PMS polyimide columns without the retention gap.

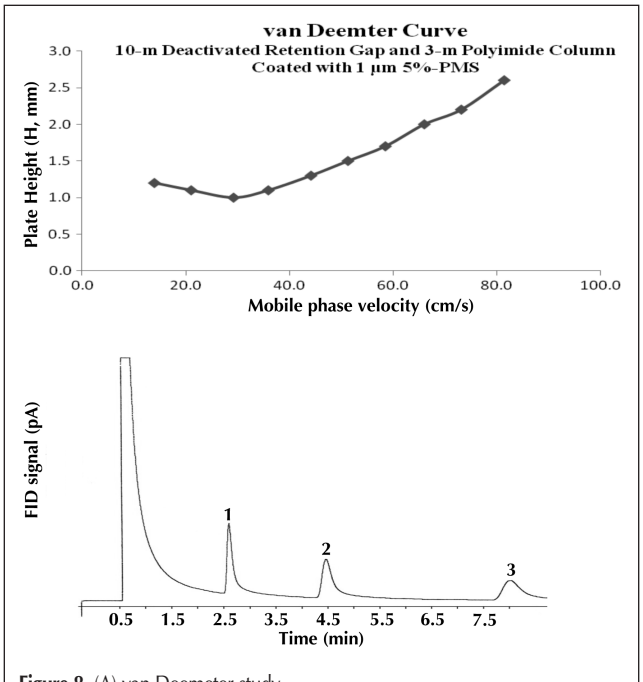

Figure 8. (A) van Deemeter study

(B) FAMEs separation on connected deactivated fused-silica retention gap and 5%-PMS polyimide column. Peaks: 1 = methyl decanoate; 2 = methyl undecanoate; 3 = methyl dodecanoate. Conditions: Isothermal 100°C; mobile phase velocity at the optimum, 30 cm/s.

Headspace applications of the retention gap-5%-PMS polyimide coated column

Representative workplace samples such as BTEX and a clearcoat automotive paint sample, which could potentially be analyzed by a portable GC instrument, were analyzed by headspace GC in just a few minutes (Figures 9A and 9B). The separation of the solvents benzene and toluene was possible but the ethylbenezene and xylene peaks overlap. This is consistent with a previously reported chromatogram showing close elution of ethylbenzene and *m*,*p*,*o*-xylenes (19). Four of the five solvents in the clearcoat paint sample were resolved by the 3-m 5%-PMS polyimide column; ethanol and methyl ethyl ketone are close in boiling points and were not distinguished. Positive identification of the solvents in the clearcoat paint sample was made by mass spectrometry using the GCD instrument. The material safety data sheet for this product, checked after the chromatography, showed the presence of these same solvents and no others (20).

Conclusion

The major result of this study is that the 0.32 mm i.d. polyimide polymer columns coated with the PMS stationary phases were shown to be capable of performing reasonable and reproducible separations on three classes of volatile organic probes: alkanes, amines, and FAMEs. They were also able to retain and

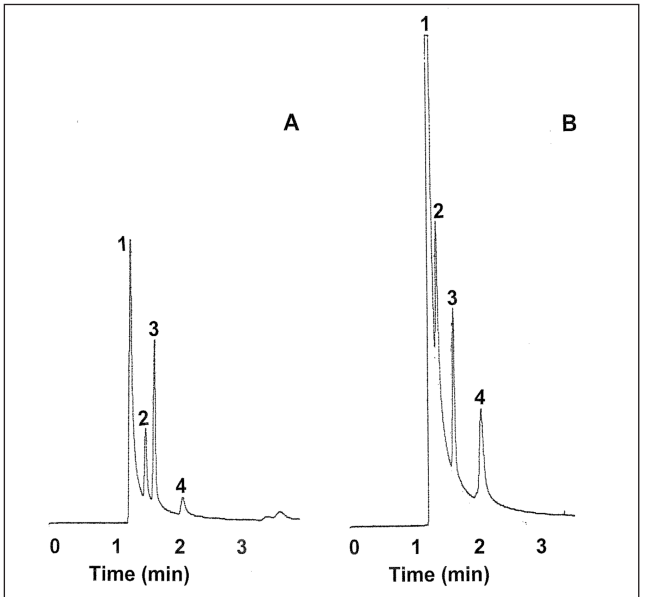

Figure 9. (A) Headspace BTEX separation on connected retention gap and 5%-PMS polyimide column. Peaks: 1 = solvent; 2 = benzene; 3 = toluene; 4 = ethylbenzene and xylenes. Conditions: Isothermal 30°C, 5 µL injection, flow rate 30 cm/s.

(B) Headspace clearcoat automotive paint separation on connected retention gap and 5%-PMS polyimide column. Peaks: 1 = ethanol and methyl ethyl ketone; 2 = methyl isobutyl ketone; 3 = toluene; 4 = ethyl 3-ethoxypropionate. Conditions: Isothermal 30°C, 5 µL injection, flow rate 30 cm/s.

elute individual aldehydes, alcohols, and acids, though it was not determined what separation ability these columns have for a range of these compounds.

The column cleaning, annealing, and temperature testing worked reproducibly on all columns. No column bleed was observed for the coated columns during the isothermal separations. When the optimum flow as determined to be 30 cm/s by the van Deemeter study was achieved with the use of a deactivated retention gap in conjunction with the polyimide coated capillary, the efficiency as measured by *H* improved to about 1 mm. This *H* value is still larger than that (0.3 mm) found for previously reported 0.25 mm i.d. fused silica capillary columns coated with SE-30 and markedly larger than that expected for a commercial column with a similar i.d. and film thickness. Future characterization of these columns should be performed on a more modern GC instrument so a column restrictor or a retention gap is not required to maintain optimal flow conditions.

There are many interesting avenues for further development of these columns. One of these would involve development of improved bonding of the polyimide with stationary phases, perhaps enhanced by chemical treatment of the polyimide surface. Developing methods for cross-linking the stationary phase surface would improve the ability of the columns to be used at higher temperatures without bleed. A collaborative project involving resistively heated polyimide capillary using an internal nickel wire, similar to a recent report using fused silica capillary (21), is also envisioned.

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