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Development and evaluation of gold-centered monolayer protected nanoparticle stationary phases for gas chromatography

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Abstract

The current status for the development of novel open-tubular gas chromatography (GC) stationary phases consisting of thin films of gold-centered monolayer protected nanoparticles (MPNs) is reported. Dodecanethiol MPNs, in which the monolayer is dodecanethiol linked to the gold nanoparticle, have shown great promise as a GC stationary phase with efficient columns having been produced in a variety of capillary i.d.'s with stationary phase film depths ranging from 10 to 60 nm, ±2 nm at a given film depth. Stationary phase operational parameters are discussed including maximum operating temperature, sample capacity, and stationary phase lifetime and robustness. An overview of the general method employed for column production is also included. The sample capacity was determined for a 2.5 m, 250 μm i.d. column with a stationary phase film thickness of 40 nm, at 50 °C using anisole (k' = 1.86) as the probe analyte. The sample capacity was experimentally found to be 2.3 ng under these conditions, similar to values reported for thicker, polymer stationary phases. The efficiency of the dodecanethiol MPN stationary phase was determined with a 100 μm i.d. capillary and found to have a reduced plate height h_{min} value of 0.95 for octane (k' = 0.68). Areas of application illustrated and discussed utilizing the dodecanethiol MPN stationary phase include complementary separations such as two-dimensional GC (GC × GC), potential utilization within a model system for a micro-fabricated GC (μGC), as well as efficient single dimension high-speed separations. Initial development of polar stationary phases utilizing 4-chlorobenzenethiol MPNs and 4-(trifluoromethyl)benzenethiol MPNs is discussed. Included is a selectivity comparison of the retention behavior of the 4-chlorobenzenethiol MPN stationary phase and the dodecanethiol MPN stationary phase.

Keywords: Nanoparticles; Stationary phases, GC; Selectivity

1. Introduction

For decades, chromatographers have utilized nanometer-sized materials in the development of highly efficient chromatographic stationary phases. These materials offer a variety of advantages from improved mass transfer characteristics to greater stability of traditional polymer phases by incorporating nanoparticle additives. Beginning in the early 1960's, stationary phases consisting of a core substrate with nanoparticle spheres arranged in various manners on the surface of the core substrate were being implemented in chromatographic systems. Kirkland [1–3] developed superficially porous silica microspheres in this manner using a non-porous silica core with nanometer-sized silica spheres attached to the core. Typically, this results in a 0.5–1 μm layer of silica of a porous nature with pore sizes on the order of 30 nm [4]. Initially developed for the separation of small solutes, this phase has been marketed commercially as "PoroShell" and is used today for the analysis of macromolecules [5].

For anion chromatography, a cation-exchange resin core particle is used to electrostatically attract a monolayer of nanometer-sized anion-exchange resin particles [6]. This type of stationary phase was developed by Small and Stevens, initially using a sulfonated core particle with 500–2000 nm sized resin particulates on the surface of the core particle [7]. Continued refinement of this type of stationary phase has resulted in a variety of ion exchange pellicular phases with surface particles as small as 20 nm with applications in areas such as trace metal analysis and carboxylic acid separations

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[8–11]. Nanoparticles on the order of 10 nm in diameter have also been used to stabilize polymer stationary phases for gas chromatography (GC), similar in concept to that for support-coated open tubular columns [12].

More recently, the unaccompanied use of nanoparticles as chromatographic stationary phases has been put forth. Both silica and polymer nanoparticles have been applied in electrophoretic chromatography as a stationary phase [13–15]. Ultrahigh-pressure liquid chromatography has also taken advantage of nanoparticles by packing organo-silica particles approximately 670 nm in diameter into a capillary with an internal diameter of 50 μm [16]. Microseparations have also utilized nanomaterials such as the use of 75 nm quaternary ammonium latex particles as an open-tubular stationary phase for on-chip liquid chromatography [17]. Thus, there is a long history for the use of nanomaterials for enhancing chromatographic performance. It is not surprising that nanoparticles have and will continue to provide advances in the development of small-scale chromatographic systems such as those achieved through microfabrication and capillary chromatography, as well as in the more traditional-scale chromatographic systems that already employ their use.

As noted in a recent review on high-speed separations, the need for more selective and efficient stationary phases increases as scientists push the envelope of chromatography and hence the need to focus on novel stationary phase development [18]. The call for new stationary phases for gas chromatography is not limited to high-speed GC (HS-GC) but also complementary separation techniques such as comprehensive two-dimensional GC (GC × GC) [19–22] as well as miniaturized chromatographic systems [23–25]. All of the above areas of interest have contributed significantly to a recent surge in novel stationary phase development ranging from in-column polymerized stationary phases for micro-GC to liquid ionic stationary phases [26–29] to our recent work in nanoparticle-based GC stationary phases [30,31]. The nanoparticles we have been studying are known as gold-centered monolayer protected nanoparticles (MPNs) that consist of a gold core with a thiol-linked monolayer of organic molecules on the surface of the gold core. The chemical characteristics of these types of materials have been well documented in the literature as summarized by Daniel and Astruc in a recent review [32]. MPNs are of particular interest because their properties can be influenced by the structure of the monolayer forming molecules and the surface monolayer stabilizes them relative to aggregation as compared to bare gold nanoparticles [33–36]. The selectivity achieved for chemical sensing with a gold-centered MPN is dominated by the chemical structure and functionality selected for the organic surface layer [37]. The MPNs appear to have useful thermodynamic and mass transfer properties that are ideally suited for application as a GC stationary phase. This report details the results to date for the development of GC stationary phases utilizing dodecanethiol MPNs. Potential areas of application for MPNs are demonstrated including complementary separations such as GC × GC, exploration of a model system for use in micro-fabricated GC systems, as well as efficient single dimension, high-speed GC separations. Initial work toward the development of two polar MPN stationary phases is also reported.

2. Experimental

2.1. Reagents and chemicals

All chemicals were reagent grade or higher grade. Triethylamine, toluene, and chlorobenzene were purchased from Baker (J.T. Baker, Phillipsburg, NJ, USA). Cyclopentane, methylene chloride, acetone, ethyl formate, hexene, hexyne, 1,1,1-trichloroethane, 1-chlorobutane, *n*-butylamine, 1,2-dichloroethane, heptene, proprionitrile, 1-heptyne, 2-butanol, 2-pentanone, methylcyclohexane, 1,2,3-trichloroethane, nitroethane, 2-pentanol, cycloheptane, *cis* and *trans*-1,2 dimethylcyclohexane, 1-bromopentane, 2-hexanone, 1-chlorohexane, cyclohexylamine, *p*-xylene, ethylbenzene, 1-pentanol, 1-nonene, cyclooctane, 2-heptanone, 1-nonyne, 1-nitrobutane, anisole, bromohexane, bromobenzene, 3-octanone, cyclohexanol, 1,3,5-trimenthylbenzene, decane, and 1-bromoheptane were all purchased from Aldrich (Aldrich, Milwaukee, WI, USA). Trichloromethane, tetrahydrofuran, hexane, cyclohexane, benzene, acetonitrile, heptane, pyridine, and 1-butanol were purchased from Fisher (Fisher Scientific, Fairlawn, NJ, USA). Ethyl acetate, butyl formate, butyl acetate, hexanal, heptanal, 1-hexanol, and octanal were purchased from Poly-Science (AccuStandard Inc., New Haven, CT, USA). Water used in the production of the columns was filtered using a NANOpure II filter system (Barnstead/Thermolyne Corp., Dubuque, IA, USA). UHP grade hydrogen (99.999% pure) was used as the GC carrier gas (AirProducts, Allentown, PA, USA).

2.2. Nanoparticle synthesis

The synthesis of the gold-centered MPNs used herein was initially developed by Brust and Schiffrin and later modified by Wohltjen and Snow [34,38]. The basic formula for the synthesis is shown below.

$$HAuCl_4 \cdot 3H_2O + RSH \xrightarrow[NaBH_4]{(C_8H_{17})_4NBr} Au:SR$$

The details for the synthesis and characterization of the dodecanethiol nanoparticle material used herein is provided in our previous report, and not repeated here for brevity [30]. The resulting solid material is black in color and easily dissolves in methylene chloride. The nanoparticles were in part analyzed by transmission electron microscopy (TEM) (Model JEM 2010, JEOL, Tokyo, Japan), a representative image of which is shown in Fig. 1. The average diameter of the poly-disperse dodecanethiol MPNs was previously determined to be 3 nm. The density of the thiol-linked monolayer on the surface of the gold cores has not been determined

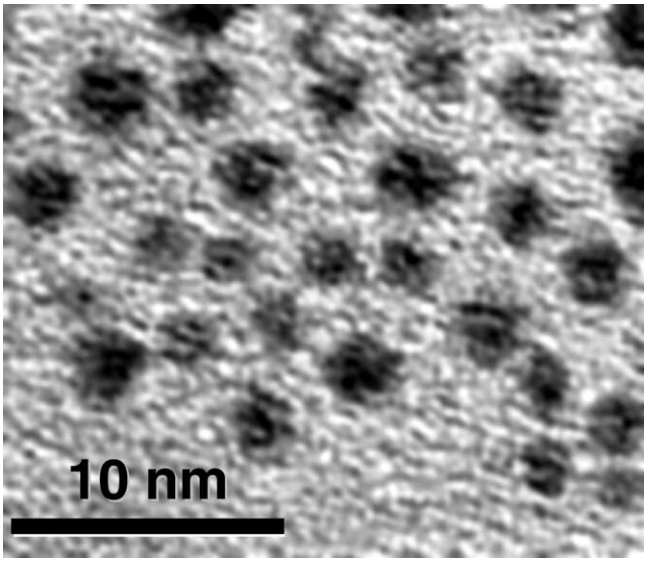

Fig. 1. Transmission electron microscope (TEM) image of the dodecanethiol MPNs used in the production of the novel nanoparticle GC stationary phase. This image was obtained using a copper grid airbrushed with a dilute solution (0.2% by mass) of the nanoparticles dissolved in dichloromethane. The nanoparticles are polydisperse with an average core diameter of 3 nm. Reprinted with permission from Ref. [31].

for these particles. A variety of chemical and physical characteristics of various MPN materials are well documented [37,39–41]. Similar methods were used in the synthesis, purification and characterization of the 4-chlorobenzenethiol and 4-(trifluoromethyl)benzenethiol MPN materials. In general, these "more polar" materials are more difficult to purify than the dodecanethiol MPNs and continued work toward establishing a satisfactory method to prepare GC columns with them is currently being refined, with only initial studies reported and discussed herein.

2.3. Column preparation

Open tubular MPN column production involves the use of deactivated silica capillary for the dodecanethiol MPN stationary phase; however some variation is necessary for the initial work being carried out for the newly developed polar MPN stationary phases. All capillaries employed for this work were purchased from Supelco (Bellefonte, PA, USA) with the exception of the studies with the square internal diameter capillary that was purchased from Polymicro (Polymicro Technologies, Phoenix, AZ, USA). All deposition methods initially begin with deactivated silica capillaries in order to avoid mixed-mode separations. Experiments utilizing the deactivated silica capillaries without modification, "blank" columns, resulted in no discernable separation for a variety of analyte mixtures.

A method for MPN column production is outlined below and is employed for all MPN columns discussed herein. The capillary is washed with three volumes of methylene chloride, 20 μl each, and similarly with three volumes of water and then baked in an oven at 300 °C for 1 h. A ∼5 mg quantity of dodecanethiol MPNs is placed in a 100 μl conical insert inside a standard injection vial (Agilent Technologies, Palo Alto, CA, USA). Approximately 50 μl of methylene chloride is added to the vial. A 5 μl aliquot of the resulting nanoparticle solution is introduced into the column via capillary action. With the column in a vertical position, using gravity to move the plug of nanoparticle solution, the nanoparticles are deposited in the capillary via evaporation. The column is inverted so that the stationary phase is uniformly distributed within the capillary. Thus, nanoparticles are deposited on the capillary walls as the solvent evaporates during the movement of the solution plug. The total time for stationary phase deposition in this manner is variable depending upon the capillary i.d., but can be completed in a few minutes for smaller i.d. capillaries. Small i.d. capillaries only require a few passes of the nanoparticle solution plug while large i.d. capillaries require deposition of multiple plugs of solution in order to achieve the desired stationary phase depth. If an acceptable level of chromatographic efficiency is obtained for a column the film depth is measured at random lengths along the capillary using SEM as detailed below. Methodology for nanoparticle deposition was established in this manner.

Column length studied was variable, with lengths ranging from approximately 1 m to as great as 3 m having been produced. This gravity-driven method of stationary phase deposition is used due to the low viscosity of the nanoparticle solution. An attempt to use nitrogen to move the solution plug was found to cause non-uniform deposition due to the tendency of the plug to "spurt" along the length of the column with solvent evaporation occurring rapidly at the front end of the capillary. For this reason, a constant force approach (gravity) is used instead of the constant velocity approach typically employed for stationary phase deposition. Particular details for the columns discussed in this report are shown in Table 1. Initial characterization of each column produced is done using four mixtures of varying chemical classes, similar to the method used in reference [30], and is not included here for each column, for brevity.

2.4. SEM imaging of the MPN stationary phase within the capillary column

All images were obtained using a Siron XL 30 (FEI Company, Hissboro, OR, USA) after sputter coating the capillaries with a 5 nm Au layer using a SPI bench top module sputter coater (Structure Probe Inc., West Chester, PA, USA). The Au layer is uniformly present over the surface of the capillary being imaged and served only as a contrasting agent to enhance the image by increasing the electrical conductivity of the sample, while not introducing any bias in the measured thickness of the MPN film depth. Randomly selected pieces of capillary, taken from varying locations along the column of interest were analyzed in this manner. Images were taken using an end on view of a given capillary.

Table 1
Dimensions and stationary phases used for the MPN columns reported herein

Stationary phase	i.d. (μm)	Length (m)	Film depth (nm)	N_t (efficiency/s), octane
(1) Dodecanethiol MPN	250	2.5	40	3080 (k' = 0.60)
(2) Dodecanethiol MPN	100	1.5	10	865 (k' = 0.68)
(3) 4-Chlorobenzenethiol MPN	250	1.8	Variable	1945 (k' = 0.10)
(4) 4-(Trifluoromethyl)benzenethiol MPN	200	2.0	–	243 (k' = 0.37)
(5) Dodecanethiol MPN	100 square	1.3	15	3990 (k' = 0.22)

N_t is the efficiency, N, divided by the retention time for octane at the specified retention factor.

2.5. Chromatographic instrumentation

All chromatograms were obtained with an Agilent 6890 gas chromatograph using a standard commercial FID detector and injector with ChemStation computer control (Agilent Technologies, Palo Alto, CA, USA). The instrument was modified to use a high-speed micro diaphragm valve mounted internally in the oven as a secondary injector (VICI, Valco Instruments Co. Inc., Houston, TX, USA) [42]. This injection system was used for all the experiments discussed herein. The high-speed injection method was applied in order to minimize band broadening due to sample injection. This also helped to control the amount of sample introduced onto the thin film stationary phase. The connecting column from the standard Agilent injector to the high-speed valve was deactivated silica capillary, 300 μm i.d. × 25 cm long. An analytical column replaced this connection line during GC × GC experimentation. The valve was controlled with a valve controller box, developed in house, with an injection pulse width of 15 ms and a sample loop of 1.3 μl [43]. For GC × GC experiments, the valve was actuated at 1 s intervals with a 20 ms actuation. All data were collected from the FID using ChemStation and then imported into Matlab (MathWorks, Natick, MA, USA) and saved for subsequent analysis.

2.6. Chromatographic experiments

All chromatograms were obtained with an injection source and FID temperature of 250 °C. The inlet pressure was maintained at 48,000 Pa with a variable split as stated, while the auxiliary pressure (column pressure) was varied independently as dictated by the experimental method being employed. The oven temperature was constant at 50 °C unless otherwise noted. For the GC × GC experiments, either a 4 or 15 m poly(ethyleneglycol) column with a 250 μm i.d. and 0.2 μm film thickness (IMMOWax, Agilent Technologies, Palo Alto, CA, USA) was used as the first column of the GC × GC system, and a dodecanethiol MPN column as the second column.

3. Results and discussion

3.1. Analysis of operational parameters

While several different applications of the dodecanethiol MPN stationary phase have been reported including a comparison to a commercial stationary phase, additional in-depth analysis of the operating parameters of the phase was warranted and is presented here. Reproducible column production with the dodecanethiol MPN material has proven to be quite successful with high efficiency columns in a variety of i.d. and length dimensions achieved. Capillaries with an i.d. ranging from 530 down to 100 μm have all been successfully prepared and studied with film thicknesses ranging from 60 to 10 nm, respectively. The maximum operating temperature was initially established using thermal gravimetric analysis (TGA). Analysis of the three different types of monolayers discussed herein shows that organic monolayer loss typically begins around 150 °C, as shown for the dodecanethiol MPN phase in our previous work [30]. While TGA allowed an estimate of the maximum operating temperature, a more traditional GC determination of the maximum operating temperature of the dodecanethiol MPN stationary phase had not yet been completed. Using a step-wise temperature program (25 °C step every 15 min for 100–250 °C), it was found that stationary phase loss does begin to occur at 150 °C with significant loss of stationary phase occurring at 175 °C. Hence, for future stationary phase development using MPNs, TGA characterization can continue to be used as an estimate of the appropriate temperature operation range for these materials. In order to overcome the loss of the chemically selective monolayer and thus, to expand the useful operational temperature range of these types of stationary phases, new avenues of exploration for materials synthesis are required.

The sample capacity of the dodecanethiol MPN material was determined for a 250 μm i.d., 2.5 m column with a MPN film thickness of ∼40 nm (Fig. 2). The column used in the sample capacity study performed well. An example of a high-speed separation is shown in Fig. 3 for a series of alkanes on the 250 μm i.d. column. The sample capacity is defined here as the maximum amount of a given analyte that can be injected onto a column that leads to a 10% increase in peak width. Using anisole (k'= 1.86) as the probe analyte at 50 °C, the dodecanethiol MPN stationary phase sample capacity was found to be 2.3 ng. The sample capacity study results for anisole are highlighted in Fig. 4. It is interesting to note that as the column becomes overloaded the anisole peak becomes more fronted. This can be seen quantitatively by comparing the skew, γ_s, values for the two peaks shown, calculated at the level of 10% of the peak height [44]. The top peak (36 pg injected mass) has a skew value of 1.1 indicating an acceptable degree of tailing and good peak shape, with a

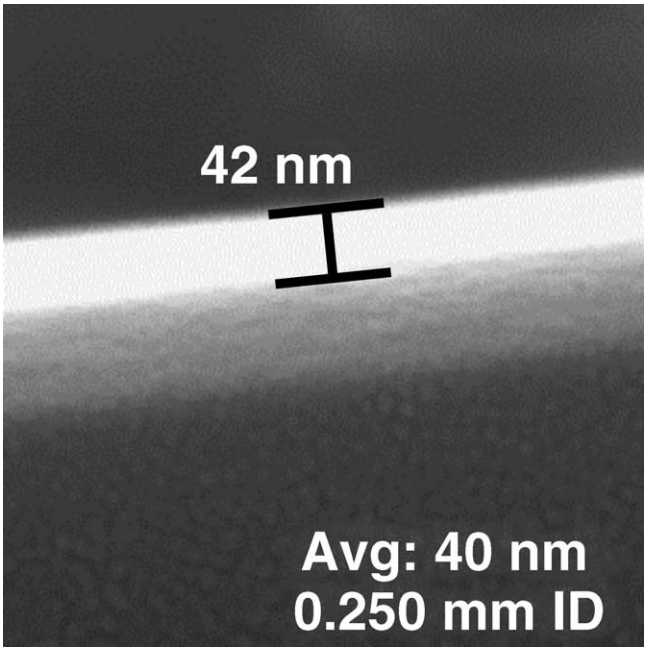

Fig. 2. Scanning electron microscope (SEM) image of the MPN stationary phase within the 250 μm i.d. capillary. Nine measurements from various locations along the length of the column resulted in an average film thickness of 40 nm (±2 nm).

skew value of 1 being the ideal. This is similar to skew values determined for the 530 μm column reported earlier [31]. Strikingly, the skew value for the 2.3 ng peak is 0.6, indicating that the peak is extremely fronted while still being only 10% wider. This clearly demonstrates why sample overload is so detrimental and why traditionally, extremely thin film stationary phases have been so difficult to work with. Thus, while 2.3 ng is a similar value to those reported for other thin film GC stationary phases, the fact that it was achieved with a 40 nm film thickness is significant because it is much thinner than most polymer phases employed [45,46]. This is one of the advantages of MPN stationary phases: a thin film as desired for efficient separations with a sample capacity that is similar to the more traditionally used polymer phases.

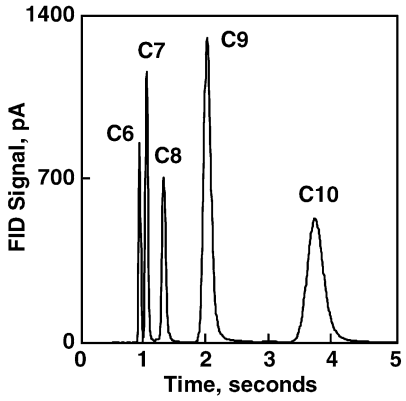

Fig. 3. Alkane series separation (C6–C10) performed on the 250 μm i.d. dodecanethiol MPN stationary phase column with a 40 nm film, 2.5 m length. The separation was obtained at an oven temperature of 50 °C with a constant pressure of 170,000 Pa (~1200 cm/s) utilized for the analysis. The inlet and detector were held constant at 250 °C with a 0.5 μl injection with a 40:1 split.

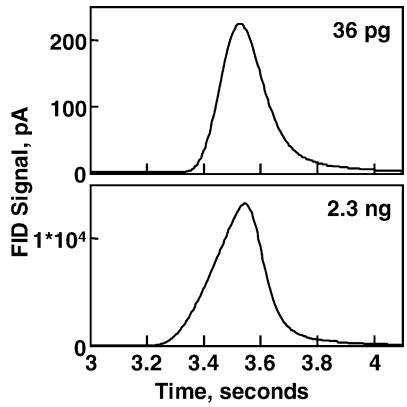

Fig. 4. Chromatographic data demonstrating the introduction of column overloading on a 40 nm film thickness with the dodecanethiol MPN stationary phase within a 250 μm i.d. × 2.5 m column at 50 °C. The sample capacity was determined to be 2.3 ng injected mass (bottom peak), which has a skew value of 0.6 indicating that as the sample overloading capacity of the column is approached a significant amount of peak fronting occurs. The 36 pg peak has a skew value of 1.1.

The operating parameters determined are summarized in Table 2. Also listed are values for the lifetime of the columns produced to date. For example, for experiments conducted with the original 530 μm i.d. dodecanethiol MPN column, it was found that there was little to no loss of efficiency over a 4-month period with over 650 injections having occurred within that time frame [30]. For the 250 μm column reported in this report, a 4-month period of storage occurred between initial production and the studies conducted and reported herein. In that time, a loss of stationary phase efficiency was not observed. Further studies on dodecanethiol MPN stationary phase robustness should include expanded studies on extended storage and use of dodecanethiol MPN stationary phase columns, as well as extending to other MPN stationary phases shown to have additional application possibilities.

Table 2
Summary of the operating parameters determined for the dodecanethiol MPN stationary phase

Dodecanethiol MPN stationary phase characteristics	
Stationary phase film thickness (range)	10–60 nm
Variation of stationary phase film thickness, average S.D.	2 nm
Capillary i.d.'s utilized	530–100 μm
Maximum operating temperature	150 °C
Temperature with significant stationary phase loss	175 °C
Sample capacity (40 nm film)	2.3 ng
Robustness	
Column use without loss of efficiency	4 months
Injections per single column without loss of efficiency	650+
Longest shelf life to date	4 months

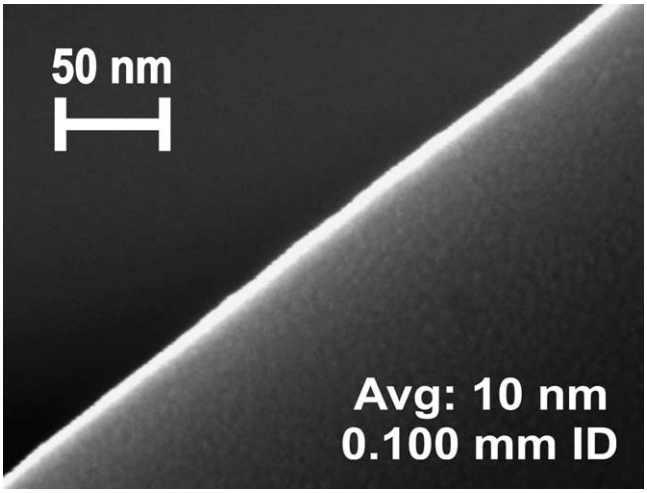

Fig. 5. SEM image of the MPN stationary phase within the 100 μm i.d. round capillary. Nine measurements from various locations along the length of the column resulted in an average film thickness of 10 nm (±0.9 nm).

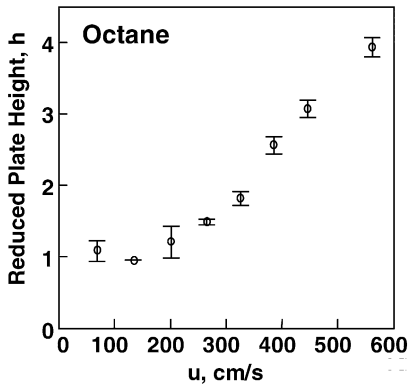

Fig. 6. The van Deemter plot for octane (k = 0.68) on the dodecanethiol MPN stationary phase within the 100 μm i.d. × 1.5 m round capillary column. The standard deviation error bars were calculated from sets of three runs at each linear flow velocity. The inlet and detector were held constant at 250 °C with a 150:1 split on the inlet for a 0.5 μl injection. The chromatogram was obtained isothermally at 50 °C. See Fig. 7 for example chromatogram.

3.2. Stationary phase relationship to separation efficiency

Initial development of the dodecanethiol MPN material took place in larger i.d. capillaries (300 μm and above). While working with the larger i.d. capillaries, a visible color change was observed as the column was produced, i.e. as the MPNs were deposited within the capillary. In this way, the color of the capillary became a qualitative indicator of the stationary phase thickness and uniformity, which are indicators of the anticipated separation efficiency. Typically, however, small i.d. capillaries are employed for systems requiring extremely efficient separations. When capillaries become this small, 150 μm or less, visual inspection of the column is no longer possible for determining the extent and uniformity of MPN stationary phase deposition during column production. However, the columns are produced very quickly and once an efficient separation is obtained using a potential column, SEM analysis can be used to confirm the presence of MPNs within the capillary. An example of a small i.d. capillary column with an efficient dodecanethiol MPN thin film can be seen for a 100 μm i.d. round column shown in Fig. 5. This column was produced in order to explore the use of dodecanethiol MPNs in smaller i.d. capillaries and the resulting effects on separation efficiency as compared to previous work with the dodecanethiol MPN stationary phase. Using SEM analysis the average film depth was found to be 10 nm ± 0.9 nm, a film depth slightly greater than three times the size of a single nanoparticle (3 nm). This is an extremely thin and uniform film and the resultant efficiency can be seen in the van Deemter plot in Fig. 6 showing the relationship between the reduced plate height, h, and the average linear flow velocity, $\bar{u}$, for octane as the test analyte. The reduced plate height, h, is the experimentally determined plate height, H, divided by the inside diameter of the capillary. Using reduced plate height plots, comparison between different systems with varying column diameters is straightforward and more objective. The minimum reduced plate height, h_{min}, is obtained at the optimum linear flow velocity. An h_{min} less than or equal to one is indicative of a high performance open tubular GC system [47]. The minimum theoretically obtainable h_{min} for open tubular chromatography under ideal conditions is 0.8 [48,49]. The h_{min} value of 0.95 obtained for octane (k' = 0.68) on the 100 μm i.d. column is very close to the h_{min} value of 0.90 obtained for chlorobenzene (k' = 0.79) on the 530 μm i.d. dodecanethiol MPN stationary phase column originally reported [30]. This indicates that the efficiency of the dodecanethiol MPN stationary phase is not significantly affected by variations in column-to-column film depth and i.d. of the capillary. Consequently, the dodecanethiol MPN stationary phase columns have the potential to be very reproducible, which is essential for applying to established chromatographic methods.

An efficient and small i.d. column such as the 100 μm i.d. round capillary column is ideal for use in high-speed separations. For example, this column baseline separated six analytes in less than 4 s (Fig. 7). At 10 nm, the MPN phase is an extremely thin film and the potential for stationary phase overloading is high. Fortunately, the skew values for these analytes (∼1.2 for most) are quite satisfactory for many applications. Thus, the 100 μm i.d. column has proven to provide similar skew values as other dodecanethiol MPN columns, and can be applied accordingly with confidence. These results demonstrate the versatility of the dodecanethiol MPN material to produce an efficient, thin film stationary phase in a variety of capillary dimensions, or as discussed next, in different forms of implementation.

3.3. Example application: a model for chip-based gas chromatography

Early in the development of the dodecanethiol MPN stationary phase, it was recognized that the deposition proper-

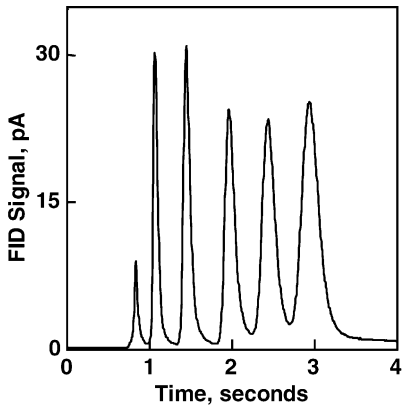

Fig. 7. Six-component separation utilizing the 10 nm dodecanethiol MPN stationary phase film within a 100 μm i.d. × 1.5 m round capillary column. The chromatogram was obtained isothermally at 50 °C with a column pressure of 140,000 Pa (∼270 cm/s). All other chromatographic parameters are the same as those in Fig. 6. Retention order: tetrehydrofuran, octane, chlorobenzne, anisole, bromobenzene, decane.

ties of the MPNs (i.e. extremely thin and reasonably uniform film deposition properties, especially in corners) may provide a distinct advantage over other types of GC stationary phases for use in microfabricated gas chromatography (μGC) systems [23,50]. Microfabricated GC systems result in angular or square cornered channels in contrast to the traditional round capillary used for most open tubular GC columns [51]. In order to explore the concept of an MPN stationary phase within an angular microchannel configuration while focusing the attention on the performance of the stationary phase and not the rest of the μGC system, the MPN stationary phase was deposited within a 100 μm × 100 μm square capillary that has a 363 μm round o.d., making the capillary amenable to a traditional GC system for injection, detection, flow rate and thermal control (Fig. 8A). The square capillary can then be used as a model for a μGC system with angular cornered channels.

We recently reported aspects of the square capillary work, and a more in-depth discussion of these results can be found therein [31]. Using SEM analysis it was found that the film thickness of the dodecanethiol MPN stationary phase was on average 15 nm along the wall of the capillary (Fig. 8B). Some thickening of the stationary phase was observed in the corners of the capillary, however, from the point within the capillary where the stationary phase is significantly thicker, to the center of the corner, it is only 5 μm of the 100 μm wall length. Along the majority of the length of the capillary walls the stationary phase thickness is very uniform with only small variations. Overall, an efficient chromatographic system was obtained with a minimum reduced plate height, h_{min}, of 1.2 for octane (k' = 0.22). This result is confirmed by the chromatographic performance achieved with the square capillary MPN column as demonstrated in the 2 s separation of seven components (Fig. 9). These and other square capillary results are extremely promising, but the role that MPNs will play in μGC development is yet unknown and will require

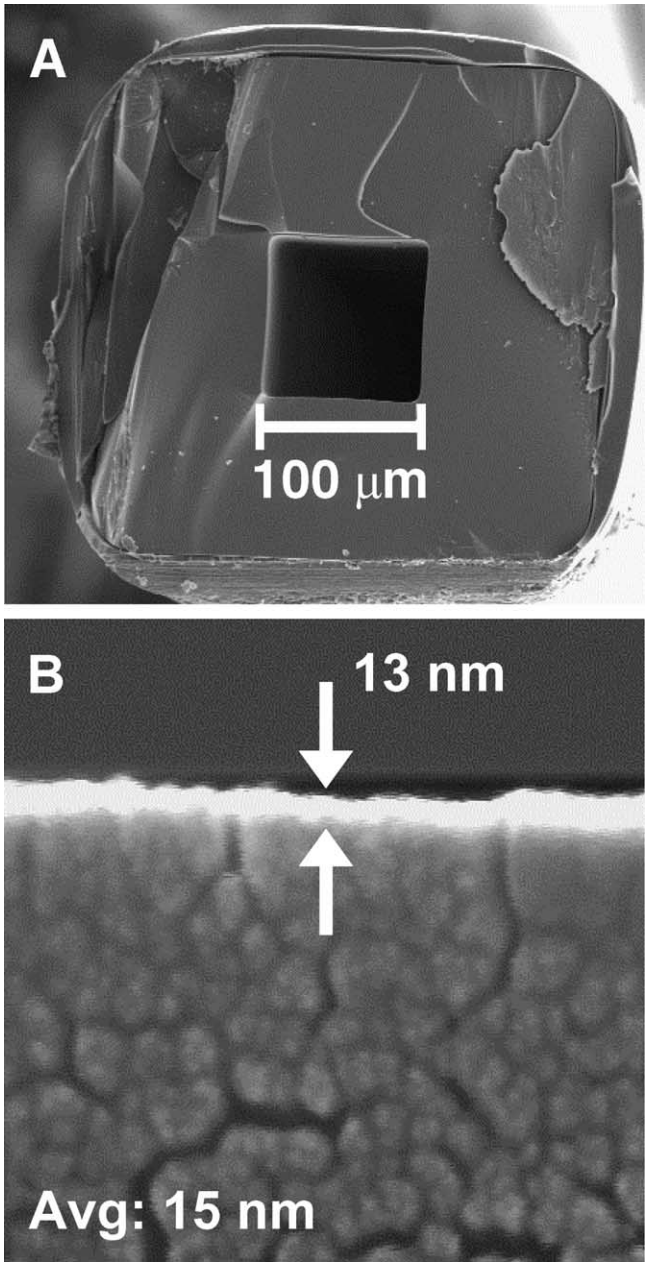

Fig. 8. (A) SEM image of the MPN stationary phase within the 100 μm × 100 μm square capillary. (B) Representative view of the MPN stationary phase along the capillary wall. Fourteen measurements from five locations along the column resulted in an average film thickness of 15 nm (±4 nm). Reprinted with permission from Ref. [31].

further evaluation and implementation of them within a truly microfabricated system to fully understand their potential.

3.4. Example application: two-dimensional separations

While MPNs possess favorable deposition properties, another advantage of MPNs is the large variety of potential organic monolayers, since the monolayer selection dictates the chemical selectivity. This versatility is very appealing for application of MPN stationary phases within chromatographic

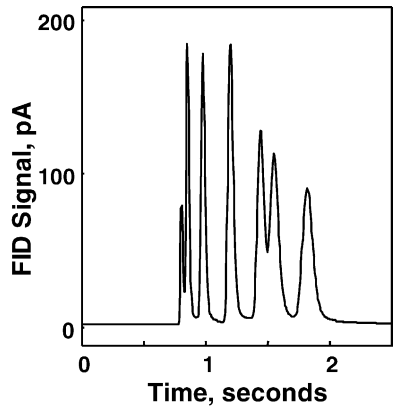

Fig. 9. High-speed separation of seven components is shown using the dodecanethiol MPN stationary phase within the 100 μm square capillary. The separation was obtained using a 1.3 m, 100 μm square capillary column with dodecanethiol MPN stationary phase at 75 °C operated under constant pressure conditions at 170,000 Pa (~200 cm/s hydrogen gas). The following is the retention order: methyl ethyl ketone, benzene, octane, chlorobenzene, anisole, 3-octanone, and decane. Reprinted with permission from Ref. [31].

systems utilizing complementary separation schemes. For example, complementary stationary phase systems, which are required with comprehensive two-dimensional gas chromatography (GC × GC), have successfully separated such complex samples as jet fuels, essential oils, pesticides, fragrances and other petroleum distillates [19–22,52–54]. Coupled with chemometric analysis and a variety of detection schemes, GC × GC has proven to be a very powerful analysis tool [21,55–58]. As shown in Fig. 10, the complementary stationary phases used for GC × GC analysis not only provide for a greater amount of separations space, but also give chemical class information based on how the analytes separate in the two-dimensional space. Often, the first column of a GC × GC system utilizes a non-polar separation scheme. However, the efficiency and speed achieved with the dodecanethiol MPN stationary phase in the 100 μm i.d. capillary with a short column length (1.5 m) dictates that it be used as the second column. For this reason, the GC × GC chromatograms shown herein are in a "reversed" format from those often shown, with the polar poly(ethyleneglycol) stationary phase as column 1 (4 m, 250 μm i.d., 0.2 μm film in Fig. 10) and the non-polar dodecanethiol MPN stationary phase as column 2. Note that under these separation conditions neither column provides enough resolution between all of the 16 components to allow for reliable analyte identification. This could be seen by summing the resultant two-dimensional separation onto either axis to obtain the ensuing separation for the two columns individually (not shown for brevity).

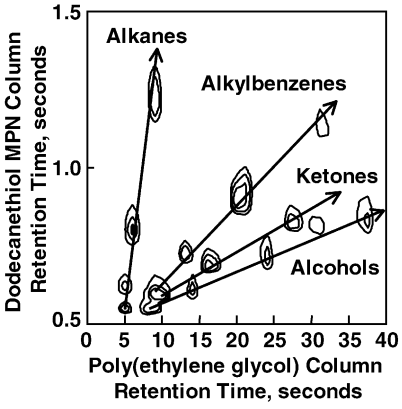

Fig. 10. The GC × GC separation of 16 components of four chemical compound classes using the dodecanethiol MPN stationary phase (100 μm i.d. round capillary) as the second dimension separation is shown. This separation was obtained using a 4 m poly(ethyleneglycol) column (250 μm i.d., 0.2 μm film) as the first column at 34,000 Pa (~40 cm/s) with 1.5 m of the dodecanethiol MPN 100 μm i.d. round capillary column as the second column operated at 240,000 Pa (~440 cm/s). A temperature ramp of 50 °C/min from 40 to 75 °C was used with the FID and inlet temperatures at 250 °C. A 0.5 μl injection was introduced with a 600:1 split on the inlet. The valve injection onto the second column had a 20 ms injection pulse width, a 1.3 μl loop with a 1 s modulation period.

Another advantage of two-dimensional separations is the ability to analyze complex samples in less time than is traditionally the case with one-dimensional GC. For the demonstration applying the dodecanethiol MPN stationary phase in the second dimension of a GC × GC separation of gasoline, the same 250 μm i.d. poly(ethyleneglycol) column used previously for column 1 with a longer length (15 m) was used with a 2.5 m, 250 μm i.d. dodecanethiol MPN stationary phase column as column 2. This arrangement afforded a greater amount of sample capacity as well as provided a slightly longer column for analysis. The resultant gasoline separation chromatogram is shown in Fig. 11A. From previous work with these types of natural gas separations, it is known that the detector response range for the hydrocarbon components is very broad, making visualization of all of the peaks difficult. For this reason, a Matlab "peak find" program written in-house was used to locate all discernible peak maxima above a set threshold for the gasoline separation shown (Fig. 11B). It can be seen then that the separation space of the chromatogram is well utilized with a large number of smaller analytes also successfully separated using the dodecanethiol MPN stationary phase column as the second dimension of a GC × GC instrument.

3.5. Polar MPN stationary phase development

With successful results for the non-polar dodecanethiol MPN GC stationary phase in a variety of applications, the development of a polar stationary phase utilizing MPNs as a thin film is now of great interest. Another type of nanoparticle currently being examined for application as a GC stationary phase is 4-chlorobenzenethiol MPNs. Traditionally, polar GC stationary phases have proven to be more difficult to develop [59–61]. The electronic interactions of the polar stationary phase material with itself and/or the capillary wall, tend to cause non-uniform deposition within the capillary. After initial failures for satisfactory polar MPN column production using the procedure established for the dodecanethiol MPN column production, it was determined

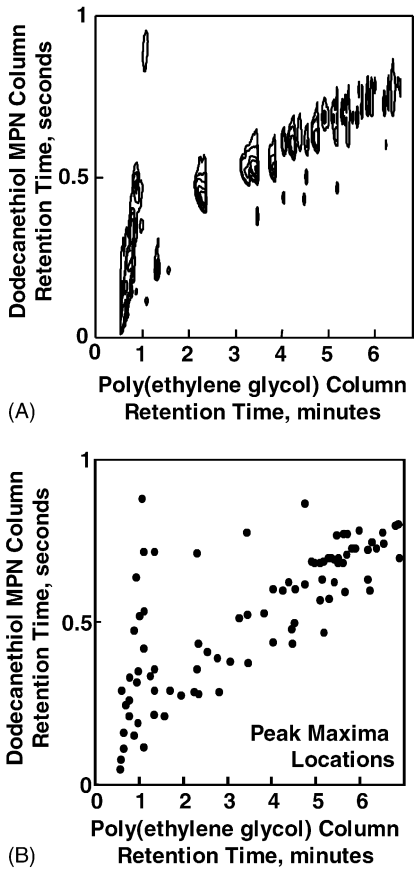

Fig. 11. (A) The GC × GC chromatogram of a commercially available gasoline sample. Separation was achieved using a DB-Wax column for column 1, 250 μm i.d., 0.250 μm film × 15 m, with column 2, a 250 μm i.d. × 2.5 m column with dodecanethiol MPN stationary phase, with a 7 min temperature program (40 °C to start, hold for 2 min, ramp for 5 min to 140 °C at 20 °C/min). The detector and injector were both at 250 °C with the injector held at 34,000 Pa (∼40 cm/s for column 1) and with a 0.5 μl injection volume and the auxiliary hydrogen flow for column 2 at 140,000 Pa (∼625 cm/s for column 2). The valve injection onto the second column had a 20 ms injection pulse width, a 1.3 μl loop with a 1 s modulation period. (B) Peak maxima locations for the chromatogram shown in part A with a threshold of 5 pA chosen. Removing the overwhelming detector response of the more common analytes such as the hydrocarbons more readily shows the presence of smaller analytes.

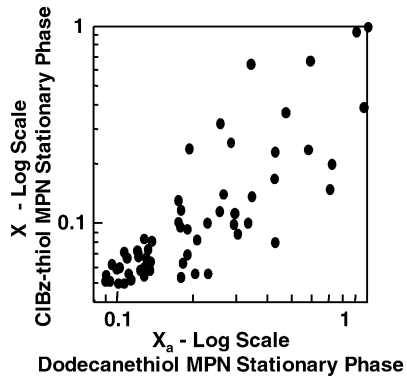

Fig. 12. Stationary phase selectivity plot of X_a values (log scale) showing the relative retention characteristics of the dodecanethiol MPN stationary phase vs. the 4-chlorobenzenethiol MPN stationary phase. All analytes were collected under similar conditions to those stated in Fig. 3 with the exception of the column pressure utilized. For the dodecanethiol MPN analysis a constant pressure of 100,00 Pa (∼450 cm/s) while a constant pressure of 55,000 Pa (∼400 cm/s) was used for the 4-chlorobenzenethiol MPN data collected. The analytes used for this comparison as well as the X_a values obtained are listed in Table 3.

that a "slightly polar" capillary would be used instead of the deactivated silica usually purchased for column preparation (at 250 μm i.d.). The risk of analyte interaction with a small fraction of non-deactivated silica sites was seen as necessary in order to achieve reasonable MPN film deposition along the entire length of the capillary. The main failure of all previous attempts had resulted in bare silica spots present at irregular intervals along the column. While bare silica patches were no longer observed, even during SEM analysis, the efficiency of the columns produced in this manner proved to be lower than desired, with lower efficiencies, N, and less-Gaussian peak shapes. Closer inspection of the stationary phase using electron microscopy showed that the 4-chlorobenzenethiol MPNs had not deposited as a uniform thin film like that observed with the dodecanethiol MPN films.

However, despite the efficiency being lower than that which we typically employ with MPN columns, the fact that no bare silica spots were present along the length of the capillary allows for comparison of the retentive properties of the 4-chlorobenzenethiol MPN stationary phase column with the 250 μm i.d. dodecanethiol MPN stationary phase column. The chemical selectivity of these two stationary phases relative to each other can be compared using $X_{a,}$ a range-scaling transformation [62]. This transformation was applied to the retention time data of 58 probe analytes of varying chemical make-up. To calculate X_a, one first makes a list of the relative retention times of all analytes in the study, with the relative retention time equal to the retention time minus the dead time. The X_a for a given analyte is calculated by dividing the relative retention time for the analyte by the relative retention time of the longest retained analyte (Table 3). This normalization approach allows for an objective comparison between two stationary phases. In this instance the longest retained analyte was 1-hexanol for both stationary phases. A log-plot of the X_a values for the dodecanethiol MPN stationary phase versus the X_a for the 4-chlorobenzenethiol MPN stationary phase shows that considerable selectivity differences between the two phases exist (Fig. 12). A large amount of scatter is seen, with the dodecanethiol MPN phase being slightly more retentive. This result shows the potential for application of MPN stationary phases for both dimensions of a GC × GC system.

Great promise can be seen to this end with current work focusing on improvements for the 4-chlorobenzenethiol MPN stationary phase discussed above, as well as new work on a third stationary phase consisting of 4-(trifluoromethyl)-benzenethiol MPNs. A preliminary chromatogram using the 4-(trifluoromethyl)-benzenethiol MPN material is shown in Fig. 13. The phase appears to be highly selective for polar

Table 3
Values for the comparison of the 4-chlorobenzenethiol MPN stationary phase (ClBz) to the dodecanethiol MPN stationary phase (C12)

Probe analyte	Boiling point (°C)	X_a-C12	X_a-ClBz	k'-C12	k'-ClBz
Cyclopentane	50	0.089	0.051	0.385	0.345
Ethyl formate	53	0.109	0.067	0.472	0.355
Trichloromethane (chloroform)	61	0.106	0.072	0.462	0.356
Hexane	64	0.093	0.051	0.403	0.358
Tetrahydrofuran	66	0.099	0.059	0.429	0.490
Hexane	69	0.101	0.050	0.440	0.305
Hexyne	71	0.127	0.054	0.551	0.335
1,1,1-Trichloroethane	75	0.113	0.052	0.492	0.373
1-Chlorobutane	77	0.130	0.067	0.567	0.337
Ethyl acetate	77	0.111	0.056	0.483	0.475
Cyclohexane	78	0.106	0.050	0.461	0.369
n-Butylamine	78	0.120	0.073	0.522	0.398
Benzene	80	0.121	0.068	0.525	0.348
Acetonitrile	81	0.090	0.055	0.393	0.475
1,2-Dichloroethane	83	0.102	0.060	0.444	0.354
Triethylamine	89	0.179	0.053	0.780	0.337
Heptene	94	0.123	0.058	0.535	0.362
Proprionitrile	97	0.095	0.062	0.414	0.499
Heptane	98	0.121	0.071	0.526	0.369
1-Heptyne	99	0.127	0.060	0.551	0.365
2-Butanol	99	0.136	0.064	0.590	0.424
2-Pentanone	101	0.128	0.084	0.556	0.472
Methylcyclohexane	101	0.134	0.058	0.583	0.327
Butyl formate	107	0.137	0.081	0.596	0.421
Toluene	110	0.182	0.063	0.793	0.452
1,1,2-Trichloroethane	114	0.191	0.093	0.830	0.461
Nitroethane	114	0.132	0.074	0.576	0.475
Pyridine	115	0.175	0.102	0.760	0.627
1-Butanol	118	0.264	0.141	1.151	0.675
2-Pentanol	118	0.257	0.116	1.120	0.648
Cycloheptane	119	0.204	0.056	0.890	0.342
trans-1,2 Dimethylcyclohexane	123	0.191	0.070	0.830	0.352
1-Bromopentane	126	0.208	0.083	0.906	0.532
Butyl acetate	126	0.178	0.096	0.773	0.644
2-Hexanone	127	0.179	0.118	0.779	0.820
cis-1,2 Dimethylcyclohexane	129	0.230	0.056	1.000	0.380
Hexanal	131	0.174	0.131	0.759	0.804
Chlorobenzene	132	0.293	0.112	1.274	0.734
1-Chlorohexane	133	0.229	0.101	0.995	0.560
Cyclohexylamine	134	0.342	0.638	1.488	3.828
p-Xylene	135	0.332	0.101	1.444	0.713
Ethylbenzene	136	0.292	0.099	1.269	0.651
1-Pentanol	137	0.472	0.365	2.054	1.673
1-Nonene	146	0.302	0.088	1.315	0.514
Cyclooctane	149	0.429	0.080	1.869	0.355
2-Heptanone	149	0.258	0.322	1.124	2.225
1-Nonyne	150	0.343	0.137	1.491	0.798
1-Nitrobutane	153	0.194	0.239	0.846	1.446
Heptanal	153	0.285	0.259	1.239	1.775
Methyl phenyl ether (anisole)	154	0.427	0.229	1.859	1.402
Bromohexane	155	0.423	0.168	1.840	0.991
1-Hexanol	156	1.000	1.000	4.354	5.384
Bromobenzene	156	0.578	0.237	2.519	1.455
Cyclohexanol	160	0.907	0.944	3.949	4.390
1,3,5-Trimethyl benzene (mesitylene)	165	0.722	0.201	3.141	1.186
Octanal	171	0.591	0.670	2.572	4.193
Decane	174	0.708	0.148	3.083	0.885
1-Bromoheptane	180	0.979	0.388	4.263	2.281

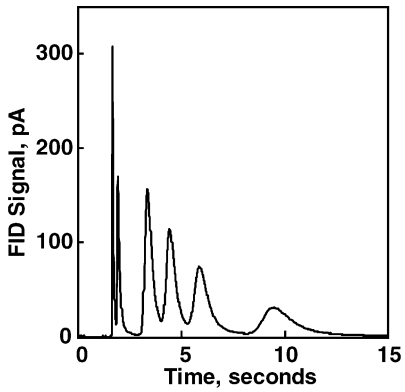

Fig. 13. Separation obtained utilizing a new nanoparticle stationary phase being developed using 4-(trifluoromethyl)benzenethiol MPNs. This chromatogram was obtained at an oven temperature of 100 °C with all other parameters the same as those listed in Fig. 3 with a resultant linear flow velocity of ∼300 cm/s. Retention order: hexane, methyl ethyl ketone, decane, chlorobenzene, 3-octanone, 1-propanol.

analytes, which could prove to be very useful in a two-dimensional separation, as well as potentially applicable as a highly selective high-speed GC stationary phase. However, continued refinement of synthesis, purification and column production for the 4-(trifluoromethyl)benzenethiol MPN material is necessary before serious application of it as a stationary phase can take place.

4. Conclusions

Historically, the application of nanomaterials has proven to be advantageous to development of efficient and unique stationary phase for different chromatographic disciplines. Building on this foundation, we are developing novel GC systems using dodecanethiol MPNs as a thin film stationary phase. The stationary phase is efficient and the sample capacity is comparable to a commercially available stationary phase but with an extremely thin MPN film depth. Application of this novel stationary phase within a variety of areas has proven to be quite successful. This success warrants continued development and analysis of the dodecanethiol MPN stationary phase, as well as prompting more in-depth work with other MPN stationary phases utilizing other monolayers on the nanoparticle center. This could include a study of the affect of chain length on the chemical selectivity for alkanethiols other than dodecanethiol. Overall, the use of MPN materials as GC stationary phases appears promising in a variety of areas including high-speed GC, microfabricated-GC, as well as GC × GC.

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