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Monolayer-protected gold nanoparticles as an efficient stationary phase for open tubular gas chromatography using a square capillary Model for chip-based gas chromatography in square cornered microfabricated channels

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Abstract

The application of a dodecanethiol monolayer-protected gold nanoparticle (MPN) stationary phase within a microchannel environment was explored using a square capillary column as a model for high-speed, microfabricated gas chromatography (μGC). Successful deposition and evaluation of a dodecanethiol MPN phase within a 1.3 m long, 100 μm × 100 μm square capillary is reported. The thickness of the MPN phase was evaluated using SEM analysis. An average thickness of 15 nm along the capillary walls was determined. While the film depth along the walls was very uniform, the corner depths were greater with the largest observed depth being 430 nm. Overall, an efficient chromatographic system was obtained with a minimum reduced plate height, h_{min}, of 1.2 for octane ($k = 0.22$). Characterization of the MPN column was completed using four compound classes (alkanes, alcohols, ketones, and aromatics) that were used to form a seven-component mixture with a 2-s separation. A mixture consisting of a nerve agent simulant in a sample containing analytes that may commonly interfere with detection was also separated in only 2 s, much faster than a similar separation previously reported using a μGC system requiring 50 s. A comparison of the MPN stationary phase to phases employed in previously reported μGC systems is also made. Application of the square capillary MPN column for a high-speed separation as the second column of a comprehensive 2-D gas chromatography system (GC × GC) was also explored.

Keywords: Stationary phases, GC; Nanoparticles; Chip technology; Instrumentation

1. Introduction

The development of novel stationary phases for gas chromatography (GC) is an ongoing interest due to the broad scope of applicability of GC methods. Recently, we reported the use of dodecanethiol monolayer-protected gold nanoparticles (MPNs) as a stationary phase for open tubular GC [1]. The MPN material provided comparable separation efficiencies as a commercial polymeric stationary phase and was satisfactorily robust with a useful lifetime. The previously reported MPN column had a 60 nm thick MPN stationary phase within a 2 m × 530 μm i.d. capillary. With these promising initial results, it was of great interest to apply MPNs within a smaller i.d. capillary, recognizing that the deposition properties of the MPNs (i.e., an extremely thin and reasonably uniform film with respect to capillary i.d. was readily achieved) may provide a distinct advantage over other types of GC stationary phases. As such the MPN materials may be ideally suited for use in microfabricated gas chromatography (μGC) systems [2–4]. Microfabricated GC systems result in angular or square cornered channels in contrast to the traditional round capillary used for bench-top open tubular GC columns [5]. 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

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has a 363 μm round o.d., making the capillary amenable to a traditional GC system for injection, detection, flow rate and thermal control. The round o.d. allows for the use of standard fittings with the internally square capillary within a standard instrumental design. The square capillary can then be used as a model for a μGC system with angular cornered channels.

Microfabricated GC was introduced over 20 years ago, but only recently has the development of μGC begun to rapidly progress [6]. However, as recently as 2002, even the most successful applications of μGC result in relatively low separation efficiency, which is usually attributed to the shortcomings of the stationary phase [3,5–8]. Therefore, it is critical to continue to explore and develop efficient and robust stationary phases for μGC. Recent advances include a bonded amino acid phase, in-channel polymerized phases, metal anchored phases, roughened channel walls for polymer deposition, as well as the use of microspheres for packed bed μGC [9–14]. The impetus for this interest in μGC stationary phase development arose because traditional polymer GC stationary phases in an angular cornered channels do not result in a uniformly thick stationary phase, i.e., the polymer phase tends to be significantly thicker in the corners of the channel. This heterogeneity in the stationary phase thickness results in a less efficient separation. Due to their unique deposition properties, we hypothesize that the use of MPNs within an angular channel system, in this case a square cornered capillary, will result in a relatively more uniform and significantly thinner stationary phase than traditional polymer phases and offer more efficient chromatographic performance.

We report herein recent results supporting this hypothesis including images of the MPN stationary phase within a square capillary column and the resulting chromatograms from test mixture separations. Characterization of the square capillary MPN column using four different compound classes is reported, as well as studying the separation efficiency and mass transfer characteristics of the MPN phase as a function of linear flow velocity. The square capillary MPN column was then used to separate a nerve agent simulant in a mixture containing common hydrocarbons. Multi-dimensional separation schemes would also benefit from an efficient thin film stationary phase and so the square capillary MPN column was utilized as the second column in comprehensive 2-D gas chromatography (GC × GC) [15–17].

2. Experimental

2.1. Reagents and chemicals

All chemicals were reagent grade or higher grade. Methyl ethyl ketone, 1-propanol, toluene, 1-butanol, and chlorobenzene were all purchased from Baker (J.T. Baker, Phillipsburg, NJ, USA). Chlorobutane, 1,1,2-trichloroethane, octane, 2-hexanone, *p*-xylene, ethylbenzene, 1-pentanol, nonane, anisole, 4-ethyltoluene, mesitylene, 3-octanone, 1,2,4-trimethylbenzene, decane, and bromoheptane were purchased from Aldrich (Aldrich, Milwaukee, WI, USA). Methylene chloride, hexane, and benzene were purchased from Fisher (Fisher Scientific, Fairlawn, NJ, USA). 2-Butanol, 3-heptanone, and 1-heptanol were purchased from PolyScience (AccuStandard, New Haven, CT, USA). Water used in the production of the column was filtered using a NANOpure II filter system (Barnstead/Thermolyne, Dubuque, IA, USA). Industrial-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 MPNs used herein was initially developed by Brust and Schiffrin and later modified by Wohltjen and Snow [18,19]. 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 nanoparticle material used herein is provided in our previous report, and not repeated here for brevity [1]. 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 dodecanethiol MPNs was previously determined to be 3 nm. A variety of chemical and physical characteristics of various MPN materials are well documented [20–23].

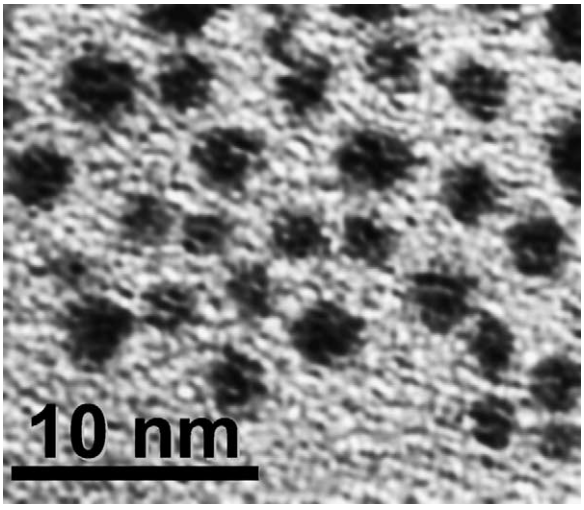

Fig. 1. Transmission electron microscopy (TEM) image of the dodecanethiol MPNs used in the production of the novel nanoparticle GC stationary phase. This image was obtained using a copper grid airbrushed with a dilute solution (0.2% by mass) of the nanoparticles dissolved in dichloromethane. The nanoparticles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

2.3. Column preparation

A square deactivated silica capillary, 100 μm width, was used for the production of the open tubular MPN column (Polymicro Technologies, Phoenix, AZ, USA). The capillary was washed with three volumes of methylene chloride, 20 μl each, and similarly with three volumes of water. The capillary was then baked in an oven at 300 °C for 1 h. A 5 mg quantity of dodecanethiol MPNs was placed in a 100 μl conical insert inside a standard injection vial (Agilent Technologies, Palo Alto, CA, USA). Approximately 50 μl of methylene chloride was added to the vial. The resulting nanoparticle solution was introduced into the column via capillary action, with 5 μl of solution introduced in this manner. With the column in a vertical position, using gravity to move the plug of nanoparticle solution, the nanoparticles were deposited in the capillary via evaporation. The column was inverted so the stationary phase was uniformly distributed within the square capillary. Thus, nanoparticles were deposited on the capillary walls as the solvent evaporated during the movement of the solution plug. In order to achieve a thin MPN film and thus, efficient separations, the column was only inverted once and the MPN solution was allowed to evacuate the capillary. The total time for stationary phase deposition in this manner was less than 1 min. To avoid clogging, no MPN solution was allowed to pass into a 50 mm portion of the end of the capillary that was inserted into the flame ionization detection (FID) system. The final column length was 1.3 m. This gravity-driven method of stationary phase deposition was 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) was used instead of the constant velocity approach typically used for stationary phase deposition.

2.4. Scanning electron microscopy (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–Pd layer using a SPI bench top module sputter coater (Structure Probe, West Chester, PA, USA). The Au–Pd 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 thickness. In this manner the surface characteristics of the silica capillary relative to the MPN stationary phase film can be more clearly distinguished. Five randomly selected pieces of capillary, taken from varying locations along the column were analyzed. Images were taken using an end on view of the capillary.

2.5. Chromatographic instrumentation

All chromatograms were obtained with an Agilent 6890 gas chromatograph using a standard commercial FID system 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, Houston, TX, USA) [24]. This injection system was used for all the experiments discussed herein. This was done in order to minimize band broadening due to sample injection. This also reduced 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, 35 cm × 200 μm i.d. 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 [25]. All data were collected from the FID system 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 150:1 split, while the auxiliary pressure (column pressure) was 170,000 Pa (∼200 cm/s) unless otherwise noted. The oven temperature was constant at 75 °C unless otherwise noted. Acetone was used as the dead time marker. For the GC × GC experiment, a 4 m poly(ethylene glycol) column with a 200 μm i.d. and 0.2 μm film thickness was used (IMMOWax, Agilent Technologies).

3. Results and discussion

Evaluation of the presence of a gold MPN thin film within the square capillary (Fig. 2A) was of great interest as well as the deposition properties of MPN at the capillary corners versus the walls. Using SEM, the presence of a thin film of MPNs was confirmed inside the square capillary. It can be seen that only a thin film of MPNs is present in the capillary corners, although it is thicker than areas along the capillary wall (Fig. 2B and C). Using several images at five random locations along the column it was determined that the MPN phase thickness was on average 15 nm (±4 nm, a variation slightly larger than the size of 1 nanoparticle having an average diameter of 3 nm) on the walls of the capillary and no greater than 430 nm in the corners. 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 (Fig. 2C). Along the majority of the length of the capillary walls the stationary phase thickness is very uniform (15 nm average) with only small variations

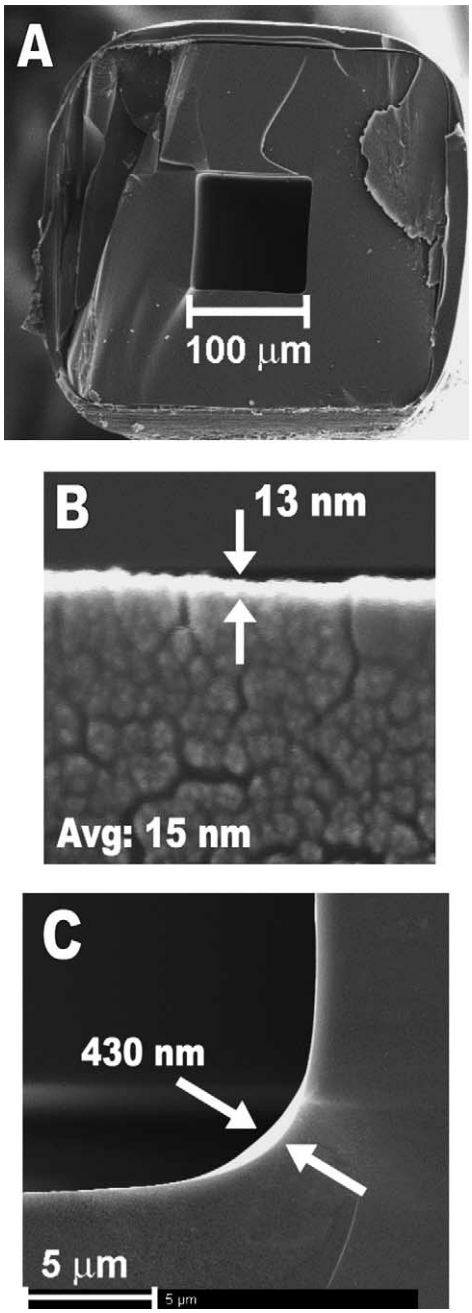

Fig. 2. (A) Scanning electron microscopy (SEM) image of the MPN stationary phase within the 100 μm square capillary. (B) Representative view of the MPN stationary phase along the capillary wall. Fourteen measurements from five locations along the column resulted in an average film thickness of 15 nm (±4 nm). (C) Magnified view of the capillary corner showing MPN deposition within the corner (430 nm maximum thickness) relative to the adjacent walls. The corner stationary phase, although much thicker than along the walls, constitutes ∼10% of the total stationary phase surface area.

due to limited MPN clumping, possibly due to the roughness of the silica walls within the capillary. We shall see that the chromatographic performance of the square capillary MPN column was good, even though the thickness in the corners was higher than along the walls.

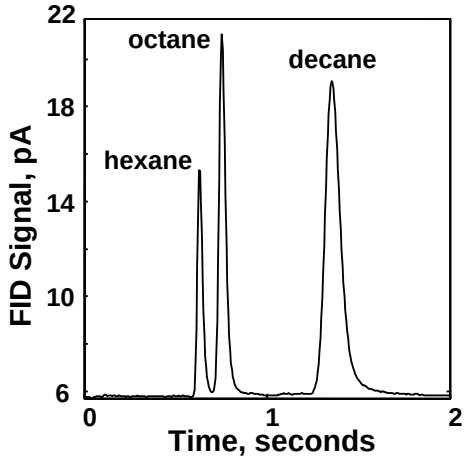

Fig. 3. Chromatogram of the separation of the alkane series (hexane, octane, decane) is shown. The separation was obtained using a 1.3 m × 100 μm square capillary column with dodecanethiol MPN stationary phase at 75 °C operated under constant pressure conditions at 170,000 Pa (∼200 cm/s hydrogen gas). The other compounds, listed in Table 1 were separated under the same conditions (chromatograms not shown for brevity).

The chemical selectivity of the square capillary MPN column was examined using four different classes of compounds: alkanes, aromatics, ketones, and alcohols. A representative separation showing the alkanes is presented in Fig. 3, while the retention data for the other compounds are summarized in Table 1, for brevity. The separation patterns for the test compound mixtures were very similar to those achieved with the previous MPN column work using a round capillary [1]. However, the alkane separation that previously required 35 s on a 60 nm thick stationary phase in a 2 m × 530 μm i.d., round capillary column is now much faster, being achieved in less than 2 s on a nominally 15 nm thick stationary phase in a 1.3 m × 100 μm square capillary. This alkane separation confirms the presence of a dodecanethiol

Table 1
These twelve components were chosen for analysis of the retention behavior of the dodecanethiol MPN stationary phase within the square capillary

	b.p. (°C)	t_r (s) (MPN)	k (MPN-square)	k (MPN-round)
Hexane	69	0.63	0.02	0.01
Benzene	80	0.70	0.14	0.06
Methylethyl ketone	80	0.69	0.12	–
1-Propanol	97	0.69	0.12	–
Octane	126	0.75	0.22	0.21
Chlorobenzene	132	0.94	0.53	0.65
1-Pentanol	138	1.03	0.67	0.51
3-Heptanone	148	0.92	0.50	0.42
Anisole	154	1.12	0.82	0.82
3-Octanone	168	1.21	0.97	0.71
Decane	174	1.35	1.20	1.47
1-Heptanol	175	2.75	3.47	3.27

The retention factors were calculated using acetone as the dead time marker. The k (MPN-round) data was reported in [1] and shown here for comparison.

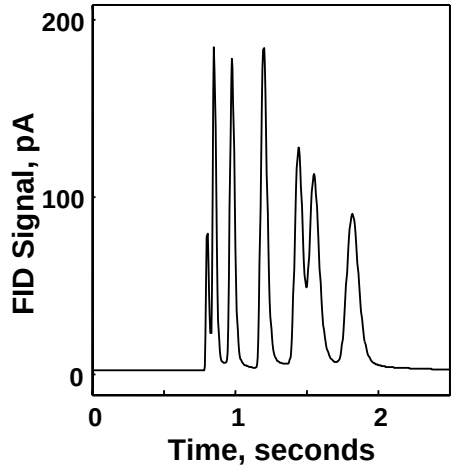

Fig. 4. High-speed separation of seven components (subset of Table 1) is shown using the dodecanethiol MPN stationary phase within the 100 μm square capillary. The following is the retention order: methyl ethyl ketone, benzene, octane, chlorobenzene, anisole, 3-octanone, and decane. Chromatographic parameters are the same as those for Fig. 3.

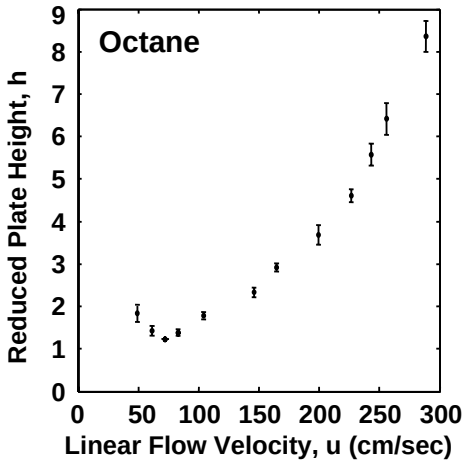

Fig. 5. The van Deemter plot for octane ($k = 0.22$) on the dodecanethiol MPN stationary phase within the square capillary column. The standard deviation error bars were calculated from sets of three runs at each linear flow velocity. All other chromatographic parameters are the same as those in Fig. 3.

MPN film as the stationary phase governing the separation. The dodecanethiol MPN phase is a predominately non-polar as previously reported [1]. Reasonable agreement is obtained between the retention factors for the round versus square capillary MPN columns, even though the instrumentation and experimental conditions were not identical.

A mixture consisting of seven components from three of the compound classes (from Table 1) was readily separated in less than 2 s with acceptable resolution (Fig. 4). The peak shapes obtained with the square capillary MPN column were reasonably good, yet, some tendency toward non-Gaussian peak shapes was apparent. One possible reason for this tendency may be due to modest deposition irregularity of the MPN phase within the capillary. Another explanation is that for short columns operated at high linear flow velocity, such as in this study, band broadening mechanisms contribute to slightly asymmetric peaks [26]. Calculated skews, γ_s, for analyte peaks for prior work with the dodecanethiol MPN phase were typically around 1.2, indicative that the MPN phase is capable of producing good peak shapes [1,27]. Further characterization of the MPN stationary phase is needed but must take these effects into consideration. Studies are also currently underway to investigate the selectivity achieved for the dodecanethiol MPN stationary phase relative to other MPN stationary phases for use in multi-dimensional GC, the capacity of the different stationary phases as a function of film thickness and column temperature, column robustness over a broad temperature range, as well as evaluation of the intermolecular interactions of the MPN stationary phase using statistical methods [28,29].

Before expanded utilization of the square capillary MPN column it was of interest to explore the mass transfer and band broadening characteristics as a function of linear flow velocity. Obtaining the Van Deemter plots for several representative analytes facilitated this study. For brevity, only the plot for octane ($k = 0.22$) is shown in Fig. 5. The mass transfer behavior of the MPN stationary phase in the square capillary column responds classically, as seen by the shape of the Van Deemter curve as a function of linear flow velocity. From this plot it can be seen that the optimal linear flow velocity, the most efficient flow velocity for this system, is ~70 cm/s. For ease of comparison, the reduced plate height, h (calculated plate height, H, divided by the relative radius of the capillary), was calculated for the Van Deemter plot studies. Theoretically, a capillary-based chromatographic system with a reduced plate height ~1 is considered efficient [30]. The Van Deemter plot for octane shows that this system is efficient with an $h_{min} \sim 1.2$ obtained. For comparison, Wiranto's smallest reported plate height, H, for a microengineered open tubular GC system utilizing a dimethylsiloxane stationary phase was 0.57 mm as compared with the minimum plate height obtained with the current dodecanethiol MPN square capillary GC system of 0.14 mm [7]. It should be noted that chromatograms reported herein (Figs. 3 and 4) were at significantly higher flow rates than the optimum indicated by the Van Deemter plots. What this tells us is that the useful linear flow velocity range for the square capillary MPN column is fairly broad while still offering efficient separations. This flexibility will allow for the applications of the square capillary MPN column within high-speed GC systems such as the GC sensor as well as being promising for the use of MPN stationary phases within angular microfabricated channels [24].

Over the past few years, the scientists at Sandia National Laboratories have made many advances in the realm of μGC, with their device referred to as the μChemLab [2,8,9,31]. To better put the potential of the square capillary MPN column into context, it was applied for a chemical separation of interest to the developers of the μChemLab and related analytical GC systems. An example chromatogram to be

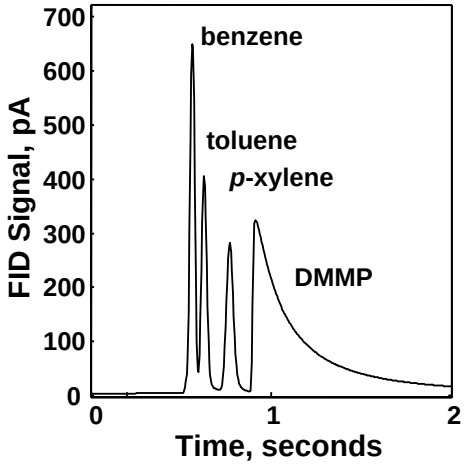

Fig. 6. Separation of a simulated nerve agent from a hydrocarbon background in less than 2 s is shown. Dimethylmethyl phosphonate (DMMP) is a model for the nerve agent Sarin while benzene, toluene, and *p*-xylene simulate common interferences for nerve agent detection in gasoline. The same chromatographic parameters as with Fig. 3 were applied except under constant pressure conditions at 240,000 Pa (~240 cm/s).

compared to the square capillary MPN column is the separation of benzene, toluene, *p*-xylene, and dimethylmethyl phosphonate (DMMP) [32]. This sample mixture is representative of a chemical nerve agent, simulated by DMMP, in a typical interference background simulated by common aromatic compounds. Using the MPN stationary phase within the square capillary a nearly resolved separation of the four compounds was achieved in under two seconds at a linear flow velocity of approximately 240 cm/s (Fig. 6), well above the optimal linear flow velocity of this system. Despite this, the separation shown still has an efficiency, N, of 3040 (*p*-xylene, $k = 0.45$). This separation is very similar, i.e., the same compounds and nearly the same resolution, to that shown by Sandia in reference 32 but in a fraction of the time. The separation on the 1.4 m square capillary MPN column required ~2 s while ~50 s were required for the 1 m microfabricated GC system reported by Sandia. The stationary phase used by Sandia was OV1 (polydimethyl siloxane) and an unstated temperature program [8]. Other experimental parameters were not available for comparison. It should be noted that the DMMP separation done on the MPN stationary phase was achieved isothermally. These results support the idea that MPN materials may prove to be viable and efficient stationary phases for use in angular cornered GC systems such as microfabricated chromatographic channels.

It is interesting to compare the performance of the square capillary MPN column to other previous reports of μGC systems as well. A μGC system utilizing a 0.2 μm thick copper phthalocyanine phase has been reported with separations taking on the order of 30 min [14,33] in contrast to the seconds required for separations with the dodecanethiol MPN stationary phase. Results obtained with polymer films are usually much faster than 30 min but stationary phase film depths and depth uniformity are rarely reported within the literature. A polymer film for possible application as a stationary phase within microchannels was recently reported with an ideal film depth of 100 nm but was not applied for chromatographic separations [13]. While polymer stationary phases continue to be more widely chosen due to the variety of chemical selectivity available, they are still often described as predominantly non-uniform for microchannel deposition and inefficient as compared to theoretical results for the μGC systems being developed [7,8].

Implementation of MPN materials in small dimensional capillaries for use in multi-dimensional GC systems such as GC × GC is also of interest [15–17,34]. The GC × GC system relies upon having a highly efficient stationary phase within a short, smaller dimensional capillary as the second column, and a more traditionally sized capillary for the first column. The two columns should provide complementary chemical selectivity in order to more fully utilize the peak capacity of the 2-D separation. Often, a non-polar stationary phase is used for the first column, but since the square capillary MPN column is more appropriately configured for the second column, a polar poly(ethylene glycol) column was used for the first column in the present investigation. This "reversed" stationary phase pairing provided an excellent comprehensive 2-D separation for the twenty-four-component mixture shown in Fig. 7. Only two sets of analytes were too overlapped for visual analyte identification: benzene and heptyne, toluene and 2-butanol (Table 2). However, these analytes could be readily mathematically resolved using

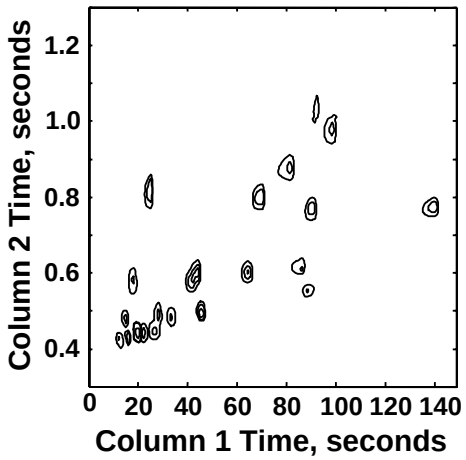

Fig. 7. The GC × GC separation of 24 components (Table 2) using the dodecanethiol MPN stationary phase within a square capillary system as the second dimension separation is shown. Two pairs of components are not totally resolved (benzene and heptyne, toluene and 2-butanol) resulting in only 22 visually resolved contour spots. This separation was obtained using a 4 m poly(ethylene glycol) column (200 μm i.d., 0.2 μm film) as the first column at 34,000 Pa (~40 cm/s) with 0.9 m of the dodecanethiol MPN 100 μm square capillary column as the second column operated at 210,000 Pa (~235 cm/s). The oven was held constant at 60 °C with the FID and inlet temperatures at 250 °C. A 0.5 μl injection was introduced with a 150:1 split on the inlet. The valve injection onto the second column had a 15 ms wide injection pulse width, a 1.3 μl loop with a 1 s modulation period.

Table 2
Retention times and boiling points of the 24 components separated using GC × GC utilizing the dodecanethiol MPN stationary phase within a 100 μm square capillary as the second column, 0.9 m in length with a 15 nm stationary phase thickness

	b.p. (°C)	t_r (s)			b.p. (°C)	t_r (s)	
		Column 1	Column 2			Column 1	Column 2
Hexane	69	12.5	0.43	Chlorobenzene	132	64.2	0.61
Chlorobutane	77	16.1	0.43	*p*-Xylene	135	44.1	0.61
Benzene	80	20.2	0.45	Ethylbenzene	136	42.2	0.58
1-Propanol	97	29.1	0.45	1-Pentanol	137	84.5	0.61
1-Heptyne	99	19.7	0.45	Nonane	151	18.0	0.58
2-Butanol	99	27.0	0.48	Anisole	154	139.6	0.77
2-Pentanone	101	22.0	0.44	4-Ethyltoluene	162	69.0	0.81
Toluene	110	28.5	0.49	Mesitylene	165	75.5	0.85
1,1,2-Trichloroethane	114	88.5	0.55	3-Octanone	166	90.5	0.77
1-Butanol	118	45.3	0.49	1,2,4-Trimethylbenzene	169	98.5	0.99
Octane	126	15.0	0.48	Decane	174	25.0	0.82
2-Hexanone	127	33.2	0.49	Bromoheptane	180	92.3	1.04

The first column was a poly(ethylene glycol) column, 4 m in length with a 200 μm i.d. and a 0.2 μm film thickness. The separation was obtained isothermally at 60 °C with a 15 ms injection pulse width to the second column every 1 s.

chemometric analysis if quantification or unknown identification was desired [15,16,35]. Also of interest in this separation is the short analysis times achieved: less than 120 s for the first column and less than one second for the second column (the square capillary MPN column). These results demonstrate the utility of the implementation of the dodecanethiol MPN stationary phase material within high-speed, multi-dimensional GC systems such as GC × GC.

4. Conclusions

The use of dodecanethiol MPNs as an efficient stationary phase in a 100 μm square capillary has been demonstrated. The relatively uniform thin film deposition of the MPNs within the square capillary supports the potential utility of this material within μGC systems. The square capillary MPN system was also successfully implemented in a GC × GC format, demonstrating the utility of the dodecanethiol MPN stationary phase within a multi-dimensional GC instrument. The role that MPNs will play in μGC development is not fully known and will require implementation within a truly microfabricated system to more fully understand their potential. Continued development of novel MPN stationary phases, including those previously not reported as well as the current dodecanethiol phase, is warranted so that the full promise of these materials may be realized, whether within a μGC system or other analytical gas phase analyzers and sensors.

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