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Micromachined GC Columns for Fast Separation of Organophosphonate and Organosulfur Compounds

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This article demonstrates how to prepare microfabricated columns (microcolumns) for organophosphonate and organosulfur compound separation that rival the performance of commercial capillary columns. Approximately 16 500 theoretical plates were generated with a 3 m long OV-5-coated microcolumn with a 0.25 μm phase thickness using helium as the carrier gas at 20 cm/s. Key to the advance was the development of deactivation procedures appropriate for silicon microcolumns with Pyrex tops. Active sites in a silicon−Pyrex microcolumn cause peak tailing and unwanted adsorption. Experimentally, we found that organosilicon hydride deactivation lowers adsorption activity in microcolumns more than silazane and silane treatments. But without further treatment, the phosphonate peaks continue to tail after the coating process. We found that heat treatment with pinacolyl methylphosphonic acid (PMP) eliminated the phosphonate peak tailing. In contrast, conventional resilylation employing *N,O*-bis(trimethylsilyl)acetamide, hexamethyldisilazane, and 1-(trimethylsilyl)imidazole does not eliminate peak tailing. Column activity tests show that the PMP treatment also improves the peaks for 2,6-dimethyl aniline, 1-octanol, and 1-decanol implying a decrease in the column's hydrogen bonding sites with the PMP treatment. FT-IR analysis shows that exposure to PMP forms a bond to the stationary phase that deactivates the active sites responsible for organophosphonate peak tailing.

Miniature gas chromatographs (μGC) with microfabricated columns have received considerable interest for the analysis of toxic chemicals, explosives, disease markers, and other analytes.[1–59] At present though, only Sacks and co-workers,[3,9,58] Manginell and co-workers,[10,14,18,24,59] and Radadia et al.[4] have reported microfabricated columns that are able to show sig-

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nificant separation of organophosphonates. In all the cases the organophosphonate peaks show significant tailing due to unwanted adsorption to the active sites present in the microcolumn. For example, Figure 1 shows a fast μGC chromatogram taken from our previous presentation.[4] Notice that the dimethyl methyl phosphonate (DMMP), diethyl methyl phosphonate (DEMP), and diisopropyl methyl phosphonate (DIMP) peaks tail considerably. That makes the microcolumns less than optimal for fast portable GC.

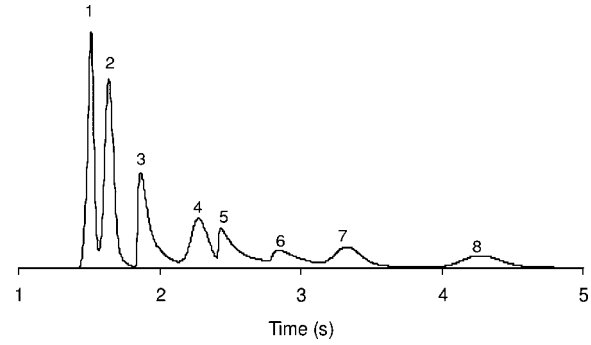

Figure 1. Chromatogram showing a 4 s separation obtained in the OV-5-coated microcolumn described by Radadia et al. (ref 4). The separation was obtained by injecting 1 μL of headspace vapor with a split of 100:1 (injector temperature 250 °C); the column inlet pressure was held at 25 psi, and oven temperature was ramped from 90 to 98 °C at 120 °C/min. Hydrogen was used as the carrier gas. Peaks represent (1) diethyl ether, (2) toluene, (3) dimethyl methyl phosphonate, (4) diethyl methyl phosphonate, (5) *n*-octanol, (6) diisopropyl methyl phosphonate, (7) 1,6-dichlorohexane, and (8) dodecane. Notice that the dimethyl methyl phosphonates, diethyl methyl phosphonate, octanol, and diisopropyl methyl phosphonates peaks tail, leading to an apparent nonzero baseline between 2 and 3.3 s.

A similar situation occurred in the early days of capillary GC. Researchers were able to separate organophosphonates, but significant tailing was seen.[60] Eventually column manufacturers were able to develop capillary columns that produced sharp phosphonate peaks. Unfortunately, the methods were never published in the open literature.

The objective of the work described in this article was to develop a procedure that would allow sharp GC peak elution for organophosphonate and organosulfur compounds on microfabricated columns. We tried the deactivation procedures recommended by several GC manufacturers[61,62] but never were able to obtain the sharp peaks we desired. Finally, we discovered a novel procedure, deactivation with an alkylating phosphonate—pinacolyl methylphosphonic acid (PMP) (CAS: 616−52−4). The PMP (Scheme 1) reacts with the active sites responsible for phosphonate peak tailing resulting in sharper peaks.

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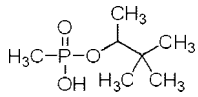
Scheme 1. Pinacolyl Methylphosphonic Acid



The objective of this article is to describe the procedure and also to explain how the chemistry works, so the procedures may be generalized.

EXPERIMENTAL SECTION

Microcolumn Fabrication. Microfabrication started with a double-side-polished 4 in. (5−20 Ω·cm) p-type silicon wafer from SiliconQuest. The wafer was coated on both the sides with Shipley SPR220−7 photoresist at 3000 rpm. Double-side photolithography was performed to obtain an image of 100 μm wide and 3 m long serpentine channel on the front side and 210 μm access port holes on the back side. The patterned photoresist was baked at 140 °C for 30 min to withstand deep reactive ion etching (DRIE). The channel patterns were etched 100 μm deep using DRIE. Then access holes were etched into the channel from the back side of the wafer. Four 3 m long columns were obtained from processing one silicon wafer. The resulting columns were cleaned with Shipley Microposit Remover 1165 at 120 °C followed by a standard clean 1 (SC-1) at 73 °C. Pyrex 7740 glass pieces of the size of the silicon die were cut out from wafers using a diamond wheel cutter, followed by an SC-1 clean. Silicon channels were anodically sealed with the cleaned Pyrex glass at 400 °C with 900 V bias. The bonded column was then deactivated and packaged in a manifold (shown in Figure 2C) for the coating and testing process.

Deactivation. Three different deactivation procedures were compared: silylation, persilylation, and organosilicon hydride treatment. Silylation was performed with a 10% dimethyldichlorosilane (DMDCS) (Gelest, ≥99%) solution in toluene, passed through a column heated on a hotplate at 100 °C for 8 h, followed by a toluene, methanol, and ether rinses of 0.5 mL each. The column was then dried for 1 h under 5 psi nitrogen flow at 100 °C in the GC oven prior to testing.

Persilylation and organosilicon hydride deactivation were performed using 1,2-diphenyl-1,1,3,3-tetraphenyldisilazane (DPTMDS) (Fluka, ≥97%) and phenyltris(dimethylsiloxy)silane (Ah3P) (Gelest), respectively. The deactivation was performed by dynamically coating the surface with a one column length plug of neat reagent. A brass reservoir manifold containing the solution was attached on one of the microcolumn access ports, and the plug was pulled using a 660.4 mmHg vacuum at the second access port. After the liquid plug evacuation the column was heat-treated in a vacuum annealer (300 μm of Hg) at a rate of 8 °C min^{-1} to 375 °C with a hold time of 4 h. The vacuum annealer was purged with nitrogen for 10 min before applying vacuum to ensure absence of oxygen. The column was cooled to room temperature before being exposed to atmosphere. The column was connected to 0.5 m long fused-silica transfer lines (i.d. 100 μm, o.d. 200 μm, Restek, IP-deactivated) using a brass manifold as shown in Figure 2C. A two-ferrule design was used to make a connection to the microcolumn chip as shown in Figure 2D. During assembly when the ferrule nut was screwed down the polyimide ferrule deformed the poly(tetrafluoroethylene) (PTFE) ferrule to make a leak-tight seal between the fused-silica capillary and the chip. The packaged column was rinsed with one column volume of methanol, one column volume of pentane, and one column volume of air at 25 μL/min using a syringe pump.

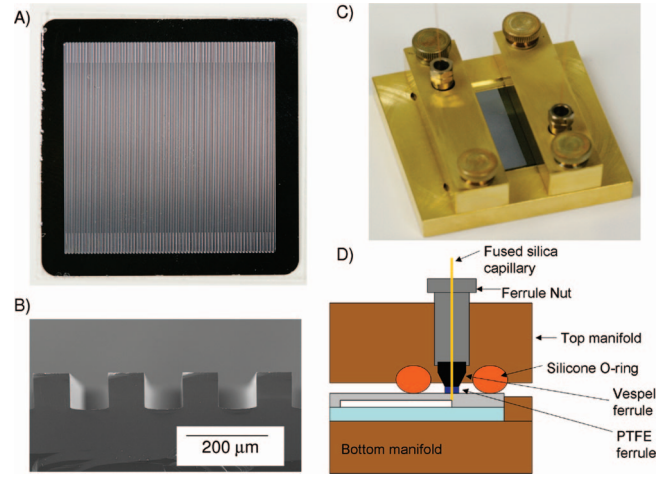


Figure 2. (A) Three meter long micromachined serpentine column on a 3.2 cm square and 500 μm thick silicon piece anodically bonded to 1 mm thick Pyrex 7740, (B) scanning electron micrograph of 100 μm wide and 100 μm deep channels, (C) brass manifold packaging for a microcolumn, and (D) details of a low dead volume connection to the microcolumn.

Stationary Phase Coating. A 5% polar phase was chosen to achieve separation of phosphonates. The 4% (w/v) coating solution was prepared by dissolving OV-5 (Ohio Valley) vinyl phase in pentane in a sonicator bath. Dicumyl peroxide (DCP) (Sigma Aldrich, >99%) in the form of 2% (w/v) toluene solution was added to the coating solution to achieve a final concentration of 0.2% (w/w) in the deposited stationary phase. The microcolumns were filled with the coating solution, which was dynamically driven out with air at a rate of 25 μL/min. The coated microcolumn was then connected to a conventional GC to perform cross-linking at 140 °C for 1 h in flowing hydrogen with an inlet pressure of 10 psi. Next, the microcolumns were conditioned by heating the microcolumn to 200 °C for 4 h in flowing hydrogen with an inlet pressure of 40 psi. Next, the microcolumns were cooled and the fused-silica connection lines were replaced with new deactivated fused-silica lines. The latter procedure ensures the true measurement of the microcolumn's performance. The fused-silica legs were trimmed to the shortest length (~20 cm) required for connecting the microcolumn to a conventional GC.

Postcoating Treatments. Two postcoating treatments were evaluated, one with PMP (Sigma Aldrich, CAS 616−52−4, 97%) and another one with Rejuv-8 (Sigma Aldrich, a commercial resilylating mixture of *N*,*O*-bis(trimethylsilyl)acetamide, hexamethyldisilazane, and 1-(trimethylsilyl)imidazole). The PMP treatment was performed on a conventional GC at 110 °C by injecting 1 μL of liquid in the splitless mode (injector temperature of 250 °C) with a hydrogen flow at 40 psi followed by a stabilizing time of 1 h with the hydrogen flowing. The column was reconditioned at 200 °C with 40 psi inlet pressure for 4 h. The completion of reconditioning process was checked with the presence of a stable FID baseline.

The resilylation treatment with Rejuv-8 was performed by four injections each 1 h apart as recommended in the product specification. Each injection consisted of 5 μL of liquid at 100 °C

Table 1. Components of the Organophosphonate and Organosulfur Compound Mixture

no.	compound
1	2-chloro-2-methylpropane
2	ethyl ether
3	isooctane
4	diisopropyl sulfide
5	chloroethyl methyl sulfide
6	nonane
7	dimethyl methyl phosphonate
8	isopropane sulfonyl chloride
9	decane
10	diethyl methyl phosphonate
11	diisopropyl methyl phosphonate
12	undecane
13	triethyl phosphate
14	menthone
15	isoborneal
16	dodecane

with inlet pressure of 10 psi. The resilylation treatment was followed by a reconditioning treatment as stated earlier.

Microcolumn Testing. An Agilent 6893N GC/FID-MS, with 7683B autosampler was used for all the separations. The packaged column was placed in the GC oven and connected to the split inlet and FID using Restek deactivated guard columns. Hydrogen was used as carrier gas in all tests except when carrying out column activity tests using Agilent column test mix injections. Helium was used in the latter case. Headspace injections of DIMP (Alfa Aesar, 95%), and *n*-octanol (Sigma Aldrich, ≥99.7%) were performed to check column activity. DIMP was used a model phosphonate tracer. Octanol was used as a tracer because it is very commonly used as a sensitive probe of improper column deactivation and of column performance. The extent of deactivation check was performed on 35 cm long microcolumns by injecting 5 μL headspace (sampling vial at ~20 °C) with a split of 50:1 (injector temperature at 250 °C) and oven temperature and inlet pressure held at 75° and 5 psi, respectively.

The effect of postcoating treatment on phosphonate activity was studied on 3 m long, OV-5-coated microcolumns by injecting 5 μL of a saturated DIMP headspace vapor (sampling vial at ~20 °C) with a split of 50:1 (injector temperature at 250 °C) and column temperature and pressure at 110 °C and 20 psi. Detailed study of column adsorption activity was performed using DB-5 microbore column test mix supplied by Agilent. The 1 μL of test mix liquid was injected with a split of 1000:1 (injector temperature at 250 °C). The inlet pressure was adjusted to achieve a helium carrier gas velocity of 20 cm/s. The oven temperature was adjusted to 120 °C to achieve a retention factor of ~6 for tridecane.

In the experiments reported here, DMMP (Sigma Aldrich, ≥97%), DEMP (Sigma Aldrich, ≥97%), DIMP, and triethyl phosphate (TEP) (Sigma Aldrich, ≥99.8%) were used to evaluate the ability of the column to separate organophosphonates. Isopropyl sulfide (IPS) (Sigma Aldrich, 99%), chloroethyl methyl sulfide (CEES) (Sigma Aldrich, 98%), and isopropyl sulfonyl chloride (IPSC) (Fluka, ≥97%) were used to evaluate the ability of the column to separate organosulfur compounds. In detail, a mixture of the reagents listed in Table 1 was prepared. One μL of the headspace vapor of the mixture (sampling vial at 20 °C) was injected with a split of 120:1 (injector temperature at 250 °C), the oven temperature held at 110 °C, and inlet pressure ramped from 40 to 50 psi at the rate of 150 psi/min.

The chromatograms were analyzed using Agilent's MSDChem data analysis software (version D.01.02.16). The number of microcolumn plates were calculated using the tridecane peak in the Agilent column test mix injection by

$$N = 5.54\left(\frac{t_R'}{W_h}\right)^2 \quad (1)$$

where t_R' is retention time of the tridecane minus methane retention time and W_h is the width of the tridecane peak, taken at the half-peak height.

Infrared Analysis. Fourier transform infrared spectroscopy (FT-IR) was performed on silicon samples to further understand the effect of the PMP treatment. A double-side polished 4 in. silicon wafer was spin-coated with neat Ah3P solution at 3000 rpm for 40 s. The coated wafer was then heated in a vacuum annealer as previously described for the column deactivation. OV-5 coating solution was prepared as mentioned earlier for stationary phase coating procedure. Deactivated wafer pieces were spin-coated with the coating solution at 3000 rpm followed by a cross-linking treatment in a vacuum annealer at 140 °C for 1 h. PMP treatment of the coated silicon piece was performed by spin coating neat PMP solution at 3000 rpm followed by heat treatment at 200 °C in the vacuum annealer. PMP vaporization was found to be complete in a control experiment using a silicon wafer under the latter treatment conditions. This was confirmed with FT-IR. The treated surfaces were analyzed using a Nicolet Nexus 670 FT-IR in the transmission mode. IR spectra were collected in the transmission mode with 64 scans from 800 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. ACD/SpecManager software was used to perform suitable background correction to the IR spectrum.

RESULTS

Microfabrication. Figure 2 shows images of the microfabricated column (A and B) and column holder (C). The column consists of a series of 100 μm wide, 100 μm deep channels on a 3.2 × 3.2 cm^2 silicon wafer. The channels are arranged in a serpentine pattern. The total column length is 3 m. The channels were sealed by anodically bonding a 7740 Pyrex cover glass on top of the channels. Capillaries were attached to the back of the column using an in-house made manifold as indicated in Figure 2D. Restek (no. 560292) deactivated guard columns (i.d. 100 μm, o.d. 200 μm) were used to make all connections.

Effects of Deactivation. Figure 3 shows how three different deactivation procedures, silylation, persilylation, and Ah3P treatment, affect the *n*-octanol and DIMP peaks seen on columns with no stationary phase. The DIMP injection on nondeactivated microcolumn results in two peaks, a relatively sharp peak at 2.4 s and a highly tailing peak at 7.8 s. DIMP injection on microcolumns silylated with dichlorodimethylsilane (DMDCS) resulted in only one slightly sharper peak at 2.4 s. DIMP elutes on diphenyltrimethyldisilazane (DPTMDS)-persilylated microcolumns as one relatively big peak at 2.7 s. However, the DIMP peak has a half-peak width of 0.9 s and shows significant tailing. The DIMP injections on the microcolumn deactivated with Ah3P resulted in a sharp peak at 2.4 s with a peak width of 0.4 s.

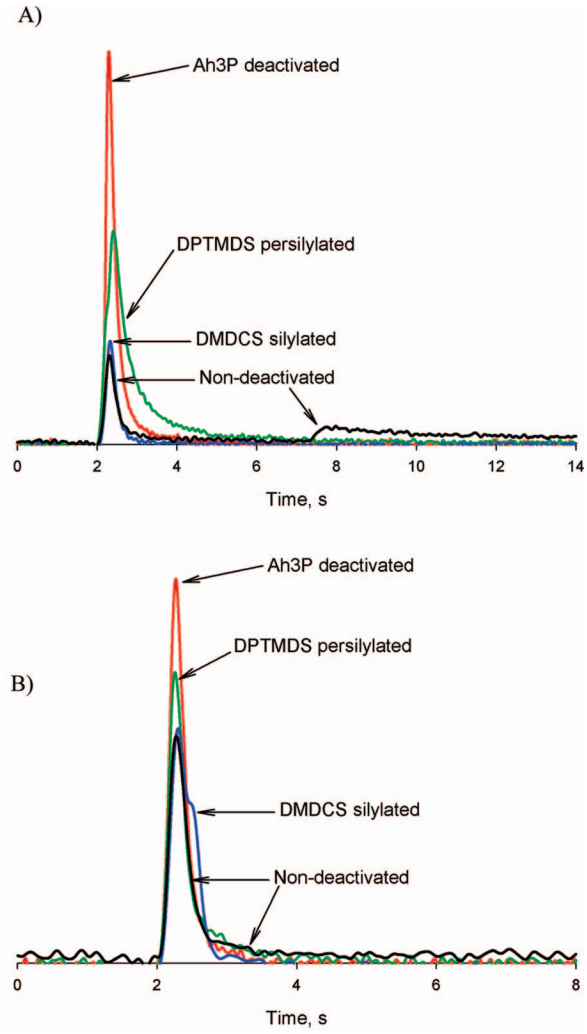


Figure 3. (A) Diisopropyl methyl phosphonate and (B) *n*-octanol injections on nondeactivated silicon, persilylated, and Ah3P-treated microcolumns prior to coating stationary phase. Headspace (5 μL) of compound was injected on 35 cm long microcolumns with a split of 50:1 (injector temperature 250 °C), and oven temperature and inlet pressure were held at 75 °C and 5 psi, respectively. Hydrogen was used as the carrier gas.

The octanol injections on nondeactivated column resulted in a peak at 2.4 s with considerable tailing. No additional peaks were observed with octanol injections as compared to DIMP. The octanol injections on the DMDCS silylated microcolumns with a peak at 2.45 s with a slightly higher peak height and a shoulder. The peak shows less tailing characteristics compared to the nondeactivated microcolumns. The octanol peak on DPTMDS-persilylated microcolumn elutes at 2.35 s and is higher in peak height and peak area compared to silylated and nondeactivated microcolumns. The octanol peak on Ah3P-deactivated microcolumn eluted at 2.4 s and showed the highest peak height among all the deactivations.

Effects of Postcoating Treatments. The results in Figure 3 were for columns with no stationary phases. Figure 4 shows effects of two postcoating treatments: Rejuv resilylation and PMP treatment on columns with OV-5 stationary phase coated on Ah3P-deactivated walls. DIMP injections on freshly coated microcolumn resulted in a peak at 18.1 s that tails tremendously. Resilylation of the coated microcolumn resulted in the faster elution of the

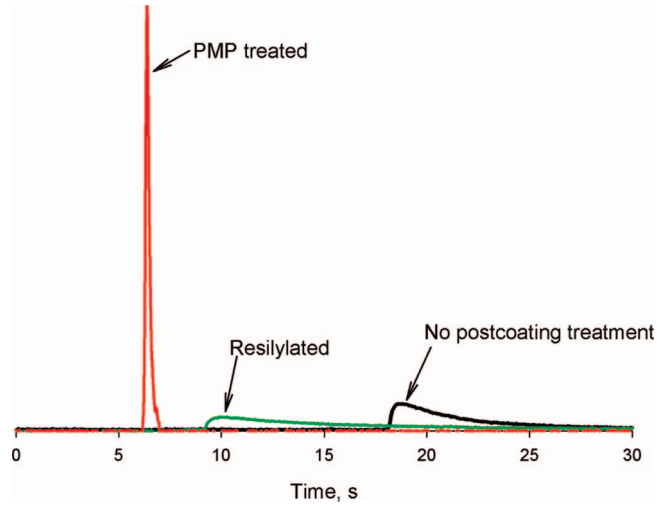


Figure 4. Diisopropyl methyl phosphonate headspace injection on Ah3P-deactivated, OV-5-coated microcolumns without further treatment and with further heat treatment with resilylating agent (Rejuv-8) and pinacolyl methylphosphonic acid (PMP). The test was carried out on coated, 3 m long microcolumns by injecting 5 μL of headspace with a split of 50:1 (injector temperature 250 °C), and oven temperature and inlet pressure were held at 120 °C and 10 psi, respectively. Hydrogen was used as the carrier gas.

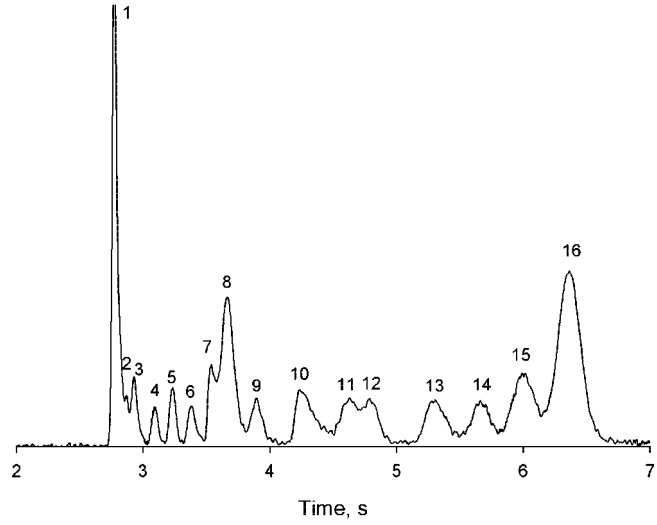


Figure 5. Separation of the phosphonate and sulfur compound mixture described in Table 1 on the pinacolyl methylphosphonic acid treated microcolumn. Testing was carried out using hydrogen as carrier gas. Headspace vapor (1 μL) of the mix was injected with a split of 120:1 (injector temperature 250 °C), the oven temperature was held at 110 °C, and inlet pressure ramped from 35 to 45 psi at the rate of 150 psi/min.

DIMP peak at 9.8 s. However, the DIMP peak was smaller in height and exhibited even more pronounced tailing than the freshly coated column. PMP treatment on freshly coated column decreased the retention time of DIMP peak to 6.7 s. The DIMP peak was also much sharper, only slightly asymmetric, and showed negligible tailing. The peak width at half-height of the DIMP peak was 0.15 s.

Figure 5 shows the separation of an organophosphonate (OP) and sulfur compound mix (described in Table 1) on the PMP-treated microcolumn. The fast GC chromatogram shows readily resolvable and less tailing peaks of OP (peaks 7, 10, 11, 13) and

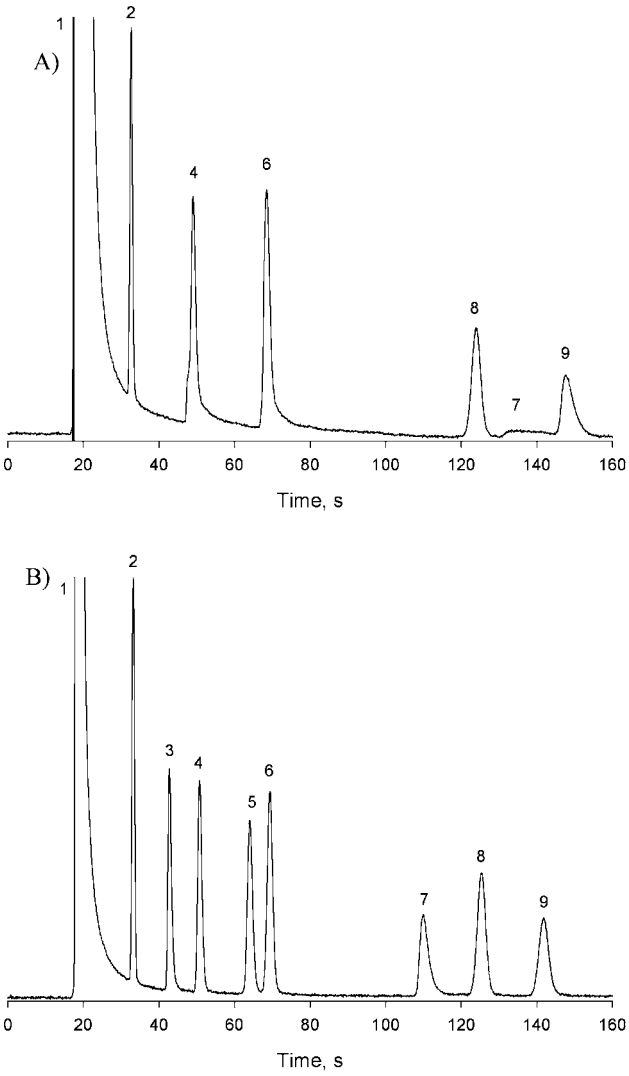


Figure 6. Separation of test mixture described in Table 2 on Ah3P-deactivated and OV-5-coated columns: (A) without PMP treatment and (B) with PMP treatment. Test mixture liquid (1 μL) was injected in split mode (1000:1 split; injector temperature 250 °C), column temperature was held at 120 °C, and inlet pressure adjusted to achieve a helium carrier gas velocity of 20 cm/s.

Table 2. Column Test Mixture Components (Agilent Technologies, No. 200-0010)

no.	compound
1	hexane
2	decane
3	*n*-octanol
4	2,6-dimethyl phenol
5	2,6-dimethyl aniline
6	napthalene
7	*n*-decanol
8	tridecane
9	methyl decanoate

organosulfur (OS) compounds (peaks 4, 5, 8). Peak 10 corresponding to diethyl methy phosphonate (DEMP) shows an asymmetric peak showing some residual activity. The separation of compounds was obtained within a 4 s window.

Column Test Mix Results. Figure 6 shows the column activity testing results obtained by injecting Agilent's DB-5 microbore column test mix (contents listed in Table 2). The mix is formulated to detect the presence of different characteristic active sites in the column. The mix contains *n*-octanol and *n*-decanol for the detection of hydrogen bonding sites such as silanol (Si−OH) groups. 2,6-Dimethylphenol and 2,6-dimethylaniline are used for Lewis acidic and basic active site detection. The metal adsorptive sites are detected using napthalene. The methyl decanoate and alkanes are used for computing column efficiency and checking presence of dead volumes and column overloading.

Test mix injection on freshly coated microcolumn showed strong adsorption of *n*-octanol, *n*-decanol, and 2,6-dimethylaniline peaks. The *n*-octanol peak was present in tailing parts of peak 4, which was confirmed using mass spectrometry. The *n*-decanol peak eluted as a shoulder to the baseline at 135 s on the chromatogram. The napthalene peak exhibit slight tailing characteristics. The number of theoretical plates were calculated based on the tridecane peak. The methane retention time was adjusted to 0.295 min. The tridecane peak showed an adjusted retention time (t_R) of 1.773 min and a peak width of 0.034 min. With the use of eq 1 the number of theoretical plates was calculated to be ~15 000.

Test mix injection on the PMP-treated microcolumn exhibited sharp peaks for *n*-octanol, *n*-decanol, and 2,6-dimethylaniline. *n*-Decanol does exhibit slight tailing. The methane retention time was adjusted to 0.287. The tridecane peak eluted at a retention time of 1.802 min and a peak width of 0.033 min. The number of theoretical plates on the PMP-treated column were calculated to be ~16 500. The theoretical number of plates on a 3 m column increases with PMP treatment by ~1500. This corresponds to an increase of 3% in theoretical plate numbers on a 1 m basis. This may be due to swelling of the stationary phase or inconsistency in the dynamic coating process.

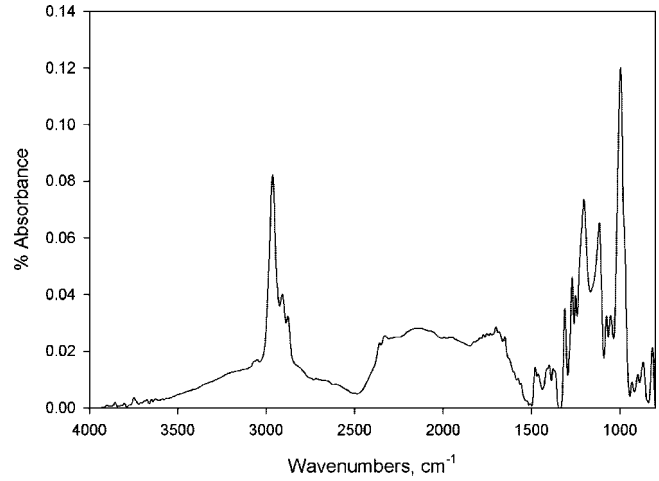


Figure 7. Fourier transform infrared spectrum of the PMP-treated OV-5 film.

FT-IR. Figure 7 is obtained by subtracting the FT-IR results for PMP-treated from nontreated OV-5-coated silicon surface. Strong phosphoryl stretching vibrations (P═O) are evident at 1205 cm^{-1}. This indicates the presence of adsorbed phosphonate species on the surface. The spectrum region from 3000 to 2800 cm^{-1} shows a typical fingerprint exhibited by CH_3O and CH_3P

vibrations in the condensed-phase PMP spectrum.[63] The spectrum shows presence of pinacolyl skeletal vibrations from 1240 to 1270 cm^{-1}.

Interpretation of the spectra of compounds containing both P−OH and P−OR functionalities in alkyl hydrogen methylphosphonates is complicated by the fact that they give rise to strong P−O− stretching vibrations which are common to both groups. In the spectrum, the presence of the P−O−C group produces a strong absorption band in the region of 1000 cm^{-1}. Unlike the liquid PMP spectrum showing three broad peaks around 1000 cm^{-1}, the spectrum in Figure 7 shows only one absorption band. This along with the absence of O−H stretching absorption peak in the region of 2525−2780 cm^{-1} implies the acidic proton in the PMP has been lost, and the PMP has reacted with the active sites in the column to form a stable phosphonate compound.

DISCUSSION

The work here demonstrates that it is possible to create microcolumns that efficiently separate phosphonates. We find that our 3 m long OV-5-coated microcolumns have approximately 16 500 theoretical plates using helium as the carrier gas at 20 cm/s. That corresponds to 5500 theoretical plates per meter. By comparison, Agilent reports that commercial GC columns with phase thicknesses similar to ours (0.25 μm) show 4630 theoretical plates per meter.[64] To the best of the authors' knowledge the current article reports the largest number of theoretical plates per meter for a silicon microcolumn.

Key to the better performance was developing a deactivation procedure for the microcolumns. Deactivation of fused-silica columns is very well studied, but there has been little work on micromachined columns. Micromachined columns are commonly made of trenches in silicon sealed with Pyrex 7740 glass slides. The Pyrex is designed to produce strong anodic bonds and is not easy to deactivate. In particular, the Pyrex contains alkali ions that diffuse to the surface during the anodic bonding process. The alkali ions are critical to the formation of a strong anodic bonds, but they make the surface of the Pyrex hard to deactivate.

The DIMP injections on nondeactivated column results in elution of two peaks. A plausible explanation for two peaks is the saturation and desaturation of reversible phosphonate adsorptive sites. Activity test results for deactivated microcolumns shows improvement over nondeactivated microcolumns. DMDCS silylation eliminates the reversible phosphonate binding sites and hence shows only one DIMP peak. DPTMDS persilylation produces better response and hence better deactivation to DIMP and octanol injections compared to DMDCS silanization treatment. This is due to the mere fact that persilylation produces a denser film over the surface compared to silylation and hence provides lower gas permeability toward the surface. For DPTMDS and Ah3P deactivations, the irreversible phosphonate adsorption sites are being blocked along with the reversibly binding sites. Ah3P deactivation blocks the irreversible sites more efficiently than DPTMDS and hence results in a better deactivation. Ah3P deactivation produces better response to DIMP and octanol injections than DPTMDS. A possible cause would be the same reason why persilylation is better than silanization.

The octanol injections on nondeactivated column exhibited extreme tailing and did not produce two peaks as with DIMP. This shows presence of active sites apart from hydrogen bonding sites, which are actively adsorbing phosphonates and not adsorbing *n*-octanol. The DMDCS silylation procedure produces a peak with slightly higher peak height and reduces the peak tailing present in peaks eluting from nondeactivated columns. DPTMDS persilylation and Ah3P deactivation produces a higher level of deactivation with Ah3P-deactivated microcolumn's response being the best. Figure 3 shows that injection of DIMP headspace vapor is a very sensitive tracer for phosphonate adsorptive sites in the microcolumn compared to *n*-octanol.

The difficulty with the Ah3P coating is that the column does not stay deactivated after the stationary phase is added. Instead, we see evidence of acid and alkali sites in the "deactivated" column. Column test mix results show that freshly coated microcolumn with Ah3P deactivation shows high adsorption activity for *n*-octanol, *n*-decanol, and 2,6-dimethylaniline indicating acid and alkali sites.

We tried several methods to remove the metal impurities. Boiling the devices in acid and similar methods created leaks through the anodic bonds, so the column did not work properly. Among the postcoating treatments, resilylation reduces the phosphonate retentive nature of the column. However, the tailing behavior remains. Heat treatment with PMP shows reduction in DIMP peak tailing and produces a sharp peak profile. It also suppresses the column activity toward octanol, decanol, and dimethylaniline by poisoning the active sites.

We propose that the PMP reacts with the active sites to poison them. FT-IR results indicate that the PMP loses its acidic hydrogen during the treatment of the column. Evidently, the PMP is reacting with the alkali ions and other active sites in the column to poison them for further adsorption.

This result seems to be unique to PMP and other acidic phosphonates. We have also injected DMMP, DIMP, DEMP, or TEP and find that there is no significant improvement of the performance of the column after 10 min. PMP on the other hand, loses a proton and stays in the column. We found that injecting PMP did give good peak shapes for subsequent organophosphonate headspace injections and also the column activity remained suppressed after holding the column at 100 °C with hydrogen carrier pressure of 10 psi for 8 days (our longest measurement).

This suggests that one can extend the method to other difficult systems where conventional deactivation methods do not work. The idea simply is to use a poison to block active sites in a column. Obviously, the poison might change as the impurities change. However, it is likely that the method can be extended to deactivate surfaces in a variety of microsystems

CONCLUSIONS

The results in this article show that it is possible to create a silicon microcolumn with performance that rivals that of a conventional column. We observe 5500 theoretical plates per meter, compared to 4630 reported by Agilent. The deactivation procedure was key to this performance. Test results presented in the article show that Ah3P deactivation renders the nondeactivated column surface more inert to OP and sulfur compounds, compared to persilylation and silylation methods of deactivation. Also, DIMP is a better probe for indicating column activity toward

(63) Aldrich Library of FT-IR Spectra; Vol. 2, (1); p 1560:B.
(64) http://www.chem.agilent.com/Scripts/Generic.ASP?lPage=60009&indcol=N&prodcol=YREF (accessed Jan 28, 2008).

OPs compared to *n*-octanol. Coated columns show activity toward phosphonates, which can be reduced by heat treatment with PMP. Resilylation has a negligible effect on the activity of a freshly coated column toward OP compounds. Commercial column test mix injection shows decrease in column's hydrogen bonding sites of acidic nature with PMP treatment. Application of the findings of this work would render microcolumns to be used in fast μGCs to separate highly active OP and sulfur compounds.

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