Hybrid integration of injector and detector functions for microchip gas chromatography

Abhinav Bhushan,†a,b,c Dawit Yeman,ab Scott McDaniel, b Jost Goettert, a Michael C. Murphyc and Edward B. Overtonb

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Hybrid microchips containing high aspect ratio gas chromatograph (GC) columns with an integrated on-chip split injection and a flame ionization detector were developed. Two different column configurations, spiral and serpentine, both 1 m long by 50 μm wide and 500 μm tall, were fabricated out of electrodeposited nickel. The hybrid chip allowed injection plugs on the order of 1–2 ms, which lowered the height equivalent to theoretical plates (HETP) and allowed a comparison of system level band broadening between the two column configurations. The gas phase band broadening was estimated by measuring the flow characteristics and peak broadening of an unretained compound, and the results were compared with kinetic models. Experimental results show that both spiral and serpentine column layouts had similar flow and band broadening, suggesting that gas phase band broadening may be independent of column layout. The necessity for narrow injection bands for fast micro-chip chromatographic analysis was demonstrated, which emphasized the importance of component integration in designing powerful micro-analytical systems.

Introduction

More than 50 years after Golay demonstrated the higher performance of capillary gas chromatograph (GC) columns over packed columns,1,2 and 30 years since the advent of reliable manufacturing of fused silica capillary columns,3 the field of gas chromatography is poised for another significant innovation, the transformation of GC hardware into the realm of micro-fabricated systems. The recent rise in interest in rapid, on-site chemical analysis for homeland security,4–8 environmental monitoring9–14 and point-of-care medical diagnostics15–22 has prompted the development of several novel approaches toward building GC-based sensors. The primary reason motivating the interest in the micro analytical world is that the current instruments are not well-suited for rapid on-site chemical analysis because of their size and power consumption, which also limits the speed of analysis. Specifically for gas chromatography, recognition that both fast and high-resolution analysis may not be possible is growing.23 This trade-off stems from the reduction of the column diameter increasing separation efficiency, but reducing the flow rate and enabling extra column effects to become important contributors to peak broadening. Portable GCs circumvent this problem to some extent by redesigning the GC using improved manufacturing techniques, mainly to reduce the form and speed factors. However, quite often, in doing so, the instrument functionality is restricted. For instance, while the Agilent 3000 MicroGC and Varian CP-490 Micro-GC are portable and weigh under 20 lbs, they are limited to running isothermal analyses, and have an analytically limited detection limit of around 1 ppm using a thermal conductivity detector.24–26

Newer instruments with resistively heated columns that allow the temperature-programming mode27–32 are promising but their limited speed of analysis, use of consumables, and energy consumption limit their deployment. Following the pioneering work at Stanford on the first microfabricated GC over 30 years ago,33 current ongoing research at universities, national laboratories, and start-up companies presents the exciting possibility for the development of the next generation of microfabricated GC-on-a-chip chemical sensors.24,33–40

Fast GC is typically carried out using a combination of short, narrow-bore capillary columns, hydrogen carrier gas, and fast temperature programming.41–47 However, fast GC analysis on capillary columns can suffer from a lower peak capacity and less efficient separation than that achievable through a slower analysis on the same column. Rectangular cross-section columns have been proposed as an alternative to circular ones to accommodate both high resolution and high flow rates.48,49

Initial attempts to make the rectangular cross-section columns had limited success because the mechanical shaping processes lacked the accuracy necessary to generate tubes of uniform cross-section.50,51 Microelectromechanical systems (MEMS) technology offers more control over dimensional variation for fabricating square and rectangular cross-section columns. The typical approach has been to use wet bulk silicon micromachining.52,53 More recently, deep reactive ion etching (DRIE),54–57 and non-silicon micromachining techniques have also been used to fabricate high aspect ratio (HAR) columns.58,59 The HAR columns are typically 0.5–3 m long, 50–300 μm wide, and 100–600 μm tall, arranged on a small footprint microchip.

Narrow injection plug widths are necessary to increase chromatographic efficiency in fast GC analyses.52 The length, width,
and cross-section of a HAR column influence the shape and size of the sample plug traversing the column and contribute to the separation efficiency. In microfabricated GC systems, the column layout can cause band broadening as well. Squeezing a 1–3 m long column on a few square centimeters microchip footprint leads to convoluted column layout geometries that can influence the flow characteristics through the column and the shape of the injected sample plug. In the work published on MEMS GC columns, there is little agreement as to the best column layout; column layouts have ranged from circular and rectangular spirals to serpentine and corrugated configurations. Since the geometric layout of the column can potentially affect the peak band broadening, it is important to understand and quantify its effect on column performance.

Split injection is commonly employed in both capillary GCs and microfabricated GCs to inject a narrow band sample. In this case, the front end of the column connects directly to the injector. In microfabricated columns, the typical approach is to use circular capillary tubing and small connectors to connect the injector to the microfabricated column, and the microfabricated column to the detector (see Fig. 1a). This process of transferring analytes from the injector to the column head can induce band broadening due to the mismatch between the internal volume of the injector and the column as well as dead volume in the column/injector connections. Moreover, the off-the-shelf splitters and detectors, such as the flame ionization detector (FID), are off-chip, which increases the form factor and contributes to band broadening.

The real strength of MEMS is in realizing a complete analytical system that includes not only the column, but also the monolithic and/or hybrid integration of the injection and detector functions integrated on a single chip. A step was taken towards realizing a ‘GC on a chip’ by on-chip integration of the important connections between the split and the HAR column, as well as an FID make-up and fuel gas with a separation column. Uncoated GC chips were used to demonstrate the influence of column layout on band broadening of high aspect ratio serpentine and spiral column chips. The efficiency of the columns was compared with the theoretical kinetic models. The effectiveness of the uncoated GC chips in minimizing peak broadening due to gaseous flow disturbances and extra column effects was addressed, while other issues such as stationary phase coating and its effect on separation will be presented in a future manuscript.

**Experimental**

**Column design**

One meter long, 50 μm wide by 500 μm tall high aspect ratio column tubes were laid out in an ~2 cm² chip area. Two types of columns were designed, one with the channels in a serpentine configuration, and the other where the channels were arranged in a double spiral in/spiral out configuration as is shown in Fig. 2. In addition to the separation column, the GC chip contained two wider channels running perpendicular to the column inlet and outlet (see Fig. 1b and Fig. 2). The column runs from points A to D, the on-chip split occurs at point A, and the split flow is regulated by an off-chip needle valve at vent point B. The FID fuel makeup gas is introduced at point C to mix with the column effluent and provide non-diffused combustible mixture to the FID tip at point D. The analytically important connections at the injector and detector ends of the HAR column are included in the GC chip design.

**Column fabrication**

The columns were fabricated using X-ray LIGA (lithography, electroplating, molding) through a process that has been

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Fig. 1 (a) Microfabricated GCs typically have external connections going from the injector to the column and from the column to the detector that lower column performance due to the increased dead volumes and flow disturbances. Gas supply to the detector is made externally directly to the detector assembly. (b) Illustration of a representative column layout for a serpentine column chip that, by incorporating the critical analytical components on the chip, reduces the number of external connections and improves performance. The spiral GC chips have a similar layout except for the different column geometry.

Fig. 2 Micrographs of the nickel spiral and serpentine columns. The columns are 50 μm wide, 500 μm tall, and 1 m long. The design includes on-chip split and detector fuel gas ports.
described in detail elsewhere. Briefly, to fabricate the X-ray mask, an optical photomask containing the column design was used to lithographically pattern 12 μm of SPR-220 photoresist (Rohm and Haas, Marlborough, MA) on a silicon wafer with a 2 μm thick layer of low stress PECVD silicon nitride (DIMES, Delft, The Netherlands). Gold (Technic, Cranston, RI) was electrodeposited into the developed pattern to a thickness of 10 μm forming the absorber pattern. A backside etch was performed in a 30% KOH solution to remove the silicon, leaving the gold pattern suspended on the silicon nitride membrane.

The patterns on this X-ray mask were transferred into a thick, high molecular weight poly(methyl methacrylate) (PMMA) (Vistacryl, CQ, Vista Optics, Widnes, UK) resist using X-rays from a CAMD bending magnet source. The PMMA disks were bonded to silicon wafers coated with a thin layer of oxidized electron-beam evaporated titanium. After exposure, the resist was developed in alternating cycles of developer and rinse solutions, rinsed in deionized water, and immediately immersed in a nickel sulfamate electrodeposition bath. Nickel was electrodeposited at a constant current density of 10 mA/cm² to fill the resist mold and plated over the resist to seal the top of the columns. The overplated layer was planarized to a ±5 μm end-to-end thickness variation on a GC chip using 10, 5, and 1 μm diamond particle slurries in sequence on a Hyprez lapping system (15LM-115V, Engls, Wheeling, IL). After etching the silicon substrate to release the columns, nickel was electrodeposited on the etched surface to seal the other side of the column chips. The encapsulated PMMA resist was removed by heating the columns slowly over a period of 4 h to 450 °C. The pneumatic connections to the GC chips were made by attaching thin walled 0.016” O.D., 0.012” I.D. stainless steel capillary tubes (Small Parts, Miami Lakes, FL) to the GC chips using JB Weld, a polyamide-based epoxy (JB Weld, Sulfur Springs TX).

**Apparatus**

A commercially available microFAST GC (MFGC, Analytical Specialists, Inc., Baton Rouge, LA), was modified to conduct experiments using the microfabricated GC chips. All of the flows and pressures, except the split flow needle valves, were controlled through the MFGC electronics and were accessible via a dedicated microcomputer data processing system. During the sample loading cycle, an atmospheric pressure gas sample of natural gas was injected into the 2 μl sample loop of a 10-port diaphragm valve (VICI, Houston TX) that connected ports 2 and 6 of the injection valve as shown in Fig. 3. During loop loading, a continuous flow of the carrier gas, hydrogen, was maintained to the GC chip. Upon actuating the diaphragm valve for 200 ms, hydrogen was diverted through the sample loop, via ports 4-3-6-5, to inject a part of the sample loop volume into the GC chip.

**Fig. 3** (a) Schematic of the experimental setup used to test the GC chips. A microFAST GC was modified to incorporate the MEMS columns instead of the capillary columns, and include a diaphragm valve sample loop injector. The two configurations shown are for loading the sample loop and injecting the sample into the column. (b) A close-up view of the pneumatic connection and the on-chip FID with an external collector electrode.
This narrow plug was further split between the column and injector vent using the on-chip split. The width of the plug injected onto the high aspect ratio column was estimated to be 1–2 ms wide when using split flows above 200 ml/min. When the split flow vent valve was fully open, vent flow rates of 30 sccm at 20 psi source pressure and 400 sccm at 50 psi source pressure were obtained. For measurement of the peak widths, the concentration of the methane in the gas sample was adjusted to give a methane peak height that was between 30% and 80% full scale regardless of the vent flow. All retention time and peak width measurements were done in duplicate with selected data points run in triplicate. Error bars in the data represent a 95% confidence level.

An on-chip FID complete with the makeup and fuel gases was integrated on the GC chip. As shown in Fig. 3b, hydrogen gas was connected to the makeup gas port of the GC chip (‘C’ in Fig. 1b) to sweep the eluting compounds into the FID tip and provide hydrogen fuel to support combustion at the tip of the detector at the outlet end of the on-chip column. The hydrogen flame at the tip was burned using room air as the oxidizer that was available in the ambient air environment around the small FID tip. The body of the FID tip was used as the negative electrode for the detector, and a conductive wire loop, positioned around the outlet flame tip, served as the anode, floating at 230 V DC above ground (Fig. 3b).

Materials and procedures

House natural gas, which was approximately 98% methane, was used in all of the experiments. Hydrogen was used as the transport gas since an optimum HETP (Height Equivalent to Theoretical Plates) can be maintained for a wider range of operating pressures.65 Further, since hydrogen is needed as a detector fuel, its use as the carrier and detector fuel eliminates the need for two compressed gas sources. Chromatographic data acquisition from the FID was provided by a 24-bit, 1 kHz A/D electrometer board, which was interfaced to a laptop computer using software developed in-house. Peak widths and retention times were manually measured in duplicate from the chromatographic data using the MFGC’s data acquisition software, and all calculations were performed using Microsoft Excel 2007 (Redmond, WA). Flow rates were measured with a digital flow meter (Model 6000, Restek, Bellefonte, PA) and automatically converted to sccm by the flow meter.

Results and discussion

A hybrid platform using a commercial valve with an integrated on-chip split to produce narrow injection peaks of the order of 1–2 ms was developed. The platform was used to compare the band broadening in two configurations of microfabricated columns: spiral and serpentine. There have been relatively few studies of gas phase band broadening in GC columns,66 and no studies of microfabricated devices. If flow disturbances produce broad peaks, irrespective of liquid phase coating efficiencies, the ultimate column separation efficiencies will be limited, constraining use of the micro-chip columns for high resolution separation of compounds in complex mixtures. The overall efficiency of a GC column depends on the size of the analyte plug, at injection and at the outlet. The peak width of the analyte plug is directly responsible for the efficiency of the column or HETP. The HETP, a measure of the efficiency of a gas chromatograph column separation system, is calculated from the retention time, \( t_0 \), of an analyte peak or the holdup time of an unretained peak, and the peak width at half height, \( w_{1/2} \), as is shown in eqn (1), where \( l \) is the column length. The HETP \( (H) \) is represented as a cumulative measure of band broadening as an infinitely narrow ideal plug travels from the inlet of the column through the detector as a function of the average carrier gas velocity, \( u \),66,68,69,99 and can be calculated from the general expression as shown in eqn (2). The first term on the right hand side of eqn (2) describes band broadening due to longitudinal diffusion as analytes move through the column, the second term accounts for band broadening due to interaction of the analytes with the mobile phase in the columns, and the third term represents the interactions between the analytes and the liquid phase of the column.

\[
H = \frac{l}{5.54} \left( \frac{w_{1/2}}{t_0} \right)^2 \quad (1)
\]

\[
H = \frac{A}{u} + B\bar{u} + Cu \quad (2)
\]

To test the effect of column geometry on column performance independent of coating issues, methane was used as the unretained species. The GC chips were tested with many different test bed designs and connector configurations in an effort to minimize the influence of the testing apparatus on peak width measurements. When determining flow disturbances using an unretained peak with short 1 meter long HAR column chips, the ability to deliver narrow injections to the GC column was found to be the most significant contributor to gauging column performance. This has significant implications for evaluating the performance of microchip GC columns compared to theoretical predictions. If injected plugs are too broad, the HETP measurement, meant to measure column efficiency, will be obscured by the extra column effects at the injector. If the injected plug does not meet this requirement of being an ‘infinitely narrow’ plug, the HETP values will be larger than those calculated from chromatographic theory and an additional term will be required in eqn (2) to represent the broadening of the finite volume of the gas plug.66 Through this setup, 1–2 ms injected plugs were achieved, which made an insignificant contribution to the overall HETP, allowing the evaluation of contributions from other sources, such as column geometry, to band broadening.

Many different models have been proposed to estimate the HETP for high aspect ratio rectangular cross-section columns, starting with Golay,49 followed by a modified model proposed by Spangler,48 and progressing to a more sophisticated mathematical model by Ahn and Brandani that incorporated the effects of adsorptive capacity in the coated corners of the channel.44 Spangler proposed a modification to Golay’s model with changes to coefficients \( A, B, \) and \( C \) of eqn (2).99 Table 1 compares the coefficients in all three models modified for an unretained analyte, such as methane. These models do not account for the column layout configurations, and would predict the HETP...
values based solely on column dimensions (length, width, and height) at various flow velocities. The experimental HETP values for 1 meter, 50 μm by 500 μm GC chips values were estimated by measuring the measured peak width at half height, \( w_{1/2} \), and the holdup time, \( t_0 \), and using eqn (1). The influence of on-chip split flow on column performance was studied as was the variation in performance due to changes in the column head pressure. The experimental HETP observations for the spiral and serpentine column configurations were compared with the values predicted by the Golay, Spangler, and Ahn and Brandani models.

### Influence of split flow on column performance

The split flow was regulated by adjusting the needle valve at point B in Fig. 1b to obtain the desired vent flow rate. Two sets of experiments were performed: (1) an open split vent that allowed variation of the split flow by adjusting the inlet pressure; and (2) a constant split flow of 30 sccm maintained for all inlet pressures. The variation of the average carrier gas velocity with the source pressure for the two column configurations and two split flow conditions is plotted in Fig. 4. An increase in the source pressure led to a corresponding increase in the column head pressure, which increased the average carrier gas velocity, and reduced the holdup time independent of the split flow. However, as shown in Fig. 4, reducing the split flow rate at a particular source pressure caused a decrease in the column head pressure, which reduced the average carrier gas velocity and increased the holdup time at the constant source pressure. These results demonstrate the potential flexibility of the setup with two different approaches for modulating the column holdup time: one by increasing the source pressure that provides a larger operating range for laboratory conditions, and the other by modulating the split flow rate at a constant pressure which may be an option for gas discharge from a portable source for in-field analytical applications.

The variation of HETP for the two columns under a split flow of 30 sccm is plotted in Fig. 5. The two column configurations, spiral and serpentine, have very similar HETP values, suggesting that the column layout on the chip does not significantly influence gas phase band broadening. However, in each case, the HETPs increase at high pressure drops across the columns. For high pressure drops across the column (Fig. 1b), the inlet volumetric flow is significantly lower than the outlet volumetric flow because of the compressibility factor. Consequently, the width of the injection plug is relatively wider for higher than for lower pressure drops, increasing the HETP for high volumetric flows. Therefore, the HETP increases at high pressures are a function more of injector effects than column effects.

### Table 1

Coefficients from the Golay, Spangler, and Ahn and Brandani models corresponding to the variables \( A, B, \) and \( C \) in eqn (2) for the flow of unretained species, i.e., the retention factor = 0. Here, \( D_g \) is the gas phase binary diffusion coefficient, \( b \) is the column half-width, \( D_s \) is the solid phase diffusion coefficient, \( l \) is the column length, and \( a \) is the column aspect ratio, defined as the ratio of the column height to the width.

<table>
<thead>
<tr>
<th>Model</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Golay</td>
<td>( 2D_g )</td>
<td>( \frac{0.9}{96} \frac{4b^2}{D_s} )</td>
<td>0</td>
</tr>
<tr>
<td>Spangler</td>
<td>( \frac{0.9}{96} \frac{4b^2}{D_s} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahn and Brandani</td>
<td>( \frac{1}{105} \left( \frac{2a^2}{(a + 1)^2} \right) \frac{4b^2}{D_s} )</td>
<td></td>
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</tr>
</tbody>
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![Fig. 4](image-url) Variation of the average carrier velocity with source pressure for (a) spiral and (b) serpentine columns compared for two cases – open split and split flow set to 30 sccm.

![Fig. 5](image-url) Variation of HETP with average carrier velocity for spiral and serpentine columns for a split flow of 30 sccm.
Influence of pressure drop on column performance

In this case, the needle valve was set at a fixed resistance allowing for a vent flow at all source pressures. The inlet pressure was varied from 20 to 80 psi, and the retention times and peak widths at half height of methane were recorded. In Fig. 6, the HETPs for the two column configurations are displayed as a function of average carrier gas velocities. The experimental HETP values were compared to the calculated values using the Golay, Sanger, and Ahn and Brandani models, corrected for unretained compounds, $k = 0$, as shown in Table 1. The experimental data closely fits the models, suggesting that the losses in the GC chip are minimal. Furthermore, the data in Fig. 6 show that both the spiral and serpentine column configurations have a similarly shaped Golay plot, and similar minimum values, establishing that the column layout configuration does not significantly influence band broadening for these configurations. Moreover, the close fit between the experimental and theoretical HETP suggests that the band broadening due to extra column effects, as well as the influence of the experimental test bed, have been minimized in this hybrid design. The results are important because the injection with the test apparatus results in an effectively ‘narrow’ injection plug. This injection of an narrow plug allowed measurement of gas flow efficiencies through the GC chips that showed no significant broadening due to the on-chip connections, the column layout, and the rectangular configuration fabrication process.

To date, most micro-chip GC research has focused on the development of microfabricated GC columns, and the testing of these columns has been performed with conventional GC hardware.33-40 The use of conventional GC hardware to test microfabricated columns by themselves does not allow for detection of the inefficiencies caused by the microfabricated system components such as the injector or detector. The over-riding importance of the injector bandwidth considerations compared to column configuration issues when designing microfabricated GC instrumentation was clearly demonstrated. Additionally, the impact of dead volumes from connecting circular tubing to rectangular cross-section columns was shown to cause negligible band broadening when critical connections at the injector split and detector have been designed into the GC chip. System integration issues such as this will be important to overall instrument design if very small GC sensor-type instrumentation is to become a reality.

The widths of the injection peaks are determined by the extra column effects in the injection system. For non-ideal injections, the observed band broadening was not substantially caused by flow issues within the column. Examination of Fig. 5 and Fig. 6 indicate that an increase in the split flow generally leads to a lower HETP due to the injection of a narrower plug. Further, under the open split condition, the HETP curve has a relatively shallow slope. This may result from the injection of very narrow bands entering the head of the column regardless of the column head pressure when using high split flows as opposed to any effect from band broadening in the column itself. However, a shallow HETP curve is advantageous for maintaining efficient performance over the wider range of operating conditions that may be encountered in on-site analysis.

Conclusions

Microfabricated GC chips with integrated sample injection, column, and flame ionization detector functions were prepared. The GC chip columns were 50 μm wide by 500 μm tall by 1 m long and arranged in both serpentine and spiral layout configurations. The band broadening of the sample plug was studied by observing the HETP of the unretained gas flow through the column chips. Within the measurement accuracy, there was no significant difference between the performance of serpentine and spiral column layouts. The system-level losses were minimized by integrating the critical functions of the injector split and the detector on to the chips, which allowed performance of the columns to approach that predicted by theoretical models. These results show that system integration of the complete GC system, including injector and detector functions are essential for high resolution performance of the microfabricated GC columns. Research is on-going to coat these columns with different stationary phases as well as to evaluate system performance with compounds that are retained by the GC liquid phase.

This lays the groundwork for a more comprehensive computational fluid dynamic model to better understanding of the microflows in different chip configurations, including the effects of the inlet and detector flows. Developing fast temperature programming capability for micro-chip GC columns is also desirable to reduce peak widths of later eluting compounds by lowering the capacity factors as a function of temperature rather than as a function of the injection system.

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