System optimization for realizing a miniaturized gas chromatograph sensor for rapid chemical analysis

Abhinav Bhushan
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SYSTEM OPTIMIZATION FOR REALIZING A MINIATURIZED
GAS CHROMATOGRAPH SENSOR FOR RAPID CHEMICAL ANALYSIS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical Engineering

by
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December, 2006
Dedication

To my wife and friend,
Teesta
Acknowledgements

This journey from my re-joining Graduate School to finishing my dissertation would not be possible without the help and support of many, whom I wish to acknowledge here.

I would like to thank my committee members, Dr. Michael Murphy, Dr. Jost Goettert, Dr. Edward Overton, Dr. Judy Wornat, and Dr. George Stanley for being positive and cooperative. Words cannot describe the guidance and patience of Dr. Murphy. His positive attitude, constant motivation, and far sightedness are unparalleled. Whatever I have achieved today would not have been possible without him. Dr. Goettert provided constant motivation in setting personal goals and provided all of the opportunities for professional and technical developments one can ask for from a supervisor. No one understands gas chromatography better than Dr. Overton does. I am fortunate to have worked with him for the past few years.

I could not have done this without the constant support of my colleagues, Dawit, Sebina, Lena, Khalef, Scott, Andrew, and Arun. Dawit in particular has patiently tolerated me for over five years, been there to offer quick solutions to my silly questions and of course, for the constant supply of trance music. I thank Dr. Joe Simonson at Sandia National Laboratory for shouldering the duties of the principal investigator for the current grant. His goal-oriented approach has been very inspiring. I cannot thank enough Dr. Joshua Whiting at Sandia National Laboratory for patiently explaining me the intricacies of gas chromatography and for sharing the theoretical models. I am indebted to the inspiring tutelage under Dr. Michael Cohn at MicroAssembly Technologies.

I thank the CAMD staff, especially Mr. Craig Stevens for solving all of the administrative issues, Ms. Caryl Boyet for purchasing, and Ms. Lee Ann Murphey for all travel and organizational issues. The support of the CAMD microfabrication staff and Mr. Zhong Geng Ling for X-ray exposures is appreciated. This journey would not be possible without the support of
my friends Datta, Vikram, Mayank, and their families who have always been there for me since my arrival to the United States.

Getting this far would not be possible without the strong support from my family. They have patiently encouraged my decisions and I am glad things have worked out positively. Teesta’s high energy level and constant motivation was a big factor in my being able to devote large amounts of time towards achieving my goals. Finally, I thank financial support from the National Science Foundation EPSCoR, Johnston Science Foundation, and Defense Advanced Research Projects Agency (DARPA).
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Abstract

Rapid and comprehensive on-site analysis of chemicals in applications ranging from industrial process control to homeland security is of significant importance to improve the environment and save human life. The need for sensors that are fast, reliable, and portable has never been greater. For the challenging task of on-site instrumentation, where power sources can be limited, shrinking the size of the device is the most effective way to conserve power. Although gas chromatography is a mature technique well suited for these applications, current instrumentation has deficiencies that limit its usage. Speed of analysis and non-portability are severe hindrances to using the bench top and portable instruments for on-site applications. This focus of this research is to provide a transition from a portable gas chromatograph (GC) instrument to a handheld GC sensor.

The significant issues for realizing a handheld GC sensor were addressed. One important design criterion was that the sensors have the same analytical capability as a commercial GC instrument. Of the many components of a GC, the separation column primarily defines the resolution and the analysis time. Thorough theoretical analysis led to the conclusion that high aspect ratio, rectangular cross-section columns have a distinct advantage over capillary columns. A column including an on-chip sample loop and a makeup gas manifold were designed. Previously reported attempts to fabricate rectangular columns have focused on low aspect ratio or square cross-section columns. Contrasting all prior efforts, significant strides in process development were made to realize nickel GC columns using the LiGA technology with aspect ratios as high as 20. Through process control, a device yield of over 90% was achieved. Tests on these columns yielded more than 20,000 plates for unretained species. Four hydrocarbons were separated in less than 2 s at 100 °C on a 50 μm wide by 600 μm tall by 0.5 m long coated LiGA column. For the first time reported, 2-D GC was implemented using MEMS columns.
1 Introduction

Rapid and comprehensive on-site analysis of chemicals in applications ranging from industrial process control to homeland security is of significant importance to improve the environment and ensure a better life. A gas chromatograph (GC), often-termed “a needle in a haystack” instrument [1], is one of the most widely used analytical devices, with applications in the chemical process industry, oil exploration, environmental monitoring, purification of substances, and general organic compound analysis. Apart from these traditional uses, GCs are playing an important role in the detection of chemical warfare agents, the detection of diseases [2], and even in quality control of coffee beans [3]. Industrial process control is one of the big industrial applications of a GC, with the instruments in the chemical plants continuously monitoring chemical processes and contributing in quality control. The combination of a GC and a mass spectrometer can identify, qualitatively and quantitatively, constituents of samples.

While credit for discovering gas chromatography is disputed [4], from the discovery of chromatography in the early 1900’s to the first use of packed GC columns to the emergence of capillary GC, a tremendous amount of work has gone towards advancing the technique [5, 6]. For their work in developing partition chromatography to separate amino acids, Martin and Synge won the Nobel Prize in 1952. Introducing gas liquid chromatography, Martin and James performed separation on a stationary liquid phase coated on an inert support with a gaseous mobile phase, giving rise to the packed bed column. The analytical power of this technique is illustrated in the chromatogram shown in Figure 1-1 [Agilent Technologies, Santa Clara, CA]. In this example, a standard GC instrument, 5973 GCD [Agilent Technologies] was used to analyze a broad range of volatile organic compounds (VOCs). A typical GC consists of an injector, a separation column, a detector, and electronics for control and data processing. The peaks show different compounds present in the sample, the x-axis shows the absolute time when the
compound eluted from the column and the y-axis shows the relative magnitude of the analytes present in the sample.

1.1 The Need for Portability

After mass spectrometers, GCs are one of the most reliable and versatile analytical instruments. The reliability is due to the large dynamic range of a GC, which means that GCs can analyze a large group of chemical compounds without much instrumental modification. The primary industrial uses of GCs are in the chemical manufacturing industry, for environmental analysis, and oil exploration. The type of GC instrument used depends on the application. A look at Table 1-1 identifies the important specifications for various applications [7].

**Fast Chromatography—60 VOC Compounds**

1. Trichlorofluoromethane
2. 1,1-Dichloroethene
3. 1,1-Dichloroethane
4. Benzene
5. 1,2-Dichloropropane
6. Toluene
7. 1,2-Dibromoethane
8. o-Xylene
9. 1,4-Dichlorobenzene
10. Naphthalene

![Chromatogram showing analysis of 60 volatile organic compounds](image)

**GC:** 5973 GC
**Sample:** 10 ml split (ratio 40:1)
**Carrier:** Helium, 0.65 ml/min constant flow
**Column:** HP-624, 25 m x 200 μm x 1.12 μm, (Part No. 19091V-402)
**Injection:** HP 7695 Purge & Trap
**Oven:** Temperature program shown above

**Figure 1-1:** A chromatogram showing analysis of 60 volatile organic compounds obtained on the HP 5973 GC (Agilent Technologies).
Table 1-1: Desired specifications for various analyses suitable for a GC [7].

<table>
<thead>
<tr>
<th>Analysis type</th>
<th>Analysis time</th>
<th>Sensitivity</th>
<th>Peak capacity</th>
<th>Compounds</th>
<th>Additional critical spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental</td>
<td>2-10 min</td>
<td>ppb</td>
<td>100</td>
<td>C₂ to C₃₀</td>
<td>Power, portability</td>
</tr>
<tr>
<td>Oil and gas</td>
<td>5-15 min</td>
<td>ppm-ppt</td>
<td>50-100</td>
<td>C₁ to C₂₀</td>
<td>Size, power</td>
</tr>
<tr>
<td>Breath analysis</td>
<td>1–3 min</td>
<td>ppb-ppt</td>
<td>100</td>
<td>C₂-C₂₀</td>
<td>Cost</td>
</tr>
<tr>
<td>Process monitoring</td>
<td>.5 to 1 min</td>
<td>ppt</td>
<td>50</td>
<td>C₁ to C₁₀</td>
<td>Size, Power, Cost</td>
</tr>
<tr>
<td>Warfare agents</td>
<td>&lt;10 sec</td>
<td>ppt</td>
<td>50-100</td>
<td>C₁-C₁₂</td>
<td>Size, power, portability</td>
</tr>
<tr>
<td>Space applications</td>
<td>&lt;1 min</td>
<td>ppt</td>
<td></td>
<td>C₂ to C₃₀</td>
<td>Size, power, portability</td>
</tr>
</tbody>
</table>

For instance, to control the process in a chemical manufacturing plant, real-time feedback is desired. In the case of monitoring pollutants in the air, most of the sampling will involve long periods and will not necessarily require real-time feedback. For homeland security applications, it may be desired to have a two-tier response – a fast yes/no signal to mobilize the first responders on a possible threat, and a slightly delayed, more detailed signature of the involved chemicals for appropriate countermeasures [8]. Significant savings in time and money in oil exploration will result if a quick yes/no answer can be obtained from an instrument in oil wells. The current practice is to drill a hole, collect samples, bring them to the lab, and analyze them. The time involved can be shortened by having a quick in situ analysis, to help identify potential drilling sites. Space exploration is another potential area where a portable GC will have a big impact. The high cost of sending deep space missions has led NASA and other space agencies to play it safe with well-proven technologies. For example, the Cassini-Huygens gas chromatograph-mass spectrometer probe with three GC columns weighed more than 17 kg and consumed an average power of 41 W [9]. The GC, which collected atmospheric data during the descent, could not be used any further since it was destroyed on landing due to the high inertial
impact. Certainly, after making a decade long journey, one would expect the sensors to survive longer than a few hours. The main limitation of using mass spectrometers is that they need vacuum pumps for operation, so they remain bulky and power hungry [10, 11, 12]. Mass spectrometers will have limited on-site/portable applications until the development of a high performance micro vacuum pump.

One common theme amongst all of the applications is the large range of compounds to be detected and the short analysis time. Additionally, to be used in the field, the “GC sensor” should be small, weigh less, and operate on very little power. For civilian responders, a reliable low false positive, high false negative analysis is extremely important to mitigate fear and panic. Moreover, the instrument will have to be small, providing immediate information, and use limited consumables.

1.2 Historical Background on Fast GC Efforts

The chromatogram in Figure 1 shows the current state-of-the-art. The current gas chromatography systems, such as the one above or the HP 6890 series GC (26”x20”x18.5”), are bulky (weight > 100 lbs), slow (30-120 minutes per analysis cycle), laboratory based, and too costly to be used on-site for chemical process and environmental monitoring and for remote operation in remote and hostile environments. As another example, the Clarus 500 Gas Chromatograph (Perkin Elmer, Wellesley, MA) is widely used for EPA analysis and collection of compounds ranging from C$_2$-C$_{20}$. The instrument uses a flame ionization detector (FID) to detect volatile organic compounds (VOCs) and has the option of using a mass spectrometer for detailed analysis or for NOx detection. This instrument takes up to 120 minutes per analysis cycle, consumes up to 3 kW per cycle, and needs a 120 V power supply for operation and is certainly not portable.
Although current needs for on-site analysis are greater than ever, the fascination with fast gas chromatography is not new. The credit for the first fast chromatogram goes to Golay, who demonstrated separation of five analytes – air, acetone, carbon disulfide, methanol, and methylene chloride in less than 10 seconds [13]. A breakthrough bigger than the fast separation was the manner in which it was achieved: instead of using the packed columns commonly available at that time, Golay used a 32 ft long, 254 μm diameter thin film capillary column under a head pressure of 15 psi. The use of these capillary columns was a revolutionary concept, which significantly improved the separation efficiency while reducing the analysis time as compared to packed bed columns. Using capillary columns, Desty separated isometric heptanes in under a minute [14]. At around the same time, Scott et al. separated five compounds in five seconds using a 2.75 m long column [15]. The other significant development in capillary GC came through the development of fused silica capillary columns [16]. Before that, the use of glass and metal columns for capillary GC had serious limitations. The metal columns were too chemically active for polar compounds, while the glass capillaries were too fragile. Almost all of capillary GC nowadays takes place on the easy to deactivate and flexible fused silica columns.

Since the beginnings of fast separation by Golay, efforts have continued to reduce the chromatographic analysis time. In 1982, four straight chain hydrocarbons C1-C4 were separated in 150 ms on a 32 mm by 1.19 mm packed bed column at 150 °C [17]. Under turbulent flow conditions, separation of four compounds (straight chain C5-C7 and toluene) on a 5 m by 0.32 mm column with a 120 nm stationary phase (film) was conducted under a pressure of 50 bar [18]. Another fast analysis on 1 m by 50 μm capillary column with a 50 nm film, separating benzene, toluene, and m-xylene in 1.9 seconds yielded good results [19]. Desty demonstrated rapid separation of 15 components mixture in 2 seconds on a 1.2 m long column [20]. The most common approach for fast chromatography is to use short columns - typically less than 1m long.
An advantage of using short columns with a high linear velocity is the significant lowering of elution temperatures [24]. The use of an ultra narrow bore 5 m by 50 μm capillary column with a 0.05 μm film was reported for very fast separation of complex hydrocarbon fuel samples [25].

These results point to the fact that fast GC is possible, but two distinctions should be made. Firstly, most of the above results are on laboratory instruments, which are not amenable for on-site applications. Secondly, fast GC using narrow bore capillary columns is not necessarily high resolution GC. Fast GC analysis typically suffers from lower peak capacities and resolution than slower analysis on the same column. The resolution of a circular capillary increases with decreasing column diameter, which translates into increased analysis time. Since the gas flow rate through the column is inversely proportional to the fourth power of the column diameter, reducing the diameter, for most practical purposes, limits the flow rate through the column, increasing analysis time. As such, most applications use capillary columns of 100 μm diameter or more. Comprehensive 2D gas chromatography is one way to improve resolution by incorporating two columns in series [26]. The instrumentation for such a setup is quite complex and certainly not suitable for sensor applications in the current form. As an alternative to using capillary columns, Golay and Spangler suggested that high aspect ratio rectangular, cross-section GC columns offer the potential for high resolution, governed by the narrow dimension, and high carrier flow rates governed by the wide dimension [27, 28]. Rectangular columns have an additional degree of freedom such that the column resolution and the analyte volume flow rate can be tailored independently.

1.3 The Quest for a Micro GC Sensor

Current GC instrumentation can be divided into three groups: bench top instruments, like the HP 6890 and Clarus 500 GC; portable GCs like the ones developed by ASI [29], Wanekaya
Dziuban [54], and others; and micro GC sensors like those developed by SLS Microtechnology, Z-nose, and C2V, which are primarily in the developmental stage. A small, fast, dual column GC developed by ASI Limited uses conductively-heated, dual narrow bore columns, a solid sorbent trap injector, and dual FIDs, to achieve very rapid temperature programmed GC analysis of volatile and semi volatile compounds in an instrument configuration that uses less than one square foot of bench space [29, 30]. Identification and detection of VOC’s using a GC-multi array polymer sensor detector was demonstrated by separating a mixture in a GC column and using multi-array polymer sensors for detection [31]. The polymer sensor array consists of polypyrrole, a conducting polymer, which was sensitive to a wide range of vapors. The system compared well to a conventional GC-TCD system. A mixture of methanol, 1-pentanol, and 1-heptanol was separated in under 300 seconds using both the instruments. A field GC-MS analyzer containing a concentrator-thermo-desorber (CTD), magnetic sector mass spectrometer, and a multi-collector ion detector was shown to screen toxic substances in air in about 100 seconds [32]. The CTD is a thin-walled metal tube which can be flash heated to introduce a narrow sample plug (<1s) into the column. The rapid heating also minimizes thermal decomposition of the analytes. The heated sample was led into a mass spectrometer for mass based analysis. Sarin (125 m/z), soman (126 m/z), mustard gas (158 m/z), and VX (114 m/z) were separated in about 100 seconds. Fast screening of tributyl phosphate at low parts per trillion in air was also demonstrated at a frequency of one sample/min.

The portable GC analyzers are still large for on-site applications because they use conventionally manufactured components, their size, weight, and power consumption are often serious limitations to true portability. With the use of MEMS (Micro Electro Mechanical Systems) technology, the concept of analysis-on-a-chip can be realized. Having a small sensor also enables interesting and conveniently applicable concepts for 2D GC (shown in Chapter 5). The one
notable aspect of these bench top instruments is that they produce a high resolution analysis. To be effective, it is extremely important that all future portable and micro GC instrumentation maintain the analytical integrity of analysis. To achieve this, the primary functional units of a GC instrument will have to be redesigned.

1.3.1 Injectors

Since the total analysis time of a high-speed chromatograph can be very small (< 1 second), in order to have a high chromatographic resolution, the peak width should be extremely narrow (of the order of 1 ms). Researchers at the University of Washington reported extremely narrow injection widths of the order of 1-5 ms using a synchronized dual valve injection arrangement, which resulted in peak widths of less than 10 ms and total analysis time of less than 400 ms [33]. Chromatographic analysis of 15 compounds in less than 5 seconds was shown by using a diaphragm valve-based rapid injection system and conventional short capillary columns with very high carrier flow velocities [34]. The diaphragm valve provides small injection pulses, which, when passed through a 2 m, 180 µm diameter capillary column, gives the spectra of separated components in ~ 5 seconds. This method was good for separating simple mixtures; for complex mixtures, the partially separated compounds (overlapping peaks) were further analyzed using chemometric tools. These techniques to produce a narrow injection plugs utilize exotic arrangements of valves with high pressure gas supplies, things which may not be available in the field.

1.3.2 Detector

GC detectors can be either universal or be compound specific. The Thermal Conductivity Detector (TCD), Flame Ionization Detector (FID), Helium Ionization Detector (HID) are examples of universal detectors, while Nitrogen Phosphorous Detector (NPD) (selective for compounds containing nitrogen and phosphorous) and Flame Photometric Detector (FPD) (for sulfur
containing compounds) are compound specific detectors [35]. Apart from the selectivity, the response time and the dynamic range characterize detector performance. For minimum peak distortion, the detector response time should be at least one order of magnitude faster than the width of the eluting peak. Equation 1-1 gives the detector response time in which the peak distortion is less than 1%. For a retention time, of 0.5 seconds and 3000 plates, a detector response time of 9 ms is required.

\[ R_t = \frac{t_r}{\sqrt{N}} \]

The dynamic range of a detector is the concentration range over which the detector elicits a measurable (S/N > 3), generally linear response.

Being one of few miniaturized detectors, the TCD is one of the most commonly available non-selective detectors capable of detecting ppm concentrations. New class of detectors such as Surface Acoustic Wave (SAW) devices [36, 37, 38, 39, 40] and carbon nanotubes based ionization detectors [41] offer promise of miniaturization and integration with columns. In a SAW device, the shift in the resonant frequency of a vibrating MEMS element when analyte molecules adsorb over the coated surface is measured and is a characteristic of the analyte. While miniaturized SAW devices are sensitive in the attogram range [42, 43], their main drawbacks are that they are non-selective and difficult to coat. Coating the SAW devices is necessary to make the sensor chemically selective; without coating, it remains only a mass sensitive, non-selective detector. If selectively coated, potentially an array of hundreds of SAW devices can help in parallel detection of compounds in a multi-dimensional detector capacity, which will reduce the false positives [44]. Actually, in such a case, the SAW array may act as a standalone sensor, foregoing the need for a separation column. Of course, the limitations in making this feasible are the difficulties in addressing the individual SAW devices in the array.
during coating and the elimination of cold spots and associated dead volumes on the SAW device package. Further, if a SAW device is used in series with a GC, the adsorption-desorption cycle should have a time response of the order of the time between two consecutive eluting GC peaks. Being a slow process, surface adsorption limits the performance and sensitivity of the SAW device [45]. Since the FID has sub-millisecond response times, has a large dynamic range, and is relatively easy to implement, it was selected to be used in this research.

1.3.3 Column

The column is the most critical component of the system, defining the resolution and the analysis time. Since the late 1970’s, MEMS technology has long been deemed applicable to developing GC columns [46]. Most of the development has been geared towards improved columns. The driving factor to build MEMS GC columns is the fact that a very high driving pressure is required to obtain a high resolution separation from a capillary column. Theory developed half a century ago suggests using rectangular cross-section columns instead of capillary columns, where the column width will govern the resolution while the volumetric flow rate will be determined by the cross-sectional area of the rectangle [27, 28].

Researchers at the University of Michigan [47, 48] have achieved 1000-3000 plates/m using 3 m long, 150 μm wide, and 240 μm tall columns. These columns, fabricated by deep reactive ion etching (DRIE) of silicon, are arranged in a square spiral pattern on a 3.2 cm square silicon substrate. Isothermal separation of 20 compounds (methanol to butyl acetate / chlorobenzene) was performed in 4 minutes by using hydrogen carrier gas and in 10 minutes by using air carrier gas. By temperature programming, both, the separation time and the peak capacity showed significant improvement. Interfacing the microfabricated column with a microfabricated differential mobility spectrometer enables detection of both positive and negative ions in a single experiment [48]. Ultrafast chromatography using 100 μm wide by 100
μm deep by 50 cm long silicon micromachined columns coated in situ with chemical vapor deposited carbon nanotubes was shown to separate straight chain alkanes, C₆⁻C₁₀, in under one second isothermally (140 °C) and with temperature programming (60 °C/s) [49]. The slow adsorbing desorbing characteristics of the nanotubes and the fact that the nanotubes covered only one column wall limited the performance of the column (broad peaks). Much discussions have centered on the ability to coat these very narrow columns and the effects of the flow dynamics on the column’s Height Equivalent to a Theoretical Plate (HETP) associated with the square ends of rectangular columns [50, 51].

1.3.4 Micro GC Instrumentation

A few efforts using MEMS components for GCs have been commercialized. A handheld MEMS-based GC analyzer board, GCM 5000, developed by SLS Micro Technology (Hamburg, Germany), can analyze ppm levels of permanent gases [52]. The GC sensor uses an electromagnetic valve injector, a silicon micromachined column, and a MEMS TCD (Thermal Conductivity Detector) as the primary components, integrated with COTS fluidic and electronic modules on a printed circuit board. Another handheld GC, developed by C2V incorporates a conventional narrow bore capillary column, integrated with MEMS micro valves, and a MEMS micro-TCD [53]. The assembly was in a 4” by 6” package, called the microDelta platform, with provisions for fluidic and electrical connections. The detection sensitivity is at ppm levels, with a maximum operating temperature of 200 °C, and analysis mainly under isothermal conditions. This sensor was suitable for primarily analyzing volatile compounds. Another portable GC with MEMS components was shown to separate compounds in 400-700 seconds using a silicon micromachined injector, a capillary column, and a double TCD [54]. The results of this unit compare well with the conventional GC analyses. A portable GC consisting of a direct resistively heated stainless steel column coated with polysiloxane and a SAW detector was used for
analyzing explosives and chemical warfare agents [55, 56]. The Z-nose instrument uses a 1 m long column and reported analysis time of 10 seconds with $20^\circ$C/s temperature programming rate. Since the SAW is a nonspecific detector, a components library was used to obtain the correlation between elution time and the shift in the resonance frequency.

One of the most advanced miniaturized GC instrument is the MicroChemLab System developed at Sandia National Laboratories. The optimized handheld sensor monitors low concentrations of dangerous gases in public areas in real-time with a cycle time of about 1 min [57]. The instrument consists of a thin film, membrane-based silicon micromachined pre-concentrator, a silicon micromachined chromatographic column, and a quartz surface acoustic wave based detector array [58]. Each of these components has selective coatings contributing to the selectivity and low false alarm rates of the sensor. The column, operated under vacuum outlet conditions, uses air as a carrier gas. The prototype instrument can detect volatile chemical warfare agents with a very low rate of false position identifications [59].

Figure 1-2: MicroChemLab system developed by Sandia National Laboratories [57].
1.4 Outline of the Dissertation

To develop field portable sensors for future applications, the field of gas chromatography is currently undergoing a new wave of innovations in component design and analysis techniques, driven largely by the micro-manufacturing technologies. The architecture of the primary component, the column, is the most critical development necessary since it controls the analysis time, the resolution, and the overall system efficiency. This thesis addresses design of high resolution, high aspect ratio rectangular cross-section, GC columns; MEMS process development for stable fabrication of these columns; and experimental results. These advanced MEMS columns will be the key component of a handheld GC sensor.

Chapter 1 motivates the development of fast and portable instrumentation. The scientific basis of GC separations is summarized in Chapter 2. Factors affecting resolution and speed are discussed and the limitations of the capillary columns in increasing both the speed of analysis and the resolution are identified. Chapter 3 discusses the design of rectangular cross-section columns. The advantages of high aspect ratio columns, along with the effects of different physical and operational parameters on column performance are discussed. The effect of dead volumes is incorporated into the design. In Chapter 4, steps leading to a stable MEMS process to fabricate the columns are discussed. Integrated features, such as on-chip split and detector manifolds, are discussed. The use of ultrasonic microscopy and quick chromatographic measurements to assess device quality are presented. Chapter 5 provides background on the column coating procedures and outlines the progress made in deactivating and coating rectangular metal columns. Experimental data on characterizing the columns, as well as comparing columns of different widths and lengths are presented. Chapter 6 summarizes the research effort and provides an outlook towards realizing a full GC sensor.
2 Basic Concepts of Gas Chromatography

A gas chromatograph is a tool for separating mixtures of organic compounds, be it solids, liquids, or gases. In all cases, the compounds of interest have to be converted into the gaseous phase before they can be analyzed. Factors important for a particular analysis can set requirements for column performance. For example, in environmental analysis, it may be useful to run a high sensitivity analysis to cover all of the pertinent compounds even if it increases the analysis time. On the other hand, for a life-threatening emergency, like a chemical leak, it may be better to get a speedy analysis of the pertinent chemical signatures.

2.1 Gas Chromatography

Important aspects of GC theory directly affect the ability to perform fast chromatography. The compounds of a mixture separate based on their boiling points and/or relative affinity for a stationary phase lining the walls of a capillary tube [60]. The schematic of a gas chromatograph system shown in Figure 2-1 consists of an injector, a separation column, a detector, fluidic manifolds including valves, pressure sensors and flow regulators, and electronics for data processing and overall system control. The sample is collected by means of a pump - for volatile compounds or for unattended ambient analysis, a syringe - for manual injection of volatile and non-volatile compounds, or auto samplers such as e.g., I-AS by Agilent Technologies, Santa Clara, CA and Cobra L/S by Central Development LLC, Baton Rouge, LA. The collected sample is usually adsorbed on an adsorbent (like Tenax™) followed by thermal desorption. Common commercial GC columns are 100-320 μm diameter and 1-30 m long capillaries made out of fused silica, glass, or metal. The separating medium for GC columns is either a packed bed of solid adsorbents, packed bed column, or a thin layer coated on the column wall, capillary column.
Since the advent of fused silica columns and wall-coated stationary phases, these columns are preferred over packed bed columns because of better performance [61].

The separation in a column can occur under various operating modes: isothermally, where the column temperature is held constant over the duration of the separation [60]; temperature programming, where the column temperature is raised at a constant rate from the beginning to the end of the separation [62, 63]; and gradient temperature programming, where the column temperature varies along the length of the column and is also increased at a constant rate during separation [64]. To change the column temperature, the column is generally either installed in a convection oven as in the HP 5890/6890 GCs (Agilent Technologies, Santa Clara, CA) or assembled with a resistive heating element as in the microFast GC (ASI Inc., Baton Rouge, LA).

Figure 2-1: Schematic of the primary components of a typical gas chromatograph.
The sample is either driven through the column by a pressurized carrier gas, pressure driven mode, or pulled through by a vacuum pump located at the end of the column, vacuum outlet mode. In both cases, gas velocities assume a parabolic profile in accordance with Hagen-Poiseuille flow and the flow rate through the column can be estimated using basic fluid mechanics principles [65]. In pressure driven mode, increasing the head pressure linearly with time during the separation improves column efficiency [66, 67]. The analytes are transported through the column via a mobile phase, carrier gas, which typically is a low viscosity gas such as helium or hydrogen, although air is also commonly used. There are many types of stationary phases, including polar, non-polar, chiral, and ionic. The choice of a stationary phase will depend, among other things, on the volatilities and the polarities of the analytes. The greater the interaction of a species with the stationary phase, more retained, the slower the compound will advance through the column. Lightly retained compounds elute from the column first. For straight chain hydrocarbons, the volatility decreases with an increasing number of carbon atoms in the molecule. Detectors, either generic, or specific to the functional groups present in the analytes, identify the eluting samples. The output of a GC is a chromatogram, which is a distribution of the time an analyte spends in the column and the quantity of that analyte detected by the detector, which is proportional to the amount present in the sample.

2.2 Background

The physical problem in chromatography is the separation of substances or analytes. The molecular basis for the chromatographic process is the dynamic interaction of the solutes with the stationary and mobile phases. The driving force of these interactions is the systems’ tendency to reach chemical equilibrium at all locations in the column. The concentration of each analyte in the stationary and mobile phases adjusts continuously at all points in the column such that the chemical potential of each solute in the stationary phase equals that in the mobile
Consider a closed system, $S$, containing two phases, $a$ and $b$. The chemical potential of a compound $i$ dissolved in a phase $a$ is:

$$\mu^a_i = \mu^{0a}_i + RT \ln c^a_i$$

(2-1)

where, $\mu^a_i$ is the chemical potential of analyte $i$ in phase $a$, $\mu^{0a}_i$ is the standard chemical potential of substance $i$ in phase $a$, $R$ is the universal gas constant, and $c^a_i$ is the concentration of analyte $i$ in phase $a$. For an analyte which is in chemical equilibrium between the two phases,

$$\mu^a_i = \mu^b_i$$

(2-2)

On combining Equations 2-1 and 2-2 and rearranging, Equation 2-3 results.

$$\left(\frac{c^a_i}{c^b_i}\right)_{eq} = \exp\left(\frac{-\Delta \mu^0_i}{RT}\right) = K$$

(2-3)

where, $\Delta \mu^0_i = \Delta \mu^{0b}_i - \Delta \mu^{0a}_i$ and $K$ is the partition coefficient or the distribution coefficient. In chromatography involving gas and liquid phases, the convention is to take phase $a$ as the stationary phase and phase $b$ as the mobile phase. The partition coefficient depends on the analyte, the nature of the stationary phase, and the temperature of the system. Even though complete equilibrium is beyond reach in any chromatographic system because the mobile phase continuously transports the solute molecules that are in that phase to new portions of the stationary phase, partitioning is a very fast, first order, process, so the movement of the individual bands occurs at very close to the equilibrium. The equilibrium concentrations are good approximations to the actual distribution of the analytes within the system.

At a particular temperature, let $V_a$ and $V_b$ be volume of the analyte in phases $a$ and $b$ respectively. The total moles of solutes in the two phases are $c^a_i V_a$ and $c^b_i V_b$. The ratio of the number of moles in phase $a$, $n^a_i$, to the number of moles in phase $b$, $n^b_i$, is given by Equation 2-4.
The retention factor or the capacity factor, $k$, and the phase ratio, $\beta$, can be written as Equations 2-5 and 2-6.

\[
\frac{n_i^a}{n_i^b} = \left(\frac{c_i^a}{c_i^b}\right) \cdot \frac{V_a}{V_b}
\]

Differences in $k$ are the basis for chromatographic separation. The retention factor represents the relative molar fraction of the analyte in the stationary phase (Equation 2-7)

\[
k = \frac{K}{\beta}
\]

A solute molecule travels along the column only during the time when it is in the mobile phase. During the time that the molecule is in the stationary phase, either it does not have a net displacement along the column or the net displacement is orders of magnitude lower than that in the mobile phase since there is no driving force other than diffusion in the stationary phase.

The total time, $t_r$, an analyte spends in the column, called the retention time, is the sum of the column holdup time, which is the time it spends in the mobile phase, $t_m$, and the adjusted retention time, which is the time it spends in the stationary phase, $t'_r$.

\[
t_r = t'_r + t_m
\]

Another interpretation for the retention factor is the relative time fraction that the average molecule spends in the stationary phase, as expressed in Equation 2-9.

\[
k = \frac{t_r - t_m}{t_m}
\]
2.3 The Separation Process

The movement of an analyte through the column is always associated with broadening of
the analyte band by dispersive transport. The performance of a column is often expressed in
terms of the number of peaks that can be resolved in a chromatographic run. This means that
the narrower the peaks, i.e. less band broadening, the greater the number of peaks that can be
resolved and the better the efficiency. The relation between the retention time and the width of
the analyte band is a measure of the separation efficiency. As discussed above, even though
partitioning in a GC is a fast process, the analyte concentration between the mobile and
stationary phases does not reach equilibrium. The column can be considered divided into a
number of plates, a term derived from distillation column theory. The assumption is that the
solute molecules reach equilibrium between the two phases in each theoretical plate. As one
can expect, the larger the number of plates, the more the number of equilibrium steps and
better the separation. For a distillation column, if \( a \) is the amount of analyte in the stationary
phase in plate number ‘0’ during the first extraction step, and \( b \) is the amount in the mobile
phase, then \( a/b = k \) and \( a+b = 1 \), normalized to the total amount of the analyte in the system.
For such a case, the amount of solute in plate \((r+1)\) after passage of \( n \) mass balance and
equilibrium steps is given by Equation 2-10 [68].

\[
Q_{r+1} = \frac{n! a^{n-r} b^{r}}{r! (n-r)!}
\]

Equation 2-10

For a total number of plates, \( r+1 \), where \( r \) is large, Equation 2-10 can be expanded by the
Binomial Theorem and approximated as shown in Equation 2-11.

\[
Q_{r+1} \approx \frac{1}{\sqrt{2\pi r}} \exp \left( -\frac{(n_{\text{max}} - r)^2}{2r} \right)
\]

Equation 2-11
where, \( n_{max} \) is the number of plate volumes required to transport the mass center of the band to the last plate. Equation 2-11 is similar in form to the familiar expression for a Gaussian probability distribution (Equation 2-12).

\[
y = \frac{1}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(\bar{x} - x)^2}{2\sigma^2}\right)
\]

where, \( y \) is the independent variable, \( \bar{x} \) is the center of mass of the independent variable, and \( \sigma^2 \) is the variance of the distribution. The maximum is given by Equation 2-13.

\[
y_{max} = \frac{1}{\sqrt{2\pi}\sigma^2}
\]

From this discrete multistage model, a continuous flow model was developed [69, 70] which led to a Poisson type distribution. For a large number of extraction or equilibrium steps, the Poisson distribution also approaches a Gaussian distribution. Both these theories suggest that an ideal chromatographic zone follows a Gaussian distribution. Comparing Equation 2-11 and 2-12, the standard deviation of the band in plate units can be derived as Equation 2-14.

\[
\sigma = \sqrt{\bar{r}} = \sqrt{N}
\]

Each plate has a finite “height” or length, called the Height Equivalent to Theoretical Plate (HETP) or \( H \), which is related to \( N \) by the simple expression in Equation 2-15.

\[
N = \frac{L}{H}
\]

After van Deemter et al. developed the first general rate theory, Golay applied that theory towards capillary columns. Aris showed that for a column of any cross-section, the total dispersion is simply a sum of the contributions arising from the mobile and stationary phases and the interfacial mass transfer resistance between the two phases [71]. The ordinary
diffusional effects are additive for each of the phases. Over the years, all of the published modifications to that theory have had the basic form of Equation 2-16.

$$H = \frac{B}{u_o} + Cu_o + Du_o^2$$

where, $u_o$ is the column outlet flow velocity. The underlying premise of these theories is that the different processes that contribute to peak broadening are independent of one another. Further, it assumes that each one of them generates a Gaussian probability distribution. According to the central limit theorem, the resulting overall distribution is also Gaussian. The variance of the resulting distribution is the sum of the variances of the individual processes that generate the distribution (Equation 2-17), which on combining with Equation 2-16 leads to Equation 2-18.

$$\sigma_{total}^2 = \sum_{i} \sigma_i^2$$

$$H_{total} = \frac{\sigma_{total}^2}{L} = \sum_{i} H_i$$

Each of the three terms of Equation 2-16 arise from an independent process that contributes to the peak broadening: the first term on the right hand side describes the longitudinal diffusion of an analyte band as it traverses the column; the second term accounts for the interaction between the carrier gas and the analyte, that between the analyte and the stationary liquid phase, and the interfacial resistance to mass transfer between the stationary and mobiles phases; and the third term considers band broadening effects due to components and factors other than the column.

As a sample volume containing analytes moves through the column, it interacts with the carrier gas and the stationary phase on the column walls. All substances have an inclination to
diffuse into their surrounding matter. An analyte band will also diffuse axially along the column.

In one-dimension, the diffusive behavior follows the diffusion equation derived from Fick’s second law (Equation 2-19).

\[
\frac{\partial c_{i,j}}{\partial t} = -D_{i,j} \frac{\partial^2 c_{i,j}}{\partial x^2}
\]  

where, \(c_{i,j}\) is the concentration of analyte \(i\) in analyte \(j\) and \(D_{i,j}\) is the binary diffusion coefficient of the analyte \(i\) in analyte \(j\). The general solution to this PDE is an exponential response similar in form to a Gaussian distribution (Equation 2-20).

\[
c_{i,j} = \frac{1}{\sqrt{4\pi D_{i,j} t}} \exp \left( -\frac{(\bar{x} - x)^2}{4D_{i,j} t} \right)
\]

with the maximum concentration shown in Equation 2-21.

\[
c_{i,j,max} = \frac{1}{\sqrt{4\pi D_{i,j} t}}
\]

Comparing Equation 2-21 with Equation 2-13, yields Equation 2-22.

\[
s_{i,j,axial,max}^2 = 2D_{i,j}t
\]

Equation 2-22 is the Einstein’s equation for Brownian motion. If \(\bar{u}\) is the average velocity through the column,

\[
H_{i,j,axial} = \frac{s_{i,j,axial}^2}{L} = \frac{2D_{i,j}t}{L} = \frac{2D_{i,j}}{\bar{u}}
\]

On accounting for the axial diffusion of the analyte in the stationary phase, Equation 2-23 takes the form of Equation 2-24.

\[
H_{i,j,axial} = \frac{2(D_{i,j,o} + kD_{i,j})}{\bar{u}} = \frac{B_{i,j,o}}{\bar{u}}
\]
The axial diffusion is proportional to the residence time of the analyte in the mobile phase. Since diffusion in the mobile phase is orders of magnitude higher than diffusion in the stationary phase, the longitudinal diffusion in the stationary phase is generally neglected. The binary diffusion coefficient in Equation 2-25 is a least-squares approximation to the experimental values with a 5% average error [72].

\[
D_{i,j} = 10^{-3} T^{1.75} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2} \frac{p \left[ (\Sigma_i \nu_i)^{1/3} + (\Sigma_j \nu_j)^{1/3} \right]^2}{(\Sigma_i \nu_i)^{1/3} + (\Sigma_j \nu_j)^{1/3}}
\]

Here, \( M_i \) is the diameter of the analyte molecule, \( p \) is the pressure, and \( \nu_f \) is a special diffusion parameter summed over atoms, groups, and structural features of the diffusing species in terms of three arbitrary exponents. The diffusion coefficient for two species depends on the pressure and temperature, which in turn means that it depends on the position of the analyte along the column. Since the linear gas velocity also varies with column pressure, the ratio \( D_{i,j}/\bar{u} \) is constant throughout the column as long as the temperature is constant and the compressibility effects are neglected.

The second term in Equation 2-16 describes the dispersion of the analyte band that arises because of the fact that the mass transfer processes are not instantaneous. This term encompasses three independent resistance to mass transfer coefficients: \( C_{i,m} \), resistance to mass transfer in the mobile phase; \( C_{i,s} \), resistance to mass transfer in the stationary phase; and \( C_{i,t} \), the interfacial resistance to mass transfer arising from the finite rate constant for the partitioning process. The analyte molecules diffuse and mix in the mobile phase because of Brownian motion (given by Einstein’s equation). Although the flow characteristics and the velocity profile of an analyte band are discussed later in this chapter, it is sufficient to know for now that the band velocity has a parabolic profile across the cross-section of the column.
governed by Poiseuille’s equation [65]. In addition, the flow regime is laminar. Under these conditions, the concentration of the analyte varies across the transverse direction in the band (Figure 2-2). Analyte molecules close to the column center axis travel faster than those near the stationary phase. This concentrates the analytes in the leading edge of the band at the center axis of the column and creates a concentration gradient from the center axis to the column wall, across the column diameter $d_c$, causing radial diffusion that in turn partially offsets the laminar flow effect. If the column diameter is large, the time for a molecule to diffuse from the center to the wall will be larger. This can be interpreted as a finite probability that some fraction of the analyte always diffuses towards the center axis and moves faster than the average analyte band, while another fraction stays close to the column wall and stationary phase, while moving slower than the average analyte band, leading to zone dispersion. By formulating these effects mathematically into a single equation, the variance for circular cross-section columns is (Equation 2-26) [73]:

$$\frac{\sigma_{i,m,\text{radial}}^2}{L} = \frac{1 + 6k_i + 11k_i^2}{(1 + k_i)^2} \frac{d_c^2 u_o}{96 D_{i,\text{radial}}} = H_{i,m,\text{radial}} = C_{i,m} u_o$$

A higher diffusion rate between the analyte and mobile phase will obviously reduce this band broadening, so will a column with a smaller diameter. Of course, using a narrower bore column will, for the same pressure drop, have a lower velocity also, further reducing the band broadening. The overall effects of reducing the column diameter are quite interesting, as later discussions will demonstrate.

Similar to the analyte diffusion in the mobile phase, an analyte concentration gradient exists across the stationary phase. This diffusion generates a distribution of the time required by the individual molecules to diffuse back to the interface and partition into the gas phase, causing band broadening.
Figure 2-2: Schematic showing the concentration gradients occurring across various regions of the column cross-section. The analyte concentration varies in the axial and transverse directions of the velocity profile and across the stationary phase.
Again, it is obvious that the diffusion time across a thinner stationary phase film, \( d_f \), will be smaller than for a thicker layer. As with all other diffusion constants, the gas-liquid diffusion coefficient, \( C_{i,s} \), is proportional to the temperature, so increasing the column temperature can reduce this band broadening. Mathematically, the variance due to resistance in mass transfer due to the stationary phase can be written as Equation 2-27:

\[
\frac{\sigma_{i,s,radial}^2}{L} = \frac{2k_i d_f^2 u_o}{(1 + k_i)^2 D_{i,s}} = H_{i,s,radial} = C_{i,s} u_o
\]

For circular columns with \( d_f \ll d_c \):

\[
d_f^2 \approx d_c^2 \beta^2
\]

The rate of interfacial process is the same as a reversible rate constant for mass transfer from the stationary phase to the mobile phase. Although a mathematical formulation of the effect exists [74, 75], the measurement of this term is extremely difficult because it has the same effect as the resistance to mass transfer terms due to radial diffusion. Aris was the first one to derive an expression for this term (Equation 2-29) [71].

\[
H_{i,i} = \frac{2k_i d_f}{(1 + k_i)^2 k_{d,i}} u_o = C_{i,i} u_o
\]

In the majority of the cases, since the resistance to mass transfer in the mobile phase dominates the resistance to mass transfer terms, the contribution of the finite rate of the interfacial process is usually neglected.

### 2.4 Extra-Column Effects

The third term in Equation 2-16 factors in the effects other than the column that contribute to analyte band broadening. Fast capillary GC has suffered because of the lack of adequate instrumentation. Instrument contributions to band broadening, commonly termed
extra-column effects, become critical in fast chromatography and may limit efficiency [76]. Some of the primary sources of extra-column effects are dead volumes at the injector and detector, finite injection plug width, uncoated connecting tubes, and significant changes in areas between the different connecting components. The rule of thumb is that any uncoated surface that an analyte passes through will contribute to band broadening. At the column outlet, the uncoated part of the column from the column outlet to the detector contributes to band broadening. Further, Equation 2-16 assumes that the injected sample plug has the distribution of a delta function, i.e., zero width. In practice, an injected sample always has a finite width and the injection process occurs over a finite length of time. The leading edge of the analyte band that enters the column first moves through the column before the trailing edge of the sample plug enters the column. This length of the plug depends on the mode of injection and is independent of the column.

Since the equipment contributions to band broadening are generally independent of the column contributions, the second moment of these extra-column effects are added to the second moment of the column. The extra-column terms are quantities in either in time units (e.g., finite injection plug width) or in length units (e.g., dead volumes). Converting the contributions from the time units into the length domain helps to add them to the variance of the column. The variance in the time and length domains, \( \nu_{\alpha,t} \) and \( \nu_{\alpha,l} \), are related as shown in Equation 2-30.

\[
\sigma_{\text{ec,l}}^2 = \frac{\sigma_{\text{ec,t}}^2}{(1 + k)} u^2
\]

The velocity in Equation 2-30 should correspond to the section of the instrument where the extra-column effect resides. For example, it is the inlet velocity for the variance due to the injector volume while for variance dealing with detector issues should use the column outlet.
velocity. In a pre-concentrator or an absorbent trap, it takes a $t_{pc}$ seconds to desorb off the analytes and inject into the column. The extra-column contribution of this time in the length domain is shown in Equation 2-31.

$$\sigma_{ec,t}^2 = \left[ \frac{t_{pc}}{1 + k_i} \right]^2$$

For the extra-column contributions that are in the length units, the approach is slightly different. For a dead volume $V_{d,i}$, the extra-column contribution can be written as Equation 2-32.

$$\sigma_{ec,t}^2 = \left[ \frac{V_{d,i}}{Q(1 + k_i)} \right]^2$$

where, $Q$ is the volumetric flow rate. For the particular case of injecting a plug of a finite volume through a sampling valve or a split flow, the variance in the time domain can be written as Equation 2-33 [77].

$$\sigma_{ec,t}^2 = \frac{\tau^2}{12}$$

where, $\tau$ is the ratio of the sample volume to the volume flow rate carrying the sample. If the split flow rate is $SR$, this is given by Equation 2-34.

$$\sigma_{ec,t}^2 = \frac{1}{12} \left[ \frac{V_{d,i}}{Q(SR + 1)(1 + k_i)} \right]^2$$

Having a split flow at the column inlet can reduce the effects of the inlet dead volumes, though, at the expense of losing some of the valuable collected sample. Assuming that the peaks eluting from the column are Gaussian, the extra-column contribution of the detector, $V_{d,o}$, with a makeup gas flow, $Q_{mg}$, is presented in Equation 2-34.

$$\sigma_{ec,t}^2 = \frac{1}{36} \left[ \frac{V_{d,o}}{Q + Q_{mg}} \right]^2$$
It is common practice to add makeup gas to the detector to sweep all of the eluting analytes to the detector, thus reducing the dead volume contributions. Combining all of the band-broadening terms, the overall HETP equation can be written as Equation 2-36.

\[ H_i = \frac{2(D_{i,j,o} + k_i D_{j,s})}{u_i} + \frac{1 + 6k_i + 11k_i^2}{(1 + k_i)^2} \frac{d^2 \bar{u}}{96 D_{i,j,o}} + \frac{2k_i}{(1 + k_i)^2} \frac{d^2 \bar{u}}{D_{i,s}} + \frac{\sigma_{ec}^2}{L} \]  

For compressible flows, modifications to the HETP equation were suggested by Giddings [78] by incorporating pressure correction factors \( f_1 \), the Giddings-Golay compression coefficient given by Equation 2-37 and \( f_2 \), the Martin-James gas compressibility coefficient, given by Equation 2-38.

\[ f_1 = \frac{9\left(\frac{p_r}{p_i} - 1\right)\left(\frac{p_r^2}{p_i^2} - 1\right)}{8\left(\frac{p_r^3}{p_i^3} - 1\right)^2} \]  
\[ f_2 = \frac{3\left(\frac{p_r^2}{p_i^2} - 1\right)}{2\left(\frac{p_r^3}{p_i^3} - 1\right)} \]

Here, \( p_r \) is the pressure ratio, \( p_i/p_o \). In such cases, the average flow velocity, \( \bar{u} \), can be written in terms of the outlet velocity, \( u_o \):

\[ \bar{u} = f_2 u_o \]

Equation 2-40 gives the retention time for an analyte, \( t_o \).

\[ t_o = \frac{L}{\bar{u}} \]

The modified HETP equation in terms of the outlet gas velocity is given in Equation 2-41.

\[ H_i = \frac{2(D_{i,j,o} + k_i D_{j,s})}{u_o} f_1 + \frac{1 + 6k_i + 11k_i^2}{(1 + k_i)^2} \frac{d^2 u_o}{96 D_{i,j,o}} f_1 + \frac{2k_i}{(1 + k_i)^2} \frac{d^2 u_o}{D_{i,s}} f_2 + \frac{\sigma_{ec}^2}{L} \]
Figure 2-3 shows a typical plot, called the Golay plot, between the HETP and average column velocity. The velocity at which the HETP reaches a minimum is called the optimum velocity. Operating the GC at this condition will yield the maximum efficiency. This figure also shows the variation of the three main band broadening terms – longitudinal diffusion, the interaction between the carrier gas and the analyte, and that between the analyte and the stationary liquid phase.

2.5 Optimum Column Velocity

Differentiating Equation 2-16 with respect to the column velocity gives an expression for the optimum velocity (OPGC) necessary for achieving minimum HETP. On neglecting the extra-column, the OPGC is given in Equation 2-42 and the corresponding HETP by Equation 2-43.

\[
OPGC = \sqrt{\frac{B}{C}}
\]

Figure 2-3: A typical Golay plot for naphthalene through a 50 μm diameter, 1 m long capillary column with 0.1 μm OV-1 stationary phase using hydrogen carrier gas at 100 °C.
In a plot of HETP versus column velocity, the OPGC corresponds to the maximum column efficiency, often termed as the van Deemter minimum [60]. If the extra-column effects are taken into account, partially differentiating Equation 2-16 with respect to the velocity results in a third order equation. To simplify solving this equation, Gasper introduced the idea of the time necessary to generate a Theoretical Plate (TH) (Equation 2-44) [79].

\[ T_H = \frac{\sigma^2}{t_R} \]

which on substituting in Equation 2-16 takes the form of Equation 2-45.

\[ T_H = \frac{B}{u^2} + C + Du \]

\( T_H \) has a minimum at the optimum velocity (OPGC') given by Equation 2-46.

\[ \text{OPGC} = \left(\frac{2B}{D}\right)^{1/3} \]

The plate height at this velocity \((H')\) is shown in Equation 2-47. The OPGC shows that for most cases in a real system, \( \text{OPGC}' > \text{OPGC} \), i.e., the column efficiency increases as the velocity is increased from OPGC to OPGC' and decreases after that.

\[ H' = \frac{3}{2} (2B)^{2/3} D^{1/3} + \frac{C}{D^{1/3}} (2B)^{1/3} \]

2.6 Column Velocity - Hagen-Poiseuille Flow

For an incompressible flow, on neglecting the variations in fluid viscosity with pressure at constant temperature, the Navier-Stokes Equations can be reduced to the form of Equation 2-48 [65].
\[ \rho \frac{D \vec{V}}{Dt} = -\nabla P + \rho \vec{F} - \mu \nabla^2 \vec{V} \]

where \( D/Dt \) denotes the material derivative, \( \vec{V} \) is the velocity vector, \( \mu \) is the kinematic viscosity and \( \vec{F} \) is the external force factor. For a Newtonian fluid, the viscous shear stress is proportional to the viscous shear strain and written in terms of the fluid viscosity and the velocity gradient.

\[ \tau_{\text{shear}} = \mu \frac{du}{dr} \]

Assuming no motion in the transverse direction, the force acting in that direction is neglected and the pressure varies only along the column length. The standard form of the governing equation describing the flow becomes Equation 2-50.

\[ \frac{1}{\mu} \frac{dP}{dz} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \]

The flow velocity at a distance \( r \) from the center of a circular cross-section of radius \( R \) can be derived from Equation 2-50.

\[ u(r) = -\frac{1}{8 \mu} \frac{dP}{dz} (R^2 - r^2) \]

The pressure difference per unit length can be calculated based upon the maximum flow velocity which occurs at \( r = 0 \). For compressible flows, the pressure gradient across the column, in terms of \( P_i \), the pressure at the column outlet and \( P_0 \), the head pressure at the column inlet, is shown in Equation 2-52.

\[ \frac{dP}{dz} = \frac{(P_i^2 - P_o^2)}{2LP_o} \]

The velocity at the center axis of the column then becomes the expression in Equation 2-53.
This expression shows that the flow velocity has a parabolic profile across the cross-section of the column. This flow pattern, typical in laminar flows, is known as the Hagen-Poiseuille flow. Incorporating the compressible effects, which become significant for pressure drops over three atmospheres, the velocity of an analyte varies non-linearly with distance along the column (Equation 2-54). This implies that each analyte will attain OPGC only at a particular position along the column and deviate from it at all other locations.

From the van Deemter curves for hydrogen, nitrogen, and air as carrier gases, it can be deduced that the slope of HETP versus average carrier gas velocity is a minimum for hydrogen, meaning that column velocity can be maintained within a small range of OPGC’, resulting in higher efficiency [82].

2.7 Isothermal and Temperature Programming

Guiochon [80] and Said [81] have discussed optimization of isothermal separations in terms of the analysis time in detail. The resolution of a column improves by either reducing the column diameter or by increasing the column length. The consequences of these changes are a longer separation time and an increase in the column head pressure. Given an infinite amount of time and an infinitely long column, the optimal separation occurs under isothermal conditions [62]. For sensor applications, it is desirable to perform the analysis in a short amount of time while consuming minimal power. For isothermal separations, although shorter columns and higher carrier gas velocities result in faster separations, the principal drawback is that the later
eluting peaks are much broader than the early eluting ones. The reason for this is that the longer the analytes spend in the column, the greater the contributions of axial diffusion and resistance to mass transfer in the mobile phase. An increase in the separation temperature sharpens the analyte peaks, but the resolution decreases, causing early eluting analytes to coelute. Temperature programming introduces a degree of freedom during the separation. Numerous studies suggest the benefits of temperature programmed separation over isothermal separations [83]. On increasing the column temperature during a chromatographic run, the retention factor of an analyte and the diffusion coefficients decrease, increasing the rate of separation. Each analyte attains a characteristic temperature and moves along the column, unretained, on attaining that temperature. For high-speed separations using fast temperature programming, the retention times are far less dependent on column length and carrier gas velocity than for high speed isothermal separations [83]. Blumberg and Klee showed that the optimum temperature programming rate was 10 °C/holdup time [63]. A programming rate faster than this would not contribute to improving the resolution. This rate is important since for a faster ramp rate, it is possible that the temperature program will finish before any or all of the analytes have eluted from the column. For a sensor with a separation time of less than 10 seconds, the holdup time will be on the order of 250-1000 ms and the ideal temperature-programming rate 10-40 °C. Again, OPGC’ will only be attained at a particular position along the column. An interesting variation promising improvement over temperature programming was proposed where the temperature of the column would be a function of the distance along the column as well as time [64]. For a positive temperature gradient in the direction of the carrier gas flow, the leading edge of a peak travels more slowly than the receding edge, sharpening the analyte band. This technique, implemented by physically moving a column through a convection oven during the run [84], is not practical for a sensor application.
2.8 Column Efficiency

The performance of a chromatographic column can be evaluated in a number of ways including resolution, peak capacity, separation or Trennzahl number, and separation time. Column selectivity depends on the magnitude of the individual energies of interaction and governs the spacing of the eluting peaks. The separation factor, given by Equation 2-55, defined as the relative retention of two peaks A and B in the chromatograph, gives a measurement of the separation between the peak maxima. By convention, separation factors are always greater than one, compound A is retained more than B.

\[
\alpha = \frac{t^r_A}{t^r_B} = \frac{k(A)}{k(B)}
\]

The resolution \( R \), given by Equation 2-56, quantifies the amount of peak overlap and is given by Equation 2-56.

\[
R = 1.2 \frac{t^r_B - t^r_A}{w_h(B) + w_h(A)}
\]

where, \( w_h \) is the peak width measured at half height. For peaks with baseline separation, a resolution of 1.5 or more is necessary, which represents a peak overlap of less than 1%. The most commonly used expression for peak capacity in an isothermal separation can be written in terms of the number of plates, the holdup time, and retention time (Equation 2-57).

\[
n = 1 + \frac{\sqrt{N}}{4} \ln \left( \frac{t_r}{t_m} \right)
\]

The number of plates can be estimated by using Equation 2-58.

\[
N = 5.54 \left( \frac{t_r}{w_h} \right)^2
\]
In order to double the peak capacity, the number of plates, and the column length, will have to increase four-fold. The peak capacity for a temperature programmed separation can be derived from the Trennzahl number, $TZ$, which is measured as the ratio of separation time for the two adjacent reference $n$-alkanes to the sum of their peak widths at half height [85, 86, 87]. The peak capacity can be obtained by summing the $TZ+1$ values for adjacent pairs of $n$-alkanes (Equation 2-59) [88].

$$TZ = \frac{\Delta t_R}{\sum W_h} - 1$$

Here, $\Delta t_R$ is the difference in retention times for pairs of analytes and $\sum W_h$ is the sum of their peak widths at half height. A new measure of separation describes the separation, $S$, of two peaks in units of standard deviation and is given by Equation 2-60 [89].

$$S = \int_{t_a}^{t_b} dS = \int_{t_a}^{t_b} \frac{dr}{\sigma}$$

where, $\sigma$ is, as before, the standard deviation. The ratio $1/\sigma$ is simply the number of $\sigma$-intervals that the analysis can produce per unit time.

### 2.9 Calculation of Peak Capacity

As can be appreciated from Equation 2-41, designing an optimum column is a multi-parameter problem. To separate a set of analytes on a chosen column type, the peak capacity depends on the column dimensions: length, width, and height; temperature and temperature programming rate; and the film thickness. The separation efficiency will be the highest when the operating conditions are close to the Golay minimum [60]. The Golay minimum is the velocity at which the HETP reaches a minimum value, which translates into the maximum number of plates for that column under those conditions. The estimation of peak capacity for isothermal separations is quite straightforward, since the operating temperature
and related parameters such as diffusion constants, carrier gas viscosity, and retention factors are constant during the run. In temperature-programming mode, however, these parameters change with time. The retention factor, for example, is calculated from temperature dependent variables such as the distribution coefficient, gas viscosity, and velocity [90, 91, 92]. One of the methods to estimate the peak capacity ($TZ+1$) is to divide the column into a large number of small sections in the time domain [93, 94]. The viscosity, gas phase and liquid phase diffusion coefficients, band velocities for each analyte, and the carrier gas, are calculated for each column sub-section. These are used to calculate the $B$, $C$, and $D$ terms in Equation 2-16, which are summed over all of the subsections.

2.10 Circular Column - Time vs. Resolution

The resolution and separation time of circular cross-section capillary columns were calculated using Pro ezGC version 2.2 (Restek, Bellefonte, PA). Two operation modes were considered: 1) when the column head pressure was held constant and 2) when the holdup time was held constant. Columns with diameters of 50 μm, 100 μm, and 200 μm, 2 m long, with a 0.1 μm thick RTX-1 stationary phase were used. A temperature-programming rate of 15 °C/s was picked to separate straight chain alkanes C$_1$-C$_{12}$. The starting temperature was ambient at 25 °C and the pressure was atmospheric at 14.7 psi. The retention time, peak width at half heights, and resolution of each compound were recorded and plotted in Microsoft Excel. Figure 2-4 shows the retention time of all of the analytes for the three columns under a head pressure of 30 psi. As expected, retention time of compounds increases with decreasing column diameter. In addition, the heavier compounds, higher $k$ values, take longer to elute than those less retained, as predicted by Equation 2-9. As shown in Figure 2-5, the column resolution increases with reducing column diameter.
Figure 2-4: Variation of retention time with column diameter for straight chain alkanes C\textsubscript{1}-C\textsubscript{12} through a 2 m long circular column under a 15 ° C/s ramp rate for a 30 psi head pressure.

Figure 2-5: Variation of resolution with diameter for straight chain alkanes C\textsubscript{1}-C\textsubscript{12} through a 2m long circular column under a 15 ° C/s ramp rate for a 30 psi pressure.
Figure 2-6 and Figure 2-7 show the variation of retention time and column resolution, respectively, for the case when the holdup time through the column is constant at 70 ms by varying the head pressure. As the column pressure is increased to maintain the holdup time for the smaller diameter column, the retention time for the other compounds reduces by a factor of 4 or more as compared to those in Figure 2-4. However, the price paid is the high inlet pressure shown in Figure 2-8. One solution to this problem is to use rectangular cross-section columns as suggested by Golay and Giddings. The design of such columns follows in the next chapter.

2.11 Concluding Remarks

Equation 2-36 shows that the performance of a GC column depends on a number of physical and operational parameters. Temperature is the primary factor as the carrier gas velocity, the diffusion coefficients, the retention factors, all vary with temperature. The resolution of the early eluting compounds reduces with increasing temperature of an isothermal separation; at lower temperatures, the later eluting compounds show broadening. To overcome this, temperature programming is frequently employed. Column resolution improves by reducing the column diameter. The column efficiency depends on the carrier gas velocity. For high resolution analysis, a narrow column is desired, while for a fast analysis, either a high column head pressure or a large diameter column is desired. The solution to this conundrum is to use rectangular cross-section columns, where the width and height can be tailored independently.
Figure 2-6: Variation of retention time with diameter for straight chain alkanes $C_1$-$C_{12}$ through a 2m long circular column under a 15 ° C/s ramp rate for a 30 psi head pressure for a holdup time of 70 ms.

Figure 2-7: Variation of resolution with diameter for straight chain alkanes $C_1$-$C_{12}$ through a 2m long circular column under a 15 ° C/s ramp rate for a 30 psi head pressure for a holdup time of 70 ms.
Figure 2-8: Variation of the outlet flow rate and the required column head pressure with column diameter to maintain a holdup time of 70 ms.
3 Design of the GC Sensor

A micro GC system consists of all of the necessary components of a bench top GC in a miniaturized form, promising enhanced performance in terms of size, power consumption, resolution, and speed. However, transitioning from bench top, laboratory-based systems to portable devices with similar or superior performance poses significant challenges. Separation columns have to be significantly smaller and shorter to reduce the analysis time to a few seconds and still ensure good separation. For example, a high resolution column may produce peak widths of a few tens of milliseconds. In such a case, the peak width of the injected plug has to be an order of magnitude less to maintain the resolution. This can be a challenge if a large collected sample volume has to be concentrated, since that sample volume has to be “shrunk” down and concentrated to a few milliseconds wide pulse. Most operations involving short injection pulse widths use a system of dual-valves or split injection, causing loss of the collected sample. This can be a potential problem when detecting analytes in low concentrations. Since the associated flow velocities in fast chromatography are much higher than those in traditional GC, the relative contributions of the extra-column effects are pronounced in fast GC. The overall performance of the GC sensor will depend not only on the performance of the individual components but also on how these components interface with one another. Building up on the discussion of column design issues, this chapter focuses on the design of rectangular cross-section columns.

3.1 Rectangular Cross-Section Columns

In 1983, Giddings et al. postulated that the plate height for an open parallel plate column of width \( w \) and an open tubular column of diameter \( d_c \) for liquid chromatography were related by Equation 3-1 [78]. By using a rectangular cross-section column, an additional degree of
freedom is introduced since the column width governs the resolution while the column height establishes the volumetric flow rate. A narrow, high aspect ratio column enables fast diffusion of the gas molecules in and out of the stationary phase, improving the separation efficiency, while the taller column allows lower pressure drops and higher gas volume in the column, to offset any loss in resolution due to the smaller sample volumes because of the reduced width.

\[
\frac{HETP_{opp}}{HETP_{OTC}} \propto \left( \frac{w^2}{d_e^2} \right)
\]

While these results were postulated for liquid chromatography, the theory developed suggests that a similar trend can be expected for gas chromatography [27, 95].

### 3.2 Speed and Separation Efficiency of Rectangular Columns

Consider a gaseous analyte flowing through a rectangular cross-section column of width \(2b\), height \(2h\), and length \(L\). The HETP of rectangular cross-section columns has the familiar form of Equation 3-2.

\[
H = \frac{B}{u_o} + Cu_o + Du_o^2
\]

The column performance is connected to the gas velocity. Equation 3-3 estimates the velocity of a gas, \(u_z\), at a distance \(z\) along the column length [95]. Here, \(dP/dz\) is the pressure gradient along the column, and \(K_p(x, y)\) is the column permeability across the column cross-section given by Equation 3-4.

\[
u_z = \frac{K_p(x, y) \frac{dP}{dz}}{2 \mu \nu_o}
\]

\[
K_p(x, y) = \frac{b^2d^2}{2(b^2 + d^2)} \left[ 1 - \frac{x^2}{b^2} - \frac{y^2}{d^2} \right]
\]
On integrating Equation 3-3 along the column width and height, the expression for the velocity is given by Equation 3-5.

\[ u_x = \frac{1}{12\mu} \frac{b^2 d^2}{(b^2 + d^2)} \frac{dP}{dz} \]  

Since the flow in the microfabricated columns is compressible [Appendix A], the pressure gradient across the column is given by Equation 3-6 (same as Equation 2-52).

\[ \frac{dP}{dz} = \frac{(P_1^2 - P_0^2)}{2L P_0} \]  

The nonlinear profile of the pressure along a 50 μm by 600 μm by 1 m long column is clear from Figure 3-1. The rate of change of pressure with distance along the column \( (dP/dz) \) is shown in Figure 3-2. The sharp increase in the pressure gradient towards the end of the column results in a higher gas velocity at the exit and enhances the parabolic nature of the velocity profile. Figure 3-3 shows a plot of the function \( K_v(x, y) \), which gives the three-dimensional profile of the plug velocity, at different stages along the column. Figure 3-4 helps visualize this by separating the velocity profile along the width and height. For high aspect ratio \( (b<<d) \) fluidic channels, the expression for velocity in Equation 3-3 reduces to Equation 3-7. The flow rate at the column outlet will simply be the cross-sectional area times the outlet flow velocity at \( z = L \).

\[ u_x = \frac{b^2}{12\mu} \frac{dP}{dz} \]  

The low values of the Reynolds numbers, less than 10 for pressures of up to 80 psi, calculated using Equation 3-8 suggest the flow is highly viscous and laminar [65].

\[ Re = \frac{\bar{u} D_h}{v} \]
Figure 3-1: Variation of the column pressure along a 50 μm wide by 600 μm tall by 1 m long column for hydrogen flow for an inlet pressure of 45 psi at room temperature.

Figure 3-2: Variation of the pressure gradient along a 50 μm wide by 600 μm tall by 1 m long column for hydrogen flow for an inlet pressure of 45 psi at room temperature.
Figure 3-3: Three-dimensional velocity profile at increments of 9 cm along the column length for a 50 μm wide by 600 μm tall by 1 m long column for 45 psi hydrogen flow at room temperature.

Figure 3-4: Change in the velocity profile shown separately for the column height and width at increments of 9 cm along the length for hydrogen flow through a 50 μm wide by 600 μm tall by 1 m long column for an inlet pressure of 45 psi at room temperature.
Here, \( D_h \), is the hydraulic diameter, given by Equation 3-9, and \( v \), the kinematic viscosity.

\[
D_h = \frac{4 \times \text{cross sectional area}}{\text{wetted perimeter}} = \frac{4bh}{2(b+h)}
\]

The Knudsen number was calculated to be less than 0.01 [96], signifying that the flow regime was continuum with no slip [97]. Golay approximated the rectangular cross-section column as infinite parallel plates, neglecting the effect of the shorter sidewalls [27]. Equation 3-10 shows the modified Golay equation to calculate the HETP for rectangular cross-section columns valid for compressible flows [50].

\[
H_i = \frac{2(D_{i,j,o} + k_i D_{i,s})}{u_o} f_1 + \frac{1 + 9k_i + \frac{51}{2}k_i^2}{105(1 + k_i)^2} \frac{4b^2u_o}{D_{i,j,o} f_1} + \frac{2k_i}{3(1 + k_i)^2} \frac{(b + d)^2 h_f^2 u_o}{D_{i,s} f_2} + \frac{\sigma_{cc}^2}{L}
\]

The high aspect ratio affects the gaseous diffusion constant. While the pressure drop for a high aspect ratio column approaches that of two infinite parallel plates without sidewalls, the axial dispersion coefficient converges to a value \( \sim 8 \) times that for the infinite parallel plate without sidewalls (Equations 3-11 and 3-12) [71].

\[
D_{axial,\infty} = \frac{1}{210} \frac{u_o^2 w^2}{D_{i,j,o}} \quad \text{for infinite parallel plates with no sidewalls}
\]

\[
D_{axial,\infty} = \frac{7.9512 u_o^2 w^2}{210} \frac{D_{i,j,o}}{D_{i,s}} \quad \text{for high aspect ratio column with sidewalls}
\]

These results are true for dispersion in an uncoated column and apply to the axial dispersion in the column. The contribution of the coated sidewalls for fluids in general has been studied extensively [50, 51, 98]. Giddings and Myers studied this effect for liquid chromatography and derived an expression to account for the effect of the sidewalls [78]. Similar to the circular cross-section capillary columns, the non-uniformity in the velocity profile in a rectangular cross-section columns leads to an additional mass transfer contribution. Poppe solved the
transport equation numerically to derive expressions for different coating strategies - coating on a single wall, coating on two walls, and coating on all four walls. The results, expressed as an equivalent height in Equation 3-13, replace the second term of the HETP equation

\[ h = \frac{F_0 + F_1 k_i + F_2 k_i^2}{N_c(1 + k_i)^2} \]  

where, \( F_0, F_1, F_2, N_c \) were calculated as functions of the column aspect ratio. An analytical solution to this problem, derived by Ahn et al. [50] based on theory proposed by Dutta et al. [51], modifies the resistance to mass transfer in the mobile phase to Equation 3-14.

\[ C_m(k_i) = \frac{1}{6} \left( \frac{k_i}{1 + k_i} \right)^2 g_1(\alpha) + \frac{1}{105} g_2(\alpha) + \frac{1}{15} \left( \frac{k_i}{1 + k_i} \right) g_3(\alpha) \]

\[ g_1(\alpha) = \frac{2\alpha^2}{(\alpha + 1)^2} \]

\[ g_2(\alpha) \approx \frac{(7.951 - 1.759)(\alpha - 1)^2}{(\alpha - 0.1)^2} + 1.759 \]

\[ g_3(\alpha) \approx \frac{(4.151 - 0.938)(\alpha - 1)^2}{(\alpha + 0.2)^2} + 0.938 \]

where, \( \alpha \) is the aspect ratio. It is interesting to note that for the limiting case when \( \alpha \to \infty \), \( g_2(\alpha) \to 7.951 \), which is the limit derived by Aris. Substituting the three constants above in Equation 3-14 leads to Equation 3-15 [50]:

\[ C_m(k_i) = \frac{1}{96(1 + k_i)^2} \left\{ \frac{32}{35} g_2(\alpha) + \left[ \frac{64}{35} g_2(\alpha) + \frac{32}{5} g_3(\alpha) \right] k_i \right\} \]

\[ + \left[ 16 g_1(\alpha) + \frac{32}{35} g_2(\alpha) + \frac{32}{5} g_3(\alpha) \right] k_i^2 \]

The different approaches taken by Poppe and Ahn result in very similar expressions for the contribution to plate height. Table 3-1 compares the values of \( F_0, F_1, F_2 \) in Equation 3-13 with the corresponding terms in Equation 3-15 for different aspect ratios. The values show
convergence of the results from the two methods. Both of these approaches predict higher values for the mass transfer in the mobile phase for high aspect ratio columns, which means that the efficiency of the high aspect ratio columns will be less than that predicted by Golay and Giddings. As expected from Equation 3-10, the performance of a rectangular cross-section column is heavily dependent on the gas velocity, which in turn depends on the column dimensions. Another important factor that can affect column performance is the dispersion caused by the physical configuration of the column.

### 3.3 Effect of Turns on Column Performance

In capillary GC, columns as long as 50 m, coiled in a circular or a helical arrangement, are commonly used. There have been numerous studies evaluating the effects of this coiling on column performance [99, 100, 101, 102]. Due to the parabolic profile of the laminar gas flow in the column, the gas velocity is a maximum at the center axis. As the analytes pass around a turn, the centrifugal forces offset the maximum velocity zone towards the outer wall, deforming the symmetry of the velocity profile [101]. Secondary flows develop across the cross-section and separate into two halves.

<table>
<thead>
<tr>
<th>f's from Poppe</th>
<th>Corresponding terms from Equation 3-15</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect ratio = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.80</td>
<td>1.76</td>
<td>1.02558</td>
</tr>
<tr>
<td>10.20</td>
<td>10.08</td>
<td>1.01131</td>
</tr>
<tr>
<td>17.14</td>
<td>17.08</td>
<td>1.00404</td>
</tr>
<tr>
<td>Aspect ratio = 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.10</td>
<td>7.05</td>
<td>1.00666</td>
</tr>
<tr>
<td>39.00</td>
<td>38.97</td>
<td>1.00075</td>
</tr>
<tr>
<td>62.00</td>
<td>61.76</td>
<td>1.00394</td>
</tr>
<tr>
<td>Aspect ratio = 256</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.94</td>
<td>7.91</td>
<td>1.00345</td>
</tr>
<tr>
<td>44.79</td>
<td>44.66</td>
<td>1.00287</td>
</tr>
<tr>
<td>71.59</td>
<td>71.48</td>
<td>1.00140</td>
</tr>
</tbody>
</table>

Table 3-1: Comparison of values of constants for Poppe and Ahn.
The centrifugal forces are balanced by a pressure, which has its maximum at the outer bend. Summation of the velocity vectors of the axial and the secondary flows results in a helical displacement of a fluid element along the column [103, 104]. While the capillary columns are manufactured by drawing a wire over an appropriate mandrel, most of the processes to realize rectangular cross-section columns are derived from lithography, where the columns are arranged in a particular pattern on a substrate or a “chip,” and cannot be wrapped like a tube.

One of the first decisions in any microfabricated column design concerns the column configuration, the arrangement of the column on the chip. The columns, which typically range from 0.5-5 m, are fit on a chip of a few square centimeters area. In the published work on MEMS columns, there is no agreement on a column layout. The group at the University of Michigan has used circular and rectangular spirals, the researchers at Sandia National Laboratory a circular spiral, Professor Masel’s group at University of Illinois at Urbana Champaign a tightly wound serpentine [105], SLS Microtechnology (Hamburg, Germany) a corrugated design in one of their silicon columns, and all prior work at LSU has been on serpentine columns. The one common feature of all of these layouts is that a long column is packed into a small footprint, which means that there must be turns. Whenever there are turns in a gas flow path, flow disturbances in the form of dispersion, separation and eddy formation, and mixing can take place. For a technique such as gas chromatography, the efficiency of which is highly dependent on the shape of the sample plug as it travels through the column, it is important to identify the effect of turns on the column performance.

The amount of skew due to the turns can be studied through the 2D, non-dimensionalized advection-diffusion equation (Equation 3-16) [106, 107]. Here, \( c \) is the concentration of the species, \( t \) is the time, \( x \) is the axial channel dimension, \( y \) is the traverse channel dimension, \( L \) is the length of the curved section, \( w \) is the channel width, \( u \) is the velocity
and the superscript ‘ denotes the normalized component. This equation reflects two transport mechanisms: the term labeled ‘1’ in this equation is the advective transport - in the axial direction; the terms labeled ‘2’ and ‘3’ are the contributions from the axial and transverse diffusion, due to concentration gradients, respectively.

\[
\frac{\partial c}{\partial t} - U \frac{\partial c}{\partial x} = \frac{1}{\text{Pe}_w} \left[ \frac{w}{L_s} \left( \frac{\partial^2 c}{\partial x^2} \right) - \frac{L_s}{w} \left( \frac{\partial^2 c}{\partial y^2} \right) \right]
\]

The Peclet number, a non-dimensional parameter that characterizes the ratio of the rates of advection to diffusive transport for analytes, is given by Equation 3-17.

\[
\text{Pe} = \frac{Uw}{D_g}
\]

Here \(U'\) is the maximum velocity difference along the direction transverse to the microchannel which, under no-slip flow conditions, equals the maximum velocity in the channel occurring at the central axis of the channel. For pressure-driven flows, this velocity depends on the column dimensions, the pressure gradient, and the analyte since all analytes travel with different velocities due to the different retention factors. The Peclet number for an analyte will vary with the band position along the column since the band velocity increases along the column length. There are three primary regions depending upon \(\text{Pe}_w\) and \(L/w\) that are relevant to dispersion studies of dilute solutes [107].

\(\text{Pe}_w < 1\): For the case when \(\text{Pe}_w\) is small, the diffusive terms dominate the dispersion of the analyte band. Since the flow velocity, which is a function of the channel dimensions, affects the advective transport most profoundly, the channel geometry has little effect on dispersion when \(\text{Pe}_w < 1\).
$L/w > Pe'_w > 1$: In this flow regime, both advection and transverse diffusion are important to the evolution of the analyte band. While transverse diffusion prevents asymmetric stretching of the band, the contribution due to axial dispersion exceeds that due to axial diffusion alone. This is commonly termed as Taylor’s dispersion and is accounted for by using an effective diffusion coefficient. It has been shown that the effective diffusion constant in the Taylor-Aris limit is \( \sim 8 \) times the normal diffusion constant.

$Pe'_w > L/w$: Here, since the advective transport dominates the diffusion terms, the channel geometry has a significant influence on the evolution of the analyte band.

Computing the Peclet number gives a sense of the geometric dispersion of the analyte band. For complementary turns, as in a serpentine layout, it has been suggested that if the time required for a molecule to diffuse across the channel width is at least 100 times longer than the time required for the analyte band to cover the distance between two turns, the dispersion caused by the first turn will be “reversed” by the second turn [108]. This reversed flow also takes place for a spiral layout in which the flow starts and ends at the outer turn of the spiral, after changing direction at the center (see Figure 3-5). This condition can be written mathematically as Equation 3-18, where \( L_{st} \) is the length of the straight section between two turns for a serpentine layout or the length of the spiral from the inlet to the point where the flow is reversed.

\[
Pe'_w \equiv \frac{100 \, L_{st} \, w}{W}
\]

The variation of $Pe'_w$ for an unretained analyte for different column dimensions is shown in Figure 3-6. The Peclet number decreases for narrower columns, primarily because of the reduction in the axial velocity of the analyte.
Figure 3-5: Schematic of a spiral column layout showing the important dimensions. $L_{bt}$ is the length of the channel from $p_o$ to $O$. 
In addition, as shown in Figure 3-7, the Peclet number for an unretained analyte is more than that of a retained one, naphthalene in this case, because the retained analytes move slower than unretained ones. For serpentine columns, the maximum geometric dispersion due to the turns can be calculated by considering the difference in path length between the inner and outer turns at the curved section of the channel. If $\theta$ is the angle subtended by the curved portion of the channel, the difference in length between the inner and outer turns can be written as Equation 3-19 [108].

$$\delta l = \theta w$$

3-19

For a column with $n_{se}$ turns, a plug broadens by a total of (Equation 3-20)

$$\Delta l = n_{se} \theta w$$

3-20

For a column with mean turn radius of curvature thickness $r_m$, the number of turns can be written as in Equation 3-21.

$$n_{se} = \frac{L}{2(2L_{bt} + 2\pi r_m)}$$

3-21

For a spiral column layout, the band broadening due to the racetrack effect will be the difference between the outer and the inner path lengths. For the layout in Figure 3-5, if $p_o$ is the outer point along the axis at the outermost turn, $p_i$ the inner point along the axis at the innermost turn of a column with a wall thickness of $w_{wall}$, the number of turns is given by Equation 3-22.

$$n_{sp} = \frac{(p_o - p_i)}{(w + w_{wall})}$$

3-22

For a spiral of the form of Equation 3-23,
Figure 3-6: Variation of the Peclet number for an unretained analyte as a function of the gas pressure for 1 m long columns with different widths and aspect ratios at 50 °C.

Figure 3-7: Comparison of the Peclet numbers for an unretained analyte and naphthalene with time through a 50 μm by 600 μm by 1 m column under a 30 °C/s ramp rate.
\[ \tau = \sigma \theta + p_c \]

where, \( \tau \) is the turn radius, \( \sigma \) is a constant, \( \theta \) the angle, and \( p_c \) is the distance from the center of the spiral to the first turn, the length of the spiral can be calculated by Equation 3-24.

\[ L = \int_{\theta_1}^{\theta_2} \sqrt{r_0^2 + \left( \frac{dr_0}{d\theta} \right)^2} \, d\theta \]

Here, \( \theta_1 \) and \( \theta_2 \) are the angles subtended at the start and end of the spiral, related by Equation 3-25.

\[ \theta_2 = \theta_1 + 2\pi n_{sp} \]

For the outer spiral,

\[ r_0 = -\frac{w\theta}{\pi} + p_o \]

while for the inner spiral,

\[ r_0 = -\frac{w\theta}{\pi} + p_o - w \]

The integral in Equation 3-24 evaluates to Equation 3-27.

\[ L = 2\pi r_0 w \]

The difference between the length of the outer spiral and the inner spiral will simply be given by Equation 3-28.

\[ \Delta l = 2\pi n_{sp} w \]

The wider the spiral, the less the required number of turns will be, resulting in less band broadening. From Equations 3-20 and 3-28, the band broadening for two columns of the same
length and the same width, one arranged as a serpentine and the other as a spiral, can be related by the Equation 3-29.

$$\frac{Broadening_{sp}}{Broadening_{se}} = \left( \frac{n_{sp}}{n_{se}} \right)^2$$

For a Gaussian probability distribution, the second moment introduced due to the increase in the analyte plug length, $\Delta l$, shown in Equation 3-30, can directly be added to the HETP equation.

$$\sigma_{\text{turn}}^2 = \frac{\Delta l^2}{12}$$

Two additional non-dimensional numbers, the Dean number ($De$) and the Schmidt number ($Sc$), characterize the presence of secondary flows. The Dean number, given by Equation 3-31, is the ratio of the centrifugal to viscous forces - the higher the Dean number, the greater the effect of curvature. The Schmidt number in Equation 3-32, characterizes fluid flows with simultaneous momentum and mass diffusion convection processes. Here, $R_c$ is the mean radius of curvature of the turn.

$$De = \frac{\tau Ud}{\rho} \sqrt{\frac{w}{2R_c}}$$

$$Sc = \frac{\rho}{\tau D_g}$$

There are two primary flow regimes in channels with turns: the turns affect the flow if $De > 0.2$ [109] and coiling effects become significant for cases when $De^2Sc > 10$ [110].

### 3.4 Design of a High Aspect Ratio Rectangular Column

The performance of a column is evaluated in terms of the analysis time and the peak capacity. A number of physical parameters - column length, width, height, geometry, and
operational parameters - pressure, temperature, gas type, stationary phase type/thickness, affect column performance. To understand better the effect of all of the involved parameters, a code written in Matlab (The Mathworks, Natick, MA) was used to derive solutions. For all of the models in this section, methane and naphthalene (C_{10}H_{8}) were the first and the last eluting analytes respectively. Methane represents the unretained species while naphthalene represents boiling point of up to dodecane. In addition, unless otherwise noted, the following parameters were kept constant: column height – 600 μm, column length – 1 m, and an OV-1 type stationary phase film thickness – 0.1 μm. Figure 3-8 shows the variation of the holdup time and retention time of naphthalene with column for a 1 m long, 600 μm tall column for two pressures under an isothermal separation of 100 °C and 200 °C. As the temperature is increased, the retention factor of a compound decreases, which means that it is less retained in the column. At high temperatures, a compound will move faster through the column and its retention time will be reduced. At lower temperatures, the elution of naphthalene takes much longer than at higher temperatures. Figure 3-9 shows the variation of the number of plates for a column with and without a 5 μl inlet dead volume (D_i) for different column widths of a 1 m by 600 μm tall column for an isothermal separation at 200 °C. The inlet dead volume causes a significant decrease in the column performance. More importantly, the column width for the maximum peak capacity shifts to a larger value on considering an inlet dead volume. This suggests that for a real system, there is no distinct column width for optimal separation.

3.5 Comparison between Circular, Square, and Rectangular Columns

Consider two columns with the same hydraulic diameter and same length of 1 m, one a 50 μm diameter circular column and the other a 50 μm side square column. Figure 3-10 plots the number of plates for naphthalene versus average velocity at 100 °C.
Figure 3-8: Variation of the holdup time and the retention time for naphthalene with column width for 1 m long, 600 μm tall columns for two different pressures and two temperatures.

Figure 3-9: Variation of the number of plates with column width for 1 m long, 600 μm tall columns for two different pressures, with and without an inlet dead volume ($D_i$), at 200 °C.
The performance of the circular column is slightly better than the square column because in the square column the analytes have to travel a larger distance along the diagonal to reach the stationary phase. The efficiency of the rectangular column is lower than the square column (see Figure 3-11). For the square and rectangular columns, which are similar to each other except for the height, the velocity and the retention factor are the only two parameters influencing the HETP. One noticeable fact is that for the same pressure drop, the average velocity for the rectangular column is almost twice that of the square and circular columns. If the higher order terms are neglected, the retention factor of rectangular cross-section columns, derived from Equation 2-7, leads to Equation 3-33.

\[
k_i \propto \frac{1}{\beta} = \frac{2d_f(b + d)}{bd}
\]

For the same film thickness, the phase volume ratio for the 50 μm square column is 1.85 times that of the rectangular column. A look at the first two curves in Figure 3-12 begets the question: what is the advantage of a high aspect ratio column. Figure 3-12 explains that all real systems encounter dead volumes and extra-column effects. The extra-column effects that have a fixed volume are inversely proportional to the gas flow rate (see Equation 2-32). The length of the injected plug depends on the injected volume and the column cross-sectional area. For the same injected volume, the smaller the column cross-sectional area, the longer the injected plug, and the lower the efficiency.

Figure 3-13 compares the performance of columns of similar cross-sectional areas with different widths for an ideal system with no dead volumes. As expected, a narrow column has a better performance than a wider column. On considering an inlet dead volume \( (Di) \) of 2 μl, the efficiency of all of the columns decreases (see Figure 3-14). Since the cross-sectional areas are the same for all of the columns, the contribution of the inlet dead volume will be the same.
Figure 3-10: Comparison of performance between 1 m long circular and square columns with hydraulic diameters of 50 μm for naphthalene with hydrogen carrier gas on an OV-1 column with a 0.1 μm film thickness at 100 °C.

Figure 3-11: Comparison of performance between circular, square, and rectangular columns. For the same pressure, the average velocity for the rectangular column was twice that of the square column, while the efficiency is lower. The compound used was naphthalene with hydrogen carrier gas on an OV-1 column with 0.1 μm film thickness at 100 °C.
Figure 3-12: Plots of the number of plates for two 50 μm wide, 1 m long columns with different heights, with and without extra-column effects. With an inlet dead volume (Di), the efficiency of the low aspect ratio column decreased significantly, mainly because of the smaller cross-sectional area.

Figure 3-13: Comparison of performance of columns with the same cross-sectional areas but different widths for the ideal case defined by Golay’s equation (Di=0).
Figure 3-14: Comparison of performance of columns with the same cross-sectional areas but different widths with a 2 µl inlet dead volume ($D_i$).
Figure 3-15 compares the unretained HETP of columns with different widths. The narrower columns have a slightly lower HETP, which can be derived by substituting \( k = 0 \) in Equation 3-16. The corresponding Golay plots for naphthalene at 200 °C are given in Figure 3-16.

Figure 3-17 compares the holdup times for columns for different columns for temperature-programmed separations. Figure 3-18 compares the peak capacity for the same set of columns, showing that the column performance is better for narrow columns. Again, fixed volume extra-column effects will hamper the performance of a low aspect ratio column more than a high aspect ratio one. Figure 3-19 shows the variation of the retention time of methane and naphthalene with column widths for pressures of 40 psia and 80 psia, respectively under temperature programming of 40 °C/s. The retention times for this case are slightly lower than for the isothermal case, because the viscosity of a gas is proportional to the temperature. Figure 3-20 plots the variation in peak capacity for two different pressures with and without a 5 μl inlet dead volume. The peak capacity shows a significant jump at higher pressures though volumetric extra-column effects at the inlet cause a significant drop and shifts the optimum width to a wider column, although, incorporating a split injection mitigates the effect of the inlet extra-column effects (see Equation 2-32). Figure 3-21 shows the peak capacities for different split ratios for a 5 μl inlet dead volume; the peak capacity for the case without the dead volume is 129. It shows that a high split ratio (>20) is required to achieve the maximum efficiency.

Figure 3-22 shows the variation of the peak capacity with and without geometric dispersion arising from a serpentine column with a hundred 180 ° turns. The percentage contribution of the reduction in peak capacity due to the geometric dispersion is plotted on the secondary axis. This shows that the turns do contribute to the band broadening. The contribution of the geometric dispersion will become more evident as the components of the GC sensor are integrated leading to minimal dead volumes.
Figure 3-15: Golay plots for 600 μm tall by 1 m long columns of different widths for methane using hydrogen carrier gas at 30 °C.

Figure 3-16: Golay plots for 600 μm tall by 1 m long columns of different widths for naphthalene using hydrogen carrier gas at 200 °C.
Figure 3-17: Variation of the holdup time with head pressure for different columns under a 40 °C/s ramp rate from 25 °C to 250 °C.

Figure 3-18: Variation of peak capacity with head pressure for different columns with a 0.1 μm thick OV-1 stationary phase under a 40 °C/s ramp rate from 25 °C to 250 °C.
Figure 3-19: Variation of the column holdup time and retention time of naphthalene with column width for head pressures of 40 psi and 80 psi through a 1 m long, 600 μm tall column and a 40 °C/s ramp rate.

Figure 3-20: Variation of peak capacity on a 1 m long, 600 μm tall column for two pressures and a 40 °C/s ramp rate, with and without a 5 μl inlet dead volume.
Figure 3-21: Effect of the split flow ratio on peak capacity for a 1 m long, 600 μm tall column with a 5 μl inlet dead volume.

Figure 3-22: Effect of the number of turns on peak capacity of a 1 m long, 600 μm tall column for different pressures and a 40 °C/s ramp rate.
These results reemphasize that the performance of a column depends on many parameters, including column width, height, and length, head pressure, film thickness, temperature, temperature programming rate, and extra-column effects. Other extra-column effects such as the outlet dead volume cause similar reduction in the peak capacity, stressing the importance of good system design. In addition to the design considerations, to realize the column, the capabilities of the fabrication process should be considered also. Considering previous experience with fabricating these columns, 30 μm, 40 μm, and 50 μm widths and lengths ranging from 0.5-2 m were designed. The discussion on the various designs and the process development leading to fabricating these columns follow in the next chapter.

3.6 Chapter Summary

Modeling results for both isothermal and temperature programming show that column performance is lower for a system with dead volumes than for an ideal system. In a real system, a narrow width, high aspect ratio column will perform better than similar dimension circular and square columns. The band broadening due to column geometry when flow reversal does not occur was estimated for serpentine and spiral column layouts.
4 Fabrication of the GC Sensor

The GC column is the most critical component of a GC sensor. Most of the discussion on realizing the sensor will focus on the design and fabrication of the GC column, which, as discussed below, consists of the column and added functionality in the form of sample injection loop, integrated split flow, a placeholder for integrating the detector, and strategies for thermal management. Apart from the high aspect ratio, the column walls should be as parallel as possible to maintain resolution. Just 1% of taper in a column with an aspect ratio of 100 would increase the diffusion coefficient by 17.5 times compared to a parallel wall column. This effect increases quadratically with increasing sidewall taper [27]. Due to these constraints, the most appropriate methods to fabricating the columns derive from lithography and MEMS processes. Standard machining tools for micro-milling and drilling are limited to depths not more than three times the nominal diameter of the cutting tool and will produce a taper in the machined parts. A number of fabrication techniques, including, stereolithography, silicon bulk micromachining, silicon deep reaction ion etching (DRIE), silicon DRIE polymer vapor deposition, and LiGA have reportedly been used to fabricate GC columns, a brief overview of which follows. The discussion will cover the detailed description of the involved fabrication steps and the process development steps carried out.

4.1 Background

The first non-circular columns were fabricated by Papendick et al. in the late 1970’s by reworking 1 mm i.d. coated steel and copper capillary columns through a “micro-mangle” to obtain 200-300 μm wide, 400-600 μm tall, elliptical columns [111]. While pooling of the stationary phase during column coating at the sharp corners could be avoided in the elliptical profile, the fabrication approach was not successful as 1) the heat generated from the reshaping
process destroyed the column coating, 2) connections to the column were difficult because of the resulting awkward geometry, causing large dead volumes, 3) quality control was difficult with the fabrication process, 4) a lack of precise control over the formed rectangular column geometry resulted in overly-flat columns which increased the required column head pressure, and 5) the cross-section was not uniform along the column length. Another approach to realizing noncircular, crinkled columns was discussed by Desty et al. [112]. The motivation for using such columns was to enhance the transverse mixing without causing additional longitudinal broadening. These elliptical cross-section columns with width and height of up to 70 μm and 660 μm, respectively, were coated with a crystalline stationary phase with promising preliminary results. Some success in lowering the HETP due to the reduction in mass transfer in the gas phase was reported, but the columns faced the same limitations as those developed by Papendick.

At around the same time, Terry et al. demonstrated a microfabricated column by silicon bulk micromachining [46]. The system consisted of an injection valve, a 1.5 m long, 40 μm deep, 200 μm wide rectangular cross-section column, and a thermal conductivity detector (TCD) on a silicon wafer. The lack of a technique for coating a rectangular cross-section column reduced device performance. In addition, capillary connections to and from the column to the external components introduced dead volumes and cold spots that decreased performance. Although the initial system was not widely adopted, descendants of the micro GC with thermal conductivity detectors are commercially available and in use in miniaturized and full-scale GC systems today.

From Terry’s original idea, a number of research groups have used MEMS techniques to fabricate micro GC columns in silicon [109, 113, 114, 115, 116, 117], parylene [118, 119], porous silicon [120], carbon nanotubes [49], polymer resin via stereo lithography [122], SU-8 via UV-
LiGA [123] and metal [124]. Microfabricated silicon columns have gone through over 25 years of design and development. These columns, typically with an aspect ratio of 1-4, consist of a silicon substrate micromachined using the DRIE process and a cover sheet of Pyrex®, bonded anodically to yield a sealed GC column. The most recent reported tests on a 150 μm wide by 240 μm deep by 3 m long columns show separation of 20 compounds ranging from methanol (Kovats RI 305 on a non-polar OV-1 column [125]) to chlorobenzene (Kovats RI 827 on a non-polar OV-1 column [125]) in 600 seconds under isothermal conditions, yielding 2700 plates/m. Problems with controlled deposition of the stationary phase are suggested as the cause for the poor performance [114]. There are two issues related to the fabrication process that will limit the performance of the silicon columns. First, the low aspect ratio columns do not fully exploit the advantages of the rectangular cross-section configuration. The reported sidewall taper of up to 2% can also degrade performance as suggested by Golay. Second, while significant progress has been made with the anodic bonding process, there are reports of failure during the high temperature operation due to thermal expansion mismatch [126], higher residual thermal stresses with higher temperature-higher strength bonding processes [127, 128], and the dependence of bond strength on the cooling rate [129] that indicate that additional work is needed before it is a reliable method of sealing columns over large areas.

The parylene columns, fabricated by vapor deposition of parylene in a silicon mold fabricated by DRIE, were sealed by laminating with a parylene cover. The 50 μm wide by 300 μm tall by 1 m long columns with a 10-50 μm thick wall yielded good separation results for light compounds on a variety of stationary phases. The parylene column by itself has low thermal capacitance, but the thin walls deform under gaseous pressure, changing the column cross-section and performance. The low capacitance advantage is lost if the structure is supported on thicker walls or by metal interlayers. The fabrication process is quite expensive and serial in
nature since the silicon mold acts as a sacrificial template which has to be etched away to utilize the parylene column.

A gas sensor based on a porous silicon film detected NOx, CO, SO2, and NH3 in ppm concentration in less than 10 minutes. The resistance of the micro/nano porous silicon layer, which acted as a high surface area adsorbent, changed when analytes pass over it and was used as a marker for a particular gas. Diffusion during adsorption and release of the analyte to/from the surface limited the performance of the device. The advantages of the device are its small size and easier integration since the fabrication process is compatible with the CMOS process. The 500 μm wide by 1000 μm tall by 1 m long columns fabricated by stereolithography are of academic interest only since the low dimensional tolerance of the fabrication process cannot produce narrow width, high performance gas chromatograph columns.

As an alternative, high aspect ratio, metal columns for gas chromatography fabricated using the LiGA process were introduced. The LiGA technique is well suited to fabricate complex, narrow, high aspect ratio structures [130, 131, 132, 133] with excellent vertical side wall quality [134, 135], and is scalable for high volume production through injection molding using molds made by the LiGA process [136]. One of the principal advantages of LiGA is the wide choice of working materials such as nickel, copper [137, 138], nickel-iron [139, 140], ceramics [141], and polymers. Previous work at LSU with the LiGA columns has focused on flow and thermal modeling and fabrication of columns with an aspect ratio of up to four. The columns described here were typically 2 m long, 50 µm wide, and up to 650 µm tall. For a structure like the micro GC column, which should have good thermal properties along with structural rigidity, metal columns are an interesting alternative to the silicon columns. There is a distinct advantage to using metal columns because of their higher thermal conductivity compared to the silicon-glass composite. Consider a column heated by a heater placed at its bottom as shown in Figure 4-1.
The column stack comprises the top cover, the column, and the bottom cover. The three cases considered are a nickel top, nickel column, and nickel bottom; a copper top, copper column, and copper bottom; and a glass cover, silicon column, and glass cover. Table 4-1 lists the physical parameters. A simple heat balance for each of the blocks yields Equation 4-1.

\[
S_f = h_c A_1 (T_1 - T_\infty) + \frac{1}{R_1} (T_1 - T_2) + C_1 \frac{dT_1}{dt}
\]

\[
\frac{1}{R_1} (T_1 - T_2) = h_c A_2 (T_2 - T_\infty) + C_2 \frac{dT_2}{dt}
\]

\[
\frac{1}{R_2} (T_2 - T_3) = h_c A_3 (T_3 - T_\infty) + C_3 \frac{dT_3}{dt}
\]

where, \(S_f\) is the heater flux, \(h_c\) is the convective heat transfer coefficient, \(T_\infty\) is the temperature of the surroundings, \(T\) is the temperature of the block, \(R\) is the thermal resistance between adjacent blocks in terms of its length, \(L\), cross-sectional area, \(A\), and resistivity, \(k\), and \(C\) is the thermal capacitance of the block in terms of its mass, \(m\), and specific heat capacity, \(c_p\).

\[
R = \frac{L}{kA}, \quad C = mc_p \Delta T
\]

These equations, solved using the ode45 solver in Matlab gave the dynamic temperature response of each block. Figure 4-2 shows a plot of the dynamic response for an input heat flux of 15 W for nickel columns with nickel top and bottom covers. Figure 4-3 and Figure 4-4 show the respective response curves for copper columns with copper covers and silicon columns with glass covers. The low heat transfer rate of the glass covers is the primary cause of the slow response of the silicon columns, rendering them suitable for only isothermal operation and not for temperature programming operation with fast cycle time and low power consumption. This may also limit their operation to primarily separating compounds with high vapor pressures.
Figure 4-1: Schematic of the thermal model.

Table 4-1: Material and physical properties for the thermal model [142].

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\text{kg/m}^3$</th>
<th>$c_p$ $\text{J/kg K}$</th>
<th>$k$ $\text{W/m K}$</th>
<th>Top cover thickness</th>
<th>Column thickness</th>
<th>Bottom cover thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>8900</td>
<td>444</td>
<td>90.1</td>
<td>100 $\mu$m</td>
<td>600 $\mu$m</td>
<td>100 $\mu$m</td>
</tr>
<tr>
<td>Copper</td>
<td>8230</td>
<td>380</td>
<td>401</td>
<td>100 $\mu$m</td>
<td>600 $\mu$m</td>
<td>100 $\mu$m</td>
</tr>
<tr>
<td>Silicon</td>
<td>2300</td>
<td>712</td>
<td>148</td>
<td></td>
<td>600 $\mu$m</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>2230</td>
<td>840</td>
<td>1.005</td>
<td>100 $\mu$m</td>
<td></td>
<td>100 $\mu$m</td>
</tr>
</tbody>
</table>
Figure 4-2: Temperature response of a nickel column with nickel top and bottom covers for an input power of 15 W. The convective heat transfer coefficient is 50 W/m²K.

Figure 4-3: Temperature response of a copper column with copper top and bottom covers for an input power of 15 W. The convective heat transfer coefficient is 50 W/m²K.
4.2 Column Fabrication

LiGA is a micromachining process, which makes use of a synchrotron, an electron storage ring [143]. Changing the path of this electron beam orbiting the ring at relativistic speed releases photons tangential to the direction of the beam. The wavelength of these photons ranges from infrared to hard X-rays (5 Å). Fresnel diffraction from this broad spectrum causes a blur in the edge of the exposed resist, which can be up to 0.1 μm for a 500 μm thick resist, which is still minimal as compared to UV lithography. The short wavelength of the X-rays reduces diffraction effects in patterning materials, while the high energy enables deep penetration into the material. Under normal operating conditions, the electron ring at CAMD operates at 1.3 GeV energy.

Like all MEMS processes, the LiGA process starts with the fabrication of an optical lithography mask in a pattern generator, or direct writing of an intermediate mask with an electron beam. Transferring the pattern from the optical or intermediate mask to an X-ray mask
enables patterning of X-ray sensitive material [134]. Exposure of the positive PMMA resist to X-rays through the mask causes scissions in the long polymer chains, reducing the average molecular weight of the exposed resist. The low molecular weight PMMA is removed by alternating between GG developer and GG rinse solutions. Metal electrodeposition into the resulting templates forms either structures or mold inserts for hot embossing and injection molding. Figure 4-5 shows the schematic of the fabrication process.

4.2.1 Device Substrate Preparation

An ideal substrate for LiGA should have sufficient electrical conductivity for electrodeposition, provide good adhesion for the PMMA during developing and electrodeposition, minimize the effects of fluorescence during X-ray exposure, be rigid enough to withstand stresses coming from metal electrodeposition, and be selectively etched to release the structures if necessary. It should also be sufficiently flat and smooth to yield good quality structures. The typical process for substrate preparation is to glue (bond) a PMMA disc to a conductive substrate using one of the two gluing methods: solvent bonding involving methylmetaacrylate (MMA) [145] and a PMMA glue containing 15% of 950k PMMA resist and 85% MMA. Seven substrate types were evaluated: silicon wafers (525 μm +/- 25 μm, TTV 20 μm, bow/warp <40 μm, 1-100 Ohm resistivity, single side polished, TYGH Silicon, Livermore CA) coated with 2 μm of nickel, 2 μm of titanium, and 1 μm of titanium oxide attached through solvent bonding, silicon wafers coated with 2 μm of nickel, 2 μm of titanium, and ~1 μm of titanium oxide layer bonded using the PMMA glue, and bulk titanium wafers (Vulcan materials, Birmingham, AL) bonded using the PMMA glue. The titanium oxide substrates were prepared by electron-beam deposition of a 2 μm thick titanium layer on a silicon substrate and oxidizing it for up to 5 minutes in an alkaline-peroxide solution containing 0.1 M sodium hydroxide (NaOH) and 30 % hydrogen peroxide (H₂O₂) at 65 °C.
Figure 4-5: Schematic of the column fabrication process by LiGA.

Step 1: Expose PMMA on a Si substrate

Step 2: Develop exposed PMMA

Step 3: Electrodeposit nickel and planarize

Step 4: Etch substrate, electrodeposit nickel on the bottom face

Step 5: Heat to remove the PMMA
The PMMA glue comprised 15% PMMA, 85% MMA by weight, with benzyl peroxide, dimethyl aniline, and methacryloxypropyl-trimethoxysilane (MEMO) used as additives to improve cross-linking between the glue and the PMMA. The PMMA resist (Vistacryl, CQ-grade non-UV; Vista Optics, Stockport, UK) was cut into 3.8” diameter discs, annealed in a convection oven at the rate of 1 hr/1 mm thickness at 88 °C, bonded to the substrates, and flycut (Precitech Optimus flycutting machine, Keene, NH) using a diamond tool (Contour Tooling, Jackson, MI) to thicknesses ranging from 300 to 700 μm with an accuracy of +/- 6 μm.

For a test mask, features in the shape of thin lines, 50 μm wide by 1.5 cm long, were placed on an optical mask and the X-ray mask fabricated on a silicon nitride membrane. The substrates were exposed with a top to bottom dose of < 5 and developed in alternating cycles of GG developer (20 min) and GG Rinse (40 min) until the resist was developed completely. Any delamination in the resist during development was treated as a device failure. Table 4-2 lists the obtained results. The prepared titanium oxide layers on the bulk titanium and e-beam deposited titanium substrates gave the best results.

Table 4-2: Evaluation of resist bonding methods for different substrates.

<table>
<thead>
<tr>
<th>Seed layer</th>
<th>Bonding method</th>
<th>Results (300 μm – 700 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Solvent bonding</td>
<td>Delamination during resist development</td>
</tr>
<tr>
<td></td>
<td>PMMA glue</td>
<td>Delamination during resist development</td>
</tr>
<tr>
<td>Titanium</td>
<td>Solvent bonding</td>
<td>Good for up to 300 μm thick resist</td>
</tr>
<tr>
<td></td>
<td>PMMA glue</td>
<td>Delamination during resist development</td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>Solvent bonding</td>
<td>Good for up to 300 μm thick resist</td>
</tr>
<tr>
<td></td>
<td>PMMA glue</td>
<td>Excellent adhesion up to 700 μm thick resist</td>
</tr>
<tr>
<td>Bulk titanium</td>
<td>PMMA glue</td>
<td>Excellent adhesion up to 700 μm thick resist</td>
</tr>
</tbody>
</table>
Further, the bottom surface of the structures on the bulk titanium substrates was much rougher
(Ra ~ 800-1000 nm) as compared to that from the silicon-titanium oxide layer (Ra ~ 300 nm).
Consequently, silicon wafers with a titanium-oxide seed layer were picked as the substrate for
routine fabrication.

4.2.2 X-Ray Mask Fabrication

All of the mask designs used in this research were drawn in AutoCAD (AutoDesk, CA). Industry
standard clear field chrome-on-soda-lime glass optical masks, 0.09” thick, 5” by 5” in
dimensions, with right reading chrome down, were purchased from Advanced Reproductions
(North Andover, MA). The two types of X-ray mask membranes used were graphite and silicon
nitride. The use of graphite as a membrane for X-ray masks has been discussed in detail
elsewhere [144].

The X-ray mask fabrication process on a 2 µm thick, low stress silicon nitride membrane
(DIMES, Delft, The Netherlands) was a three-mask process (see Figure 4-6). A positive resist,
SPR-220 (Rohm and Hass, Marlborough, MA), was spin coated on a silicon nitride wafer at 1100
rpm for 30 seconds, let sit on a leveled surface for 6 minutes to relieve stress in the coated layer,
and baked at 105 °C for 3 minutes on a hot plate. The resulting resist layer was 13 +/- 1 µm
thick. The edge bead was removed by exposing the resist with 3900 mJ/cm² energy on a Quintel
UV alignment system (Quintel, Morgan Hill, CA). Removal of the edge bead was critical to
getting a good contact exposure for the mask pattern. The edge bead mask consisted of an
annular ring with an outer diameter of 4.1” and inner diameter of 3.7”. The exposed areas were
developed for ~10 minutes in a mixture of 50% MF-321 and 50% MF-322 developers (Rohm and
Hass, Marlborough, MA). The mask containing the column design was centered on the mask
wafer, exposed to UV light with a dose in the range of 350-430 mJ/cm², and developed for 4-6
minutes. Gold, because of its high molecular weight and a high absorption coefficient, is the
most commonly used absorber for X-rays. About 10 μm of the absorber was electrodeposited into the resist pattern from two types of commercially available gold electrodeposition solutions based on gold sulfite (Na₃Au(SO₃)₂) chemistry, Type TG25E-RTU (Technic, Irving TX) at 48 °C and Neutronex 309 (Enthone, West Haven CT) at 55 °C, both using a galvanostatic, pulsed current cycle and a platinized mesh anode. The back of the gold electroplated wafer was coated with S1818 resist (Rohm and Hass, Marlborough, MA) at 3000 rpm for 30 seconds, baked in a convection oven for 30 min, backside aligned and exposed for 30 seconds, and developed for ~10 minutes in MF-321 to reveal the silicon nitride layer. The mask pattern for this layer included windows corresponding to the pattern on the front of the mask. The silicon nitride layer was etched in a RIE system at the Nanofabrication Center, University of Minnesota, exposing the underlying silicon surface. After etching the exposed silicon in a KOH bath at 85 °C, it was mounted on a 4” NIST ring to form the X-ray mask. The nickel structures fabricated using the silicon nitride mask have better sidewall roughness (Ra=150 nm) as compared to those from the graphite membrane (Ra=500 nm).

4.2.3 X-Ray Exposure

Exposing the resist to X-rays is a process step critical to the sidewall slope and the quality of the structures. The typical procedure to estimate the energy required for exposure is to fix the energy required to expose the bottom of the resist. The top surface of the resist receives a higher intensity of radiation than the bottom surface. The intensity of X-rays decreases as they pass through different media including, membranes, resists, filters, and plating bases. Equation 4-2 shows the relationship between the rate of change of intensity with resist thickness [146].

\[ P_\alpha \left( z \right) = P_\alpha \left( 0 \right) e^{-z\xi} \]
Figure 4-6: Schematic of the silicon nitride X-ray mask fabrication process.

1. Coat silicon nitride wafer with photoresist
2. Remove edgebead and pattern wafer
3. Electrodeposit gold
4. Cover front with resist, pattern backside
5. Etch nitride, etch silicon, remove all resist
Here, $P_{ev}(0)$ is the incident radiation, $z$ is the resist thickness, and $P_{ev}^z(z)$ is the radiation at a thickness $z$. The total energy required for exposure is then an integration of the area of the $P$-$z$ curve. Figure 4-7 shows the critical regions of the resist-substrate pair concerning X-ray exposures. The top dose and the bottom doses are defined as the radiation energy per unit volume absorbed by the top surface of the resist and the bottom surface of the resist respectively. An important exposure parameter is the top dose to bottom dose ratio (TBR). Adding filters before the mask reduces the percentage of the soft X-rays reaching the resist surface and reduces the TBR. This shifts the radiation spectrum absorbed in the resist to a narrower, higher energy region, resulting in a more uniform energy deposition along the resist height. The unwanted consequence of adding filters is that the energy reaching the resist reduces, aka, the total energy and the time required for complete exposure increases. The high dose can lead to cracks in the resist and reduce the shelf life of the resist after exposure. While a TBR of five or less is the reported optimum for PMMA [134], exposures without the use of filters with a TBR of up to 20 are also common for exposing resist layers 200 μm and thicker at CAMD [147]. The absorbed dose in the areas under the gold absorber must be lower than 100 J/cm$^3$ for good contrast between the exposed and unexposed regions.

DoseSim® (version 4.0.0, IMT, Karlsruhe, Germany) was used to estimate the energy required to expose PMMA resist [148]. The two exposure methods followed were: 1) adding filters that maintained the TBR below five with the bottom dose at 3500 J/cm$^3$ and 2) no filters with the bottom dose at 2500 J/cm$^3$. Bubbling of the PMMA resist was observed at high values of the top doses (more than 20,000 J/cm$^3$), which caused cracks in the PMMA. Both exposure modes gave good results. To save exposure time and to reduce the hard X-rays reaching the resist, the routine process used the latter exposure method.
Figure 4-7: Conditions for the absorbed doses at different points on the resist layer.
4.2.4 Column Layout

Four different masks were fabricated, each with a number of column designs. Table 4-3 lists the details of these designs. The layouts included sensor “chips” containing columns, which were 30-50 μm wide, 0.25-2 m long, in spiral and serpentine configurations. Each iteration was a design modification either based on process development or incorporated increased functionality on the column chip. Figure 4-8 shows a representative sensor chip, which incorporates a sample inlet loop with split flow, interface for adding makeup gas at the outlet, and inlet/outlet ports for fluidic connections on both side.

Table 4-3: Dimensions of the different columns designs patterned on the mask.

<table>
<thead>
<tr>
<th>Column width (μm)</th>
<th>Column lengths (m)</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.25-2m</td>
<td>Serpentine</td>
</tr>
<tr>
<td>40</td>
<td>0.25-2m</td>
<td>Serpentine</td>
</tr>
<tr>
<td>50</td>
<td>0.25-2m</td>
<td>Serpentine and Corrugated</td>
</tr>
</tbody>
</table>

Figure 4-8: Schematic of a representative column layout showing a 50 μm wide, 2 m long column. The size of the column chip is 2 cm by 4 cm.
Previous results on the test mask indicated that for 600 μm tall columns, the wall thickness should be four times the thickness of the columns to avoid delamination during resist development, based on the critical aspect ratio criteria [149, 150]. Additionally, drying the structures after the developing cycle caused the resist structures to collapse because of stiction. Consequently, the substrates were electrodeposited right after developing the resist, without drying. To avoid delamination of the resist structures due to thermal expansion coefficient mismatch between the developer/rinse at 25 °C and the sulfamate based nickel electroplating bath which was typically operated at 55 °C [151, 152], a process was developed to electrodeposit nickel at 35-40 °C [149]. Nickel was electrodeposited at a current density of 10-15 mA/cm² in the developed PMMA mold and overplated to form a three-sided structure (Step 3 in Figure 4-5). After planarizing the overplated regions to +/- 20 μm, the structures were released by etching the silicon substrate in a 30% potassium hydroxide, KOH, bath at 85 °C. The titanium oxide seed layer was also etched in the KOH bath. Close inspection of the surface at the bottom of the structures (substrate interface) revealed thin metal bridges (see Figure 4-11). One possible source of these defects was the damage to the PMMA glue layer caused by secondary fluorescence radiation resulting in its partial development and subsequent underplating [153].

One method to remove these metal bridges was to remove about 25 μm by polishing the surface. The other method was to electrodeposit a copper sacrificial layer before electrodepositing the nickel device layer. A copper-nickel selective etchant (Transene, Danvers, MA) helped etch the copper sacrificial layer after releasing the structures from the substrate. Although both of these techniques gave good results, polishing the released structures was adopted for the routine process.

To satisfy the condition in Equation 3-18 for the 50 μm wide column, the maximum value for \( L_{tx} \) is 3 μm, which for serpentine columns means that the dispersion is not reversed
by the opposing 180° turns. The Dean number and the parameter $De^2Sc$ are plotted for different column dimensions in Figure 4-9. Since the flow in the columns is laminar, shown by the low $Re$ values, and the curved areas of the serpentine columns make up less than 3% of the total column length, the effect of secondary flows, if present, will be negligible on the designed columns. At the higher temperatures experienced during temperature programming separations, $De$ and $De^2Sc$ will be smaller than those plotted since both, the velocity and the diffusion coefficient, increase with temperature, further lowering the effect of the secondary flows.

4.2.5 Sealing the Metal Columns

There were two choices to sealing the columns. One was to fabricate free standing structures, without a supporting substrate, and seal the columns either by mechanical methods such as fasteners or by diffusion bonding. The other choice is to seal one side by electrodeposition (overplating), leaving one open side which can be sealed by electrodeposition [154, 155], laser welding [156, 157], and diffusion bonding [158]. Laser welding often requires a filler material, e.g., carbon black, for bonding [157], which can interfere with sensitive GC analysis. Diffusion bonding and its derivatives have applications in 1) packaging MEMS inertial sensors via gold thermo compression bonding [159] and 2) nickel-nickel diffusion bonding [160]. The use of electroplating to seal MEMS devices is a simple, low-cost, scalable, and effective process, which is surprisingly not commonly used.

Freestanding columns have a distinct advantage over columns that have an inherent substrate. While they have the potential of eliminating the “pooling” effect of stationary phase films, there are two drawbacks to using freestanding columns. The first is that due to the residual stresses from electrodeposition and substrate removal, the nickel column walls, mechanically equivalent to cantilever beams, tended to curve upon release.
Figure 4-9: Variation of the Dean number for an unretained analyte through 1 m long columns with different widths.

Figure 4-10: Variation of the factor $D_e^2Sc$ for an unretained analyte through 1 m long columns with different widths.
This creates a problem in sealing these columns by diffusion bonding. The remedy is to reduce the “channel length” (see Figure 4-8) which increases the stiffness of the cantilever beams.

Surface preparation for sealing the freestanding columns via mechanical fasteners or diffusion bonding is another limitation. The surface planarity and the average surface roughness value requirements for metal-to-metal seal are very high (total thickness variation < 1 μm and Ra < 10 nm). This is very challenging for a device as a column with a large surface area (up to 4 cm²). To avoid the challenges of freestanding columns, the nickel columns were sealed via electroplating. Two methods were used - one in which the channels were filled with a wax and the other where the PMMA resist itself was used as the filler material.

To use wax as the filler material, the PMMA from the overplated columns was flood exposed and developed. The column was placed on a hotplate at 150 °C and wax shavings were placed on the chip, where they melted and filled up the column. The columns were then planarized and overplated with nickel. The process is shown in Figure 4-14. To drive the wax out without burning it, the column chip was heated to 150 °C and nitrogen gas at 100 psi was applied at the ends. This was not very successful. Due to the high fluidic impedance of the columns, the applied pressure was not sufficient to drive the wax out completely or the fluidic connections were not strong enough to withstand the high pressure under temperature. Another problem during filling the column with the wax - the wax layer formed a negative meniscus, which was difficult to fill-up completely, even after the covered surface was polished. There were always areas where the wax had broken off from the channel.

These shortcomings were eliminated by using an alternate method. The columns after the X-rays exposure, development, and electrodeposition were overplated, with the PMMA resist still in place. Through this step, called the 2nd overplating step (step 5 in Figure 4-5), 500-800 μm thick nickel covers were formed on the column and lapped to the desired thickness
Figure 4-11: Columns with thin nickel bridges (first image) which were removed by polishing (second image).

Figure 4-12: Serpentine and corrugated columns, 50 μm wide and 600 μm tall, fabricated using the LiGA process.

Figure 4-13: a) SEM of the cross-section of a 50 μm wide and 600 μm tall column and b) SEM image of the sidewalls and the bottom of the columns.
Single side sealed columns

Replace PMMA with wax and planarize

Overplate nickel and remove wax

Figure 4-14: Schematic of the process for sealing the columns using a wax filler.

on a Hyprez Lapping System (15LM115V, Engis, Wheeling IL), resulting in an end-to-end flatness of +/- 5 µm across the sample.

After opening the column inlet/outlet ends at the sides with a Dremel (Racine, WI), the columns were heated in a Thermolyne 1300 atmospheric furnace (Dubuque, IA) to 425 °C (step 5) for four-six hours to remove the PMMA by pyrolysis and allowed to cool down to room temperature.

To test internal leaks in the column, methane gas plugs were introduced into the column in a flow of hydrogen carrier gas. Figure 4-15 shows a schematic of the experimental setup. The column chip has four inlet/outlet ports: the inlet split flow at port A, the vent at port B, the makeup gas (hydrogen) introduced at port C, and the column outlet at port D. External connections to the sealed columns were made by attaching stainless steel capillaries with o.d. of 0.016” and i.d. of 0.012” (Small Parts, Miami Lakes, FL) to the inlet and outlet ports. Hydrogen leak detectors (Restek, Bellefonte, PA and Gow-Mac, Bethlehem, PA) tested the leaks at the inlet/outlet connections. A 2 µl methane sample loop installed in a ten-port mini diaphragm electrostatic valve (Valco Instruments, Houston, TX), was filled up loaded with methane using a
syringe. On actuating the valve, the sample volume was injected into the column inlet with a 50:1 to 100:1 split flow ratio, controlled by a needle valve at port B. The eluting unretained peak was detected using a FID, which was connected to a Keithley 6517A Electrometer/High Resistance Meter (Keithley, Cleveland OH), from where the data were transferred using an A/D board at a sampling rate of 125 Hz, and displayed on a PC using the GageScope software (version 2.2.00, Gage Applied Sciences, Dallas TX). A single peak would indicate a perfectly sealed column, while a double or triple peak registered at the detector would indicate multiple flow paths (leaks) in the column. For the column design in Figure 4-8, a peak doublet was recorded (see Figure 4-16).

To investigate the issue further, failure analysis techniques such as a SEM, X-ray imaging, and Surface Acoustic Microscopy (SAM) were considered. While a SEM provides sub-micron resolution, unlike X-ray imaging or SAM, it is a destructive technique. In addition, locating the delamination in a sealed column can be difficult in SEM with the information can easily be lost during sample preparation. X-ray imaging was not useful for this application, because X-rays in normal synchrotron operation do not have sufficient energy to penetrate the 200-600 μm thick nickel layers. In contrast, SAM utilizes differences in acoustic impedances (density*acoustic velocity) of the materials at an interface to detect the presence of flaws. The use of SAM as a failure analysis tool has been widespread in the semiconductor industry since the early 90s [161]. The principle behind ultrasonic inspection is that a portion of the ultrasound reflects at a material boundary, while the remainder propagates through it. Voids and delaminations, which are strong reflectors, appear bright on a SAM image. The larger the differences in acoustic impedance, the greater the amount of sound reflected. In the pulse echo mode, the reflected sound is digitized to produce images of internal interfaces. An electronic gate helps collect data at a specified depth and an image results on scanning the sample.
Figure 4-15: Schematic of the experimental setup to test the sealing of the microfabricated GC columns.

Figure 4-16: Response of a defective LiGA column to a methane plug showing the presence of multiple peaks.
Figure 4-17: An ultrasonic horn used to image the sealed nickel columns via acoustic microscopy.

Figure 4-18 shows the SAM image, obtained at Sonix Inc. (Springfield, VA) using a 110 MHz, 8 mm focal length transducer with a resolution of 20 μm by 20 μm, for a section of the column in Figure 4-8. The “bright” areas on the SAM image indicate the presence of air. There were two potential causes for the observed delaminations [162]. During PMMA pyrolysis in Step 5 of the fabrication process, the decomposing PMMA in the stress-relieving windows expanded but did not have a vent to accommodate the increased volume, causing pressure to build-up (see Figure 4-19). The high pressure eventually caused the gases to break across the electroplated nickel layer, which show up as “white” areas on the SAM image (see Figure 4-18). The stress-relieving windows are necessary to reduce the stress in the PMMA during the exposure and developing processes. The other delamination occurred across a large area across the columns (Figure 4-20). Surface contamination on the column before the second electrodeposition was the primary cause of this defect. These impurities caused a weak bond between the electroplated layers, which readily debonded apart under increased temperature. After inspection under the SAM, the delaminated areas were marked on the column chip, cross-sectioned, and observed in a SEM, confirming the hypothesis (see Figure 4-21). Images from the first electrodeposited surface did not show any delamination.
Figure 4-18: SAM image showing the break in the nickel wall caused by pressure buildup during PMMA pyrolysis. The areas in white are “air,” those in dark are nickel.

Figure 4-19: A close-up view of the structures necessary to relieve stress during resist exposure and development.
Figure 4-20: SAM image of the cross-section of a delaminated area of a sealed column due to surface contamination.

Figure 4-21: SEM image of the area corresponding to the large delamination in Figure 4-20.
In the layout in Figure 4-22, the design was modified to combine all of the stress-relieving windows into a single structure and providing exit paths to the sides of the chip. Figure 4-23 shows the SAM image of this design. The response to a methane injection resulted in only one peak, confirming that the columns were sealed (see Figure 4-24). Figure 4-25 shows the SEM images of the cross-section of the sealed columns. Following this modified design and fabrication process, high aspect ratio nickel columns with typical channel width of 50 \( \mu \text{m} \), 600 \( \mu \text{m} \) and more tall, and 0.5 to 2m long are now routinely fabricated at CAMD.

4.2.6 Column Layout Revisited

In the column design in Figure 4-8, the sample inlet loops can serve as an enclosure for a Solid Phase Micro Extraction (SPME) type concentrator. At the other end, adding the makeup gas directly to the column chip can reduce the number of capillary connections. Providing the sample inlet at the side of the chip rather than the more traditional top-of-the-chip enables a stacked architecture for further integration and a more compact design. The corrugated configuration in Figure 4-26 provides better rigidity during the development and electroplating processing steps because of the smaller effective channel length. The inlet and outlet connecting channels on these columns are 300 \( \mu \text{m} \) wide with the ends tapering to 500 \( \mu \text{m} \) to accommodate a 0.016” diameter capillary connections.

Subsequent designs served to study the effect of column width on performance. Columns 30 \( \mu \text{m} \), 40 \( \mu \text{m} \), and 50 \( \mu \text{m} \) in lengths ranging from 0.25 – 1 m were designed. For the column in Figure 4-27, the sample inlet loop was thermally isolated from the column by air gaps. By temperature cycling independent of the column, the sample loop, filled with an adsorbent, will act as a second stage concentrator. On heating the sample loop, the sample will desorb off the adsorbent and inject into the column, which may be at a different temperature.
Figure 4-22: Layout of the modified 50 μm wide, 2 m long column where the individual stress-relieving windows were connected and extended to the edge of the chip to allow for the melted or vaporized PMMA to flow out.

Figure 4-23: SAM image of the modified column design with continuous stress-relieve structures. The interface between the column and the second electrodeposition was perfect with no signs of any delamination.
Figure 4-24: Response to a methane sample on a perfectly sealed column showing only one eluting peak.
Figure 4-25: SEM images of the sealed 50 μm wide and 600 μm tall columns showing the extremely parallel side walls.

Thermal simulations for a 2 second flash heating of the adsorbent and subsequent temperature programming of the column show very little heat transfer between the two parts [163]. The inlets on this column are different from those in the previous designs. Since the wall of the connecting capillary tubing is 50 μm thick, there will always be some dead volume associated with this connection in case of a tapered inlet. The inlets in this design were modified a 450 μm wide, 3 mm long section, leading to a 200 μm wide sample loop. For a 600 μm tall column, the hydraulic diameter of the sample loop is 300 μm. A capillary with 425 μm o.d./300 μm i.d. will connect well to the column since 1) the flow rate mismatch between the inlet to the sample loop is eliminated and 2) the dead volume will be negligible if the tube is flush with the inlet to the sample loop.

The columns were fabricated using the fabrication process described in Figure 4-5. All of the columns were tested for internal leaks by flowing methane and recording the peaks on the described experimental setup. With a growing understanding of the factors influencing the process parameters, a fabrication yield of over 90% has been achieved over the past two years.
Figure 4-26: Layout of a 50 μm wide, 0.5 m long corrugated column.

Figure 4-27: Layout of a 50 μm wide, 0.5 m long column with air gaps that thermally isolate the inlet sample loop from the column.
5 Column Coating and Experimental Results

To effect separation on the fabricated sensors, a thin layer of a stationary phase should cover the column walls. The stationary phase coating is an important component of the column and determines the separation performance of a column. GC columns are commonly deactivated to neutralize the chemically active sites before coating. Procedures to deactivate and coat capillary columns have been commercialized. The following sections give a brief background on stationary phase coatings and discuss the issues concerning coating of rectangular cross-section nickel columns. Procedures to deactivate and coat the LiGA columns are introduced and the separations performed on the LiGA columns are presented.

5.1 Coatings

The stationary phase is typically an organic compound, a layer of which coats and adheres to the column walls. Since the retention factor is a function of the coating type and thickness, changing the type and thickness of the stationary phase alters the performance of a column. Thick coatings increase the residence time of the analytes, which increases the separation time, making them suitable for analysis of more volatile analytes. For high temperature isothermal or temperature-programmed separations, it is important that the coating compounds have a low vapor pressure and do not decompose. Instability at high temperatures is the main reason limiting the use of packed-bed coating materials in capillary columns. The primary concern in capillary columns is the uniformity of the stationary phase coating on the inner surface of the column. A thin phase coating may leave some of the active sites on the surface uncovered, resulting in peak tailing. A thin phase may lead to a fast separation but with a reduced column capacity. The interactions of the solutes with the stationary phase are due to dispersion, induction, orientation, and donor-acceptor interactions [164, 165, 166]. These factors determine
the “polarity” of the stationary phase towards a solute. The type and concentration of the
stationary phase and the column temperature influences column selectivity.

There are many types of stationary phases, including polar, non-polar, chiral, and ionic, all
classified on the basis of their polarities. The polarity of a column can be evaluated via the
McReynolds system [167, 168]. To obtain the McReynolds number, the Kovats retention
indexes of 10 solutes are computed in the stationary phase of choice and in squalane, which
serves as the reference stationary phase [169]. The differences in the Kovats’ retention indices
for the two phases for each of the 10 solutes are summed up to give an overall polarity of the
stationary phase. The McReynolds constants can also guide in selecting a column that will
separate compounds with different functional groups, such as ketones from alcohols, or, esters
from nitriles. Of the 200 phases analyzed by McReynolds, four phases: OV-101, OV-17, OV-225,
and Carbowax 20M, can provide satisfactory GC analysis for over 85% of the applications [170].

The rule for selecting a stationary phase is that “like dissolves like” – for polar solutes, a
polar stationary phase should be used, while the exact type can be fine-tuned according to the
McReynolds constants. Another criterion is the lifetime of the coating: polar phases are
generally slightly less efficient than non-polar ones and have a shorter life at elevated
temperatures. Non-polar phases are more resistant to oxidation and hydrolysis than polar
phases. Polysiloxane phases are the most commonly used stationary phases because of their
high thermal stability and the wide range of polarities. Figure 5-1 shows the molecular structure
of a polysiloxane molecule [60]. Coatings formed by this molecule are termed 100% non-polar.
Replacing the methyl groups with other functional groups changes the polarity of the polymer.

There are two methods commonly used to coat capillary columns: 1) static and 2) dynamic.
In static coating, the stationary phase is dissolved in a solvent and introduced to the column
[116, 171]. One end of the connection tubing is closed; the other end is attached to vacuum.
As the solvent is pulled out of the column under vacuum, a thin layer of the stationary phase is left on the column walls. The film thickness in static coating is a function of the concentration of the coating solution, $C_{cs}$, determined by a simple mass balance (Equation 5-1).

$$h_F = \frac{\text{volume of column}}{\text{surface area of column}} * C_{cs}$$

In dynamic coating, the column head pressure drives a plug of stationary phase dissolved in a solvent. This causes a thin layer of the stationary phase to adhere to the column walls. Repeating the process multiple times results in the desired stationary phase thickness. The film thickness in this case is given by the Fair-Brother equation (Equation 5-2).

$$h_F = \frac{r C_s}{200} \left( \frac{u \eta}{\gamma} \right)^{1/2}$$

Here, $r$ is the radius of the column or the hydraulic diameter for a rectangular column, $u$ the velocity, and $\gamma$ the surface tension between the coating solution and the column.

While coating circular capillary columns has been commercialized over the past 30 years, coating on rectangular cross-section columns has not been studied much and comes with its own issues. There are two main factors for consideration: 1) pooling of the liquid in the corners of the microfabricated columns and 2) thickness uniformity over the entire column. Pooling of the stationary phase in the corners of the rectangular cross-section columns...
enhances the coating problems [110]. The pooling results in an uneven stationary phase layer which can cause peak broadening.

Among the first reported instances of coated microfabricated columns, 300 μm wide, 10 μm tall, 0.9 m long silicon columns were vapor deposited, before sealing them with anodic bonding, with a 2000 Å thick layer of α-phase Copper phthalocyanine (CuPc) to serve as a solid adsorbent in separating NO$_2$ from a gas sample [126, 127]. Under a head pressure ranging from 20-40 psi and a temperature of 80 °C, NH$_3$ and NO$_2$ were separated in about 30 minutes. The peaks showed significant amount of broadening and tailing, suggesting dead volumes. Another solid stationary phase, plasma-polymerized fluoropolymer, deposited on 100 μm wide, 10 μm tall, 2 m long silicon micromachined columns by RF sputtering, was reported useful for environmental applications since it showed little response to water vapor, although no separation data were presented [172, 173]. A PDMS-like film was deposited by the PECVD process on the silicon micromachined columns [174]. Descendents of this column and coating form the separation column in the credit-card GC from SLS Microtechnology (Hamburg, Germany). The techniques for depositing stationary phase on columns before sealing will not work for the present LiGA columns since the columns are filled with the resist until they are sealed. More recently, success in static and dynamic coating procedures on 150 μm wide, 240 μm tall, 1-3 m long silicon DRIE columns has been reported [114, 116]. Initial problems with cavitation at the sharp corners on the microfabricated columns resulted in a non-uniform film. This problem was partially solved by adding dicumyl peroxide, a cross-linking agent, to the stationary phase before coating. The cross-linking agent stabilizes high temperature operation of the coated columns. Coating thicknesses of 0.1-1 μm using the static coating procedure and 1-2 μm via the dynamic coated procedure were achieved. Temperature programmed separation of straight chain alkanes from C$_1$-C$_{12}$ on the 3m long column was obtained in about 500 seconds.
To monitor volatile organic compounds, 50 μm wide, 40 μm deep, 2 m long silicon columns, fabricated by a two-step fabrication procedure using KOH isotropic etching and DRIE, were coated with a sol gel containing two metal alkoxide precursors: tetraethoxysilane (to form the silica matrix on the column walls) and perfluorooctyltriethoxysilane (to form the stationary phase) [175]. Separation of a BTX mixture (benzene, toluene, p- and o-xylenes) was carried out at room temperature in about 120 seconds.

The parylene columns developed by Noh et al. were coated via vapor deposition and both, static and dynamic, coating techniques [119]. Additionally, parylene was coated on silicon DRIE columns by injection coating, which is similar to dynamic coating. Under dry coating, plasma polymerization of fluorocarbon and chemical vapor deposition (CVD) of parylene functionalized with an amine group were carried out. Under wet coating, OV-1 type PDMS stationary phase was used. Although the column performance improved with temperature programming the chromatographic run, plate numbers less than 5% of those expected were recorded mainly due to dead volumes and non-uniformity in and pooling of the coating layer.

Metal capillary columns were common before the advent of silica columns. They were more difficult to coat because of the presence of a large number of active sites on the surface. These active sites react with the polar analytes, increasing their adsorption, which leads to peak tailing. Deactivating the active sites before coating will reduce the surface interactions. The deactivation, in some cases, also serves to make the column wall more wettable to the stationary phase. The main idea behind deactivation is to cover the nascent column surface with a non-active chemical/coating, which for most of the cases is some form of a silanol group. Glass columns can be silanated by filling them with a mixture of vapors of hexamethyldisilazane and trimethylchlorosilane in a 5:1 ratio and heating to 150 °C for 48 hours or coating with allyltrichlorosilane and curing under oxygen flow at 150 °C for 2 hours [176]. The use of
polymethylhydrosiloxanes and silanol is common for deactivating fused silica columns [177].

Other methods to deactivate include thermal degradation of polysiloxanes [178], poly ethylene glycols (PEGs), octamethylcyclotetrasiloxane (D₄) [179, 180], Carbowax 20M [181]. Deactivating a column using a polar compound, such as PEG, may alter the polarity of the stationary phase coating, especially for thin coatings. Other compounds like Carbowax may produce an acidic column [182]. Deactivating the column and immobilizing the stationary phase in a single step is an alternative procedure commonly practiced [60]. In a recent interesting experiment, carbon nanotubes grown in the vapor phase in situ capillary columns worked as a stationary phase [49, 183, 184].

Commercial solutions to deactivated metal columns include Ultimetal (Varian, Palo Alto, CA), Silico-steel (Restek, Bellefonte, PA), and Ultra Alloy (Frontier Lab, Fukushima, Japan). These processes are suitable for deactivating stainless steel columns but not for nickel columns [185].

The most common approach to deactivate nickel columns is to deposit a thin layer of silicon, in either a gaseous phase [186] or an aqueous phase [187], on the column. In the gaseous-phase deposition technique, full concentration silane is run through the column at 380 °C for 3 hours, which deposits a 50-100 Å layer of silicon on the column walls. The stationary phase readily adheres to this silicon layer using traditional coating chemistries. The chemicals used in most of the deactivation procedures are highly toxic and may not be suitable for common laboratory use. A more amenable process to deactivate is to use a mixture of 0.5% silane in helium instead of pure silane [188]. The aqueous process for deactivation uses a layer of perhydropolysilazane (PSZ), an inorganic polymer containing silicon, which forms amorphous silica when heated to 400 °C in air. Another promising class of aqueous materials to deactivate metal columns is silicon-on-glass.
5.2 Fluidic Connections and Column Deactivation

To connect the column to the outside world, steel tubing with 0.016” o.d. and 0.012” i.d. (Small Parts, Miami Lakes, FL) was attached by either JB Weld (JB Weld, Sulfur Springs TX) or Ohmex AG (Omega, Stamford CT). Due to the mating of a rectangular cross-section with circular tubing, dead volumes were inherent (see Figure 5-2). Deactivating the LiGA columns had another challenge arising from the issues related to fluidic connections. One drawback of the deactivation procedures mentioned above is that they require temperatures of around 400 °C.

The epoxies used to attach the tubing disintegrated at temperatures above 300 °C. Three methods identified to attach tubing to the columns that would withstand a high temperature and be leak-free were: 1) laser spot welding, 2) electroplating, and 3) a combination of both. The steel tubing was laser welded (Mezzo Technologies, Baton Rouge, LA) using a nickel wire as a filler material (see Figure 5-3). The high temperature during laser welding made the thin tubing brittle and fragile at the interface. The connections, in most instances, broke off at the slightest torque and were unusable. At other times, the tubing wall melted at the interface, blocking the column outlet.

For the electroplated connections, the capillary tubing inserted in the column opening was held in place by PMMA glue. The jig shown in Figure 5-4 was designed to cover all areas of the chip except the four ends, facilitating selective nickel electroplating between the opening in the chip and the tubing. After electrodeposition, the column chip was heated to 300 °C in a furnace to remove the PMMA glue. While the electroplated bond was intact after this process, quite often, one or more of the connections would come undone during electroplating, causing the electrolyte to seep in and block the opening. To correct this problem, the electroplating procedure was performed on the laser welded chips. The electrodeposited nickel supported and strengthened the laser welded joint, while the laser welding prevented the electrolyte from
Figure 5-2: Dead volumes on connecting a rectangular cross-section with a circular cross-section column.

seeping into the chip (see Figure 5-5). While the welded-electroplated connections were mechanically robust, withstood temperatures of up to 450 °C without delamination, and did not produce any leaks, the overall process suffered from the low yield of the laser welding process. More process optimization for laser welding is required, including using thicker walled tubing.

To counter the problems with making connections that can withstand 400 °C, the LiGA columns were deactivated by three alternative chemical treatments: 1) methylsiloxane spin-on-glass (11F, Filmtronics, Butler PA), 2) silicate spin-on-glass (15A, Filmtronics), and 3) D4. JB Weld was the preferred method for connecting the tubing for these cases because of the lower deactivation temperatures. The 50 μm wide by 600 μm tall, 0.5 m serpentine columns were used as test structures to study the deactivation process. The chemical activity of the nascent column surface was evaluated by checking separation of a mixture of equal concentrations of hexane and decane at 110 °C. Any separation may indicate presence of active sites.
Figure 5-3: Image of a steel capillary laser-welded to a nickel column.

Figure 5-4: Image showing the different steps taken to attach tubes to the column via nickel electrodeposition. In Step 2, the tubes of appropriate length were cut. In Step 3, the tubes were held on the chip in a mechanical jig, which insulated the chip, leaving only the four outlets exposed for electrodeposition.

Figure 5-5: Image showing nickel electroplating over a laser-welded capillary connection.
5.3 Experimental Apparatus

A HP 5890 GC was modified for use as an experimental test stand as shown in Figure 5-6. The setup is shown schematically in Figure 5-7. Samples in the gaseous (methane) and liquid phases were injected through syringes. The pressure at the injection port was maintained 5-10 psi. The injected sample vaporized on entering a 1 ml volume heated chamber maintained at 150 °C. The flow from this chamber was split between a sample loop and a vent, with the vent flow maintained at 50 ml/min. The 2 µl sample-loop was filled up in the “load loop” configuration of a Valco ten-port mini diaphragm electrostatic valve (Houston, TX).

The carrier gas, hydrogen for these experiments, entered the valve at port 4, the sample entered at port 7, and port 2 was connected to the vent. During the “loop load” cycle, the sample went through the ports 7-6-sample-loop-3-2-valve vent. On actuating the valve using an external trigger (not shown), the quantity in the sample loop traveled through ports 3-sample-loop-6-5. In the microfabricated columns, the sample coming from port 5 of the valve was split at the on-column split. A needle valve attached at the other end of the inlet sample loop on the column chip regulated the split ratio. The split flow rate at the column inlet was kept between 0-450 ml/min, corresponding to 0-100% closure of a needle valve. By splitting the injected sample volume twice, a very narrow sample plug (around 1 ms wide) was injected into the column. This was a significant improvement over the normal injection mode of the HP 5890 GC which gives injection peak widths of 30 – 60 seconds. In addition, the current method using the on-column split is a step forward over the proposed dual valve system [33]. For this range of split flows, the width of the sample plug injected into the column was estimated to be ~ 1 ms.

The column head pressure was read off at port 4. At the outlet of the microfabricated columns, makeup gas was added through the space provided on-chip. A FID, maintained at 120 °C, was
Figure 5-6: An image showing the modified HP 5980 GC which was used to test the LiGA columns.

Figure 5-7: Schematic of the experimental setup to test the LiGA columns.
used as the detector. Before evaluating column activity and performance, the effect of the split ratio and the makeup gas pressure on performance was evaluated.

5.3.1 Effect of Split Ratio on Column Performance

A 50 μm wide, 600 μm tall, 2 m long column was installed in the 5890 GC. About 5 μl of methane gas was injected into the column using a syringe. The split flow rate was varied from 100-450 ml/min by operating the split needle valve. As shown in Figure 5-8, the volume flow rate at the split valve varied linearly with the opening of the split needle valve. The calculated HETP, plotted in Figure 5-9, shows that the maximum efficiency was achieved when the valve was 75-100% open.

5.3.2 Effect of Makeup Gas Pressure on Column Performance

The retention times and peak widths at half height of the eluting methane peaks were recorded while the makeup gas pressure was varied from 5 to 25 psi. The column head pressure was kept constant at 45 psi with the split needle valve 100% open. The HETP, calculated from the recorded retention time and the peak width at half height, dropped continuously with increasing makeup gas pressure (Figure 5-10). The retention time and half heights for different makeup gas pressures in Figure 5-11 explained this behavior. An increase in the makeup gas pressure increased the back pressure at the column outlet (see Figure 5-7), causing a reduction in the column flow rate and an increase in the holdup time. Adding the makeup gas efficiently sweeps the effluent towards the detector, reducing the peak width at half height. At low makeup gas pressures of 0-10 psi, the peak broadening is quite significant. The overall effect here is that the HETP decreases by increasing the makeup gas pressure. A constant makeup gas pressure of 15 psi was used in all of the subsequent experiments. These results show that the on-column split and makeup gas functionalities incorporated on the chip work as intended.
Figure 5-8: Variation of the split flow rate with the opening in the split needle valve.

Figure 5-9: Variation of HETP for methane with split flow rate through a 50 μm by 600 μm by 2 m column at room temperature for a 15 psi makeup gas pressure.
Figure 5-10: Variation of HETP with makeup gas pressure for methane through a 50 μm by 600 μm by 2 m column at room temperature. The split flow was constant at 100% open.

Figure 5-11: Variation of retention time and peak width at half height with carrier gas velocity at different makeup gas pressures through a 50 μm by 60 μm by 2 m column for a 60 psi column head pressure at room temperature.
In addition, using such architecture eliminates the use of two zero dead volume T-junctions and numerous extra connections normally needed to implement similar effects (as seen later in Figure 5-18 for the tests on capillary columns).

5.4 Results on Column Deactivation

To check the chemical activity of the columns, a mixture of hexane and decane was run through the 50 μm wide, 600 μm tall, 0.5 m long test columns at 110 °C. Although no separation was observed, the peak for hexane showed some tailing, suggesting presence of some active sites. Both types of spin-on-glasses were coated by pushing the solution through the column using a syringe and heating the column to 300 °C for 20 minutes in an oven. D4 was coated in a similar manner but the columns were not heated after the treatment.

Hexane and decane were separated on the columns treated with the spin-on-glass while no separation was observed on the column with D4. Since D4 deactivated the column to some degree, all further columns were treated with D4 before coating the stationary phase.

5.5 Coating of LiGA Columns

The static coating technique was used to coat each set of columns treated with D4. Based on the experience with capillary columns and meeting the requirements for fast separation times of less than 10 seconds the stationary phase film on the LiGA columns between 0.05 – .2 μm was targeted. The columns were filled up with a coating solution comprising 0.04 mg of OV-1 stationary phase in mixture of 0.5 ml methylene chloride and 0.5 ml pentane through a capillary washing reservoir (SGE, Austin, TX). Three ends of the columns were sealed, while the fourth was connected to a vacuum pump. The columns were conditioned by pulling out air for 4 hours using a vacuum pump. According to Equation 5-1, 0.1 μm a film is expected for the 50 μm by
600 μm column, 0.4 μm for the 300 μm by 600 μm inlet sample loop, and 0.05 μm for the connecting tubing.

5.5.1 Results on the 0.5 m LiGA Columns

Figure 5-12 shows the Golay plots for unretained species on serpentine and corrugated columns. Both the columns show a similar characteristic curve and the same van Deemter minimum. This shows that the band broadening undergoes partial reversal in the turn of the corrugated columns, mainly because of the shorter “channel length” than the serpentine columns. As discussed in Chapter 4, corrugated columns are more stable than serpentine columns during the fabrication process. Their layout is also more compact than serpentine columns. Since both the columns have similar performance, incorporating the corrugated columns may lead to a new generation of columns with even higher aspect ratios. Figure 5-13 shows the separation of hexane and decane at 110 °C on one of the coated serpentine columns. The two compounds co-elute at higher pressures. Figure 5-14 shows the separation of the two compounds at different temperatures under isothermal conditions. As expected, the column resolution decreases with increasing temperature. Figure 5-15 shows the separation of hexane, octane, decane, and dodecane on another coated serpentine column.

5.5.2 Results on the 1 m LiGA Columns

Columns with widths 30 μm, 40 μm, and 50 μm and 600 μm height were tested for activity before treating with D4 and OV-1 stationary phase. Figure 5-16 compares the Golay plots for these columns for methane at room temperature. The performance of the three columns with different width seems very similar to one another. On the uncoated columns, the velocity is the primary parameter determining performance. Interestingly, hexane and decane separated on the uncoated, undeactivated 50 μm by 600 μm by 1 m column (see Figure 5-17).
Figure 5-12: Golay plot for unretained species on 50 μm by 600 μm by 0.5 m serpentine and corrugated columns room temperature. The split flow was set at 100% open and the makeup gas at 15 psi.

Figure 5-13: Separation of hexane and decane on a 50 μm by 600 μm by 0.5 m serpentine column coated with OV-1 stationary phase under different pressures at 110 °C. The split flow was set at 100% open and the makeup gas at 15 psi.
Figure 5-14:  Separation of hexane and decane on a 50 μm by 600 μm by 0.5 m corrugated column coated with OV-1 stationary phase at different temperatures. The column head pressure was 60 psi, the split flow was set at 100% open, and the makeup gas pressure was 15 psi.

Figure 5-15:  Separation of four hydrocarbons on a 50 μm by 600 μm by 0.5 m serpentine column coated with OV-1 stationary phase. The separation was performed at 80 °C and a pressure of 40 psi.
Figure 5-16: Golay plots for 600 μm tall by 1 m long columns of different widths. The split flow was set at 100% open and the makeup gas at 15 psi.

Figure 5-17: Separation of hexane and decane on uncoated 50 μm by 600 μm by 1 m columns. The split flow was set at 100% open and the makeup gas at 15 psi.
This may suggest two things: one that the column has active sites and the other that there is residual carbon from the PMMA pyrolysis. The deactivated and coated 1 m columns did not perform as good as the 0.5 m column. Presence of bubbles in the column during the coating process can result in a bad coating. To check the source of separation on the undeactivated columns, the chemical activity of three commercial capillary columns was studied.

5.5.3 Commercial Capillary Tubing

Figure 5-18 shows the schematic of the experimental apparatus to test the capillary columns. The setup was configured to mimic that for testing the LiGA columns. To simulate the on-column split, a zero-dead volume T-junction (Valco Instruments, Houston, TX) was added. The pressure drop in the column for these large diameter capillary tubing was very small. On adding a T-junction to add the makeup gas, the column outlet was no longer at atmospheric pressure. In fact, due to the low hydraulic resistance, the column outlet pressure was quite high, and caused backflow into the makeup gas tubing. Due to this, makeup gas could not be used in this configuration. Lack of makeup gas does not affect the goal of the experiment, which was to check the activity of commercial capillary columns.

Three types of columns were evaluated: 1) 320 μm diameter, 5 m long, deactivated silica tubing (Supelco, St. Louis, MO), 2) 380 μm diameter electroformed nickel tubing (Valco Instruments, Houston, TX), and 3) 400 μm diameter, 36” long stainless steel tubing (Small Parts, Miami Lakes, FL). The deactivated tubing did not show any separation between hexane and decane (see Figure 5-19). The electroformed tubing and the stainless steel tubing showed separation of hexane and decane. These experiments confirmed that the 1 m undeactivated LiGA columns had active sites, which can cause separation, even without the presence of solid organic, carbon like, adsorbents.
Figure 5-18: Schematic of the experimental setup to test the circular capillary columns

Figure 5-19: The 320 μm diameter, 5m long deactivated, uncoated fused silica column did not separate hexane and decane at 110 °C with a 100% open split flow.
Figure 5-20: Separation of hexane and decane at 110 °C on a 500 μm diameter, 5m long electroformed nickel tubing with a 100% open split flow without makeup gas.

Figure 5-21: Separation of hexane and decane at 110 °C on a 200 μm diameter, 36" long stainless steel tubing with a 100% open split flow without makeup gas.
5.5.4 Results on the 2 m LiGA Columns

Like the 1 m columns, the 50 μm by 600 μm by 2 m undeactivated columns were used to separate hexane and decane (see Figure 5-22). Figure 5-23 compares the Golay plots for the three lengths of the 50 μm columns. The van Deemter minimum for the three columns occurs at very similar positions. Under optimum conditions, the 0.5 m column gives 5,000 plates, the 1 m column 10,000 plates, and the 2 m column 20,000 plates for unretained compounds. This showed that the longer columns had more number of plates than the shorter columns. Figure 5-25 shows the theoretical plot for methane (unretained) through 50 μm wide by 600 μm tall columns of different lengths at room temperature. The trend in the relative HETP values for the three columns is the same as that derived experimentally.

5.6 Two-Dimensional GC

A two-dimensional GC prototype was implemented using two MEMS columns as shown in Figure 5-26. This column assembly replaced the single column in Figure 5-7. After injecting the sample into the first column, the split was injected into the second column. The split for the second column was set to 100% split needle valve. The eluting gas streams from both the columns were combined and directed to the FID. The 2D C was used to separated hexane and decane through a combination of coated and uncoated columns. Distinguishing peaks from individual columns for complex mixtures can be difficult using a single detector, having two detector channels, say a TCD and a FID, will help in better identification.
Figure 5-22: Separation of hexane and decane on a 50 μm by 600 μm by 2 m long column at 50 psi head pressure and 110 °C. The split flow was set at 100% open and the makeup gas at 15 psi.

Figure 5-23: Golay plots for methane through 0.5 m, 1 m, and 2 m long, 50 μm wide, 600 μm tall columns. The split flow was set at 100% open and the makeup gas at 15 psi.
Figure 5-24: Number of plates for methane through 0.5 m, 1 m, and 2 m long, 50 μm wide, 600 μm tall columns. The split flow was set at 100% open and the makeup gas at 15 psi.

Figure 5-25: Theoretical plot of HETP for 50 μm wide by 60 μm tall columns of different lengths for an unretained analyte at room temperature.
Figure 5-26: Implementation of 2D GC using a single injection, single detector on two LiGA columns. The split sample from the first column (50 μm by 600 μm by 0.5 m coated with 0.1 μm of OV-1) was injected into the second column (50 μm by 600 μm by 1 m, uncoated). The outlets for the two columns were joined using a T-junction and channeled to the detector.

Figure 5-27: Separation of hexane and decane using 2D GC on a 50 μm by 600 μm by 0.5 m first column, coated with 0.1 μm OV-1 and an uncoated 50 μm by 600 μm by 1 m second column. The column head pressure was 40 psi, the split for the second column was set to 100% open, and the makeup gas pressure for both the columns was set at 15 psi.
6 Conclusions

High aspect ratio, rectangular cross-section gas chromatograph columns were fabricated using the LiGA process. Process developments to find the substrate with a good adhesion, optimize dose for X-ray exposures, optimize developing conditions, and low temperature nickel electrodeposition were the key factors in helping realize the columns. After detailed investigation, a two-sided nickel electrodeposition process was determined to be effective and reliable to seal the nickel GC columns. Two test procedures – one using scanning acoustic microscopy and the other an experimental apparatus, were developed as process control tools to locate leak free columns. These developments resulted in 30-50 μm wide, 600 μm tall, and 0.5-2 m long columns with aspect ratios of 12-20. Starting with a process yield of less than 10% a few years back, the presented process development efforts have increased the column fabrication yield to over 90%.

Techniques to attach capillary tubing to the columns were investigated, with a combination of laser welding and electroplating giving the best results. These connections withstand temperatures of at least 450 °C. Procedures to deactivate the columns were studied and the columns were coated via static coating. An experimental test platform was built by modifying the HP 5890 GC. This apparatus will form the basis for the next generation GC instrumentation using microfabricated columns. A technique using on-column split injection was used to inject injection plugs of around 1 ms into the column. This is a significant improvement over the several seconds wide injection plugs normally possible in the bench top GCs.

The effects of the on-column split and makeup gas were experimentally determined. A mixture of four compounds from octane to dodecane was separated in under 2 seconds at 100 °C on a 50 μm by 600 μm by 0.5 m long, statically coated column. The efficiencies of 30 μm, 40 μm, and 50 μm wide by 600 μm tall by 1 m columns were compared for unretained species.
The performance of the serpentine columns was similar to that of the corrugated columns. This is important in case higher aspect ratio columns are desired since the corrugated columns have better rigidity during the fabrication process and have a smaller footprint than the serpentine columns. The 50 μm by 600 μm by 2 m long columns results in 20,000 plates for unretained species under isothermal conditions. A configuration of 2D GC using one coated and one uncoated column was demonstrated.

Following these efforts, two primary areas need further developments to realize a high resolution GC column. The first is temperature programming. The factors concerning temperature programming are the ease of integration and the reliability of the thin film heaters [163]. The second is the development of an integrated check valve between the sample loop and the column inlet is essential to inject a sharp sample plug into the column. The formidable challenges of integrating a check valve with the column have so far prevented on-chip injection.

Any attempt to commercialize the columns will require fabricating the MEMS columns at a price comparable to the capillary columns. Large volume production of the columns is one way to reduce costs. The transition from high yield fabrication to a more cost effective process like molding needs research. With a routine fabrication process, prompt processing and analysis of data requires a technical solution. Currently, each column undergoes up to six experiments with 10 data points before coating. By the time a column is characterized for routine use, it will have up to 20 datasets, each with 10 or more data points. Clearly, expedited data analysis is desired.

The main component of the detector electronics is a fast electrometer, which is currently of a cigar box size. If the GC sensor itself is a smaller than that, the associated electronics too will have to be miniaturized. One concern for on-site autonomous sensors is that of reliability, false positives or true negatives. The use of 2D GC with dual detectors will be a step forward in assuring reliability of analysis.
References


7. E. B. Overton, *private communication*.


17. R. J. Jonker, H. Poppe, and J. F. K. Huber, “Improvement of speed of separation in


19. H. M. McNair and G. L. Reed, “Flash chromatography: use of fast oven temperature
programming,” 21st International Symposium on Capillary Chromatography &
Electrophoresis, Park City, Utah, 1999.


22. A. van Es, High speed narrow bore capillary gas chromatography, Wiley Interscience,


24. A. B. Fialkov and A. Amirav, "Identification of novel synthetic organic compounds
with supersonic gas chromatography-mass spectrometry," J. Chromatogr. A., v 1058,

analysis with a 50 µm ID column: theory, practical aspects, and application to a highly


27. M. J. E. Golay, “The height equivalent to a theoretical plate of retentionless


31. A. K. Wanekaya, M. Uematsu, M. Breimer, O. A. Sadik, “Multicomponent analysis of
alcohol vapors using integrated gas chromatography with sensor arrays,” Sensor

32. A. L. Makas and M. L. Troshkov, “Field gas chromatography-mass spectrometry for


52. http://www.sls-micro-technology.de/


103. J. Eustics, Eng., v 120, pp 604, 1925.


http://webbook.nist.gov


147. Z. G. Ling, personal communication.


159. http://www.microassembly.com


166. H. Lamparczyk, “,” *Chromatographia*, v 20, pp 283, 198.5


185. Restek Corporation, *private communication*.


188. R. J. Simonson, private communication.
Appendix: Gas Compressibility Effects in Microfluidics

The change in density of a fluid in motion is a common measure of characterizing fluid compressibility, a criterion captured by the Mach number, $Ma$. Defined as the ratio of the velocity of a fluid to the velocity of sound in the same fluid, the premise behind this dimensionless quantity is that the density of a moving fluid, $\rho$, is different from when it is stationary, $\rho_0$. For isothermal or adiabatic flow, the ratio of the densities in the two cases is given by Equation A 1.

$$\frac{\rho_0}{\rho} = \left(1 + \frac{\gamma - 1}{2} Ma^2\right)^{-\frac{1}{\gamma-1}}$$

where, $\gamma = c_p/c_v$. For a less than 5% change in fluid density, which corresponds to a Mach number of less than 0.3, treating the fluid as incompressible is a valid assumption. Compressible flows occur for Mach numbers greater than this because of the significant variation in the fluid density.

The above criterion does not incorporate the effects of fluid viscosity on the fluid velocity. The majority of fluid flow in the microfluidic domain is termed as viscous flow, characterized by low Reynolds numbers. Under these conditions, a large pressure differential may exist along the channel, which can cause a significant variation in the density of the fluid. For cases where viscous forces dominate, a modified expression given by Equation A 2 determines the change in density between moving and stationary fluids [A-1].

$$\frac{\Delta \rho}{\rho_0} \sim \frac{\Delta P}{\rho a^2} \sim \frac{L \, Ma^2}{d_0 \, Re}$$

The criterion for fluid incompressibility then becomes the expression in Equation A 3.
Table A-1 lists the density variation for hydrogen flow through different microchannel geometries. As seen clearly, even at low Mach numbers, the flow undergoes significant changes in density, suggesting that the flow field is compressible.

Table A-1: Change in density for different columns showing that the flow is compressible because of the significant change in density from the inlet to the outlet conditions.

<table>
<thead>
<tr>
<th>b (μm)</th>
<th>d (μm)</th>
<th>Dh (μm)</th>
<th>uavg (cm/s)</th>
<th>Ma</th>
<th>Density variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>173</td>
<td>173</td>
<td>173</td>
<td>471</td>
<td>0.0037</td>
<td>68.55%</td>
</tr>
<tr>
<td>123</td>
<td>246</td>
<td>164</td>
<td>381</td>
<td>0.0030</td>
<td>61.70%</td>
</tr>
<tr>
<td>100</td>
<td>123</td>
<td>110</td>
<td>189</td>
<td>0.0015</td>
<td>67.83%</td>
</tr>
<tr>
<td>50</td>
<td>600</td>
<td>92</td>
<td>78</td>
<td>0.0006</td>
<td>39.95%</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>67</td>
<td>63</td>
<td>0.0005</td>
<td>61.70%</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>33</td>
<td>12</td>
<td>0.0001</td>
<td>47.46%</td>
</tr>
</tbody>
</table>

Vita

Abhinav Bhushan was born in Moradabad, Uttar Pradesh, also known as the brass capital of India. After completing his high school in Allahabad, India, he joined Motilal Nehru Regional Engineering College, Allahabad, India, where he earned the Bachelor of Engineering (Honor’s) in Mechanical Engineering. He joined the Department of Mechanical Engineering at Louisiana State University in Fall 1998. After graduating with a Master of Science degree in Mechanical Engineering in 2001, he joined MicroAssembly Technologies in Richmond, CA where he worked on MEMS packaging solutions. He left MicroAssembly Technologies in 2002 and joined CAMD, LSU as a full-time Research Associate. He formally enrolled into the Ph.D. program at the Department of Mechanical Engineering in 2004 and expects to be awarded at the commencement of December 2006. Currently, as a Research Associate at CAMD, he is developing the next generation of high-resolution gas sensors.