DESIGN, TESTING, AND SIMULATION OF
MICROSCALE GAS CHROMATOGRAPHY COLUMNS

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Abstract

A microscale gas chromatography column is one component in a microscale chemistry laboratory for detecting chemical agents. Several columns were fabricated using the Bosch etch process which allows deep, high aspect ratio channels of rectangular cross-section. A design tool, based on analytical models, was developed to evaluate the effects of operating conditions and column specifications on separation resolution and time. The effects of slip flow, channel configuration, and cross-sectional shape were included to evaluate the differences between conventional round, straight columns and the microscale rectangular, spiral columns. Experimental data were obtained and compared with the predicted flowrates and theoretical number of plates. The design tool was then employed to select more optimum channel dimensions and operating conditions for high resolution separations.

I. Introduction

Sandia National Laboratories is currently developing a microscale chemistry laboratory (μ ChemLab). The goal is to build a handheld unit for detecting chemical agents such as sarin and soman nerve agents. Part of the system will be a gas chromatography (GC) column that will separate chemical species for detection. Typical GC columns used today for separating chemicals are silica tubes ranging from 50 to 500 microns in diameter and 30 m in length. These columns have a thin liquid layer absorbed onto the walls, typically 1-10 nm thick, where chemical separation occurs due to differences in the equilibrium absorption coefficients for each chemical species flowing through the column. For the Sandia μ ChemLab project, it is desired to reduce the dimensions of the column to fit on a 1 cm² silicon chip while maintaining good separation efficiency in a reasonable time.

Several design issues result from the microscale constraint. The columns will be etched on silicon wafers. Thus, the geometry will be more complicated than conventional straight columns with circular cross-sections.

First, the column width will be on the order of tens of microns while the depth will be hundreds of microns thus yielding high aspect ratio channels. Second, the column will have a rectangular cross-section. Third, the column will be in a spiral configuration as shown in Figure 1. System design constraints, such as the gas injection system and pump design, affect the operation of the GC column. Thus, an optimum GC column design must address these fabrication and operating constraints. Design parameters must be selected based on an obtainable flowrate, which is limited by the pump performance, and yield the best separation resolution in a reasonable total time.

A modeling tool has been developed to aid in the design of microscale GC column configurations. The design code to predict GC column performance employs the compressible flow equations with slip at the wall and the Golay¹ equation with Giddings² pressure correction. The Golay equation describes the quality and time required for a particular separation for both round and rectangular cross-section columns. Experimental measurements of flowrates and separations in conventional columns and in the microscale spiral columns are compared with model predictions. These comparisons validate the model and allow us to understand and characterize the flow and separation phenomena.

II. Fabrication

The microscale GC columns are fabricated at Sandia using a reactive ion etch process which etches deep, narrow, rectangular cross-section channels in a spiral shaped pattern as shown in Figure 1. Several spiral configurations have been fabricated with a width of 10 to 40 μ m, depth of 80 to 250 μ m, and length of 0.3 to 1 m. The separation distance between the rings varies such that the entire column fits in a 1 cm² area. In 1975, Terry³ etched 200 μ m wide and 20 μ m deep channels. The Bosch⁴ etch process enables our deep channels and thus, smaller chip areas.

Starting with a commercial 3 inch silicon wafer, a mask is prepared for the deep etch by patterning a relatively thick photoresist of 10 to 12 μ m, which config-

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ures the channel width and length. The patterned wafer is etched using a plasma process developed by Bosch⁴ that cycles between etching and a polymer deposition to maintain the vertical side walls of the channel while the channel bottom continues to etch. After the etch, the photoresist is removed from the wafer in the last step for the silicon slice.

The etched channel area is anodically sealed with a cover slip that has preprocessed through holes for access to the channel. The Pyrex wafer, which is also 3 inch, is machined by grinding through holes with a 15 mil burr at appropriate locations, so that channel ends will align to the holes. The Pyrex and silicon are prepared for anodic bonding by cleaning in a piranha solution, rinsing, and drying. After the glass is aligned to the silicon, the assembly is heated to about 300°C and then bonded under a high potential. Whole wafers have been successfully fabricated through the bonding step before sawing to separate individual devices. Finally, for each device, capillaries for test fittings are attached to the holes in the Pyrex glass.

Channels must be coated to form the necessary stationary phase for separation optimization and to tailor the separation mechanisms. We are currently in the process of investigating various coating procedures for uniformity, thickness, and separation performance. One spiral has been coated with OV-1.

Since the width is a critical dimension in the analytical model, some spirals were sawed in half to precisely determine their dimensions. The width of a nominal 40 μm spiral channel can actually range from 44 to 60 μm whereas the length is fairly constant. The SEM (Scanning Electron Microscope) image of the sawed edge of a nominal 55 μm wide spiral is shown in Figure 2. Channel etch looked quite uniform from the outer to inner channels of the device. The width at the top of the channel was 55 μm from the side view (same as the top view). The width at the bottom of the channel was about 50 μm . Typically, the etch width at the bottom of the channel is about 90% the width at the top. Also from this sawed device, the depth of the channel is 280 μm compared to the nominal 250 μm .

III. Experiment

A. Flowrate

Flow in both the capillary and microscale spiral columns was characterized using the system illustrated in Figure 3. Gas flow into the column was controlled with a low pressure (0-40 psi) regulator that was connected through a short cross fitting to a pressure transducer, a vent valve, and the column. A soap-bubble flow meter was attached to the discharge end of the column to measure the volumetric flow rate. Three meters were available to cover five ranges of flow volume: 0.1 ml, 0.5 ml, 1 ml, 10 ml, and 50 ml. To minimize the influence of

pressure drift within the system, the volume was selected to provide a collection time of about one minute. The pressure transducer provided an uncertainty of about 1.5% after it was calibrated with a dead-weight comparator. The accuracy of the flow meters was estimated to be better than 1%. Tests were conducted in ambient air where the temperature was nominally 23°C and the pressure at the discharge of the bubble flow meter was nominally 83.4 kPa (12.1 psi). Precise measurements of ambient conditions were made on each day of testing.

B. Separation

Experiments for determining the retention factors and number of theoretical plates were performed on a Hewlett Packard 6890 Gas Chromatograph (GC) using a flame ionization detector (FID). Flow measurements were taken at the exit of the FID with only the carrier gas flowing (fuel gases and make-up gas turned off.) The GC was equipped with a HP Automatic Liquid Sampler and all injections were performed using a split injection technique. The commercial columns used in these tests were 5% phenyl-methyl polysiloxane coated capillaries with 100 μm internal diameter and 0.1 μm film thickness of Supelco SPB-5. Liquid samples were prepared from reagent grade chemicals purchased from Aldrich Chemical Company. A mixture was prepared of n-octane, n-decane, n-dodecane and dimethyl methyl phosphonate (DMMP). The concentration of each compound in the carbon disulfide solvent was approximately 0.1% by weight. All carrier gases were Matheson ultra high purity grade and all tests were run isothermally using constant carrier gas pressure during the run. Column length, column temperature, carrier gas type and carrier gas pressure were the experimental variables in these tests. Test repeatability was indicated by two or three runs at each condition.

The retention factor, k , was calculated using the carbon disulfide as the unretained peak, t_M , and the retention time of the various normal alkanes⁵:

$$k = \frac{t_R}{t_M} - 1$$

The number of theoretical plates, N , was calculated using the peak retention time, t_R , and the peak width at half peak height, w_h ⁵:

$$N = 5.545 \left(\frac{t_R}{w_h} \right)^2$$

Measurements were not taken on the DMMP peaks since the polar compound "tailed" significantly on this column and therefore would not present a symmetrical peak for measuring consistent widths at half peak height.

IV. Analytical Model

A design tool based on analytical models was developed to compute the carrier gas velocity, the theoretical

number of plates, and the total separation time in GC columns with round and rectangular cross-sections. The program is written in Fortran. The equations are given in Table 1. Input values can easily be changed to evaluate the effect of different carrier gases, analytes, operating conditions, coatings, and column geometries on separation, as indicated by the theoretical number of plates.

A. Flowrate

The flow model was developed employing the Navier-Stokes equations with slip, which may become important as the size of the channel decreases. Arkilic, Breuer, and Schmidt⁶ developed a slip flow model based on a momentum balance at the wall and compared with data. The Navier-Stokes with slip model assumes steady, isothermal, laminar, compressible 2D flow and a diffuse gas-surface interaction, which is valid for most surfaces. A factor, based on the aspect ratio of the rectangular channel, is applied to approximate 3D flow⁷. The equations for the velocity at the outlet of round and rectangular columns are given in Table 1. The slip term is only included in the expression for the rectangular columns as they may have very small widths. This is the term with Kn_o , the Knudsen number at the outlet, defined as λ/H , where λ is the mean free path of the gas. The Navier-Stokes equations are valid in both the continuum ($Kn < 0.01$) and slip-flow ($0.01 < Kn < 0.1$) regimes. For no-slip, Kn_o is set to zero.

B. Separation

The modified Golay¹ equation, for open tubular columns of uniform cross-section and isothermal operation, with a pressure correction per Giddings² and an additional term for the instrumental contribution to band broadening⁸, describes the theoretical plate height, h , in Table 1. The four terms in the Golay equation represent the static and dynamic diffusion of the analyte in the carrier gas, diffusion of the analyte in the stationary layer, and the band broadening due to the sum of the instrumental dead times, respectively. For zero instrumental dead time, the optimum velocity resulting in the minimum plate height is obtained by solving $dh/du_o = 0$ as shown in Table 1.

The third term in the Golay equation, C_s , describes diffusion in the stationary retentive layer and is often neglected implying just an adsorption-desorption mode of retention at the surface of the stationary phase and instantaneous (versus an actual slow) diffusion into the bulk of the material. Reston and Kolesar⁹ attribute four orders of magnitude difference between their theoretical and experimental separation factors to this term. Also, per Golay, this term can dominate in simple capillary columns and thus, we must try to evaluate it in our design studies.

C. Transport Properties

Coefficients of viscosity and diffusion are required to compute the velocity of the carrier gas and the theoretical plate height, respectively, as shown in Table 1. The coefficient of viscosity of the carrier gas, μ , is computed from the kinetic theory for rigid-sphere molecules¹⁰:

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{M_g T}}{\sigma_g}, \text{ g/cm-s}$$

The diffusion coefficient of the analyte, a , in the carrier gas, g , is computed using the Fuller-Schettler-Giddings equation³:

$$D_g = \frac{0.001 T^{1.75} (1/M_a + 1/M_g)^{1/2}}{p [(\sum v_a)^{1/3} + (\sum v_g)^{1/3}]^2}, \text{ cm}^2/\text{s}$$

where M = molecular weight, T = temperature (K), σ = molecular diameter (angstroms), p = pressure (atm), and $\sum v$ = sum of atomic volume increments. D_g is evaluated at the same location as the velocity (we choose the column outlet) such that the static and dynamic diffusion terms in the Golay equation are constant along the column, i.e., the diffusion coefficient is inversely proportional to pressure (or density) and pu is constant along the column. The diffusion coefficient of the analyte in the stationary phase, D_s , is user-specified in the program. Some empirical equations for n-alkanes in silicone phases or phenyl-methyl silicones are given in ref. 12 as a function of carbon number and temperature.

V. Code Validation

A. Flowrate

Data was first obtained on conventional GC columns to gain confidence in both the experimental setup and the analytical model. Flowrates of air measured in 1 m long round, straight capillary columns compared well with the model, as shown in Figure 4a. Data were also obtained using argon carrier gas and compared well with model predictions. An uncertainty of about 1 μm in the capillary diameter is small compared to the uncertainty in the dimensions of the etched microscale spiral columns and thus, not a significant source of discrepancy between the model and data. Flowrates measured in uncoated and coated columns were the same within the experimental uncertainty as shown in Figure 4a.

The same test setup was used to measure the flow through the etched spiral columns and to assess three effects which distinguish the spiral column from conventional columns: slip flow, spiral channel configuration, and rectangular cross-sectional shape. Flowrates were measured through four spiral columns 40 μm wide. The maximum Knudsen number for these cases is 0.0008 which indicates the continuum flow regime. There was negligible difference in the flow rates computed with slip and no-slip. Another test set employed a vacuum

operation where the inlet pressure was atmospheric and outlet pressure was 6 psi less. The maximum Knudsen number in these cases is 0.004 and the flowrates with and without slip differed by less than 2%. Thus, for these conditions and geometries, the no-slip assumption seems reasonable. One spiral column was fabricated with a width of 10 μm . The data for this spiral is not presented as SEM images revealed sections which were not etched through thus causing some flow blockage. Slip flow does become important at 10 μm such that the difference in volumetric flowrates with and without slip was 12%.

The analytical model for flowrate was developed for flow through a straight channel while the data were obtained for flow through spiral configurations. The measured flowrates of air through four spirals are compared to the model predictions in Figure 4b. Three of the spirals are 1 m long but differ in the separation distance between the rings, 40, 100, or 160 μm . The fourth spiral is 0.3 m long with a separation distance of 160 μm . All four spirals have a nominal width of 40 μm and nominal depth of 250 μm . The model compares well with the shorter column and the 1 m long column with a separation of 160 μm . The flowrate through the other two 1 m long columns appears to be severely underpredicted.

Uncertainty in the channel dimensions will affect the flow rate. Since the volumetric flowrate goes as the cube of the width, an uncertainty of 50% in channel dimensions can yield a factor of three difference in the flowrates. All four spirals were cut and dimensions measured using a SEM. The two spirals which did not compare with the model had a measured width of 50 μm . When this width is input to the model, the data and predictions agree well as shown in Figure 4b. Since the model agrees well with the data, negligible effect of the spiral curvature on flow is assumed and the rectangular cross-section is sufficiently modeled.

B. Separation

Separations were obtained using the conventional capillary columns with lengths of 1 and 10 m and nitrogen and hydrogen carrier gases. The retention factors of octane, decane, and dodecane in the 0.1 μm thick SPB-5 coated columns are shown in Figure 5 as a function of temperature for nitrogen carrier gas. The column temperature was 40, 60, 80, or 100°C, the outlet pressure was atmospheric (~12.1 psi), and the inlet pressure was varied from 13.2 to 67.2 psi. The retention factors in hydrogen carrier gas were the same as those in nitrogen within the experimental uncertainty. The experimentally determined retention factors are inputs to the design tool to predict the theoretical number of plates.

The predicted and experimentally determined number of theoretical plates on the two capillary columns are compared in Figure 6. Diffusion in the stationary layer was negligible due to the thin coating and relatively large diffusion coefficients in the SPB-5 coating. An in-

strumental dead time of 200 ms gave the best comparison of the model with the data. The model compares fair within the uncertainty in the data and seems to predict the proper trends. Additional data will assist in characterizing and understanding the interaction of the many parameters defining separation performance.

Separations were also demonstrated on a 1 m long, 40 μm wide, 250 μm deep rectangular cross-section spiral column coated with OV-1. The separations were adequate but at a reduced performance compared with the conventional capillaries. Since the retention factor is a function of the analyte, temperature, coating type, and coating thickness to column width ratio (w/d), it can be adjusted by changing these parameters. Work is in progress to increase the separation performance by improving the coating uniformity and to employ the design tool to guide selection of the column dimensions.

VI. Design Studies

To specify the mask for the next generation of etched microscale spiral GC columns, the column length and width were varied to determine an optimum design. For these design studies, the pressure drop was constrained to 6 psi due to the current pump performance. Thus, all cases assumed an inlet pressure of 14.7 psi and outlet pressure of 8.7 psi. The following assumptions were also made: nitrogen carrier gas, DMMP analyte with a retention factor of 5, temperature of 300 K, an instrumental dead time of 100 ms, a column depth of 250 μm , and instantaneous diffusion in the stationary layer.

Increasing the column length increases the optimum width, number of plates, and total separation time as shown in Figure 7a. If a column length of 1.5 m is selected, the optimum column width is 52 μm yielding 14,000 plates and a total separation time of 0.4 min. Since the retention factor and instrumental dead times vary with analyte or are unknown, they were varied as shown in Figure 7b to evaluate the change in performance and optimum width for the 1.5 m long column. An increased dead time shifts the optimum design to smaller column widths. This is only significant for small retention factors as the dead time term in the Golay equation is inversely proportional to $(k+1)^2$. Increasing the retention factor from 5 to 50 increases the total separation time from 0.4 to 4 min for a 1.5 m long, 52 μm wide column.

Three other parameters were varied to determine their effect on the GC column performance. For small column widths (or diameters), columns with rectangular cross-sections perform better than round cross-sections as shown in Figure 8; also, nitrogen is a better carrier gas than hydrogen, as shown in Figure 9, although hydrogen yields faster separation times. The cross-over points for both cases depend on the column length and operating conditions. Finally, diffusion in the stationary phase was evaluated to determine its impact on separa-

tion resolution. The maximum number of plates decreases and shifts to smaller optimum widths with increasing coating thickness and decreasing diffusion coefficient. Since these parameters can have a large impact on the optimum design, more data is being obtained to characterize and control them.

VII. Conclusions

Several microscale spiral GC columns were successfully fabricated using the Bosch reactive ion etch process. The advantage of the Bosch process is that it allows deep, high aspect ratio channels to maximize the column area per chip area. SEM images were required to accurately determine the channel dimensions which are used to compute the flowrates. Comparisons of computed flowrates with data on the microscale spiral columns indicated that slip flow at the wall and the spiral curvature had negligible effect on the flow. Separation data obtained on conventional capillary columns coated with SPB-5 compared best with the analytical model assuming an instrumental dead time of 200 ms. Separation was demonstrated on an OV-1 coated spiral column at a reduced performance compared to the conventional columns and thus, work is ongoing to improve the coating process and uniformity. To specify the mask for the next generation of etched spiral microscale GC columns, the analytical model was used to select the optimum column dimensions and to evaluate off-design performance.

VIII. References

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Table 1: Compressible Flow and Golay Equations

	Round	Rectangular
u_o	$\frac{d^2(P_i^2 - P_o^2)}{64 \mu L P_o}$	$\frac{d^2(P_i^2 - P_o^2 + 12Kn_o P_o^2(P-1))}{24 \mu L P_o} \left(1 - 1/(AR)^2\right)$
B	$2D_g$	$2D_g$
C_g	$\frac{\left(1 + 6k + 11k^2\right)\left(\frac{d}{2}\right)^2}{24(k+1)^2 D_g}$	$\frac{4\left(1 + 9k + \frac{51}{2}k^2\right)\left(\frac{d}{2}\right)^2}{105(k+1)^2 D_g}$
C_s	$\frac{2kw^2}{3(k+1)^2 F^2 D_s}$	$\frac{2kw^2}{3(k+1)^2 F^2 D_s} \left(\frac{H+d}{H}\right)^2$
E	$\frac{(\Delta t)^2}{L(k+1)^2}$	
f_1	$\frac{9(P^4 - 1)(P^2 - 1)}{8(P^3 - 1)^2}$	
f_2	$\frac{3(P^2 - 1)}{2(P^3 - 1)}$	
h	$f_1 \frac{B}{u_o} + f_1 C_g u_o + f_2 C_s u_o + (f_2 u_o)^2 E$ GOLAY Equation	
u_{opt}	$\sqrt{\frac{B}{C_g + (f_2/f_1) C_s}}$	
h_{min}	$2\sqrt{f_1 B (f_1 C_g + f_2 C_s)}$	
t_{total}	$(k+1) \frac{L}{f_2 u_o}$	

where

u_o = gas velocity at outlet

P = inlet to outlet pressure ratio, P/P_o

Kn_o = Knudsen number at outlet

k = retention factor

Δt = sum of instrumental dead times

w = thickness of stationary layer

F = effective to actual surface area of stationary layer

μ = viscosity of carrier gas

D_g = diffusion coefficient of analyte in carrier gas

D_s = diffusion coefficient of analyte in stationary layer

t_{total} = total separation time

h = theoretical plate height

H = column height

L = column length

d = column width or diameter

AR = aspect ratio of channel, H/d

Figure 1. Spiral Microscale GC Column

Figure 2. SEM: Rectangular Cross-Section GC Column

Figure 3. System for Flow Measurements in GC Columns

Figure 5. Temperature Effect on Measured Retention Factor

(a) Straight, Round Cross-Section Column
(Air, $L=1m$)

(b) Spiral, Rectangular Cross-Section Column
(Air, $40μm \times 250μm$)

Figure 4. Volumetric Flowrates: Model vs. Data

(a) 10 m Column Length

(b) 1 m Column Length

Figure 6. Theoretical Number of Plates: Model vs. Data

(a) Effect of Column Length

(b) Effect of Retention Factor and Dead Time

Figure 7. Spiral Design Study

Figure 8. Round vs. Rectangular Columns

Figure 9. Nitrogen vs. Hydrogen Carrier Gas