DESIGN, MODELING AND FABRICATION OF MEMS-BASED MULTICAPILLARY GAS CHROMATOGRAPHY COLUMNS

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ABSTRACT

This paper describes different approaches to achieve high-performance microfabricated silicon-glass separation columns for micro gas chromatographic (μ GC) systems. The capillary width effect on the separation performance has been studied by characterization of 250 μ m-, 125 μ m-, and 50 μ m-wide single-capillary columns (SCCs) fabricated on a 10×8 mm² die. To address the low sample capacity of these narrow columns, the paper presents the first generation of MEMS-based "multicapillary" columns (MCCs) consisting of a bundle of narrow-width rectangular capillaries working in parallel. The theoretical model for the high-equivalent-to-a-theoretical-plate (*HETP*) of rectangular MCCs has been developed, which relates the *HETP* to the discrepancies of the widths and depths of the capillaries in the bundle. Two-, four-, and eight-capillary MCCs have been designed and fabricated to justify the separation ability of these columns. These MCCs capable of multi-component gas separation provide a sample capacity as large as 200 ng compared to 10 ng for 50 μ m-wide single capillary columns.

INTRODUCTION

Gas Chromatography is a unique and versatile technique for separation and identification of volatile and semivolatile organic mixtures. As an analytical tool, which was introduced in the 1950s, GC has a wide range of applications in the pharmaceutical industry, environmental monitoring, petroleum distillation, clinical chemistry, and food processing.

In a GC system, the mixture to be separated and analyzed is vaporized and injected into a column whose walls are coated by a polymer called stationary phase. The mixture components traverse the length of the column in a mobile phase (i.e., carrier gas) at rates determined by their retention in the stationary phase. If the column length and differences in the retention times are sufficient, a complete separation of components is possible. The separated components pass over a detector such as a flame ionization detector (FID), which generates a signal corresponding to the mass of the components in the mobile phase [1, 2].

Conventional GCs provide accurate analysis of complex mixtures but at the expense of using large, power-hungry, and relatively expensive table-top instruments. MEMS technology has already demonstrated the possibility of realizing micro gas chromatography systems (μ GC) which exhibit faster analysis times, lower power consumption, and higher portability compared to bulky conventional GCs.

The development of high-speed and high-performance separation columns is of paramount importance in the world of μ GC especially for public safety, homeland security, and environmental monitoring applications. The reported MEMS-based columns for high-speed GC (HSGC) have achieved separation of a few analytes in seconds but they have not been able to demonstrate highly efficient separations (complex mixture analysis) due to their significantly reduced column length (<50 cm) and their large channel width (>100 μ m). This paper addresses this situation by first demonstrating the successful design, fabrication, and stationary phase coating of very narrow-width columns. A new class of microfabricated columns called

multicapillary, consisting of a bundle of very narrow-width rectangular capillaries working in parallel, is also reported. The presented multicapillary columns enhance sample capacity and alleviate the stringent requirements on the amount of analyte that can be analyzed when using only a single narrow-width capillary column.

THEORY

I. Single-Capillary Column (SCC)

Analysis time, separation efficiency, and sample capacity are the main factors that need to be considered in the design and development of μ GC columns for real-time trace analysis. Analysis time for a mixture is defined by the retention time, t_R , of the last target component peak to elute from the column [1, 3]:

$$t_R = \frac{L}{u}(k+1) \quad (1)$$

where u is the average linear carrier gas velocity, L is the column length, and k is the retention factor for the component, which depends on column temperature and stationary phase properties. For a given column cross section, the retention time can be decreased by operating at (1) a higher carrier gas velocity, (2) a higher temperature, or (3) using a shorter column. MEMS technology affords very high temperature programming rates (~600 °C/min) using on-chip heaters for ultra-low mass short separation columns [2, 4]. The major difficulty of using short columns for HSGC is the significant loss in column separation power. This amplifies the importance of using conditions that provide the maximum possible column efficiency.

The efficiency of GC columns is expressed by the height-equivalent-to-a-theoretical-plate (*HETP*). For rectangular channels, *HETP* is given by [5]:

$$HETP = \frac{2D_g}{u} f_1 f_2 + \left[\frac{(1+9k+25.5k^2)}{105(k+1)^2} \frac{w^2}{D_g} \frac{f_1}{f_2} \dots + \frac{2}{3} \frac{k}{(k+1)^2} \frac{(w+h)^2 d_f^2}{D_s h^2} \right] u \quad (2)$$

where D_g and D_s are the binary diffusion coefficients in the mobile and stationary phases, respectively, d_f is the stationary phase thickness, w and h are the channel width and height, respectively, and f_1 and f_2 are the Gidding-Golay and Martin-James gas compression coefficients, respectively. Consequently, the number of theoretical plates (N) can be calculated using *HETP* value:

$$N = L/HETP \quad (3)$$

Considering the second term in equation (2), it becomes clear that narrower columns (smaller w) provide a smaller $HETP$ or better separation efficiency. The downside of using HSGC columns with small widths is that for a given stationary phase thickness, the sample amount that can be injected without overloading the column is limited to several nano grams. The sample capacity drastically drops for narrow-width columns having a small cross-section area and small $HETP$ (large N) [6]. Another limitation of narrow-width columns is that the volumetric flow rate can be very low [1], which in turn puts limitations on the detector sensitivity. The following section addresses these problems by introducing the first generation of MEMS-Based multicapillary columns.

II. Multicapillary Columns (MCC)

The idea of multicapillary columns was introduced by Golay in 1975 to increase the column separation efficiency without sacrificing sample capacity [3]. The main concept is that the reduced sample load, caused by using narrow-bore fused silica capillary columns, is compensated by increasing the number of capillaries, n , which work in parallel. Therefore, the sample capacity and flow rate can be theoretically increased by a factor of n . The $HETP$ for a GC column is defined by the following equations [1]:

$$HETP = L \frac{\sigma^2}{t_R^2} \quad (4)$$

where σ^2 is the peak variance. The $HETP$ for MCCs can be defined in terms of the performance of its single capillaries, the stationary phase properties, and the structure features. By ignoring the details of derivation, an MCC with an average linear gas velocity of u_o has the following $HETP$:

$$HETP = \frac{u_o^2}{L[1+k_o]^2} \sigma_o^2 + L \left(\frac{\sigma_h}{h_o} \right)^2 + L \left(\frac{\sigma_w}{w_o} \right)^2 \quad (5)$$

where $(\sigma_h/h_o)^2$ and $(\sigma_w/w_o)^2$ are cross-section height and width variances normalized by the average height (h_o) and width (w_o), respectively. k_o is the retention factor in a capillary with cross-section area of a_o ($h_o \times w_o$). In this equation, the first term, $HETP_o$, refers to the $HETP$ of a capillary whose dimensions are the average of the dimensions of all capillaries in the bundle and can be calculated from equation (2). The other terms is related to the band broadening caused by inhomogeneity of the channels. If all the capillaries in the bundle have exactly the same dimensions ($\sigma_h = \sigma_w = 0$), the second and third terms of the MCC performance equation would be zero, which means that MCC has an $HETP$ equal to that of the single capillary while its sample capacity is multiplied by the number of capillaries in the bundle. Conventional MCCs comprising a bundle of round capillaries show a dispersion of 3-4% [7]. As shown later, highly homogenous rectangular capillaries can be fabricated by MEMS technology in order to minimize the second and third term in equation (5) and to increase the separation performance.

FABRICATION

In order to study the width effect on $HETP$, SCC columns with three different capillary widths (50, 125, and 250 μm) were designed. Moreover, two-, four- and eight- capillary MCCs were fabricated to characterize the MCC performance.

Fig. 1: Fabrication process flow for MEMS-based multicapillary columns. The column formed from silicon wafer etched using deep reactive ion etching (DRIE) technique (a-b) and bonded to a Pyrex wafer(c).

All the columns had a length of 25 cm and all the MCCs had a constant total width of 250 μm . The fabrication of both silicon-glass SCCs and MCCs started with cleaning a silicon wafer in a Piranha solution. Then, a 10 μm -thick layer of AZ9260 photoresist was spun on the wafer at 3 krpm for 60 seconds. After patterning the photoresist (Fig. 1a), the wafer was etched to a depth of 250 μm using deep reactive ion etching (DRIE) technique to form channels with aspect ratios varying between 1 (for 250 μm -wide columns) and 5 (for 50 μm -wide columns) (Fig. 1b). After stripping the resist, the silicon wafer was anodically bonded to a Pyrex 7740 substrate (Fig. 1c). The final step is dicing the wafer to form $10 \times 8 \text{ mm}^2$ chips, a picture of which is shown in Fig. 2. Fig. 3 shows SEM images of SCCs and MCCs before the channels were sealed. It should be mentioned that the serpentine design of the microfabricated columns compensates the peak broadening caused by turn-effect and equalize the length of all the capillaries in MCCs.

In order to connect the chips to the GC system, fused silica capillary tubing with 167 μm -O.D. and 100 μm -I.D. was used. The tubing was first deactivated at 400 $^\circ\text{C}$ with octamethylcyclotetrasiloxane (D4) as the deactivation agent using a previously published procedure [8]. After deactivation, the tubing was washed with 0.5 mL of methylene chloride and then

Fig. 2: GC column fabricated on an 8 mm square die after anodic bonding and attaching capillary tubes.

Fig. 3: SEM images of columns before anodic bonding. (a) Single Capillary Column (SSC), shows the vertical channels with aspect ratio of more than seven(onset) and (b) Cross-section view of 4-channel Multicapillary Column (MCC), top view (onset)..

purged with helium at 220 °C for 60 minutes. The tubing was then attached to the microfluidic ports of the chip using two-part adhesive (Epoxy 907, Miller-Stephenson). The deactivation procedure was repeated a second time to ensure deactivation of the chip. Due to temperature limitations of the epoxy, the deactivation procedure was performed at 250 °C, instead of 400 °C, for 90 minutes. The washing and purging procedures were also repeated. Then, a solution of polydimethylsiloxane (OV-1) dissolved in n-pentane was used to fill the column while one end of the column was blocked by pushing a small amount of wax into the capillary tubing. The concentration of the coating solution was calculated in the range of 4 mg/ml and 8 mg/ml for different columns in order to achieve an optimum coating thickness mentioned above. A vacuum was then applied to the other end while the column was kept in a water bath at 35 °C. This resulted in slow evaporation of the solvent leaving behind a thin layer of stationary phase on the column walls. In order to obtain a stable film, the OV-1 stationary phase was cross-linked by passing a vapor of azo-tetrabutane (AZT) through the column for 60 minutes. Finally, the column was sealed at both ends and heated at 220 °C for 60 minutes.

RESULTS AND DISCUSSION

Table 1 summarizes the channel dimensions and statistical dispersion factors for different microfabricated MCCs. The cross-sectional dispersion of these MEMS MCCs is about 0.5% and is significantly lower than that of conventional columns (3-5%) [7]. Considering equation (5) and according to Table 1, the peak broadening resulting from inhomogeneities in the capillaries' dimensions (second term of equation 5) is one order of magnitude

less than that from the peak broadening resulting from a single capillary (first term).

In order to evaluate the capabilities of the microfabricated columns, several experiments were conducted using a conventional GC system (5890 Series II GC, Hewlett Packard) having a split inlet (200:1) and flame ionization detector (FID). The capillary column inside the GC was replaced by the MEMS column. The GC autosampler (7673B, Hewlett Packard) was used to inject the samples. Air was used as a carrier gas. All gases were purified with filters for water vapor and hydrocarbons. The injector and FID temperature were maintained at 280°C.

To determine the sample capacity, solutions of dodecane ($C_{12}H_{26}$) in methylene chloride were prepared in increasing concentrations from 250 ng/µL to 10 µg/µL and the *HETP* was calculated for each sample by an injection of 1 µl of the solution at 60 °C with a split ratio of 200:1. The maximum sample amount without significant change in the *HETP* (less than 10%) was used to determine the column sample capacity. Table 2 lists the measured sample capacities of the columns. MCC columns are promising in that they can provide high efficiency of narrow columns while providing larger sample capacities. As listed in Table 2, the columns having more capillaries demonstrate higher sample capacity. The MCC with four 65 µm-wide capillaries presented a much larger sample capacity (20 fold) compared to the 50 µm-wide SCC.

The separation performance of the MCCs have been explored by separating a high-concentration gas mixture containing indoor air components (Sigma-Aldrich Inc., MO, US), in the conventional GC oven. Fig. 6 shows the chromatogram obtained using two-

Table 1: Statistical data obtained by SEM images to characterize the homogeneity of channels in different microfabricated MCCs at different cross sections.

MCC	Statistical Data to qualify fabrication process						H_o cm	$L \left[\left(\frac{\sigma_h}{h_o} \right)^2 + \left(\frac{\sigma_w}{w_o} \right)^2 \right]$ mm
	Average channel width(W) µm	Average width dispersion ($\frac{\sigma_w}{W}$) %	Average channel depth(D) µm	Average depth dispersion ($\frac{\sigma_D}{D}$) %	Average cross-section area(A) (µm) ²	Average area dispersion($\frac{\sigma_A}{A}$) %		
2-capillary	126.5	0.27	256.7	0.43	32466	0.53	0.014	0.006
4-capillary	65.3	0.47	244.7	0.26	15983	0.51	0.009	0.007
8-capillary	36.2	0.52	231.4	0.19	8388	0.55	0.007	0.008

Table 2: Sample capacity measured using dodecane injection at 60°C, air as the carrier gas at 10psi column inlet pressure.

Column Design- Channel width(um)	Sample Capacity(ng)
SCC-50	10
SCC-125	12
SCC-250	19
MCC-125 (2-capillary)	50
MCC-65 (4-capillary)	200

channel MCC at a 30 °C/min temperature programming rate. The injection volume was 2 µl which can easily overload all the fabricated SCCs.

It should be emphasized that uniform stationary phase coating is a challenging step in the development of rectangular µGC columns. It becomes even more challenging for MCC columns with numerous parallel capillaries since all capillaries should have similar coating thickness to optimize the column performance. The primary experimental measurements of minimum *HETP*, under the same conditions mentioned above, showed a value of 0.05 cm and 0.12 cm for two- and four-capillary MCCs, respectively. This deviation from theory (see Table 1) is mainly attributed to the nonuniformity of the stationary phase coating. Work is currently under way to develop novel techniques based on self-assembly deposition of nano-structured materials to achieve a uniform thin layer of stationary phase in all the capillaries of the bundle in the presented microfabricated MCCs.

Fig.4: Chromatogram of high concentration standard mixture of indoor air components obtained by 2-channel MCC at a temperature rate of 30°C. Image onset is the first 1.2 min. of the analysis time.

CONCLUSION

This paper has presented the development of silicon-glass high-efficient µGC columns. The tradeoff between separation efficiency and sample capacity has been addressed by presenting the MCCs. General correlations for the efficiency of rectangular

cross-section MCCs have been developed. The efficiency of such columns depends on the dispersion of the capillary dimensions in the bundle as well as the coating technique. The compatibility with unpredictable amount of environmental samples indicates the promise of MCCs for applications in environmental monitoring and homeland security.

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