Micro-Fabricated Packed Gas Chromatography Column Based on Laser Etching Technology

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Abstract

In this work, a micro packed gas chromatograph column integrated with a micro heater was fabricated by using laser etching technology (LET) for analyzing environmental gases. LET is a powerful tool to etch deep well-shaped channels on the glass wafer, and it is the most effective way to increase depth of channels. The fabricated packed GC column with a length of over 1.6 m, to our best knowledge, which is the longest so far. In addition, the fabricated column with a rectangular cross section of 1.2 mm (depth) × 0.6 mm (width) has a large aspect ratio of 2:1. The results show that the fabricated packed column had a large sample capacity, achieved a separation efficiency of about 5,800 plates/m and eluted highly symmetrical Gaussian peaks.

21 **Keywords:** Micro packed gas chromatography column; Separation efficiency; Micro
22 gas chromatography system; Laser etching technology

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1. Introduction

With increasing demands for real-time environmental samples monitoring, micro/portable gas chromatography (GC) instruments with high sensitivity were in urgent need to be developed [1, 2]. However, the development of micro gas chromatography systems was limited due to large volume and high power consumption of traditional chromatography columns. Owing to the development of MEMS technology, micro gas chromatography columns have a brighter prospect with some advantages of smaller volume, more rapid analysis and less power consumption [3-11]. In addition, the micro GC columns can be easily integrated with different GC components (e.g. pre-concentrators and detectors), enabling the realization of a field portable system for real-time sample analysis. Therefore, the miniaturization of GC columns has been the main subject of recent research focus.

After ten years of development, the micro gas chromatography columns have been widely used for separating gas mixtures in several fields. The development can be roughly divided into three phases. The micro open tubular GC columns acted as focus were firstly developed. However, the separation efficiency is relatively poor due to the limited sample capacity. It is well known that the volume of column has great influences on the sample capacity. In order to improve the sample capacity, in recent years, micro semi-packed GC columns [12, 13, 14] and micro multicapillary GC columns [15] were developed, which can yield efficiencies of over 9000 plates/m. However, the gas mixtures separated by the above micro GC columns are predominantly VOCs gaseous, and the coated stationary phases are mainly stationary

65 liquids, such as the OV-1, OV-101, PDMS, etc. It is very difficult to separate the
66 permanent gases (CO, CO₂, O₂, N₂, etc.) and low carbon hydrocarbons (CH₄, C₂H₂,
67 C₂H₄, C₃H₆, etc.). In order to solve the problem, micro packed columns filled with
68 chromatographic packing were proposed. However, the development of them
69 encountered a bottleneck as it is very difficult to uniformly fill chromatographic
70 packing in the folding or bending shallow channels, resulting in a limited length of
71 micro packed columns. J.Sturmann [16] developed a silicon micro-machined packed
72 GC column integrated with a solid-state metal oxide semiconducting (MOX) gas
73 sensor for GC analysis. S. Zampolli reported [17] a packed column with a length of
74 75 cm. However, longer packed columns were rarely reported.

75 It is well known that the separation efficiency depends on the length and the aspect
76 ratio (defined as the ratio of depth to width) of the columns, so it is very important to
77 fabricate micro packed GC columns with long and large aspect ratio channels.
78 Generally speaking, reducing width and increasing depth of the channels can improve
79 the aspect ratio, obtaining larger plates. However, it is very difficult to uniformly fill
80 chromatographic packing in narrow channels as they can be easily blocked by the
81 packing. Therefore, in order to improve the separation performance, increasing depth
82 of the channel was the most effective way. In recent years, Laser etching technology
83 (LET) has become an important etching method. As it can easily etch deep channels
84 on glass wafers as well as on silicon wafers, the column depth can be substantially
85 increased by bonding the channels on the silicon wafer together with the channels on
86 the glass wafer. Consequently, the column can achieve a channel with a depth of 1.2

mm-1.5 mm, which greatly enhances the aspect ratio and the sample capacity, improving the separation efficiency of micro packed GC columns. In this work, a micro packed GC column based on LET with a length of 1.6 m was reported, the length, to our best knowledge, is the longest so far.

2. Experimental Section

2.1. Materials and reagents

In this work, Sample I (Beijing Hua Yuan Gas Chemical Industry Co., Ltd) contains 500 ppm CO and CH₄ gas **balanced in helium gas**. Sample II (Beijing Hua Yuan Gas Chemical Industry Co., Ltd) was composed of 8 compounds (CO, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₁₀, the concentrations are 10.0 ppm, 9.95 ppm, 10.15 ppm, 10.0 ppm, 10.1 ppm, 9.9 ppm, 10.25 ppm and 11.0 ppm, respectively). Porapak Q with a diameter of 100 μ m was purchased from Sigma-Aldrich (St. Louis, Mo, USA).

2.2. Experimental setup

In this paper, the samples were analyzed utilizing a mini GC system based on a micro thermal conductivity detector (μ TCD) [18] (Fig.1). The proposed μ TCD was characterized with a large linear range of 10^5 and a detection limit less than 5 ppm. The sample injected by a sampling pump was transported into the packed column through a valco valve. Pure hydrogen gas with a large thermal conductivity coefficient was used as carrier gas, the flow rate of which was controlled by a pressure regulator.

2.3. Fabrication of the micro packed GC column

2.3. 1. Fabrication of the channels

In this work, instead of the conventional methods (such as chemical etching or deep reactive ion etching, with which it was very hard to fabricate deep well-shaped channels on glass wafer), LET was used to fabricate the channels. The details of the fabrication process of the column are presented as follows. Firstly, the column configuration was drawn by AutoCAD. Subsequently, rectangular micro channels with a cross section area of 0.6 mm×0.6 mm were etched on the silicon and glass wafer by LET based on the configuration (Fig.2) , respectively. However, some burrs were left on the edge of these channels due to laser ablation, result in low yield rate when packaging the devices. Therefore, the surfaces must be polished before bonding. In addition, a micro filter was fabricated and located at the outlet, which can prevent the chromatographic packing loss.

2.3. 2. Fabrication of the micro heaters

In order to make the column with fast self-heating capability, micro heaters were integrated on the backside of the column. The heater with resistance of 8 Ω was fabricated by sputtering a 20 nm/250 nm Cr/Pt stack and then applying a lift-off process. The heater can increase temperature at a speed of 5°C per second and the highest temperature can be raised up to 200°C in 100 seconds. Then, the channels on the silicon wafer were aligned and bonded with the counterparts on the glass wafer. The depth and length of the column are 1.2 mm and 1.6 m, respectively, and the aspect ratio is 2:1. Fig.3 shows the heaters, the fabricated micro GC column and the micro TCD integrated with the fabricated packed column.

2.3. 3. Packing the GC column

In order to separate the permanent gases and low carbon hydrocarbons, Porapak Q acting as the stationary phase was packed in the column. The packing process is detailed as follows. First, the outlet of the column was connected with a pump through a capillary, and the inlet was directly emerged into the porapak Q powder. Then, the pump was turned on and the porapak Q powder was transported into the channels. In order to uniformly pack the column, the column needs to be gently beaten during the packing process. After filled with the porapak Q powder, the fabricated column was put into a temperature programmed oven which was filled with the nitrogen ambient, and the temperature of the column was successively increased to 80°C, 120°C and 220°C for 4 hours of stationary phase aging, respectively.

3. Results and Discussion

3.1. Column efficiency

A more realistic description of the processes at work inside a column takes account of the time taken for the solute to equilibrate between the stationary and mobile phase. The resulting band shape of a chromatographic peak is therefore affected by the rate of elution. It is also affected by the different paths available to solute molecules as they travel between particles of the stationary phase. Therefore, Van Deemter equation relates height equivalent to a theoretical plate (*HETP*) of a GC column to various flow and kinetic parameters which cause peak broadening, as follows [19, 20]:

$$HETP = A + \frac{B}{u} + Cu \quad (1)$$

The *HETP* is typically calculated experimentally from a chromatogram using equations (2) and (3).

$$HETP = L/n \quad (2)$$

Where *L* is the column length and *n* is the plate number. The plate number can be calculated based on the retention time (*t_R*) of peak [21].

$$n = 5.54 \left(\frac{t_R}{w_{1/2}} \right)^2 \quad (3)$$

Where *t_R* is the retention time, and *w_{1/2}* is the width of the peak at half height. The Van Deemter curve calculated for the fabricated packed column was shown in Fig.4.

The minimum *HETP* value, *H_{min}*, found at the optimal average carrier gas velocity, *u_{opt}*, gives the maximum number of theoretical plates. For the fabricated packed column a minimum *HETP* of 0.015 cm (6,700 plates/m) at a linear gas velocity of 11 cm/s can be expected from the calculations.

3.2. Separation chromatograms

To evaluate the performance of the micro-fabricated packed GC column, some key parameters were studied, such as sample capacity, separation efficiency, and repeatability. These experiments were carried out at a linear flow velocity of 11 cm/s, at the temperature of 100°C, with the carrier gas of H₂. The gas was a mixture of CO and CH₄ with concentration of 500 ppm. In general, the larger sample capacity of the GC column, the greater output response the detector has. Therefore, the sample capacity is an important factor of the GC column. However, when the injected sample

was over the sample capacity of GC column, the chromatographic peak would cause serious peak tailing or leading peak, thus affecting the resolving power. In order to evaluate the sample capacity of the fabricated column, three different volumes of samples (0.5 ml, 1.0 ml and 1.2ml) with same concentration were injected into the column, respectively. Fig. 5 shows the signal outputs of the detector with different sampling volume. As we can see from chromatograms, the output response was able to improve by increasing injected sample when the sample capacity was large enough. Moreover, the peak tailing didn't occur, even when the sampling volume reached 1 ml. However, the peak broadening and peak tailing obviously occurred when the sampling volume was 1.2 ml, which indicated the injected sample was over the sample capacity of the column.

In order to evaluate the repeatability of the fabricated packed column, 3 repeated experiments were performed with a sampling volume of 1 ml. These experiments were carried out with the same conditions of flow rate (11 cm/s) and the temperature of column. Fig. 6 shows the chromatograms of the 3 repeated experiments. As we can see from the chromatograms, the proposed column completely separated CO and CH₄ with very high repeatability, and the resolution of the two chromatographic peaks is over 1.5.

In order to evaluate the performance of the micro packed column for complicated gas mixtures, a sample (sample II) composed of 8 components was used to perform the experiment, where the column temperature was 100°C, the sampling volume was 1ml, H₂ was acted as carrier gas and the flow rate was 11 cm/s. Fig. 7 shows chromatogram

of these complicated gas mixtures, indicating that the fabricated column completely separated these components in 100 seconds with resolution over 1.4 for these adjacent peaks. In addition, the fabricated column yielded efficiencies of 5,800 plates/m at the carrier gas velocity of 11 cm/s, and the measured plates were close to the calculated value.

4. Conclusion

This study demonstrated a LET based micro packing GC column. LET was a powerful tool to etch deep well-shaped channels on glass wafer, leading to a large aspect ratio. The micro packed GC column with a length of 1.6 m, to our best knowledge, is the longest so far. Based on the above experimental results, the micro-fabricated packed column had a large sample capacity, and was able to completely separate 8 components with separation efficiencies of 5,800 plates/m.

In order to achieve optimal separation efficiency, an effective method is used to reduce the packing diameter down to 5 to 10 microns. In theory, the separation efficiency can be improved up to 10,000 plates/m. However, the pre column pressure will increase significantly when the column was filled with smaller particles packing, which was unfavorable for portable/micro GC system due to their limited carrier gas pressure.

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Figure.1. Schematic of the mini GC-μTCD system.

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289 Figure.2. Configuration of the micro packed column: (a) the channel on the wafer, (b)

290 the channel filled with chromatographic packing.

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296 Figure.3. (a) The heaters, (b) the fabricated micro GC column filled with porapak Q,
297 and (c) the micro TCD integrated with the packed column.

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Figure.4. The Van Deemter curve calculated for the fabricated packed column.

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Figure.5. The outputs of the detector with different sampling volume.

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Figure.6. The chromatograms of the 3 repeated experiments.

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Figure.7. Separation of complicated gas mixtures of CO, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₁₀. The sample volume was 1 ml, the velocity was 11 cm/s and the column temperature was 100°C.