



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 5800 plates/m and eluted highly symmetrical Gaussian peaks.

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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 [12–14] 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 liquids, such as the OV-1, OV-101, PDMS, etc. It is very difficult to separate the permanent gases (CO, CO₂, O₂, N₂, etc.) and low carbon hydrocarbons (CH₄, C₂H₂, C₂H₄, C₃H₆, etc.). In order to solve the problem, micro packed columns filled with chromatographic packing were proposed. However, the development of them encountered a bottleneck as it is very difficult to uniformly fill chromatographic packing in the folding or bending shallow channels, resulting in a limited length of micro packed columns. Sturmman [16] developed a silicon micro-machined packed GC column integrated with a solid-state metal oxide semiconducting (MOX) gas sensor for GC analysis. Zampolli reported [17] a packed column with a length of 75 cm. However, longer packed columns were rarely reported.

It is well known that the separation efficiency depends on the length and the aspect ratio (defined as the ratio of depth to width) of the columns, so it is very important to fabricate micro packed GC columns with long and large aspect ratio channels. Generally speaking, reducing width and increasing depth of the channels can improve the aspect ratio, obtaining larger plates. However, it is very difficult to uniformly fill chromatographic packing in narrow channels as they can be easily blocked by the packing. Therefore, in order to improve the separation performance, increasing depth of the

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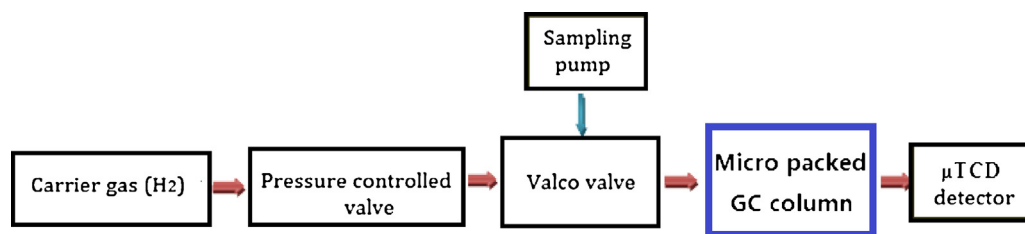


Fig. 1. Schematic of the mini GC- μ TCD system.

channel was the most effective way. In recent years, Laser etching technology (LET) has become an important etching method. As it can easily etch deep channels on glass wafers as well as on silicon wafers, the column depth can be substantially increased by bonding the channels on the silicon wafer together with the channels on the glass wafer. Consequently, the column can achieve a channel with a depth of 1.2 mm to 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

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 10⁵ 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 \times 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 $^{\circ}$ C per second and the highest temperature can be raised up to 200 $^{\circ}$ C in 100 s. 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 $^{\circ}$ C, 120 $^{\circ}$ C and 220 $^{\circ}$ C for 4 h 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 Eqs. (2) and (3).

$$HETP = \frac{L}{n} \quad (2)$$

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].

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

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