LOW PRESSURE DROP MICRO PRECONCENTRATORS WITH A COBWEB TENAX-TA FILM

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ABSTRACT

This paper reports the design, simulation, and experimental evaluation of high performance low pressure drop ($<100\text{Pa/cm}$) micropreconcentrator (μPC) chips ($7\text{mm}\times 7\text{mm}\times 0.38\text{mm}$) for micro total analytical systems. The μPC 's high performance is attributed to the multiple inlets/outlets, novel high-aspect-ratio ($380\mu\text{m}$) parabolic reflectors, and cobweb configuration of adsorbent films all in which promote the adsorption of chemical species. Flow pattern simulations were used to verify the underlying concept of the design. The adsorption capacity of hydrocarbons was used to evaluate the μPC s experimentally. The performance of the new design was found to be more than 2 orders of magnitude higher than the first generation reported previously.

INTRODUCTION

Generally speaking, preconcentrators (PCs) are concentration amplifiers used to improve the detection limit of analytical systems such as spectroscopy [1], mass-spectrometry [2], and chromatography [3]. They are also an integral part of handheld chemical detection systems. However, to meet the size and power constraints, handheld systems rely on microfabricated components (fluidic ports/channels, pumps, valves, etc.) which operate at low pressures. For example, a state-of-the-art micromachined pump designed for micro gas chromatographers can only provide a maximum back pressure of 7 kPa [4] whereas a typical MEMS-based μPC can introduce large pressure drop as high as 14 kPa [5]. Therefore, reducing the pressure drop in μPC s is a key development in handheld systems.

Conventional PCs are troubled by large pressure drop, dead volume, and high power consumption. Microfabrication technology has enabled high efficiency preconcentration in terms of sample capacity, device size, and the energy consumed. Recently, our group and others have utilized 3D microstructures embedded within a microcavity and coated with adsorbent films to realize low pressure drop μPC [6-8]. The microstructures provide large surface-to-volume ratio and low flow resistance compared to conventional microporous granular packing arrangement. This paper reports the design, simulation, and experimental evaluation of high performance low pressure drop μPC chips for micro analytical instruments including a micro gas chromatography system (μGC) [9]. In addition to our unique design enabling very low pressure drops, less than 100Pa/cm , we present a new deposition method which results in a cobweb structure of the adsorbent material, thereby significantly increasing the concentration efficiency without obstructing the gas flow.

The new design consists of an array of parabolic reflectors embedded within a $7\text{mm}\times 7\text{mm}\times 0.38\text{mm}$ cavity. The unit cell of the array consists of three reflectors as shown in Fig. 1. The reflectors are arranged to split the flow in the forward direction and combine them back in the reverse direction. The spacing between the reflectors (side and middle spacing) was varied to investigate its effect on the device performance. Table 1 list the different spacing values for both side and middle spacing along with the symmetry ratios (SR) of different designs. The SR was defined as the ratio of side to middle spacing. High SR represents narrow passage of flow which increases the probability of molecules

scattering and interacting with the adsorption surface. Full scale (actual chip size) computational fluid dynamics (CFD) simulation was consummated to investigate the flow behavior in such geometries. To establish confidence in the CFD model, calculated flow rates were compared with experimental results as shown in Fig. 2. The CFD results of the flow velocity profile showed high velocity in the middle spacing region of PC100 design as presented in Fig. 3. The data suggested that high SR value is desirable. The CFD results confirmed the anticipated flow behaviors. The simulated pressure drops in the different designs are listed in Table 1. The pressure drop profile is shown in Fig. 4 indicates uniform pressure drop which is also desirable.

Figure 1: The μPC unit cell. Arrows indicate the flow direction.

Table 1: Different spacing arrangements and their corresponding symmetry ratio along with the simulated pressure drops at 1.5mL/min flow rate.

Design Label	Middle spacing (μm)	Side Spacing (μm)	SR	Pressure drop (Pa)
PC100	100	250	2.5	145
PC200	200	200	1	97
PC300	300	150	0.5	94

Figure 2: Comparison of calculated and experimental flow rates to establish confidence in the CFD model

Figure 3: Simulation of the flow profile through different design spacing arrangements

Figure 4: Pressure-drop profile in the μ PC

The microstructures were realized according to the process flow in Fig. 5. The process starts with (a) photolithography of microstructures and fluidic ports on 4 inches test grade silicon wafer using high resolution, superior aspect ratio thick film photoresist (PR9260). This step was followed by (b) etching the patterned wafer using deep reactive ion etching (DRIE) to form 380 μm deep 3D structures. Tenax-TA particles were dissolved in dichloromethane at 50 mg/mL concentration to create a solution to fill the etched cavity with. Adsorbent deposition (c) was achieved by adding drops of 2-propanol into solution before it evaporates from the cavity. Cobweb Tenax-TA evolves when 2-propanol contacts Tenax-TA solution. The cobweb structure anchors to the sidewalls once the solvent evaporates as shown in Fig. 6. The cavity was then sealed (d) by anodic bonding the silicon substrate to a Pyrex wafer at 1250 V and 300°C instead of conventional 350-400°C bonding temperature to avoid damaging the polymer. The expansion reservoirs shown in Fig. 7 were incorporated into the inlet/outlet design to prevent the sealing adhesive from overflowing into the inner cavity. This was a new addition to the first generation design reported previously [7]. The silicon-Pyrex stack was then diced into individual devices like the one shown in Fig. 7. Each device was connected on both sides with 300 μm -OD, 170 μm -ID deactivated fused silica tubing using high temperature ceramic based adhesive. The addition of Tenax-TA did not create a measurable difference in the flow rate. Fig. 8 presents a scanning electron microscopy (SEM) image of cobweb Tenax-TA

Figure 5: μ PC fabrication process flow

Figure 6: Optical image of the cobweb Tenax-TA.

Figure 7: 3D rendering of the μ PC, insets are SEM micrographs of the fabricated microstructures

Figure 8: SEM image of cobweb Tenax-TA on the micro parabolic reflectors

The μ PCs were evaluated experimentally by using the adsorption capacity as a figure of merit. The testing was performed inside a temperature controlled chamber to accurately maintain the testing temperature at 35°C. An electronic gas flow controller was used to supply and control the carrier gas which was selected to be nitrogen to resemble actual field operation conditions. The flow rate through the μ PC was set to constant 1 mL/min. A flame ionization detector (FID) was utilized to detect the hydrocarbon samples used in the experiments. An off-board high-performance ceramic heater (ultra-fast ramp rate) was used for thermal desorption along with K-type thermocouple for manual temperature monitoring and control. In future work, on-chip thermal desorption capability will be added to the μ PCs. The chips were saturated with benzene at 35°C and then desorbed at 100°C/sec to 250°C. The FID peak area is proportional to the analyte concentration. The benzene concentration in the desorption peak reflects the sample amount collected by the device. It is evident from Fig. 9 that the SR parameter has a significant effect on the performance of the parabolic reflectors design. Moreover, Fig. 9 shows that the performance of PC100 design is more than 2 orders of magnitude higher than the micro pillar design presented in HiltonHead'08 [10]. In the first generation design inkjet printing of Tenax-TA was used to provide uniform film deposition. Cobweb Tenax-TA offers better utilization of the space between the microstructures with the μ PC

cavity. Reproducibility of the results in terms of peak area was 10% relative standard deviation (RSD) with more than 10 manual injections is shown in Fig. 10.

Figure 9: Benzene desorption concentration for the three designs as well as the first generation design

Figure 10: Reproducibility of μ PC desorption pulses

For proof of concept, the μ PC was put in series with a 1m 100% methylpolysiloxane microfabricated column [11] to demonstrate the possibility of μ PC- μ GC integration. Under the same loading/desorbing conditions as the benzene test, the μ PC was loaded with a mixture of toluene, nonane, decane, undecane, dodecane, tridecane, tetradecane, and pentadecane diluted in pentane at 1ppm concentrations. The sample concentration was below the FID detection limit; thus, preconcentration was needed to make the sample detectable. Fig. 11 illustrates a chromatogram of the preconcentrated sample injected into the micro column via thermal desorption. The initial and final temperatures of the column were 35 °C and 150 °C at 30 °C/min. The carrier flow rate was 1mL/min.

CONCLUSIONS

The performance of analytical instruments especially handheld systems can be improved with sample pretreatment techniques such as preconcentration. This paper has demonstrated the possibility of developing lower pressure drops, small sizes, and high performance MEMS-based μ PCs. This was realized by utilizing findings from previous designs, novel parabolic reflectors configuration, and cobweb Tenax-TA. The simulation analyses verified by experimental results have shown the effect of the SR parameter in the parabolic reflectors design. Future work will aim to better understand and model the behavior of the μ PCs under different conditions. The reproducible desorption peaks needed for fast on-field analytical analysis has been demonstrated by the μ PC.

The presented device was successful in concentrating a diluted multi-compound hydrocarbon mixture.

Figure 11: Preconcentration and separation of a mixture of (1) toluene, (2) nonane, (3) decane, (4) undecane, (5) dodecane, (6) tridecane, (7) tetradecane, and (8) pentadecane diluted in pentane below the FID detection limit.

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