

Multiple-Stage Microfabricated Preconcentrator-Focuser for Micro Gas Chromatography System

Wei-Cheng Tian, *Member, IEEE*, Helena K. L. Chan, *Student Member, IEEE*, Chia-Jung Lu, Stella W. Pang, *Fellow, IEEE*, and Edward T. Zellers

Abstract—The design, fabrication, and characterization of a multiple-stage Si microfabricated preconcentrator-focuser (μ PCF) for a micro gas chromatography (μ GC) system that can provide real-time quantification and identification of complex organic vapor mixtures are presented. The μ PCF consists of a Si microheater loaded with Carboxen B, Carboxen X, and Carboxen 1000 carbon adsorbent granules, and a Si micromachined cover plate. Deep reactive ion etching is utilized to produce mechanically robust fluidic interconnection adapters hermetically sealed to fused silica capillary tubing for connection to the other components in the μ GC. This three-stage device is designed to capture compounds spanning up to 4 orders of magnitude in volatility. The dead volume, thermal mass, heating efficiency, and pressure drop of the three-stage μ PCF are improved significantly over its single-stage μ PCF predecessor. We demonstrate the successful capture, desorption, and high-resolution chromatographic separation of a mixture of 30 common organic vapors using our three-stage μ PCF in a conventional GC system. The peak width at half height is <2.05 s for all compounds after elution from the GC column. [1280]

Index Terms—Adsorbent, gas detection, micro gas chromatography (μ GC), microelectromechanical systems (MEMS), microheater, preconcentrator-focuser (PCF).

I. INTRODUCTION

A HIGHLY portable micro gas chromatography (μ GC) system produced using micromachining technologies to determine contamination of air has been an ongoing area of multidisciplinary research in biomedical diagnostics, environmental monitoring, industrial processing, and food inspection. Traditionally, the analyzes of contaminated air samples are performed by the conventional bench-top gas chromatography

(GC) system in the laboratory. Recent efforts have been made to develop field-portable and meso-scale GC systems to provide portability and near real time analysis capability [1], [2]. However, these portable GC systems are large and require large power supplies. They also have long analysis cycle times and require large sampling volumes. Therefore, there is considerable interest in a fast, lower power, highly portable μ GC system that can provide real time monitoring for quantification and identification analysis of complex compound mixtures.

A preconcentrator-focuser (PCF) in a high-performance GC system is required when the resolving power of the GC column or the sensitivity of the detector is limited by the low parts per billion (ppb) concentrations of analytes. The principle of PCF operation is that as the low-concentration complex compound mixture passes through the device, these compounds will be captured over time for subsequent rapid thermal desorption. The thermally released compounds provide narrow desorption peaks with relatively high concentration. The narrow desorption peak increases the separation efficiency of the GC column and the high concentration peak increases the sensitivity of the analysis.

Conventional stainless-tube preconcentrators used in U.S. Environmental Protection Agency analytical methods are large in size and consume high power during thermal desorption. They also suffer from large dead volume and limited heating efficiency due to their large thermal mass [3], [4] and therefore required an additional liquid nitrogen focusing stage. A microfabricated preconcentrator-focuser (μ PCF) using micromachining technology can overcome these limitations by significantly reducing the device size, dead volume, thermal mass, and power consumption and thus increase the performance of the device. Previously, microfabricated preconcentrators with a thin layer of adsorbent film on a heated-membrane were developed at Sandia National Laboratories for a μ -ChemLab designed to detect specific chemical warfare agents [5]. However, the devices were not designed to provide large adsorbent capacity for preconcentration of complex organic mixtures or uniform heating of large amount of adsorbent granules, which are the targets for our project.

This work is part of an effort to develop a μ GC system for the analysis of low ppb of volatile organic compounds in indoor air. The ultimate goal of this wireless microsystem is to analyze 30 to 50 compounds in 10 min with a small sample volume of 50 ml and low power consumption of 10 mW. We developed a thick, high aspect ratio microheater to provide a large adsorbent capacity and large heating surface for a single-stage μ PCF,

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W.-C. Tian, H. K. L. Chan, and S. W. Pang are with the Engineering Research Center for Wireless Integrated Microsystems, Department of Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan 48109 USA (e-mail: pang@eecs.umich.edu).

C.-J. Lu is with the Engineering Research Center for Wireless Integrated Microsystems, Department of Environmental Health Sciences, The University of Michigan, Ann Arbor, Michigan 48109 USA.

E. T. Zellers is with the Engineering Research Center for Wireless Integrated Microsystems, Department of Environmental Health Sciences and Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109 USA.

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which was discussed previously [6]–[8]. These novel microheaters provide both large interstitial volume between heating elements for large adsorbent capacity and large heating surface for uniform heating of the adsorbents. To further enhance the performance obtained with our single stage μ PCF, we optimized the design and placed three different adsorbents in the microheater to form a high-efficiency multiple-stage μ PCF. The device design, including the adsorbent material and capacity, the microheater, and the microfluidic interconnection, will be discussed. The fabrication technology, the thermal measurements, and the desorption performances of the μ PCF will be presented.

II. DESIGN OF THREE-STAGE MICROFABRICATED PRECONCENTRATOR-FOCUSER

Microfabricated preconcentrator-focuser design involves the choice of adsorbent materials and capacity, microheater, and microfluidic layout. The choice of adsorbent materials for the desired flow rate, sampling time, and input concentration levels dictates the required adsorbent capacity of the device which, in turn, determines the μ PCF geometrical dimensions. The microheater was designed to provide large adsorbent capacity and uniform heating of adsorbents. Mass of the μ PCF and heat transfer between the gases and the μ PCF determine the microfluidic layout for the device.

A. Adsorbent Materials and Capacity

Instead of using one adsorbent material as in the single-stage μ PCF, three different adsorbent materials, Carbo-pack B, Carbo-pack X, and Carboxen 1000 (Supelco, Bellefonte, PA), are chosen in the three-stage μ PCF because each adsorbent has its specific surface area, pore morphology, and pore size distribution which enables it to handle compounds with a particular range of vapor pressures [9]. The 3 adsorbents have different surface area (100 m²/g for Carbo-pack B, 250 m²/g for Carbo-pack X, and 1200 m²/g for Carboxen 1000) and are used to trap compounds with different volatilities.

Adsorbents with large surface area are used to trap compounds with high volatility. These large surface area adsorbents are usually placed downstream in the sampling gas flow path so that the low volatility compounds will not be trapped in these adsorbents. The adsorbents and their masses are chosen based on the desorption peak width, chromatographic peak shape, and breakthrough volume [9]. Testing of the adsorbents considered in this study with a wide range of vapors has resulted in the following rough guidelines: compounds with vapor pressures in the range between 0.01 and 29 torr will be trapped by Carbo-pack B (100 m²/g) in the first stage, compounds with vapor pressures between 29 and 95 Torr will be trapped by Carbo-pack X (250 m²/g) in the second stage, and higher volatility compounds with vapor pressures between 95 to 231 Torr will be trapped by Carboxen 1000 (1200 m²/g) in the third stage. The gas flow path is reversed during thermal desorption to avoid trapping of the low volatility compounds in the adsorbents with large surface area.

The characterization of the adsorptive performance of these adsorbents has been performed by doing breakthrough measurements using a bench top GC system [9]. The derivation of the

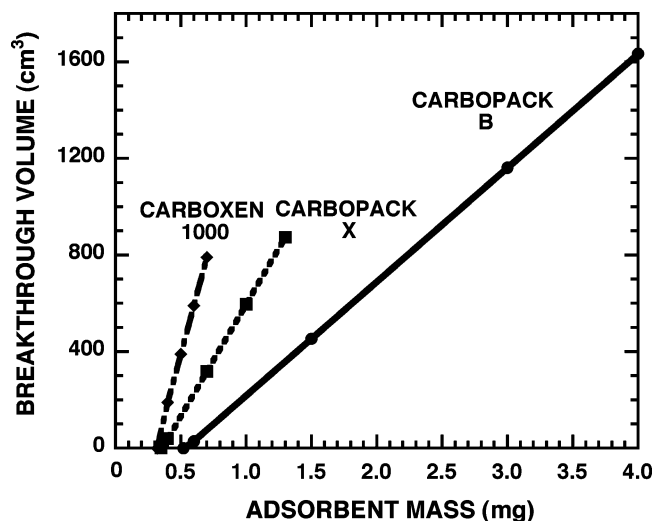


Fig. 1. The relationships between 10% breakthrough volume and adsorbent mass for the three adsorbents: Carbo-pack B, Carbo-pack X, and Carboxen 1000.

breakthrough time and breakthrough volume using the Wheeler model has been presented previously [8]–[10]. The Wheeler model provides a useful framework for assessing performance in terms of the relevant design and operating variables of the μ PCF: [11], [12]

$$t_b = \frac{\rho_b W_e}{C_0} \left[\tau - \frac{1}{k_v} \ln \left(\frac{C_0}{C_x} \right) \right] \quad (1)$$

where t_b is the time (min) required for breakthrough to occur, which is usually defined as when the ratio of outlet and inlet vapor concentrations (C_x/C_0) reaches 10%, ρ_b is the packed-bed density (g/cm³), W_e is the equilibrium saturation capacity defined as adsorbate mass per adsorbent mass (g/g), $\tau = W_b/(\rho_b Q)$ is the bed residence time (min), Q is the volumetric flow rate (cm³/min), W_b is the adsorbent mass (g), k_v is the kinetic rate constant (min⁻¹), C_0 is the inlet concentration (g/cm³), and C_x is the outlet concentration (g/cm³). The breakthrough volume in cm³ is then defined as

$$V_b = t_b \times Q \quad (2)$$

where V_b is the breakthrough volume and is a function of the adsorbent mass W_b .

The Wheeler model cannot be applied readily to mixtures of vapors where there is competition for adsorption sites. Therefore, adsorbent masses must be determined by experimental testing. Such testing was performed in [13] and the results were extrapolated to the anticipated sample volumes to be used in the current microsystem. Results for the three different types of adsorbent are plotted in Fig. 1. It indicates that for a 44-compound mixture concentration of 100 ppb and assuming a sampling flow rate of 25 cm³/min and sampling time of 10 min (sampling volume or minimum breakthrough volume of 250 cm³), the required carbon adsorbent mass is 1.10 mg of Carbo-pack B, 0.66 mg of Carbo-pack X, and 0.45 mg of Carboxen 1000 for a breakthrough volume of 250 cm³. To ensure that we are operating without any breakthrough, we can

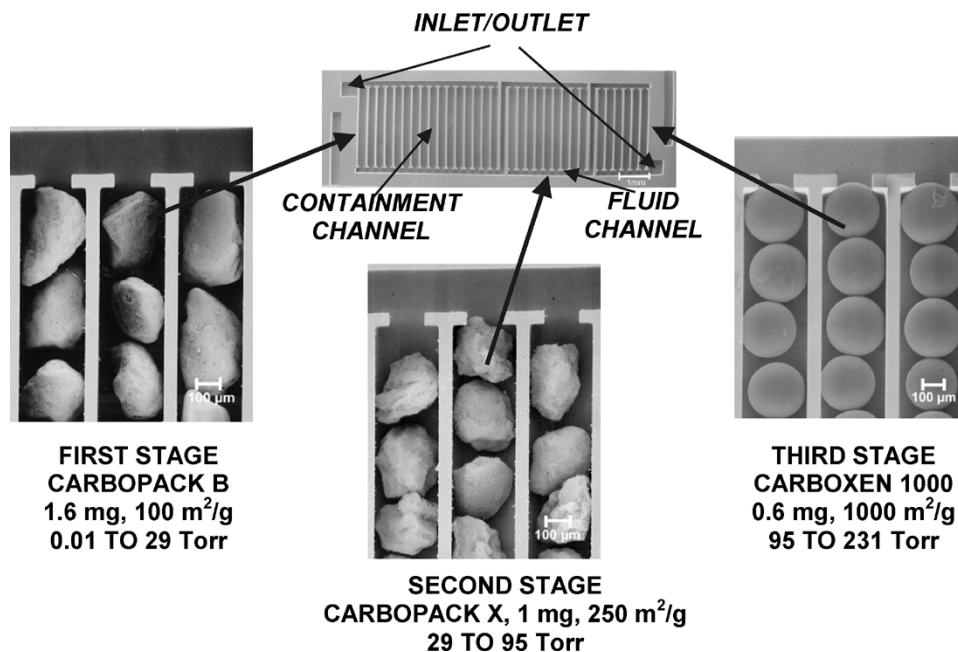


Fig. 2. Three-stage microfabricated preconcentrator-focuser using thick microheater (upper center) packed with three carbon adsorbents to cover a wide range of compound volatilities.

increase the adsorbent mass by 50% to 1.6, 1.0, and 0.6 mg for each of the three adsorbents.

B. Microheater Design

Due to the large adsorbent mass required to provide sufficient capacity for preconcentration of a complex vapor mixture at the concentration levels tested, thermal desorption with a thin-film microhotplate design is not appropriate. Instead, a thick, three-dimensional (3-D) microheater with large surface area for efficient thermal conduction of heat from a Joule heated membrane via tall slats to the carbon adsorbents is utilized. Our novel microheaters provide a large adsorbent capacity and uniform heating of adsorbent granules for the μ PCF. Two microheater designs have been explored: one employing a heavily doped membrane and the other a lightly doped membrane. Both designs have 50 μm thick Si membranes. Several experiments have been performed to demonstrate that the membrane-confined current path of the heavily doped design enables it to have more uniform heating.

The top view of our microheater is shown in the upper center of Fig. 2. The thick microheater structure consists of large surface area Si heating slats, fluid flow channels for low pressure drop and uniform gas flow, and containment channels for single rows of adsorbent granules. The heating slats are 380 μm tall, 50 μm wide, and 3000 μm long while the containment channels for the adsorbents are 220 μm wide and 3000 μm long. As shown in Fig. 2, the microheater is divided into three stages, one for each type of adsorbent. The size of each stage is dictated by the adsorbent mass of the particular adsorbent necessary for the given vapor pressure range of compounds. Sixteen adsorbent containment channels comprise the first stage with 1.6 mg of Carbo-pack B, while the second stage has nine channels with 1 mg of Carbo-pack X, and the third stage has six channels with 0.6 mg of

Carboxen 1000. These dimensions are designed to accommodate sufficient adsorbent capacity of each stage as predicted by the Wheeler model, which was described in the previous section. The packing density of the adsorbents may be varied but the slat height can be adjusted to meet the required adsorbent capacity.

Two-dimensional (2-D) ANSYS simulations have been performed to verify the microfluidic layout of the device with open channels for uniform fluid flow, absence of shorted flow paths, and low pressure drop [14]. A shorted flow path between the inlet and outlet means the air flows directly across the μ PCF without passing through all the flow channels, therefore preventing the complete trapping of compounds. As shown in Fig. 2 the slats have been designed with T-shaped ends to prevent adsorbents in the containment channels from blocking the fluid flow channels along the top and bottom of each stage. The utility of these fluid flow channels is to direct fluid flow into the parallel adsorbent channels which each have equal cross-section are giving the same pressure drop under ideal conditions. The 150 μm wide fluid flow channels between the μ PCF walls and the heating elements are used to reduce the pressure drop through the device. Furthermore, the inlet and outlet are in opposite corners to prevent shorted flow paths.

C. Microfluidic Interconnection

The main considerations for fluidic interconnection between the μ PCF cover plate and the fused silica capillary tubes are hermetic sealing ability, mechanical reliability, and low dead volume. A plasma etched, mechanically robust microfluidic adapter ring on the cover plate of the PCF was designed and fabricated for the fused silica capillary tubes [15], [16]. This design provides the advantages of being leak-proof upon application of polyimide as a sealant, giving mechanical strength to

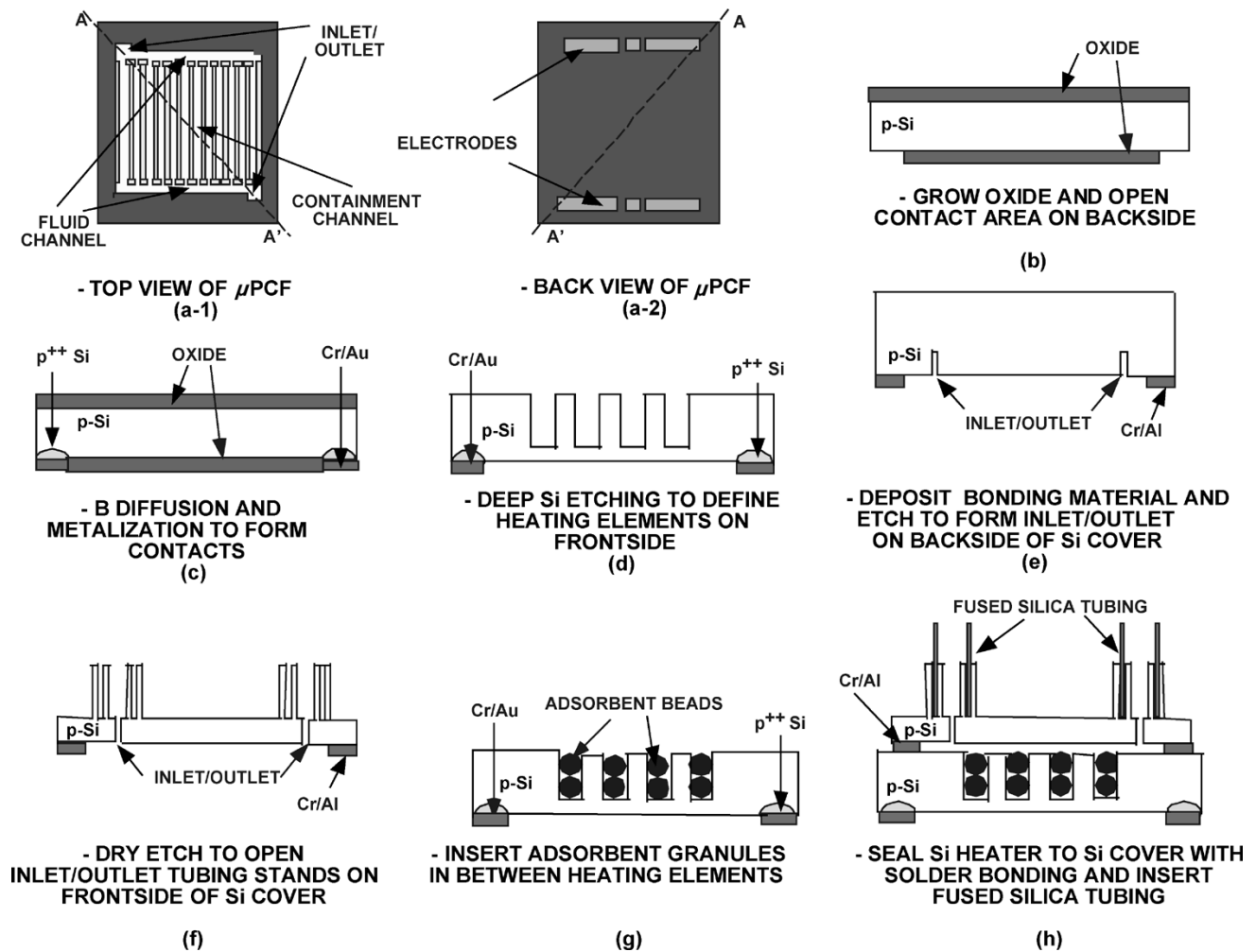


Fig. 3. Schematics for fabrication of the sealed preconcentrator-focuser.

the tubing and cover plate interface, and preventing clogging of the inlet or outlet by polyimide.

III. FABRICATION TECHNOLOGY OF THREE-STAGE PRECONCENTRATOR-FOCUSER

The μ PCF consists of a thick Si microheater for adsorbent loading and a Si cover plate for fluidic interconnection to the other components of the μ GC. In order to fabricate the thick microheater and the cover plate, deep reactive ion etching was developed to provide vertical sidewall and smooth morphology of these two components. After the carbon adsorbent granules were loaded into the microheater, the cover plate was solder bonded using Al to the microheater to seal the structure. Double-side polished p-type $\langle 100 \rangle$ Si wafers of 100 mm diameter and 475 μm thickness were used as the starting substrate for both the microheater and the cover plate.

A. Deep Reactive Ion Etching

The Bosch dry etching process has been used to ensure fast Si etch rate, smooth morphology, and vertical profile [17], [18]. In this work, the dry etching conditions were optimized to reduce the bowing effect while preserving the etch rate for the deep trenches. Bowing is the erosion of the sidewall passivation

layer due to ion bombardment along the sidewalls and lower ion flux at the bottom edges of the trenches [19]. The resulting optimized etch conditions call for stage power reduction as a function of etch time to reduce the effect of the etch cycle as the etch progresses and the depth increases. This reduces the energy of the ions impacting the sidewalls and provides a vertical etch profile for deep trenches.

The optimized dry etch conditions are: an etch cycle time of 13 s, source power of 800 W, stage power of 12 W, pressure of 25 mTorr, and a SF_6 flow rate of 85 sccm. The stage power is ramped down at a rate of -0.1 W/min. The passivation cycle duration is 7 s, and uses 600 W of source power with no stage power, pressure of 15 mTorr, and a C_4F_8 flow rate of 85 sccm. These optimized etch and passivation cycles were applied to fabricate both the Si microheater and the cover plate. For 380 μm deep Si trenches, the average Si etch rate was 2.5 $\mu\text{m}/\text{min}$ while the photoresist mask etch rate was 13 nm/min.

B. Microheater

The microheater fabrication is a four-mask double-sided process and the major process steps are shown in Fig. 3(a) to (d). Fig 3(a-1) and (a-2) show the top and back view of the microheater. Cross section of AA' direction is chosen to describe this double-sided process. First, a 2- μm -thick thermal

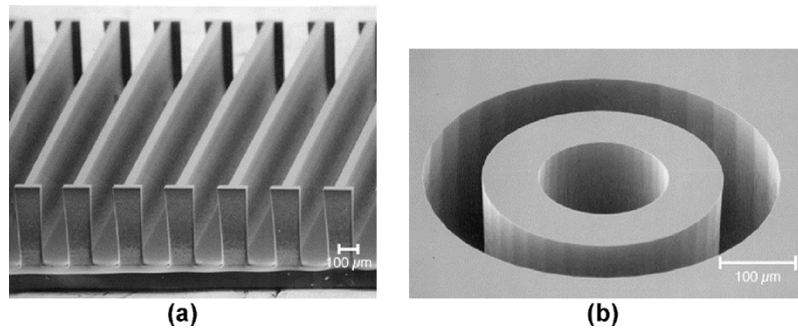


Fig. 4. (a) Thick Si microheater with large heating surface. The widths of the containment channels at the ends are reduced to confine the adsorbents inside the channels. (b) Leak-proof inlet/outlet fluidic adapter ring on the cover plate. The fused silica tubing is inserted into the ring for fluidic interconnection.

oxide was grown at 1100°C for 10 h and patterned for use as a doping mask. Then deep boron diffusion (pre-deposition for 5 h, constant source diffusion, and drive-in for 5 h) for a junction depth of $10\ \mu\text{m}$ was performed for ohmic contact (for the heavily doped design, the junction depth also determines the volume through which there is Joule heating). The backside processing was completed with the evaporation of a 20 nm Cr adhesion layer followed by 200 nm of Au to form the ohmic contacts. On the frontside of the substrate, as shown in Fig. 3(d), the $380\text{-}\mu\text{m}$ -thick and $50\text{-}\mu\text{m}$ -wide heating slats, and $220\text{-}\mu\text{m}$ -wide channels for the carbon adsorbents were etched using the optimized etching described in the previous section. The fabricated thick microheater with tall heating slats is shown in Fig. 4(a). The width of the Si slats at the two ends was increased from 50 to $120\ \mu\text{m}$, forming a T-shape end, to confine the adsorbent inside the containment channels.

C. Cover Plate

The same optimized etch conditions described above were used to fabricate the Si cover plate. Figs. 3(e) to (f) show the three-mask process for the cover plate. On the backside of the cover plate substrate, a $0.2/3\text{-}\mu\text{m}$ -thick layer of Cr/Al was evaporated and patterned to form the solder bonding rings. Following the previous solder evaporation, a dry etch was performed on the backside to define the inlet and outlet to the device. Finally, on the frontside a dry etch was done to reduce the thermal mass, open the inlet and outlet, and form the inlet and outlet fluidic adapter rings, as shown in Fig. 3(f). The fabricated inlet and outlet fluidic adapter rings for the fused silica capillary tubes are shown in Fig. 4(b). These adapter rings enhance the mechanical support of the capillary tubing and make the fluidic interconnects more reliable.

D. Microfabricated Preconcentrator-Focuser

Following the plasma etching to define the microheaters, the three types of carbon adsorbents were loaded into their respective sections of the microheater, as shown in Fig. 3(g). When loading a given adsorbent, a Si stencil plate with dry etched openings was used to cover the other two stages of the μPCF to prevent contamination or adsorbent mixing in the other parts of the μPCF . Significant mixing of the adsorbents into other sections will broaden desorption peaks and degrade the performance of the μPCF .

Bonding of the Si cover plate to the adsorbent loaded microheaters (Fig. 3(h)) was done in a rapid-thermal annealing chamber at 800°C for 3 min using Ar as the purge gas due to its inertness to the carbon adsorbents [20]. Passivated fused silica capillary tubing with an inner diameter of $320\ \mu\text{m}$ and an outer diameter of $430\ \mu\text{m}$ were inserted into the inlet and outlet fluidic adapter rings and sealed with polyimide. For electrical connections, the Cr/Au contact pads on the backside of the preconcentrator were Al wirebonded to a printed circuit board.

IV. THERMAL MEASUREMENTS OF MICROHEATERS

Both the steady state and transient thermal response of the microheaters are important for the overall desorption performance of the μPCF . A fast and uniform heating of the microheater is necessary for simultaneous desorption of compounds from the three types of adsorbent contained in the channels. Prior tests indicated that a temperature from 250 to 300°C would be sufficient for complete desorption. From the transient thermal response, we characterize the heating rate of the device for a given applied electrical power and this dictates the minimum heating time during desorption.

A. Steady-State Response

The temperatures of the unloaded heavily doped and lightly doped microheaters were imaged by using a commercial infrared (IR) camera (FLIR Systems, Portland, OR). For both designs, electrical power was applied to the device in increments of 300 mW and the IR image was recorded after the microheater reached its steady state temperature. Fig. 5(a) shows an IR image of the lightly doped microheater. The temperature variation of the device is within 15% and the average temperature is 261°C when the input electrical power is 1.5 W. For the heavily doped microheater, the temperature variation is within 5% and the average temperature is 269°C at input power of 1.5 W.

This more uniform heating was shown with heavily doped membrane because the current flow and heating are confined to the surface of the membrane as defined by the doped junction depth of $10\ \mu\text{m}$. From this heated membrane the Si slats conduct the heat away from the membrane to the adsorbents. For the microheater with lightly doped membrane, in addition to the membrane, current flows through the walls bounding the adsorbent containment area. This results in a less uniform heating of the microheater area than the heavily doped membrane design.

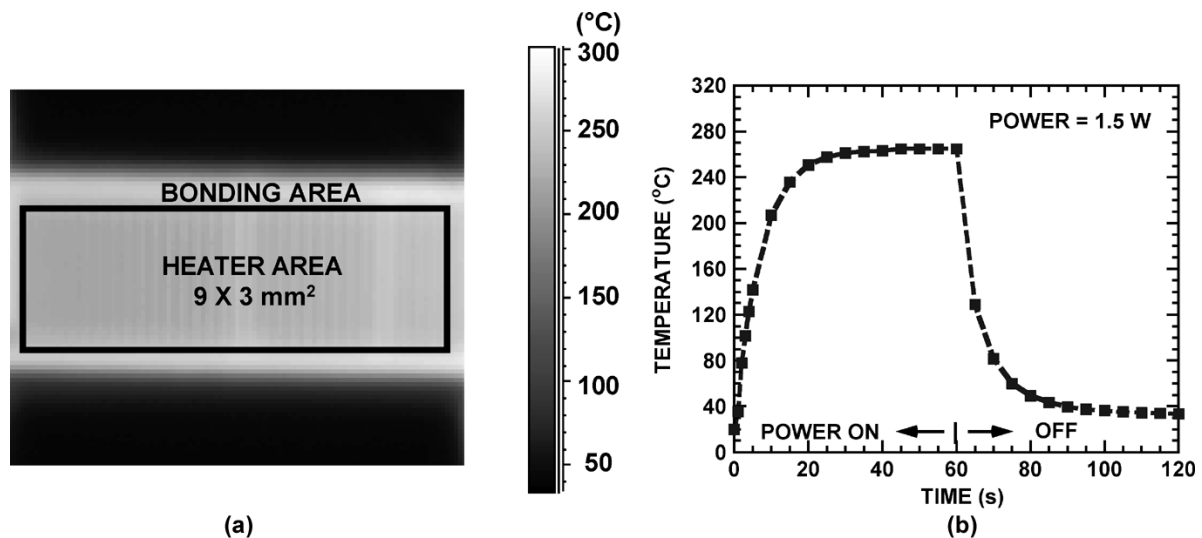


Fig. 5. (a) Thermal image of the lightly doped microheater using a commercial infrared camera. (b) Transient thermal response of the heavily doped microheater.

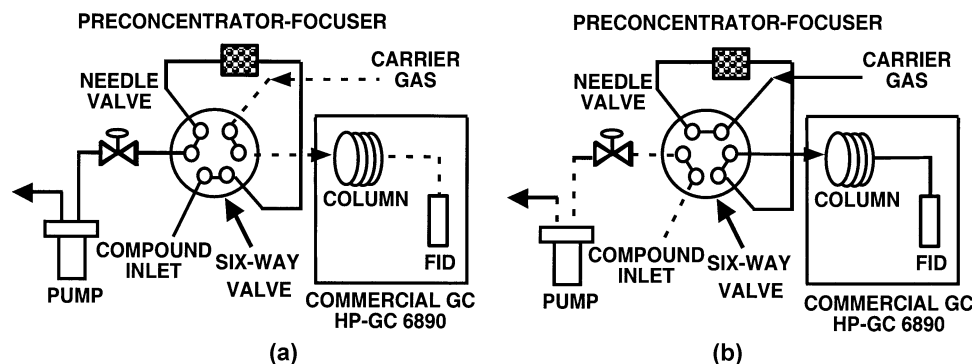


Fig. 6. Measurement setup for (a) compound sampling and (b) thermal desorption.

B. Transient Thermal Response

The transient thermal responses measured with the IR camera for the heavily doped microheater are shown in Fig. 5(b). The heating rate of the heavily doped microheater obtained from the slope of the transient is $12.1\text{ }^{\circ}\text{C/s}$ with an applied power of 1.5 W . The heating rate is determined by the thermal mass of the device, the applied electrical power, and thermal isolation of the device. For the transient shown in Fig. 5(b), the minimum power required to reach a steady state temperature of $250\text{ }^{\circ}\text{C}$ was applied for 1 min and then monitored for an additional minute after the power was turned off.

Faster heating rates can be achieved by applying an initially higher power to ramp up the temperature and then reducing the power to maintain the steady-state temperature at $250\text{ }^{\circ}\text{C}$, which is chosen as the temperature for desorption. This application of higher power during temperature ramp up and lower power for steady-state temperature maintenance naturally occurs for the case of the lightly doped microheater when a constant current is maintained through the device in these two operating regimes. As the device is heated, its resistance first increases due to the decrease in carrier mobility with temperature. The Si carrier mobility decreases because the lattice scattering increases with temperature in lightly doped Si microheater. However, when the temperature exceeds $200\text{ }^{\circ}\text{C}$, the significant increase of intrinsic carrier concentration with temperature starts to dominate and thus decreases the device resistance [21], [22].

TABLE I
COMPARISONS OF SINGLE-STAGE AND THREE-STAGE MICROFABRICATED PRECONCENTRATOR-FOCUSER

Type of μPCF	1 Stage	3 Stage
Heater Mass/Stage (mg)	28.6	10.1
Temperature Uniformity (%)	>95	>95
Heating Rate ($^{\circ}\text{C/s}$)	18	100
Power/Stage (W)	2.1	0.8
Dead Volume/Stage (μl)	8.16	2.62
Pressure Drop/Stage (KPa)	13.80	2.11
Peak Width at Half Height (s)	0.80	0.44
Preconcentration Factor	5600	>5600

The resistance of the lightly doped ($\sim 10^{16}\text{ cm}^{-3}$) microheater during temperature ramp up is greater than its resistance at $250\text{ }^{\circ}\text{C}$ because the intrinsic carrier concentration exceeds the background doping concentration. Thus, by keeping the applied current the same throughout the ramping and steady-state operating regimes, the applied power is initially larger for ramping when the resistance is higher and then the power becomes smaller due to the lower resistance at higher temperature. For a lightly doped microheater with a minimum power of 1.5 W for steady state and a current of 73.6 mA , the heating rate is $35.4\text{ }^{\circ}\text{C/s}$ and the time needed for heating the microheater to $250\text{ }^{\circ}\text{C}$ is 6.5 s .

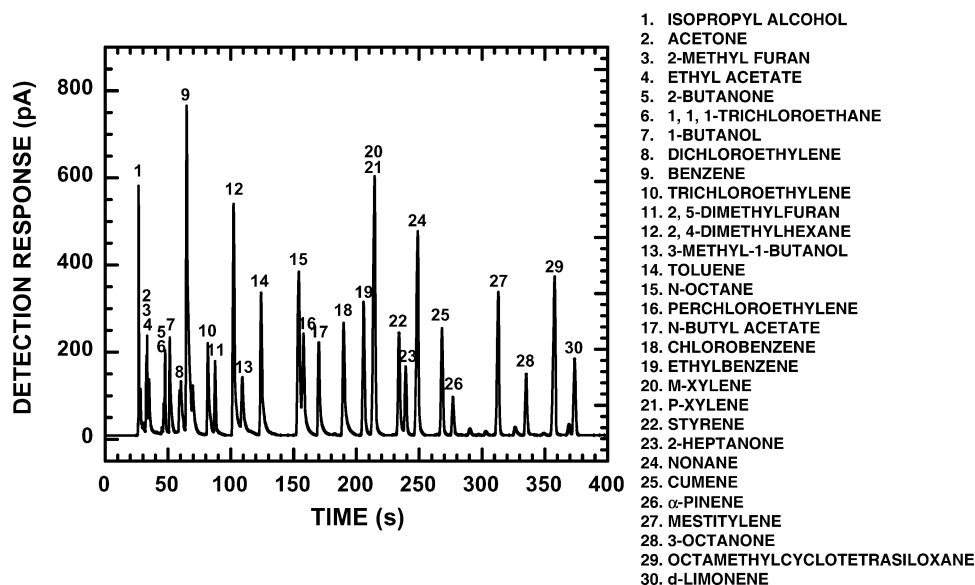


Fig. 7. A chromatogram showing successful separation of 30 organic vapors using three-stage microfabricated preconcentrator-focuser with a conventional gas chromatography system.

V. DESORPTION PERFORMANCE

Figs. 6(a) and (b) show the setup used to measure the desorption performance of the μ PCF. The μ PCF is connected to a six-port valve to switch between sampling the 30-compound mixture and desorption to a commercial gas chromatography system with a flame-ionization detector (FID). The 30-compound mixture for sampling is prepared by injecting liquid compounds into a Tedlar bag with pre-filled known volume of clean and dry air.

A. Experimental Description

The operation of the μ PCF consisted of adsorbing analytes in the μ PCF followed by stop-flow for heating the microheater and then desorption of compounds into the commercial GC system. As shown in Fig. 6(a), 0.25 cm³ of the 100 parts per million (ppm) compound mixture was injected by gas-tight syringe into the inlet. The compound mixture was carried through the PCF by an air flow of 25 cm³/min for 10 min, drawing a total volume of 250 cm³. This corresponds to a sampled mass-equivalent of 100 ppb for each compound at the sampling volume of 250 cm³. After sampling, the flow was stopped (stop-flow condition) for 20 s while the electrical power was supplied to the device to reach the desorption temperature (typically 250 to 300 °C). We have demonstrated that the stop-flow condition facilitates sharper peak widths for certain compounds [8]. Once we resumed the carrier flow, an additional 20 s was needed to desorb compounds completely. Fig. 6(b) shows the resulting chromatogram. This helium carrier gas was in the reverse direction (from sampling) through the device to flow the desorbed compounds into the GC for detection. In the multiple-stage μ PCF, the flow reversal from sampling to desorption cycles, or backflushing, is necessary to prevent lower volatility compounds from re-adsorbing into the Carboxen 1000.

B. Performance of Microfabricated Preconcentrator-Focuser

Better performance was obtained using the three-stage μ PCF than with its single-stage μ PCF predecessor (see [8]) as shown in Table I. For the thermal measurements of the two devices, IR imaging showed good temperature uniformity across both devices and the variation was within 5%. The heating rate of the single-stage μ PCF was 18 °C/s and the power required for desorption at 300 °C was 2.1 W. Compared to the single-stage μ PCF, the heating rate and power consumption of the three-stage μ PCF were 100 °C/s and 0.8 W per stage at a desorption temperature of 250 °C. These substantial improvements were achieved by lifting the three-stage μ PCF to reduce the conductive heat loss to the underlying package substrate. Moreover, the thermal masses of the heater and cover plate were reduced from 28.6 to 10.1 mg per stage in the three-stage design and this also improved the heating efficiency.

Through proper design of the μ PCF to eliminate the non-functional empty space inside the device, the dead volume for the three-stage μ PCF was reduced from 8.16 to 2.62 μ l/stage. For the characterizations of these two μ PCFs, pressure drop and desorption peak measurements were performed. As shown in Table I, the pressure drop of the three-stage μ PCF is \sim 7X lower than that of the single-stage μ PCF. The significant lower pressure drop in the three-stage device was obtained by properly arranging the fluid channels between the μ PCF walls and the heating elements inside the device. In addition, the peak width at half height (PWHH) of the desorbed compounds was improved significantly in the three-stage μ PCF. The minimum peak width of 0.8 s is obtained using Benzene in single-stage μ PCF while the peak width of 0.44 s is obtained using Isopropyl Alcohol in a three-stage μ PCF. The preconcentration factor of the three-stage μ PCF cannot be determined at present due to the breakthrough of high volatility compounds resulting from uneven packing of adsorbents in the channels. Our future work includes the investigation of μ PCF designs that will provide more uniformity adsorbent packing to avoid the breakthrough problem.

TABLE II
DESORPTION PEAK WIDTHS OF 30 COMPOUNDS

Organic Compound	Vapor Pressure (Torr)	PWHH (s)	Organic Compound	Vapor Pressure (Torr)	PWHH (s)
Isopropyl Alcohol	43	0.44	Perchloroethylene	18.5	1.91
Acetone	231	0.61	n-Butyl Acetate	12	1.78
2-Methyl Furan	200	0.75	Chlorobenzene	11.8	2.03
Ethyl Acetate	95	0.78	Ethylbenzene	10	1.73
2-Butanone	91	0.69	m-Xylene	8	1.75
1, 1, 1-Trichloroethane	124	0.67	p-Xylene	9	1.75
1-Butanol	91	0.96	Styrene	6	1.73
Dichloroethylene	88	1.12	2-Heptanone	3.9	1.62
Benzene	95	1.49	Nonane	4.3	1.88
Trichloroethylene	47	1.43	Cumene	3.5	1.76
2, 5-Dimethylfuran	66	1.03	α -Pinene	5	1.82
2, 4-Dimethylhexane	35	1.62	Mesitylene	2.5	1.73
3-Methyl-1-Butanol	2.4	1.66	3-Octanone	1.3	1.66
Toluene	28.5	1.70	Octamethylcyclotetrasiloxane	3	1.90
n-Octane	14	1.78	d-Limonene	3	1.79

C. Chromatogram Measurements

In the single-stage μ PCF, 10 different common organic compounds were well separated and desorption peak widths were very narrow (0.8 to 2 s), as presented in [23]. The extension of volatility range is demonstrated by the composite of four chromatograms showing the desorption of 30 organic compounds by the three-stage μ PCF as shown in Fig. 7. The 10 compounds tested for the single-stage prototype are also included in the 30 compound samples. The 30 compounds are separated into four groups for sampling/desorption in order to avoid co-elution of compounds on the chromatogram. The most volatile compound desorbed is acetone with a vapor pressure of 231 torr while the lowest volatility compound is 3-octanone with a vapor pressure of 1.3 torr. A desorption flow rate of 2 cm³/min was used, which is the desired flow rate based on the system requirements of the micromachined GC column. The total heating time was 40 s with 20 s for stop-flow and 20 s for carrier gas flow. The power required to achieve 300 °C with carrier gas flow was 0.8 W/stage. In order to get a fast and high resolution compound separation, the operating temperature of the GC column was optimized. The initial and final temperatures of the column were 25 and 90 °C with a temperature ramp rate of 10°C/min. As shown in Fig. 7, the total separation time for 30 compounds was within 400 s. The PWHHs for all of the compounds were <2.05 s at a flow rate of 2 cm³/min, as shown in Table II.

Higher volatility compounds such as acetone and isopropyl alcohol elute rapidly through the GC column. Thus, their peak widths largely depend on the desorption efficiency of the μ PCF. As can be seen in Table II, peak widths of early eluting compounds are <1 s which indicate the sufficient desorption and heating performance of this newly designed μ PCF. Low-volatility compounds such as 3-octanone and d-limonene desorb relatively slowly from the μ PCF, but they are refocused on the column at initial stage of separation while the column is cold. The low volatility compounds are retained strongly on the GC column and as the column temperature rises gradually, they elute as sharp peaks. All of these low-volatility compounds have similar peak widths of 1.62 to 1.90 s.

In order to study the desorption efficiency, the same measurement is performed without reloading the compounds into the

μ PCF and GC after obtaining the 30-compound chromatogram. No desorption peaks are observed on the chromatogram and thus 100% desorption efficiency is demonstrated.

VI. CONCLUSION

A high efficiency three-stage μ PCF with large adsorbent capacity and uniform heating of adsorbents for quantitative analysis of a wide volatility range of complex organic mixtures for a μ GC was presented. Optimized etching conditions were developed to fabricate the thick microheater and the cover plate for the μ PCF. Microheaters with different designs were investigated to compare the heating efficiency. Our three-stage device is designed to extend the detection range of the compounds to cover up to 4 orders of magnitude in volatility, from 0.04 to 231 torr. In addition, the dead volume (from 8.16 to 2.62 μ l/stage), thermal mass (from 28.6 to 10.1 mg/stage), heating rate (from 18 to 100°C/s), and pressure drop (from 13.80 to 2.11 KPa/stage) of the single-stage μ PCF were improved significantly in the three-stage μ PCF and thus the device performance was improved substantially. Thirty organic compounds have been separated successfully with small PWHHs (0.44 to 2.05 s) using our three-stage μ PCF in a commercial GC system. Further improvements include design optimization and thermal isolation of the μ PCF to increase the separation and power efficiency of the μ GC system.

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Wei-Cheng Tian (M'00) was born in Taipei, Taiwan, R.O.C., in 1973. He received the B.S. degree in electrical engineering from National Taiwan University (NTU) in 1995 and the M.S. and Ph.D. degrees in electrical engineering and computer science from the University of Michigan, Ann Arbor, in 2000 and 2003, respectively.

At University of Michigan, his research focused in the advanced MEMS technology development, dry micromachining technologies of high aspect ratio micro/nanostructures, microsystem prototype development, and microfabricated preconcentrator/focuser in micro gas chromatograph. In 2001, he received a distinguished achievement award for graduate student in the College of Engineering. He joined General Electric Global Research Center, Niskayuna, NY, in 2003 to work on capacitive micromachined ultrasound transducers, humidity/gas sensors, and novel micro/nanofabrication integration technologies development. In 2004, he is awarded GE company certification as a green belt in the Six Sigma quality management program. He has 12 publications in journal/conference proceedings and seven patents pending. His research interests include micro/nanofabrication technologies and design for MEMS/transducers.

Dr. Tian is a Member of the American Vacuum Society.



Helena K. L. Chan (S'97) received the B.Sc. degree in electrical engineering and computer sciences from the University of California, Berkeley, in 2000 and the M.Sc. degree in electrical engineering from The University of Michigan, Ann Arbor in 2001. She is currently working toward the Ph.D. degree in electrical engineering at The University of Michigan.

During her undergraduate career, she interned at Motorola, Austin, TX, where she developed an analog circuit design handbook for SOI technology, and investigated power handling and electromigration problems in standard cells for the M³CORE microcontroller. At the Berkeley Sensor and Actuator Center (BSAC), she researched flip-chip bonded RF MEMS batch transfer microrelays.

Ms. Chan is the recipient of the 2004 Distinguished Leadership Award given by The University of Michigan College of Engineering, and the 1996 Olin E. Teague Memorial Scholarship awarded by the National Space Club, Washington, D.C. She served as the President of the IEEE Student Branch at the University of California, Berkeley from 1997–98.



Chia-Jung Lu received the B.S. degree in chemistry from Fu-Jen Catholic University, R.O.C., in 1991 and the M.S. degree in analytical chemistry from National Taiwan Normal University, R.O.C., in 1993. He recently received the Ph.D. degree from the Department of Environmental Health Sciences, working with Dr. Zellers on a portable GC for indoor air quality applications that employs tunable separation methods in conjunction with surface-acoustic-wave sensor array detection as his dissertation.

From 1993 to 1994, he was an Associate Researcher at Material Research Labs in the Industrial Technology Research Institute (ITRI), Taiwan, where he worked to develop impedance-type polymer humidity sensors. From 1994 to 1997, he worked for the Center of Industrial Safety and Health Technology within ITRI and focused on vapor sampling methods, remote sensing Fourier Transform Infrared Spectroscopy, and gas monitor evaluations. From 1997 to 1998, he worked at the Energy and Resource Labs in ITRI on miniaturized oxygen sensors. He is currently an Assistant Professor in the Department of Chemistry, Fu-Jen Catholic University.



Stella W. Pang (S'81–M'82–SM'91–F'99) received the Sc.B. degree in electrical engineering and computer science from Brown University, Providence, RI, in 1977 and the M.Sc. and Ph.D. degrees in electrical engineering and computer science from Princeton University, Princeton, NJ, in 1978 and 1981, respectively.

From 1981 to 1989, she was with Lincoln Laboratory at the Massachusetts Institute of Technology (MIT), Cambridge, and in 1990, she joined the University of Michigan, Ann Arbor. Currently, she is a

Professor in electrical engineering and computer science and the Associate Dean for graduate education in the college of engineering. Her research interests include nanofabrication technology for microelectromechanical, microelectronic, and optical devices. She has over 300 technical papers, book chapters, and presentations and is the editor and author of 16 books, journals, and conference proceedings.

Dr. Pang has served as conference organizer for the American Vacuum Society (AVS), Electrochemical Society (ECS), Electronic Materials Conference, Institute of Electrical and Electronics Engineers (IEEE), International Symposium on Electron, Ion, and Photon Beam Technology and Nanofabrication, Material Research Society, and SPIE. She has taught 20 short courses on microfabrication technology for microelectronic manufacturing and microelectromechanical systems. She is a Fellow of the ECS and AVS.



Edward T. Zellers received the B.A. degree in chemistry from Rutgers University, New Brunswick, NJ, in 1978 and the M.S. and Ph.D. degrees in environmental health sciences from the University of California, Berkeley, in 1984 and 1987, respectively.

From 1978 to 1981, he worked at Bell Laboratories, Murray Hill, NJ, on the synthesis and characterization of electrically conductive organic materials. He joined the faculty at the University of Michigan, Ann Arbor, in 1987 and is currently a Professor in the Department of Environmental Health Sciences and the Department of Chemistry. He is Director of the Occupational Health Program in the Department of Environmental Health Sciences and is Group Leader of the Environmental Sensors and Subsystems Thrust within the Michigan Engineering Research Center for Wireless Integrated Microsystems. He has been involved in research on microfabricated chemical sensors, sensor arrays, and miniaturized instrumentation for over 20 years.