Zebra GC: A Fully Integrated Micro Gas Chromatography System

Apoorva Garg[1], Muhammad Akbar[1], Shree Narayanan[1], Leyla Nazhandali[2], and Masoud Agah[1]
[1]VT MEMS Laboratory, [2]SEPAC Laboratory, Virginia Tech, Blacksburg, USA
Email: {agarg88, makbar, snsnair, leyla, agah} @vt.edu

***Abstract*—This paper reports the development of a fully controllable micro gas chromatography (µGC) system. The system, named Zebra GC, uses a microfabricated preconcentrator (µPC) for sample collection, a microfabricated separation column with an on-chip thermal conductivity detector (µSC-TCD) for analyte separation and detection, a flow controller unit, flow and thermal management units, and user interface unit. The system has an internal flow manipulation scheme which yields sharp analyte injection from µPC to µSC-TCD with widths as narrow as 0.36 s and significantly suppresses flow variations observed by the µTCD resulting in the generation of stable chromatograms. All microfabricated components have their own on-chip heaters and sensors enabling low-power high-speed temperature control during desorption and separation phases. The performance of this ready-to-deploy Zebra GC system has been demonstrated through the analysis of a gas mixture containing aromatic volatile organic compounds (VOCs).**

I. INTRODUCTION

Hazardous air pollutants, such as aromatic volatile organic compounds (VOCs), are known to have serious environmental and health effects. Exposure to these toxicants may cause adverse health effects [1]. Most of these pollutants emerge from man-made sources and activities including emissions from automobile, refineries, factories, and power plants. To safeguard the health of exposed individuals and to ensure that the concentrations of these VOCs do not exceed the permissible exposure levels set through federal regulations, it is critical to monitor exposure to these compounds.

Among various analytical methods, gas chromatography (GC) has been the established method for assessing the presence and concentration of VOCs in the environment, and GC coupled to mass spectrometer (GC-MS) is one of the most prevalent tool. Such practices typically require collection of a sample in the field using a canister or sorbent tube, transport to the lab, and then perform analysis using conventional GC equipment. These techniques are labor-intensive, costly, and do not provide real-time information about the environment while suffering from the possibility of sample contamination or degradation during transport. There have been attempts at miniaturizing GC-MS systems [2], but such systems are still bulky, expensive, and consume high amount of power.

A versatile solution for detection of VOCs is based on portable gas chromatography systems leveraging micro-fabricated components to achieve a small form factor, less power consumption and reduced cost. The current trend in µGC is more directed towards the development of novel components enabled by microelectromechanical systems (MEMS) fabrication processes and nanotechnology including preconcentrators (µPC) [3, 4], separation columns (µSC) [5, 6], and gas detectors [7]. Integration of the various components into a workable system [8] is a critical yet underexplored aspect.

In this work, we present an innovative µGC architecture, which leverages monolithic integration of a separation column with micro-thermal conductivity detectors (µSC-TCD) [9] to minimize band broadening and chip-to-chip fluidic interfaces. The integration reduces the formation of cold spots by minimizing transfer lines. Another innovative aspect of this architecture is a method to perform very sharp injections from the µPC even in the presence of flow-sensitive gas detectors like TCD. This innovative system design relaxes constraints on the design of the µPCs by mitigating the effect of vapor desorption on the injection-plug width. The design enables us to achieve low detection limits suitable for environmental monitoring applications. We report in this article the system design, prototypal implementation, operation, and analytical performance of the proposed µGC system, dubbed Zebra GC.

II. SYSTEM ARCHITECTURE

A. Microfabricated components

The fabrication process of the µPC and µSC-TCD has been described in our previous publications [9-11] in details. The µPC is a 13 mm×13 mm silicon-glass chip and consists of an array of high aspect ratio micro-posts inside its 1 cm square cavity. The micro-posts are realized by bulk micromachining of a 4 inch silicon wafer utilizing a deep reactive ion etching process to achieve a depth of 240 µm, followed by dicing of wafer into individual chips. A 1-µm thick plasma enhanced chemical vapor deposition (PECVD) oxide layer that acts as an insulator is deposited on the backside. The micro-posts are coated with a thin film (~200 nm) layer of Tenax TA adsorbent and capped with a Borofloat wafer via anodic bonding. A 40 nm/230 nm of Cr/Ni stack is deposited which serves as a heater and temperature sensor on the backside of the chip using an e-beam evaporator (PVD-250, Kurt Lesker). The nominal resistance of the heater and sensor is around 15 Ω and 250 Ω, respectively. Finally, fused capillary tubes are inserted and epoxied to the inlet/outlet ports.

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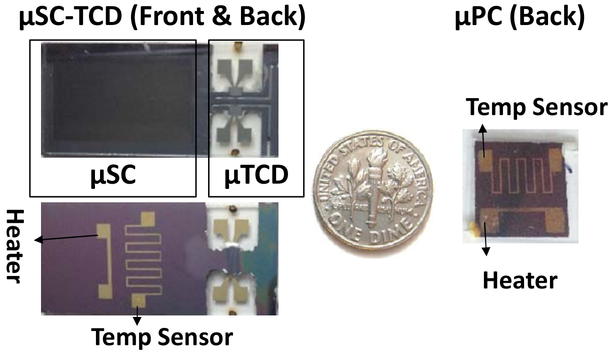

Figure 1: Optical images of microfabricated components

For the µSC-TCD, two-step anisotropic etching of silicon is performed. First, a shallow depth of 2–3 µm is achieved which prevents the contact between the metal interconnects on the Borofloat wafer and the walls of the separation column in silicon upon bonding. Second, a 2 m long, 70 µm wide and 240 µm deep channel is etched into silicon wafer. TCD resistors are fabricated on a glass substrate using a lift-off process for a 40 nm/100 nm/25 nm Cr/Ni/Au stack deposited employing the e-beam evaporator. The glass and silicon substrates are then aligned and bonded together. The heaters and temperature sensors are fabricated on the backside of the chip using stainless steel shadow mask. Afterwards, the capillary tubes are epoxied into the inlet/outlet ports. The chip is finally coated with a thin layer (~250 nm) of polydimethylsiloxane (PDMS or OV-1) on the walls of the column channel. Optical images of chips are shown in Fig. 1.

B. *Integrated electronic module*

The microfabricated components, integrated with the pump (Parker Hannifin Co.), multi-way valves (The Lee Co.), and a portable helium cylinder, are controlled through an integrated electronic module managed by an 8-bit micro-controller (ATmega640, Atmel Corporation). Magnetic latching solenoid valves are selected to optimize power consumption and controlled by applying a 5 V DC pulse through an H-Bridge. The pump flow rate is adjusted by varying the pulse-width modulation (PWM) duty cycle, which is an important parameter during sample collection. The on-chip temperature sensor is connected in a 3-wire resistance temperature detector (RTD) configuration by using two well-matched current sources with a high precision 24-bit ADC. The reference voltage for the ADC is also generated using these matched current sources, through a precision resistor and applied to the differential reference pins of the ADC. This scheme ensures that the span of the analog input voltage remains ratio-metric to the reference voltage and any error in the former due to temperature drift of the excitation current is compensated by the variation of the latter. On chip heaters are controlled through PWM channels and a digital proportional control system is implemented as part of the embedded firmware, which generates different profiles for temperature reference signal based on the user input (initial temperature, step, ramp, final temperature).

The µTCD is connected in a Wheatstone bridge, driven by 7.5 V DC, with low noise thin film resistors (PF1260 series, Riedon Inc). The differential signal is conditioned and filtered prior to feeding into an ultra-low noise 24bit ADC (AD7793, Analog Devices). The signal is further filtered digitally, using an on-chip low pass modified Sinc3 filter that also provides 60 Hz rejection. The TCD, along with the entire system, is operated at a data rate of 10 Hz, which provides substantial resolution for the peaks. Fig. 2 shows the implementation of integrated electronic module on a double sided printed circuit board.

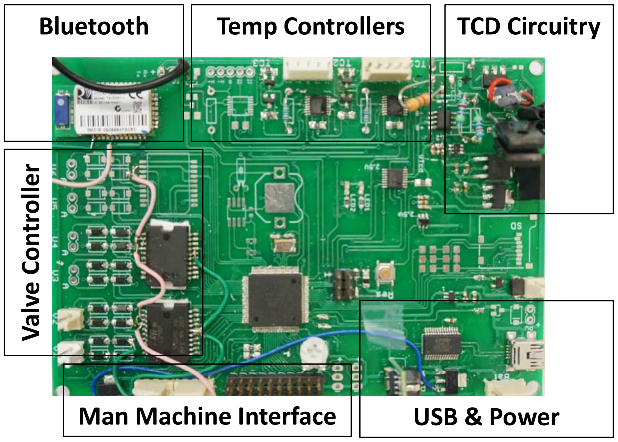

Figure 2: Integrated electronic module realized on a 2-layer printed circuit board.

C. *Integration and operation*

Microfabricated components along with the flow controllers, integrated electronic module, and user interface circuitry are assembled in a 12”×6”×4” box, schematically shown in Fig. 3. The box also houses a lithium ion battery (2200 mAh) pack and a small helium cylinder (95 mL, 2700 psi) to make Zebra GC highly portable (~4 lbs). The system can be operated in a manual or automatic mode using the LCD/Keypad based human-machine interface, which has a menu driven system. Once the mode is selected, the screen shows the state of the system in terms of valve positions, temperature readings, pump duty cycle, and sensor value. Sensor data can be visualized and recorded in the Labview application, which receives data packets through USB or Bluetooth interface.

Zebra GC implements the following automated stages: loading, injection, analysis, and cleaning. In loading stage, the µPC is loaded with VOCs present in the air sample by the mini diaphragm pump. Once sufficient sample is loaded in the µPC, the valves are switched to flow helium through the bypass path into the µSC-TCD. In order to ensure a sharp injection plug, the µPC is heated first at a rate of 25 °C/s to 200 °C without flow, and then the valve is switched to inject analytes into the µSC-TCD. This stage typically lasts 10-12 s. Once the analytes are injected, they get separated and simultaneously detected in the µSC-TCD. This separation for the analytes of interest takes ~1-2 min; the µSC can be operated at higher temperatures to reduce the analysis time or to resolve higher boiling compounds. Once the analysis phase is complete, the valves are switched back to flow helium at a rate of 3 mL/min through the µPC. The µPC is heated in this stage to remove any residual analyte from previous loading stage. Typically, one temperature cycle (10-12 s) is sufficient to desorb the remaining analytes because of the high desorption efficiency of our silicon-based µPC.

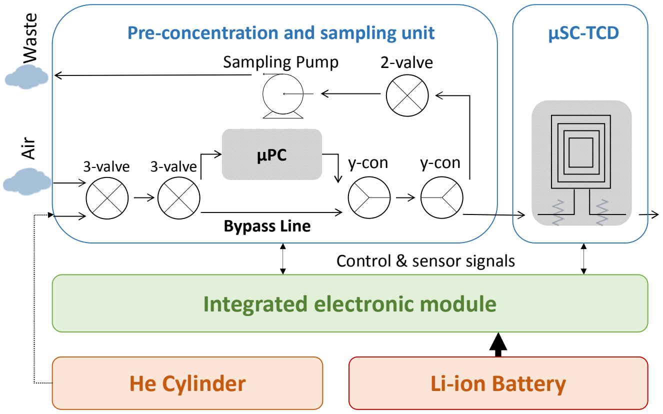

Figure 3: Zebra GC system schematic.

III. RESULTS AND DISCUSSION

A. *Experimental Setup*

The analytical performance of µPC, µSC-TCD and integrated Zebra GC system was evaluated by performing experiments using a conventional GC system (Agilent GC-7890A) equipped with an electronic pressure controller, flame ionization detector (FID), and an autosampler (G-4513A). Both injector and detector temperatures were maintained at 280 °C during testing. All chemicals used for chromatographic testing were of analytical standard (>99% purity) and purchased from Sigma-Aldrich.

For accurate temperature measurement, on-chip sensors were calibrated by placing the microdevices in the GC oven to characterize sensor resistance that responded linearly with respect to temperature with correlation coefficient of (R^2) >0.99. The calibration was completed by updating the firmware with calibration slope and offset, which were computed from the resistance vs temperature data

B. *µPC and µSC-TCD testing*

An important parameter for µPC testing is the width of the desorption peak, as it directly influences the chromatographic resolution achieved by the separation column. Initially, a desorption peak width of ~4 s was attained by the µPC at a heating ramp rate of 25 °C/s and flow rate of 1 mL/min. This was reduced by adopting a flow manipulation technique, which required heating the µPC without the carrier gas flowing followed by passing the carrier gas through when the chip reached its final temperature. This flow-manipulation technique resulted in a reduction of the peak width at half height (PWHH) from 4 s to ~0.8 s. As shown in Fig. 4, a minimum PWHH of ~ 360 ms was achieved when the desorption flow rate was increased to 2.5 mL/min. It is notable that 99% desorption efficiency for the analyte of interest was achieved by heating the µPC to 200°C. The remaining amount was removed by subsequent heating of the µPC prior to another run to minimize carry over from the previous adsorption run

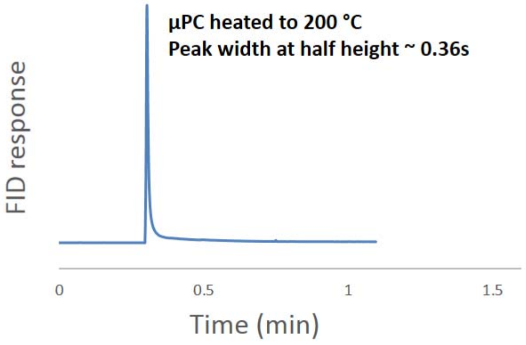

Figure 4: Injection plug from the µPC using the flow manipulation technique.

Further, we tested the µSC-TCD by evaluating its separation and detection performance. A mixture of 6 compounds (headspace), containing benzene, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, and p-xylene, was injected (1 µl) by autosampler through the heated injection port. The peaks were found to be well resolved and the separation required less than 2 minutes. Next, a calibration curve showing the µTCD's output (peak area) vs VOC's injected mass was obtained. For that purpose, a headspace sample of tetrachloroethylene was prepared and tested. As shown in Fig. 5, the injected mass was varied from 3 to 9 ng, and detector response was found to be linear with R^2 >0.99.

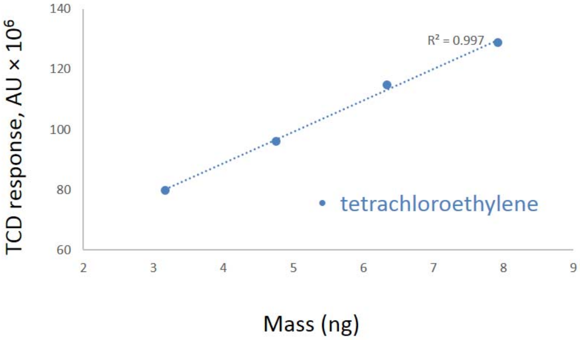

Figure 5: µTCD response (area units) vs VOC injected mass.

Next, the µPC was connected upstream of µSC-TCD to integrate the two components. The flow rate was set to 1 mL/min, for which the PWHH was measured to be 0.8 s from the µPC and the µSC exhibited well resolved peaks for the analytes of interest. An alternate flow path for the µPC was provided to maintain a steady flow in the µSC-TCD during the injection stage as TCD is a flow sensitive detector.

C. *Zebra GC testing*

The components of the Zebra GC were assembled as schematically shown in Fig. 3. The system was tested by loading it with a mixture of five VOCs with mass ranging from 5-20 ng, which corresponds to 2-3 min loading of ~1 ppmv concentration. The chromatogram in Fig. 6 shows that the system was able to successfully separate and identify the compounds in the mixture. This demonstrates the full operation of the entire system from injection to detection and the functionality of the supporting microcontroller circuitry.

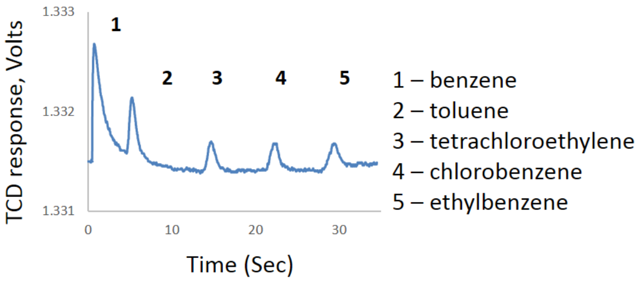

Figure 6: Chromatogram showing loading, separation and detection of a mixture of five VOCs generated from the Zebra GC system.

The average running time and power consumption for one complete measurement cycle, assuming 2 minutes loading and 2 minutes separation time, are 4.4 minutes and 1.7 watts, respectively. Each battery charge (capacity – 2200mAh) and helium refill (95ml, 2700psi) will last more than 150 and 8000 complete measurement cycles respectively.

IV. CONCLUSION

In conclusion, a hybrid portable chemical sensing system has been developed, incorporating monolithically integrated components, for portable on-site gas analysis. The system leveraged micro-machined components to achieve low power consumption and fast analysis time.

REFERENCES

[1] S. T. Vater, S. F. Velazquez, and V. J. Cogliano, "A Case Study of Cancer Data Set Combinations for PCBs," *Regulatory Toxicology and Pharmacology,* vol. 22, pp. 2-10, 8// 1995.

[2] L. Gao, Q. Song, G. E. Patterson, R. G. Cooks, and Z. Ouyang, "Handheld Rectilinear Ion Trap Mass Spectrometer," *Analytical Chemistry,* vol. 78, pp. 5994-6002, 2006/09/01 2006.

[3] M. Akbar, D. Wang, R. Goodman, A. Hoover, G. Rice, J. R. Heflin*, et al.*, "Improved performance of micro-fabricated preconcentrators using silica nanoparticles as a surface template," *Journal of Chromatography A,* vol. 1322, pp. 1-7, 12/27/ 2013.

[4] B. Alfeeli and M. Agah, "MEMS-Based Selective Preconcentration of Trace Level Breath Analytes," *Sensors Journal, IEEE,* vol. 9, pp. 1068-1075, 2009.

[5] S. Ali, M. Ashraf-Khorassani, L. T. Taylor, and M. Agah, "MEMS-based semi-packed gas chromatography columns," *Sensors and Actuators B: Chemical,* vol. 141, pp. 309-315, 8/18/ 2009.

[6] D. Wang, H. Shakeel, J. Lovette, G. W. Rice, J. R. Heflin, and M. Agah, "Highly Stable Surface Functionalization of Microgas Chromatography Columns Using Layer-by-Layer Self-Assembly of Silica Nanoparticles," *Analytical Chemistry,* vol. 85, pp. 8135-8141, 2013/09/03 2013.

[7] S. Narayanan and M. Agah, "Fabrication and Characterization of a Suspended TCD Integrated With a Gas Separation Column," *Microelectromechanical Systems, Journal of,* vol. 22, pp. 1166-1173, 2013.

[8] W. R. Collin, G. Serrano, L. K. Wright, H. Chang, N. Nuñovero, and E. T. Zellers, "Microfabricated Gas Chromatograph for Rapid, Trace-Level Determinations of Gas-Phase Explosive Marker Compounds," *Analytical Chemistry,* vol. 86, pp. 655-663, 2014/01/07 2013.

[9] S. Narayanan, B. Alfeeli, and M. Agah, "Two-Port Static Coated Micro Gas Chromatography Column With an Embedded Thermal Conductivity Detector," *Sensors Journal, IEEE,* vol. 12, pp. 1893-1900, 2012.

[10] M. Akbar and M. Agah, "A Microfabricated Propofol Trap for Breath-Based Anesthesia Depth Monitoring," *Microelectromechanical Systems, Journal of,* vol. 22, pp. 443-451, 2013.

[11] B. Alfeeli, L. T. Taylor, and M. Agah, "Evaluation of Tenax TA thin films as adsorbent material for micro preconcentration applications," *Microchemical Journal,* vol. 95, pp. 259-267, 7// 2010.