

A FACILE, STANDARDIZED FABRICATION APPROACH AND SCALABLE ARCHITECTURE FOR A MICRO GAS CHROMATOGRAPHY SYSTEM WITH INTEGRATED PUMP

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ABSTRACT

This paper reports a micro gas chromatography (μ GC) system that includes a microfabricated Knudsen pump, preconcentrator, separation column, and discharge-based detector. All four components are co-designed and co-fabricated on the same glass wafer by a 3-mask lithographic process, and fit within a footprint of 1.8×1.8 mm². Each component is tested individually: the motionless Knudsen pump provides 0.4 sccm air flow rate with 1 W input power; the preconcentrator demonstrates a fully desorbed heptane peak at 170 °C; the column and the detector demonstrate successful separation and detection of three alkane species. A stackable architecture is proposed as the system integration scheme and a future goal of this effort.

KEYWORDS

Micro gas chromatography, Knudsen pump, stackable architecture, microplasma emission, pulsed discharge.

INTRODUCTION

The miniaturization of GC components and systems has been pursued since the 1970s when Terry *et al.* reported a μ GC system with three microfabricated components: a sample injection valve, a separation column and a thermal conductivity detector [1]. A number of μ GC systems have been reported since then, particularly in the past decade. The μ ChemLab system reported by Lewis *et al.* includes a preconcentrator, a separation column, and a surface acoustic wave (SAW) array detector [2]. A μ GC system reported by Zellers *et al.* includes a microfabricated preconcentrator, valves, columns, a chemiresistive sensor array and a peristaltic micropump [3]. A continuing challenge to microsystem integration has been that not all the components have been miniaturized, and each has been fabricated by a different approach. An inexpensive and commercially compatible microfabrication process that can be shared by multiple μ GC components may facilitate wider adoption. In addition, the integration of four key elements is desirable for realizing a full system: the preconcentrator, the separation column, the detector, and the pump. The use of Knudsen pumps for μ GC systems has been previously established [4], but the pumps utilized were large, not lithographically micromachined, and not designed for integration.

This paper explores such a lithographic and standardized fabrication approach, using metallization and sandblasting of glass die, to manufacture the element structures of the four key μ GC components. The metal layer is patterned to form heaters, temperature sensors and

discharge electrodes, whereas the sandblasting is used to micromachine gas flow channels and thermal isolation cutouts. The μ GC components can be integrated into a system in the form of direct stacking, eliminating the need of capillary tubes for gas flow connections.

CONCEPT AND DESIGN

The Knudsen pump operates by thermal transpiration across a stack of nanoporous mixed cellulose ester (MCE) membranes [5] with an active pumping area of 1.2×1.2 mm². The membrane stack is sandwiched by lithographically metallized glass die and sealed around the perimeter. Arrays of through-holes and grooves are micromachined on these glass die to facilitate gas flow through the MCE membrane stack. With no moving parts, the Knudsen pump provides a highly reliable solution for integration in the μ GC system.

The preconcentrator has an 11 mm³ chamber packed with ≈ 120 μ m diameter Carbograph-2 granules (Grace Davison Discovery Sciences, IL) as the sorbent material. The chamber is designed with a sorbent loading port as well as arrays of pillar/post structures located in the vicinity of the gas inlet and outlet of the preconcentrator to confine the sorbent granules. During operation, the preconcentrator adsorbs vapor-phase analytes at room temperature. To initiate analysis, these analytes are injected into the downstream components by a thermal pulse.

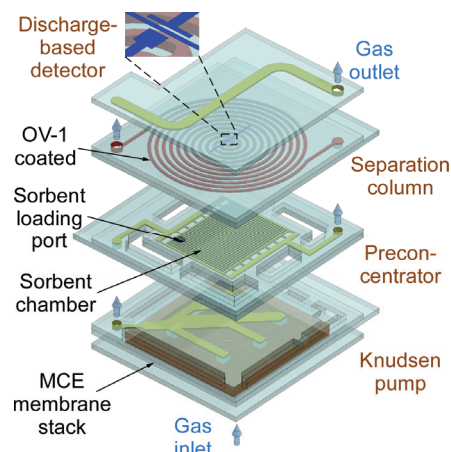


Fig. 1: The schematic of the discharge-based detector, the separation column, the preconcentrator, the Knudsen-pump, and their possible stacking scheme.

The separation column is a long channel (length ≈ 25 cm, hydraulic diameter ≈ 300 μ m) designed in a double-spiral pattern, and coated with ≈ 0.2 μ m thick OV-1 stationary phase on its inner wall. During operation, gas

analyte molecules that interact with the stationary phase are separated by their specific retention time.

The discharge-based detector uses high voltage pulses to create microdischarges between two thin film metal electrodes spaced 50 μm apart. The microplasma generates optical spectra, in which the emission band representing carbon species can be used to provide a chromatogram [6].

The stacking scheme (Fig. 1) illustrates a chip-scale integration approach for the μGC system. The four components form a serially connected gas flow path in the order of Knudsen pump (upstream), preconcentrator, separation column and detector (downstream). A number of spacers, micromachined using the same sandblasting process, can be inserted between adjacent components to reduce thermal crosstalk.

FABRICATION

The common fabrication process for all four components utilizes one mask for thin film metalization on a glass wafer, and two masks for a front-and-back sandblasting process that is commercially available (Fig. 2). The process starts with a metal layer (Ti/Pt 50/200 nm) deposited by thermal evaporation and patterned by liftoff on a 500 μm thick glass wafer. The metallized wafer is subject to two sandblasting steps (micro abrasive jet machining from Bullen Ultrasonics Inc., OH): one step creates 150-300 μm deep grooves for in plane gas flow, whereas the other creates through-wafer vias for inter-layer gas flow and cutouts for thermal isolation.

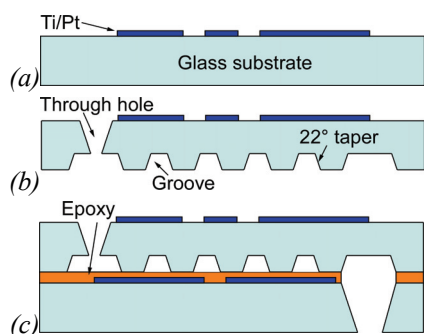


Fig. 2: The fabrication process shared by the discharge-based detector, the separation column, the preconcentrator and the Knudsen pump. (a) Deposit and pattern a Ti/Pt layer on the glass substrate. (b) Create grooves and through-holes by a two-step sandblasting process. (c) Bond two sandblasted die to form gas flow channels.

With all the μGC components fabricated on the same wafer, the die are singulated by dicing and assembled using epoxy bonding. For the separation column, a thin layer (<10 μm thick) of SU-8 (MicroChem, MA) is spin-coated on the mating surfaces. The two die are pressed together and permanently bonded by curing the SU-8 under ultraviolet exposure and heat. Some degree of softbaking prior to bonding helps stabilize the fluid SU-8 layer, preventing it from blocking the column. For the other components, low-viscosity epoxy Epotek-377 (Epoxy Technology, MA) is applied to the perimeter of assembled die, from where it is drawn into the seams by

capillary force. Leak free bonding is achieved after curing at 150 $^{\circ}\text{C}$. For the Knudsen pump, a stack of cut-to-size MCE membranes (105 μm thick, 25 nm pore diameter, 70% porosity, Millipore, MA), is sandwiched between glass die and sealed at the perimeter by a viscous epoxy Stycast2850FT (Henkel, Düsseldorf, Germany). Capillary tubes can be attached to the inlet/outlet of the components for further processing or testing using the epoxy Stycast2850FT.

The separation column and the preconcentrator require post-assembly processing. A static coating method [7] is used to coat the column with a ≈ 0.2 μm thick layer of stationary phase. A solution of OV-1 (Ohio Valley Specialty, OH), dissolved in pentane, is filled in the column, which is then placed in a vacuum chamber with one end of the column sealed. The vacuum evaporates the solvent pentane from the unsealed end of the column, leaving a layer of OV-1 coated on the column inner wall as the stationary phase. For the preconcentrator, the sorbent granules are drawn into the sorbent chamber from the loading port by applying a gentle vacuum at the inlet/outlet of the preconcentrator [8]. After sorbent loading, the loading port can be easily sealed by thermal tape or epoxy. The images of the fabricated devices are shown in Fig. 3.

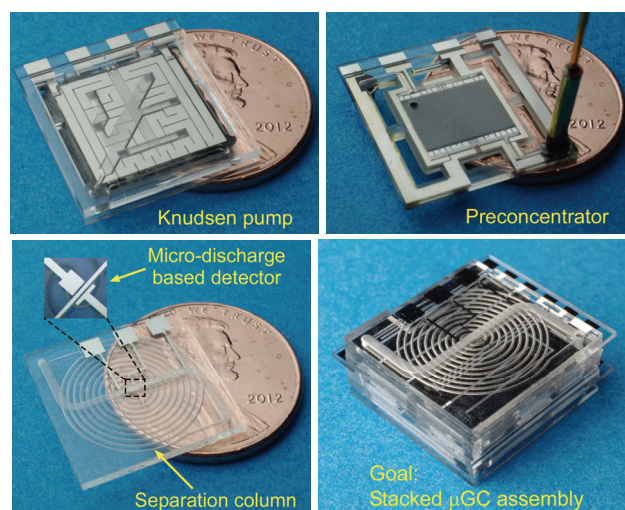


Fig. 3: Images of the discharge-based detector, the separation column, the preconcentrator, and the Knudsen pump. A stacked assembly of the complete system illustrating a future goal.

EXPERIMENTAL RESULTS

This paper describes the individual tests of the four μGC components; the system level operation remains a future goal.

The steady state operation of the Knudsen pumps was tested by attaching various capillary loads at the outlet while leaving the inlet open to the ambient at atmospheric pressure. A pressure sensor (Model # MPX5010DP, Freescale Semiconductor, AZ) was used to measure the pressure at the pump outlet and a flow meter (Part # FMA-1603A, Omega Engineering, CT) provided the gas flow rate. With 1 W input power, the Knudsen pump generated 0.42 sccm air flow rate against a ΔP of 329 Pa; with the outlet sealed – i.e., in the zero flow condition –

the Knudsen pump created an equilibrium ΔP of 993 Pa. The characteristic curve of the Knudsen pump is shown in Fig. 4.

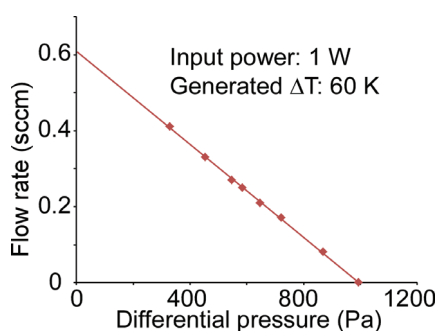


Fig. 4: The Knudsen-pump performance curve with 1 W power input.

The separation column was tested with the assistance of the injection port and the flame ionization detector (FID) in an Agilent 6890 GC system with N_2 used as the carrier gas. A syringe was used to sample the headspace of a sample vial that was filled with the mixture of pentane, hexane and heptane, and then inject the vapor into the separation column operating at room temperature. As shown in a typical FID chromatogram (Fig. 5), the analytes were separated in the column with retention times of 18 s, 22 s, and 35 s, respectively. The retention peaks showed good symmetry without much fronting or tailing.

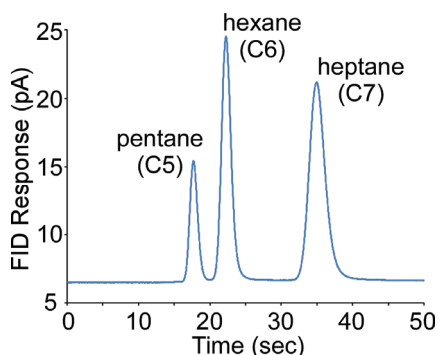


Fig. 5: Experimentally observed separation of a C5-C7 alkane mixture obtained by the micromachined column followed by a commercial flame ionization detector.

The performance of the preconcentrator is reflected by thermal desorption chromatogram of heptane (Fig. 6). The preconcentrator was used to collect the heptane vapor drawn from a dilution bottle by an external vacuum pump. To evaluate desorption, the preconcentrator was connected into the Agilent 6890 GC system, similar to the arrangement for the separation column. The gas flow direction for desorption was the same as that for sampling, in accordance with overall gas flow in the μ GC architecture. With a N_2 flow rate of 1 sccm and a thermal pulse at 170 °C, the preconcentrator typically provided a desorption peak with half-height width of 1.4 s. The response showed modest tailing. The flow rate was measured by the flow meter FMA-1603A. The temperature of desorption was controlled by the on-chip heater, either the on-chip thermistor or an external

thermocouple attached to the preconcentrator, a data acquisition card (DAQ, Model # USB-6259, National Instruments), as well as a closed-loop algorithm in a LabVIEW® program. When the preconcentrator was subject to a second thermal pulse, it did not show an additional desorption peak, verifying that full desorption was performed during the first thermal pulse.

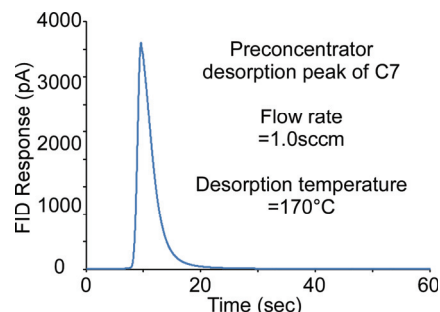


Fig. 6: An experimentally obtained thermal desorption peak of a preconcentrator showing the injection of a mixture of C5, C6 and C7 alkanes.

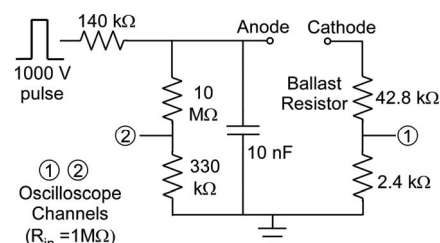


Fig. 7: The control circuit for the discharge-based detector.

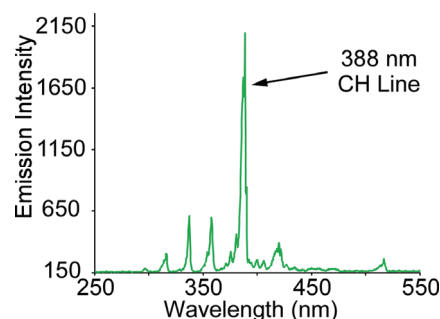


Fig. 8: A typical optical spectrum generated by the discharge-based detector with alkane plugs in N_2 .

The discharge-based detector created pulsed microdischarges with the circuit as illustrated in Fig. 7. A high voltage pulse charged the 10 nF capacitor and initiated a microdischarge once the breakdown voltage between the anode and the cathode was reached. The 42.8 k Ω ballast resistor, together with the 2.4 k Ω resistor, limited the discharge current while the 140 k Ω resistor at the anode limited the charging rate of the capacitor. The two resistive dividers (10 M Ω /330 k Ω and 42.8 k Ω /2.4 k Ω) were connected with the oscilloscope channels to monitor the anode and cathode voltages as well as the discharge current. In such a circuit, the detector created microdischarges of \approx 2 ms duration consuming 13 mJ energy per discharge (including the energy consumed by the circuit elements). The optical emission generated by the microplasma was guided by an optical fiber into a

handheld spectrometer (Model # USB 2000, Ocean Optics, FL) that produced optical spectral data collected by a laptop computer. With an elevated concentration of alkane presenting in nitrogen, the CH spectral bands (388 nm, 418 nm, 516 nm) showed a significant response against the N₂ bands (315 nm, 337 nm, 357 nm) as illustrated in Fig. 8.

The performance of a sub-system comprised of the micromachined column combined with the microdischarge-based detector was also evaluated. The column and the detector were connected by a capillary tube. The injection port of the Agilent 6890 GC was used as the source. The detector was fired at a rate 2 pulses/second. In the resulting spectra, the CH band at 388 nm was selected to provide the chromatogram. The separation and detection of a C5-C7 alkane mixture are evident in Fig. 9. Due to the pulse-to-pulse deviations in the pulsed microdischarges, the detector responses at high alkane vapor concentration showed a certain level of fluctuation. However, the separation was still evident with significant and symmetric retention peaks. As described in plate theory, ideal GC retention peaks approach Gaussian shapes [9]; thus the detector data were fitted by Gaussian functions in Fig. 9.

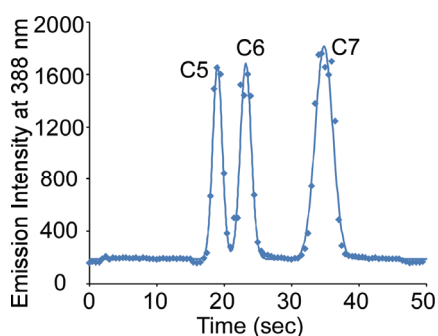


Fig. 9: Experimentally observed separation and detection of a C5-C7 alkane mixture performed by the sub-system comprised of the micromachined column combined with the microdischarge-based detector.

CONCLUSION AND DISCUSSION

This paper describes a standardized fabrication approach that can be shared by four μ GC components – the Knudsen pump, the preconcentrator, the separation column and the discharge-based detector, and presents a scalable μ GC architecture featuring direct component stacking. The four μ GC components, co-designed and co-fabricated for system integration, are tested individually and their preliminary performance is reported.

The approach described in this paper uses an assembly process where all the components are fabricated from the same wafer and assembled after dicing. However, a batch mode process can also be envisioned where each component is replicated exclusively on the full wafer, and wafer-to-wafer bonding is used to assemble the system prior to dicing. Furthermore, the glass wafer used in this paper can be replaced with less expensive or higher performance material, such as a ceramic.

Future efforts include integrating all the μ GC

components into a stack and testing the performance of the full system.

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