

AN ALL ELECTRONIC, FULLY MICROFABRICATED MICRO GAS CHROMATOGRAPH

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ABSTRACT

This paper reports a full micro gas chromatograph (μ GC) in which all the components are electronic. All components, including a Knudsen pump, a preconcentrator, separation columns, and capacitive gas detectors, form a complete μ GC system that has no moving parts, uses room air as carrier gas, and can be fabricated by a common low-cost process. The preliminary system has experimentally demonstrated sampling, separation, and detection of 12 chemicals with 1-10 ppm concentrations. The calculated detection limit is expected to reach as low as 20 ppb.

KEYWORDS

Capacitive gas sensor, chemical sensing, Knudsen pump.

INTRODUCTION

A variety of micro gas chromatographs (μ GCs) have been reported since the late 1970s [1]. In gas chromatography, complex vapor mixtures are separated into individual species, which are characterized by elution time that is measured using a detector located downstream of the separation column. For detection of vapors with low concentration, preconcentrators are often used to sample vapor molecules and inject a highly concentrated peak into the separation column. The sampling and separation require gas flow that is typically generated by gas pumps.

Many μ GCs reported hitherto relied on external macro components. In particular, almost all μ GCs used external, commercial gas pumps [2-4]. Our group has previously demonstrated the integration of microfabricated gas pumps (*i.e.*, Knudsen pumps) into μ GCs (*i.e.*, *iGC1* and *iGC2*). However, these μ GCs used gas detectors based on microdischarge emission spectroscopy, which relied on an external optical spectrometer [5, 6]. Some other μ GCs used electrically driven micro gas pumps and detectors, but only demonstrated partial system operation; for these, macro-scale injectors were used for vapor injection [7]. Partial miniaturization limits the integration of μ GC systems, and the resulting reduction in cost.

To address the primary challenge in our prior work on *iGC1* and *iGC2* [5, 6], the microdischarge-based detector must be replaced with another detector with electronic interface. Various electronic μ GC detectors have been reported, including the thermal conductivity detector (TCD) [8], the discharge photo ionization detector (DPID) [9], the heterodyne graphene detector [10], the surface acoustic wave (SAW) detector [2], the metal oxide semiconductor (MOX) detector [3], the chemiresistor [4], and capacitive detectors [11, 12]. The TCD, DPID, and heterodyne graphene detector relied upon the use of external Helium as either carrier gas or

auxiliary gas, whereas the other detectors could be used with air as the carrier gas in the context of a μ GC. Compared to the alternatives, the capacitive detectors have several advantages in device implementation: (1) commercially available low-cost electronic interface; (2) room temperature operation; (3) simple fabrication.

Several types of capacitive detector structures have been reported. The parallel plate structure reported in [11] had a polymer film sandwiched by a perforated top plate and a flat bottom plate. The perforations provide access of vapor to the polymer. A majority of capacitive detectors use a simpler structure with on-substrate interdigitated electrodes covered by a polymer film [12-15]. Upon vapor adsorption, the polymer undergoes swelling and permittivity change. Both effects vary the electric field line distribution, and hence the capacitance. Compared to the parallel plate structure, the interdigitated structure generally provides lower sensitivity (as a fraction of the electric field lines are guided through the substrate and not used for sensing) but faster response (as the entire polymer film is exposed to the vapor to facilitate diffusion). The latter property makes the interdigitated structure more attractive for μ GC applications.

This paper reports the *iGC3.c1*, a system that integrates a Knudsen pump, a preconcentrator, separation columns, and a capacitive detector. The capacitive detector uses the simple on-substrate interdigitated structure. The detector response is directly measured by a commercial integrated circuit chip. This approach achieves a complete, easily manufacturable μ GC that does not rely on external optical instruments or carrier gas supplies.

DESIGN AND FABRICATION

The *iGC3.c1* system architecture includes two modules: the chromatography module and the Knudsen pump module (Fig. 1). The former includes a two-stage preconcentrator, separation columns, and a capacitive detector; whereas the latter is a two-stage, bi-directional Knudsen pump. The system is partitioned mainly because the Knudsen pump requires external heat sinks, which are unnecessary for the other components. Additionally, the modular design provides reconfigurability.

The preconcentrator contains two segments of sorbents, Carbo-pack-B and Carbo-pack-X (Sigma Aldrich, WI), which target a wide range of vapor species. The sorbents are packed into a U-channel, which is cantilevered above a glass spacer, isolating it from the substrate. This design relieves thermal stress and reduces heat loss through the anchor (Fig. 2). The separation columns are meandering channels with hydraulic diameter $\approx 230 \mu\text{m}$ and total length $\approx 60 \text{ cm}$. The interior of these channels is coated with $\approx 0.2 \mu\text{m}$ thick OV-1 stationary

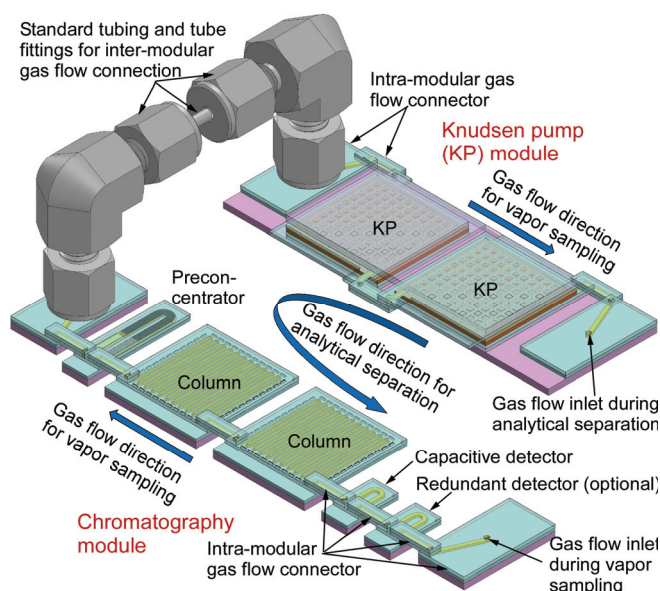


Fig. 1: Architecture of the full μ GC system.

phase (Ohio Valley Specialty, OH).

The capacitive detectors use patterned thin-film metal (Ti/Pt, $\approx 25/100$ nm) to form interdigitated electrodes (with width and gap ≈ 1 μ m) on glass. Although two detectors are provided for redundancy, only one detector is used. Its electrodes are covered by an OV-1 layer (of thickness ≈ 0.25 μ m). When exposed to vapors, it undergoes changes in thickness, permittivity, and consequently capacitance. In principle, additional detectors with different coating material or thickness can be used to enhance signal identification.

The Knudsen pump generates gas flow by thermal transpiration, which occurs in a narrow channel, with hydraulic diameter comparable to or less than the gas mean free path, where gas molecules tend to move against the temperature gradient along the channel [16]. In this work, each stage of the Knudsen pump uses a stack of nanoporous mixed-cellulose-ester membranes of total thickness ≈ 500 μ m, pore diameter ≈ 25 nm, porosity $\approx 70\%$ (Millipore, MA) to provide thermal transpiration [17]. The membranes are sandwiched between glass dice from above and below, both

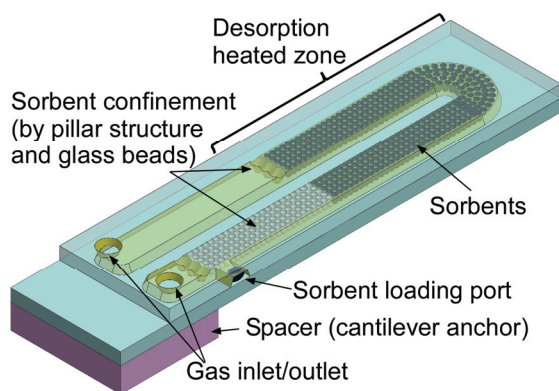


Fig. 2: Preconcentrator designed as a cantilever structure (which also applies to the separation columns)

with embedded Ti/Pt heaters and flow channels. External heat sinks are attached to the glass dice. By selectively heating one side of the membrane stack, flow can be generated in either direction. This permits the flow direction to be reversed when switching from sampling to separation. Two pumping stages are used to increase the output pressure head for the separation columns. The system can be readily reconfigured with more separation columns and more Knudsen pump stages.

All components are arranged in a planar fashion, which provides superior thermal isolation than the stacked approach in [5, 6]. The two modules are connected by compression tube fittings (Fig. 1). Within each module, the components are connected by microfabricated connectors.

All the *iGC3.c1* components are co-fabricated using a low-cost process adapted from [5]. The flow channels are created in glass substrates of thickness ≈ 500 μ m using sandblasting (Bullen, Inc., OH). The heaters, thermistors, and capacitor electrodes are created by metallization on non-sandblasted glass substrates (Fig. 3). Compared to our previous approach of sequentially applying metallization and sandblasting to the same substrate, this parallel approach accelerates the fabrication and reduces the risk. The dice are assembled into components and held in place by epoxy. For the capacitive detectors, the metallized substrate is coated with 10 nm-thick Al_2O_3 using atomic layer deposition. This is an optional, precautionary step to prevent potential shorting caused by dust, *i.e.*, it can be excluded if the assembly is performed in a clean environment. Then an OV-1 layer is spin-coated on the metallized substrate before the sandblasted substrate is bonded.

The components in the chromatography module are mounted on a printed circuit board (PCB), whereas these in the Knudsen pump module use a hybrid platform with PCB-heat sinks. Lead transfer between the components and PCBs is provided by commercial pins and headers directly soldered to the components. A preliminary version of system is shown in Figs. 4-5.

EXPERIMENTAL RESULTS

The preliminary system has demonstrated sampling, separation, and detection of 12 chemicals with 1-10 ppm concentrations, using room air as carrier gas (Fig. 6). The 12 chemicals included non-polar alkanes, benzene, toluene, *m*-xylene, *o*-xylene (BTX), α -pinene, and mildly-polar hexanal

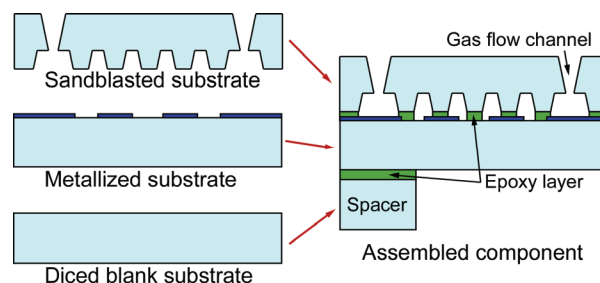


Fig. 3: Fabrication and illustrative assembly process of the μ GC components

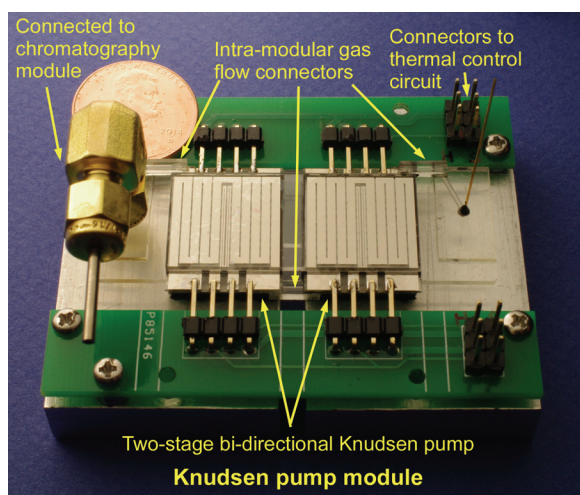


Fig. 4: Photo of a preliminary Knudsen pump module (with footprint $\approx 7 \times 5 \text{ cm}^2$, top heat sinks removed for clarity)

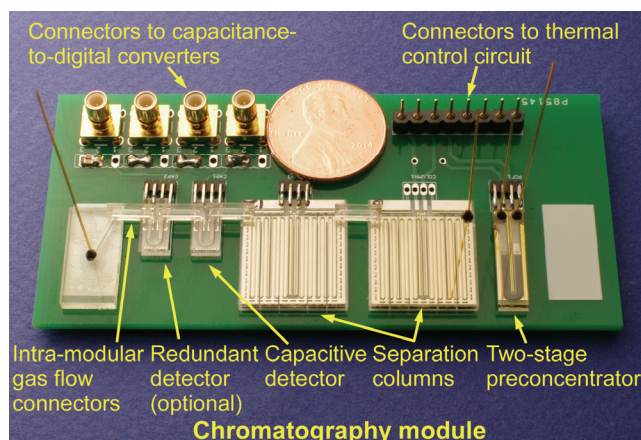


Fig. 5: Photo of a preliminary chromatography module (with footprint $\approx 9 \times 4 \text{ cm}^2$)

and 2,4-dimethyl-3-pentanol.

The tested vapor samples were prepared by injecting a measured volume ($\approx 1 \mu\text{L}$) of the 12-chemical liquid mixture into a 2 L dilution bottle prefilled with room air. After the mixture fully evaporated in the bottle, the resulting vapor concentration was 10 ppm for each non-polar species and 1 ppm for each mildly-polar species. The term “ppm” used in this paper is defined as the number of molecules of each chemical divided by the number of molecules of air in the prepared vapor and multiplied by 10^6 .

During vapor sampling, the bottle was connected to the port upstream of the capacitive detectors. The Knudsen pump module provided 0.2 sccm flow for 10-20 min., drawing the vapor through the detectors, the separation columns, and into the pre-concentrator. The flow rate was measured by a commercial flow meter (Model # MW-20SCCM-D, Alicat Scientific, Inc., AZ) connected downstream of the pump. During analytical separation, the dilution bottle was removed. Starting 10 s after the beginning of signal recording (Fig. 6), the pump provided 0.2 sccm flow, pushing room air through the chromatography module

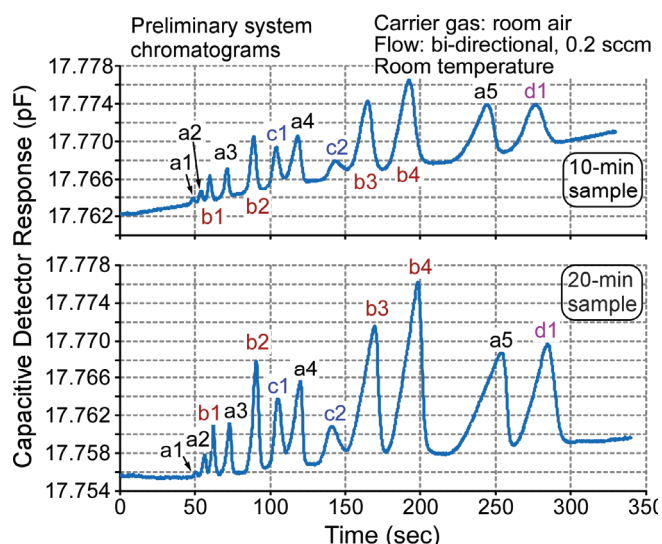


Fig. 6: Preliminary chromatograms of 12 chemicals provided by the system. a1-a5: alkanes C5-C9 (each 10 ppm); b1-b4: benzene, toluene, m-xylene, and o-xylene (each 10 ppm); c1-c2: hexanal and 2,4-dimethyl-3-pentanol (each 1 ppm); d1: α -pinene (10 ppm).

in the reverse direction. The preconcentrator was heated to 250°C at 20 s after the pumping was initiated (Fig. 6) to provide thermally inject the sampled vapor into the column. The columns and detector were operated at room temperature. The detector response was directly measured by a commercial capacitance-to-digital converter chip (AD7746, Analog Devices, MA) on its evaluation board. The detection rate was $\approx 7 \text{ Hz}$.

As evident in Fig. 6, most of the 12 chemicals were baseline-separated within 5 min., i.e., baseline was reached between two adjacent peaks. Compared to the results of 10-min. sampling, the 20-min. samples provided peak heights that were twice as high. This indicates that the detector response varied linearly with chemical quantities.

The detector noise was measured by reading 1000 continuous data points of the detector capacitance at zero-flow condition (Fig. 7). The absence of flow ensured that the measurement was immune to the vapors that could cause

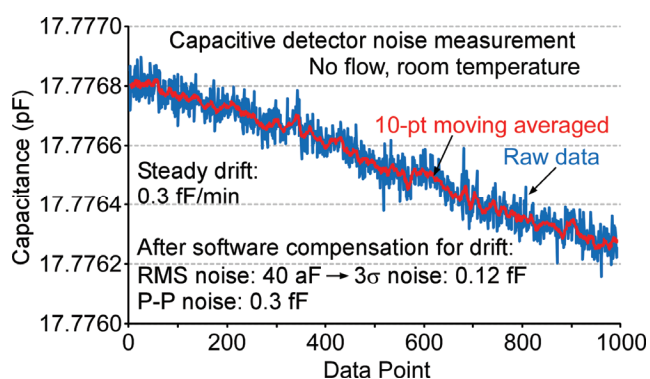


Fig. 7: Detector noise measured by a commercial capacitance-to-digital converter (Part # AD7746, Analog Devices, MA). The measured 3σ noise is $\approx 0.12 \text{ fF}$.

signal fluctuation. After linear compensation for the steady drift in Fig. 7, the root-mean-square noise, as denoted by the standard deviation (σ), was ≈ 40 aF. Based on the commonly used criterion of 3σ noise, *i.e.*, ≈ 0.12 fF, the expected detection limits were calculated to be 2 ppm for pentane, 230 ppb for benzene, 70 ppb for *o*-xylene, and 20 ppb for hexanal.

DISCUSSIONS AND CONCLUSION

The results demonstrated the viability of a μ GC system in which all the components are microfabricated and electronically interfaced. The system has no moving parts, uses room air as carrier gas, and all the fluidic components can be co-fabricated by a common low-cost process. These features reduce the cost of the system.

Current results are based on a preliminary system (Figs. 4-5). The chromatograms show baseline drift, which is likely caused by impurities in the carrier gas. This can be digitally compensated by software.

The system platform can be improved in various aspects. For example, multiple detectors with different polymer coating can be easily integrated to enhance vapor recognition. More preconcentrators or separation columns can be added to enhance the chromatography. Other gas micropumps can also be integrated to accelerate the analyses.

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