Microfluidic integration of µPID on µcolumn for ultracompact micro-gas chromatography

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ABSTRACT

Microfabricated gas chromatography (µGC) offers a powerful portable vapor analysis solution for various field applications. Here, we developed a microfluidically integrated architecture of a microfluidic photoionization detector (µPID) on a microfabricated column (µcolumn) via a silicon-on-insulator platform. By eliminating the off-chip interconnects, the microfluidically integrated column PID (iCPID) demonstrated a narrow peak width compared to the off-chip benchmark µPID. Furthermore, the iCPID sensitivity as a function of the bias voltage and temperature were characterized. Finally, an ultracompact (0.9 L, 0.9 kg), automated, and battery-operated µGC system without any benchtop components was constructed based on the iCPID. Rapid (2 min) isothermal separation of eight volatile compounds at room temperature was demonstrated.

1. Introduction

Lab-on-a-chip microfabricated gas chromatography (µGC) [1] has revolutionized the analysis of volatile organic compounds (VOCs) by enabling compact, low-power, and rapid analysis in diverse field applications, including environmental monitoring [2–5], biomedical diagnosis [6–8], homeland security [9–12] and space exploration [13, 14]. To date, the majority of µGC devices rely on a hybrid integration approach [1–5,10,12,15–25], in which individual components (i.e., preconcentrators, columns, and detectors, etc.) are fluidically connected using off-chip interconnects (e.g., guard columns and universal connectors, etc.). Although this approach offers advantages such as eliminating thermal crosstalk between components that usually operate at different temperatures and providing greater freedom to optimize and change individual components, it also poses several challenges. First, manual assembly of a hybrid integrated µGC is labor-intensive, costly, and susceptible to human errors, making it incompatible with mass production. Second, fluidic interfacing methods [26] commonly used in hybrid integration (e.g., epoxy, Nanoport [27], metal fittings [12,28,29], and manifolds [3,4,12,25,30], etc.) can either introduce mechanically weak points at the connecting junctions or significantly increase the footprint of presumably miniaturized components. Finally, the hybrid configuration can generate cold spots and dead volumes between transfer lines, thereby causing band broadening and degrading overall chromatographic separation ability of µGC. Consequently, monolithically integrated µGC has been pursued, with a focus on integrating separation micro-columns (µcolumns) and respective detectors on a single chip [11,30–36]. Table 1 compares recent µGC systems and modules employing different integration schemes. Compared to hybrid integration, monolithic integration could range from only merging two devices (or partial components) together to an entire system level integration of multiple devices on the same chip. It is widely observed that integration in µGC systems often includes additional packaging post-fabrication for inevitable off-chip interconnections (fluidics, ionization sources, etc.).

Various types of gas detectors, including thermal conductivity

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detectors (TCD) [11,34,35], optical interferometric sensors [31], pivot plate resonators [30], photoionization detectors (PID) [32,33] have been integrated monolithically with μcolumns owing to their microfabrication compatibility. Among these integrated detectors, PIDs have emerged superior due to their fast response, high sensitivity, and ability to detect a broad range of chemical compounds. Recently, μGC integrated with a micro helium discharge photoionization detector (μPDID) showed rapid separation and detection of alkanes and aromatics with a detection limit of 10 pg [32,33]. However, the μPDID requires a separate high-purity helium cartridge as an auxiliary flow during operation, which inevitably increases the footprint and weight of the entire system, restricting certain field applications. In contrast, vacuum ultraviolet (VUV) lamp based PIDs avoid the need for bulky helium cartridges and can potentially be integrated with μGC. Although the lower VUV photon energies generated from the VUV lamp (10.6 eV for Krytron lamps and 11.7 eV for Argon lamps) may limit the range of detectable chemical compounds, they allow for the use of ambient air (after removal of hydrocarbons and drying) as the carrier gas without interfering with analysis of target compounds since oxygen and nitrogen ionization potentials are higher than 11.7 eV. This further reduces the μGC system’s footprint by eliminating any carrier gas cartridges. Finally, the plasma in lamp-based PIDs is confined inside the lamp and not in direct contact with the electrodes (as in the case of μPDID [39,40]), which prevents the potential degradation of the electrodes (both excitation and sensing electrodes) exposed to plasma over time.

Conventional PIDs using VUV lamps are still relatively bulky, and their configuration is not designed for μGC integration. Zhu et al. and Li et al. developed a lamp-based microfluidic PID (μPID) with rapid response and high sensitivity. This μPID was fabricated on a silicon wafer using etched parallel silicon channel walls as the electrodes on a glass substrate [18,41], paving a way for potential μGC integration. Very recently, a lamp-based PID (arrayed integrated photoinitiation detector, AiPD) using coplanar metal sensing electrodes has also been explored in an attempt for integration with μcolumns [16]. In the μPDID-μcolumn work [32,33], the microfabrication process for monolithically integrating the μPDID and μcolumn, although relatively simple (i.e., a two-mask process), was yet not amicable for wafer-scale batch production due to the need for dicing the silicon and glass wafers into separate individual pieces before anodic bonding (in order to expose the excitation/sensing electrodes for packaging) and the simplified process disallowed an on-chip heater [34] conventionally integrated on μcolumns [32,33]. Similarly, the AiPD-μcolumn device [16] currently was only realized by manually gluing individually microfabricated dies on a larger substrate using epoxy, which may hinder large-scale manufacturing [16]. Furthermore, coplanar metal electrode design as in both μPDID and AiPD [16,32,33], while relatively simple to fabricate, would result in non-uniform electric fields that may lead to a sublinear response to analyte concentrations [16]. On the other hand, for the μPID using parallel silicon electrodes that generate a strong and uniform electric field [18,41] overlapping entirely with the photoionization area, its integration requires an appropriate design that can achieve fluidic connection between the μPID and μcolumn while maintaining electrical isolation.

Here, we developed an integrated μGC architecture based on a silicon-on-insulator (SOI) structure that enables monolithic integration of the parallel-plate silicon electrodes on μcolumn with an on-chip heater, realizing microfluidic integration of a VUV lamp based μPID with additional microfluidic packaging (i.e., VUV lamp, fused silica capillaries) off-chip. In this article, we first detail the design, fabrication, and characterization of the integrated μcolumn and μPID (i.e., iCPID). It is shown that at lower injection masses (<10 ng), the iCPID maintained a sensitivity similar to the stand-alone μPID [18,41], which possesses a single-digit-picogram detection limit, and that the peak widths detected by iCPID were narrower than those by the off-chip stand-alone μPID due to the monolithic integration. Finally, an ultracompact, fully-automated,

<table>
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<th>Table 1</th>
<th>Comparison of μGC systems and modules.</th>
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<td>μGC integration</td>
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<tr>
<td>Grag et al. [34]</td>
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<td>Akbar et al. [32]</td>
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<td>Qin et al. [2]</td>
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<td>Liao et al. [16]</td>
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<td>Li et al. [18]</td>
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<td>Whiting et al. [38]</td>
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* not applicable as a module.
** Air** denotes operation without a gas cartridge.
*** including 0.45 kg batteries and associated electronics in a 0.34 L battery chamber.
battery-powered μGC system was constructed based on the iCPID. The entire system was self-contained within a 3D-printed box with a volume of only 0.9 liters and a weight of 0.9 kg and used ambient air as the carrier gas. A rapid separation of eight VOCs in two minutes isothermally at ambient temperature was demonstrated.

1.1. Integrated μ-column and μ-PID (iCPID) device architecture and working principle

As illustrated in Fig. 1, the iCPID is fabricated on an SOI platform with a top-down architecture, where the μ-PID (in the device layer) resides on top of the μ-column (in the handle layer). At the inlet and outlet of the μ-PID, there are two etched-through vertical pass-through holes that termed as “microfluidic vias”. The first one connects the upstream μ-column (in the handle layer) to the μ-PID (in the device layer) and the second one is routed towards the outlet of the iCPID (in the handle layer). The μ-PID and μ-column are electrically isolated by the buried oxide (BOX) on SOI. A glass layer is anodically bonded to the SOI to seal the μ-column. The heater of μ-column is patterned on top the device layer of the SOI with an additional layer of SiO$_2$ to provide electrical isolation. A VUV lamp (Krypton for 10.6 eV or Argon for 11.7 eV) is hermetically mounted on the μ-PID by epoxy and serves as the photoionization source. To prevent outgassing from the epoxy used in lamp packaging, a micromachined insulation silicon wedge (inset of Fig. 1 (B)) is inserted to the side of microfluidic vias before applying epoxy. The monolithic batch microfabrication process of iCPID is depicted in Fig. 2 and described in “Experimental”.

During operation, the gas mixture enters the inlet of the iCPID, and is subsequently separated by the μ-column whose temperature is ramped by the integrated heater. Towards the end of the μ-column, the separated molecules flow up through the microfluidic via and are then detected by the μ-PID before flowing back down towards the outlet of the iCPID. This top-down architecture of the iCPID minimizes the overall footprint by allowing the μ-PID to be stacked directly on the μ-column while avoiding any interconnection in between. It also takes advantage of flow-through and nondestructive nature of the μ-PID, which allows for further downstream analysis (such as connecting the outlet of the iCPID to a 2nd-dimensional column [17]).

2. Experimental

2.1. Materials

Analytical standard-grade benzene, hexamethyldisilazane (HMDS), and the eight VOCs listed in Supplementary Table S1 were purchased from Sigma-Aldrich (St. Louis, MO). 400 μm thick, double-side polished Si wafers (<100>, p-type, 0.001–0.005 Ω·cm and <100>, p-type, 1–10 Ω·cm) were purchased from Ultrasil LLC. 550 μm Borofloat 33 glass (P/N 517) were purchased from UniversityWafer. A 10.6 eV VUV Kr lamp with a MgF$_2$ window was purchased from Mtronix (P/N 043–257). Guard columns for fluidic packing and interconnections were purchased from Restak (P/N 10011). UV curable epoxy (NOA 68 T) was purchased from Norland Product Inc. Carbopacks B (P/N 20273) and X (P/N 10437-U) were purchased from Sigma-Aldrich. Additional accessory materials that used to build the system are provided in Table S2. All materials were used as purchased without further purification or modification.
Fig. 2. Schematics outlining the microfabrication process for iCPID. (1) Thermal oxide was grown on a Si wafer. (2) An SOI wafer was created by fusion bonding the oxidized wafer to a highly doped Si wafer. The conductive wafer serves as the device layer and the oxidized wafer serves as the handle layer. (3) The oxide on the handle wafer was patterned via photolithography and RIE to create a hard mask for the pchannel, inlets, and pass-through microfluidic vias. (4) The inlets and pass-through vias were etched with DRIE while the pchannel was protected with photoresist. (5) After stripping the photoresist, DRIE was continued using the oxide hard mask to etch the pchannel while the inlets and pass-through vias were etched to the buried oxide layer (BOX). (6) Hydrofluoric acid (HF) was used to strip the thermal oxide hard mask and BOX in the pass-through vias. (7) The etched handle layer was anodically bonded to a borofloat glass wafer to seal the pchannel. (8) Plasma-enhanced chemical vapor deposition (PECVD) was used to deposit a layer of SiO$_2$ on the device layer. (9) Photolithography was used to define the pPID region where the oxide was etched by RIE. (10) A layer of Ti/Pt was patterned on the device layer using lithography, evaporation, and liftoff to define the pPID electrodes and pchannel heater simultaneously. (11) Patterned photoresist was used as a mask for the DRIE on the device layer to generate the pPID. The pPID was etched down to the BOX. After removing the photoresist, the wafer was diced into individual devices.

2.2. Microfabrication of iCPID

The monolithic microfabrication process for the iCPID is outlined in Fig. 2. Both wafers first underwent RCA clean. After a dielectric barrier discharge (DBD) of atmospheric N$_2$ plasma treatment on the bonding side of both wafers, a 400 µm thick, double-side polished Si wafer (<100>, p-type, 0.001–0.005 Ω·cm) was fusion bonded [42] to a 550 µm thick, double-side polished Si wafer (<100>, p-type, 1–10 Ω·cm) with 2 µm thick thermal oxide under vacuum at 400°C and 20 MPA for 4 hours to generate the SOI wafer where the conductive wafer serves as the device layer and the insulating wafer serves as the handle wafer. The oxide on the handle layer was then patterned using photolithography and reactive ion etching (RIE) to create a hard mask for the pchannel (3 m in length x 150 µm in width with 30 µm thick walls), inlets (400 µm in width), and pass-through microfluidic vias (550 µm in diameter). Next, photolithography was used to selectively expose the inlets and pass-through vias for a deep reactive-ion etching (DRIE) etch of ~150 µm in depth. The photoresist was then stripped and DRIE continued with the hard mask to simultaneously etch the pchannel to a final depth of 250 µm while the inlets and pass-through vias were etched. After stripping the thermal oxide and BOX on the pass-through vias with HF, the handle layer was anodically bonded [43] to a 550 µm thick borofloat glass wafer to seal the pchannel after piranha-cleaned. Next, 1 µm of SiO$_2$ was deposited on the device layer by plasma-enhanced chemical vapor deposition (PECVD) and photolithography was used to define the pPID electrodes where the oxide is etched by RIE for depositing Pt thin films to form ohmic contact on the silicon electrodes and isolate the pPID from the rest of the device layer (with PECVD oxide). The defined area is shown in Fig. 1(B) where pPID’s Pt electrodes reside. The photoresist was then stripped and a layer of Ti/Pt (30/360 nm) was patterned on the device layer using lithography, evaporation, and liftoff to define the pPID electrodes and pchannel heater simultaneously. Finally, photoresist was used as a mask for the DRIE on the device layer to generate the pPID (400 µm wide channels in an Archimedean spiral with 40 µm thick walls and a length of 3.2 cm). The pPID was etched down to the BOX (etch-stop). After removing the photoresist, the wafer was diced into individual devices with dimensions of 26.4 mm x 29.6 mm x 1.5 mm (length x width x thickness).

2.3. Microfluidic and electrical packaging of iCPID

For hermatically packaging the VUV lamp on the integrated pPID using UV epoxy, a customized silicon wedge was fabricated to underfill the etched-through inlet and outlet near the microfluidic vias before applying the UV epoxy to avoid possible clotting and outgassing from the epoxy. The insulated wedges shown in the inset of Fig. 1(B) were microfabricated using a 400 µm thick, double-side polished Si wafer that were first diced into 2 cm by 2 cm pieces. Then the piece was patterned and etched through to generate the free-standing wedges. The wedges were then conformally coated with 200 nm of SiO$_2$ by atomic layer deposition (ALD) for insulation. It should be noted that the ALD process was chosen for its ability to achieve the best conformal coating along the sidewall, although sputtering was also used to achieve the same purpose.

The coating procedure of the pchannel in the iCPID is illustrated in Figure S1. First, the guard columns were inserted into the inlet and outlet of the iCPID as well as the coating outlet port. Prior to coating, the pchannel was deactivated by eight repeated injections of HMDS into the column inlet (i.e., coating inlet) at 120 °C within 1 hour, and the coating outlet was blocked with a rubber septum during deactivation. Next, the coating outlet was hermetically connected to a vial that was linked to a pump. A coating solution (2% (w/w) of OV-5 in dichloromethane) of 100 µL was then injected from the coating inlet and dynamically coated into the 3 m pchannel. The pump’s pulling mechanism ensures the coating solution to by-pass the pPID downstream. The coating rate was controlled by adjusting the voltage of the pump, which was set at 5 cm/min. The coating process was repeated 3 times. The pchannel was subsequently treated with HMDS after each coating and then baked at 180 °C for 1 hour prior to use. The coating solution was then drained...
into the vial and can be recycled for further usage. Finally, the guard column attached to the coating outlet was removed, and UV epoxy was applied to block the outlet.

After the μcolumn coating, the iCPID was affixed to a printed circuit board (PCB), and the integrated μPID and heater were wire-bonded. The heater had a resistance of 50 Ohms. Next, the insulated wedges were fitted into the designated slots in front of the microfluidic vias in the μPID as shown in the inset of Fig. 1 (B). Finally, a 10.6 eV VUV Kr lamp was assembled on top and hermetically secured by UV epoxy along the perimeter.

2.4. iCPID operation and characterization

Packaged iCPID was operated using a μGC system platform developed in our previous work [17] which was controlled by LabVIEW™ software developed in-house. A Keithley 2400 sourcemeter was used for alternating the bias voltage between μPID electrodes. The sensitivity evaluation was performed using an Agilent 6890 benchtop gas chromatography (GC) equipped with a thermal injector operated at 250 °C and in a split mode for controlling analyte injection amount. 99.999% Helium was used as the carrier gas with a flow rate of 3 mL/min. All measurements were done at room temperature with only guard columns for fluidic connections. The heater on iCPID was driven by 5-Hz pulse-width-modulation (PWM) through an NI DAQ card. A thermocouple was used to access the temperature measurement on chip.

3. Results and discussion

3.1. Characterization of iCPID VOC detection performance

As the integrated μPID on the iCPID device has the identical design as the glass substrate based stand-alone μPID [18,41], the latter is therefore used as a benchmark to evaluate iCPID’s sensitivity and is referred to as “benchmark μPID”. The benchmark μPID was shown to have a single-digit-picogram detection limit with approximately six orders of magnitude linear dynamic range up to 1000 ng [41]. As shown in Fig. 3 (A), to ensure an accurate comparison, the iCPID were fluidically connected in series after the benchmark μPID owing to its flow-through nature. The analytes flowed through the benchmark μPID first and then the μPID on the iCPID, and finally vented out through the μcolumn on the iCPID. Such arrangement eliminates any interference effects caused by the downstream integrated μcolumn (such as peak broadening) so that the intrinsic response of the integrated μPID on the iCPID can be revealed. As shown in Figure S2, the iCPID has the same peak shape as the benchmark μPID as expected. Fig. 3(B) depicts the comparison between the response (area under a peak) of the integrated μPID on the iCPID against the benchmark μPID. Using the unity line as the reference, the integrated μPID demonstrated a sensitivity similar to the benchmark μPID at lower injection masses (i.e., benchmark μPID peak area <1 V*s, equivalent to <1 ng) without any bias voltage dependence. However, at higher injection masses, the integrated μPID’s response was observed to be sublinear and the sublinearity became more pronounced with increasing bias voltages. The baseline noise remained similar (~1 mV) to the benchmark μPID (1.9 mV) at lower bias voltages (below 8 V) but increased superlinearly up to ~40 mV at high voltages, as shown in the inset of Fig. 3 (B). The cause of the deviated performances of the integrated μPID from the benchmark μPID was attributed to the BOX layer within the SOI that is presumed to be electrically insulated and could therefore divide the chip territory into three different regions: (A) the μcolumn with the integrated heater directly on its back, (B) part of the μcolumn without the integrated heater on its back, and (C) the μPID that does not have the integrated heater. Since the μPID region cannot be directly accessed by a thermocouple after packaging a VUV lamp on top, temperatures of an unpackaged iCPID at three different regions were simultaneously measured during temperature ramping using the integrated heater, as shown in Fig. 4(A). Both the measured and simulated temperature profiles indicate that the temperature at regions B and C ramps almost the same as region A (i.e., the μcolumn with a heater on its back). The difference is only a few °C at most, suggesting that the region of the μcolumn without a heater at the backside can be adequately heated for efficient separation, but at the cost of inevitable thermal crosstalk to the microfluidically integrated μPID.

3.2. Thermal crosstalk between integrated μPID and integrated heater on iCPID

Microfluidic integration introduces inherent thermal crosstalk between the integrated μPID and heater on μcolumn. First, the heat transfer in the iCPID was studied. As illustrated in Fig. 1 (B), the integrated heater only covers two thirds of the area of the iCPID chip. We can therefore divide the chip territory into three different regions: (A) part of the μcolumn with the integrated heater directly on its back, (B) part of the μcolumn without the integrated heater on its back, and (C) the μPID that does not have the integrated heater. Since the μPID region cannot be directly accessed by a thermocouple after packaging a VUV lamp on top, temperatures of an unpackaged iCPID at three different regions were simultaneously measured during temperature ramping using the integrated heater, as shown in Fig. 4(A). Both the measured and simulated temperature profiles indicate that the temperature at regions B and C ramps almost the same as region A (i.e., the μcolumn with a heater on its back). The difference is only a few °C at most, suggesting that the region of the μcolumn without a heater at the backside can be adequately heated for efficient separation, but at the cost of inevitable thermal crosstalk to the microfluidically integrated μPID.

To evaluate the impact of thermal crosstalk on the sensitivity of the
integrated µPID, we employed the same setup as in Fig. 3(A) while maintaining the benchmark µPID at room temperature as the control to calibrate the sensitivity change in the temperature-ramped iCPID. Fig. 4 (B) shows that the sensitivity of the integrated µPID remained relatively stable during the initial ramp phase (>92% up to 75 °C), which is in agreement with our previous report [41], before gradually decreasing to ~75% at 125 °C. This sensitivity reduction was reversible, i.e., the integrated µPID sensitivity returned to the normal level when the temperature went back to room temperature. The reduction in sensitivity at high temperatures can primarily be attributed to changes in the VUV photoionization source, including transmission and generation. First, the VUV lamp window’s short-wavelength transmittance limit (116 nm or 10.6 eV for MgF₂ in this case) red-shifts as it is heated [47,48], resulting in lower transmission for high-energy VUV photons available for photoionization. Second, VUV photon generation from plasma is an isometric process inside the VUV lamp housing. The temperature increase causes a higher pressure (per ideal gas law), resulting in more collisions and hence more de-excitation of the particles capable of emitting VUV photons.

3.3. Characterization of iCPID VOC separation performance

The separation performance of the iCPID was evaluated using the setup illustrated in Fig. 5(A) (note the µcolumn of iCPID was connected upstream in contrast to Fig. 3(A)). To compare the peak shape difference between on- and off-chip detection, an off-chip stand-alone µPID was connected to the outlet of the iCPID through a 20-cm guard column as interconnection. We selected the BTEX mixture (i.e., benzene, toluene, ethylbenzene, and p-xylene) as the model analytes. Note that as the off-chip stand-alone µPID was connected in series as the benchmarking for relative performance comparison to the on-chip µPID, the actual BTEX mixture concentrations were irrelevant and therefore were not calibrated (as long as they were kept in the linear region of µPID) for simplicity. The iCPID was operated isothermally at room temperature (i.e., without temperature ramp) to simulate a field operation scheme with low power consumption.

As shown in Fig. 5(B), BTEX were effectively separated by the 3-m OV-5 integrated µcolumn with height equivalents to theoretical plate (HETP) values of 3.5 mm (benzene), 3.0 mm (toluene), 2.6 mm (ethylbenzene), and 2.4 mm (p-xylene). The off-chip stand-alone µPID detected a similar chromatogram with broader peak width for each peak. For example, the inset of Fig. 5(B) shows that the on-chip detection rendered a toluene peak 0.6 s narrower in full-width-half-maximum (FWHM).
than the off-chip detection. The corresponding differences for benzene, ethylbenzene, and p-xylene are 0.7 s, 1 s, and 0.5 s, respectively. The peak broadening effect can be attributed to the 20-cm interconnecting guard column between the iCPID and off-chip µPID. These results manifest the advantage of microfluidic integration of µcolumn and µPID by eliminating transfer lines in between. The temperature ramped effect on peak width is examined in Figure S8. It is observed that both on-chip and off-chip detection peak widths decrease due to the increased column temperature on iCPID (from room temperature to 55 °C). However, the off-chip detection peak width is broadened 20–30% over the on-chip detection peak width.

For a further benchmarking comparison, the BTEX mixture was also separated using a commercial 3-m OV-5 column with off-chip µPID detection at room temperature (Figure S9). The HETP values of benzene (35.4 mm) and toluene (7.4 mm) in the commercial column were found to be significantly larger than those in iCPID due to broader peak widths in commercial columns. Additional full-width-half-maximum (FWHM) of 4 s and 3.4 s were observed for benzene and toluene peaks, respectively. However, the HETP values of ethylbenzene (2.2 mm) and p-xylene (1.8 mm) were similar to those in the iCPID as their respective retention times in the commercial column were much longer. Both the broader peak widths in the early two peaks and longer retention times in the latter two can be attributed to the thicker coating of the commercial column (0.25 µm) than the integrated µcolumn (~0.1 µm [49]). Table S3 summarizes the detailed characteristics of the commercial column and the iCPID with on- and off-chip detection.

3.4. Construction and characterization of an ultracompact µGC system based on iCPID

We built an ultracompact µGC system based on the iCPID, dubbed integrated cube (i.e., iCube). The components and fluidic diagram for the iCube along with its operation and photo are presented in Fig. 6(A) and (B). The iCube was constructed in a 3D-printed three-layered closed-box structure, featuring a top-down configuration wherein each layer accommodated specific components (Figure S5). The system consisted mainly of a stainless steel preconcentrator, an iCPID, a pump, an air filter, two microfabricated Y-connectors (for compactness), two 3-port valves, a set of four 5500 mAh rechargeable batteries and an in-house control circuit board. Components were fluidically interconnected using flexible Polytetrafluoroethylene (PTFE) tubes and guard columns. Bias voltage for iCPID was set to 6 V to optimize the signal to noise ratio of the system. To further minimize the noise, copper mesh shields were used inside the enclosure to cover the system and major electromagnetic interference (EMI)-prone electrical components. The total size of the iCube was 0.9 L (108 mm x 94 mm x 85 mm (length x width x height)) and weighed only 0.9 kg, including 0.45 kg batteries and associated electronics in a 0.34 L battery chamber.

For iCube operation, the analytes were sampled from a gas storage bag into the preconcentrator before backflush injection into the iCPID (see the red analyzing path). Ambient air, which was filtered through an inline filter to remove moisture and hydrocarbons, was used as the carrier gas at a flow rate of ~0.9 mL/min. The sampling rate of iCube was ~8 mL/min. Separation was conducted isothermally at room temperature, and the carrier gas was air filtered to reduce noise and hydrocarbons in the instrumental system. The repeatability tests were found to be excellent as shown in Fig. S12.
temperature (~22 °C). A representative chromatogram of a standard sample containing eight VOCs (listed in Table S1) is shown in Fig. 6(C), showing that separation can be completed within 100 s. Energy consumption of the iCube was 2.53 kJ per run assuming a 6-minute operation time, which led to an estimated total working cycle of 110 (Table S4). In practice, we performed a continuous repeated operation of the iCube for up to 20 cycles as shown in Figure S12. It was observed that after a ~4-cycle of “warm-up” operation (~10 minutes of warm-up time), the system maintained stable chromatographic performance (i.e., peak height, retention time, FWHM, etc.).

The iCube features some combined advantages of recent µGC systems and modules in a few aspects as listed in Table 1. Note that the term “monolithic” used in the table indicates partial integration between two or more discrete components but not entire system. First, the iCPID eliminates the use of interconnects between the column and the detector, resulting in easier manufacturing and assembly as well as reduction in overall system volume, and it also increases robustness of the fluidic connections and hence better overall system operational reliability compared to using all stand-alone microfabricated components in hybrid integration. In addition, microfluidic integration also eliminates the potential cold spots between the column and the detector, leading to narrower chromatographic peaks. Second, the iCube utilizes ambient air as carrier gas to avoid the need for a helium cartridge, which inevitably narrows chromatographic peaks. Third, the iCube utilizes batteries, which further improves its mobility. Note that the battery set actually increases the footprint, weight, and maintenance effort (as carrier gas to avoid the need for a helium cartridge, which inevitably narrows chromatographic peaks). Second, the iCube utilizes ambient air as carrier gas to avoid the need for a helium cartridge, which inevitably narrows chromatographic peaks. Third, the iCube utilizes batteries, which further improves its mobility. Note that the battery set actually increases the footprint, weight, and maintenance effort.

4. Conclusion

This article presents a microfluidically integrated photoionization detector (µPID) on a microfabricated gas chromatography (µGC) column. The parallel-plate silicon electrodes of the µPID and the µcolumn were monolithically fabricated via wafer-level batch processing on an SOI platform, realizing microfluidic integration between the µPID and µcolumn which were previously connected off-chip through hybrid integration. The integrated chip enables an ultracompact (0.9 L and 0.9 kg), fully automated, and battery-operated µGC system. Rapid separation of eight volatile organic compounds (VOCs) in ~2 min at room temperature was demonstrated. Future work includes modified processes that can resolve the leakage in BOX, better thermal management on-chip, and new device architectures that can incorporate pre-concentrators to realize “all-in-one” monolithic µGC platform. Such integration schemes are also possible to be applied to multi-dimensional µGC architectures with integrated modulators on the same chip.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The photoionization detector (PID) technology used in the article is licensed to Nanova, RUA Diagnostics, and ChromX Health. Hongbo Zhu and Xudong Fan are the co-inventors of this technology and have financial interest in the above companies. Xudong Fan also serves as a paid or unpaid consultant to these companies.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2024.135717.

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