



# Microfluidic integration of $\mu$ PID on $\mu$ column for ultracompact micro-gas chromatography

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## ABSTRACT

Microfabricated gas chromatography ( $\mu$ GC) offers a powerful portable vapor analysis solution for various field applications. Here, we developed a microfluidically integrated architecture of a microfluidic photoionization detector ( $\mu$ PID) on a microfabricated column ( $\mu$ column) 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  $\mu$ PID. 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  $\mu$ GC 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 ( $\mu$ GC) [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  $\mu$ GC 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  $\mu$ GC 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  $\mu$ GC. Consequently, monolithically integrated  $\mu$ GC has been pursued, with a focus on integrating separation micro-columns ( $\mu$ columns) and respective detectors on a single chip [11,30–36]. Table 1 compares recent  $\mu$ GC 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  $\mu$ GC 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  $\mu$ columns owing to their micro-fabrication 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,  $\mu$ GC integrated with a micro helium discharge photoionization detector ( $\mu$ DPID) showed rapid separation and detection of alkanes and aromatics with a detection limit of 10 pg [32,33]. However, the  $\mu$ DPID requires a separate high-purity helium cartridge as an auxiliary flow during operation, which inevitably increases the footprint and weight of the entire system, and requires constant maintenance for cartridge replacement, thus 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  $\mu$ GC. Although the lower VUV photon energies generated from the VUV lamp (10.6 eV for Krypton 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  $\mu$ GC 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  $\mu$ DPID [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  $\mu$ GC integration. Zhu et al. and Li et al. developed a lamp-based microfluidic PID ( $\mu$ PID) with rapid response and high sensitivity. This  $\mu$ PID 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  $\mu$ GC integration. Very recently, a lamp-based PID (arrayed integrated photoionization

detector, AiPD) using coplanar metal sensing electrodes has also been explored in an attempt for integration with  $\mu$ columns [16]. In the  $\mu$ DPID- $\mu$ column work [32,33], the microfabrication process for monolithically integrating the  $\mu$ DPID and  $\mu$ column, 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  $\mu$ columns [32,33]. Similarly, the AiPD- $\mu$ column 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  $\mu$ DPID 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  $\mu$ PID 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  $\mu$ PID and  $\mu$ column while maintaining electrical isolation.

Here, we developed an integrated  $\mu$ GC architecture based on a silicon-on-insulator (SOI) structure that enables monolithic integration of the parallel-plate silicon electrodes on  $\mu$ column with an on-chip heater, realizing microfluidic integration of a VUV lamp based  $\mu$ PID 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  $\mu$ column and  $\mu$ PID (i.e., iCPID). It is shown that at lower injection masses (<10 ng), the iCPID maintained a sensitivity similar to the stand-alone  $\mu$ PID [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  $\mu$ PID due to the monolithic integration. Finally, an ultracompact, fully-automated,

**Table 1**  
Comparison of  $\mu$ GC systems and modules.

$\mu$ GC integration	Monolithic or hybrid	System or module	System size and weight	Battery- or wall-powered	Carrier gas	Detector	Microfabricated components and their integration
Grag et al. [34]	Monolithic	1D system	4.5 L and 1.8 kg	Battery	Helium	TCD	Precon., TCD integrated on column
Akbar et al. [32]	Monolithic	1D module	N/A*	N/A	Helium	$\mu$ DPID	Sampling loop, $\mu$ DPID integrated on column
Qin et al. [2]	Hybrid	1D module	N/A	N/A	Air**	Capacitive detector	Pump, precon., column, and capacitive detector
Liao et al. [16]	Monolithic	1D system	4.8 L, no weight reported	Battery	Air**	Capacitive detector and AiPD	Precon., column, AiPD and capacitive detector integrated using epoxy gluing on the same chip
Wang et al. [3]	Hybrid	1D system	2.7 L and 2.1 kg (sans battery)	Battery	Helium	Chemiresistor array	Precon., column, and chemiresistor array
Collin et al. [12]	Hybrid	1D system	12.4 L and 5.4 kg	Wall	Air**	Chemiresistor array	Precon., column, and chemiresistor array
Li et al. [18]	Hybrid	1D system	6.5 L, no weight reported	Wall	Helium	$\mu$ PID	Column and $\mu$ PID
Collin et al. [37]	Hybrid	2D module	N/A	N/A	Helium	Benchtop FID	Thermal modulator, columns
Whiting et al. [38]	Hybrid	2D module	N/A	N/A	Helium	Benchtop FID	Pneumatic modulator, columns
Lee et al. [20]	Hybrid	2D system	30 L and 5 kg	Wall	Helium	$\mu$ PID	Precon., column, Deans switch, and $\mu$ PID
Huang et al. [17]	Monolithic	2D system	8.4 L and 2.4 kg	Wall	Helium	$\mu$ PID	1D column, pneumatic modulator integrated on 2D column, $\mu$ PID
Zampolli et al. [25]	Hybrid	1D system	0.72 L (GC/PID), no weight reported	Wall	Helium (TCD); air (PID)**	TCD and PID	Precon., injector, column, TCD
You et al. [21]	Hybrid	1D system	15.7 L and 5 kg (sans battery)	Battery	Air**	PID	No microfabricated components
This work	Monolithic	1D system	0.9 L and 0.9 kg***	Battery	Air**	iCPID	iCPID (integrated column and $\mu$ PID)

\* 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  $\mu$ GC 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 $\mu$ column and $\mu$ 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  $\mu$ PID (in the device layer) resides on top of the  $\mu$ column (in the handle layer). At the inlet and outlet of the  $\mu$ PID, there are two etched-through vertical pass-through holes that termed as “microfluidic vias”. The first one connects the upstream  $\mu$ column (in the handle layer) to the  $\mu$ PID (in the device layer) and the second one is routed towards the outlet of the iCPID (in the handle layer). The  $\mu$ PID and  $\mu$ column are electrically isolated by the buried oxide (BOX) on SOI. A glass layer is anodically bonded to the SOI to seal the  $\mu$ column. The heater of  $\mu$ column is patterned on top the device layer of the SOI with an additional layer of  $\text{SiO}_2$  to provide electrical isolation. A VUV lamp (Krypton for 10.6 eV or Argon for 11.7 eV) is hermetically mounted on the  $\mu$ 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”.

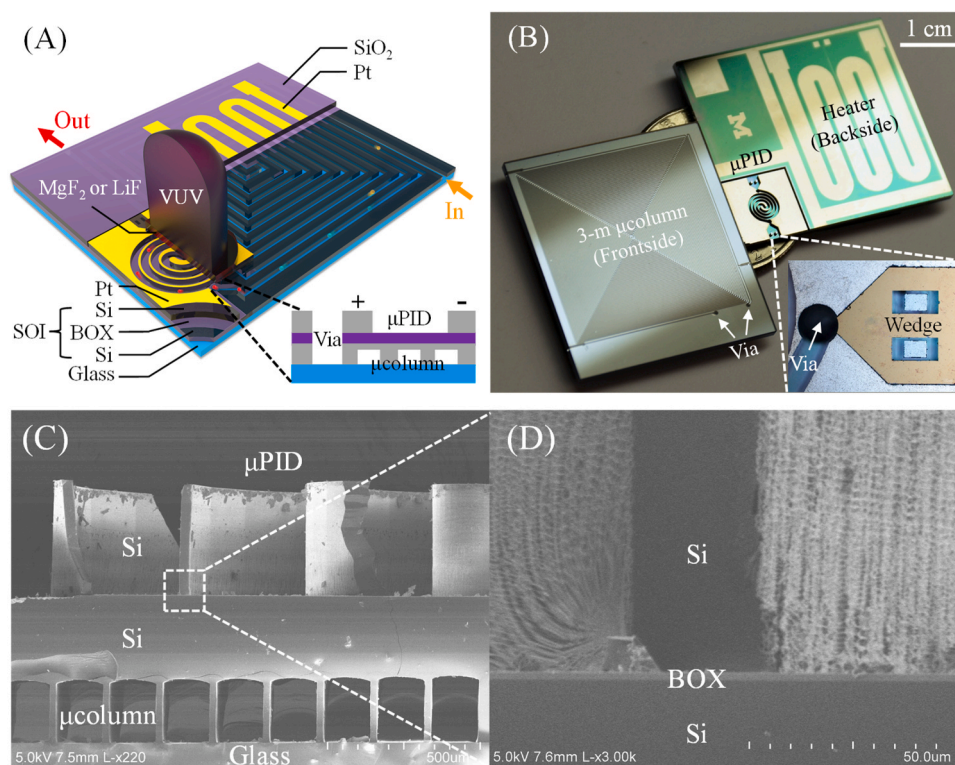
During operation, the gas mixture enters the inlet of the iCPID, and is subsequently separated by the  $\mu$ column whose temperature is ramped by the integrated heater. Towards the end of the  $\mu$ column, the separated

molecules flow up through the microfluidic via and are then detected by the  $\mu$ 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  $\mu$ PID to be stacked directly on the  $\mu$ column while avoiding any interconnection in between. It also takes advantage of flow-through and nondestructive nature of the  $\mu$ PID, which allows for further downstream analysis (such as connecting the outlet of the iCPID to a 2nd-dimensional column [17]).

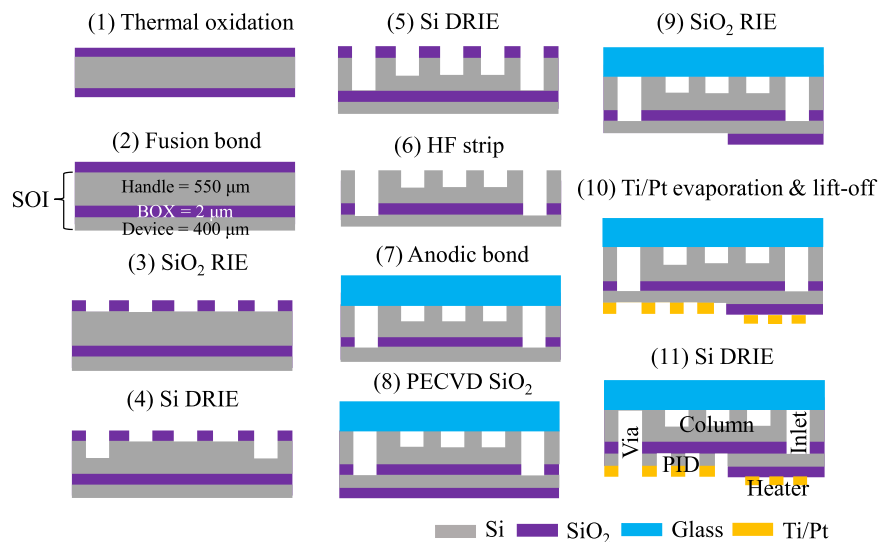
## 2. Experimental

### 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  $\mu\text{m}$  thick, double-side polished Si wafers ( $<100>$ , p-type, 0.001–0.005  $\Omega\cdot\text{cm}$  and  $<100>$ , p-type, 1–10  $\Omega\cdot\text{cm}$ ) were purchased from Ultrasil LLC. 550  $\mu\text{m}$  Borofloat 33 glass (P/N 517) were purchased from UniversityWafer. A 10.6 eV VUV Kr lamp with a  $\text{MgF}_2$  window was purchased from Mocon-baseline (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. Carboxypacks 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. 1.** (A) Architecture of the microfluidically integrated  $\mu$ column and  $\mu$ PID (iCPID) device. The iCPID is constructed on a silicon-on-insulator (SOI) platform, where the device layer consists of a  $\mu$ PID and a heater for  $\mu$ column heating, while the handle layer comprises a  $\mu$ column capped with a glass layer. Zoom-in vertical structure shows that etched-through vertical microfluidic vias fluidically connect the  $\mu$ column and  $\mu$ PID, while buried oxide (BOX) electrically isolates them. A vacuum ultraviolet (VUV) lamp (with a  $\text{MgF}_2$  or  $\text{LiF}$  window) is hermetically packaged on the  $\mu$ PID using epoxy. The gas inlet and outlet are indicated. (B) Photograph of iCPIDs (left: 3-m  $\mu$ column side up; right:  $\mu$ PID and heater side up). Inset shows an insulated silicon wedge filling up the etched-through channel opening at the inlet and outlet of the  $\mu$ PID to prevent exposure to epoxy during packaging. The holes of the wedge are aligned with the standing posts of the  $\mu$ PID to ensure proper alignment. (C) Scanning electron microscopy (SEM) of a cross-section of the iCPID featuring microfluidically integrated  $\mu$ PID on  $\mu$ column. (D) Zoom-in view of the SOI structure.



**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 layer was patterned via photolithography and RIE to create a hard mask for the  $\mu\text{column}$ , inlets, and pass-through microfluidic vias. (4) The inlets and pass-through vias were etched with DRIE while the  $\mu\text{column}$  was protected with photoresist. (5) After stripping the photoresist, DRIE was continued using the oxide hard mask to etch the  $\mu\text{column}$  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  $\mu\text{column}$ . (8) Plasma-enhanced chemical vapor deposition (PECVD) was used to deposit a layer of SiO<sub>2</sub> on the device layer. (9) Photolithography was used to define the  $\mu\text{PID}$  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  $\mu\text{PID}$  electrodes and  $\mu\text{column}$  heater simultaneously. (11) Patterned photoresist was used as a mask for the DRIE on the device layer to generate the  $\mu\text{PID}$ . The  $\mu\text{PID}$  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<sub>2</sub> plasma treatment on the bonding side of both wafers, a 400  $\mu\text{m}$  thick, double-side polished Si wafer (<100>, p-type, 0.001–0.005  $\Omega\cdot\text{cm}$ ) was fusion bonded [42] to a 550  $\mu\text{m}$  thick, double-side polished Si wafer (<100>, p-type, 1–10  $\Omega\cdot\text{cm}$ ) with 2  $\mu\text{m}$  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  $\mu\text{column}$  (3 m in length x 150  $\mu\text{m}$  in width with 30  $\mu\text{m}$  thick walls), inlets (400  $\mu\text{m}$  in width), and pass-through microfluidic vias (550  $\mu\text{m}$  in diameter). Next, photolithography was used to selectively expose the inlets and pass-through vias for a deep reactive-ion etching (DRIE) etch of  $\sim 150$   $\mu\text{m}$  in depth. The photoresist was then stripped and DRIE continued with the hard mask to simultaneously etch the  $\mu\text{column}$  to a final depth of 250  $\mu\text{m}$  while the inlets and pass-through vias were etched to the buried oxide layer (BOX), which serves as the etch-stop, with the final depth of 400  $\mu\text{m}$ . After stripping the thermal oxide and BOX on the pass-through vias with HF, the handle layer was anodically bonded [43] to a 550  $\mu\text{m}$  thick borofloat glass wafer to seal the  $\mu\text{column}$  after piranha-cleaned. Next, 1  $\mu\text{m}$  of SiO<sub>2</sub> was deposited on the device layer by plasma-enhanced chemical vapor deposition (PECVD) and photolithography was used to define the  $\mu\text{PID}$  electrodes where the oxide is etched by RIE for depositing Pt thin films to form ohmic contact on the silicon electrodes and isolate the  $\mu\text{PID}$  from the rest of the device layer (with PECVD oxide). The defined area is shown in Fig. 1(B) where  $\mu\text{PID}$ '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  $\mu\text{PID}$  electrodes and  $\mu\text{column}$  heater simultaneously. Finally, photoresist was used as a mask for the DRIE on the device layer to generate the  $\mu\text{PID}$  (400  $\mu\text{m}$  wide

channels in an Archimedean spiral with 40  $\mu\text{m}$  thick walls and a length of 3.2 cm). The  $\mu\text{PID}$  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 hermetically packaging the VUV lamp on the integrated  $\mu\text{PID}$  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  $\mu\text{m}$  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<sub>2</sub> 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  $\mu\text{column}$  in the iCPID is illustrated 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  $\mu\text{column}$  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  $\mu\text{L}$  was then injected from the coating inlet and dynamically coated into the 3 m  $\mu\text{column}$ . The pump's pulling mechanism ensures the coating solution to bypass the  $\mu\text{PID}$  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  $\mu\text{column}$  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  $\mu$ column coating, the iCPID was affixed to a printed circuit board (PCB), and the integrated  $\mu$ PID 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  $\mu$ PID 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

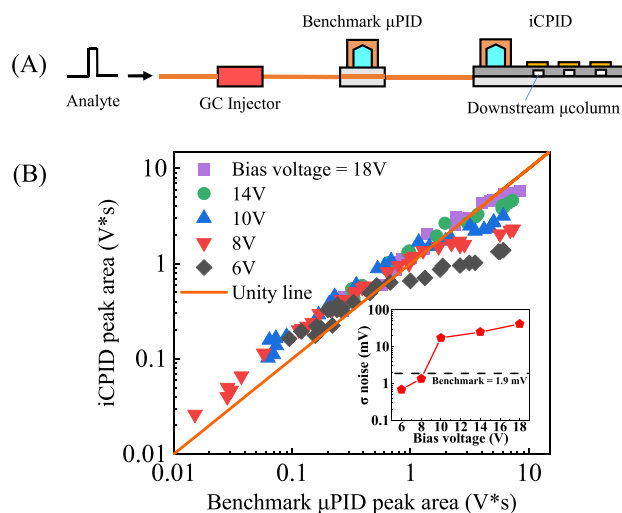
Packaged iCPID was operated using a  $\mu$ GC system platform developed in our previous work [17] which was controlled by LabVIEW<sup>TM</sup> software developed in-house. A Keithley 2400 sourcemeter was used for alternating the bias voltage between  $\mu$ PID electrodes. The sensitivity evaluation was 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  $\mu$ PID on the iCPID device has the identical design as the glass substrate based stand-alone  $\mu$ PID [18,41], the latter is therefore used as a benchmark to evaluate iCPID's sensitivity and is referred to as "benchmark  $\mu$ PID". The benchmark  $\mu$ PID 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  $\mu$ PID owing to its flow-through nature. The analytes flowed through the benchmark  $\mu$ PID first and then the  $\mu$ PID on the iCPID, and finally vented out through the  $\mu$ column on the iCPID. Such arrangement eliminates any interference effects caused by the downstream integrated  $\mu$ column (such as peak broadening) so that the intrinsic response of the integrated  $\mu$ PID on the iCPID can be revealed. As shown in Figure S2, the iCPID has the same peak shape as the benchmark  $\mu$ PID as expected. Fig. 3(B) depicts the comparison between the response (area under a peak) of the integrated  $\mu$ PID on the iCPID against the benchmark  $\mu$ PID. Using the unity line as the reference, the integrated  $\mu$ PID demonstrated a sensitivity similar to the benchmark  $\mu$ PID at lower injection masses (*i.e.*, benchmark  $\mu$ PID peak area < 1 V\*s, equivalent to < 1 ng) without any bias voltage dependence. However, at higher injection masses, the integrated  $\mu$ PID's response was observed to be sublinear and the sublinearity became more pronounced with decreasing bias voltages. The baseline noise remained similar (~1 mV) to the benchmark  $\mu$ PID (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  $\mu$ PID from the benchmark  $\mu$ PID was attributed to the BOX layer within the SOI that is presumed to be electrically insulated became leaky after fusion bonding [44] (see Section S3 for details). The leakage reduces the effective electric field generated by the parallel plates to efficiently capture the generated ions within the photoionization chamber, particularly at a high analyte concentration and a low bias voltage, and meanwhile, increases the noise when the bias voltage is high (>10 V).

In practice, the integrated  $\mu$ PID on the iCPID should therefore be operated at low bias voltages (*e.g.*, 6–10 V), which can still achieve low



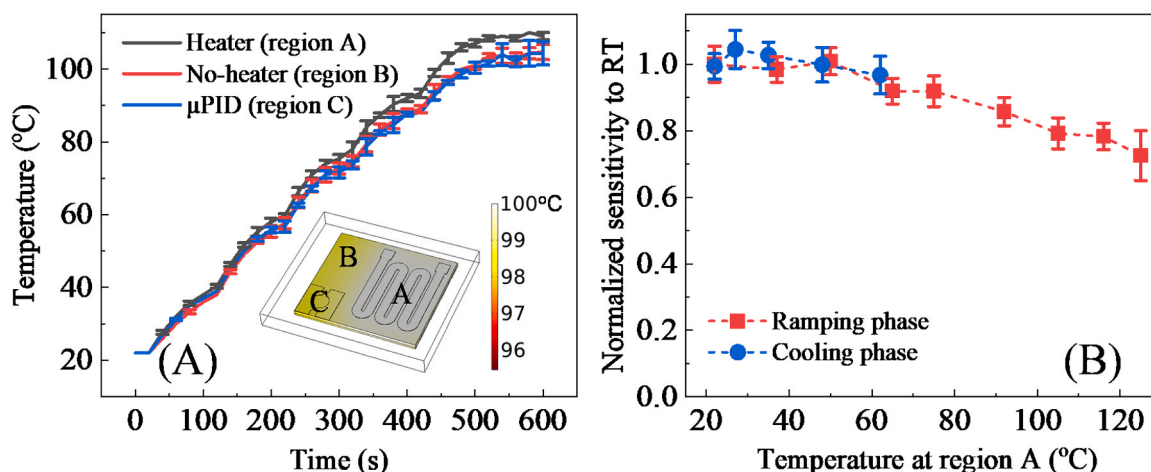
**Fig. 3.** (A) Setup to evaluate the performance of the integrated  $\mu$ PID on iCPID using a stand-alone glass substrate based  $\mu$ PID [41] as benchmark (biased constantly at 24 V). The test analyte (benzene) was injected via a bench-top GC injector. The flow-through benchmark  $\mu$ PID was connected in series with iCPID with  $\mu$ column downstream. Note that in this particular setup, the analyte entered the integrated  $\mu$ PID on iCPID before reaching the  $\mu$ column on iCPID to avoid any effects caused by the  $\mu$ column. Helium was used as the carrier gas with a flow rate of 3 mL/min. (B) Log-log plot of iCPID peak area (biased from 6 to 18 V) as a function of benchmark  $\mu$ PID peak area. Each data point represents the respective responses of iCPID and benchmark  $\mu$ PID to the same single injection. The peak area of the benchmark  $\mu$ PID, ranging from 0.01 to 10 V\*s, was calibrated to be associated with an injection mass of 0.13 ng to 130 ng, which falls within its linear response regime [41]. The inset in (B) depicts the one sigma noise of iCPID biased at different voltages. The black dashed line indicating the noise level of the benchmark  $\mu$ PID measured concurrently.

noise levels with a single digit picogram detection limit and good linearity at low analyte concentrations. At higher analyte concentrations, its sublinear response requires pre-calibration by a benchmark detector prior to use when quantitative measurement is desired. For future iterations of the iCPID, alternative microfabrication processes that produce SOI wafers with truly insulated BOX, such as separation by implantation of oxygen (SIMOX) [45,46], are worth exploring.

#### 3.2. Thermal crosstalk between integrated $\mu$ PID and integrated heater on iCPID

Microfluidic integration introduces inherent thermal crosstalk between the integrated  $\mu$ PID and heater on  $\mu$ column. 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  $\mu$ column with the integrated heater directly on its back, (B) part of the  $\mu$ column without the integrated heater on its back, and (C) the  $\mu$ PID that does not have the integrated heater. Since the  $\mu$ PID 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  $\mu$ column with a heater on its back). The difference is only a few °C at most, suggesting that the region of the  $\mu$ column 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  $\mu$ PID.

To evaluate the impact of thermal crosstalk on the sensitivity of the



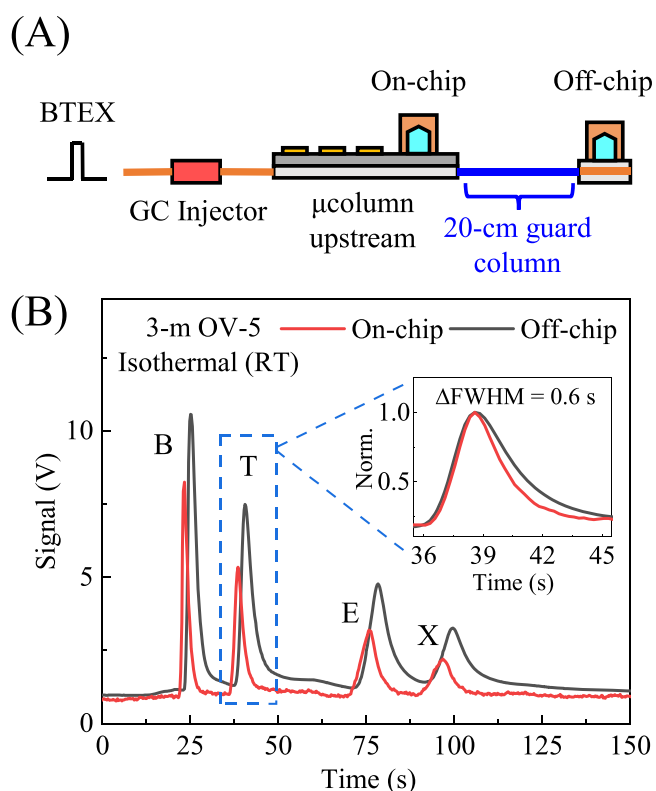
**Fig. 4.** (A) Measured temperature ramping profiles at the  $\mu$ column with (A) and without (B) the integrated heater, and  $\mu$ PID (C). The inset displays a simulated temperature profile of the iCPID with the integrated heater set to 100 °C (see S3 in the Supplemetry Information for simulation details). (B) Normalized sensitivity (relative to room temperature) of the integrated  $\mu$ PID as a function of the temperature measured at region A on the chip during both ramping and cooling phases, respectively. Error bars were obtained from three measurements.

integrated  $\mu$ PID, we employed the same setup as in Fig. 3(A) while maintaining the benchmark  $\mu$ PID 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  $\mu$ PID 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  $\mu$ PID 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  $\text{MgF}_2$  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  $\mu$ column 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  $\mu$ PID 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  $\mu$ PID was connected in series as the benchmarking for relative performance comparison to the on-chip  $\mu$ PID, the actual BTEX mixture concentrations were irrelevant and therefore were not calibrated (as long as they were kept in the linear region of  $\mu$ PID) 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  $\mu$ column 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  $\mu$ PID 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)



**Fig. 5.** (A) Setup to evaluate the separation performance of the 3-m OV-5 integrated  $\mu$ column on the iCPID using on-chip integrated  $\mu$ PID and off-chip benchmark  $\mu$ PID. The BTEX mixture was injected via a bench-top GC injector. The integrated  $\mu$ column was fluidically connected upstream and operated isothermally at room temperature. 20-cm guard column was used as the in-series fluidic interconnection between the iCPID and the off-chip stand-alone  $\mu$ PID. Helium was used as the carrier gas with a flow rate of 1 mL/min. (B) Chromatograms of BTEX generated using the iCPID and the off-chip benchmark  $\mu$ PID. The inset shows the zoom-in view of normalized toluene peaks detected by on-chip and off-chip  $\mu$ PIDs, respectively. The retention times (peak apexes) are aligned with each other for clarity.

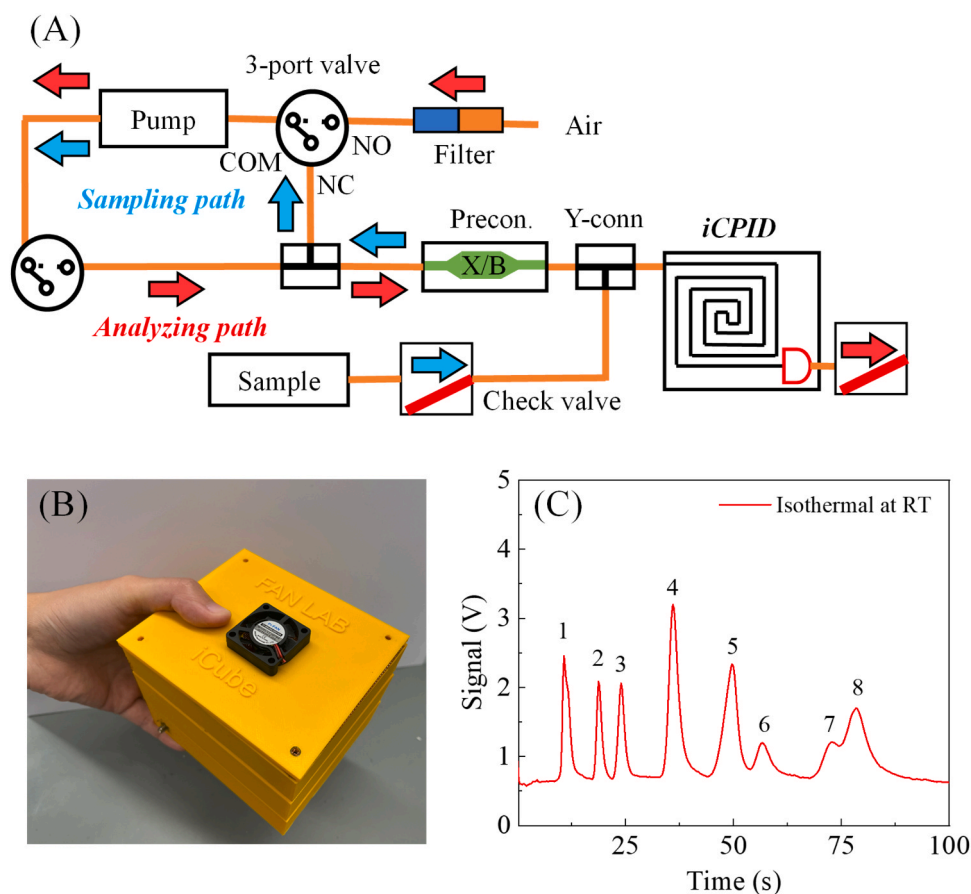
than the off-chip detection. The corresponding differences for benzene, ethylbenzene, and p-xylene are 0.7 s, 1 s, and 0.5 s, respectively. The peak broadening effect can be attributed to the 20-cm interconnecting guard column between the iCPID and off-chip  $\mu$ PID. These results manifest the advantage of microfluidic integration of  $\mu$ column and  $\mu$ PID 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  $\mu$ PID 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  $\mu$ m) than the integrated  $\mu$ column ( $\sim$ 0.1  $\mu$ m [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 $\mu$ GC system based on iCPID

We built an ultracompact  $\mu$ GC 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  $\times$  94 mm  $\times$  85 mm (length  $\times$  width  $\times$  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  $\sim$ 0.9 mL/min. The sampling rate of iCube was  $\sim$ 8 mL/min. Separation was conducted isothermally at room



**Fig. 6.** (A) System schematic of the ultracompact  $\mu$ GC device, named integrated Cube (*i.e.*, iCube). X and B: Carboxypack X and B. COM: common; NO: normally-open; NC: normally-closed; the sampling and analyzing path are indicated by blue and red arrows respectively. (B) Photograph of the iCube that occupies 0.9 L and weighs 0.9 kg. (C) Chromatogram of (1) acetone, (2) benzene, (3) heptane, (4) toluene, (5) octane, (6) butyl acetate, (7) ethylbenzene, and (8) xylene generated by the iCube. Filtered air was used as the carrier gas with a flow rate of 0.9 mL/min. Separation was conducted isothermally at 22 °C. Repeatability tests can be found in Fig. S12.

temperature ( $\sim 22^\circ\text{C}$ ). 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  $\sim 4$ -cycle of “warm-up” operation ( $\sim 10$  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  $\mu\text{GC}$  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 iCIPID 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 increases the footprint, weight, and maintenance effort (i.e., replacing cartridges) of the entire system. Third, the iCube utilizes batteries, which further improves its mobility. Note that the battery set actually occupied one third of the total weight and volume of the iCube. Further reducing them to a smaller footprint without sacrificing the power specifications can result in an even more compact system.

#### 4. Conclusion

This article presents a microfluidically integrated photoionization detector ( $\mu\text{PID}$ ) on a microfabricated gas chromatography ( $\mu\text{GC}$ ) column. The parallel-plate silicon electrodes of the  $\mu\text{PID}$  and the  $\mu\text{column}$  were monolithically fabricated via wafer-level batch processing on an SOI platform, realizing microfluidic integration between the  $\mu\text{PID}$  and  $\mu\text{column}$  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  $\mu\text{GC}$  system. Rapid separation of eight volatile organic compounds (VOCs) in  $\sim 2$  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 preconcentrators to realize “all-in-one” monolithic  $\mu\text{GC}$  platform. Such integration schemes are also possible to be applied to multi-dimensional  $\mu\text{GC}$  architectures with integrated modulators on the same chip.

#### CRedit authorship contribution statement

**Xiaheng Huang:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Shuo Yang:** Writing – original draft, Formal analysis, Data curation, Conceptualization. **Wencheng Li:** Writing – original draft, Formal analysis, Data curation. **Robert Nidetz:** Writing – original draft, Methodology, Data curation. **Ruchi Sharma:** Writing – original draft, Data curation. **Anjali Devi Sivakumar:** Writing – original draft, Formal analysis, Data curation. **Chandrakalavathi Thota:** Writing – original draft, Formal analysis, Data curation. **Hongbo Zhu:** Conceptualization. **Weishu Wu:** Writing – original draft, Data curation. **Seong-Yong Jeong:** Data curation. **Xudong Fan:** Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

#### 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](https://doi.org/10.1016/j.snb.2024.135717).

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**Supplementary Material to**  
**Microfluidic integration of  $\mu$ PID on  $\mu$ column**  
**for ultracompact micro-gas chromatography**

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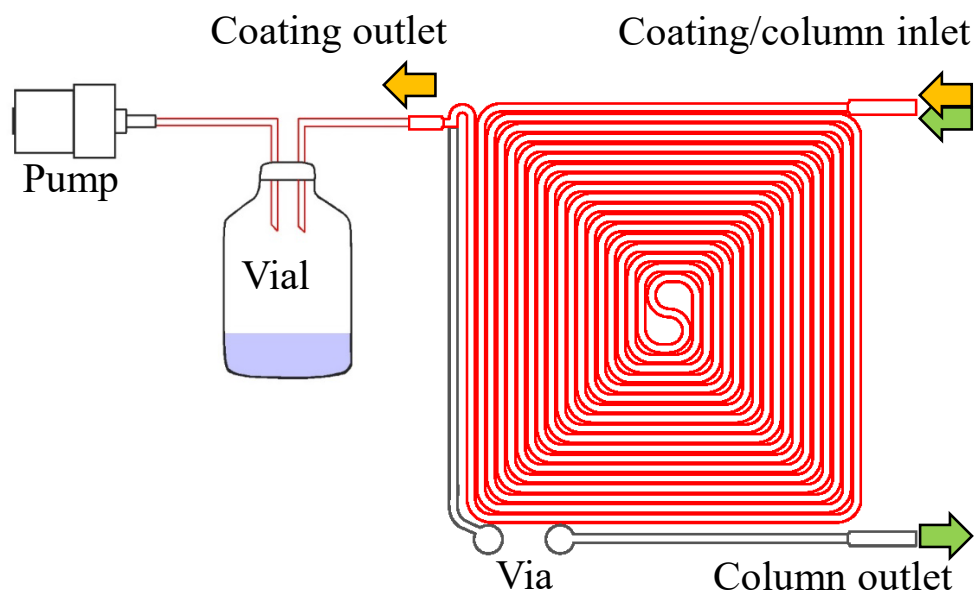
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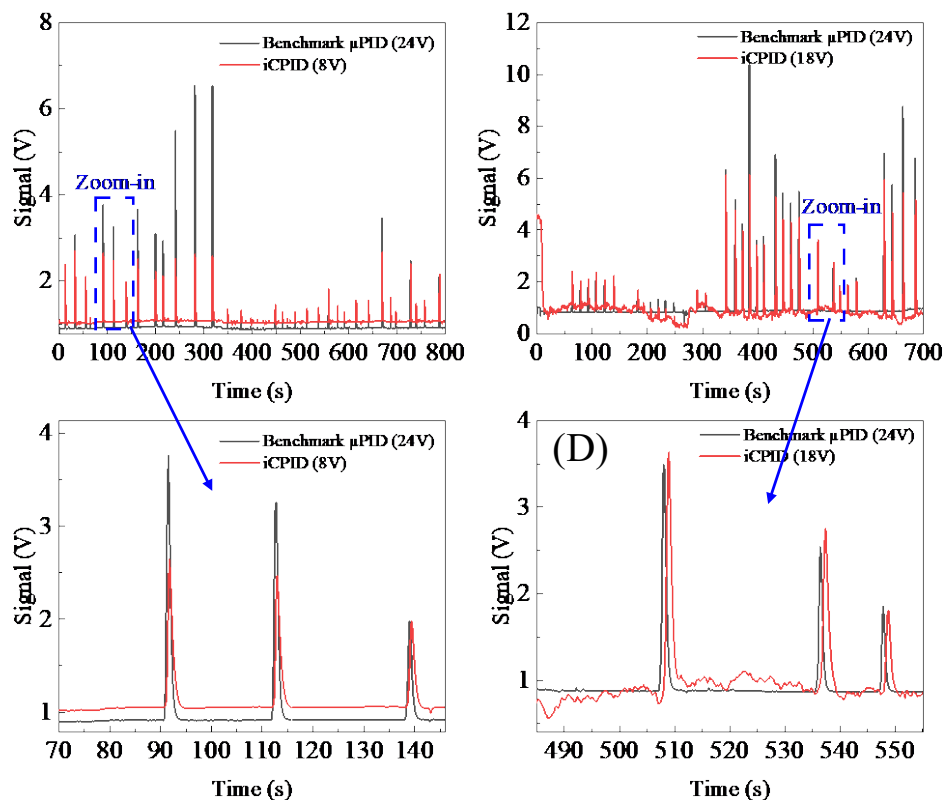
### S1. Integrated $\mu$ column coating procedure



**Figure S1.** Coating procedure for integrated  $\mu$ column on the iCPID. The coating solution (yellow arrows) was pulled by a voltage-controlled pump into the  $\mu$ column inlet and routed into the coating outlet where it then flowed into an empty vial. The red-colored region indicates the channels that are coated. Note that the green arrows indicate the gas inlet and outlet during actual iCPID operation.



## S2. Comparison between the integrated $\mu$ PID on iCPID and the benchmark $\mu$ PID

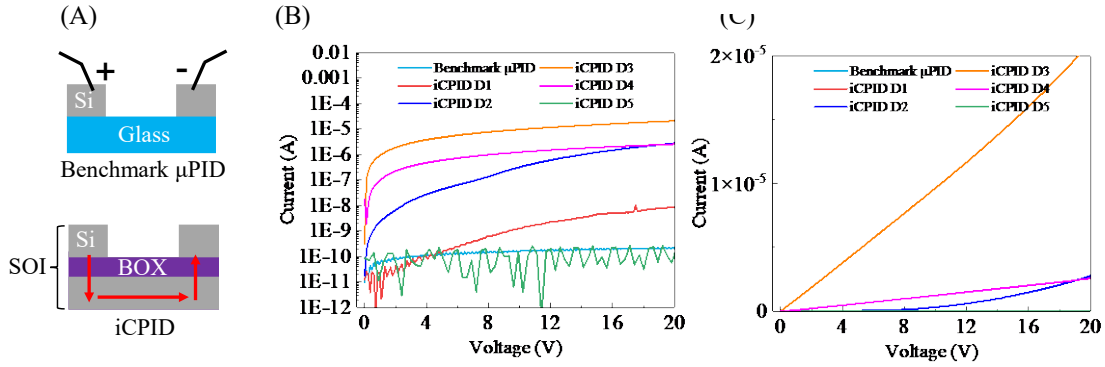


**Figure S2.** Chromatograms of the integrated  $\mu$ PID on the iCPID biased at (A) 8 V and (B) 18 V when connected in series with a benchmark  $\mu$ PID (biased at 24 V). (C) and (D) are zoom-in portions of (A) and (B). The chromatograms were generated by consecutive injections of different amounts of benzene using the setup shown in Figure 3(A) in the main text.

### S3. Cause of the leaky buried oxide (BOX) in iCPID

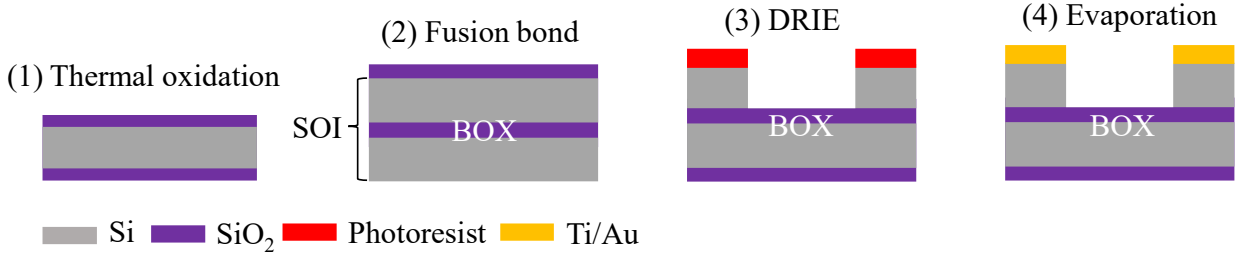
This section discusses in detail the cause of the sublinear response of the integrated  $\mu$ PID. Figure S3(A) shows the simplified device structure of the benchmark  $\mu$ PID (or glass substrate based  $\mu$ PID), which consists of two conductive silicon electrodes forming a microfluidic channel on top of an insulating glass substrate. On the other hand, the integrated  $\mu$ PID (iCPID) adopts an SOI structure where the buried oxide (BOX) serves as an insulating layer to mimic the glass substrate of the benchmark  $\mu$ PID.

To investigate the cause of the distinctive features of the integrated  $\mu$ PID, we performed current-voltage measurement to compare its intrinsic electrical characteristics with those of the benchmark  $\mu$ PID. As shown in Figure S3, it was found that most integrated  $\mu$ PID exhibited a leakage current ranging from 10 nA to 100  $\mu$ A at 20 V, whereas the benchmark  $\mu$ PID showed a constant current of 100 pA across a bias voltage from 0 to 20 V. Out of five devices constructed from two wafers, only one device (*i.e.*, iCPID D5) had an identical low and consistent current in I-V, enabling it to exhibit the same linearity as the benchmark  $\mu$ PID. The remaining four iCPIDs exhibited varying degrees of leaky I-V characteristics compared to the benchmark  $\mu$ PID. The benchmarking calibration curves presented in Figure 3 were measured using iCPID D1, which has a leaky current of up to 10 nA at 20 V and serves as a representative. The other leaky iCPIDs (*i.e.*, D2 to D4) also exhibited similar sublinear responses to concentrations.

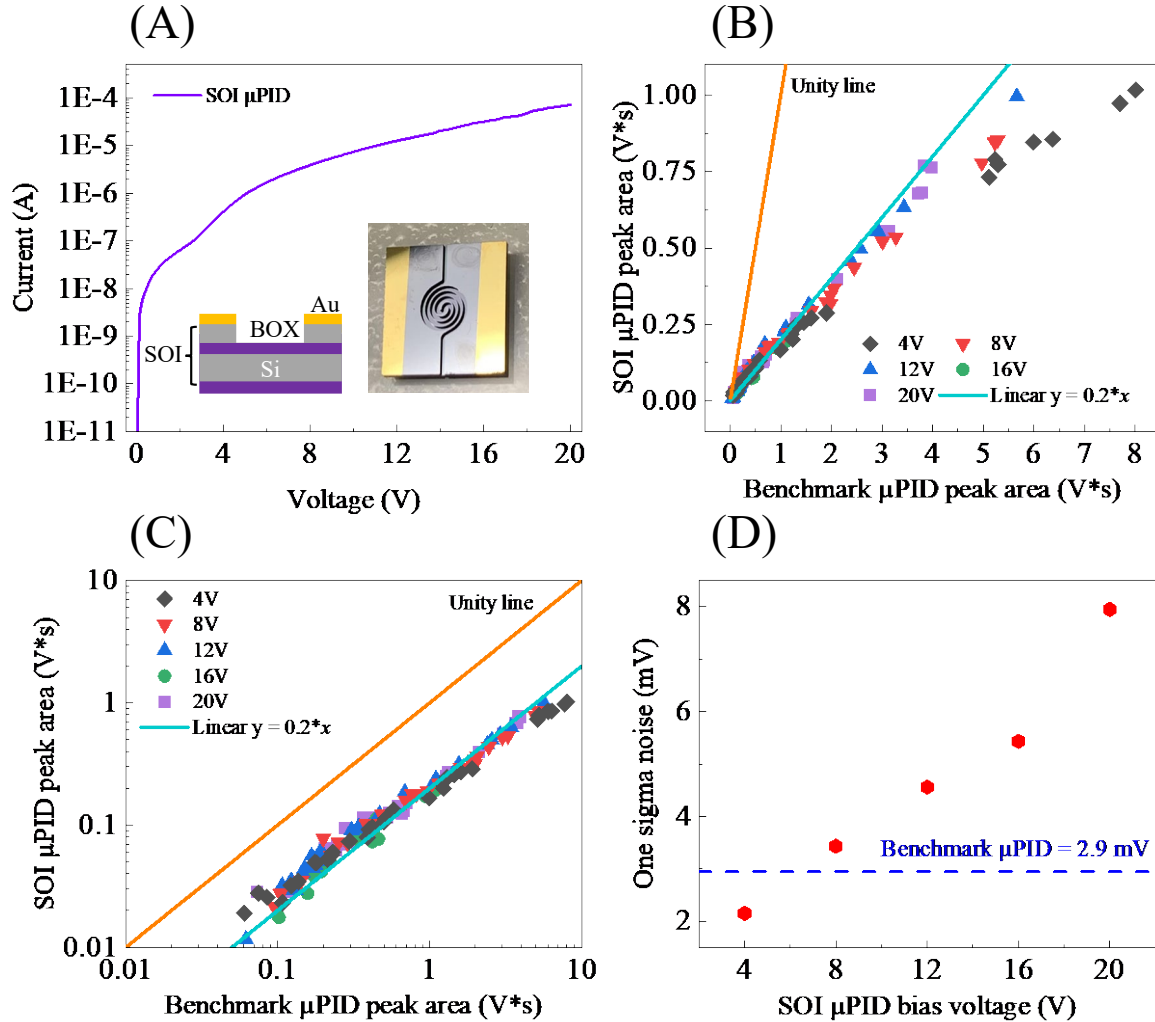


**Figure S3.** (A) Device structures of a benchmark  $\mu$ PID<sup>2,5</sup> and an integrated  $\mu$ PID within the iCPID. (B) Semi-log scale and (C) Linear-linear scale of current-voltage (I-V) characteristics of a benchmark  $\mu$ PID, and five different iCPIDs. All devices were packaged microfluidically and electrically.

To investigate the possible role of BOX in the aforementioned electrical leakage. We fabricated a stand-alone SOI  $\mu$ PID (without  $\mu$ column integration to eliminate any impact from the additional process steps). The microfabrication process (see Figure S4) was identical to a benchmark  $\mu$ PID. The only difference was the substitution of the glass substrate for an oxidized silicon wafer, which was bonded using fusion bonding. Figure S5 presents the I-V characteristics and sensing performance of a stand-alone SOI  $\mu$ PID. Similar to most of the leaky iCPIDs, this stand-alone SOI  $\mu$ PID had a high leakage current of up to 100  $\mu$ A at 20 V, resulting in 5-fold reduction in sensitivity and bias voltage dependent sublinear responses. These results suggest that the BOX within the SOI based  $\mu$ PID structure experienced leakage after fabrication, which caused sensitivity reduction and sublinear response.

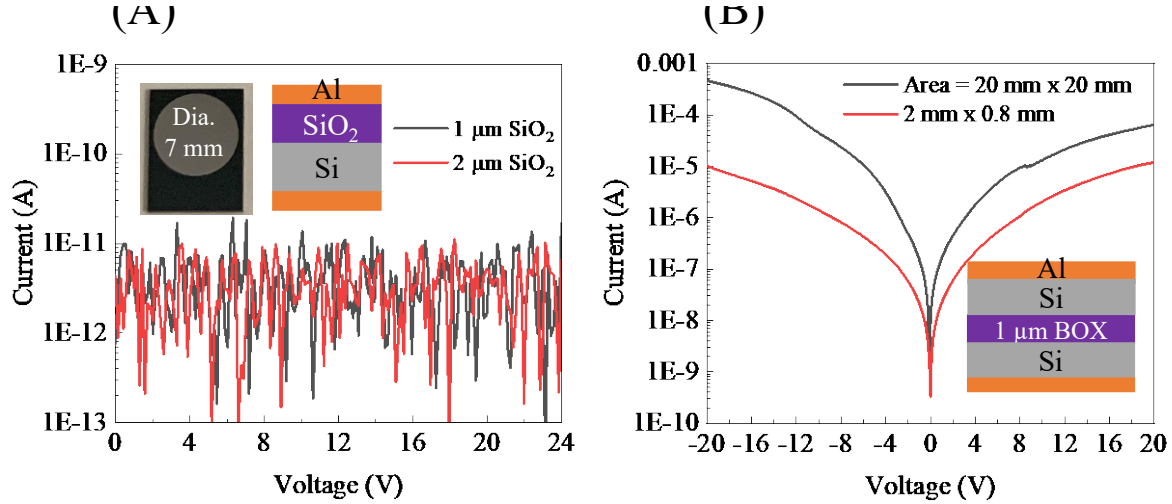


**Figure S4.** Microfabrication process of stand-alone SOI  $\mu$ PIDs. (1) Thermal oxide is grown on a Si wafer. (2) An SOI wafer is created by fusion bonding the oxidized wafer to a highly doped Si wafer. The conductive wafer serves as the device layer and the oxidized wafer serves as the handle layer. (3) Patterned photoresist is used as a mask for the DRIE on the device layer to generate the  $\mu$ PID. The  $\mu$ PID was etched down to the BOX. (4) Ti/Au is evaporated on the silicon electrodes using a Kapton tape covering the center microfluidic channels as patterning.



**Figure S5.** (A) Current-voltage (I-V) characteristics of an SOI  $\mu$ PID. Inset shows the device structure and a photograph of the SOI  $\mu$ PID. (B) SOI  $\mu$ PID peak area (biased from 4 to 20 V) vs. benchmark  $\mu$ PID peak area (constantly biased at 24 V).

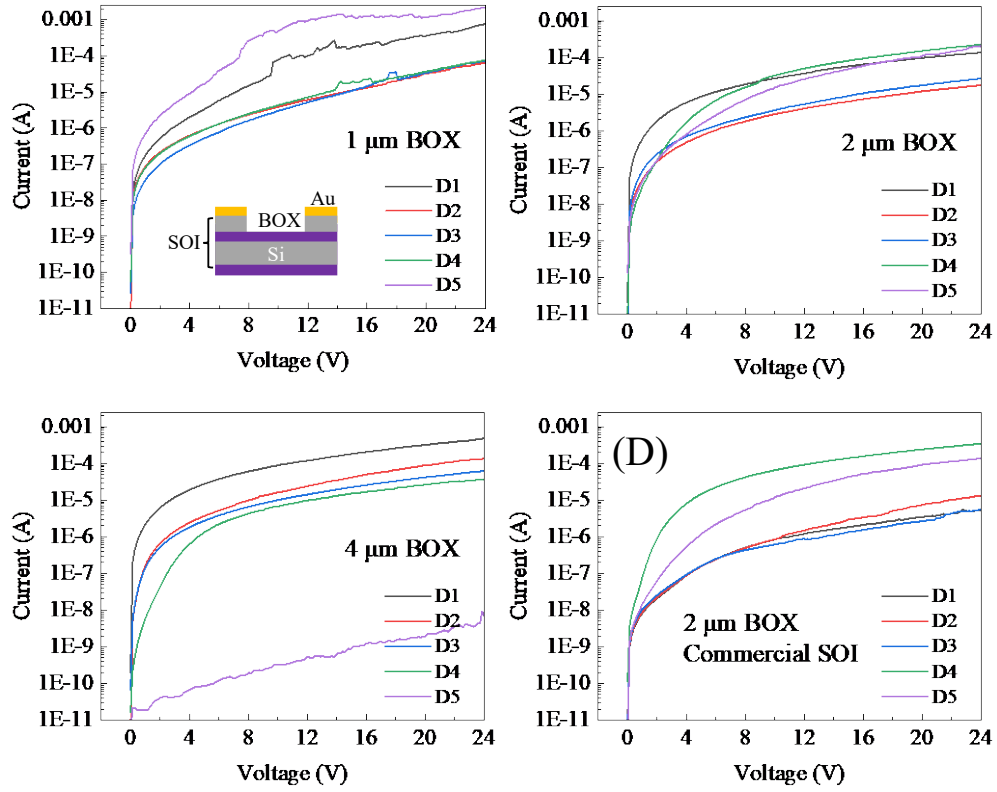
To further reveal the formation of the leaky BOX, metal-oxide-semiconductor (MOS) structures were fabricated to assess the electrical performance of BOX before and after fusion bonding. Figure S6(A) shows that the thermal oxide layer was intrinsically insulating regardless of its thickness with a flat current of several pA across the bias voltage up to 24 V. In comparison, as shown in Figure S6(B), the post-fusion bonding structure demonstrated a leaky performance indicating that the BOX layer became leaky after the fusion bonding process<sup>6</sup>. A smaller area sample also gives the leakage feature with an decreased current. This suggests that the presumably post-fusion bonding defect sites are not localized but universally existent across the BOX layer.



**Figure S6.** Current-voltage (I-V) characteristics of (A) a metal-oxide-semiconductor (MOS) structure comprising Al/SiO<sub>2</sub>/Si/Al with a device diameter = 7 mm. The thicknesses of thermal SiO<sub>2</sub> tested are 1 μm and 2 μm, respectively. Inset shows the structure and a photograph of the device. (B) Post-fusion bonding MOS structure comprising Al/Si/SiO<sub>2</sub>(BOX)/Si/Al with 1 μm of BOX. The sample areas were 20 mm x 20 mm and 2 mm x 0.8 mm. The top and bottom Al contacts were probed in these two structures.

To explore potential solutions to this issue, several strategies were explored. First, the fusion bonding was performed at an elevated temperature of 1100 °C which presumably would result in a better bond. However, the BOX still exhibited leakage. Second, the thickness of the BOX layer was increased from 2 μm to 4 μm fusion bonding two oxidized Si wafers with a 2 μm thermal oxide layer on each. As shown in Figures S7(A)-(C), all devices demonstrated varying degrees of leaky performance similar to iCPIDs. Lastly, a commercial SOI wafer (device layer: <100>, p-type, 0.001-0.005 Ω\*cm, 50 μm thick; BOX = 2 μm; handle wafer: <100>, p-type, 1-10 Ω\*cm, 500 μm thick; Ultrasil LLC) was also tested, but similar results were observed (Figure S7(D)).



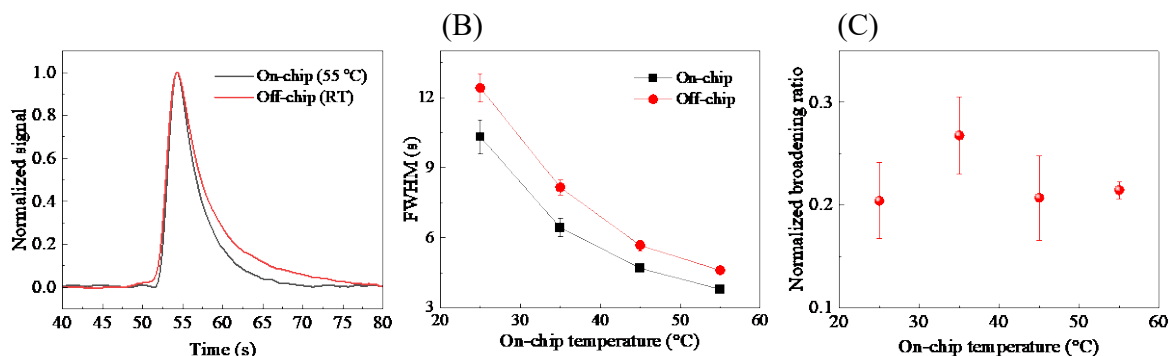


**Figure S7.** Current-voltage (I-V) characteristics of an SOI  $\mu$ PID comprising a BOX with a thickness of (A) 1  $\mu\text{m}$  (B) 2  $\mu\text{m}$  (C) 4  $\mu\text{m}$  and (D) using a BOX = 2  $\mu\text{m}$  commercial SOI wafer. Five devices out of 36 were measured from each wafer. Fusion bonding was performed at 1100  $^{\circ}\text{C}$  for 2 hours in furnaces for this batch of wafers in (A)-(C).

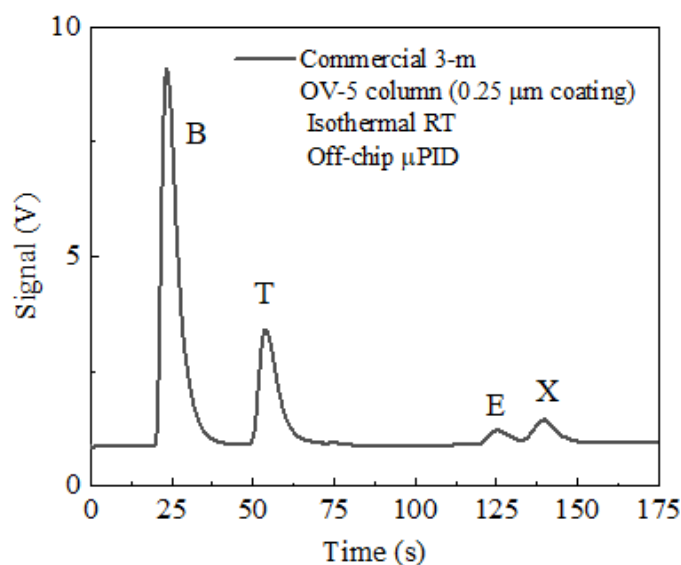
#### **S4. Thermal modeling**

We simulated heat transfer in an integrated device to obtain the temperature profile on the chip using COMSOL Multiphysics®. The results are shown in the inset of Figure 4(A). The Heat Transfer in Solids module was used in the simulation, and we considered only conduction heat transfer physics with an assumption that the other types of heat loss (convection and radiation) in the device is minimal. The geometry used in the simulation was a simplified version of the actual device structure, with an in-plane layout identical to the real device. A 0.8 mm thick silicon layer was stacked on top of a 0.5 mm thick borosilicate glass layer in the out-of-plane direction. The heat source was a patterned platinum heater (0.3 mm thick in the simulation, for simplicity) set to a temperature of 100 °C. The entire geometry was surrounded with an air cube (shown in the inset of Figure 4(A)) maintained at a constant temperature of 25 °C to provide a boundary condition and emulate the ambient environment operation of the device.

## S5. Integrated $\mu$ column separation efficiency evaluation

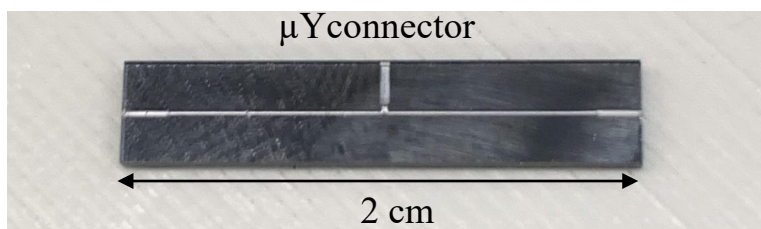


**Figure S8.** (A) Chromatograms of the test analyte, chlorobenzene, generated using on-chip and off-chip  $\mu$ PID with the iCPID ramped to 55 °C. Filtered air was used as the carrier gas with a flow rate of  $\sim 0.8$  mL/min. (B) Full-width-at-half-maximum (FWHM) of chlorobenzene from room temperature to 55 °C. (C) Normalized broadening ratio =  $(FWHM_{off-chip} - FWHM_{on-chip})/FWHM_{on-chip}$  vs. on-chip temperature. Error bars were obtained from five measurements.



**Figure S9.** A chromatogram of BTEX generated using a commercial 3-m OV-5 column (0.25  $\mu$ m coating thickness, #122-5562, Agilent Technologies) with the off-chip stand-alone  $\mu$ PID. The column was operated isothermally at room temperature. Helium was used as the carrier gas with a flow rate of 1 mL/min. The chromatographic results are listed in Table S3.

## S6. Ultracompact system - components fabrication and assembly



**Figure S10.** Photograph of a  $\mu$ Yconnector ( $\mu$ Yconn.) used in the system. The microfabrication process is reported in previous work<sup>7</sup>.

### *Preparation and operation of preconcentrator*

The stainless-steel preconcentrator was fabricated the same way reported before<sup>7</sup>.

### *Air filter preparation*

Ambient air was pumped by a pump from Artshu (#244127942) to flow through a hydrocarbon-moisture filter to generate clean and dry air to be used as a carrier gas. To build the filter, a 0.25-inch-diameter, 2-inch-long stainless steel (SS) tube from McMaster (#1443N134) was first deactivated by Silcotek Corporation. Next, we prepared a four-bed hydrocarbon-moisture filter. The first bed was silica gel beads (#FD-filter-molecular from Forensics Detectors) for trapping moisture. The second bed was a 4-angstrom pore opening molecular sieve 5A from Forensics Detectors. The third bed was a smaller granule size molecular sieve 5A, 60-80 mesh (#20302, Sigma Aldrich). The final bed was activated charcoal (#05112-100G, Sigma Aldrich). Both tube ends were closed and sealed using glass wool. The filter was preconditioned at 150 °C for 12 h under helium flow before use.

### *3D printing box procedure*

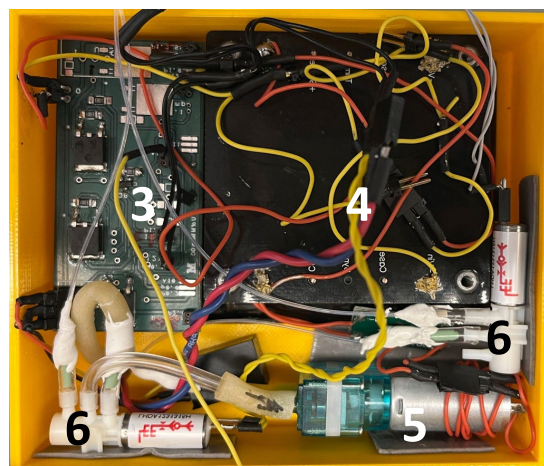
The enclosure for the iCube with dimensions 108 mm x 94 mm x 85 mm (length x width x height) was designed using Autodesk Fusion 360 and 3D printed using Ultimaker S5 3D printer with PLA (Ultimaker) as the 3D printing material.



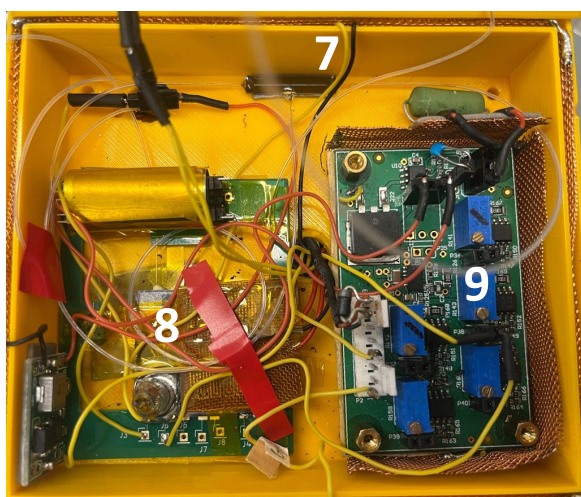
(A)



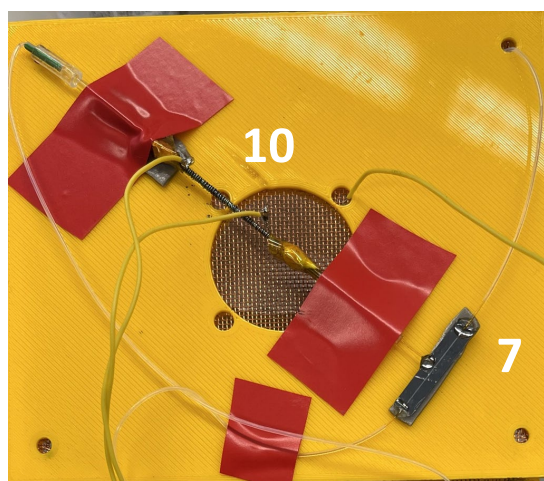
(B)



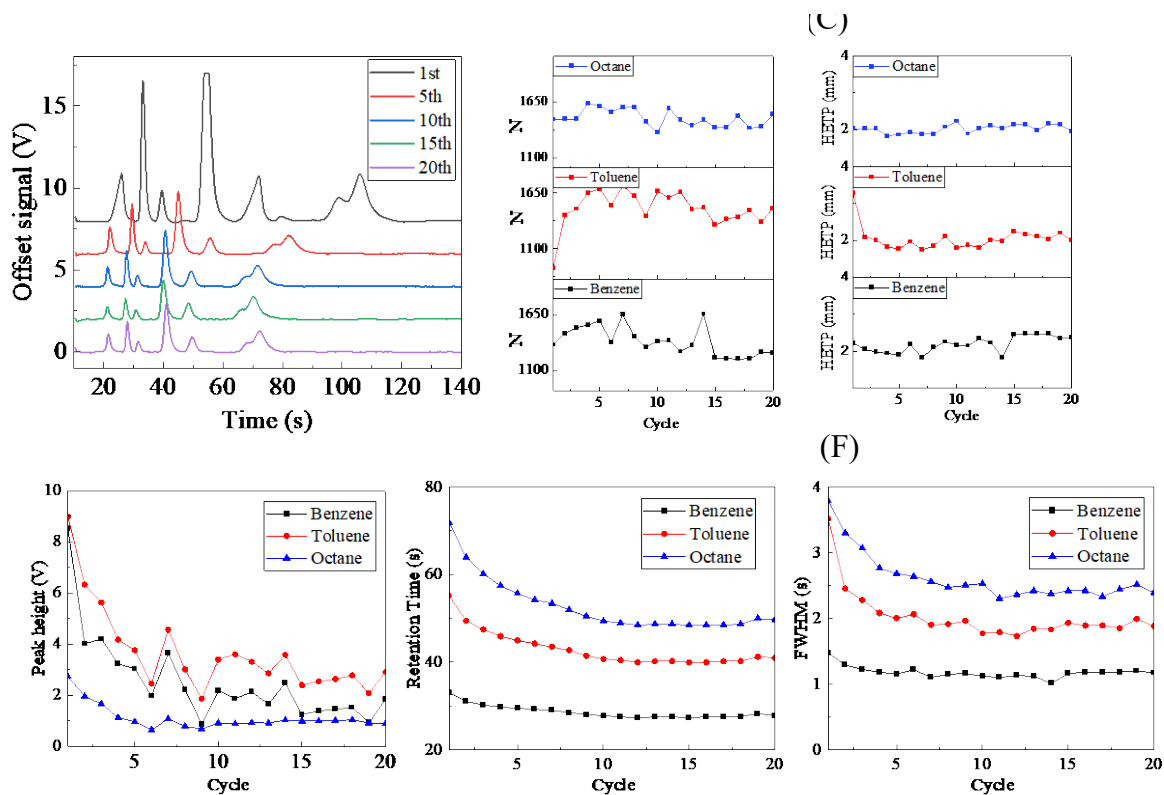
(C)



(D)



**Figure S11.** (A)-(C) First, second, and third layer of the iCube. (D) Top lid. (1) Filter. (2) Battery pack (a set of four 5500 mAh rechargeable battery). (3) Printed circuit board and data acquisition card (NI DAQ). (4) DC-DC converter. (5) Pump. (6) 3-port valves. (7)  $\mu$ Yconnector (see Figure S5). (8) Packaged iCPID (a small DC-DC converter for bias-voltage tuning on the sidewall). (9) Amplification and plasma excitation circuit for  $\mu$ PID. (10) Preconcentrator.



**Figure S12.** (A) 1st, 5th, 10th, 15th, and 20th chromatograms generated by iCube with the same mixture of chemicals sampled with the same amount each time and analyzed under identical conditions. Each analysis run was followed by a clean run. The flow rate was  $\sim 0.84$  mL/min. (B) Number of theoretical plate (N). (C) Height equivalents to theoretical plates (HETPs). (D) Peak height; (E) Retention time; and (F) Full-width-at-half-maximum (FWHMs) for benzene, toluene, and octane, which are included in this mixture.

#	Analyte	Boiling point (°C)	Concentration in bag (mg/L)
1	Acetone	56.2	0.21
2	Benzene	80.1	0.29
3	Heptane	98	0.27
4	Toluene	110.6	0.29
5	Octane	125.6	0.23
6	Butyl acetate	126.1	0.29
7	Ethylbenzene	136	0.29
8	Xylene	138.3	0.29

**Table S1.** VOC list of test compounds and the corresponding concentrations in the bag. The sampling time was 3 s at a sampling rate of 8 mL/min.

Item	P/N	Company
Norland optical adhesive 68T	68T01	Norland
Hysol 1C Epoxy	1373425	Ellsworth Adhesive
Deactivated fused silica tubing	10010	Restek
PTFE Tubing	06417-11	Cole-Parmer
Latex tubing	ZUSA-HT-227	Motion Industries
Zeus PTFE Extruded Regular Wall Tubing	SWTT-14-C	Component Supply
32-gauge nickel chromium wire	32BNC	Consolidated
Krypton lamp for PID	043-257	MOCON baseline
PCB board	Not applicable	M.A.K.S.
3-port valve	LHDA1231315H	Lee Company
Pump	244127942	Artshu
Transformer for PID excitation	CCFL FL3209	Coil Craft
DC to DC convertor	TEP 160-2415WIR	Digikey
Copper mesh	B08PT35XRD	Amazon
Battery	B098QFZW1V	Amazon

**Table S2.** Materials for the system assembly.

<b>Commercial column + off-chip <math>\mu</math>PID detection</b>	<b>RT (s)</b>	<b>FWHM (s)</b>	<b>N</b>	<b>HETP (mm)</b>
Benzene	23.0	5.9	84.8	35.4
Toluene	53.6	6.3	406.4	7.4
Ethylbenzene	125.4	8.0	1356.3	2.2
p-Xylene	139.7	8.0	1686.7	1.8
<b>iCPID with on-chip <math>\mu</math>PID detection</b>				
Benzene	23.3	1.9	867.4	3.5
Toluene	38.6	2.9	997.1	3.0
Ethylbenzene	75.9	5.3	1155.5	2.6
p-Xylene	96.9	6.5	1230.4	2.4
<b>iCPID with off-chip <math>\mu</math>PID detection</b>				
Benzene	25.1	2.6	503.6	6.0
Toluene	40.6	3.5	742.9	4.0
Ethylbenzene	78.4	6.3	871.3	3.4
p-Xylene	99.7	7.0	1120.5	2.7

**Table S3.** Retention times (RTs), full-widths-at-half-maximum (FWHMs), number of theoretical plate (N), and height equivalents to theoretical plates (HETPs) of the 3-m OV-5 commercial column using the off-chip  $\mu$ PID, and the 3-m OV-5 integrated  $\mu$ column using both on-chip and off-chip  $\mu$ PIDs, respectively. All columns were operated at room temperature.

Operation	Component	Operation time	Energy	Comment
Sampling	Pump	3 s	4.05 J	<u>Sampling Mode 1</u> Continuous sampling @1.35 W (3 V x 0.45 A)
Analyzing	Pump (carrier gas)	6 min = 360 s	480 J	@1.35 W (3 V x 0.45 A)
	Pre-concentrator	5.4 s	~2,000 J	Based on actual measurement
	PID	6 min = 360 s	45 J (@ 0.125 W)	Based on actual measurement
Total energy: 2.53 kJ				
Power supply	Battery	-	285 kJ	Battery voltage = 3.6 V Battery current = 5.5 A*H 4 batteries
Total working cycles = 110 Total working time = 11 h				

**Table S4.** iCube power consumption, and the total working cycles and time.

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