

A MICRO COLLECTOR INJECTOR (μ COIN) FOR μ GC SYSTEMS

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ABSTRACT

We report a microscale collector-injector (μ COIN) suitable for gas chromatographic microsystems (μ GC) comprising two series-coupled devices: a micro passive preconcentrator (μ PP) and a micro progressively heated injector (μ PHI). The μ PP collects volatile organic compounds (VOC) via passive diffusion. Discrete μ PPs demonstrated sampling rates close to theory, a high adsorption capacity, and efficient thermal desorption. The μ PHI accepts vapors transferred from the μ PP (by thermal desorption with pumping) and thermally generates a sharp injection. Discrete μ PHIs demonstrated capacities that varied with VOC polarity and volatility, and 190 ms injections via progressive heating.

INTRODUCTION

The direct determination of VOCs in field or clinical settings is of interest for personal exposure monitoring, point-of-care medical diagnostics, and the detection of explosives or other chemical threats. μ GC has several inherent potential advantages for such applications, and efforts to produce such microsystems have been reported [1-5]. The key analytical components of a typical μ GC comprise a preconcentrator/injector for sample capture (via pump) and introduction, a column for separation of mixture components, and a detector or array of detectors.

Typical microscale adsorbent-packed/lined preconcentrators also serve as injectors [1-7]. The dual function of such devices requires performance tradeoffs between capacity on the one hand and desorption efficiency and power dissipation on the other. Among reported micro-preconcentrators, injection band widths of VOCs are typically > 1 s, preconcentration factors are relatively low, and power consumption can be high due, in part, to the use of a mini-pump to draw air samples into the device.

The μ COIN device described here (Fig. 1) consists of a μ PP coupled to a μ PHI. The μ PP collects vapors by passive diffusion. It redesigns a predecessor technology [8] to reduce ($>10\times$) the required desorption flow rate, increase flow uniformity, and minimize energy consumption. However, the μ PP is incapable of producing sharp injections upon thermal desorption and transfer (under flow). The μ PHI, a new design that combines concepts from previously reported micro focuser-injectors [7,9], accepts the broad vapor bolus transferred from the μ PP and then is rapidly and progressively heated (under flow) to yield the sharp injection pulse needed for efficient μ GC separations with short columns. Carbon adsorbents permit trapping of vapors with a wide range of structure/volatility. This paper describes the design and preliminary characterization of discrete μ PP and μ PHI devices as well as first results from the hybrid-integrated μ COIN.

EXPERIMENTAL

Design and Fabrication

The μ PP and μ PHI devices are formed from a top silicon-on-insulator (SOI) substrate and a bottom glass substrate (Fig. 2). The top layer of the μ PP SOI substrate has a grid of 171 parallel $50\times 50\times 180$ μm ($L\times W\times H$) apertures through which vapors diffuse at a known rate according to Fick's laws. The bottom layer of the μ PP SOI substrate contains two concentric adsorbent cavities

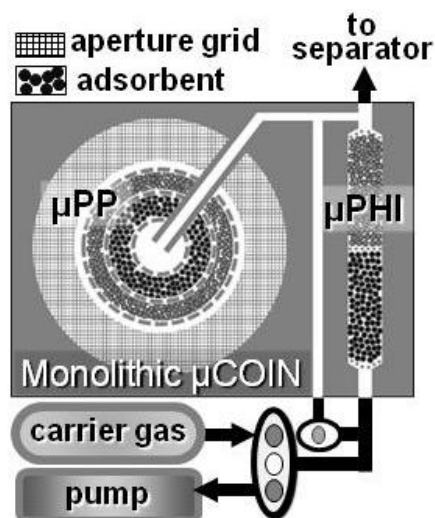


Figure 1: Conceptual diagram of monolithic 8x8 mm μ COIN.

separated by pillars and filled with ~ 800 μg of CarboPack B (C-B, surface area: 100 m^2/g , outer) and 700 μg CarboPack X (C-X, surface area: 100 m^2/g , inner). Heaters and temperature sensors (Ti/Pt) located on the top surface of the glass substrate are used for heating the adsorbents to 250 $^\circ\text{C}$ during thermal desorption.

The μ PHI has linear topology with adjacent adsorbent beds containing $\sim 500/400$ μg of C-B/C-X also separated by pillars (Fig. 2b). In the μ PHI, the adsorbent region is split into an array of 10 thermally isolated and individually addressed heaters that enable advanced (progressive) heating for compressing injection peaks.

The diffusion path through the μ PP (Fig. 2a) can be formally parsed into three segments with specific lengths and areas, L_i and A_i , through which the mass transfer of vapors is constant at steady state. The effective sampling rate, S (volume/time), can be estimated as $S=D/(L_1/A_1+L_2/A_2+L_3/A_3)$, where D is the vapor diffusion coefficient [7]. By design, S is primarily a function of the total area of the aperture grid (A_1). The capacity of the device is a function of its design as well as the nature and number of VOCs and the time of exposure. After collection is complete, the sample is transferred from the μ PP to the μ PHI under suction flow via thermal desorption.

After the sample is transferred to the μ PHI, external valves are used to introduce He carrier gas from a canister in the reverse direction (back flushing) and the μ PHI heaters are sequentially activated, progressively desorbing VOCs from inlet to outlet and "rolling up" (i.e., focusing) the mixture into a sharp injection pulse.

Discrete μ PP and μ PHI devices were created using the same microfabrication process flow. The sampling aperture grid (μ PP), adsorbent cavities and fill ports, and flow channels were fabricated using DRIE. Ti/Pt heaters/RTDs and an oxynitride overlayer were deposited on the bottom glass substrate using PVD and PECVD tools, respectively. Au-Si eutectic bonding joined the substrates (Fig. 3) [9]. Adsorbents were loaded, interconnecting capillaries were epoxy sealed, and then devices were mounted & wire-bonded onto printed circuit boards (PCB; Fig. 4).

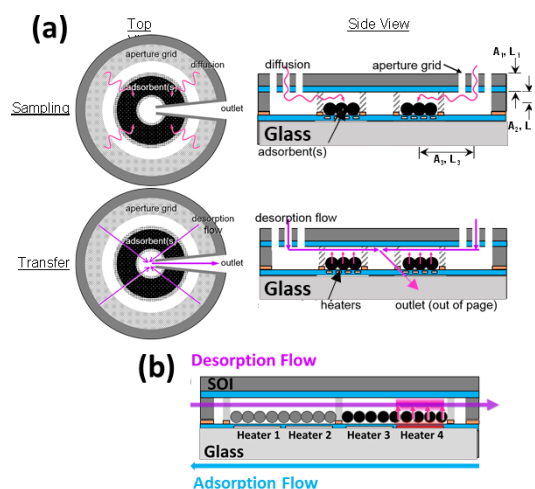


Figure 2: Design and operation of (a) μ PP (b) μ PHI.

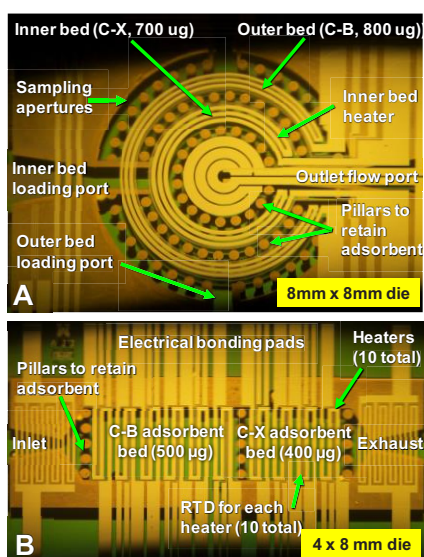


Figure 3: Optical image of fabricated (a) μ PP (b) μ PHI devices.

Discrete Device Tests

Test chemicals were obtained at high purity from standard sources and used without purification. Test atmospheres containing vapors of the test chemicals were generated from fritted-glass bubblers diluted with clean, dry air, and were verified by loop injection into a pre-calibrated GC-FID. Certain tests were performed using a thermogravimetric analyzer (TGA, Perkin Elmer). For other tests, a PCB-mounted μ PP device was mounted in a custom stainless steel chamber with electrical feedthroughs in the chamber floor. The capillary used for sample transfer was wrapped with heater coils and raised to 70 °C during transfer. Following exposure for a given time period, the chamber was purged with clean, dry air. Then, both substrate heaters were activated to heat the adsorbent beds to 250 °C while drawing air through it with a small pump at 10 mL/min. The sample was passed through a surrogate focuser [7] where the vapors were temporarily trapped and then injected into the GC-FID equipped with either a short capillary separation column or a section of (uncoated) deactivated silica guard column.

For the μ PHI, samples of the test chemicals were passed to the device as low-volume vapor boluses either from a sample loop connected to a 6-port valve or from a bench-scale GC. For the

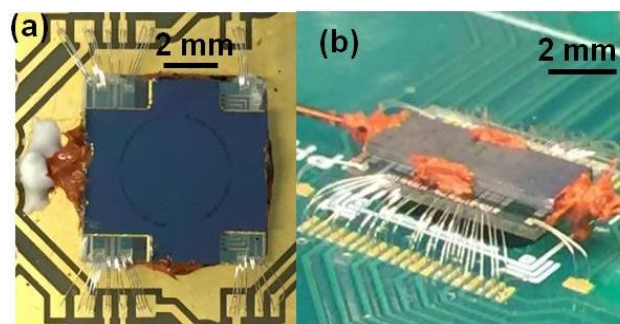


Figure 4: (a) Optical image of the wire-bonded (a) μ PP (b) μ PHI device.

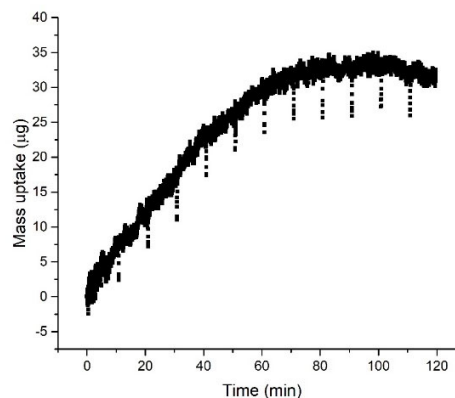


Figure 5: TGA output of suspended μ PP device showing constant sampling rate (linear mass uptake) for ~40 min and saturation at ~80 min (33 μ g of xylene at the challenge concentration of 2,000 mg/m^3).

latter the test chemical was either pure or dissolved in a volatile solvent and injected through the heated GC injection port using an autosampler syringe. The mass of test chemical was verified by pre-calibrated FID.

Device heaters were controlled and RTDs monitored by custom programs written in LabVIEW and run from laptop computers. The μ PP had feedback controlled heating (via pulse width modulation). The μ PHI had open loop heater control with independent voltages applied during the ramp up and hold periods.

RESULTS AND DISCUSSION

In initial tests, separate 3-mg samples of C-X and C-B adsorbents were loaded into a sample pan, suspended from the TGA balance, and exposed to m-xylene vapor (one of the highest-vapor pressure targets studied). After allowing uptake of relatively large masses of 5-8 μ g of m-xylene per mg of adsorbent there was no loss (bleed) of the captured vapor after two hours of purging with clean air at ambient temperature. This confirms that test vapors should be retained by the μ PP even during periods of non-exposure.

A μ PP was then device suspended in the TGA and exposed to 2000 mg/m^3 of m-xylene vapor, and mass uptake via passive sampling was measured in real time. Results are shown in Fig. 5. The sampling rate was constant for ~40 min, dropped by 30% from 40-60 min, and then dropped to zero (saturation). The total mass uptake was 32 μ g and the sampling rate was constant up to 23 μ g, which is a very high capacity. Other tests showed that capacity was inversely proportional to vapor pressure for homologous aromatic hydrocarbons, meaning that the capacity should be

sufficient for most/many VOCs of interest. TGA tests with the polar dimethylmethylphosphonate (DMMP) were not successful.

Chamber tests with the μ PP showed that the sampling rate for m-xylene was constant over 3 orders of magnitude in concentration (i.e., from 8 to 5,600 mg/m³; 15-min samples). Furthermore, tests with both m-xylene and DMMP showed that the sample rates were within 15% of those predicted by theory/modeling (see Table 1). Figure 6 shows a chromatogram from passively sampling a simple mixture of vapors with the μ PP (in chamber), transferring to the surrogate focuser, and injecting to a bench-scale GC-FID. Desorption efficiencies were 88-98%.

Table 1: μ PP sampling rate for m-xylene and DMMP.

VOC	Modeled S (mL/min)	Exper. S (mL/min)	Ratio
m-xylene	0.60	0.69	1.15
DMMP	0.44	0.48	1.09

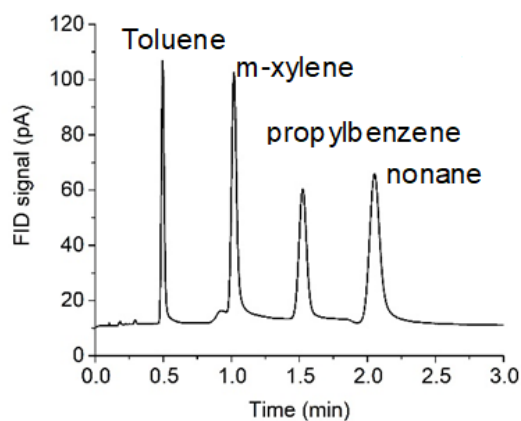


Figure 6: GC-FID chromatogram for a 4-vapor mixture passively sampled with the μ PP, transferred to a surrogate focuser and injected.

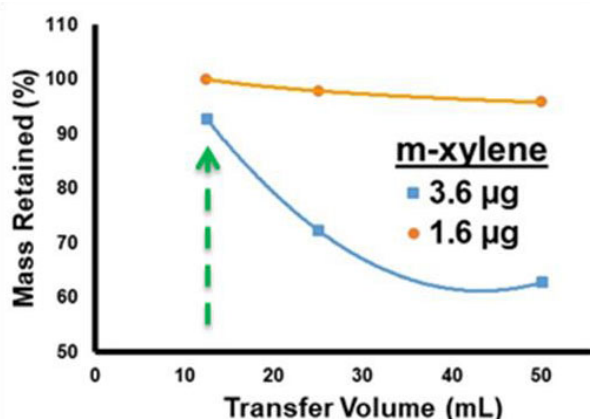


Figure 7: Plots of fractional retention (capacity) of m-xylene versus the transfer volume for the μ PHI for bolus challenges of 1.6 and 3.6 μ g at 5 mL/min. Retention is >90% for transfer volumes < 12 mL.

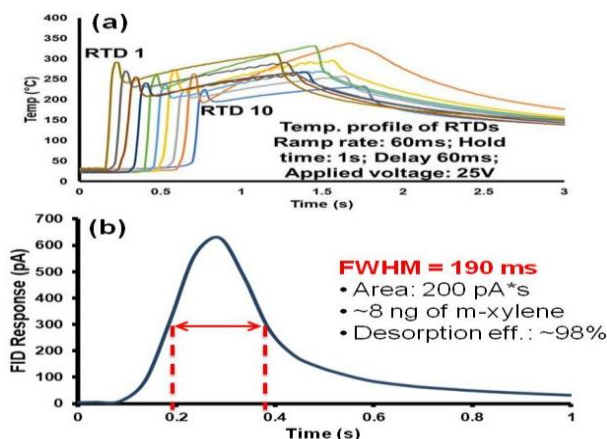


Figure 8: (a) Rapid (4000 °C/s) heating (60 ms delay time) of μ PHI bed with low thermal crosstalk (b) Sharp (full width at half maximum = 190 ms) desorption peak-width at 50 μ L/min flow during heater ramp period (~1 s) and 3 mL/min afterwards

To test of the capacity of the discrete μ PHI, breakthrough was monitored by FID using boluses of known test atmospheres passed directly through the device in a certain volume of carrier gas to mimic desorption from the μ PP. The μ PHI was subsequently heated to 250 °C using global or progressive heating to desorb the retained vapors. The percentage of mass retained was evaluated by the ratio of challenged vapor concentration/mass to the desorbed peak area.

Initial tests were performed with boluses containing 1.6 μ g and 3.6 μ g of m-xylene. These masses can be related to possible μ COIN exposure scenarios. For example, the μ PP would collect 1.6 μ g within 30 min ($S = 0.6$ mL/min) when exposed to 90 mg/m³ and it would collect 3.6 μ g in 30 min at 200 mg/m³. We anticipate that the volume of air required to transfer samples from the μ PP to the μ PHI will be < 3 mL. Figure 7 shows that the μ PHI can retain > 95% of 3.6 μ g sample of m-xylene if the transfer volume is < 12 mL. For a 1.6 μ g sample the capture efficiency is > 95% for transfer volumes as large as 50 mL! These results demonstrate excellent capacity for m-xylene with the μ PHI.

The capacity for DMMP was significantly lower than that for m-xylene, despite its vapor pressure being ~9x lower. In fact, above ~200 ng it was not possible to achieve >90% retention, regardless of the sample volume. At 75 ng of DMMP, corresponding to a 30 minute sample at 5 mg/m³ ($S = 0.44$ mL/min), the retention was 90% for a 1 mL transfer volume. Clearly, the polarity of DMMP plays a significant role in its adsorption on C-B and C-X adsorbents. We have explored the use of ionic liquid coatings as a means to enhance retention of polar VOCs on these adsorbents with modest success (data not shown). Desorption efficiencies ~98 % were observed for m-xylene and DMMP.

For desorption tests the μ PHI heaters were operated globally or sequentially. The control software allowed adjustment of the individual ramp rate, heater ON time (hold-time) and delay between adjacent heaters (Fig. 8a). Experiments were performed to assess the combination of heating and flow parameters that would provide the sharpest injection band. The best results were obtained when the residence time of vapor above each heater was held close to the firing delay between individual heaters (~100 ms). For this purpose, the flow rate was reduced to ~50 μ L/min (residence time ~300 ms) during the desorption process until all heaters reached 250 °C and the sample was completely injected, at which point

flow was increased to 3 mL/min to complete the transfer to the FID (no column was used). The full width at half maximum for the m-xylene peak was ~190 ms (Fig. 8b).

CONCLUSIONS

The concept introduced here of combining devices for passive sampling and progressively heated injection appears to be sound. Preliminary test results are promising. The capability of the μ PP to passively sampling vapors at rates close to modeled values, to retain captured vapors at high mass loading levels, and to efficiently desorb vapors thermally for transfer to the μ PHI all support its continued development. The capability of the μ PHI to retain transferred samples of volatile non-polar vapors such as m-xylene is encouraging but polar vapors are less effectively retained. The use of ionic liquid modifiers shows promise for improving the retention of polar vapors and results of such testing will be described in a future report. Regardless, the progressive heating feature of the μ PHI appears to be effective, with injection bands < 200 ms already having been achieved at low flow rates compatible with μ GC separation columns. A hybrid-integrated μ COIN prototype has been assembled but data could not be generated in time for this publication. Nonetheless, results reported here augur well for the ultimate implementation of a monolithically integrated μ COIN to serve as a collector module for future μ GC systems.

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