Passive Micro-Sampler with Facilitated On-Site Analysis for Multi-Vapor Worker Exposure Monitoring

C. Zhan,[1,5] L. Zhong,[1,5] N. Nuñovero,[1,5] R. Hower,[2] J. Potkay,[3,5*] E.T. Zellers[1,4,5*]

[1] Department of Environmental Health Sciences, [2] Department of Electrical Engineering and Computer Science, [3] Department of Surgery, [4] Department of Chemistry, [5] Center for Wireless Integrated MicroSensing & Systems (WIMS[2]), University of Michigan, Ann Arbor, USA

Introduction

Objective:

Develop and characterize a microfabricated passive sampler, called a micro Collector-Injector (µCOIN) that would 1) collect mixtures of VOCs in a worker's breathing zone for up to 8 hours, 2) be analyzed immediately in the field with a microfabricated gas chromatograph (µGC), and 3) reused indefinitely.

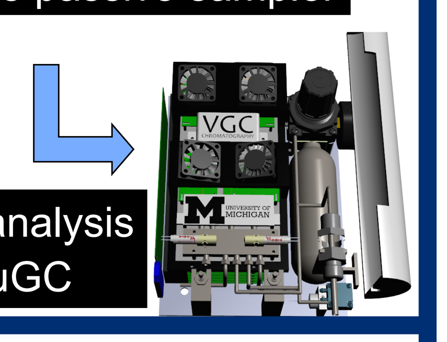
Key Features:

- Passive (diffusional) sampling with "zero" power
- High-capacity, "universal" adsorption
- Quantitative transfer from collector to injector
- Sharp injection bands via progressive heating
- Low energy per cycle via efficient design

Reusable passive sampler

Performance Goals:

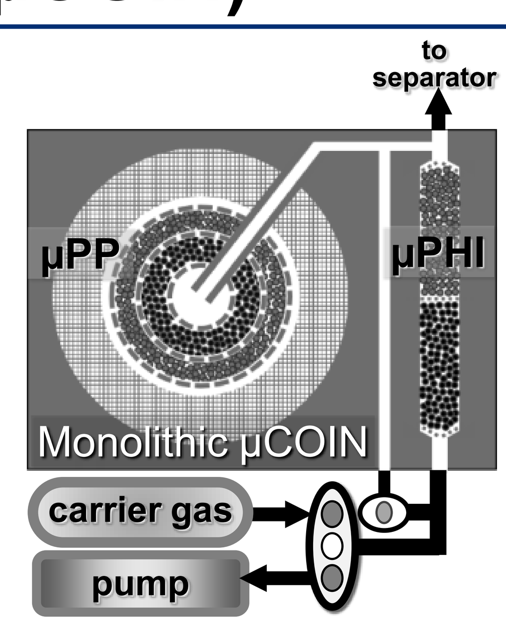
1. Quantifiable collection & injection of up to 80 compounds
2. Pre-concentration factors between 72× and 26,900×
3. Injection band widths < 250 ms
4. Up to 32 collection-injection cycles/day
5. 300 cm³ (size); 0.5 kg (wt.); 65 J/cycle (energy)



On-site analysis with µGC

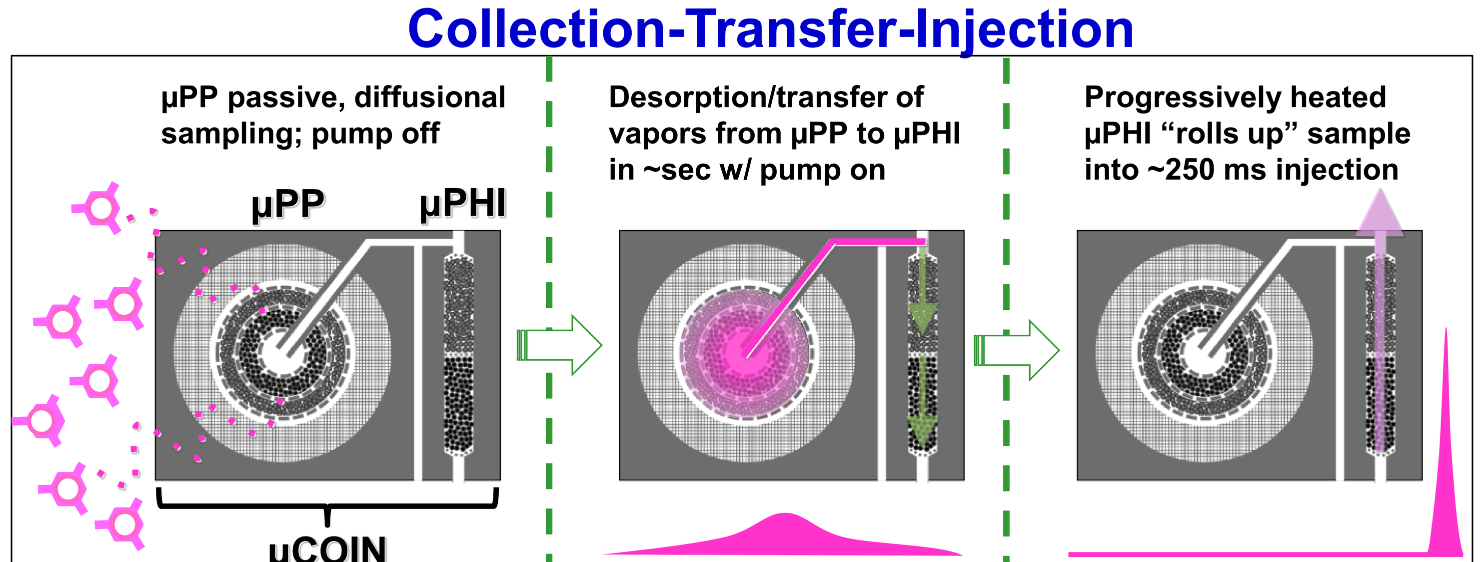
Micro Collector-Injector (µCOIN)

- **µCOIN components: µPP + µPHI**
  - µPP = micro passive preconcentrator (the collector)
  - µPHI = micro progressively heated injector (the injector)
  - Dual-adsorbent beds (concentric, adjacent)
    - Carbopack X (inner; 240 m²/g) and Carbopack B (outer; 100 m²/g)
  - Ancillary elements: carrier gas and pump
- **µCOIN-A (8 × 8 mm chip)**
  - Positive pressure, back-flushed injection
  - Split-flow injection possible
  - On-board carrier gas: for injection and purge



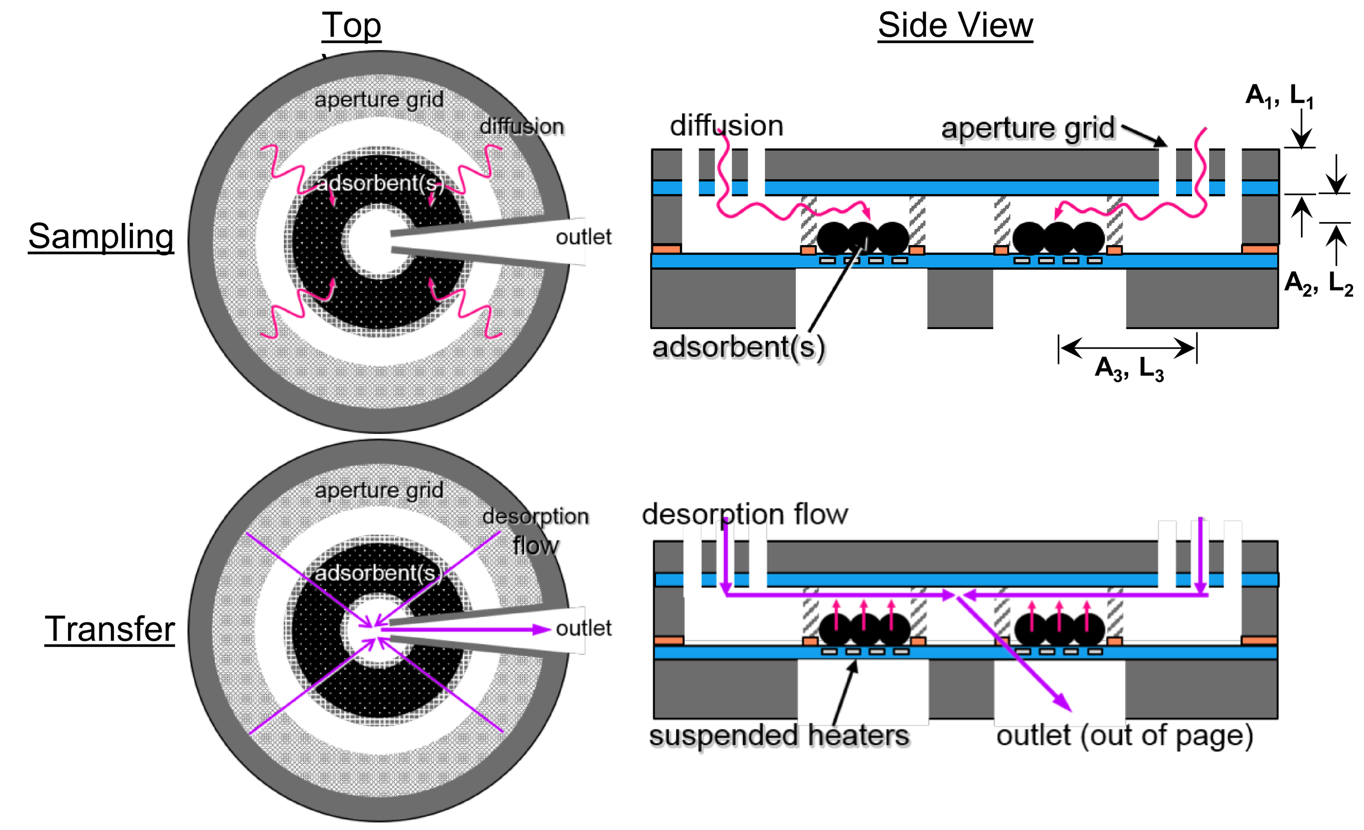
µCOIN-A*

Collection-Transfer-Injection



*adsorbent fill-ports not shown

Micro Passive Pre-concentrator (µPP)

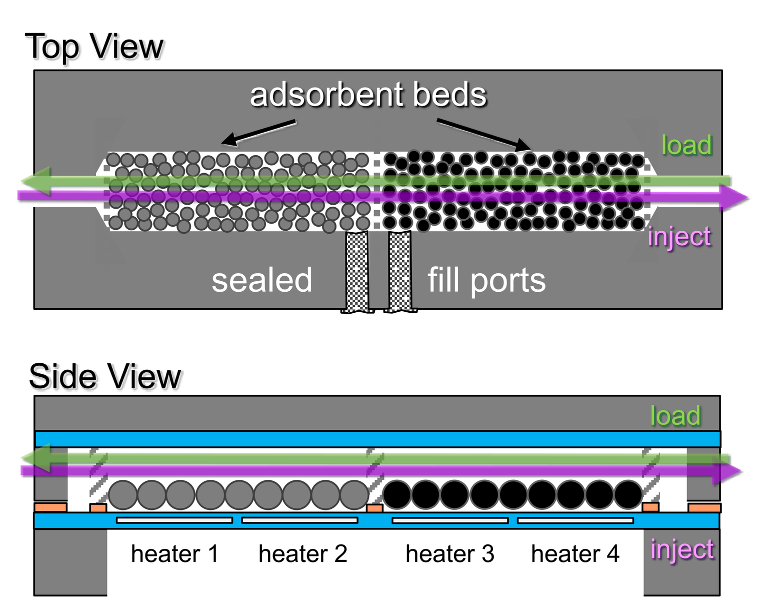


- Effective diffusional sampling rate, S_e, determined by mass transfer through a series of 3 formalized regions, S_1, S_2, S_3.
- Collected vapors are thermally desorbed via embedded heaters and transferred to the µPHI via the downstream suction pump

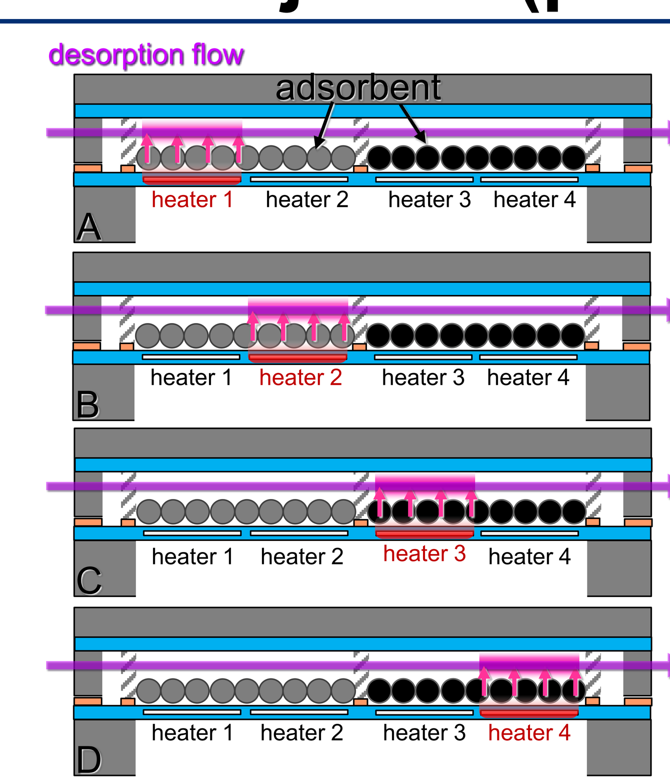
Provisional design parameters; high & low sampling rate µPPs

Parameter	High Rate Design	Low Rate Design
Sampling Rate	> 0.50 cm³/min	< 0.05 cm³/min
Min. Req. Desorp. Flow	> 3 cm³/min	< 0.2 cm³/min
Ads. Beds od/id	4.3/2.0 mm	4.3/2.0 mm
Aperture Area	2.5 mm²	0.1 mm²
$L_1/L_2/L_3$ (see Fig.)	0.20/0.22/0.84 mm	0.20/0.22/0.84 mm

Micro Progressively Heated Injector (µPHI)



µPHI diagrams of device structure, and loading and injection flow directions.

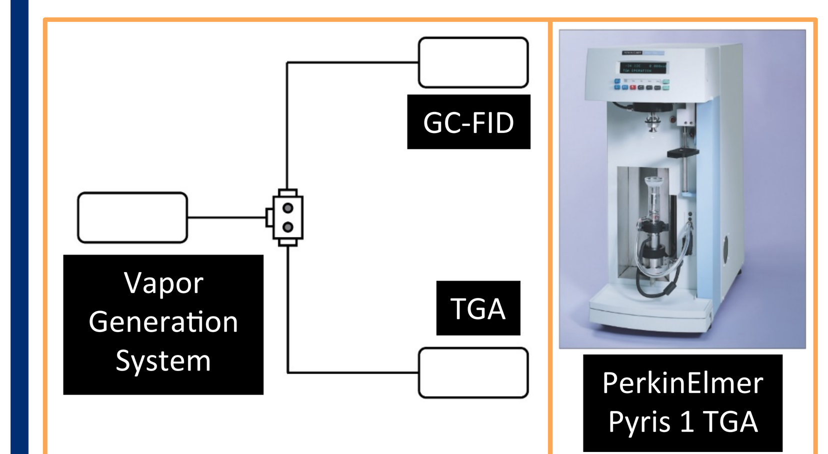


µPHI injection sequence featuring progressive heating.

Key features:

- Dual adsorbent beds for efficient adsorption and desorption
- Suspended membrane for low-power heating
- The adsorbent bed is lined with multiple independent heaters that are sequentially energized under flow to "roll up" the desorbed vapors into a sharp injection pulse

Equilibrium Adsorption Capacity Tests



- Equilibrium adsorption capacity (W_e) measured by thermogravimetric analyzer (TGA)
- Composition & concentration of test atmosphere analyzed by GC-FID

W_e vs. p_v

Compound	toluene	m-xylene
p_v (kPa)	3.78	1.01
Conc. (mg/m³)	32.6	36.3
Adsorbent mass (mg)	2.46	2.64
Uptake mass (µg)	11.4	40.3
W_e (µg/g)	4623	15234

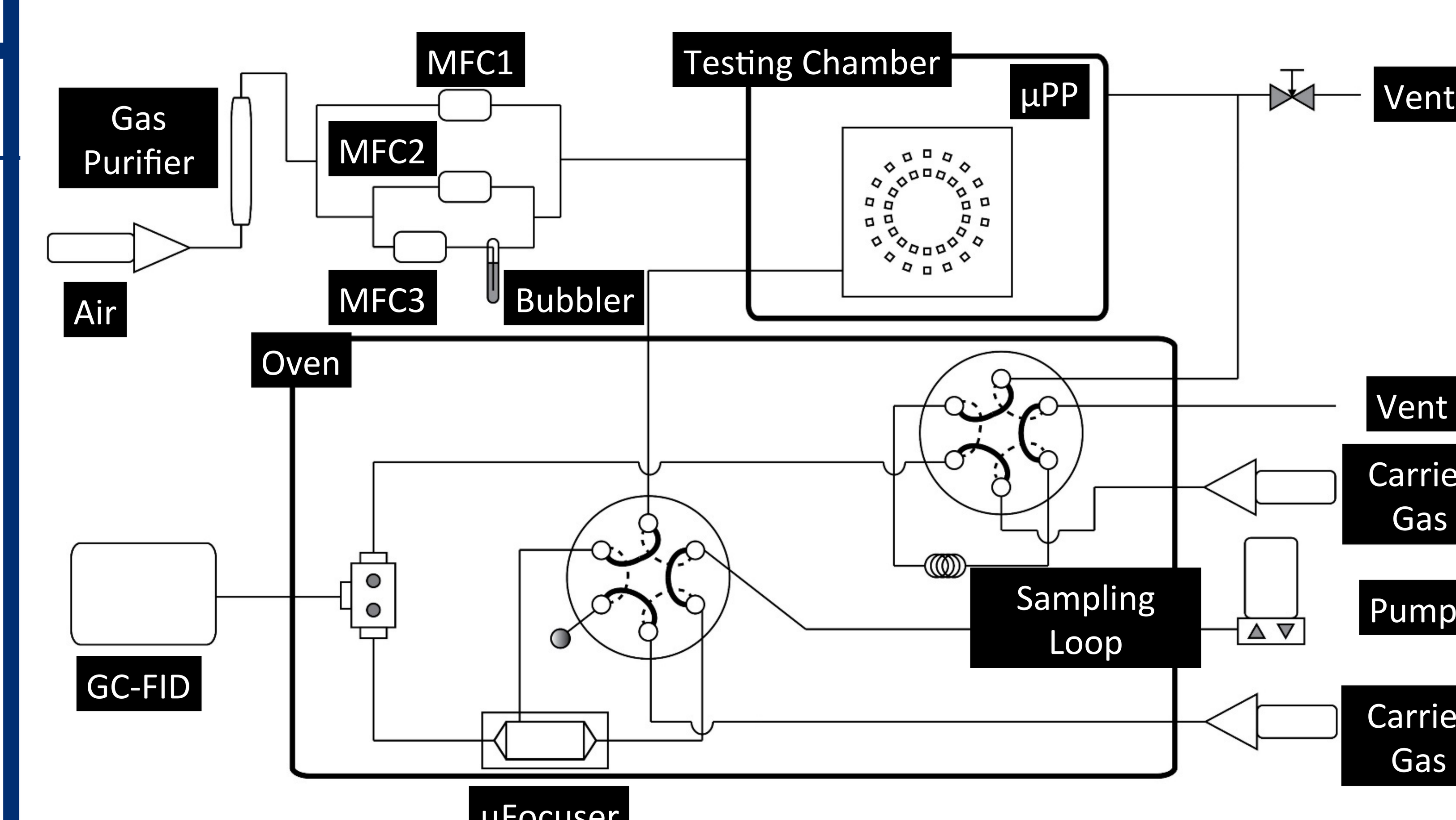
Test cmpds, vapor pressures (p_v) and TLV-TWAs (STELs)

Compound	p_v (kPa)	TLV (ppm)
trichloroethylene	6.25	10 (25)
4-methyl-2-pentanone	2.65	20 (75)
toluene	3.78	20
2-hexanone	1.46	5 (10)
butyl acetate	1.53	50 (150)
ethyl benzene	1.27	20
m-xylene	1.01	100 (150)
3-heptanone	0.187	50 (75)
1,2,4-trimethylbenzene	0.270	25
n-decane	0.191	--*
nitrobenzene	0.033	1
1,2,4-trichlorobenzene	0.039	--- (5)
n-dodecane	0.027	–*

* *no assigned TLV*

The test compounds: VOCs with a vapor pressure between 0.01-10 kPa that have TLV-TWAs within 1-200 ppm and STELs within 10-500 ppm.

Initial Testing of µPP Performance



- Sampling rates, constant-rate sampling times (capacities), and desorption flow rates, temperatures and efficiencies will be determined for individual targets and target mixtures via exposure tests and thermogravimetric analyses
- Adsorbent materials will comprise high-surface area solids either untreated or treated with surface-modifying interfacial functionalities that impart selectivity for targets or enhanced capacity.

Center for Wireless Integrated MicroSensing & Systems

Acknowledgment: Funding provided by the University of Michigan Center for Occupational Health and Safety Engineering (COHSE) and the Intelligence Advanced Research Projects Activity (IARPA).