A Wearable Microfabricated Gas Chromatography for Trace-Level Volatile Organic Compound Determinations

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Goal

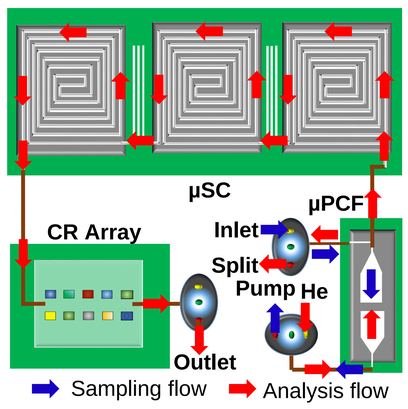
- Develop a wearable gas chromatographic micro-analytical system (μGC), referred to as a Personal Exposure Monitoring Microsystem (PEMM), for near-real-time recognition and quantification of individual volatile organic compounds (VOC) in moderately complex mixtures encountered in industrial working environments

Introduction to PEMM

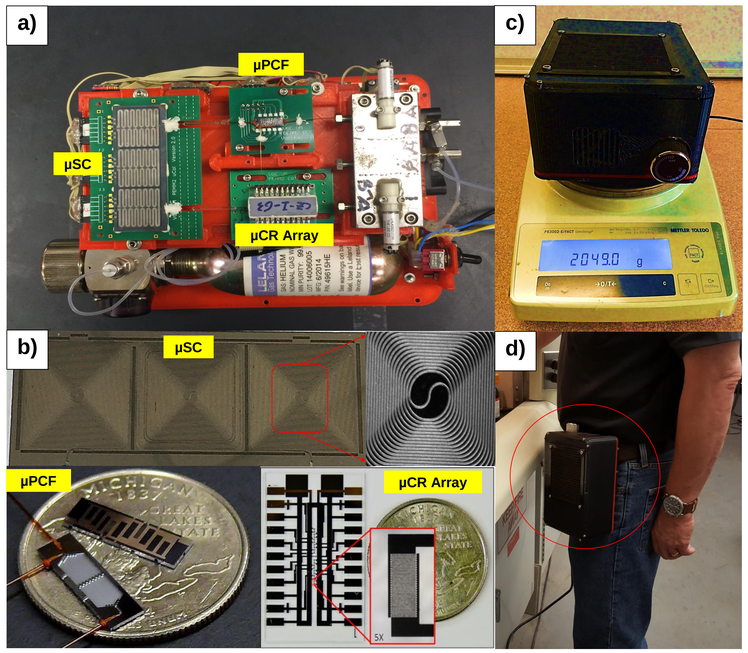
- Currently, there is no direct-reading instrumentation capable of measuring personal exposures to the components of VOC mixtures
- PEMM is designed to autonomously measure worker exposures to 10-15 VOCs every 8-10 minutes for 8 hours with detection limits in the low-ppm to high-ppb air concentration range
- Key MEMS components of the core PEMM microsystem include:
  - DRIE-Si/Pyrex dual-cavity **micro preconcentrator/focuser (μPCF)** packed with the graphitized carbons Carbopack X and Carbopack B,
    - quantitative VOC capture in specified volatility window
    - Integrated resistive heaters for desorption; optional split injection
  - DRIE-Si/Pyrex segmented, zone-heated **micro separation column (μSC)** wall-coated with cross-linked PDMS
    - independent zone heating and power efficient separation
  - Si/Pyrex **micro chemiresistor (μCR) array** coated with monolayer protected gold nanoparticles (MPNs) for VOC quantitation and recognition
    - 10 sensors available, independent grounds, response patterns
- Other features of the PEMM prototype include:
  - **Passive pre-trap** to remove low-volatility interferences
  - **On-board Helium canister** for superior chromatographic performance and low maintenance; > 1,000 analyses
  - **On-board PIC 32 + ARM microcontroller**
    - configure operating parameters; execute sampling and analysis functions; communicate with raspberry PI
  - Web based graphical user interface

PEMM Concept

Fluidic Pathways in PEMM



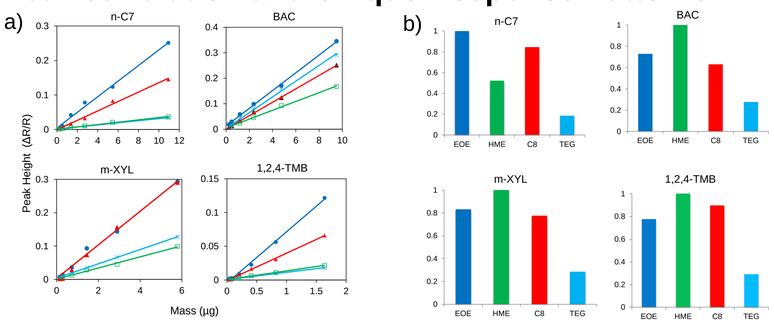
Belt-Mounted PEMM μGC Prototype



Photographs of a) PEMM prototype with cover removed; b) microsystem components; c) PEMM on electronic balance (2.05 kg); and d) PEMM mounted on a belt.

System Performance

Linear Calibration and Unique Response Patterns



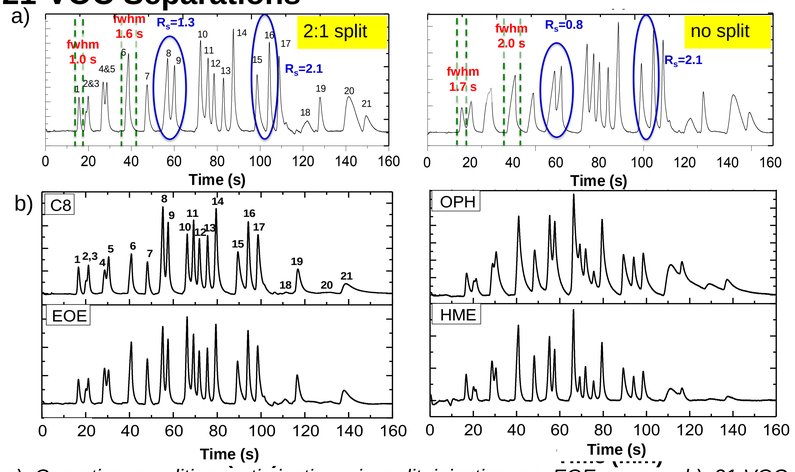
a) calibration curves based on peak heights; b) normalized response patterns for 4 compounds derived from the peak areas in a). Note: n-C7, n-heptane; BAC, butyl acetate; m-XYL, m-xylene; 1,2,4-TMB, 1,2,4-trimethylbenzene. EOE, HME, C8, TEG are acronyms for the nanoparticle functionalities.

Limits of Detection (LODs)

Compound	Limits of Detections* (ng)			
	EOE	C8	HME	TEG
n-C7	5.1	3.8	4.6	42
Toluene	4.5	3.1	2.0	18
Butyl acetate	2.8	1.9	1.1	12
m-xylene	3.8	2.4	1.9	18

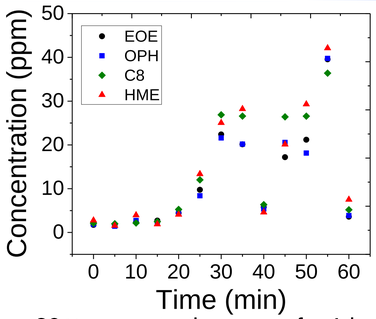
* For reference, 2 ng LOD for toluene (HME) corresponds to ~110 ppb for a 5 mL air sample

21-VOC Separations



a) Operation condition optimization via split injection on EOE sensor. b) 21-VOC Chromatograms under optimal injection condition. All conditions: ~100 ppm of each VOC; 1-min sampling @5 mL/min; μPCF: 225˚ C for 40 sec; 2:1 split injection (6:3 mL/min); Temp program: 50 sec at 30 ˚C; 50 C/min to 125 ˚C; 16 sec hold. Note: benzene (BEN); trichloroethene (TCE) ; n-heptane (C7); 4-methyl-2-pentanone (MIBK); toluene (TOL); 2-hexanone (MBK); butyl acetate (BAC); ethylbenzene (ETB); m-xylene (m-XYL); 3-heptanone (3HEP); n-nonane (C9); α-pinene (PIN); cumene (CUM); propylbenz. (PPB) ; 1,2,4-trimethylbenene (TMB); n-decane (C10); d-limonene (LIM); nitrobenzene (NBZ); n-undecane (C11); trichlorobenene (TCB); n-dodecane (C12)

Mock Field Tests



Activities

- 0-5 min: No activities
- 5-20 min: Solvent transfer (beaker to beaker)
- 20-30 min: Solvent transfer (beaker to hot plate, 80˚ C)
- 30-40 min: Solvent transfer (beaker to beaker)
- 40-55 min: Solvent transfer (beaker to hot plate, 100˚ C)
- 55-60 min: No activities

- ~20 × concentration range for 1 hour monitoring
- Good agreement among sensors, and with reference methods

Summary

- We have built the first battery powered, wearable μGC and have generated encouraging results
- Responses of μCR sensors are linear with concentration, LODs are in the low ng range for most sensors (~ high ppb air conc.), and array response patterns enhance vapor discrimination
- 21 VOC separations were achieved on 4 sensors within 3 min
- mock field tests demonstrate potential capability of PEMM for real setting multi-vapor determinations
- Retention time windowed PCA plots (not shown) facilitate overlapping peaks identifications

Center for Wireless Integrated MicroSensing & Systems

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