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# A Wearable MEMS Gas Chromatograph for Multi-Vapor Determinations

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**Abstract**

A *wearable* gas chromatographic microanalytical system (μGC) for near-real-time recognition and quantification of volatile organic compounds (VOC) in complex mixtures encountered in working environments is described. The battery powered μGC prototype measures 20×15×9 cm, weighs just 2.1 kg, has 3-D printed packaging, and can be worn on the belt to autonomously measure exposures to industrial VOC mixtures several times per hour. Novel features of the discrete DRIE-Si/Pyrex micro-component chips include a dual-adsorbent μpreconcentrator/focuser (μPCF) with split-flow injections as narrow as 600 ms (benzene), a 6-m long segmented separation μcolumn with zone heating for power efficient separations; and a fluidically redesigned array of μchemiresistors (μCR) with thiolate-monolayer protected Au nanoparticle (MPN) interface films that provide sensitive detection and diverse response patterns for recognizing eluting VOCs. Embedded microcontrol allows for continuous unattended operation and storage of data for post-exposure downloading and analysis. In our first tests of the complete prototype, we have demonstrated reproducible analyses of mixtures of up to 9 VOCs in 2.5 min (sampling and analysis), linear calibration curves, unique response patterns for mixture components, sub-ppm LODs, and stable responses for 5 days. Initial mock field tests demonstrated successful monitoring of rapidly changing concentrations of three VOCs during a solvent handling task.

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## 1. Introduction

Volatile organic compounds (VOCs) are ubiquitous, and many are toxic to humans. Collecting near-real-time *personal* multi-VOC measurements of individual exposures would greatly improve efforts to assess risks of adverse health effects, particularly in industrial workplaces. Although portable gas chromatographic (GC) instrumentation is well suited for performing multi-VOC field measurements, current instruments are too large and expensive for personal monitoring applications [1]. Despite significant advances in microfabricated GC (μGC) systems over the past decade [e.g., 2-11] a wearable μGC, suitable for routine air monitoring, has not been realized.

Here we report on a wearable μGC prototype, which we refer to as a personal exposure monitoring microsystem (PEMM), designed to analyze 10-20 VOCs per measurement, 6-8 times per hr, for any VOCs falling within a moderate volatility window defined by their vapor pressures, $p_v$. Fig. 1a shows a block diagram of the core microsystem of the PEMM. Each air sample is drawn through the inlet with the onboard mini pump and the VOCs are trapped temporarily in the μPCF. The appropriate mini valves are actuated to redirect flow, the pump is turned off, and then the VOCs are thermally desorbed and backflushed through the μcolumn for separation and detection by the μCR array on a flow of helium carrier gas from a small on-board canister. Figs. 1b-d show the core microsystem components. Fig. 1e shows the first PEMM unit (~2 kg, sans batteries), and Fig. 1f shows it mounted on the belt of one of the authors.

Novel features include: a dual-bed μPCF that quantitatively captures (and releases) VOCs with $p_v$ values < 13 kPa from sample volumes up to ~30 mL [8]; a passive pre-trap comprising a short section of PDMS wall-coated capillary removes less volatile interferences; a μcolumn chip with 6-m-long PDMS-coated channel divided into 3 thermally isolated spiral segments (2-m each) with independent heaters that can ramp the temperature of each segment (i.e., zone) with minimal cross-talk; and a μCR sensor array consisting of a set of interdigital electrodes (IDE) coated with thin films of different thiolate-monolayer protected Au nanoparticles (MPN) that yield partially selective responses from which patterns can be derived and used to recognize the specific VOCs.

## 2. Experimental

MPNs (3.5-5 nm Au core diam.) derived from the following thiols were used as μCR interface films: n-octanethiol (C8), isooctyl-3-mercaptopropionate (EOE), methyl-6-mercaptohexanoate (HME) and 1-mercapto-(triethylene glycol) methyl ether (TEG). TEG was purchased (Nanoprobes, Yaphank, NY). Other MPNs were synthesized in-house. The graphitized carbon adsorbents Carbopack X (C-X, 240 $m^2/g$), Carbopack B (C-B, 100 $m^2/g$) (Supelco Bellefonte, PA) were sieved (212-250 μm) prior to loading. PDMS was purchased (Ohio Valley Specialty Co., Marietta, OH). Pressurized He gas canisters (95 mL, 4.0 cm o.d. × 13 cm, 2500 psi) and regulator were obtained from Leland (South Plainfield, NJ).

The DRIE-Si μPCF chip (Fig. 1c) has two ~4.7 μL cavities separated by a row of 150 μm o.d. pillars, with DRIE sidewall ports for adsorbent loading (2.0 mg C-B, 2.3 mg C-X) by mild suction. Fluidic ports accommodate 250 μm i.d. fused silica capillaries. A 120-μm thick anodically bonded Pyrex plate seals the cavities/channels. A Ti/Pt

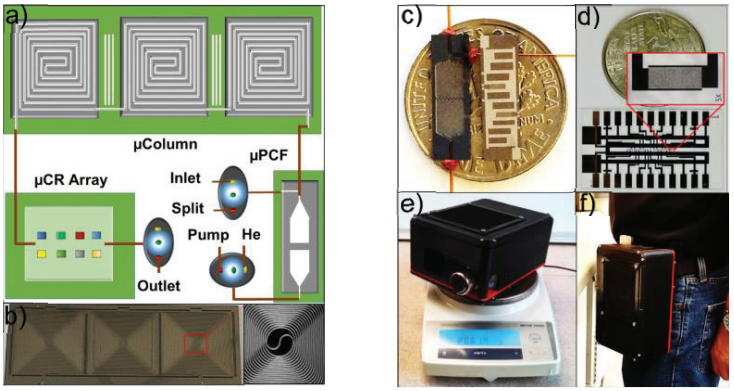


*Fig.1. (a) Fluidic layout of PEMM and; (b) photos of μcolumn; (c) μPCF and ;(d) μCR array. PEMM is (e) light enough to (f) wear on the belt.*

resistive heater and RTD were patterned onto the backside (Fig. 1c). FEM guided the heater design to minimize thermal gradients and power dissipation. The device was mounted and wire-bonded on a custom PCB.

The DRIE-Si μcolumn channel has through-wafer DRIE slots between each segment and around the periphery of the chip for thermal isolation. The 3 independent backside Pt/Ti meander-line heaters were designed to minimize gradients and power dissipation. Interconnecting capillaries were epoxied into inlet/outlet expansion ports. PDMS (0.2 μm) was statically coated on the channel walls and cross-linked for stability [2]. The μcolumn was inverted and mounted on a custom PCB, with wire bonds made to the heaters and RTDs.

The μCR array chip has 10 sets of Au/Cr (300/30nm) IDEs in a single row, with a central Au/Cr RTD, on a Pyrex substrate. Each μCR contains 27 pairs of electrodes, 5 μm wide, with 4 μm gaps, 210 μm overlap. A meander-line Pt/Ti heater was patterned on the backside. The Si lid has a 150 (d) × 350 μm (w) DRIE channel down the center (above the sensors). MPNs were drop-cast from solution to create (non-uniform) multilayer films with baseline resistances of 0.1 to 10 MΩ. Only 4 sensors were used per analysis. The lid was affixed to the substrate with double-sided tape (VHB, 3M, St. Paul, MN) and then epoxy. Interconnecting capillaries were epoxied into the fluidic ports. The lidded array was mounted on a custom PCB for electrical connections.

All devices and supporting electronic/fluidic hardware were assembled to minimize the volume of the instrument while allowing for proper cooling via on-board fans. A pair of embedded microcontrollers provides high-accuracy data acquisition, temperature control, and event scheduling. A low-power mini-computer provides a remote link for optional real-time capture of system status and data via a web-based GUI (VGC Chromatography, Dayton, OH).

Test atmospheres of VOCs were generated individually and in mixtures, with concentrations confirmed by GC-FID. Samples were captured and analyzed automatically by the PEMM after setting operating parameters. Mock field testing entailed repeatedly dipping small metal bolts into a mixture of toluene, m-xylene, and butyl acetate while wearing the PEMM. 1-min samples were collected every 6 min for 1 hr, with reference data by GC-FID.

## 3. Results and Discussion

### *3.1. Component-level testing*

Narrow injections from the μPCF are critical to achieving good chromatographic resolution. We employ an initial fast ramp of ~400 °C/sec from 30 - 100°C, followed by a PWM-controlled ramp at 150 °C/sec to 225 °C. By also using a 2:1 split-flow injection configuration (i.e., 9 mL/min total; 3 mL/min to μcolumn), the *full-width-at-half-maximum* values of benzene, toluene, and n-dodecane peaks injected separately, directly to an FID, were 0.59, 0.79, and 0.85 sec, respectively, which are remarkably narrow.

Fig.2a shows temperatures for one representative sequence of on-off heating profiles, the timing of which are guided by band trajectory models of the eluting compounds [12]. Fig. 2b shows that the retention times and peak areas are the same for "global" (simultaneous) and segmented (sequential) heating, the latter of which results in reductions in energy per analysis ranging from 21-32%, depending on the specific ramp rates employed and resulting retention times of the mixture components.

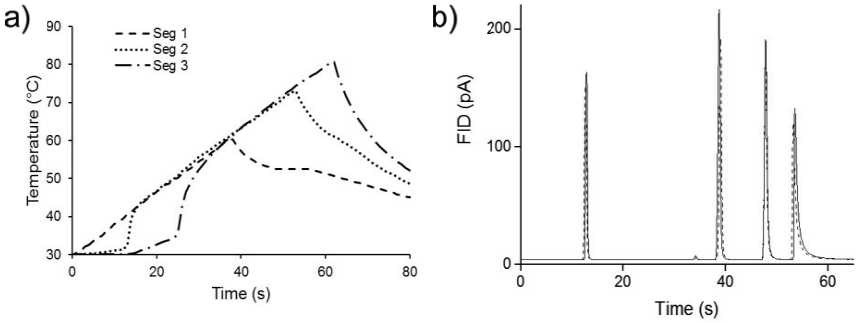


Fig. 2. (a) Temperature profiles of zone heating of the segmented μcolumn. Heating starts when the first compound enters a segment and ends when the last compound elutes out of that segment; (b) Gas chromatogram of (solid line) "global" and (dashed line) "segment" separation. Peak from left to right is solvent ($CS_2$), n-octane, ethylbenzene, and 3-heptanone.

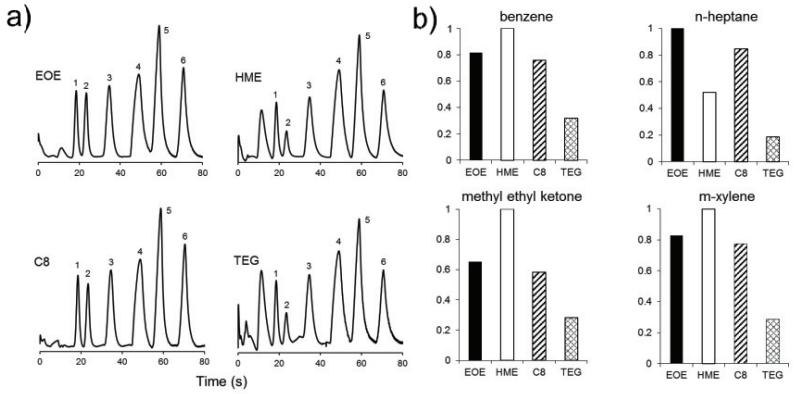


Fig. 3. (a) Chromatograms of 6 VOCs (100 ppm each) from the PEMM 4-μCR array (sample volume: 2.5 mL; μcolumn: 30 °C for 35 s, then 40 °C/min to 105 °C; μCR array: 30 °C; compounds: 1, benzene; 2, heptane; 3, toluene; 4, methyl isobutyl ketone; 5, butyl acetate; 6, m-xylene); (b) Normalized response patterns for a subset of compounds derived from peak areas in (a). Acronyms refer to the MPN interface films.

### *3.2. System-level testing*

Fig. 3a shows the 4 μCR chromatograms of 6 VOCs from a 30-s air sample (100 ppm) separated with temperature programming in < 90 s. We have also performed analyses of a 9-VOC mixture with similar resolution (not shown). Fig. 3b shows representative response patterns. Calibration curves were linear ($R^2$ >0.98) and LODs were between 1-5 ng for all VOCs on three of the sensors (exception: TEG), corresponding to 80-200 ppb air concentrations for a 5-mL air sample. Excellent medium-term stability was observed (RSD < 8% over 5 days). Mock field test results successfully demonstrated the capability for the belt-mounted PEMM to accurately track rapidly fluctuating air concentrations of the three mixture components for 1 hr. Further testing is underway.

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