



Toward a microfabricated preconcentrator-focuser for a wearable micro-scale gas chromatograph



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ABSTRACT

This article describes work leading to a microfabricated preconcentrator-focuser (μ PCF) designed for integration into a wearable microfabricated gas chromatograph (μ GC) for monitoring workplace exposures to volatile organic compounds (VOCs) ranging in vapor pressure from \sim 0.03 to 13 kPa at concentrations near their respective Threshold Limit Values. Testing was performed on both single- and dual-cavity, etched-Si μ PCF devices with Pyrex caps and integrated resistive heaters, packed with the graphitized carbons Carboxen X (C-X) and/or Carboxen B (C-B). Performance was assessed by measuring the 10% breakthrough volumes and injection bandwidths of a series of VOCs, individually and in mixtures, as a function of the VOC air concentrations, mixture complexity, sampling and desorption flow rates, adsorbent masses, temperature, and the injection split ratio. A dual-cavity device containing 1.4 mg of C-X and 2.0 mg of C-B was capable of selectively and quantitatively capturing a mixture of 14 VOCs at low-ppm concentrations in a few minutes from sample volumes sufficiently large to permit detection at relevant concentrations for workplace applications with the μ GC detector that we ultimately plan to use. Thermal desorption at 225 °C for 40 s yielded \geq 99% desorption of all analytes, and injected bandwidths as narrow as 0.6 s facilitated efficient separation on a downstream 6-m GC column in $<$ 3 min. A preconcentration factor of 620 was achieved for benzene from a sample of just 31 mL. Increasing the mass of C-X to 2.3 mg would be required for exhaustive capture of the more volatile target VOCs at high-ppm concentrations.

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1. Introduction

Measuring personal exposures to mixtures of airborne volatile organic compounds (VOCs) in working environments by standard methods entails the collection of breathing-zone air samples with adsorbent-packed devices followed by analysis at an off-site laboratory [1–4]. Since sample durations are typically several hours, only average (e.g., daily) concentrations are obtained; exposure dynamics within a work shift are lost. Gathering near-real-time measurements could improve the quality of exposure data [5]. Yet, current portable direct-reading VOC-monitoring instruments capable of quantitative multi-VOC determinations, which employ gas chromatographic (GC) separations and/or spectrometric detectors, remain too large, complex, and expensive for routine deployment as personal exposure monitors [6–9].

In attempts to address some of the shortcomings of conventional portable GC instrumentation, significant efforts by several research groups over the past four decades have been devoted to developing GC microsystems (μ GC) constructed from Si-microfabricated components, with steady progress being made toward smaller packages with lower power dissipation and greater analytical capabilities [10–22]. Most μ GC systems contain a micropreconcentrator or other on-board injection device, one or more separation micro-columns, and a microsensor or microsensor array detector, along with the necessary auxiliary hardware and software for stand-alone or computer-controlled operation. The micropreconcentrator provides the means to trap VOCs from an air sample, typically by adsorption on a granular solid, and then to thermally desorb and inject them as a focused band for subsequent separation and detection. The dual functions demanded of this μ GC component are reflected in the term “micropreconcentrator-focuser” (μ PCF) [23–25], and the range of μ PCF designs, adsorbent materials, and operating features reported over the past decade reflect the challenges to optimizing performance while minimizing size and power dissipation (for examples, see Refs. [23–38]).

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In most reported μ PCF devices, only a fraction of the mass of any targeted VOC(s) in the air passing through the device is captured and subsequently desorbed for analysis [28,30,31,33,34,37]. As with classical solid-phase microextraction (SPME) [39,40], these devices rely on the equilibrium that can be established between the VOC air concentration and the VOC surface concentration to relate the former to the latter upon subsequent quantification. Complementing such *equilibrium* μ PCFs is another class of devices that capture the entire mass of any targeted VOC(s) in the air sample [23–25,27,32,35,36]. Despite their generally larger size and consequently greater heating power dissipation, these so-called *exhaustive* μ PCFs yield much larger preconcentration factors (PF) [23,24,41,42], and the relationship between VOC air concentrations and analyzed quantities of VOCs is more direct. In fact, although significant sensitivity enhancements can be achieved with *equilibrium* μ PCF devices [31,33], since an unknown fraction of the total sampled VOC mass is lost, bonafide PF values cannot be calculated [41,42].

The design and operation of exhaustive μ PCF devices are subject to several constraints. A certain minimum sample volume is required to ensure that the mass of analyte(s) collected exceeds the limit(s) of detection (LOD) of the downstream microsensor(s), while the maximum sample volume is constrained by the inherently low capacities of the small quantities of adsorbent materials used. Flow rate, bed residence time, temperature, ambient water vapor and background VOC concentrations, adsorbent mass and specific surface area, and analyte volatility and functionality are all factors affecting capacity. Many of these same factors also affect the efficiency of thermal desorption and the minimum injection band width achievable. Thus, several aspects of μ GC system performance are contingent upon the performance of the μ PCF component.

Using the modified Wheeler Model as a guide, Lu and Zellers established relationships between the breakthrough volume (V_b), adsorbent bed mass, bed residence time (τ), and challenge concentration in their studies of small single- and multi-adsorbent packed-capillary PCF devices intended for use in portable GC instruments [23,24]. Systematic tests of capacity and desorption bandwidth for individual VOCs and VOC mixtures were performed with a selected set of adsorbents to establish the minimum required adsorbent masses and maximum allowable flow rates for exhaustive trapping and efficient desorption. These studies provided the basis for the adsorbent masses used in the first-generation μ PCF devices of the early μ GC systems developed in our group [13,25,26].

Later work by Sukaew et al. [36], examined in greater detail the relationships between values of V_b and τ of individual VOCs for a series of capillary-style PCFs and next-generation μ PCFs packed with the graphitized carbon Carboxen X (C-X). They showed that below a minimum “safe” bed residence time, τ_{safe} , the bed efficiency was <60% and the dependence of V_b on flow rate was extremely sharp and, therefore, unstable to minor fluctuations in flow rate. They recommended as a generic guideline operating at flow rates that would maintain $\tau > \tau_{\text{safe}}$. Indeed, the operating conditions of μ PCF devices incorporated into two subsequently developed application-specific μ GC systems were guided by such considerations [16,20,21,32].

In this article we describe the development and characterization of a μ PCF for use, ultimately, in a wearable μ GC system referred to as a personal exposure monitoring microsystem (PEMM), currently under development in our laboratory. The instrument is intended for generalized VOC measurements in industrial workplace environments, and we set out goals of quantitatively analyzing ~10–20 VOCs per measurement at a rate of 6–8 measurements per hour, where the VOCs would all fall within a specified volatility window defined by their vapor pressures; concentrations might range over several orders of magnitude, but for quantification most or all would be at parts-per-billion (ppb) to parts-per-million (ppm)

levels. Reconciling the constraints these place on the μ PCF with those related to the separation efficiency of the microcolumns and the sensitivities of the microsensor array to be employed required careful assessment of the tradeoffs to achieve satisfactory system-level performance. Using a set of extant μ PCF devices, we determined the adsorbent masses and operating conditions that would be required for a new dual-adsorbent μ PCF to achieve selective, exhaustive preconcentration and efficient, sharp injection of mixtures of VOCs with vapor pressures, p_v , in a designated range, at concentrations relevant to demonstrating compliance with current occupational exposure limits.

As further background for our study, in the next section we introduce the PEMM microsystem and describe the detailed competing performance criteria affecting the design of the new μ PCF. The resulting performance specifications for this application are then presented along with their rationales and associated compromises. The test set of VOCs is presented and ranges of concentrations, flow rates, and sampling times are defined on the basis of such considerations. We then proceed to describe our methodology and the results of testing with representative quantities of the adsorbent materials to be used to determine conditions for optimal desorptions/injections. The effects of key variables on the dynamic adsorption capacity are then presented followed by a final performance demonstration with a moderately complex mixture of target and interfering VOCs. Note that all testing reported here used conventional bench-scale GC instrumentation for separation and detection.

2. Experimental design and rationale

Fig. 1 shows a block diagram of one of the analytical subsystem layouts being considered for the first PEMM μ GC prototype currently being developed. The primary analytical/fluidic components

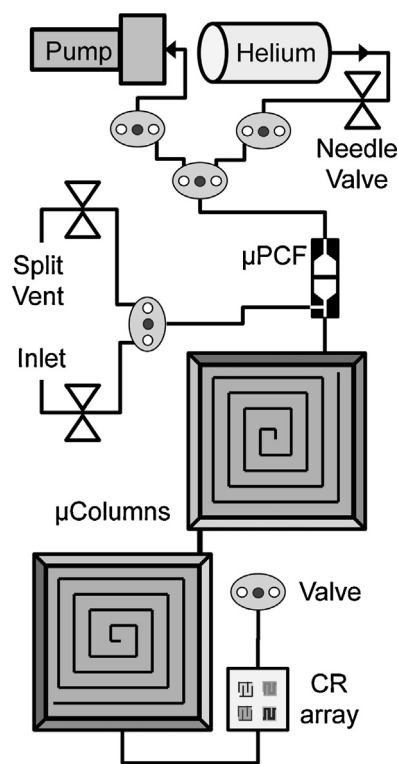


Fig. 1. Fluidic layout of the proposed PEMM μ GC. VOCs from air samples drawn through the inlet by the on-board mini-pump would be captured in the μ PCF and then thermally desorbed and backflushed into the first separation μ column on a background of He gas.

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