AN INTEGRATED MICRO-ANALYTICAL SYSTEM FOR COMPLEX VAPOR MIXTURES

Edward T. Zellers,[1,2,3] Shaelah Reidy,[1,3] Rebecca A. Veeneman,[1,3] Robert Gordenker,[1,4] William H. Steinecker,[1,3] Gordon R. Lambertus,[1,3] Hanseup Kim,[1,4] Joseph A. Potkay,[1,4] Michael P. Rowe, [1,3] Qiongyan Zhong,[1,2] Christopher Avery,[1,3] Helena K. L. Chan,[1,4] Richard D. Sacks,[1,3] Khalil Najafi,[1,4] Kensall D. Wise,[1,4]

[1]Engineering Research Center for Wireless Integrated MicroSystems, [2]Departments of Environmental Health Sciences, [3]Chemistry, [4]Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, MI, USA (Tel: 1-734-936-0766; Email: ezellers@umich.edu)

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Abstract: A micro gas chromatograph (μGC) capable of quantitatively analyzing the components of complex vapor mixtures at trace concentrations is described. The μGC features a micro-preconcentrator/focuser (μPCF), dual-column pressure- and temperature-programmed separation module, and an integrated array of nanoparticle-coated chemiresistors. The latest design modifications and performance data are presented. Highlights include a 4-min separation of a 30-component mixture with a 3-m DRIE Si/glass microcolumn, a 14-sec separation of an 11-component mixture on a 25-cm microcolumn, a complete multi-vapor analysis from a hybrid microsystem that combines analytical, rf-wireless, and microcontroller modules, and a rapid analysis driven by a 4-stage peristaltic micropump.

Keywords: gas chromatograph; micro-analytical system; integrated microsystem; gas analyzer.

1. INTRODUCTION

Building on the pioneering work of Terry et al. [1], a number of reports have appeared over the past 15 years on micromachined gas chromatographic (GC) separation channels, often coupled with devices for preconcentration, injection, and/or detection of gas-phase analytes [2-6]. Most of these efforts have focused on specific targets, such as chemical warfare agents.

We have been engaged for the past several years in an effort to develop low-power micro-instrumentation platforms for biomedical and environmental monitoring applications that couple sensing and actuation subsystems with an embedded controller, wireless transceiver, and (battery) power supply [7]. The primary focus of the environmental monitoring development effort is a versatile, high-performance micro gas chromatograph (μGC) designed for analyzing components of complex vapor mixtures at low concentrations [8-10]. Figure 1 (center) shows the fluidic layout of the analytical subsystem of the μGC. Each analysis is performed in two discrete steps. First, air samples are drawn by the pump through the inlet particulate filter, past the calibration-vapor source and through the multi-stage, adsorbent preconcentrator/focuser (μPCF). Next, vapors captured in the μPCF are rapidly thermally desorbed and back-flushed into the dual-column separation module, which can be pressure- and temperature-programmed for adjusting (i.e., tuning) retention. The compounds in the mixture are separated as they reversibly partition into the thin polymeric stationary phases lining the walls of the columns. Upon eluting from the separation module vapors pass across an array of chemiresistors (CR) coated with thin films of different gold-thiolate monolayer protected nanoparticles (MPN) whose responses vary with the nature of the transient interactions between the analyte vapors and the ligands on the nanoparticles. We recently reported on multi-vapor analyses obtained with a prototype μGC consisting of a μPCF, a single 3-m DRIE Si/glass microcolumn, and a CR-array detector [9,10]. Chromatographic retention times were used together with sensor-array response patterns to identify eluting vapors, and the magnitudes of the sensor responses wereused for quantification. Tradeoffs associated with varying different operating parameters were explored [8]. Here, we

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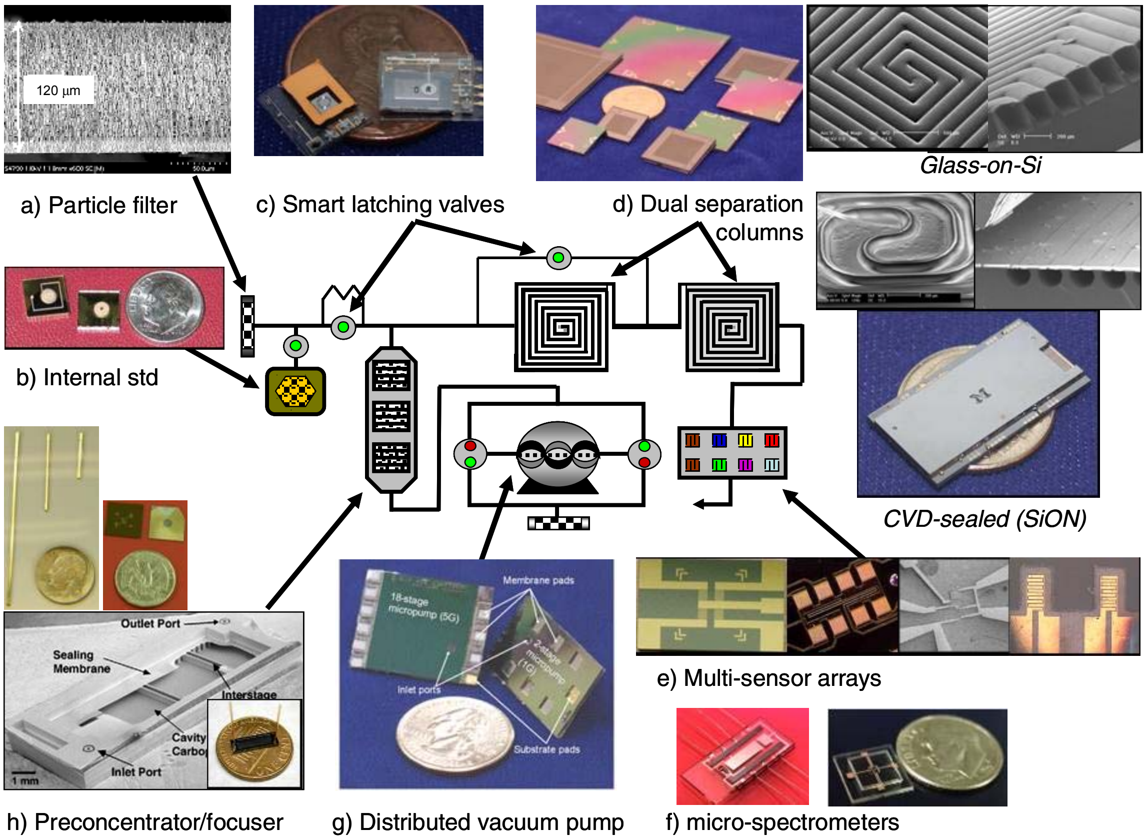

Figure 1. Layout diagram of the WIMS µGC (center) and images of the analytical components

describe some of the latest advances made toward the realization of a low-power, high-performance µGC, highlighting rapid, complex-mixture separations, and analyses performed with a complete hybrid µGC prototype and a micropump driven µGC subsystem.

2. MICROSYSTEM OVERVIEW

The inlet particle filter (Fig. 1a) consists of a macroporous silicon (PS) membrane (3.5mm diam., 120µm thick) with tortuous pores, which exhibits high capture efficiency and high capacity for submicron particles at a relatively low pressure drop (~1.2 kPa @ 25 cm^3/min) [11a]. The calibration-vapor source (Fig. 1b) is a 2-layer structure whose base contains a deep PS reservoir for retaining the volatile-liquid calibrant (e.g., n-decane) and a Si cap with a DRIE diffusion channel and exit port. The PS reservoir has straight vertical pores ~3µm in diameter [11b]. Constant vapor generation over many days of operation has been demonstrated.

The three-stage µPCF is designed to capture organic vapors quantitatively from a large sample volume (e.g., 0.25-1 L), desorb them into a small volume, and provide a sharp injection plug for chromatographic separations. Single-stage and three-stage designs have been fabricated and tested, with the latter providing efficient capture/release of 30 vapors and preconcentration factors as high as 5,000 [12]. The base of the current µPCF (Fig. 1h) is a 50-µm-thick doped-Si resistively-heated 27 mm^2 membrane. The interior is sectioned to allow packing of three different adsorbents (total mass ~ 5mg) with increasing specific surface area. Adsorbents are loaded and devices sealed at wafer level. The transient heating energy dissipation is 0.053 J/°C and 1.8W is required for steady-state heating at 300°C. Tests with n-octane (20 ppm) have given breakthrough volumes > 0.2 L. Tubular designs are also being tested.

Valves employing a thermally isolated thermopneumatic actuator, an electrostatic latch, and a capacitive position-sensing capability have been fabricated (Fig. 1c). The normally-open microvalves close in 430s at 250mW with a leak rate of 0.001 cm^3/min at 860torr and an open flow of 8 cm^3/min at 4.6torr. The current valves require a small amount of power (~mW) to maintain a seal and the plate position is determined with a sensitivity of 1.3 fF/torr.

Two discrete series-coupled separation columns are employed in our current prototype, each consisting of a convolved square-spiral DRIE-Si channel (cross-section = 150 x 240 µm), with lengths of 0.25, 0.5, 1.0, and 3.0 m (Fig. 1d). The 3-m column is contained within a square die 3.3 cm on a side [13]. The latest columns have integrated pressure and temperature sensors. Degenerative boron doping of the channel floor facilitates removal of un-needed substrate as well as subsequent column heating. Wafer-level low-pressure anodic bonding is used to seal the channel with a Pyrex cover plate and fused-silica capillaries are epoxied into recessed side ports for fluidic connections. Power for sustained heating to 100 °C is ~100 mW in vacuum [13].

Alternative, low-mass, monolithic dual-column ensembles have been fabricated from bulk-etched spiral channels with nearly circular cross-sections formed in Si by undercutting a silicon/dielectric mask. The mask openings are subsequently sealed with CVD silicon oxynitride (SiON) and excess Si is etched away to minimize mass, thereby reducing the energy required for heating. Structures having lengths of 0.5m and 1m and inner diameters of ~90 µm with integrated heaters and temperature sensors have been fabricated. Only 11mW is required to raise the column temperature by 100°C in 11s in vacuum (5mtorr). The 1-m column has been used to separate 10 volatile organic cmpds in 52s [14].

The integrated CR sensor arrays (Fig. 1e) use solvent-cast MPNs as interface layers and detect eluting vapors by the change in dc resistance of the film due to reversible vapor sorption. Characteristic response patterns are obtained for eluting vapors [15]. The response mechanism has been elucidated and a model derived relating relative resistance changes to analyte density, dielectric constant, and partition coefficient [16]. We have also e-beam patterned MPNs on a working array that has provided stable responses for ~3.5 months [17]. In a recent study focused on environmental applications, an MPN-coated CR array was used in a portable GC for analysis of environmental tobacco smoke (ETS). The instrument was able to separate two ETS markers from 34 prominent co-contaminants and achieve detection limits in the part-per-trillion range with a 1-L sample sample [18]. We have also found that incorporating Pt-olefin charge transfer complexes into the MPN layers yields remarkable selectivity and sensitivity toward each of several olefin gases and vapors [19]. We have also interfaced a commercial differential mobility spectrometer to a 3-m microcolumn (Fig. 1f) [20].

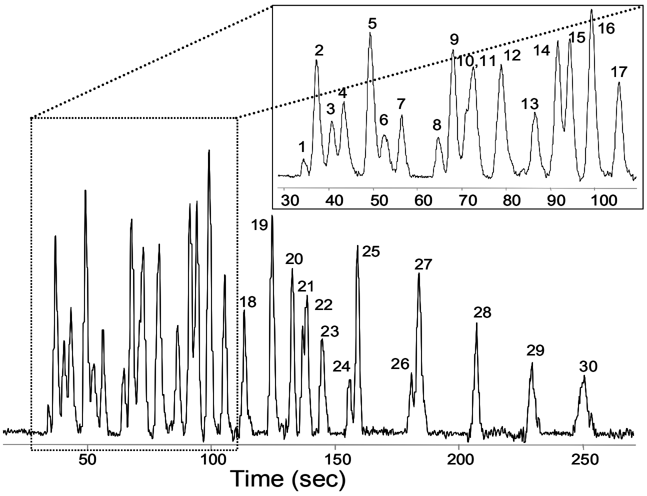

Figure 2. 30-compound mixture separated with a 3-m PDMS-coated DRIE-Si/glass column, using air as carrier gas and a linear temperature program from 30-150℃ at 30 ℃/min. The two co-elutions (10/11 & 21/22) are separable with a slower temperature ramp.

Another significant advancement has been the development of a series of high-performance multi-stage peristaltic micropumps (Fig. 1g) [21,22]. The 18-stage prototype occupies 3.8 cm^3, operates at a resonance frequency of 14 kHz, produces air flow rates up to 4 cm^3/min, generates up to 17 kPa of pressure, and requires only ~57mW of average power. A 4-stage prototype has also been produced and used in chromatographic separations, as described below.

3. MICRO-COLUMN SEPARATIONS

Figure 2 shows results obtained with a 3-m DRIE Si/glass column coated with a thin solvent-

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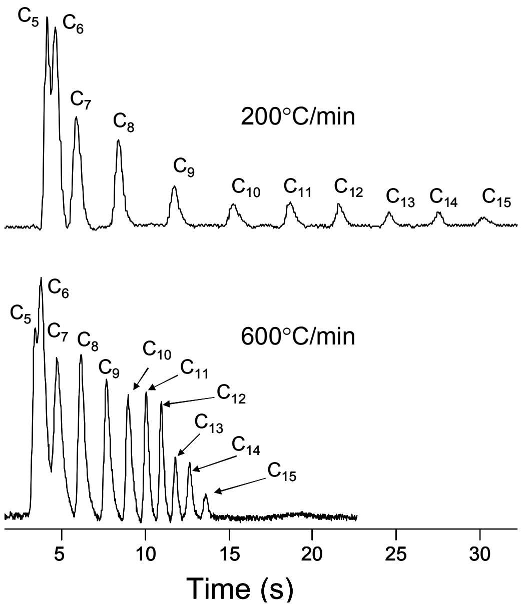

Figure 3. Chromatograms of an homologous series of n-alkanes obtained with a 25-cm-long PDMS-coated DRIE-Si/glass column and FID detector at temperature programming rates of 200 and 600 °C/min. Air was the carrier gas.

cast PDMS stationary phase. A 30-compound mixture was injected by syringe through the heated split/splitless injection port of a bench-scale GC and a flame-ionization detector was used. The analyte mixture spans five orders of magnitude in vapor pressure (i.e., from ethanal, $p_v = 743$ torr, to n-pentadecane, $p_v = 0.003$ torr). With temperature programming provided by on-board heaters and temperature sensors, this separation was completed in just 4.2 min. These columns are capable of producing 12,000 theoretical plates, making them the highest-resolution microcolumns reported to date [23].

Figure 3 shows the separation of n-alkanes using a 25-cm-long microcolumn (1-cm^2 chip) at two different temperature ramp rates. This set of compounds spans four orders of magnitude in vapor pressure. Peaks shapes are excellent and at the highest ramp the entire mixture is separated within 14sec [23].

4. µGC PROTOTYPE

Figure 4 shows our latest fully assembled µGC prototype. It contains a glass/Si electrical and fluidic integration substrate, inlet particulate filter, calibration vapor source, preconcentrator, two series coupled microcolumns with junction-point pressure control and independent temperature programming capabilities, and an integrated CR array. Short, in-plane, heated connections minimize dead volumes and wall adsorption. Commercial two-way solenoid valves direct flow, currently provided by a commercial mini-pump. Low-profile beam leads are used for several critical electrical connections. Sensor chips are inverted and bonded over a depression-etch cavity in the fluidic interconnection substrate.

The embedded µcontroller is being programmed for system control, calibration, analysis, parameter setup, sequencing instrument functions, and sensor data acquisition. At the outset of an analysis cycle, a set of operating parameters is downloaded to the program controlling the µGC. A host PC with a GUI (Labview) facilitates setting parameters, manages the wireless link(s), and provides readout of subsystem status. Preprocessing and buffering data for upload to a host controller using a ZIGBEE standard wireless link will enable deployment of multiple µGCs under control of a single user.

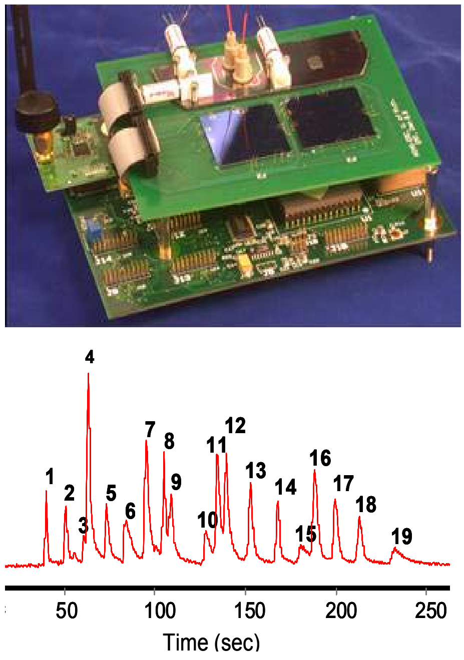

Figure 4. (top) Prototype WIMS µGC with the analytical module and rf module mounted on the microcontroller module; (bottom) chromatogram of 19 common air contaminants obtained with this prototype (FID detection).

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Figure 4 shows the results of a test designed to probe the fluidic integrity of the analytical subsystem. The 19-compound mixture comprises a set of common indoor air contaminants of anthropogenic and microbial origin. A test-atmosphere of this mixture was sampled for 5 sec and the μPCF (multi-adsorbent, tubular design) was then heated to 300 °C to inject the mixture into the separation module. The separation was completed in < 4 min using two 3-m columns coated with a non-polar PDMS stationary phase and a moderately polar poly(trifluoropropylmethyl) siloxane stationary phase, respectively [24]. Each column was temperature programmed independently. The FID trace reveals that peaks are symmetric and there is a minimum of broadening, reflecting efficient PCF injection and sample transport through the substrate and other interconnections. Similar tests run with the integrated CR array coated with electron-beam-patterned MPN interface layers produced chromatograms with slightly reduced resolution (data not shown).

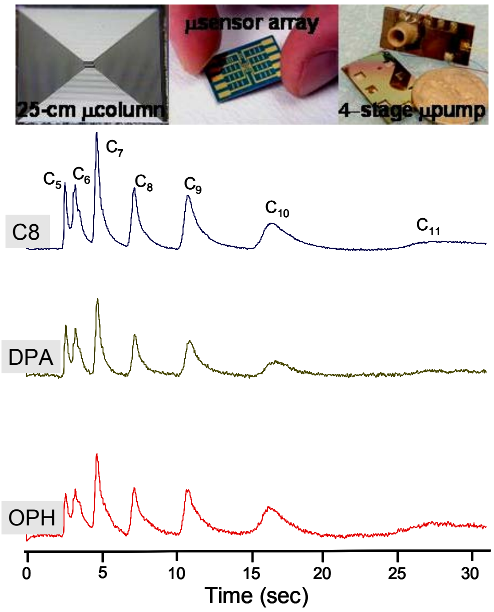

Fig. 5: (top) images of the components of a μGC subsystem comprising a microcolumn, CR sensor array, and micropump; (bottom) 30-sec temperature-programmed separation of a series of 7 n-alkanes achieved with this subsystem and air as the carrier gas. Each trace is labeled with the acronym of the MPN used on the corresponding CR sensor.

5. MICRO-PUMP DRIVEN ANALYSIS

Figure 5 shows a μGC subsystem (< 5 cm^3) consisting of a 25-cm column with a PDMS stationary phase, an MPN-coated CR array and a 4-stage gas micropump. Components were connected using passivated silica capillaries. A mixture of alkanes ranging from n-pentane to n-pentadecane (C_{15}) was injected via syringe into a heated injection port of a bench-scale GC and a tee-connection allowed for a portion of this sample to be captured by the μGC subsystem. Air was used as carrier gas and a flow rate of 0.25 mL/min (ΔP = 3.5 kPa) generated by the micropump (operated at ±100V AC) was used for the separation. The column was temperature programmed at 160 °C/min with on-board heaters. As shown, the separation of all but the least volatile pair of vapors is excellent and the separation is complete in 28sec. These results are part of a set achieved with this subsystem that comprise the first results obtained with a micro-pump driven μGC Additional results will be presented by H. Kim at this conference [25].

In summary, this work has demonstrated that rapid, quantitative analysis of complex mixtures of organic vapors with high temporal and analytical resolution is possible with a MEMS gas chromatograph. Among the notable achievements reported here are: efficient particle filtration; efficient preconcentration and thermal injection of vapor mixtures; high-resolution, high-speed, low-power separations using μcolumns equipped with on-board heaters and temperature sensors; array detectors with nanoparticle interface layers that provide characteristic response patterns and sub-ppb detection limits with modest sample volumes; a micropump capable of driving separations; and integration of fluidic, electronic, and rf-wireless modules in a hybrid prototype capable of analyzing multi-vapor mixtures.

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