A VERSATILE MEMS GAS CHROMATOGRAPH FOR DETERMINATIONS OF ENVIRONMENTAL VAPOR MIXTURES

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ABSTRACT

A microfabricated gas chromatograph (μGC) with several innovative and enabling design features is described. The microsystem incorporates capabilities for particulate exclusion, on-board calibration, sample preconcentration and thermal desorption, pressure- and temperature-modulated separations, and "spectral" detection with array of microsensors. It is intended to permit rapid determinations of complex mixtures of environmental contaminants at trace concentrations. The ultimate goal is to embed microcontroller and rf communications modules for deployment in high-performance distributed environmental monitoring networks, among other possible applications. Ultra-low power dissipation is therefore a priority. This presentation reports on progress, to date, with an emphasis on the MEMS sensors and actuators employed. Device design, processing, and integration issues are reviewed. Pressure-tuned separations with a dual micro-column ensemble are demonstrated for the first time to effect the resolution of 13-vapor mixture at room temperature in under 4 minutes. A first-generation hybrid prototype μGC capable of performing mixture separations in as little as 30 seconds with detection limits in the low part-per-billion concentration range is also presented.

INTRODUCTION

Measurements of gases and vapors in complex mixtures are critical for accurate human exposure assessments, air quality forecasting, industrial emission monitoring/ mapping, emergency spill/release response, and biomedical surveillance and diagnosis. Several portable instruments capable of multi-vapor analyses are now commercially available [**1**], but reductions in size and complexity as well as improvements in analytical performance are necessary before routine *in-situ* determinations of multiple trace-level contaminants are possible at reasonable cost.

Microsensor arrays have been applied successfully to the determination of vapors in simple mixtures [**2,3**] and to comparative analyses of mixture composites in so-called 'electronic nose' configurations [**4**]. In addition, progress continues toward micro-spectrometers based on ion-mobility [**5**], infrared absorbance [**6,7**], atomic emission [**8**], and mass analysis [**9**]. It must be appreciated, however, that quantitative analysis of vapor mixtures of complex and variable composition invariably demands temporal/spatial separation prior to measurement, regardless of the detector employed. Furthermore, for most environmental health applications a preconcentration step is required to detect vapors in the range of regulatory limits, which can be as low as a few parts-per-billion (ppb) by volume.

Since the first report by Terry et al. [**10**], a number of researchers have described micromachined gas chromatographic separation channels coupled with one or another sampling, pretreatment and/or detection devices [**11-14**]. Most notable among these is the Sandia μChemLab®, which incorporates a membrane preconcentrator with a short, DRIE-Si separation column and an integrated acoustic-wave sensor array into a fieldable hybrid microsystem designed principally for national security applications [**12,14**].

The Michigan Engineering Research Center for Wireless Integrated Microsystems (WIMS) has recently engaged in a broad-based effort to develop generic micro-instrumentation platforms for biomedical and environmental monitoring applications [**15**]. The archetypical WIMS design couples interconnected sensing and actuation subsystems, which can be customized for specific applications, with an embedded controller, RF-MEMS wireless transceiver, and (battery) power supply. The primary focus of the environmental monitoring development effort is a versatile, high-performance micro gas chromatograph (μGC).

A block diagram of the analytical components of the μGC is shown in Fig. 1 (center). Analysis requires a sequence of operations. 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). After collection of a finite sample volume, trapped vapors are rapidly thermally desorbed from the μPCF and backflushed into the dual-column separation module, which can be pressure- and temperature-programmed for adjusting (i.e., tuning) retention. The vapors in the mixture are separated spatially as they reversibly partition into the thin polymeric stationary phases lining the walls of the two columns. Compounds elute from the columns and are passed over the array of microsensors for recognition and quantification – responses from the sensors vary with the strength of the transient interactions occurring between the analyte vapors and sensor interface layers. Pressure and temperature sensors, as well as heater structures, are integrated within several devices.

MEMS processing methods are being used to fabricate the entire system with the ultimate goal of creating an autonomous micro-instrument that occupies only 1-2 cm^3, requires an average power of <<100 mW per analysis, and provides determinations of complex environmental vapor mixtures at low- or sub-ppb

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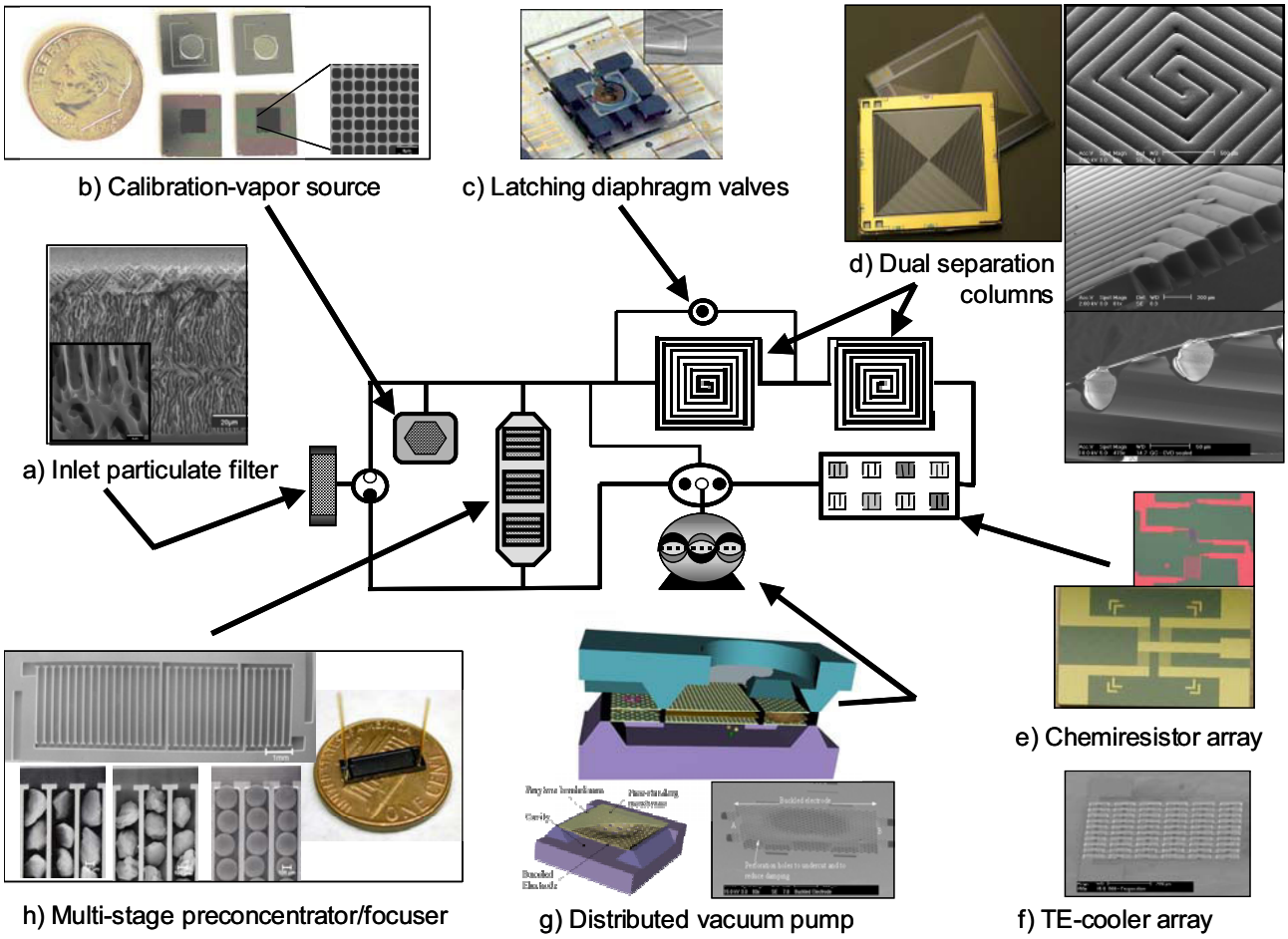

Figure 1. *Layout of the analytical components of the WIMS μGC (center); a) SEM image of a porous silicon superlattice with inset showing the tortuous-path cross section that will enhance particle collection efficiency; b) pair of calibration-vapor sources prior to sealing, with DRIE diffusion paths in top layer and PS reservoir in bottom layer (left), and SEM image of through-wafer straight-pore PS sample with uniform 3.5-μm pores (right); c) thermopneumatically actuated electrostatically latched microvalve with inset showing the elevated heater d) clockwise: photo of two 3-m Pyrex-Si DRIE columns on 3.3 x 3.3 cm die; backview of one column, cutaway showing channel cross-section, and cutaway of a 2nd-gen. ultra-low-mass CVD-sealed column; e) integrated 4-chemiresistor (CR) array with 15-μm electrode spacings (left) and CR sensors with electrode spacings of 1, 0.3, and 0.1 μm (right); f) SEM image of an array of 60 TE cooler elements for reducing sensor-array temperature; g) conceptual illustration of vacuum pump (two stages shown), and diagram and SEM image of buckled electrodes with Parylene membrane; h) 3-stage μPCF with granular adsorbents packed between transverse heat exchanger slats (left) and packaged μPCF on a U.S. penny (right).*

concentrations with a cycle time of a few minutes. Low-power interface, control, and RF-MEMS wireless communication devices to be integrated with the μGC are being developed in parallel efforts within the WIMS Center [**15,16**]. Fig. 2 presents a conceptual diagram of one monolithic μGC configuration.

Descriptions of several μGC components and subsystems can be found in recent published reports [**2,17-31**]. Here, we provide a review of current status that focuses on the important attributes of the MEMS sensors and actuators being employed, the challenges of achieving high performance at low power, and our latest results showing tuned separations and high-speed mixture analyses with a first-generation hybrid μGC prototype.

MICROSYSTEM FEATURES

Inlet Filter and Calibration-Vapor Source. An inlet filter is needed to prevent particle entrainment into the system. We are attempting to construct the filter from a large membrane of porous silicon (PS). The challenge is to create a tortuous path in order to efficiently capture particles with diameters down to the sub-micron range while maintaining sufficient porosity to minimize the pressure drop at the sampling flow rate, currently anticipated to be ≤25 cc/min. By varying the anodization conditions it is possible to adjust the size and orientation of the PS macropores with depth, alternating between regimes where pore growth is dependent on crystal orientation (anisotropic) and the direction of applied current (isotropic) [**30**]. We have succeeded in creating beds ~100 μm thick with the right morphology (Fig. 1a) and are working to extend the superlattice through the entire wafer.

The calibration-vapor source (Fig. 1b) is designed to generate calibrant vapor at a constant rate by passive diffusion from a liquid reservoir. Analysis of this "internal standard" along with vapors captured from the environment provides the means to assess and compensate for aging and drift. It is a 3-layer structure whose base contains a deep PS reservoir for retaining the volatile-liquid calibrant (n-decane for most tests to date), a Pyrex spacer layer with a wide, central aperture that defines the headspace region, and a Si cap that contains a DRIE diffusion channel and exit port. The device has a footprint of 8.5 x 9.0 mm and is 2.2 mm thick. To avoid pore-induced vapor pressure depression effects, PS reservoirs are being fabricated under conditions that yield straight vertical pores having diameters on the order of 2-8 microns (Fig. 1b) [**29**]. Constant vapor generation over many hours operation has been demonstrated with a temperature dependence that agrees closely with theory [**25**].

Preconcentrator-Focuser (μPCF). The three-stage μPCF is designed to capture organic vapors quantitatively and to thermally desorb them into a much smaller volume thereby increasing the effective concentration and providing a sharp injection plug, which facilitates high-speed chromatographic separations. Quantitative capture of vapors in complex environmental mixtures requires a large adsorbent surface area. However, subsequent desorption of trapped chemicals with a wide range of vapor pressures demands a gradient of adsorbent surface area that increases in the direction of air flow in order to avoid irreversible adsorption or thermal degradation. Rapid desorption at minimum power also requires efficient heating structures. Indeed, the demand for rapid heating represents a significant challenge to low power operation. The current μPCF (Fig. 1h) contains a set of transverse, high-aspect-ratio slat-type DRIE-Si heat exchangers, 380 (h) x 50 (w) x 3000 μm (l), spaced from adjacent elements by 220 μm. The base is a 50-μm-thick doped-Si resistively-heated membrane occupying 27 mm^2 [**26**]. The interior volume is packed with three different porous, carbon-based adsorbents (total mass ~ 5mg) in order of increasing specific surface area [**32**]. The loaded μPCF is sealed by RTA with a Si cover plate having etched grommets designed to accept the capillary interconnections. Capture/release of 30 vapors has been demonstrated but heating to 280 °C to effect desorption currently requires about 800 mW per stage. Further miniaturization and vacuum encapsulation promise significant reductions in power. Devices are also being designed to accommodate novel adsorbent materials being developed with tailored surface areas and porosities as well as high-surface-area, thermally stable materials that can be produced *in situ* within the heater structures by CVD.

Dual-Column Separation Module. The separation stage determines much of the resolution, speed, and power dissipation of the overall microsystem. Power is especially critical since the columns must be heated to ~100°C in operation, and when temperature programming is used the temperature changes can be rapid. This requires a very high thermal resistance between the columns and the ambient to achieve low power as well as ultra-low thermal mass to achieve a rapid response time. The length of the separation column, among other factors, determines the resolving power, the number of separable compounds, and the analysis time. Column length is also subject to constraint because of the pressure drop created since the pressure-driven flow provided by the micropump is limited.

To address the tradeoffs of resolution, length, and time, we are employing two series-coupled separation columns having a pressure-control valve at their junction point and independent temperature control. The two columns have complementary stationary phases so that retention differs between them for each analyte. A non-polar polydimethylsiloxane stationary phase is employed in one column and a moderately polar poly-trifluoropropylsiloxane phase in the second column. Placing a tap at the midpoint permits adjustment of the time spent in each column by the analytes. Flow can be stopped in the first column and simultaneously accelerated in the second column during an analysis, and strategically timed stop-flow intervals can enhance separations. Independent temperature control of each column provides another powerful mechanism of adjusting resolution. Collectively, these features allow maximum use of available column length and maximum flexibility for specific applications.

An initial goal for the system is to achieve sufficient resolution to separate/analyze 30 or more volatile organic compounds in a single separation of ≤10 minutes duration. Two discrete columns are employed currently, each consisting of a convolved square-spiral DRIE-Si channel 150 μm (w) x 240 μm (h), 3 m length, on square die 3.3 cm on a side [**20,21**]. To allow for peripheral inlet/outlet ports, two parallel channels were created in each column that meet at the center of the chip where the flow direction is reversed. The latest columns also 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. Fig. 1d shows front, back, and cutaway images of sealed columns having thinned Pyrex covers to reduce total mass. Power for sustained heating to 100 °C is projected at < 100 mW with proper packaging [**31**].

Stationary phases are deposited dynamically from a dilute solution under a positive pressure of inert gas and then cured to improve stability. Tests have shown that these columns can provide between 5500 and 8200 theoretical plates each. The separation of 15-20 compounds on each column in an air matrix in a matter of a few minutes has been demonstrated [**20-22**].

Fig. 3 shows the first example of a pressure-tuned separation with a dual DRIE-Si column ensemble The columns were mounted within a conventional GC oven and connected to a heated split-flow injector, compressed-air carrier gas, pneumatic mid-point valve, and a flame-ionization detector (FID). Syringe injection of a 13-compound mixture yielded the upper trace, with several co-elutions. By incorporating a series of pre-determined stop-flow intervals of a few sec each, resolution of all 13 compounds was possible in < 4 min at room temperature.

Next-generation monolithic dual-column ensembles are currently in fabrication. These low-mass columns are made from bulk-etched spiral channels with circular cross-sections formed in Si by undercutting a silicon/dielectric mask. The mask openings are subsequently sealed with CVD dielectrics. The column walls are boron-doped Si, permitting the wafer to be dissolved at end of process to yield a single-crystal Si tube supported at each end (Fig. 1d). The columns achieve minimum thermal mass and are engineered to set the tradeoffs between thermal isolation and thermal time constant. Vacuum sealing will eliminate convective losses and low-emissivity coatings minimize radiation loss. Thermal response times for heating of < 100msec and power <<100 mW are anticipated.

Chemiresistor Array. The integrated array of chemiresistors (CR) is designed to produce a "spectrum" of responses to vapors eluting from the separation module that can be combined with column retention times to identify the vapors. The magnitudes of the CR responses reflect the vapor concentrations. CR sensors consist of a set of interdigital electrodes with a thin,

chemically responsive overlayer. They are particularly well-suited for miniaturization due to the simplicity of their design and required supporting drive and measurement circuitry, ease of fabrication, and their favorable scaling laws. Work to date has focused on integrated arrays of 4 CR sensors with electrode spacings of 15 μm (Fig. 1e) and interfacial films of Au-thiolate monolayer-protected nanoclusters (MPC), 50-300 nm thick, whose dc resistances increase to different extents upon sorbing vapors [17,19,28,33]. MPCs tested include those having the following thiolate ligands: n-octanethiol (C8); 4-mercaptodiphenylacetylene (DPA); 1-mercapto-6-phenoxyhexane (OPH); and 7-mercaptoheptanitrile (CCN). The coated array is sealed with a Macor® lid to create a 3-μL detector cell. Preliminary results obtained with such arrays have been very encouraging [**17-19,28**].

With a goal of further reductions in sensor size (which will also permit a modest increase in the number of sensors in the array) we have tested CR devices with electrode spacings as small as 100 nm and found that this 150x reduction in gap size has no significant effect on sensitivity but allows a reduction in cell volume and required sample mass (which in turn will permit a reduction in the size and power requirements of the μPCF). Consistent with sorption-governed responses, sensitivity increases of 2-4x are observed upon cooling sensors by only 18 °C. Micro-thermo-electric (TE) cooling by use of arrays of Bi-Te and Sb-Te thin-film column-type TE cooling elements of micron dimensions is being investigated. Such structures have been produced by co-evaporation of the elements (Fig. 1f) and are currently being tested [**24**].

In exploring the fundamental aspects of electron tunneling through MPC films, we have observed non-linear I-V characteristics in C8-Au films on 100-nm electrode arrays even at room temperature. In addition, sensors exhibit 1/f noise that increases by ~100-fold upon toluene exposure while the resistance changes by only a factor of two [**34**].

Valves and Pump. Valves are required in three locations within the microsystem (Fig. 1). In order to minimize fluidic constrictions, valve throws > 10 μm are desirable. Actuation times <100 msec, low leakage at differential pressures of 0.5 atm, and operation at very low power are also among the design specifications. Building on prior work [**35**], we have fabricated a "smart" valve that utilizes a thermally isolated thermopneumatic actuator and an electrostatic latch, coupled with a capacitive position-sensing capability. Prototype stand-alone microvalves 1-mm in diameter (Fig. 1c) produce 500Torr of actuation pressure at 100mW of input power and provide a throw of 30 μm. The valve seat position is determined with a sensitivity of 4.3fF/Torr and the valve latches at 40V at a cavity pressure of 600Torr. Leakage is < 0.02 sccm at 0.5 atm differential pressure. Hold power (open or closed) is negligible.

Sample transport through the μGC will ultimately be provided by distributed 18-stage, peristaltic vacuum (compression) air pump currently in fabrication. Each stage comprises two checkerboard valves and an electrostatically actuated pump chamber. The overall pump dimensions are 1cm x 1cm x 1mm. Dynamic operation modeling predicts flow rates of 2-50 sccm at back pressures of 0.2-0.5 atm with a power dissipation < 40 mW [**23**]. Fabrication entails the use of Parylene membranes patterned, bonded, metallized and transferred over perforated electrodes. A novel two-sided stress-buckled (curved) electrostatic drive is also being used to create large-deflection (~8 μm) actuation at relatively low voltages (~150 V) (Fig. 1g).

1ST-GENERATION PROTOTYPE PERFORMANCE

Fig. 4 shows our first-generation prototype which combines the calibration-vapor source, μPCF, single (non-polar) column, and 4-CR array with commercial mini-valves on a Pyrex-on-Si substrate. The substrate has etched channels and micromilled access ports for fluidic interconnections, as well as metal traces for electrical interconnections to interface, control, and rf-communication boards upon which it will be mounted.

Flow velocity can have dramatic effects on desorption profiles from the μPCF, chromatographic resolution, and response profiles from the sensors. Reconciling flow velocity is one of the challenges to effective microsystem integration. Optimal flows through the μPCF during desorption are typically much higher than those providing optimal chromatographic resolution, particularly when using air as the carrier gas, however the heating rate of the μPCF, the initial separation-column temperature, and the analyte vapor pressures are all important cofactors. Models to address these issues are being developed.

Fig. 5 shows a single-sensor (OPH-Au) chromatogram obtained for a mixture of vapors captured on the μPCF and then desorbed and analyzed under one set of flow/heating conditions. These tests were performed with the same components as shown in Fig. 4 but in a slightly modified configuration. The column used a Kevlar-embedded resistive heater for temperature programming and a small commercial suction pump for air flow [**17,18**]. As shown, sharp, well resolved peaks can be produced under these conditions and the 10-compound mixture could be separated in about 2 min. This separation would require 5-10x longer on a conventional GC. Limits of detection for these vapors are all below 100 ppb assuming a 0.25-L preconcentrated air sample.

Fig. 6 shows a set of responses from the entire 4-CR array obtained under different operating conditions, adjusted to increase analysis speed for this set of more volatile vapors. A split-flow bypass (Fig. 1) was used to shunt a portion of the flow passing through the μPCF around the column so that a high desorption flow rate could be used while maintaining a lower column flow rate [**17**]. In addition a different heating profile was used for μPCF desorption. The 7-vapor mixture is separated remarkably rapidly (~30 sec), though at somewhat lower resolution. Response patterns shown for a subset of four vapors (Fig. 6) reflect the diversity of sensor responses and provide chemical information that can facilitate determinations of analyte identities [**36**].

CONCLUSIONS

This work has demonstrated that rapid, quantitative analysis of mixtures of organic vapors is possible with a MEMS gas chromatograph and that detection limits in the ppb-range can be achieved for modest sample volumes. Response patterns from the sensor array are combined with retention times to distribute the analytical burden between the separation and detector stages. Coupled with dual-column retention tuning, this microanalytical system affords unprecedented levels of performance and versatility. Achieving such high performance at the greatly reduced levels of power dissipation required for incorporation into distributed wireless environmental monitoring networks remains a formidable challenge. However, paths to lower power operation based on novel design and packaging schemes have been identified and are being implemented

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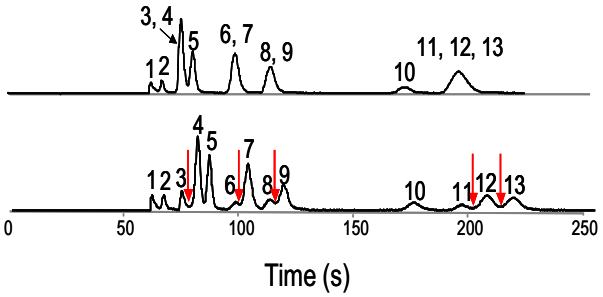

Figure 3*. 13-vapor chromatograms with dual-column ensemble (FID detection, air carrier gas). Top trace shows four co-elutions under initial conditions. Bottom trace shows resolution of compounds via brief stop-flow intervals at t = 40, 85, and 125 sec. Arrows show the resulting separations (1 acetaldehyde; 2 methanol; 3 ethanol; 4 pentane; 5 isoprene; 6 propionaldehyde; 7 cyclopentane; 8 acetone; 9 1-hexene; 10 butyraldehyde; 11 ethyl acetate; 12 benzene; 13 cyclohexene).*

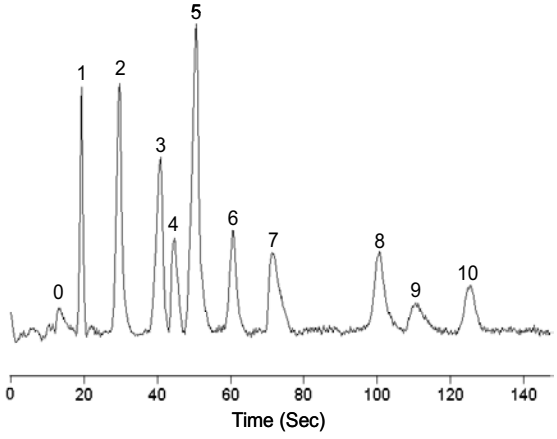

Figure 5. *10-vapor chromatogram from the μGC prototype system (only the OPH-Au coated chemiresistor response is shown), illustrating sharp, well-resolved peaks. The non-polar column was held at 25° C for 40 sec, then ramped at 0.85° C/sec to 65° C and held for the remainder of the separation. Compounds: 0 water; 1 TCE; 2 toluene; 3 perchloroethylene; 4 n-butyl acetate; 5 chlorobenzene; 6 m-xylene; 7 2-heptanone; 8 mesitylene; 9 3-octanone; 10 n-decane.*

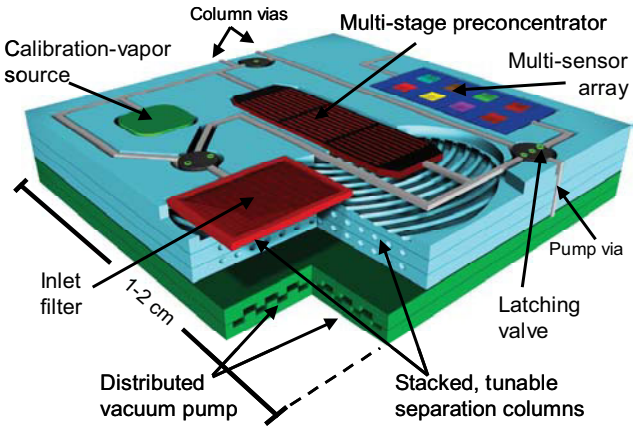

Figure 2.*. Conceptual Diagram of a Monolithic μGC.*

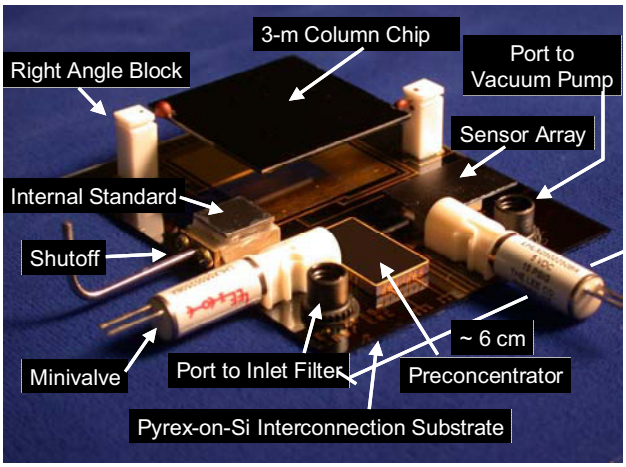

Figure 4. *1st-generation μGC prototype with MEMS and non-MEMS components on a fluidic/electrical interconnection substrate 6x8cm.*

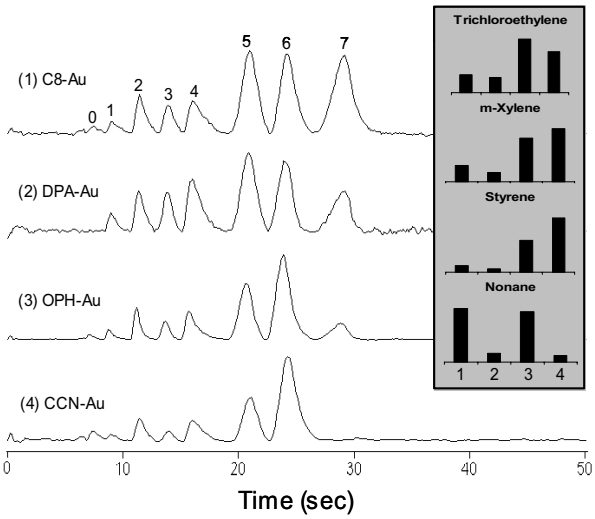

Figure 6. *High-speed 4-CR-array chromatograms of a 7-vapor mixture analyzed in 30 sec at 25 ℃ with the μGC prototype. Each trace is labeled with the corresponding nanoparticle sensor interface layer. Inset shows response patterns for a subset of vapors. Split-flow injection was employed. Cmpds: 0 water; 1 trichloroethylene; 2 toluene; 3 perchloroethylene; 4 n-butyl acetate; 5 m-xylene; 6 styrene; 7 n-nonane.*