A Programmable Palm-Size Gas Analyzer for use in Micro Autonomous Systems

Robert J. M. Gordenker and Kensall D. Wise

Center for Wireless Integrated MicroSystems, Department of Electrical Engineering and Computer Science, The University of Michigan, 1301 Beal Avenue, Ann Arbor, MI 48109-2122

ABSTRACT

Gas analysis systems having small size, low power, and high selectivity are badly needed for defense (detection of explosives and chemical warfare agents), homeland security, health care, and environmental applications. This paper presents a palm-size gas chromatography system having analysis times of 5-50sec, detection limits less than 1ppb, and an average power dissipation less than one watt. It uses no consumables. The three-chip fluidic system consists of a preconcentrator, a 25cm-3m separation column, and a chemi-resistive detector and is supported by a microcomputer and circuitry for programmable temperature control. The entire system, including the mini-pump and battery, occupies less than 200cc and is configured for use on autonomous robotic vehicles.

Keywords: Chemical sensor, gas chromatography, gas analyzer, microelectromechanical systems, microsystems

1. INTRODUCTION

During the last forty years, tremendous progress has been made in microelectronics, and today the advent of microsystems, combining low-power integrated circuits with wireless connectivity and advanced sensing technologies, is making it possible to revolutionize information gathering. Use of the lithographically-based technologies developed for integrated circuits has enabled major advances in integrated sensors, microelectromechanical systems (MEMS), and microsystems for use in inertial measurements, microfluidics, wireless systems (RF-MEMS), and some medical devices; however, relatively little progress has been made in chemical sensors, especially those capable of quantitatively analyzing unknown gaseous mixtures[1]. The problems are many, but include speed, selectivity, sensitivity, size, and stability. Of these, selectivity is typically the most serious issue. Many sensors can detect gases of interest but they also typically detect other gases, resulting in false positives that are unacceptable in many applications.

In the macro-world, the preferred approach to gas analysis involves gas chromatography (GC), in some cases working in tandem with a mass spectrometer. Gas chromatography allows quantitative analysis with the selectivity needed to separate a variety of gases, but it involves not a device but a complete system. Such systems today cost several tens of thousands of dollars and are tabletop systems too large, slow, and fragile for field deployment. This paper describes the results of a project aimed at shrinking a GC system to the size of a cell phone while speeding up the analysis cycle to a few tens of seconds and retaining detection limits of less than 1ppb.

Figure 1 shows a diagram of a microGC (μGC) system. The basic system consists of a preconcentrator, one or more separation columns, and a detector[2-5]. It uses an air carrier so that the resulting system uses no consumables. It can also employ valves, a miniature vacuum pump, and a calibration source along with pressure and temperature sensors. An embedded microcontroller, memory, and analog-to-digital converter process the sensor readouts and control the overall analysis

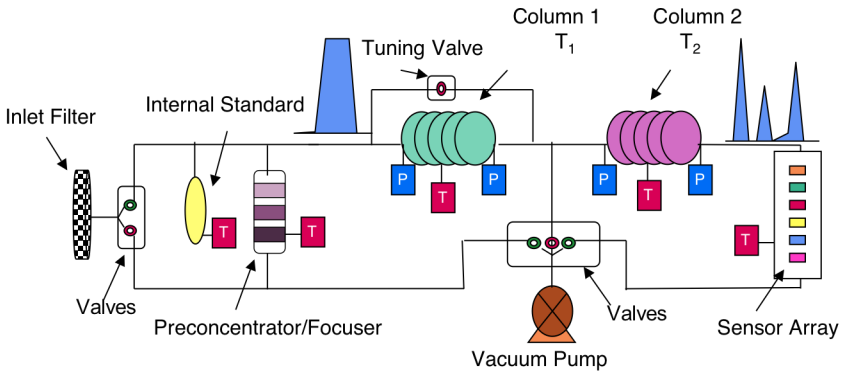


Fig. 1: Block diagram of a μGC system.

Micro- and Nanotechnology Sensors, Systems, and Applications IV, edited by Thomas George, M. Saif Islam, Achyut Dutta, Proc. of SPIE Vol. 8373, 83731O

cycle. Such systems have a host of potential applications, including food processing, the detection of biomarkers for various diseases, the mapping of environmental pollution plumes, and the detection of explosives and chemical warfare agents. In operation, the micropump pulls an air sample over a bed of carbon granules, adsorbing any volatile organic components. The analytes are then rapidly desorbed thermally into the gas stream, magnifying their concentrations and injecting them into the separation column. Their transit times through the column depend their molecular species and the amount of time they spend adsorbed on the stationary phase coating on the column wall. Thus, the different analytes emerge separated in time, and their presence at the detector is converted into an electrical signal that can be processed using software resident on the embedded microcontroller. The time delay indicates the species present and the area under the associated output amplitude curve indicates the amount of analyte present.

2. COMPONENT DEVELOPMENT

2.1 Separation Columns

The heart of the µGC is the separation column that gives the overall system its selectivity. In its simplest form (Fig. 2), the column channel is etched into a silicon wafer using deep reactive ion etching (DRIE) and is capped by a Pyrex plate[4]. A heater is integrated on the back of the silicon and the Pyrex is used to thermally isolate the column from the support base, which is maintained at ambient. Typical channel dimensions are 150µm wide by 240µm deep, although they can be scaled over a broad range. In order to reduce the column mass, improve its thermal isolation, and permit faster time constants, a boron diffusion can be used into the column and the silicon wafer can be etched back over the column area to retain only the column, removing the bulk silicon and defining the channel with a 12µm-thick single-crystal silicon wall[6] as in Fig. 3. Figure 4 shows the top view of a 3m-long etched-back column about 2cm on a side along with a cross-section. Figure 5 shows a chromatogram of thirty air pollutants spanning four orders of magnitude in vapor pressure separated with a 3m-long column coated with polydimenthlsiloxane and temperature programmed at 20°C/min. Such columns produce over 4000 theoretical plates/meter. One of the features of these very small columns is that they can be temperature programmed to avoid co-elutions and to achieve rapid separations. For example, a column separating decane in 52 sec at room temperature will separate it in 3 sec when programmed (50°C-300°C at 600°C/min). Thus, microcolumns may perform even better than some of their tabletop ancestors. Figure 6 shows the partial separation of simulants for C4, TNT, mustard gas, and sarin in less than 10 sec using a column temperature programmed to ramp between 30 and 60°C at 600°C/min, holding at 60°C[7].

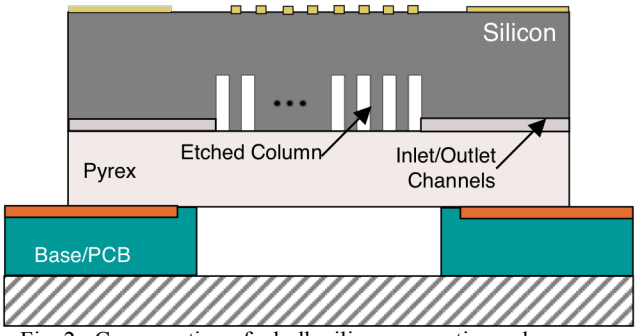


Fig. 2: Cross-section of a bulk-silicon separation column.

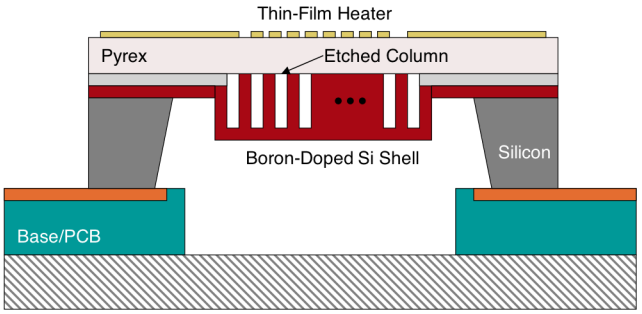
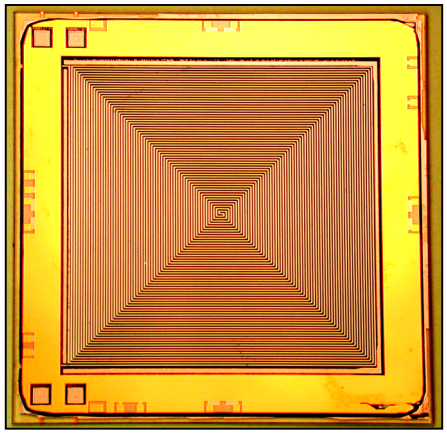


Fig. 3: Cross-section of an etched-back silicon separation column.



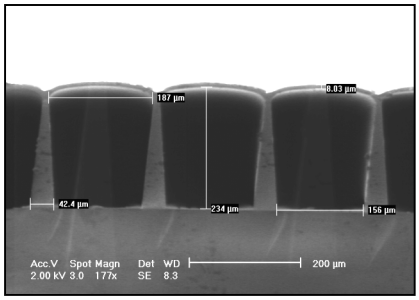


Fig. 4: Top view and cross-section of a 3m-long etched-back column.

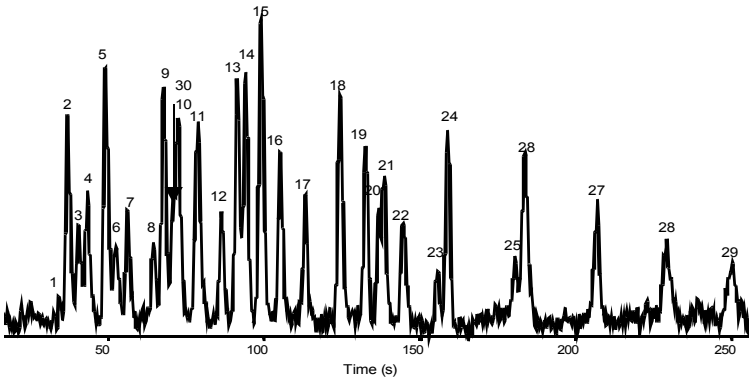


Fig. 5: Separation of 30 air pollutants in 250 sec with a 3m-long silicon microcolumn.

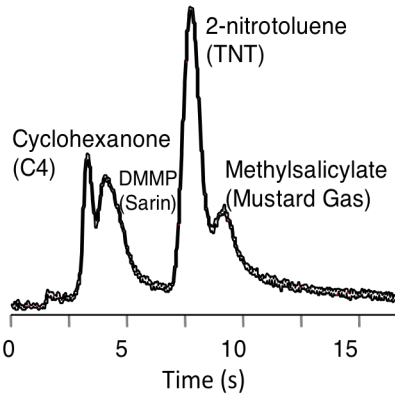


Fig. 6: A 25-cm-long microcolumn separating simulants for C4, TNT, sarin and mustard gas in less than 10 sec.

2.2 Preconcentrators

The role of the preconcentrator is to exhaustively trap the analytes to be analyzed and to subsequently desorb them rapidly into the column. It is important that the analytes be desorbed rapidly since for short columns and rapid separations, the injection plug width must be well under a second in width (e.g., 0.2-0.4sec). Typical preconcentrator structures are similar to the structures shown in Figs. 2 and 3 except that instead of a slotted channel structure, a common well forms a reservoir for the carbon adsorber. These reservoirs can be formed either as a DRIE-etched recess in the bulk silicon or as an etched-back bucket having boron-doped silicon wall. The adsorbent material has typically been carbon granules 100-150µm in diameter, although carbon nanotubes are also being explored for reduced mass and higher surface area. The current system uses thermal desorption (ambient to 250°C) alone to form the injection plug, but requires several watts when used with a bulk silicon preconcentrator. A slower and more power efficient injector could be formed using a microvalve, and devices have been demonstrated with an actuation energy of 2mJ, an actuation time of 20msec, and no hold power[8]. Figure 7 shows single-, dual, and triple-bed preconcentrators next to a U.S. penny.

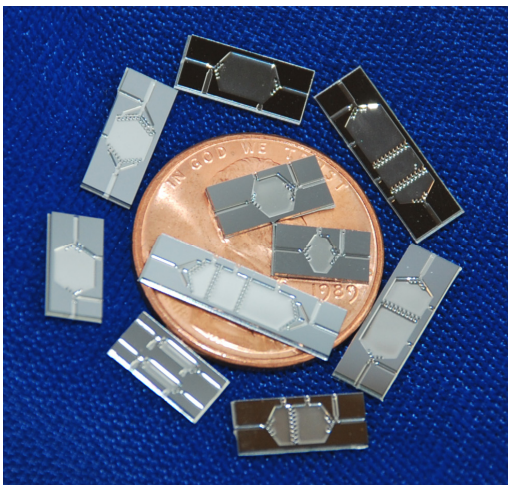


Fig. 7: Preconcentrators for use in µGC

2.3 Detectors

A variety detectors can be used with µGC systems, but thermal and chemi-resistive detectors are attractive for their ability to be miniaturized and process compatibility. The system reported here uses chemi-resistive detectors based on thin organic films containing gold-thiolate nanoclusters. The thin films rapidly absorb the gases of interest, changing their atomic separations and hence the film resistivity[9]. Detection limits are below 1ppb and in some cases below 0.1ppb. The films are positioned over interdigitated comb electrodes that can be scaled as small as 10µm on a side so that eventually such detectors could be mounted in the exit port of the column itself. Figure 8 shows a single-bed preconcentrator, a 50cm column, and a multi-element detector on a U.S. quarter.

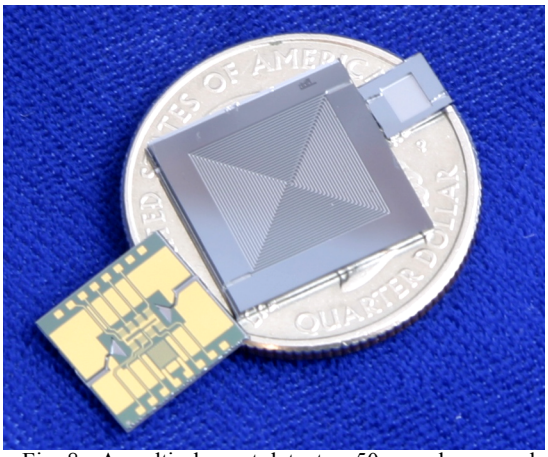


Fig. 8: A multi-element detector, 50cm column, and a single-bed preconcentrator on a U.S. quarter.

3. A PALM-SIZE µGC SYSTEM

Figure 9 shows a complete "Mercury" µGC system. The fluidic components are based on wafer-bonded silicon-glass MEMS technology as described above and consist of an off-board inlet reservoir, a single-stage preconcentrator, a 50cm-long microcolumn, a multi-element detector, and an off-board COTS mini-pump. The system is implemented on three 10cm x 4cm printed circuit boards and can be mounted on a robotic crawler in order to perform reconnaissance missions searching for explosives and chemical warfare agents that could be harmful to personnel. The top board houses the fluidics and associated electronics for sensing the component temperatures and for driving their heaters. The preconcentrator, column, and detector chips have integrated heaters and temperature sensors to allow their programmable closed-loop temperature control. This board has cutouts to thermally isolate the preconcentrator and column to reduce power and thermal time constants. The different fluidic components are interconnected via capillary tubes. The middle board contains the power electronics needed to drive the heaters and permit programmable control of the component temperatures from the main power source located on the robotic crawler. This circuitry boosts the robot battery voltage from 14V to the drive voltages needed for the heaters and must produce smooth ramps controlled by the embedded Mercury microcontroller. The bottom board contains this micocontroller (a Cypress CY8C3866-AXI) and associated circuitry to recognize commands from the robotic host, sequence through the gas analysis cycle, and return the digitized data to the robot.

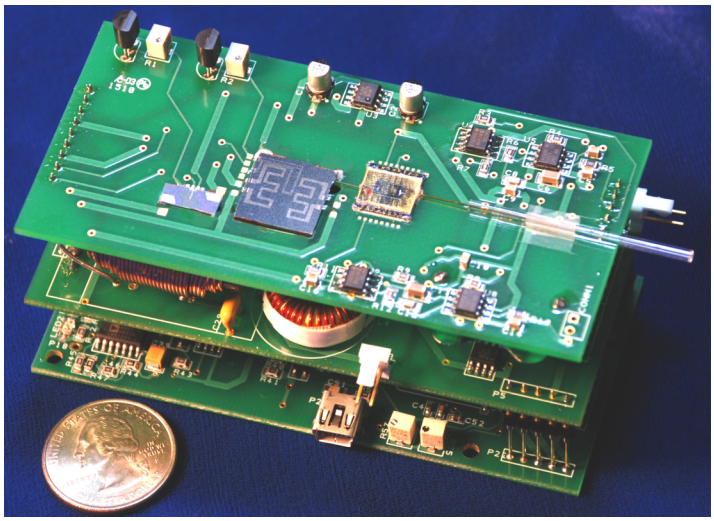


Fig. 9: The complete three-board implementation of the Mercury analysis system, shown next to a U.S. quarter.

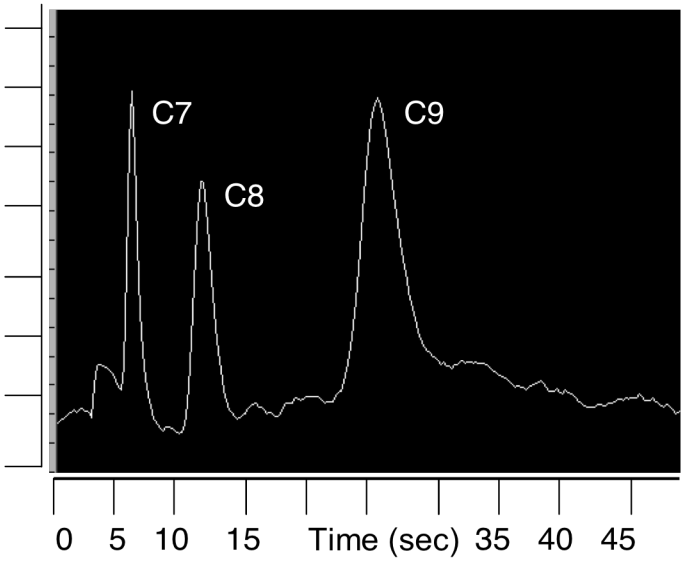


Fig. 10: A chromatogram from the Mercury µGC showing peaks for alkanes C7. C8. and C9.

The Mercury control electronics operates as a satellite (slave) to the robot processor. All signal analysis (µGC peak detection and interpretation) is done in the crawler system with the Mercury processor responding to commands from it, executing the analysis cycle, and outputting digitized data from the chromatographic detector. Commands are input from the robot using a standard USB port. For an analysis time of 40sec, the Mercury µGC has an energy dissipation of about 30J, corresponding to an average power dissipation of about 0.7W. This is dominated by the COTS mini-pump and by heating of the column. Although the peak power of the preconcentrator is several watts, it is on only briefly as the analytes are being desorbed. Figure 10 shows a chromatogram produced by the Mercury µGC running with a single-bed preconcentrator thermally desorbed to 220°C, a 50cm-long bulk separation column running at room temperature (separating heptane (C7), octane (C8) , and nonane (C9)), and a chemiresistive detector.

4. FUTURE POSSIBILITIES

The Mercury µGC is a palm-size microsystem that operates with an average power dissipation of a few watts for bulk silicon fluidic components and less than 1W with etched-back silicon components. It is capable of separating a wide

variety of analytes with detection limits of less than 1ppb and analysis times from a few seconds to a few tens of seconds. However, this system is only one step toward fluidic gas analyzers that are still smaller, more sensitive, and lower in power. The Mercury μGC is a board-level system that could be reduced to a single board with the custom integration of the integrated electronics used today; however, even with this integration, the power levels would remain relatively high. The present system also requires hand assembly of the analysis system, and the use of discrete capillary interconnects is not only tedious but also provides areas where cold spots can occur, with associated band broadening. To move to a more highly integrated fluidic system capable of operating at significantly reduced power levels (and smaller sizes), a chip-level system is needed. Here, the preconcentrator, column, and detector chips would plug into each other, eliminating any capillary tubing. Preconcentrator power can be reduced by using an etched-back thermally-isolated adsorbent reservoir and by thinning the Pyrex cap. Carbon nanotubes (CNTs) are being explored as possible lower-mass replacements for the carbon granules now used. The Pyrex cap is being completely eliminated in the separation column (Fig. 11), replaced by a deposited layer of quartz, and the resulting channels are designed to extend beyond the rim of the thermally-isolated column so that they plug into the detector and preconcentrator chips[10]. Figure 12 shows a 25cm-long column with built-in interconnects along with a cross-section of the thermally-isolated suspended column.

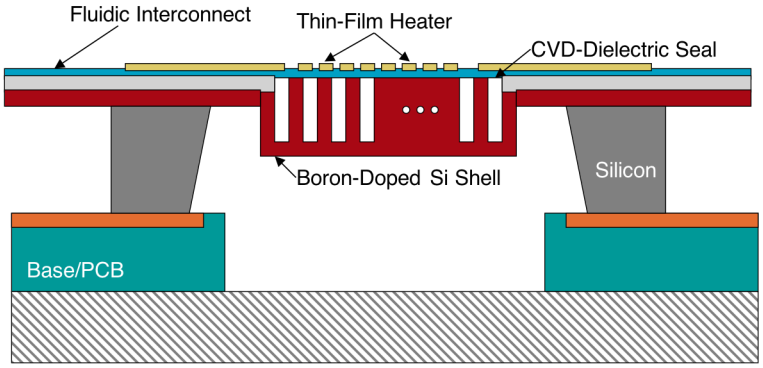


Fig. 11: Cross-section of a low-power separation column where the channel is capped with deposited dielectrics to realize a minimum-mass microstructure with built-in fluidic interconnects.

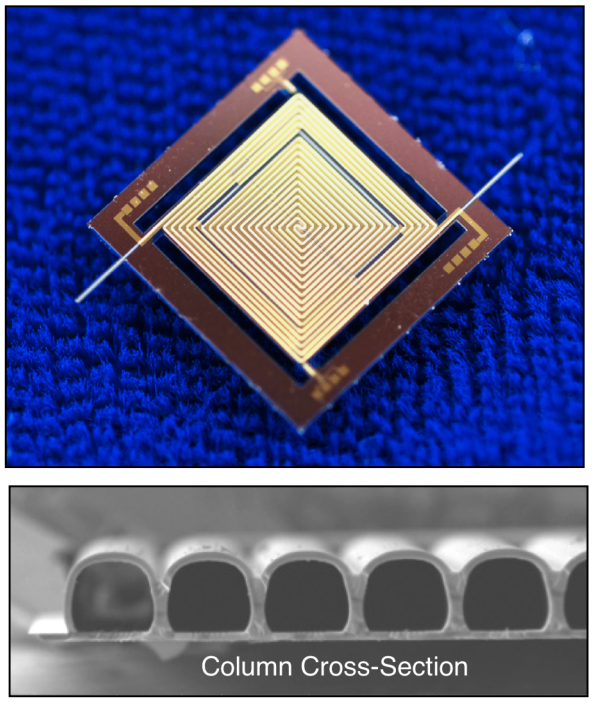


Fig. 12: Top view of a 25cm-long column sealed using deposited dielectrics and forming built-in fluidic interconnects. A column cross-section is shown below.

Figure 13 shows a prototype of the fluidic portion of a possible future μGC system[10]. A CNT-loaded preconcentrator, 25cm suspended column, and dual chemiresistive detector is shown in a micromachined alignment frame along with an alkane separation from the column (sensed using a flame ionization detector on an Agilent 6890 GC). The fluidic analysis system is sitting on a "Shuffle" MP3 player, which represents the possible size for such a system with custom integration of the associated electronics for signal processing and communication. It should be pointed out that the MEMS-based valves and pumps that would also be needed for such systems have already been prototyped[8,11]. Thus, such systems could soon become a reality for defense, homeland security, health care, food processing, the environment, and other areas[12].

5. CONCLUSIONS

This paper has described a silicon micromachined gas analyzer based on gas chromatography. The palm-size device uses no consumables and is composed of a preconcentrator, separation column, and chemiresistive detector. It has been designed for deployment on a robotic crawler capable of detecting explosives and chemical warfare agents in areas unsafe for personnel. The system separates a wide variety of compounds in seconds to tens of seconds with many detection limits below 1ppb. System power levels are a few watts using bulk silicon components and less than one watt using etched-back components. Still more advanced versions of this system could reduce power dissipation by another factor of five permitting system realization, including the pump and power supply, in the size of a cell phone.

Acknowledgments

This work was supported by the National Science Foundation under Engineering Research Centers Program under Award Number EEC-9986866 and by the U.S. Army Research Laboratory MAST CTA under Contract W911NF. The authors would like to acknowledge the many contributions of Professor Edward T. Zellers of the School of Public Health, The University of Michigan, to the work reported here. Ms. Katharine Beach and Dr. Onnop Srivannavit fabricated the devices reported here in the University of Michigan Lurie Nanofabrication Facility.

REFERENCES

[1] Wise, K. D., Ed., Special Issue on Integrated Sensors, Microactuators, and Microsystems (MEMS), *Proceedings of the IEEE*, August 1998.

[2] Reidy, S., George, D., Agah, M., Sacks, R., "Temperature-programmed GC using Si microfabricated columns with integrated heaters and temperature sensors," *Anal. Chem.*, 79, 2911 (2007).

[3] Reidy, S. M., Kim, S.-J., Beach, K., Block, B., Zellers, E. T., Kurabayashi, K., and Wise, K. D., "A Microfabricated Comprehensive Two-Dimensional Gas Chromatography System," *Digest Solid-State Sensor, Actuator, and Microsystems Workshop*, Hilton Head, S.C., (2010).

[4] Lambertus, G. R., Elstro, A., Sensening, K., Potkay, J., Agah, M., Scheuering, S., Wise, K. D., Dorman, F., Sacks, R., "Design, fabrication, and microfabricated columns evaluation of for gas chromatography," *Anal. Chem.*, 76, 2629 (2004).

[5] Zellers, E. T., Reidy, S., Veeneman, R., Gordenker, R., Steinecker, W. H., Lambertus, G. R., Kim, H., Potkay, J. A., Rowe, M. P., Zhong, Q., Avery, C., Chan, H. K. L., Sacks, R. D., Najafi, K., and Wise, K. D., "An Integrated Micro-Analytical System for Complex Vapor Mixtures," *Int. Conf. on Solid-State Sensors, Actuators, and Microsystems (Transducers'07),* Lyon, France, 1491-1496 (2007).

[6] Agah, M., Potkay, J. A., Elstro, A., L., Lambertus, G. R., Sacks, R. D., and Wise, K. D., "A High-Performance Temperature-Programmed Gas Chromatography Column," *Digest North American Sensor, Actuator, and Microsystems Workshop (Hilton Head),* 302-305 (2004).

[7] Agah, M., Lambertus, G. R., Sacks, R. D., and Wise, K. D., "High-Speed MEMS-based Gas Chromatography," *Digest IEEE Int. Electron Devices Meeting*, San Francisco, 27-30 (2004).

[8] Potkay, J. A., and Wise, K. D., "An Electrostatically-Latching Thermopneumatic Microvalve with Closed-Loop Position Sensing," *IEEE International Conference on Micro Electro Mechanical Systems (MEMS)*, Miami, Florida, 415-418 (2005).

[9] Steinecker, W. H., et al., "Chemiresistor array with nanocluster interfaces as a μGC Detector," *Proc. IEEE Int. Conf. on Sol.-St. Sensors, Actuators, and Microsystems,* Boston, 1343-1346 (2003)

[10] Beach, K., Reidy, S. M., Gordenker, R. J. M., and Wise, K. D., "A Low-Mass High-Speed μGC Separation Column with Built-In Chip-to-Chip Interconnects," *IEEE MicroElectroMechanical Systems Conference*, Cancun, pp. 813-816, January 2011.

[11] Kim, H., Steinecker, W. H., Reidy, S., Lambertus, G. R., Astle, A. A., Najafi, K., Zellers, E. T., Bernal, L. P., Washabaugh, P. D., and Wise, K. D., "A Micropump-Driven High-Speed MEMS Gas Chromatography System," *Int. Conf. on Solid-State Sensors, Actuators, and Microsystems (Transducers'07),* Lyon, France, 1505-1508, (2007).

[12] Manginell, R. P., et al., "A Monolithically-Integrated μGC Chemical Sensor System," *Sensors*, 11, 6517-6532 (2011).

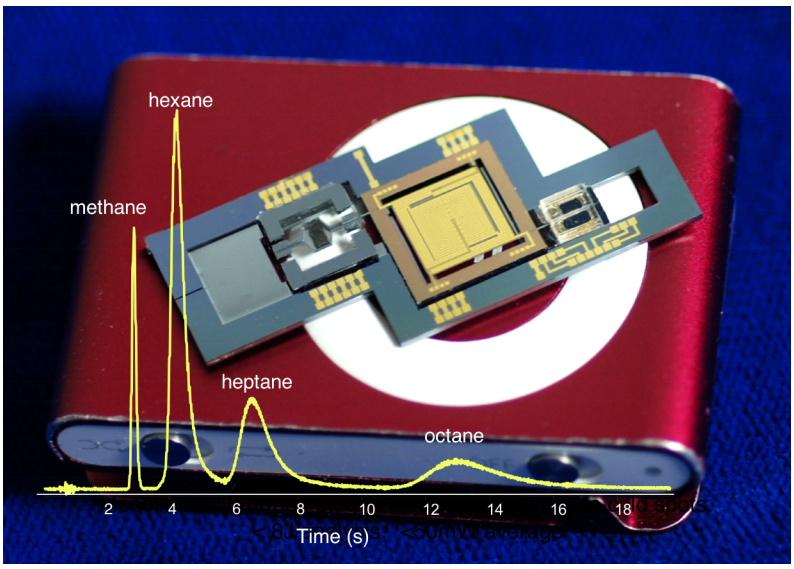


Fig. 13: A CNT-loaded preconcentrator, 25cm column, and detector is shown on a "Shuffle" MP3 player, representing the possible size of an eventual μGC-based gas analyzer. The outer ring of the white circle is about the size of a U.S. quarter. An alkane separation from the column is superimposed.