Recent Advancements in the Gas-Phase MicroChemLab

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Abstract—**Sandia's hand-held MicroChemLab system uses a micromachined preconcentrator, a gas chromatography channel, and a quartz surface acoustic wave array detector for sensitive/selective detection of gas-phase chemical analytes. Requisite system size, performance, power budget, and time response mandate microfabrication of the key analytical system components. In the fielded system, hybrid integration has been employed, permitting optimization of the individual components. Recent improvements in the hybrid-integrated system, using plastic, metal, or silicon/glass manifolds, is described, as is system performance against semivolatile compounds and toxic industrial chemicals. The design and performance of a new three-dimensional micropreconcentrator is also introduced. To further reduce system dead volume, eliminate unheated transfer lines, and simplify assembly, there is an effort to monolithically integrate the silicon PC and GC with a suitable silicon-based detector, such as a magnetically-actuated flexural plate wave sensor or a magnetically-actuated pivot plate resonator.**

Index Terms—**Acoustic detection microanalytical system, gas chromatography, gas-phase analysis, monolithic integration, pivot plate resonator, preconcentration, surface acoustic wave array (SAW).**

I. Introduction

SANDIA's MicroChemLab program was initiated in 1996 for the purpose of producing a battery-operated, hand-held microanalytical system for the selective detection of gas-phase analytes. The goal was to bring high-confidence analytical techniques to the field, rather than simply introducing a new sensor. Other groups are pursuing a similar methodology [1]. Sample introduction, preparation, separation, and detection functions are all indispensable in addressing real-world applications in which potentially interfering compounds are present, usually at much higher concentrations than the analyte of interest. These functions were performed by three microfabricated components, coupled via electrical/fluidic packaging, and housed in a hand-held system, complete with system-level control, and a rugged, simple-to-use interface.

The initial system application was the selective detection of chemical warfare agents (CWA), though the range of analytes has been expanded over the years to include pharmaceutical solvents, petrochemicals, toxic industrial chemicals (TICs) and tri-halo-methanes (THMs). In any of these cases, but particularly with CWA detection, rapid response, low power consumption, small size, and minimization of false positives are essential system requirements. Integrated sampling and sample preparation functions, as well as fast chemical separations via micro gas chromatography (GC), are likewise critical. The diversity of these attributes dictates a multidisciplinary approach: microfabrication was used to provide small, low-power critical components, synthetic chemistry provided selective coatings, and system engineering completed the microanalytical system. This approach has delivered extremely low false alarm rates and high selectivity in the field.

The MicroChemLab system uses a micromachined preconcentrator (PC), a gas chromatography channel (GC), and a quartz surface acoustic wave array (SAW) detector [2], [3]. Selective coatings placed on each of these devices contribute to the selectivity and low false alarm rate of the overall system. Hybrid integration has been used in the fielded system with great success. This approach has the benefit of allowing optimization of the individual components and enabling their replacement in a modular fashion. Initially a modified circuit board, containing both electrical and fluidic components, was developed. Recent improvements in the hybrid integration scheme consist of using passivated metal manifolds, or silicon/glass bonded manifolds. The hybrid integrated system shows superior function in field environments; however, performance could be improved by eliminating excess dead volume and cold transfer lines. Monolithic integration of the silicon PC and GC with a suitable silicon-based detector, such as a magnetically-actuated flexural plate wave sensor (magFPW), has been initiated to address these issues, as well as to ease assembly requirements and allow further miniaturization. As was previously reported [4], a PC, GC and magFPW have been monolithically integrated using Sandia's SwIFT processing architecture. Surface micromachining with Integrated Fluidic Technology (SwIFT) is a variant on Sandia's 5-layer polysilicon MEMS process. This architecture has permitted evaluation of the fabrication, packaging, and coating methods needed to make a monolithically-integrated MicroChemLab. Progress on

Manuscript received March 1, 2005; revised June 3, 2005. This work was supported by E. George of DOE CBNP (now at DHS), S. R. Long of SBCCOM (presently with DHS and RDECOM), and the Sandia National Laboratories LDRD program. The associate editor coordinating the review of this paper and approving it for publication was Dr. Giorgio Sberveglieri.

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Digital Object Identifier 10.1109/JSEN.2006.874495

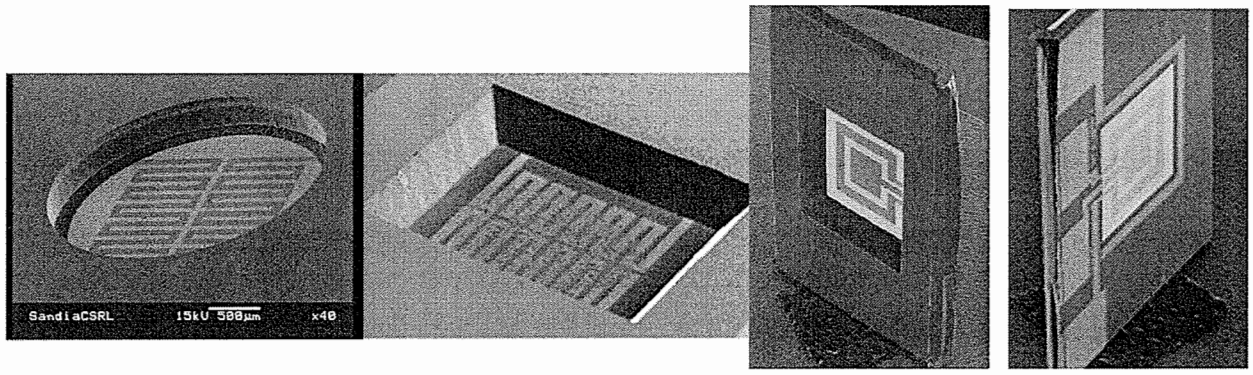


Fig. 1. (a) Bosch etched microhotplate preconcentrator. (b-d) KOH-etched microhotplate planar preconcentrators. In (b), a circular patch of adsorbent is centered on the preconcentrator. (c) and (d) show the etch side and metal side, respectively, of the same device.

this effort is described, including the use of a magnetically-actuated pivot plate resonator as a replacement for the magFPW.

II. Critical Components and Their Fabrication

A. Microfabricated Preconcentrators

Sandia's microfabricated planar preconcentrator (PC) was initially developed in 1997 to meet the need for a low-power, nonmechanical chemical preconcentrator and chromatographic injector [5], [6]. By applying a selectively-adsorbent coating to the surface of a micromachined microhotplate, selective preconcentration of target analytes, followed by rapid, thermal desorption, is achieved. The typical 2.2 mm membrane microhotplate achieves 200 °C in ~4 ms, and maintains that temperature with roughly 100 mW of electrical power. Ballistic temperature ramping enables sample thermal desorption pulse widths as narrow as ~200-ms-wide (full width at half maximum) at a typical system flow rate less than 5 mL/min.

The microhotplate PC (Fig. 1) is typically bulk micromachined using through-wafer Bosch or KOH etching, details of which are provided in [6], [7]. Since multiple wafers can be etched in parallel, and because of the higher KOH selectivity to silicon nitride (compared with Bosch etching), KOH etching is preferable. KOH etching, using a 1-μm low-stress silicon nitride mask, proceeds through the wafer, halting on the low-stress silicon nitride layer found on the opposite side of the wafer. The resultant free-standing silicon nitride membrane is typically 2.2 mm on a side. Two wafers are usually etched at a time using an etch fixture to protect the heater metallization. The thin-film heater is deposited on the silicon nitride membrane layer prior to KOH etching. It consists of a platinum layer, ~180–nm-thick, e-beam evaporated onto a titanium adhesion layer, 15--nm thick. Following device processing, the microhotplate is coated with an adsorbent layer to complete the preconcentrator. Spray coating through a mask is used to apply the adsorbent in a fairly uniform circular patch [Fig. 1(b)]. Hydrophobic surfactant-templated sol-gels are used, for example, to impart selectivity to semivolatile polar analytes relative to hydrocarbons.

Selectivity in adsorption allows the PC to pick out compounds of interest in a much higher background of interfering compounds. Fig. 2 shows overlapping analyzes.[1] In one analysis, GD (soman) is analyzed by itself; in the other, it is analyzed in a background of diesel fumes. Obviously there is no influence of the diesel, an effect attributable to the inefficient collection of the non polar constituents of diesel on this particular adsorbent. Other experiments show that humidity is likewise rejected given the adsorbent's affinity for phosphonates over water. Due to the hydrophobicity of the GC stationary phase wall coating, any water that may have been collected on the preconcentrator would pass through the column virtually unretained. While it is well documented that humidity is a common environmental interference for SAWs, the addition of a selective preconcentrator and micro GC column mitigate much of this problem. This topic is discussed further in Section IV and relevant data is presented in Fig. 11.

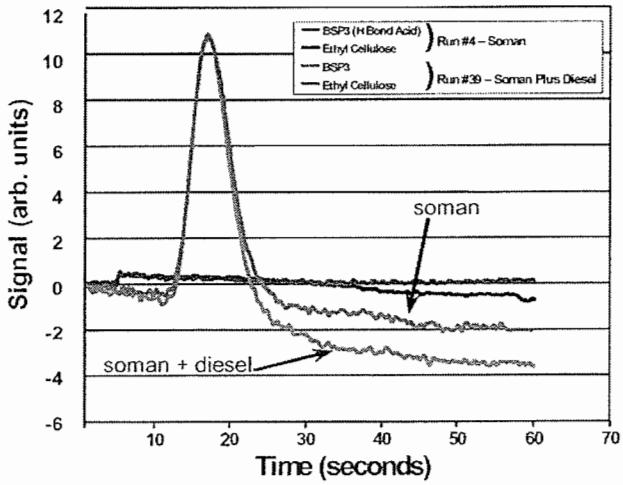
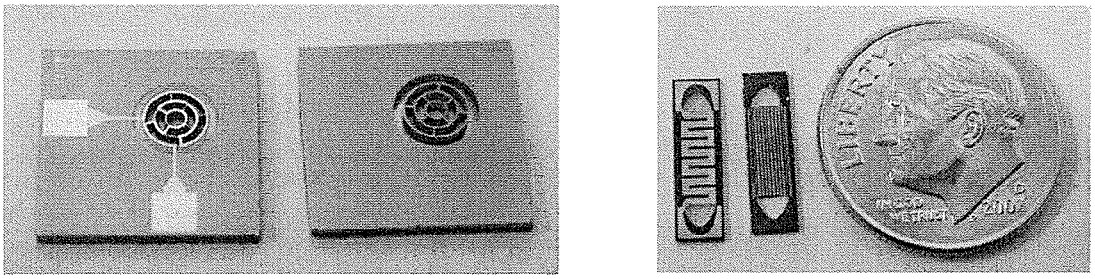


Fig. 2. Selectivity of the planar PC against soman (GD). The desorption peak of the PC as viewed by a downstream SAW shows no collection of GD. (Color version available online at http://ieeexplore.ieee.org.)

The rapid thermal desorption of the planar PC just described is extremely beneficial, providing a narrow injection pulse into the GC column. But in some cases the low surface area of the

[1]The authors regret that in Figs. 2, 6, 8, 11, and 12, the units of sensitivity are given as arbitrary due to export control limitations.



(a) (b)

Fig. 3. (a) 3D-PC with flow perpendicular to the substrate surface. Front and rear sides of the die show an adsorbent support of cylindrical cylinders of Si, all suspended by a SiN membrane. The central part of the SiN membrane is reactive-ion etched open to allow flow through the device. (b) 3D-PC with flow parallel to the substrate surface. A fin-like Si adsorbent support is suspended by a SiN membrane. (Color version available online at http://ieeexplore.ieee.org.)

design limits sample collection. Tian attempted to overcome this limitation using bulk micromachined, three-dimensional adsorbent supports [8]. While the goal of increased collection area was achieved in Tian's platform, heat conduction through the silicon suspension legs would prevent extended, portable use. To increase collection area, while minimizing power consumption, we have independently implemented the three-dimensional preconcentrator (3D-PC) designs shown in Fig. 3. Bosch etching through the wafer thickness to a silicon nitride thermal isolation membrane is used to construct the 3D-PC. This process is similar to that used for the planar device except that some silicon structures remain suspended on the central portion of the membrane to provide additional adsorbent support area. Because sample gas flow is perpendicular to the device surface, the 3D-PC of Fig. 3(a) is deemed a "perpendicular flow" device; in contrast, flow through the device of Fig. 3(b) is parallel to the wafer surface and is thus a "parallel flow" preconcentrator. Heat conduction through the silicon nitride suspensions is comparable to that of the planar device. However, the available surface area for depositing or packing in coatings has increased in our 3D-PC, up to a factor of 20, depending on the particular design, via the use of the wafer-thickness silicon structures as adsorbent supports. An advantage to this approach is that the high thermal conductivity of the silicon structures makes the temperature of the adsorbent zone much more uniform during desorption heating than the planar design. Based on modeling in ANSYS, the perpendicular-flow design of Fig. 3(a), for example, has less than a 5 °C variation in temperature in the adsorbent zone. In contrast, the planar device has a gradient of 50 °C across its active zone.

Nanoporous carbon, sol gels, and commercial packing materials have been tested with the 3D-PC devices. Fig. 4(a) compares the capacity of the planar and perpendicular-flow three–dimensional (3-D) devices for dimethyl methyl phosphonate (DMMP). The planar device loads more rapidly at first, but saturates at 2 min of collection time. In contrast, the 3D-PC takes more than 20 min to saturate. This increase in capacity enables a greater dynamic range for a microanalytical system, an increased analyte set, and/or allows expansion of the analyte set to compounds with very low volatility. Fig. 4(b) provides a comparison of the planar PC, 3D-PCs and a custom mesoscale (0.3 cm diameter by 5 cm long) desorption tube for typical toxic industrial chemicals. The parallel-flow 3D-PC has a sharper, narrower desorption peak with a FWHM of 2.3 s, compared to 3.1 s for the thermal desorption tube. Comparing the power consumption of the two devices, the parallel-flow 3D-PC displayed improved performance while consuming only 0.6 W of power at a desorption temperature of 200 °C, compared to 3 W of power for the thermal desorption tube. The planar device consumes only 100 mW and the 2–mm-diameter perpendicular-flow device uses 150 mW under the same conditions. Enhancements in the 3D-PC designs will be the subject of future correspondence.

B. Microfabricated Gas Chromatography (GC) Channels

The GC column is used to separate in time the components of the sample injected into it by the planar PC. In this fashion if more than one target chemical is collected, they can be separated from one another before reaching the detector. Likewise if a target chemical is collected on the preconcentrator with an interfering chemical they too can be separated prior to detection. The first example of a GC column etched in a silicon wafer was provided by Terry [9]. Wet etching produced 20-μm-deep, 200-μm-wide channels, onto which a Pyrex lid was subsequently bonded. The benefit of rectangular cross-section micro GC columns has been demonstrated by Overton, who primarily utilized a micro molding process to make the device [10]. We have utilized Bosch deep reactive ion etching (DRIE) to produce columns typically 400 μm deep, 100 μm wide [Fig. 5], allowing for high volumetric flow rates at reduced gauge pressures. For example, ~3 mL/min of air through the GC is achievable with 5 PSIG. This is significant since miniature commercial pumps can generate this pressure drop. Separations of 25 μm between adjacent sections of the spiral column allow for an 86-cm total length to be achieved in a chip area of about 1.44 cm^2. This GC length provided adequate separation at 5 PSIG in air in a small device footprint. After DRIE, the wafer is cleaned in piranha, and a Pyrex lid with ultrasonically-machined inlet and outlet holes is bonded to it anodically. Further processing details are provided in [3].

Once microfabricated, the walls of the GC are coated with a suitable stationary phase. The stationary phase is responsible for the chemical separating power of the GC. Representative phases from conventional chromatography, spanning the full range of polarity, have been deposited and tested. To adhere the phases to the silicon GC wall, several procedures have been implemented.

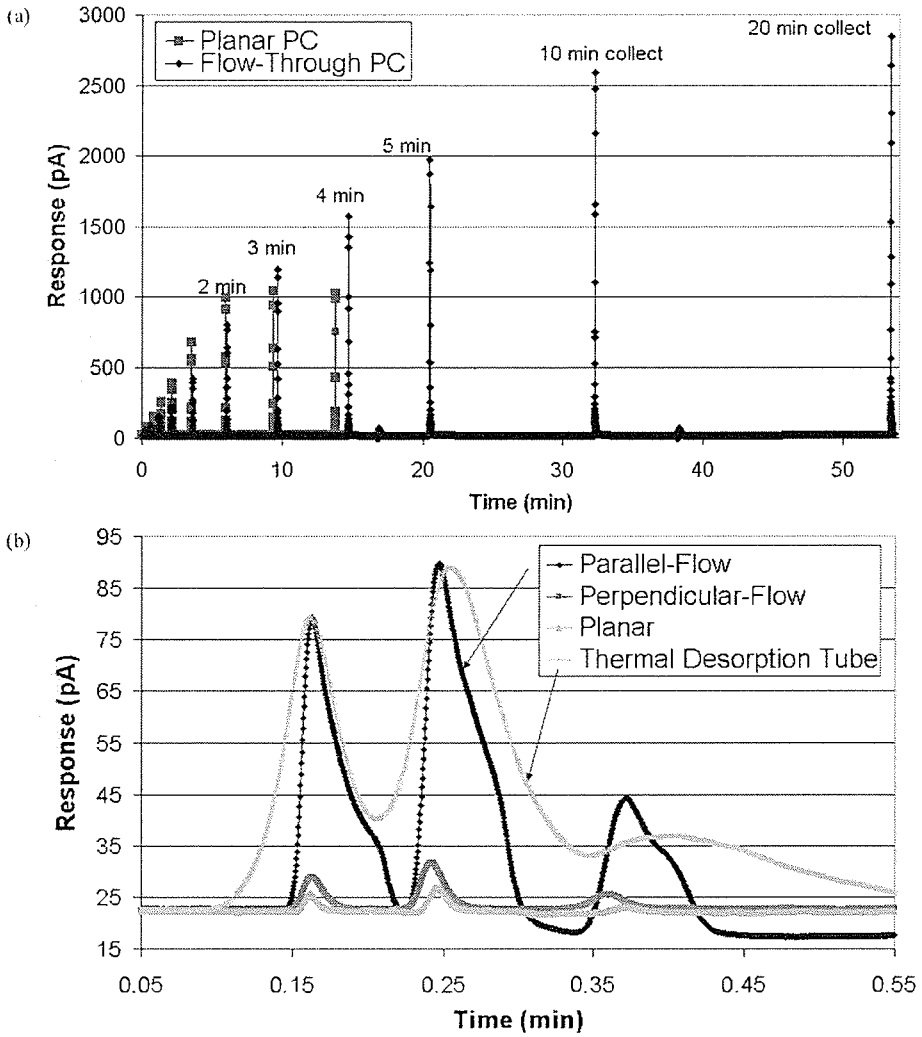


Fig. 4. (a) Desorption peaks from the planar and perpendicular flow 3D-PC as seen by a downstream flame ionization detector (FID). (b) Comparison of the desorption response of various preconcentrator devices with the adsorbent Tenax TA. Device response with TIC analytes after a 300-s collection. The parallel-flow micropreconcentrator has improved performance compared with the conventional desorption tube; the former takes 0.6 W, while the latter 3 W. (Color version available online at http://ieeexplore.ieee.org.)

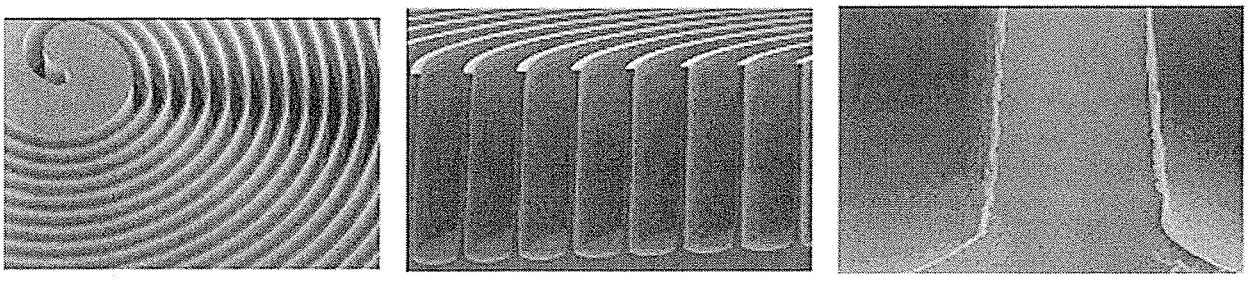


Fig. 5. SEMs of the deep-etched, spiral GC column. Far right shows a stationary phase. For scale, the channels are 100 mieron wide with 25-micron-thick walls. (Color version available online at http://ieeexplore.ieee.org.)

A modified sol-gel process has been used to passivate and coat in one step [11]. A second technique has been used to chemically bond the phase to the walls of the column using primers that enhance wetability and covalently link siloxane polymers to the oxide surface of the microfabricated column. Both chemistries enable the use of a variety of stationary phases. In general, stationary phases have a uniform thickness of 0.5 microns along the four wall surfaces of the GC column with increased thickness in the corners, sometimes double that along the walls, due to capillary action. Because measurements on the stationary phase require destruction of the GC, statistical information on coating thickness and uniformity is generally unavailable. In practice, this information is inferred from chromatography performance. The number of theoretical plates of the microGC, a measure

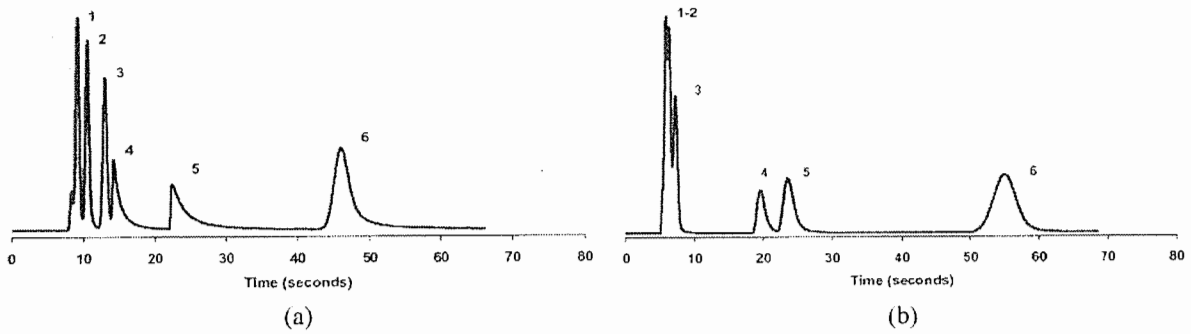


Fig. 6. Separation of several VOCs and CWA simulants using microfabricated columns with flame ionization detection; isothermal 100° C; nitrogen carrier gas 10 psig. (a) PDMS phase. (b) Carbowax 20M phase. Peak IDs: 1) benzene; 2) toluene; 3) xylene; 4) DMMP; 5)DEMP; 6) methyl salicylate. (Color version available online at http://ieeexplore.ieee.org.)

of its resolving power, is predicted to be 900, though typically 150–400 plates are obtained. The large discrepancy is attributed mainly to excess phase in the GC corners, as mentioned above.

Fig. 6 shows chromatograms produced using different stationary phases to separate VOC's and CWA's simulants. Dimethyl methyl phosphonate (DMMP) and diethyl methyl phosphonate (DEMP) are nerve agent simulants, while methyl salycilate is a simulant for sulfur mustard. Fig. 6(a) shows the separation using a non-polar OV-1 poly(dimethylsiloxane) (PDMS) phase; Fig. 6(b) shows the separation using a polar Carbowax (poly(ethylene glycol)) coating. Both materials were obtained from Supelco (Bellefonte, PA).

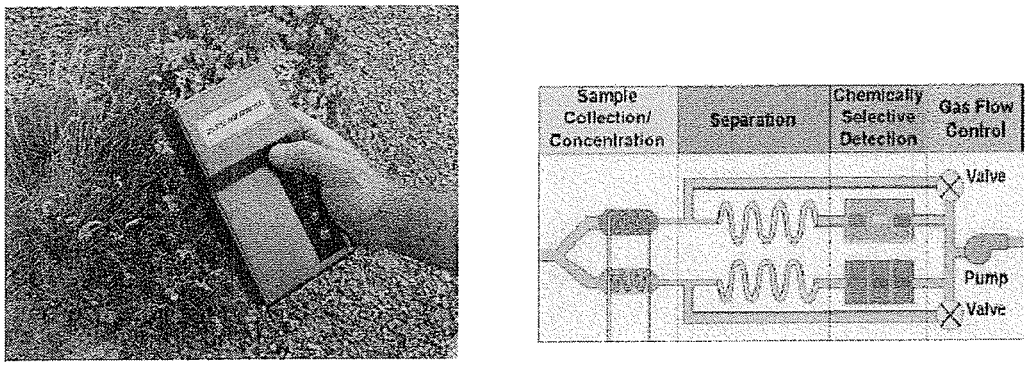
The performance of the microfabricated GC is more than adequate for field use given the selectivity in PC and GC coatings. The tradeoff in miniaturization is that the number of theoretical plates is far less than a conventional GC, yet overall analysis is much more rapid. This is where our paradigm departs from convention. While a long column is needed in a bench-top instrument to resolve the many compounds it is intended to detect, our system selectively collects only the compounds of interest. Therefore, a large number of theoretical plates are not needed. In contrast with a conventional silica GC column, the micro GC can be easily heated by the application of electrical power. Thin-film metal and polysilicon heaters have been deposited and patterned on the silicon wafer on the side opposite from the deep-etched column. Intimate contact of the heater and column is thereby achieved. The thin walls between the columns, only 25 μm thick, as mentioned above, moreover reduces the heat capacity of the micro GC. These features permit rapid thermal heating at low power. For example, 6.5 °C/s has been demonstrated with a micro GC at only 3.8 W. Higher rates are of course possible with higher power. By way of comparison, a conventional bench top GC requires hundreds of watts to achieve a modest ramp rate of 25°C/min. The ability to program a rapid temperature ramp enables the micro silicon-based GC to resolve closely eluting compounds [12]. To increase the overall GC length while maintaining the same device area, GC columns can be stacked [13].

C. Quartz Surface Acoustic Wave (SAW) Array Detector

The use of SAWs in chemical sensing is well known [14]–[16]. In the MicroChemLab system, a four-element array of surface acoustic wave detectors is used for analysis of the GC effluent: there are three active coated sensors and one uncoated reference. Chemical selectivity is built into each of the coatings. The SAW array provides high sensitivity detection, while the array provides distinct response signatures that can be used to selectively identify analytes of interest. All four elements of the array are monolithically produced by gold evaporation and liftoff on ST-cut quartz; present devices operate at 510 MHz. The SAW array is packaged with an ASIC-based phase comparator circuit, fabricated at an external foundry based on a Sandia design. The drive/sense circuitry performs multiplexed phase comparison between active and reference devices, providing a DC voltage proportional to the phase lag introduced by analyte adsorption into the SAW coatings. SAW coatings are sprayed or microdispensed onto the three delay lines following packaging of the SAW with ASICs. Typical coatings include BSP3, PECH (poly(epichlorhydrin)), ethyl cellulose and DKAP. BSP3 is a fluorinated bisphenol-containing silicone polymer useful for organophosphorous compounds [15]. DKAP, developed at Sandia National Laboratories, is similar to BSP3 but employs pendant 3,5-bis(trifluoromethyl)phenols to provide a stronger acid functionality. SAW Response patterns are given below under "System Performance".

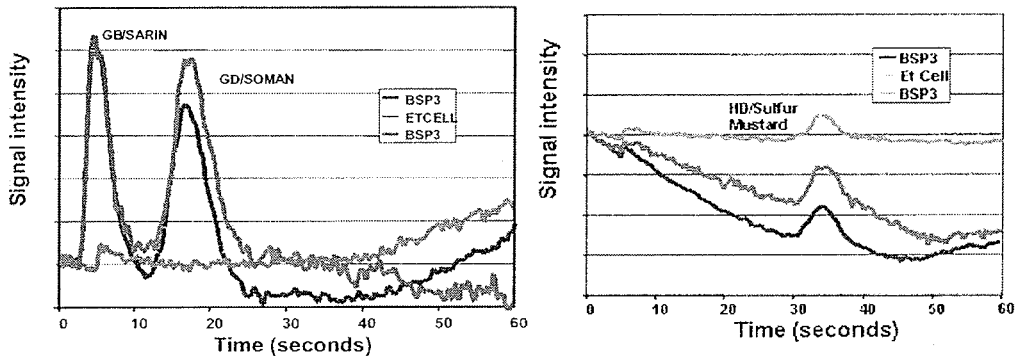
III. Hybrid Integration

A goal of the MicroChemLab system is to take the lab to the sample rather than taking the sample to the lab. Fig. 7 shows the hand-held system and a schematic representation of the portable system, which is capable of a rapid bypass collection. During sampling, a valve bypasses the GC and SAW to increase the flow across the planar preconcentrator. The result is a larger sample volume. The larger sample volume not only means that the sample is more representative of the environment in which it was taken, but also increases the overall sensitivity of the system as more analyte is collected. Pump operation in air is used to eliminate the need for a GC carrier gas supply and permit ease of use in the field. The pump currently in use (from T Squared Manufacturing, Lincoln Park, NJ) can deliver 170 ml/min of flow in the bypass mode and 3 ml/min during separations when the pressure drop is ~5 PSIG. Fig. 8 shows the response of the system to live CWA, performed at Edgewood Chemical-Biological Center (ECBC) in Edgewood, MD, in July, 2000. This figure illustrates several important aspects of the system performance. PC injection into the GC is used to obtain separate peaks for



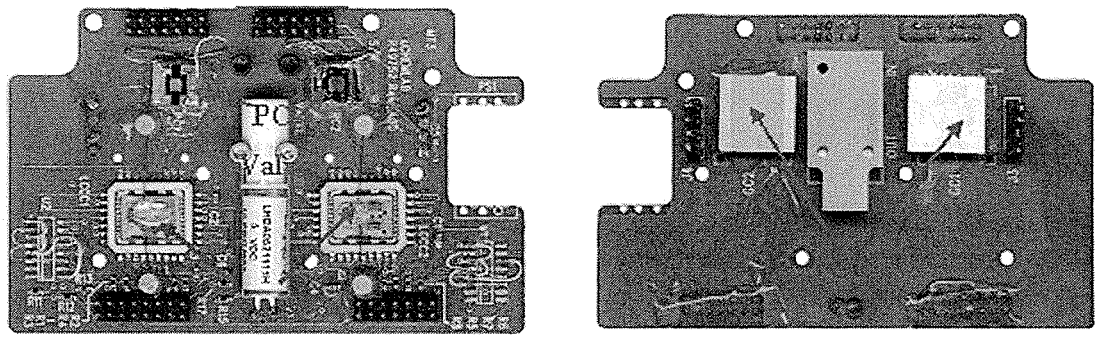
(a) (b)

Fig. 7. (a) Hand-held MicroChemLab. (b) Schematic of the system showing two analysis channels, each containing the sequential connection of a PC sample collector, GC separator and SAW array detector. Only the three active SAW delay lines are indicated, though there is a fourth reference delay line. The pump and valve are used for sample introduction and bypass functions. (Color version available online at http://ieeexplore.ieee.org.)



(a) (b)

Fig. 8. System response to live agents at ECBC. (a) Two SAW channels utilize BSP3 for redundancy in detecting sarin and soman, while the other, coated with ethyl cellulose, is insensitive to these agents. (b) Shows response at 33 s to sulfur mustard on all channels. (Color version available online at http://ieeexplore.ieee.org.)



(a) (b)

Fig. 9. Hybrid integration using a modified circuit board approach. (a) Top and (b) bottom of the circuit board are shown. Fluidic channels, in the plane and perpendicular to the plane, are formed in the circuit board process and connect the components. Two analysis channels are evident from the two sets of components, as is the miniature valve used in the bypass mode. For scale, the GC chip is 12 × 12 mm.

Sarin (GB) and Soman (GD). Peak separation is achieved in air, using the miniature pump referred to above. Analysis is completed in less than 30 s from injection. Finally, the response pattern on the SAW is indicative of these compounds; BSP3 responds strongly, while ethyl cellulose does not.

Early versions of the system hybrid integrated the microfabricated components using a modified circuit board (Fig. 9) containing both fluidic channels and standard electrical connections. The board was made from Thermount (DuPont) due to its favorable coefficient of thermal expansion, especially considering the fact that the micro components require heating during operation. Unfortunately, gold and prepreg layers exposed in manufacturing the fluidic channels in the board were incompatible with certain analytes of interest. In recent years, other manifolds have also been implemented to address these concerns. Fig. 10 shows a three-dimensional manifold made in passivated

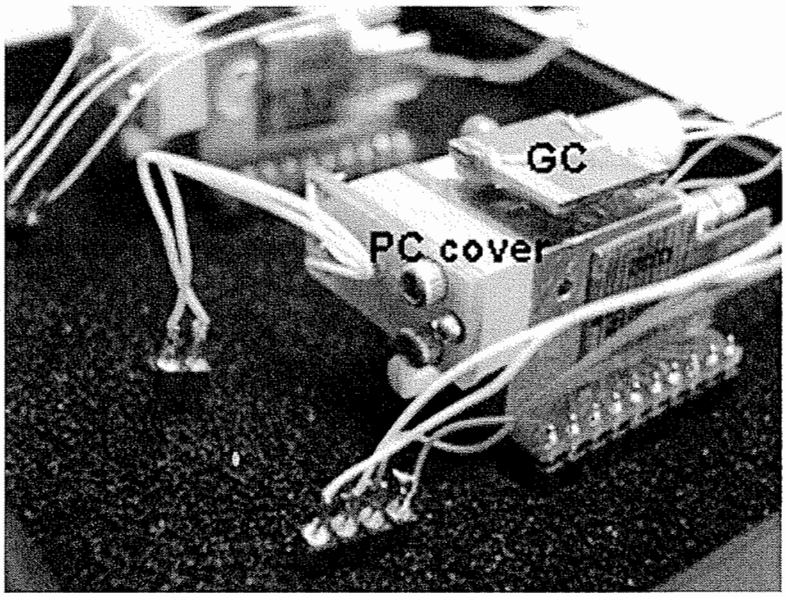


Fig. 10. Hybrid integration using a passivated aluminum manifold. The GC sits atop the manifold, the PC is beneath the front cover, and the SAW resides on the circuit board. (Color version available online at http://ieeexplore.ieee.org.)

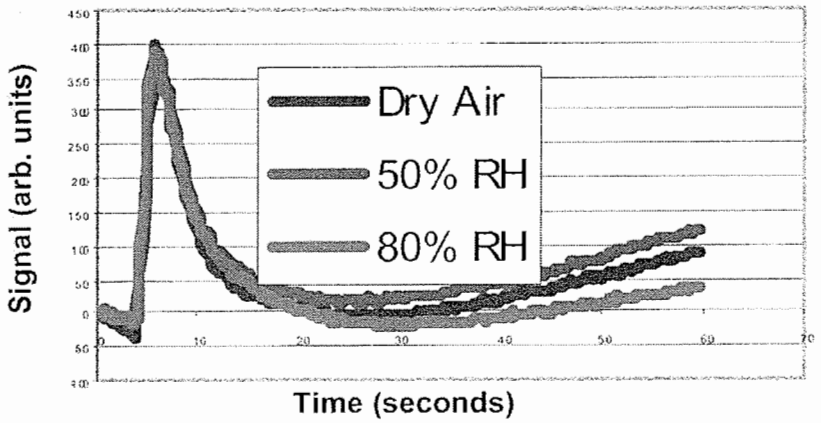


Fig. 11. System output showing overlapping analyzes with a constant concentration of DMMP and increasing amounts of humidity.

aluminum. Similar manifolds are also being made in hard plastic and in glass/silicon composites. The hybrid integration scheme allows for modular replacement of individual components and their individual optimization. One can make minor adjustments in this architecture to realize different analytical tasks. This is achieved, for example, by modifying the coatings on the individual components for selectivity to new chemicals, or, the components themselves can be replaced. For example, the 3D-PC mentioned above could be used to help address toxic industrial chemicals (see Fig. 4).

IV. System Performance

A key feature of the MicroChemLab system is the reduction of false positive readings. Current portable CWA analyzers often respond when interfering chemical signatures are present. The MicroChemLab reduces false positive readings by: 1) selective preconcentration of CWA; 2) separating CWA from interferants in the GC; and 3) discrimination of CWA and interferants via the SAW array. In each component, selective functional materials are used. As mentioned previously with regard to Fig. 2, the PC component, by nature of the physical and chemical attributes of its coating, limits uptake of non polar compounds, volatile compounds, and water. Specifically with regard to the latter, Fig. 11 shows the insensitivity of the system to water vapor interference. Current SAW-based CWA detectors show significant sensitivity to water vapor, and indeed water vapor is often the highest concentration interferent one will see in the field. As stated above, the preconcentrator, the GC column, and the selective SAW polymers work in concert for excellent rejection of water. As can been seen in Fig. 11, the system shows no effect on the detection of the CWA simulant DMMP with 50%–80% RH. While the PC imparts selectivity by rejecting nontarget compounds, the GC column also imparts of selectivity to the system both by separating target compounds from one another and by separating target compounds from interfering compounds that can be collected by the PC. An example of a class of these compounds is glycol ethers, which can be found

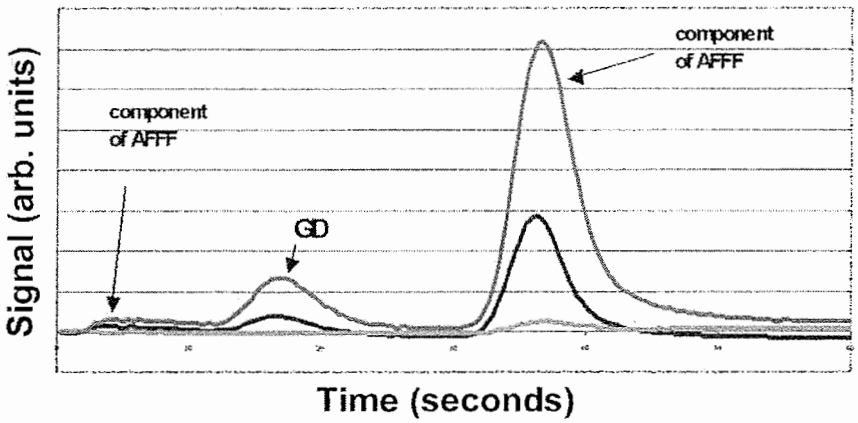


Fig. 12. System response to low levels of GD separated from high concentrations of AFFF components. (Color version available online at http://ieeexplore.ieee.org.)

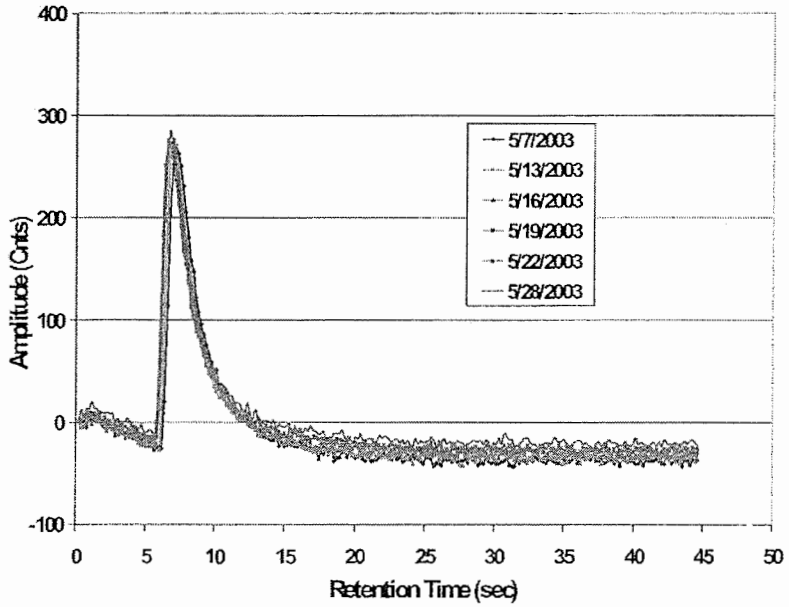


Fig. 13. Overlapping self calibration runs indicated by date acquired with DMMP analyte. Retention time and amplitude repeatability are excellent. (Color version available online at http://ieeexplore.ieee.org.)

in industrial cleaners, aqueous film forming foams (AFFF) and decontamination foams. Fig. 12 depicts a baseline separation of soman (GD) from an interfering glycol ether. It is worth noting that the glycol ether pictured in Fig. 12 is at a concentration many times higher than soman. This is yet another example of the system's overall selectivity because the materials on the PC and SAW chemistries have a lower affinity for chemicals outside of the class for which they were made. Fig. 8 gives an example of the specificity imparted to the SAW array detector by selective coatings. In the graph of the left in Fig. 8, only two of the SAW polymers respond to the two G agents in the chromatogram; however, in the graph on the right, all three elements of the array respond equally to the chemical-detected sulfur mustard.

The data shown in Fig. 13 speaks to the repeatability of the micro GC retention time and the SAW amplitude response for injections of DMMP from the microfabricated PC. Over the course of approximately four weeks, a version of the MicroChemLab known as PRO-ACT was used in the subway of a northeastern city. The DMMP self-test results in Fig. 13 were taken in air using an internal diffusion calibration standard and show that for trace concentrations, the mean retention time is 5.88 s with a standard deviation of 0.19 s. The system has operated continuously for approximately two years. An analysis cycle is completed every 2 min, bringing the total number of analyzes completed to greater than 500 000. In that time, the system has not returned a false alarm.

On a number of occasions, the system has been tested at ECBC against each of the following warfare agents: GA (tabun), GB (sarin), GD (soman), GF (cyclosarin), VX (O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate), HD (sulfur mustard) and HN3 (nitrogen mustard). Thanks to the baseline separation on the GC column, each of these was unambiguously detected. GB, GD, and HD have been tested with several interferants present, including JP8 jet fuel, diesel fuel, AFFF, xylene, ammonia, and humidity. Various results have already been shown in Figs. 2, 8, 11, and 12. In addition, Sandia has participated in five field tests at the Hazardous Spill Center at the Nevada Test Site. Of course, one of the major

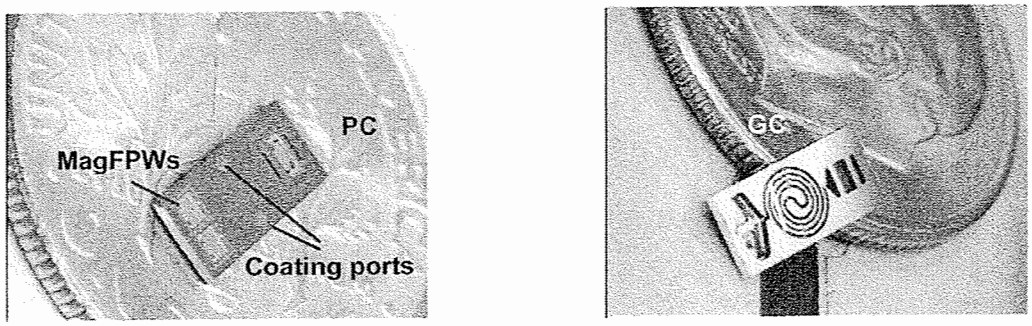


Fig. 14. First generation of monolithically-integrated MicroChemLab produced in Sandia's SwIFT technology (resting on a U.S. dime). (a) Front side surface micromachined PC, two GC coating ports and two FPWs. (b) Reverse side Bosch etch to define release holes, fluidic channels and GC. (Color version available online at http://ieeexplore.ieee.org.)

interferents in a desert environment is pervasive, fine dust. The results shown from these tests demonstrate that particulate filtering allowed the system to perform well. In one field test, triethylphosphate (TEP) was collected and detected; in another DMMP was used. In the first field test the system was 1500 ft from the explosive release of TEP with very favorable wind conditions. The MicroChemLab cycled every 2-min logging trace concentrations for the 2 h it took for the plume to disperse. In another field test, unfavorable wind conditions dominated. However, MicroChemLab, at 2000 ft from the explosive release, was still able to log down to trace-level concentrations. This release included 400 lb of cement in the explosive release, adding to the already dusty environment.

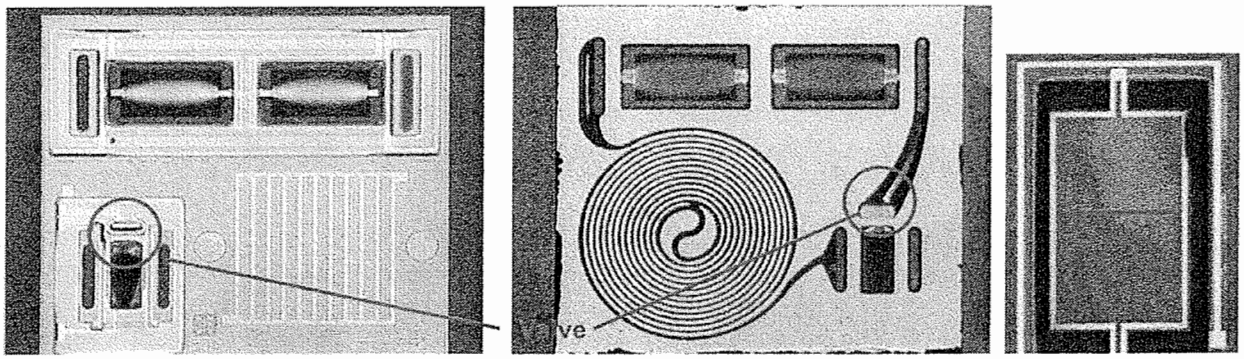
V. Monolithic Integration

There are numerous advantages to hybrid integration. In addition to modular replacement of components, thermal isolation of the individual components is much easier to accomplish when integrated in this way. Given that the individual components often have different operation temperatures, this is a very important reason for hybrid integration. However, the manifolds previously described often have cold transfer lines interconnecting the components. This can cause collection or condensation of analyte in the transfer lines, ultimately reducing sensitivity. Although the size of the manifold channels is sub-miniature, there is still excess dead volume present. Finally, assembly of the hybrid system can add to the cost of the completed system. An effort has begun, therefore, to monolithically-integrate the system for certain applications where further miniaturization is needed and performance benefits are derived. Physical isolation strategies and system timing can be used ultimately to mitigate thermal isolation issues previously mentioned for the monolithic system.

The PC and GC fabrication methods are similar, both using some form of deep etching in silicon. A suitable replacement for the quartz SAW array is necessary to effect monolithic integration in silicon. Several micromachined detectors have been investigated for this purpose, including a thermal-conductivity detector (TCD), a magFPW sensor array, and a magnetically-actuated pivot plate resonator (PPR). The TCD has also been demonstrated by Terry in an integrated micro GC system [9]. Reference [17] describes optimization on our TCD through variations in geometry and flow conditions. The TCD has promise as a general (nonspecific) detector suitable for integration with the PC and GC.

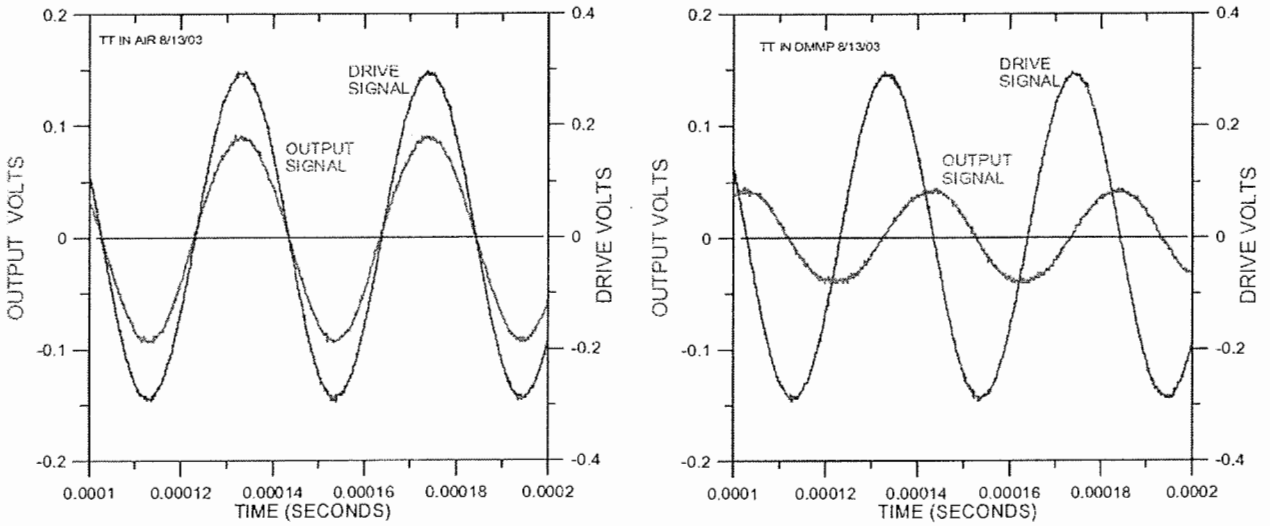
Like the SAW, the magFPW can be made selective through the use of coatings [18]. But, unlike the SAW, it can be fabricated in silicon. Because it operates at lower frequencies than the SAW, drive/sense electronics requirements are eased. In this device a magnetic field, set up by a small permanent magnet, is oriented perpendicular to current lines lithographically defined on a suspended silicon nitride membrane. Lorentz forces generated by the interaction of an imposed AC current and the magnetic field set the membrane into a flexural plate wave mode. The operational frequency depends on the physical dimensions of the membrane, transducer line spacing and membrane stiffness. The inherent sensitivity of the magFPW is in theory superior to the SAW [18], and the time response is more than adequate for analyzing the effluent of a GC. As was previously reported [4], a PC, GC, and magFPW have been monolithically integrated using both bulk micromachining and Sandia's SwIFT processing architecture. In this scheme, front-side surface micromachining was combined with back-end-of-line deep silicon Bosch etching to produce both high precision resistive heaters and transducers, and full-wafer-thickness fluidic flow channels [Fig. 14]. One important consequence of this methodology is the precise definition of thermal and acoustic boundaries for the PC and magFPW, respectively, using a sacrificial silicon dioxide layer trapped within a relatively impervious perimeter of lithographically-defined silicon-nitride. This procedure improved the acoustic performance of the magFPWs by suppressing undesired modes [4]. No perturbations to the SwIFT process were required to fabricate the magFPWs. SwIFT process modules are roughly 2.8 mm × 6.3 mm in size and permitted an important demonstration of monolithic integration of the MicroChemLab. Much was learned about the fabrication process, magFPW operation, and the coating methods needed to functionalize the components. Yet the length of GC allowable in this footprint was too short for effective separation of complicated sample mixtures.

To address these issues, a second generation of the SwIFT monolithic MicroChemLab has been developed [Fig. 15]. The use of two adjacent modules has allowed the length of the spiral GC to increase from the 2.4–cm-length fabricated in the first



(a) (b) (c)

Fig. 15. Optical photographs of the second-generation SwIFT system. (a) Front side surface micromachining is shown: dual PPR sensors are evident as are multiple oblong through-wafer access ports, a PC in the lower left, and a GC resistive heater and circular coating ports in the lower right. (b) Reverse side deep etching: the spiral GC is on the lower left. (c) Close up of the PPR, rotated 90° with respect to images (a) and(b). The direction of the magnetic field, set up by miniature magnets, is indicated by an arrow. Current lines follow the perimeter of the paddle and the two torsional suspension beams. (Color version available online at http://ieeexplore.ieee.org.)



(a) (b)

Fig. 16. Response of a sol-gel coated, magnetically-actuated PPR. (a) Basic response without analyte. (b) Phase and amplitude shift with 10 ng of DMMP present. Note, this particular device was fabricated on SOI and not in the SwiFT architecture. (Color version available online at http://ieeexplore.ieee.org.)

SwIFT design: one new design has an 8.1 cm long GC; another has an 11.8–cm-long column. These will provide useful testing for a limited analyte set. This will, in turn, permit evaluation of the functional features of the monolithic design prior to consuming the many modules needed to realize a full-length, field-deployable design. The 11.8–cm-long, 50–μm–wide GC mentioned above is integrated with a PC and dual magFPWs. The 8.1–cm, 50–μm-wide GC incorporates a novel magnetically-actuated pivot plate resonator sensor pair, described below. This monolithic chip design also incorporates a surface-micromachined bypass valve, intended to switch flow between the sampling and separation/detection portions of the overall system analysis routine. The valve consists of an electrostatically-actuated silicon nitride flap situated over the bypass port. Actuation of the flap has been demonstrated, and future improvements will increase its standoff pressure above the required 5 PSIG. Machined glass lids, baseplates, and packages have been fabricated to coat and test the monolithic system, and this work is in progress.

The PPR mentioned above is potentially more sensitive than the magFPW and, as with the magFPW, is actuated by Lorentz forces. The PPR consists of a central paddle supported by two torsional beams. AC current passing through transducer lines interact via the Lorentz force with an orthogonal, in plane magnetic field causing the paddle to oscillate about the torsional beams [Fig. 15(c)]. In separate experiments, using SOI fabrication of the PPR, its basic chemical sensitivity was demonstrated [19]. In the silicon-on-insulator process, the paddle of the PPR is formed in the silicon device layer by reactive ion etching. Then a rectangular well is Bosch etched beneath the paddle to release it for operation. The typical frequency of operation is about 26 kHz. While this design was not optimized for mass sensing (it was originally designed for another purpose), 10 ng of DMMP produces 90° of phase shift, giving a rough sensitivity estimate of 0.11 ng/degree [Fig. 16]. Accurate mechanical models of the PPR have been developed and are being used to optimize this platform for mass sensing.

VI. Conclusions

A key requirement for chemical detection in the field is improving identification and quantification by reducing the effects of interferents. The MicroChemLab system utilizes the sequential connection of three microfabricated components to achieve this goal. Each component plays a vital role not only in the overall sensitivity of the system, but also its selectivity. The sample collector, a sol-gel-coated microhotplate, not only concentrates dilute amounts of the target compounds prior to separation and detection, but also is capable of ignoring background interferents. The deep-etched GC column separates target compounds from each other. The retention time on the GC column is used to identify the target compounds as well as the pattern generated on the SAW array detector. The detector employs polymer films that are sensitive to certain classes of CWA and insensitive to interferents like fuels, organic solvents, and water vapor. In addition, the system is very adaptable, both to different sample matrices and to different target analytes. Future development of the MicroChemLab will involve even more powerful detectors and selective materials to further increase its field analytical power. Monolithic integration will be used for certain applications for further miniaturization and to reduce dead volume and improve performance.

Acknowledgment

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. The authors would like to thank M. Siegal for nanoporous carbon coating development on planar and three-dimensional preconcentrators. E. Heller and J. Blaich for processing the SAW arrays; L. J. Sanchez for processing many of the preconcentrator devices; V. Hietala for developing the SAW phase comparator; G.R. Dulleck and L.F. Anderson for developing the control circuitry of the system; M. W. Moorman for performing electro-thermal modeling of the three-dimensional preconcentrators; and H. Stewart and the staff of the Sandia's MESA microfabrication facilities for providing device processing.

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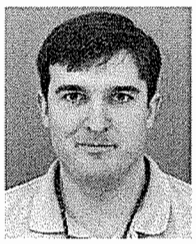

Patrick R. Lewis received the B.S. degree in physics from the University of Texas at Austin in 1990.

He has been with Sandia National Laboratories, Albuquerque, NM, for the past nine years, eight of those years developing micro analytical systems like Sandia's MicroChemLab. He has developed micro systems for the detection of chemical warfare agents, precursors, breakdown products, toxic industrial chemicals, low vapor pressure chemicals, etc. In addition, he has performed numerous tests of MicroChemLab at ECBC with actual agents, in addition numerous to field tests with chemical warfare simulants at Dugway Proving Grounds and Nevada Test Site.

Ronald P. Manginell received the B.S. degree in physics from Rochester Institute of Technology, Rochester, NY, in 1991 and the Ph.D. degree from the University of New Mexico, Albuquerque, in 1997, both in physics.

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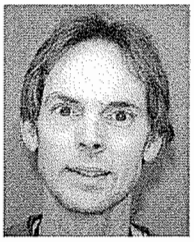

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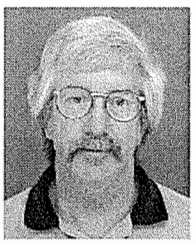

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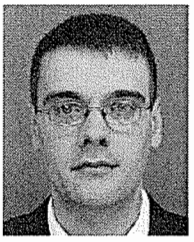

Joseph M. Bauer receeived the B.S. degree in mechanical engineering from The Pennsylvania State University, University Park, and the M.S. and Ph.D. degrees in theoretical and applied mechanics from the University of Illinois at Urbana-Champaign.

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