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GAS PHASE CHEMICAL DETECTION WITH AN INTEGRATED CHEMICAL ANALYSIS SYSTEM

Stephen A. Casalnuovo, Gregory C. Frye-Mason,
Richard J. Kottenstette, Edwin J. Heller, Carolyn M.
Matzke, Patrick R. Lewis, Ronald P. Manginell,
Albert G. Baca, Vincent M. Hietala, Joel R. Wendt,
and Douglas R. Adkins

Sandia National Laboratories
P. O. Box 5800, MS-1425
Albuquerque, NM, USA 87185-1425

ABSTRACT

Microfabrication technology has been applied to the development of a miniature, multi-channel gas phase chemical laboratory that provides fast response, small size, and enhanced versatility and chemical discrimination. Each analysis channel includes a sample preconcentrator followed by a gas chromatographic separator and a chemically selective surface acoustic wave detector array to achieve high sensitivity and selectivity. The performance of the components, individually and collectively, is described.

1. INTRODUCTION

Numerous chemical detection scenarios, for example, industrial process control and public safety applications, impose challenging requirements on the performance of chemical detection systems. These applications require detection of trace levels of specific target analytes in real-world environments that may contain more than 1000-fold higher concentrations of potentially interfering compounds. In addition, rapid analysis, instrument portability, and low rates of compound misidentification often are critically important. In an effort to address the requirements of these applications, Sandia's µChemLab™ program has a goal to develop small (palm-top computer sized), lightweight, and autonomous systems that provide rapid (1 min), sensitive, and selective detection of target analytes. Although the µChemLab™ program includes gas and liquid phase analysis systems [1], only the performance of the gas phase components is described herein.

Figure 1 shows the system design using multiple analysis channels to provide enhanced chemical discrimination and very low false alarm rates. Sensitive and highly selective detection is achieved using a small adsorbent sample preconcentrator connected to a gas chromatographic (GC) column that feeds a low dead volume surface acoustic wave (SAW) detector array. Commercially available batch microfabrication processes are employed to produce these three components, pictured in Fig. 2. Among the advantages of this approach are size and cost minimization for individual devices. The design and performance of the current component set is described below.

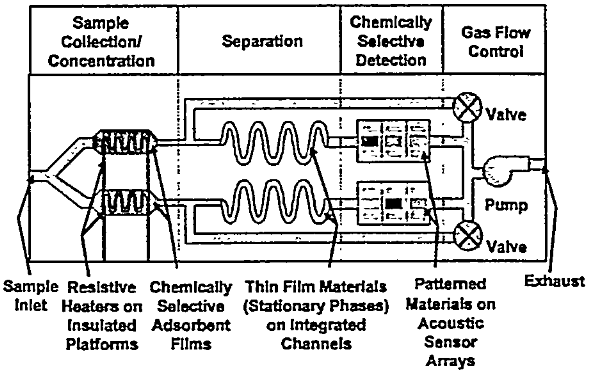

Fig. 1: Schematic of the gas-phase µChemLab™ system. The system incorporates Sandia designed and fabricated concentration, separation, and detection components (see Fig. 2) and commercially available diaphragm pumps and miniature valves.

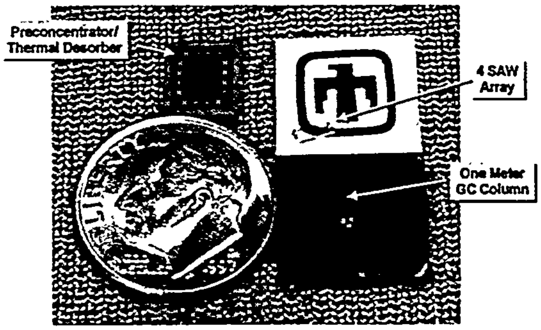

Fig. 2: Clockwise from above dime: microfabricated sample preconcentrator; four-element, 380 MHz SAW detector array, and 1 m long gas chromatograph column.

2. PRECONCENTRATOR

The preconcentrator stage collects target analytes from the air stream over an extended time and then releases them in a rapid, concentrated pulse into the GC column. The preconcentrator, in essence, is a

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microfabricated hotplate (see Figs. 3 and 4). A chemically selective layer, typically a microporous oxide, adsorbs the analytes from the environment. After sufficient analyte has been collected, an embedded Pt heater rapidly raises the temperature of the preconcentrator to desorb the analytes. Concentration enhancement factors of greater than 100 have been achieved after 40 s adsorption periods. The desorption pulse width is typically 200 ms (full width at half maximum).

The heater is fabricated on a 0.5 µm thick silicon nitride (Si_2N_3) membrane suspended over a cavity etched through a Si substrate. The 400 µm deep cavity is produced using deep reactive ion etching (DRIE) [2]. The low thermal mass and good thermal isolation of the Si_2N_3 membrane are critical for quickly heating the preconcentrator with a minimum of electric power. As shown in Fig. 5, the microhotplate requires approximately 20 ms to reach a steady-state temperature of 200°C. This steady-state temperature is sustained by 105 mW of electrical power. Thermal modeling has been used to optimize the preconcentrator design [3].

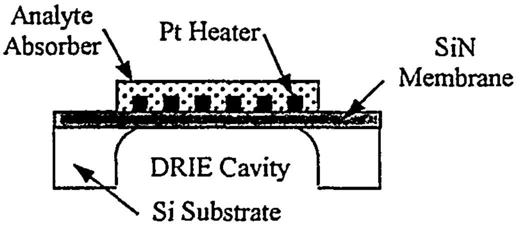

Fig. 3: Schematic cross section of the microhotplate preconcentrator stage.

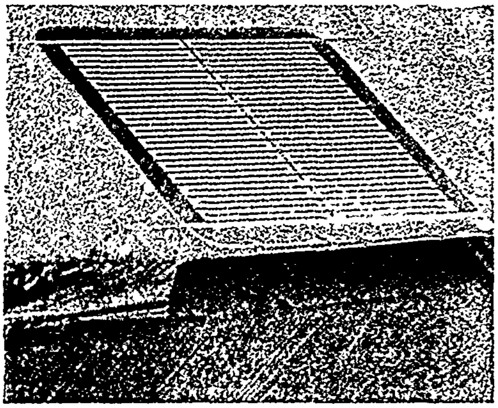

Fig. 4: Scanning electron micrograph (SEM) of the preconcentrator stage showing the micromachined SiN membrane and Pt heater. Analyte adsorbing layer is not shown.

3. GC COLUMN

A miniature GC column provides temporal separation of the analytes and any interferants that may be collected by the preconcentrator stage. A Si DRIE process, similar to that used to fabricate the preconcentrator, is employed to produce the GC column [4]. Because of the exceptionally high aspect ratio and anisotropy of the DRIE process, closely spaced, narrow gas flow channels can be etched into the Si substrate to a depth many times the channel width. This approach affords good GC performance in a small footprint while maintaining short transit times through the column. A typical column is a 1 m long spiral with 40 - 100 µm wide channels separated by 25 - 40 µm thick walls etched to a depth of 300 µm or more (see Fig. 2). It occupies a 1 - 1.5 cm^2 area. The close-up of a channel cross-section in Fig. 6 illustrates the capability of the fabrication process. After the channels are etched, the Si substrate is thermally oxidized to produce a thin, glasslike layer on the surface of the channels in order to facilitate stationary phase deposition (see below).

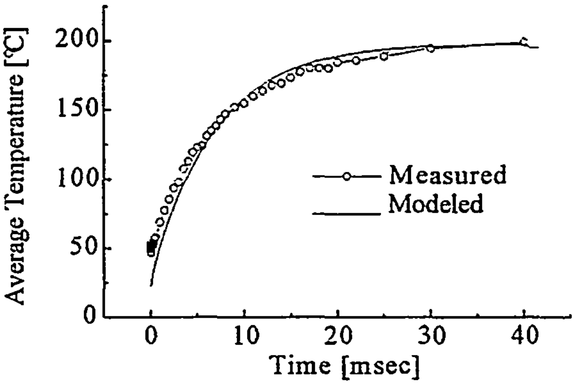

Fig. 5: Comparison of measured and modeled heating rates of the microhotplate preconcentrator during analyte desorption. The preconcentrator can be ramped from room temperature to 200°C in 20 ms, drawing 105 mW at steady state.

Fig. 6: SEM of a cross-section of a spiral GC column etched into Si using DRIE. The etch process results in deep, smooth, vertical channels.

Closed channels are produced by anodically bonding a Pyrex lid to the top surface of the Si substrate [4]. Since the bonding process is carried out at elevated temperatures, Pyrex is used because it closely matches Si's thermal expansion coefficient. PEEK stubs are adhesively bonded to this lid to provide gas interconnection.

After the channels are sealed, GC stationary phase materials are deposited on the walls using conventional polymer solution techniques as well as sol-gel coating technology. The retention of the analytes in the stationary phase produces a separation in time of the analytes arriving at the array of acoustic wave detectors. This temporal separation provides an additional means of distinguishing analytes from one another and from interferants, as shown in Fig. 7, aiding in analyte identification.

As illustrated in Fig. 1, the µChemLab™ system will have two gas analysis channels that incorporate GC columns, each with a different stationary phase. The two channels can be optimized for different analytes, increasing the functional range of the unit. The channels can also be optimized to provide two analyses for an analyte, improving the reliability and lowering the false alarm rate, as demonstrated in Fig. 8. The stationary phase selection, in this case, non-polar OV-1 versus polar Carbowax, reorders the elution times of the components.

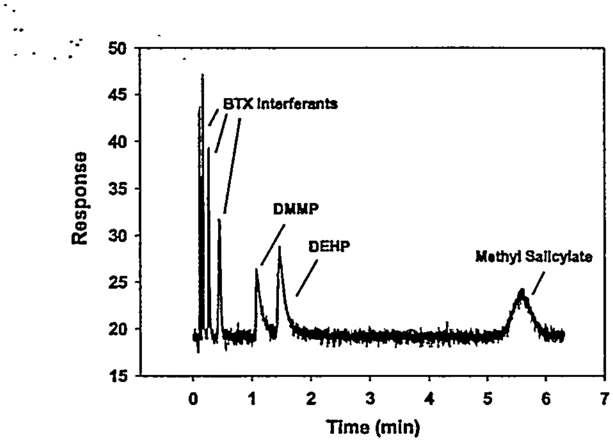

Fig. 7: Microfabricated GC column elution times for a mixture of dimethylmethylphosphonate (DMMP), diethylhydrogenphosphonate (DEHP), methyl salicylate, and benzene (B), toluene (T), and xylene (X).

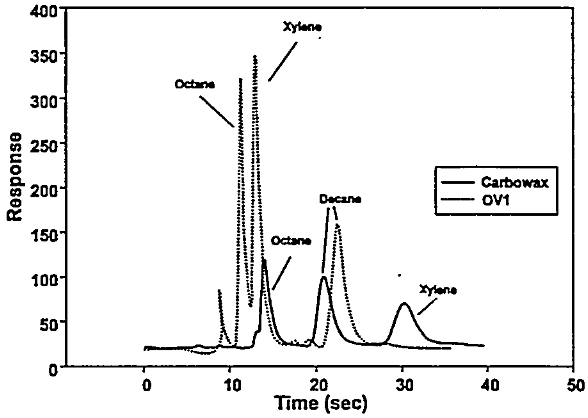

Fig. 8: Elution times for two microfabricated GC columns with different stationary phases (Carbowax and OV1). Reordering of elution times in the two channels provides confirmation of results.

4. SAW CHEMICAL SENSOR ARRAY

The use of SAW delay lines as sensitive chemical mass sensors is well known [5]. The µChemLab™ employs a 4-element quartz array in each gas analysis channel, as shown in Fig. 9. A center input interdigitated transducer (IDT) launches a SAW in both directions. Four smaller output IDTs, two on either side of the input IDT, reconvert the acoustic wave to an electric signal. Three of the SAW delay lines are coated with different chemically sorbent materials, each optimized for the analytes of interest. The fourth delay line serves as a reference. Delay lines operating between 100 MHz and 700 MHz have been designed and tested. Delay line frequency is determined by the spacing between adjacent IDT fingers and the acoustic velocity in the material.

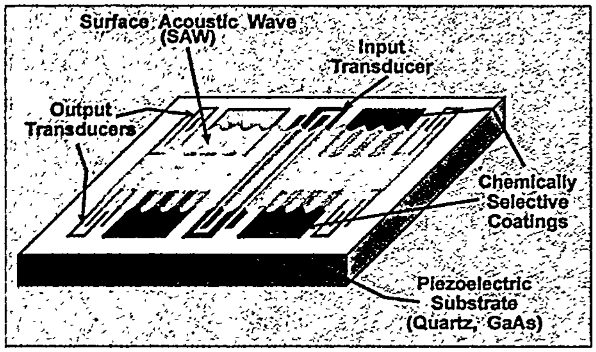

Fig. 9: Schematic representation of a 4-element SAW detector array.

The delay line frequency is a critical parameter in the design and operation of the SAW sensor array. When a delay line is configured in an oscillator circuit, the sensitivity of the oscillator frequency, f, to added surface mass density (mass/area) increases as f^2 [5]. In addition, the size of the delay line decreases as $1/f^2$. The net result is that the sensitivity to the total mass of the analyte scales as f^4, which is a strong argument for going to higher frequency. These trends are illustrated in Fig. 10.

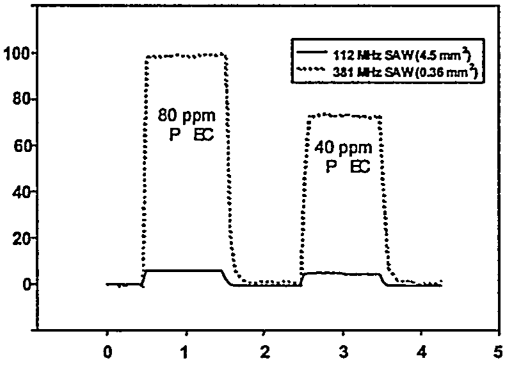

Fig. 10: Sensitivity data for two SAW devices with identical coatings when exposed to perchloroethylene vapors. The higher frequency SAW is much smaller, but exhibits a much larger response.

The attraction of higher frequency SAW sensors is reduced somewhat by the difficulty associated with packaging high frequency components. This problem is minimized if all high frequency components, including the SAW delay line, can be packaged in the equivalent of a single multichip module with only DC inputs and outputs [6]. A photograph of the multichip array configuration of the SAW sensor is shown in Fig. 11. A ST-quartz die forms the substrate for both the four-element SAW delay line array (described above) and the GaAs ICs. Circuit interconnections are made by patterning metal paths directly onto the quartz die. The ICs are connected to the quartz die by wire bonding. This device is being used in the current version of the µChemLab™.

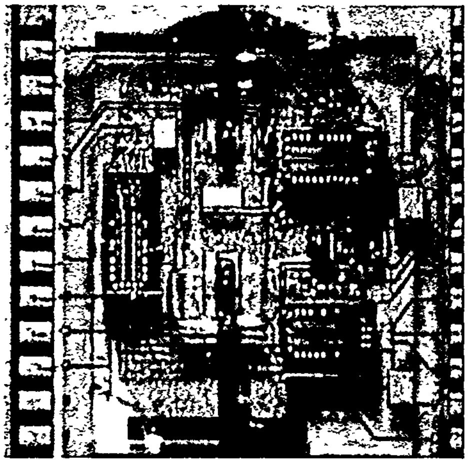

Fig. 11: Multichip module version of SAW microsensor array. The ST-quartz die size is 6.9 mm x 8.6 mm. Each of the three GaAs ICs is approximately 1 mm x 2 mm. Although the delay lines and ICs operate at 510 MHz, this module operates in a DC in/DC out mode.

One of the ICs contains an amplifier circuit that drives the central IDT and forms an oscillator with the reference SAW delay line. As analytes are sorbed onto the chemically selective coatings on the 3 sensor delay lines, the added mass produces an additional phase shift in the SAW sensors relative to the reference delay line. This phase shift is converted to a DC voltage by phase comparator circuits on the ICs. The delay lines and ICs pictured in Fig. 11 operate at 510 MHz yet the module requires only DC inputs and provides DC outputs. The three GaAs ICs draw a total of 90 mA at 2.5 Vdc. The output voltage noise for this multichip module is approximately 60 µV, or about 7 millidegrees of phase.

A fully monolithic approach that integrates the SAW delay lines and the microelectronics onto a single GaAs die is currently under development. GaAs is an ideal material for this approach because it is both piezoelectric and a semiconductor. A photograph of the monolithic die is shown in Fig. 12. Microelectronics equivalent to the 3 die in Fig. 11 is located in the corners of the die in Figure 12. The 4 SAW delay lines are placed along the diagonal of the die.

All three microfabricated components, the preconcentrator, GC column, and the multichip SAW detector module, have been assembled into a complete system. An example of the system performance, showing the temporal separation of target analytes and the varied response of two sensors of a four-sensor SAW detector array (reference and three coated sensors), is given in Fig. 13. The strong hydrogen bond of the acid coating (BSP3) provides selective detection of the DMMP while ethyl cellulose provides the largest response to methyl salicylate. The sample used for generating this data contained 75 ppb of DMMP, 1 ppm of methyl salicylate, and 74 ppm of xylene, a volatile interferant. Because of the selectivity of the preconcentrator, the xylene does not interfere with the analysis even though the concentration is almost 1000 times that for DMMP.

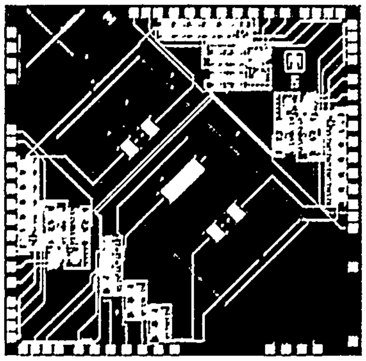

Fig. 12: Monolithic GaAs SAW Array. The large central launch transducer and 4 output transducers can be seen along the diagonal in the center of the die. The circuitry is designed to operate at 700 MHz but has only DC inputs and outputs. The die measures 4.5 mm by 4.5 mm.

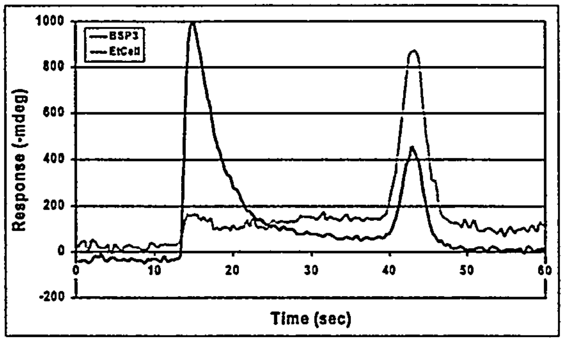

Fig. 13: SAW sensor array's unique response to mixture of DMMP and methyl salicylate after passing through the preconcentrator and GC column. Sensor array elements were coated with ethyl cellulose (Etcell), and a H-bond acid modified polymer (BSP3) [7].

6. PACKAGING AND ASSEMBLY

For assembly in the prototype µChemLab™ unit, the components described above are mounted on a novel printed circuit (PC) board that provides both the electrical and fluidic interconnects (Fig. 14). Embedded flow channels within the board and vias through the board connect the microfabricated components, mounted on either side of the board, a valve and an inlet/outlet manifold. A single board contains two gas analysis channels. The PC board shown in Fig. 14 measures 8.5 cm by 5.3 cm. Other PC boards in the prototype unit (Fig. 15) provide temperature control, A/D conversion, and system level functions. The prototype measures 20.5 cm long.

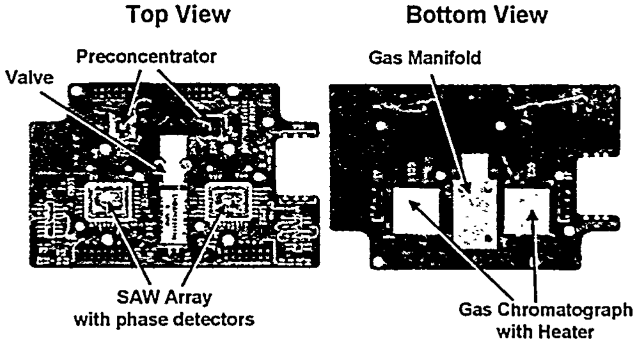

Fig. 14: Assembled PC board containing two gas analysis channels. The board provides both electrical and fluidic interconnections. It measures 8.5 cm by 5.3 cm

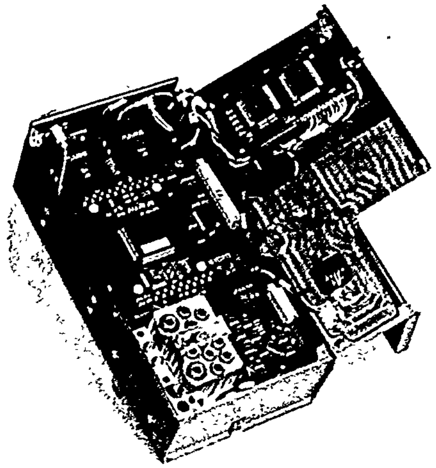

Fig. 15: View of the interior of the assembled prototype µChemLab™ unit. The gas phase analysis components are mounted on the bottom of the unit and are not visible in this picture. The unit measures 20.5 cm long.

7. CONCLUSION

Trace level chemical detection has been accomplished using microfabricated chemical analysis components. A sample preconcentrator, a gas chromatographic column, and a 4-element SAW sensor array have been combined to detect target analytes and interferants with low detection limits. Pattern recognition algorithms applied to temporally separated detector array responses provide highly reliable identification of a number of analytes. Integration of the detectors with drive and signal conditioning electronics is being explored to improve the performance of high frequency sensors and to simplify packaging.

8. ACKNOWLEDGEMENTS

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9. REFERENCES

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