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## **Microcalibrator System for Chemical Signature and Reagent Delivery**

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## Microcalibrator system for Chemical Signature and Reagent Delivery

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### Abstract

Networked systems of low-cost, small, integrable chemical sensors will enable monitoring of Nonproliferation and Materials Control targets and chemical weapons threats. Sandia-designed prototype chemical sensor systems are undergoing extended field testing supported by DOE and other government agencies. A required surety component will be verification of microanalytical system performance, which can be achieved by providing a programmable source of chemical signature(s) for autonomous calibration of analytical systems. In addition, such a controlled chemical source could be used to dispense microaliquots of derivatization reagents, extending the analysis capability of chemical sensors to a wider range of targets. We have developed a microfabricated system for controlled release of selected compounds (calibrants) into the analytical stream of microsensor systems. To minimize pumping and valve requirements of microfluidic systems, and to avoid degradation issues associated with storage of dilute solutions, we have utilized thermally labile organic salts as solid-phase reservoir materials. Reproducible deposition of tetrapropyl ammonium hydroxide onto arrays of microfabricated heating elements can provide a pair of calibration marker compounds (one fast and one slow-eluting compound) for GC analyses. The use of this microaliquot gas source array for hydrogen generation is currently under further development. The goal of the latter effort will be to provide a source of high-pressure, low viscosity GC carrier gas for Sandia's next-generation microfabricated gas-phase chemical analysis systems.

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## Nomenclature

FID	Flame Ionization Detector
GC	Gas Chromatography
HMDS	Hexamethyl disilazane
MSA	Microcalibration Source Array
PC	Preconcentrator
RSD	Relative Standard Deviation
TCR	Temperature Coefficient of Resistance
TPAH	Tetrapropyl ammonium hydroxide

## Introduction

Sandia has developed small, potentially low-cost chemical sensors for Nonproliferation and Materials Control applications and for monitoring of chemical weapons threats. Our experience with DOE sponsored nonproliferation programs and with the current accelerated needs of Homeland Defense programs has clearly indicated a need for reliable, low cost, flexible, and potentially autonomous systems for the field calibration and performance verification of such chemical sensors. In addition, the adaptation of chemical sensors for detection and monitoring of exhaled marker compounds in human breath, and potentially for liquid-phase or vapor monitoring of drugs or their metabolites from exhaled breath or from urine, could potentially be used to monitor patient health and ensure compliance with drug treatment regimens.

Useful application of chemical sensors to these problems requires all necessary components for sensor calibration, performance verification, and if necessary chemical derivatization, to be integrated with the sensor package. We therefore developed a prototype microfabricated chemical source, based on solid phase encapsulation of calibration or derivatization reagent compounds on arrays of individually addressable thermal elements. This approach could potentially provide a small, rugged, lightweight, readily manufacturable, and inexpensive source capable of delivering appropriate masses of volatile organic or other compounds for sensor calibration and/or analyte derivatization in the field.

The substrate for these devices consists of an array of metallic resistive heaters patterned on SiN membranes formed by etching of SiN/Si stack structures. These devices are essentially multiple arrays of microfabricated membrane heaters, based on a previous single-element design [1]. The microfabricated source array (MSA) device is envisioned as an extremely low-cost consumable, with replacement required after the contents of the solid-phase reservoirs are exhausted. Therefore, the ultimate cost of the MSA must be extremely low. This can only be achieved in the future by paying careful attention to manufacturability.

During the early stages of this study, we investigated the use of porous sol-gel coatings as reservoirs for 1-octanol (a relatively inert surrogate with vapor pressure similar to chemical warfare agents), but we were unsuccessful in achieving useful reproducibility of these coatings. We have therefore concentrated on the production of propene and tripropyl amine aliquots by thermal decomposition of solution-deposited tetrapropyl ammonium hydroxide on arrays of microfabricated thermal elements. The propene acts as a fast-eluting marker, and the tripropyl amine as a slow-eluting marker, in gas chromatograms using microfabricated gas chromatography (GC) components. This will be a key capability in future temperature-programmed micro-GC systems, since the pair of marker compounds can provide a measure of retention index at two points in the chromatogram.

## 1.1. Prototype substrates

Prototype devices are 2x5 element arrays of resistive heaters patterned onto thin SiN membranes, that are suspended on 1.6x1.6 cm Si die. An enlarged photo of a

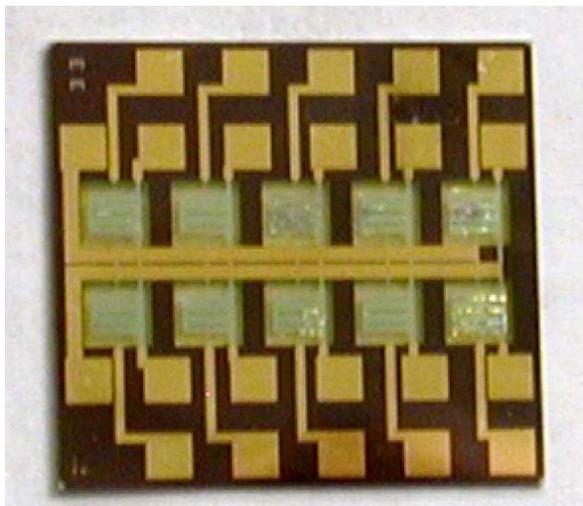


Figure 1: 2x5 prototype array

2x5 MSA prototype device is shown in Figure 1. Two parallel rows of microhotplate thermal elements (both 2.2 x 2.2 mm and 1 x 1 mm elements have been fabricated) are located along the center of the die. Each element incorporates a resistive metal heater and a separate thermistor for independent temperature measurement and feedback control, if desired. In practice, we have used the temperature coefficient of resistance (TCR) of the heater element, combined with a measurement of the input voltage and current to determine the operating temperature of the devices at given input power. Input bond pads are located along the outside edges of

the device, with common ground pads for the heater and measurement circuits at the left side of the photo. We have also fabricated the required control circuits to enable addressable thermal control of individual elements on the 2x5 MSA prototype. When set to a predetermined voltage the circuit provides a rapid (~200 msec) ramp of the selected thermal element to a specific temperature. This control relies on knowledge of the TCR of the heater and thermistor circuits patterned onto the individual elements. Accordingly, we have carefully monitored the TCR and ambient-temperature resistance values for these devices. Variance in the TCR depends on the metallization process during microfabrication. We therefore closely monitored reproducibility of TCR values for the prototype devices. Between elements of individual die the TCR values are very consistent, with relative standard deviation (RSD) between elements on the order of 0.2%. TCR RSD between individual die from a single wafer is on the order of 1-2%. However, TCR variation to date between die from different wafers has ranged up to 16%. We have therefore instituted careful monitoring of TCR values to insure accurate temperature control during desorption experiments. Ultimately, tight control of metallization steps during fabrication can be expected to produce useful devices without requiring individual measurement or calibration of thermal properties.

## 1.2. Automated drop-coating system

Reproducible deposition of solid-phase reservoir coatings on individual elements of the arrays is a key requirement for use of the devices as calibration sources. Accordingly, during FY03 we have developed an automated coating system capable of precise delivery of small-volume (~2-5 nL, depending on solution viscosity and surface wetting) droplets of precursor solutions to the active elements of our microcalibration source array (MSA) devices. The system is shown in Fig. 2. This system utilizes a pneumatically controlled pressure injector (MPPI-2, Applied Scientific Instrumentation, Eugene, OR). By monitoring working solution viscosity, pressure, and pulse duration time, we have developed methods for depositing single droplets or square arrays of droplets (up to 5x5) of several encapsulant coatings within the dimensions of the individual elements. The pressure injector feeds a capillary “pen” mounted in a motion control subsystem. The “pen” utilizes a commercially available fused silica capillary to deliver the working solution to the

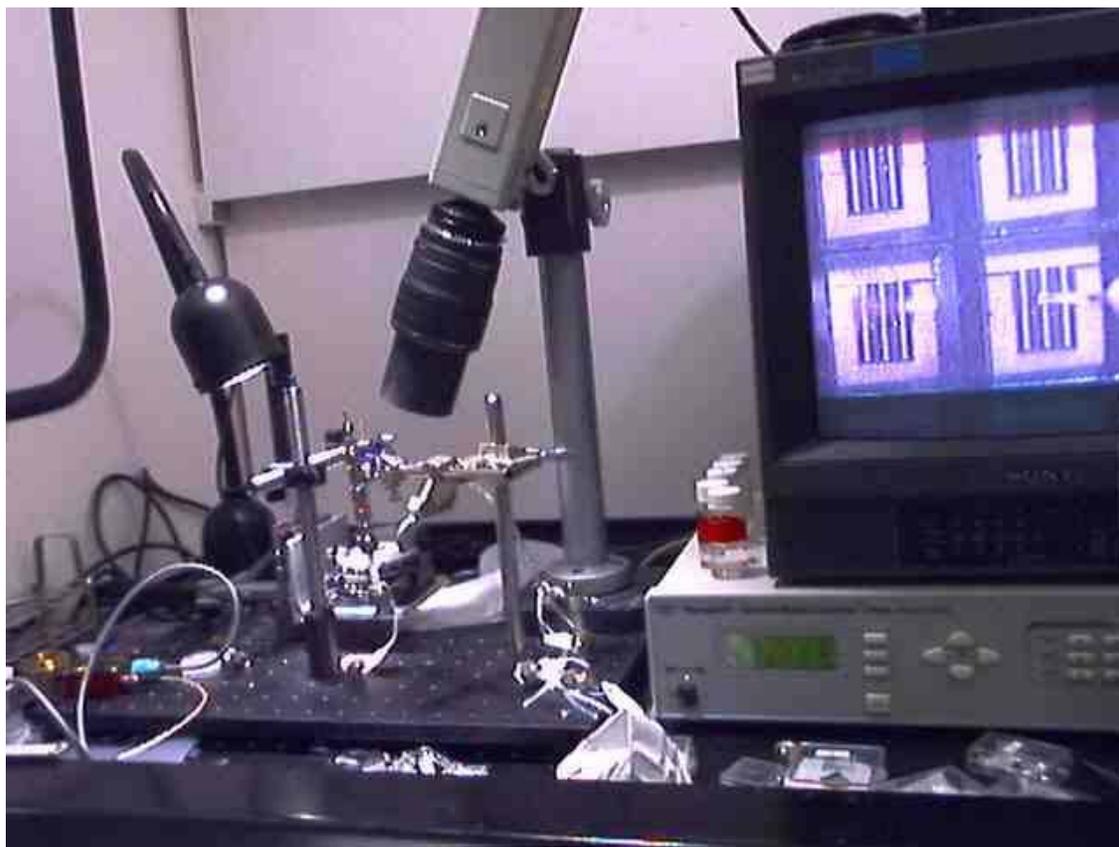


Figure 2: Automated drop-coater

substrate surface. The pen position is controlled by a Newport ESP300 three-axis motion controller with associated stepper motors, three Newport 462 linear stages, and a Newport Series 481-A rotary stage. A video camera system with a macro

lens allows for alignment and monitoring of the system, and deposition is computer-controlled by a LabView™ program through a National Instruments interface. This combination allows for precise deposition of solution precursors doped with predetermined masses of desired calibrant or derivatization reagents. The precursor solutions are then air-dried and/or thermally cured at low temperature to produce the necessary solid-phase encapsulant coatings.

The pressure injector does not drive a free droplet through the end of the capillary. Instead, the droplet meniscus at the end of the capillary “bulges” during the pressure pulse, so that the liquid surface contacts the substrate. The motion controller then withdraws the substrate away from the fixed pen position, resulting

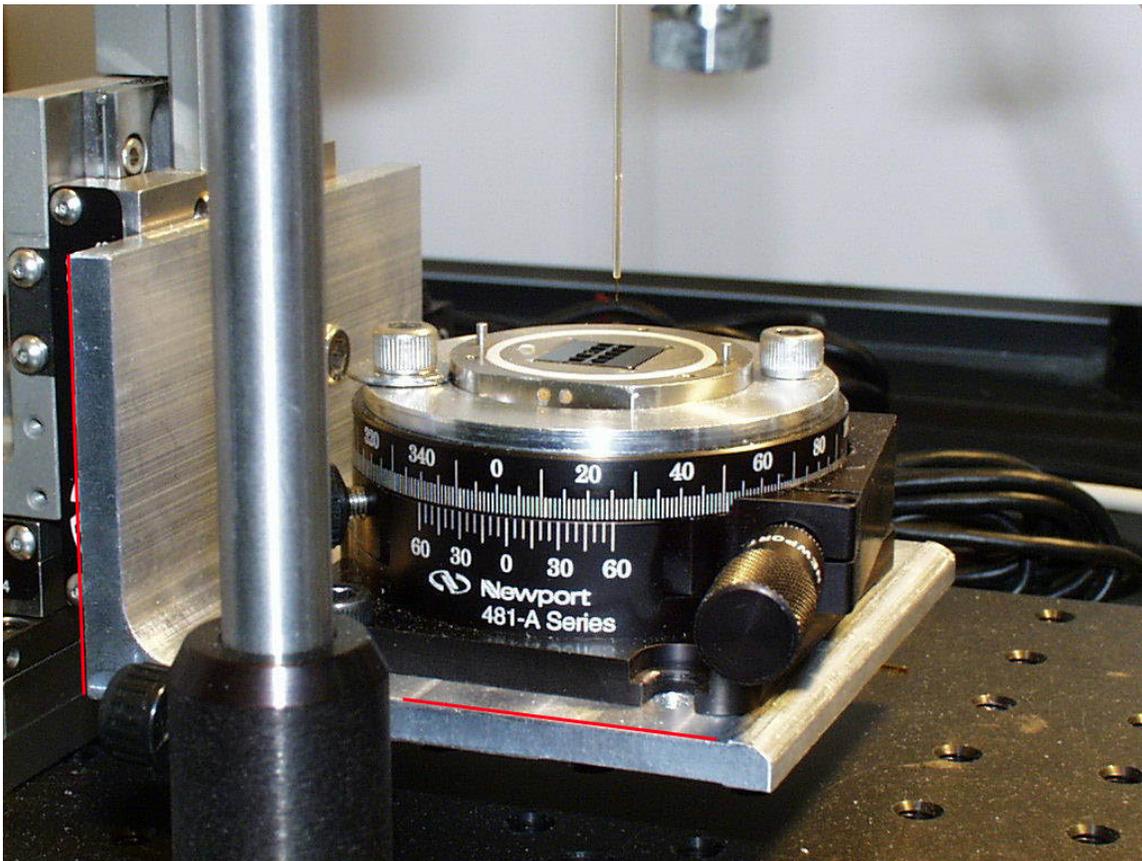


Figure 3. Drop coater capillary and sample stage

in separation of the drop and deposition onto the surface. Because of this, wetting characteristics of both the substrate and the pen surface are critical to achieve reproducible depositions with this system. The commercial capillary (shown in a closeup photo in Fig. 3) is normally coated externally with a polyimide layer to prevent breakage. In order to achieve reproducible wetting, this layer was stripped in our system by flaming the end of the capillary. The exposed glass surface was then stripped using piranha solution ( $H_2SO_4 + H_2O_2$ ). The resulting hydrophilic

surface was then allowed to stand in a solution of perfluorinated alkyl trichlorosilane. This resulted in the formation of a strongly hydrophobic self-assembled monolayer coating on the external capillary surface, which allowed for reproducible separation of droplets of aqueous or alcohol-based coating solutions.

### 1.3 Solid phase reservoir materials

During our initial attempt to develop a suitable solid reservoir film for a useful GC calibrant compound, we demonstrated thermally-controlled release of 1-octanol from solution-doped sol-gel solid films, using single-element microhotplate devices as testbeds. This compound was chosen for initial testing as a nontoxic surrogate for nerve agents, on the basis of its vapor pressure. The vapor pressure of the analyte is related to the retention index of the compound on nonpolar GC stationary phases. Upon extending this work to deposition of octanol-doped solgel films on prototype multielement arrays, we found poor reproducibility of the desorbed GC peak areas. In retrospect, this may have been due at least in part to inconsistent wetting of the deposited droplets, since these experiments were conducted before we realized the importance of surface preparation for wetting control. However, the observed effect could also be due to variations in crosslinking kinetics of the sol-gel films, which would in turn result in differences in gel pore size distributions. Therefore, we discontinued use of this approach and instead concentrated on investigation of calibrant materials based on thermally labile organic salts.

The bulk of the investigations reported here are from thermal decompositions of tetraalkyl amine hydroxide salt films to form the corresponding trialkyl amines and alkenes in the gas phase. These salts have several advantages as solid-phase calibrant gas-generating sources. The trialkyl amine and alkene products are useful calibrant compounds for nonproliferation and industrial gas monitoring applications, respectively. The salts are easily deposited as solutions in aqueous or mixed water-alcohol solutions, and have long-term stability. The alcohol or water solvents can be air-dried, and thermal disproportionation of the solid salt residue results in controlled desorption of the calibrant compounds. As an example, desorption of tripropyl amine and propene results from the thermal decomposition of tetrapropyl ammonium hydroxide:



We used gas chromatography to investigate the identity of materials emitted by this mechanism, verifying almost exclusive production of the trialkyl amine and corresponding alkene. The most appropriate tetraalkyl amine hydroxide salt can be chosen for the desired application based on the GC retention time of the resulting trialkyl amine. The retention times of several trialkyl amines under typical chromatographic conditions are shown in Table 1 (page 12). Based on this information, tetraalkylammonium hydroxide salts will be useful as calibration sources for analysis systems directed at nonproliferation applications.

## 2. Experimental Results

### 2.1. Gas chromatography results.

Several tetraalkyl ammonium hydroxide salts were anticipated to have potentially useful GC retention times. These salts and their liquid trialkyl amine counterparts were individually dissolved in ethanol and injected onto a commercial Agilent 6890 GC with 7683 autosampler and flame ionization detector (FID). All chromatography in this report was performed using this system and a 15-meter long DB-1 column (Agilent Laboratories, Palo Alto, CA) with a 530 $\mu$ m I.D. and 1.25 $\mu$ m thick stationary phase coating. In these experiments, the oven was 100°C, and the pressure was ramped from 1 to 5 p.s.i. immediately after injection of 0.2 $\mu$ L of each solution. With the split flow maximized at 200 mL/min, this chromatographic method resulted in an injection split of 62:1, preventing column overload. Through the resulting chromatograms, decomposition products were identified by retention time. Table 1 summarizes the results of these initial experiments. Here, and in subsequent experiments, the retention times of the alkenes were nearly identical under these GC conditions.

**Table 1.** GC retention times of tetraalkylammonium decomposition products

<b>Compound</b>	<b>Retention Time</b>
n-alkenes	0.63 min.
triethyl amine	1.04 min.
tripropyl amine	1.91 min.
tributyl amine	7.8 min.

### 2.2. Results with original GC fixture.

MSA devices coated with tetraalkylammonium salt films were placed in mechanical fixtures which utilized spring loaded “pogo pin” contacts to the pads on the die. The fixtures provided for carrier gas inlet flow (typically nitrogen) and outlet flow to the GC. A software controlled circuit with a serial connection was used to synchronize chromatographic data collection with the “firing” of each element on the die.

The original GC fixture for desorption testing of the MSA devices was a stainless steel block containing a U-shaped flow channel on one side, and a milled rectangular indent on the other for mechanical positioning of the die. Stainless steel was chosen in an attempt to limit gas absorption on the walls of the fixture. The device was sealed by an O-ring surrounding the entire die, with holes drilled at the ends of the U-shaped channel for connection to the GC carrier gas flow system. The flow channel did not seal directly to the face of the MSA die, relying instead on the limited gas conductance of the small gap between the face of the fixture and the die in order to control the gas flow. This flow should ideally proceed

from the inlet, around the U-shaped channel to the outlet. A sketch of this arrangement is shown in Fig. 4 along with our numbering convention for the 10 elements of the MSA die. Element 1 is taken to be the membrane closest to the outlet, while element 10 is nearest the inlet.

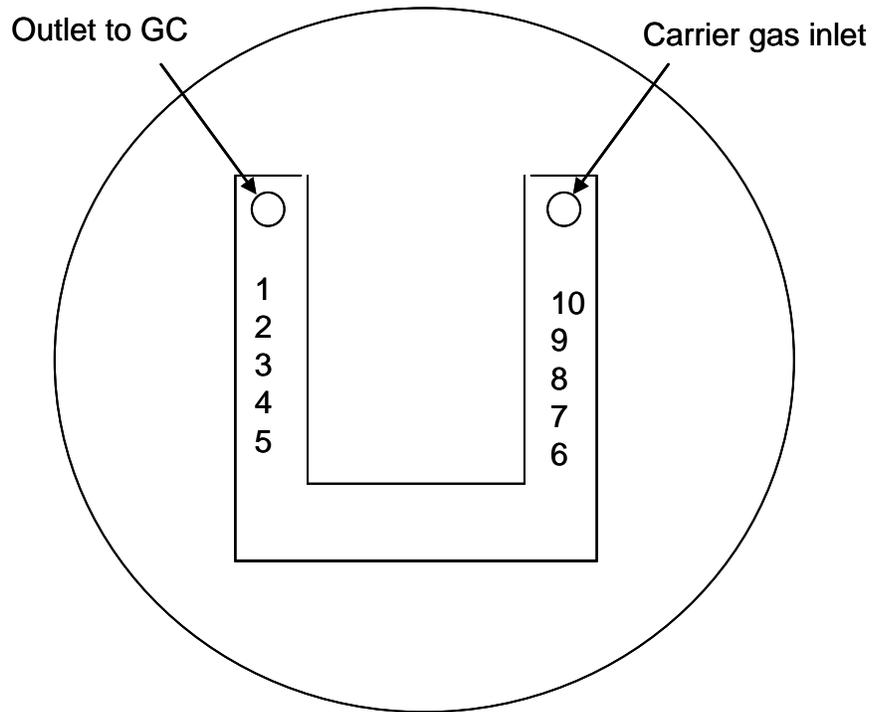


Figure 4: Sketch of original GC fixture flow channel

Chromatographic performance of devices using this fixture was unsatisfactory. An example of chromatograms for desorption of propene and tripropyl amine using this experimental arrangement is shown in Fig. 5. The oven temperature was 100°C and the pressure was 5 p.s.i.

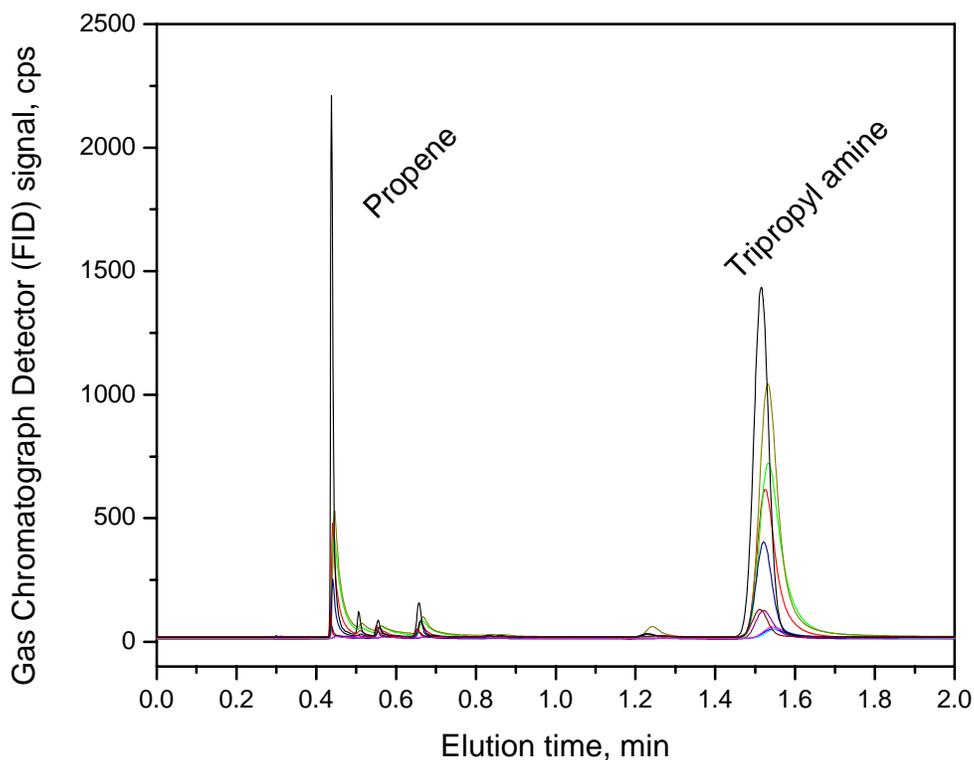


Figure 5: Chromatograms using original GC fixture

The retention times for the tripropyl amine peaks shown in Fig. 5 are relatively consistent, with a mean of 1.53 minutes and standard deviation of 0.014 minutes (RSD = 0.9%). However, the areas of the tripropyl amine peaks vary greatly, by a factor of ~9X when comparing the largest and smallest of the ten peaks. This variation may be due in part to inconsistent drop coating due to surface wetting, as described above. However, there is also leakage across the center of the intended flow path, which affects both the peak area and retention time. The latter effect is displayed in Fig. 6, where the GC peak retention times are plotted vs. the element position. To first order, the peak retention time should depend on the distance the carrier gas must flow in order to sweep the desorbed material into the GC. Referring back to Fig. 4, we would expect a monotonic increase with element number on that basis. However, the maximum retention time is for element 5, with element 10 having the shortest retention time. This is evidence that the carrier gas flow is “cutting the corner” of the idealized flow channel sketched in Fig. 4, and that the flow restriction across the fixture is not sufficient to prevent this leakage.

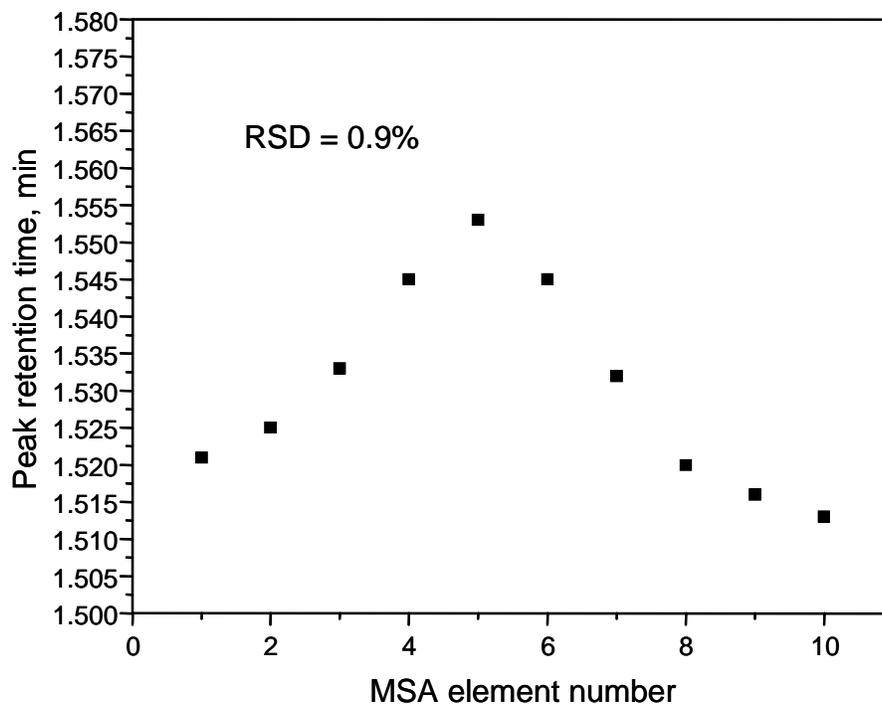


Figure 6. Peak retention times using original GC fixture

## 2.2. Results with stereo-lithographically patterned polymer GC fixture.

In order to improve the fixture performance a second design was fabricated using a commercial stereo-lithography process to form internal channels in a polymer block. This process allowed for patterning of individual flow channels connecting to a small open volume above the face of each element. The flow channels were designed in a “herringbone” pattern in an attempt to make the total flow channel lengths equal for each element in the array. The individual channels were joined at the inlet and outlet of the fixture. Elastomer gaskets were also cut to form a gas-tight seal between the modified fixture and the face of the MSA die. It would be preferable to avoid any use of elastomers if possible, since these materials often absorb significant amounts of analyte vapor, and could therefore affect the desorption results. However, the requirement for low-leakage, controlled flow channels was considered more important in this proof-of-concept study. The exposure of the elastomer gaskets to the desorbed calibrant species was limited to the edges of the gasket sheet around the individual elements. Therefore, we attempted to keep the gasket materials as thin as possible to limit the amount of gasket surface area wetted by the desorbed calibrant compounds. A photo of the polymeric fixture showing the internal gas flow channels is shown in Fig. 7. A photo of the complete fixture showing upper and lower gaskets as well as the fixture lid incorporating pogo pin electrical connections is shown in Figure 8.

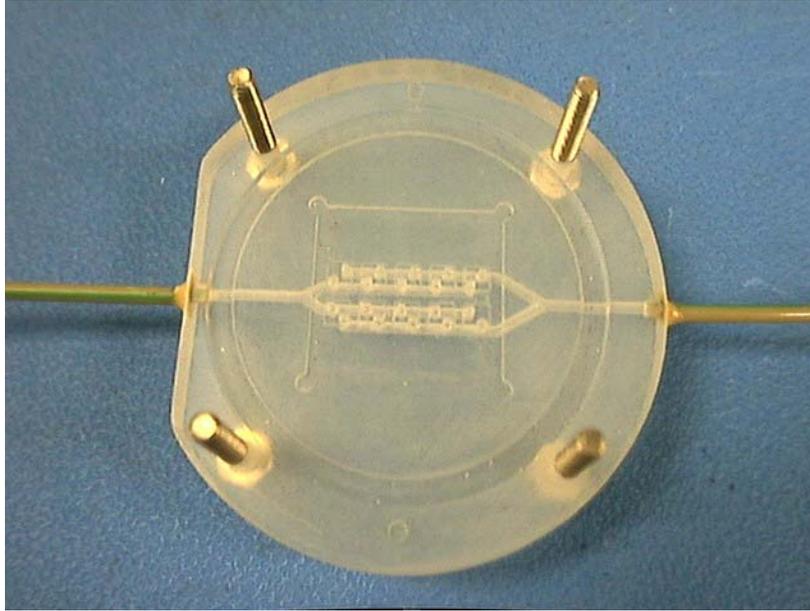


Figure 7: GC fixture showing gas channels

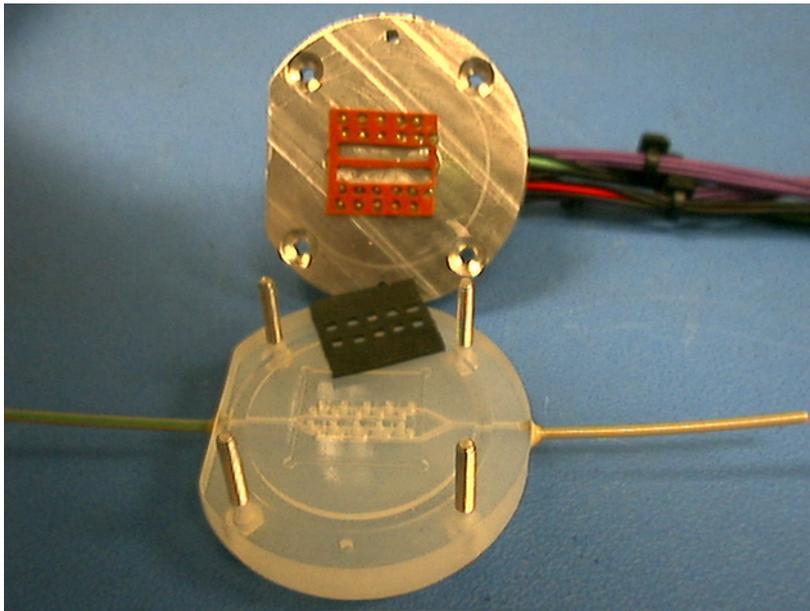


Figure 8: Complete GC fixture with lid

Fig. 9 shows a series of chromatograms of the tripropyl amine peaks desorbed from a 10-element MSA device using the fixture shown above. Due to the characteristics of the new fixture material, temperature was limited to 60°C for these and all subsequent experiments. The pressure was maintained at 5 p.s.i.

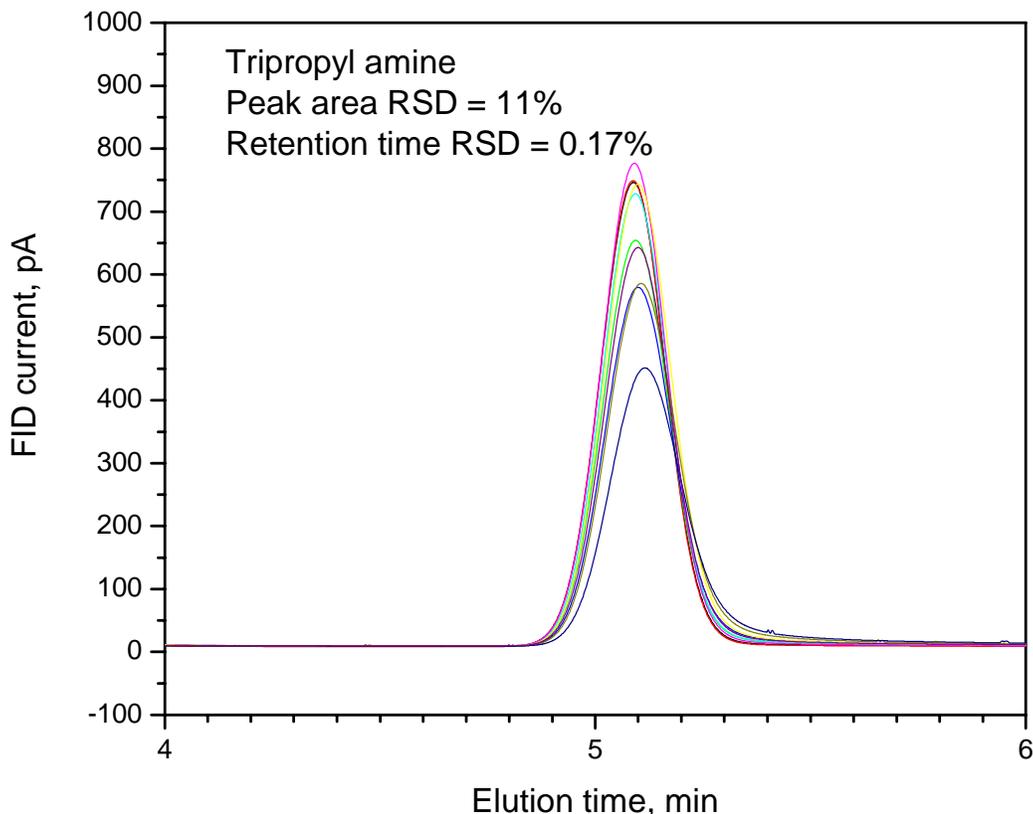


Figure 9: Tripropyl amine peaks using modified GC fixture.

Although there is still a significant variation in the measured peak areas for tripropyl amine desorption using this device (peak area RSD = 11%), the precision is vastly improved compared to the previous results (Fig. 1), where the tripropyl amine peak areas varied by as much as a factor of 9. The relative standard deviation of peak areas for the propene peaks in this data set (not shown) was 7%. While the variation of peak areas is still significant, this precision should be sufficient for useful field calibration of microscale GC instruments. The variation in peak retention times was also significantly reduced using the modified fixture. The standard deviation of the measured tripropyl amine peak retention time for the data displayed in Fig. 1 is 0.14 minutes, while that of the data displayed in Figure 9 is only 0.009 minutes.

It is worthwhile to note that while the variation of peak areas and retention times is improved by careful attention to surface wetting during deposition and by the use of the modified GC fixture, there is still a systematic variation due to position of the desorbing element on the MSA die. This is illustrated in Figures 10 and 11, which

display plots of tripropyl amine peak area and retention time for duplicate desorption runs made using two MSA die in the stereo-lithographically patterned GC fixture.

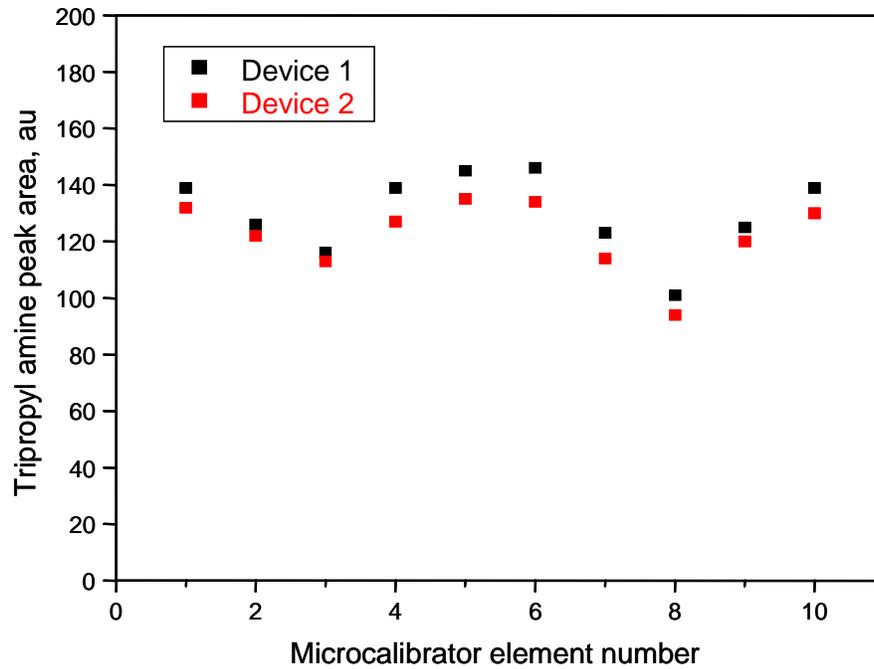


Figure 10: Peak area vs. MSA element number

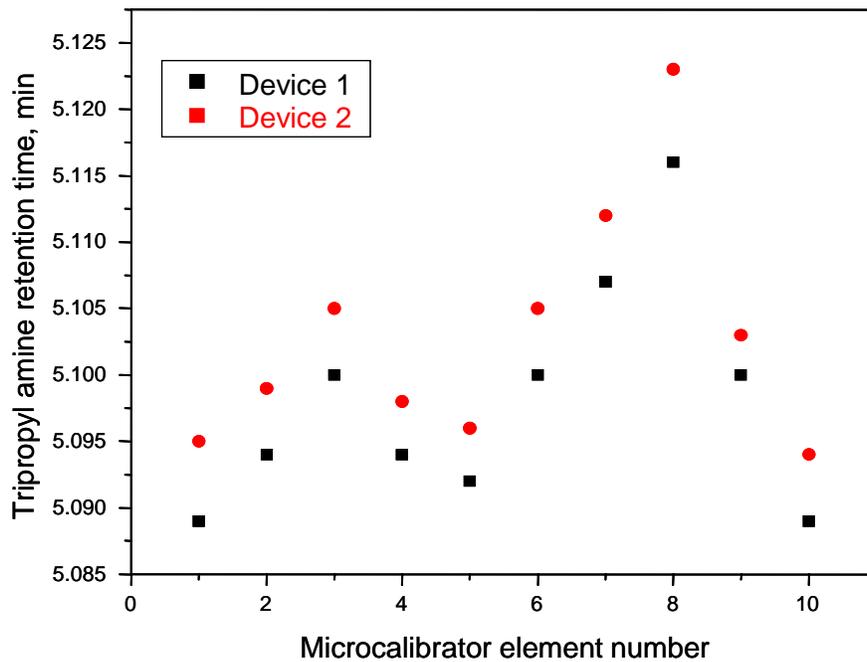


Figure 11: Peak retention time vs. MSA element number

We note that the pattern of peak retention time vs. element number is inversely correlated to that of peak area. The variation in retention time is likely to be due to variations in carrier gas flow velocity through the different elements of the device. Thus, we attribute this effect to slight variations in flow conductance through the different channels of the fixture. Comparing Figures 10 and 11, the largest desorption peaks are observed for those channels with the shortest peak retention times. This is consistent with the hypothesis that the faster carrier gas flows, which sweep the desorbed vapors out of the fixture more quickly, prevent loss of material by absorption into the polymeric fixture and/or elastomeric gasket materials.

### 2.3. Results with single element PC devices.

The multiple-element prototype die designs were based on a single element “microhotplate” preconcentrator (PC) used in Sandia National Laboratories’  $\mu$ ChemLab™ gas analyzer systems. During this study, we used these single-element devices extensively in order to test surface preparation treatments and drop deposition procedures in an attempt to achieve more reproducible deposition of alkyl ammonium salts as calibration reservoir compounds. In addition, we used these devices as substrates to determine the effect of aging (storage of coated devices under ambient conditions) on the precision of desorption peak areas.

Table 2 summarizes a single, representative set of single-element PC desorption data that illustrate the importance of reproducible surface wetting conditions for this application.

**Table 2.** Effect of surface preparation on peak areas

Run number	Propene peak area (au)	Tripropyl amine peak area (au)	Surface preparation
run 1	15.6	51.5	Piranha, HMDS  5 drops of 1% tetrapropyl ammonium hydroxide in water
	15.5	51.4	
	15.3	52.7	
	15.0	50.2	
	14.9	52.1	
<b>mean</b>	<b>15.2</b>	<b>51.6</b>	
<b>stdev:</b>	<b>0.3</b>	<b>1.0</b>	
<b>% stdev</b>	<b>1.9%</b>	<b>1.8%</b>	

Run number	Propene peak area (au)	Tripropyl amine peak area (au)	Surface preparation
run 2	18.3	57.0	Re-used surface with no washing or other prep following run 1
	17.1	53.3	
	3.5	40.5	
	5.3	62.1	
	3.2	39.9	5 drops of 1% tetrapropyl

	5.4	64.1	ammonium hydroxide in water
	6.3	74.6	
	3.6	46.4	
<b>mean</b>	<b>7.8</b>	<b>54.7</b>	
<b>stdev:</b>	<b>6.2</b>	<b>12.2</b>	
<b>% stdev</b>	<b>79.2%</b>	<b>22.2%</b>	

Run number	Propene peak area (au)	Tripropyl amine peak area (au)	Surface preparation
run 3	7.7077	45.425	Re-used surface after washing in HPLC grade water  5 drops of 1% tetrapropyl ammonium hydroxide in water
	7.792	41.316	
	8.0259	41.983	
	7.9821	42.199	
	8.3307	49.683	
	8.1906	49.689	
<b>mean</b>	<b>8.0</b>	<b>45.0</b>	
<b>stdev:</b>	<b>0.2</b>	<b>3.9</b>	
<b>% stdev</b>	<b>2.9%</b>	<b>8.6%</b>	

Run number	Propene peak area (au)	Tripropyl amine peak area (au)	Surface preparation
run 4	91.298	350.3	Re-used surface after washing in HPLC grade water, followed by air drying and HMDS vapor exposure
	99.741	350.76	
	93.518	360.37	
	95.621	350.94	
	83.436	360.83	
<b>mean</b>	<b>92.7</b>	<b>354.6</b>	
<b>stdev:</b>	<b>6.1</b>	<b>5.4</b>	Coated with 50 drops of 1% solution in water
<b>% stdev</b>	<b>6.5%</b>	<b>1.5%</b>	

Referring to Table 2, if the SiN membrane surface is not carefully cleaned and prepared before deposition of the aqueous organic salt solution, variations in surface wetting can severely degrade the reproducibility of the desorbed calibrant compound peak areas.

Conversely, when the surface of the substrate is carefully prepared between repeated coatings, the reproducibility of peak areas desorbed from single PCs is significantly improved. This is illustrated in Table 2, and also in another data set displayed in Fig. 12, which graphically indicates the repeatability of the drop coating method when other factors (surface wetting and gas flow in GC fixtures) are carefully controlled.

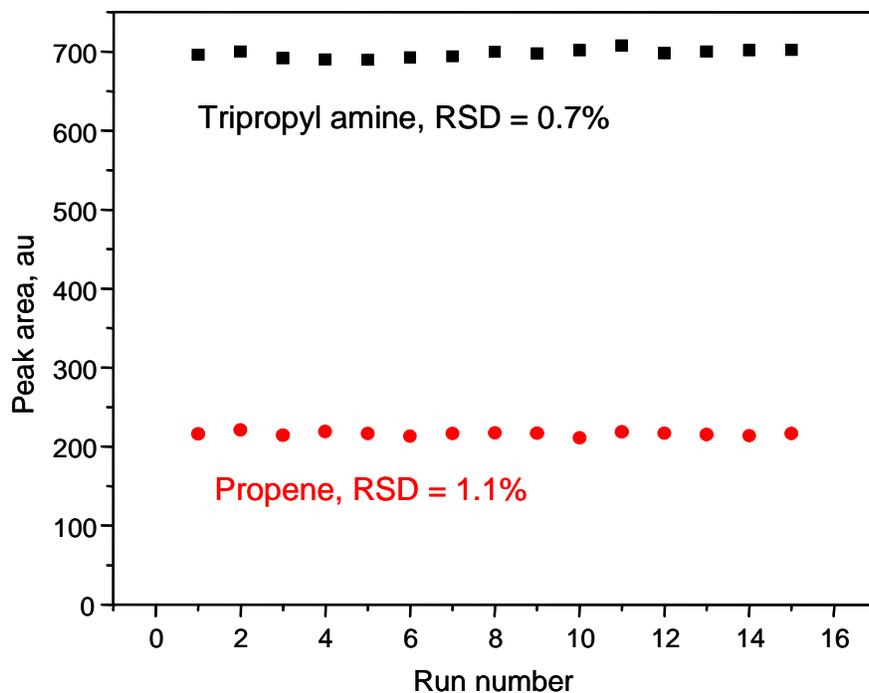


Figure 12: Tripropyl amine and propene peak areas, single PC

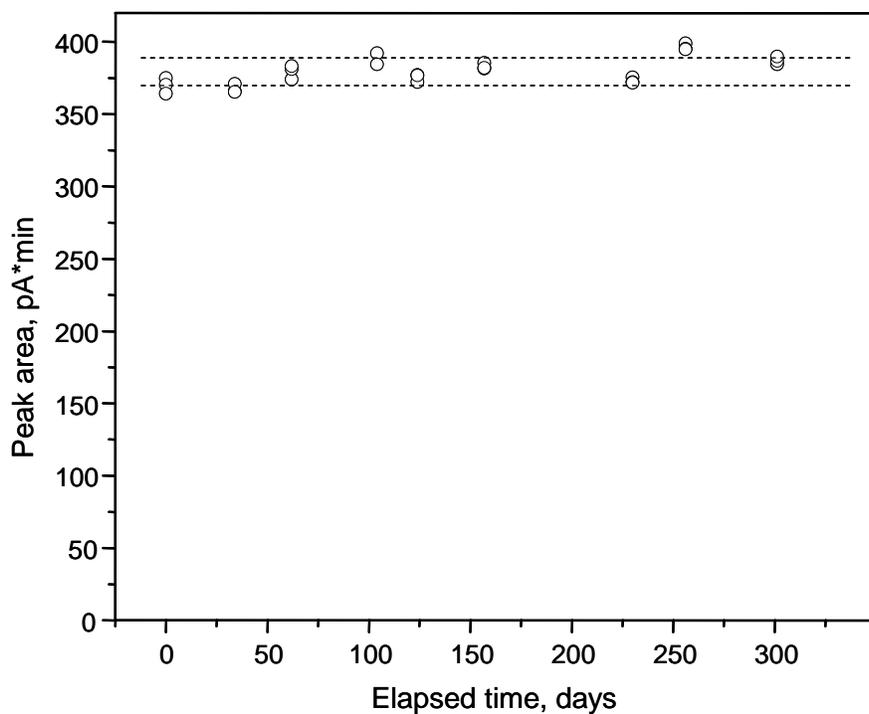


Figure 13: Effect of aging on peak area

The effect of aging of the surface coatings in ambient air on the area of the desorbed tripropyl amine peaks is shown in Fig. 13. A series of single element PCs was coated, and three of these devices were desorbed after a series of aging intervals, at 0, 34, 62, 104, 124, 157, 230, 256, and finally 301 days delay after coating. The dotted lines plotted in Fig. 13 represent plus or minus one standard deviation levels for the data set taken as a whole ( $N = 24$ ). The relative standard deviation of these data is 2.5%, significantly higher than that of the data displayed in Fig. 12 (0.7%), but still less than the 11% RSD for the multielement data displayed in Figures 9 and 10. Therefore, these data indicate that the effect of film aging can be expected to be less than the variation in peak areas due to flow velocity and absorption losses in the GC fixture for the multielement devices. In addition, these devices were coated before a full understanding of the sources of deposition variation were understood.

### 3. Future Experiments

Because the data indicate that the gas flow system contributes a large part of the variability of the system, and because the present test manifolds are too large to incorporate as part of a microfabricated GC analysis instrument, we are continuing



Figure 14: Etched gas flow channels

to investigate the use of more compact and easily assembled designs for the gas flow manifold. The next iteration of the device is based on lithographically defined, KOH-etched flow channels in a Si substrate wafer, which can then be bonded to a substrate containing via holes etched appropriately to access the desorption regions over elements of the MSA die. A photo of the etched channel structure is shown in Fig. 14. Independent channels are etched for connection to inlet and outlet gas streams. We anticipate that the flatness and surface finish of the Si substrate wafer used to produce these channels will allow us to stack the

flow channel substrate, the via-hole substrate, and the MSA die, and allow for adequate gas flow control without using elastomer gaskets between the layers of the stack. The first attempt to assemble a calibrator device based on this design is shown in Fig. 15. We have not yet obtained desorption peak data from coated devices using this design.

During the course of this development project, an alternative approach to producing a microcalibration source has also been pursued [2]. This approach is

based on an etched reservoir containing a mixture of high surface area solid support and a liquid calibrant compound. A narrow channel out of the reservoir allows diffusive leakage of the calibrant, at a rate controlled by the substrate temperature. The vapor is then “refocused” for GC injection by adsorption onto a single-element PC.

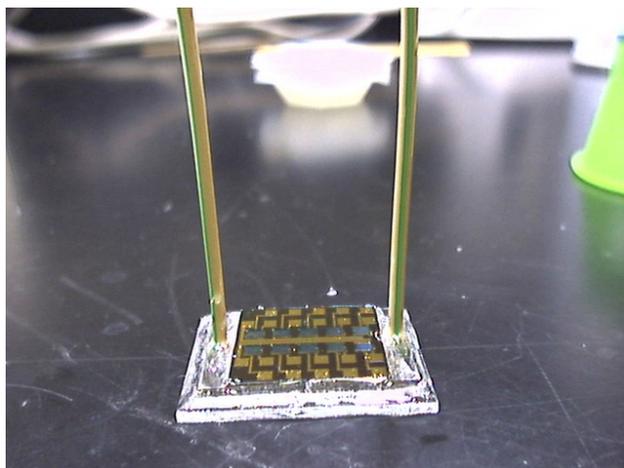


Figure 15: Prototype wafer stack microcalibrator

The latter calibration approach has proved successful in field tests. However, we intend to continue development of the solid-phase aliquot approach described here as a means of producing small volumes of high-pressure hydrogen for use as a GC carrier gas. The use of high-pressure hydrogen carrier should allow for improved chromatographic separation performance by microfabricated GC systems. Hydrogen generation in this

manner should be achievable by the thermal decomposition of solid microaliquots of magnesium borohydride diammonate or other, similar solid borohydrides.

## Conclusions

We have developed a microfabricated chemical vapor calibration source based on an array of SiN membranes with patterned resistive heater elements on a Si substrate. Thermal disproportionation of solid tetraalkyl ammonium salts deposited on these heating elements results in the reproducible production of alkenes and trialkyl amines. The production of two compounds with different retention indices is an advantage for calibration of gas chromatography data. We are extending this idea to the on-demand production of low volumes of high-pressure hydrogen, for use as a carrier gas in advanced microfabricated GC systems.

## References

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