

# Microcalibrator Chip

## Overview

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. To address these needs, Sandia has developed a microfabricated source array for controlled release of pairs of marker compounds into the analytical streams of microsensor systems to obtain calibrations of analyte separation (when appropriate) and mass response of the sensor.

Sandia has developed small, potentially low-cost chemical sensors and sensor systems for Nonproliferation and Materials Control applications and for monitoring of chemical weapons threats. The most advanced of these systems is the MicroChemLab. Our experience with DOE sponsored nonproliferation programs and with the current accelerated needs of Homeland Defense programs clearly indicate a need for reliable, low cost, flexible, and potentially autonomous systems for field calibration and performance verification of such chemical sensors. These sensors can also be adapted for human health monitoring, detecting marker compounds or drug metabolites in human breath, urine, and blood.

Field application of chemical sensors to these challenges requires that all necessary components for sensor calibration and performance verification be integrated within the sensor package. We therefore developed a prototype chemical delivery source, based on arrays of individually addressable, microfabricated, thermal elements. This approach has the potential to provide a small, rugged, lightweight, readily manufacturable, and inexpensive source capable of delivering appropriate masses of volatile organic or other compounds for sensor calibrations in the field.

## Microcalibrator Hardware

The microcalibration array is fabricated in silicon using a deep reactive ionization etch (DRIE) process or wet KOH etching. A 1-micron thick silicon nitride layer sits on top of the 400 micron wafer and serves as an etch stop and as the thermally isolating micro-hotplate membranes. A number of solid-phase, thermally activated chemistries can be placed on the micro-hotplate membranes using drop-coating, spray coating, or other methods. Producing in quantity, the microcalibration source array is envisioned as an extremely low-cost consumable, with replacement required after the contents of the solid-phase reservoirs are exhausted.

The first picture below shows a prototype device with a 2x5 array of elements. The dimensions of the die are 1.6 x 1.6 cm, and each element measures 2.2 mm on a side. A device of 1 square mm elements has also been fabricated. Each element incorporates a resistive metal heater and

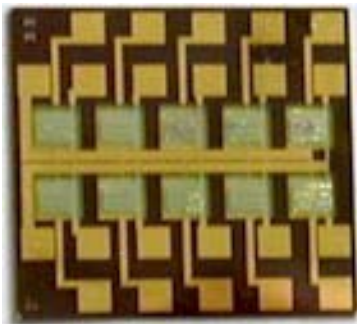
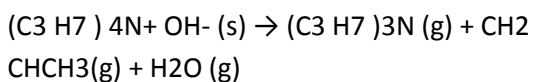


Figure 1. 2x5 prototype array.

a separate thermistor for independent temperature measurement and feedback control, if desired. Input bond pads are located along the outside edges of the device, with common ground pads for the heater and measurement circuits. When individually energized with a predetermined voltage, each hotplate element ramps to 250° C within 20 msec.

With application to gas chromatography in mind, we determined the best calibration compounds for this system. Thermal decomposition of tetraalkyl ammonium hydroxide salts form the corresponding trialkyl amines and alkenes in the gas phase. These products are useful calibrant compounds for nonproliferation and industrial gas monitoring applications, respectively. They also have several advantages as solid-phase calibrant gas-generating sources. The salts are easily deposited from aqueous or mixed water-alcohol solutions, and have long-term stability at environmental temperatures. The alcohol or water solvents can be rapidly air-dried. Rapid heating of the micro-hotplate causes complete thermal disproportionation of the solid salt, resulting in controlled generation of two calibration compounds in the gas phase. An example system of tetrapropyl ammonium hydroxide is shown here:



For gas chromatography, the propene acts as a fast-eluting marker while the tripropyl amine acts as a slow-eluting marker. This controlled reaction 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. The compounds also provide a mass calibration of the sensor.

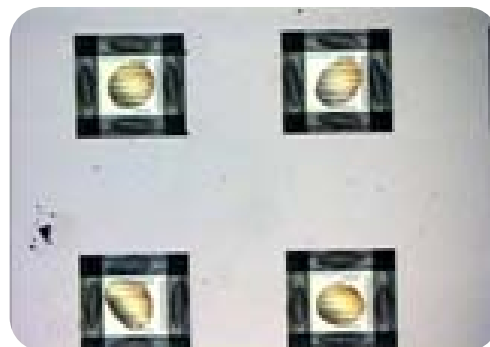


Figure 2. Tetrapropyl ammonium hydroxide.

## Experimental Results

To characterize the performance of the microcalibrators, each device was secured to a silicon gas manifold through a stainless steel gasket. The manifold provided carrier gas from a single inlet port to each array element individually, then merged the streams to a single outlet without passing calibration compounds over other elements. While epoxy held this stack together for testing purposes, the design is amenable to all-silicon fabrication.

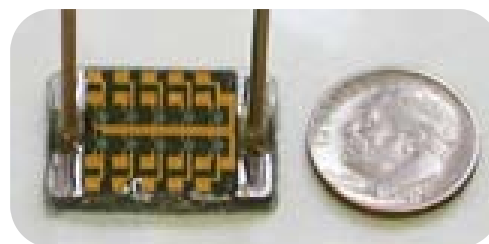
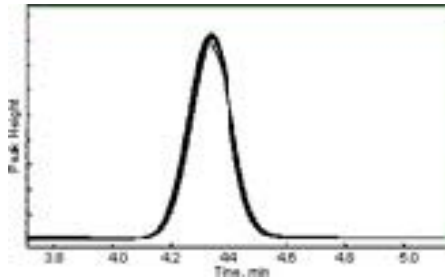


Figure 3. 2x5 array on device manifold.

Chromatography peaks from all ten elements of a single device are shown in third picture on the left. The relative standard deviations are 0.5% for peak area (mass), 1.0% for peak height, and 0.1% for retention time.



**Figure 4.** Chromatographic peaks.

The retention times of several trialkylamines under typical chromatographic conditions are shown in Table 1. The appropriate one(s) can be selected based on retention time similarity to the target analytes of the pressing application.

**Table 1.** GC retention times of tetraalkyl ammonium hydroxide decomposition products.

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

## Other Applications

Several other applications can take advantage of the multi-element hotplate format. Extending this capability, varying chemicals can be placed on the elements for different applications. Controlled dispensing of derivatization reagents in microaliquots can be used to advantageously react with specific analytes, extending the analysis capability of chemical analysis systems to otherwise inaccessible targets. Elements on the array can also be coated with borohydrides, which release hydrogen gas upon heating. Use for on-demand hydrogen generation is currently under development as a source of high-pressure, low viscosity GC carrier gas for Sandia's next-generation microfabricated gas-phase chemical analysis systems.

For additional information or questions, please email us at [MGA@sandia.gov](mailto:MGA@sandia.gov).