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Biomimetic Air Sampling for Detection of Low Concentrations of Molecules and Bioagents LDRD 52744 Final Report

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Biomimetic Air Sampling for Detection of Low Concentrations of Molecules and Bioagents LDRD 52744 Final Report

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Abstract

Present methods of air sampling for low concentrations of chemicals like explosives and bioagents involve noisy and power hungry collectors with mechanical parts for moving large volumes of air. However there are biological systems that are capable of detecting very low concentrations of molecules with no mechanical moving parts. An example is the silkworm moth antenna which is a highly branched structure where each of 100 branches contains about 200 sensory "hairs" which have dimensions of 2 microns wide by 100 microns long. The hairs contain about 3000 pores which is where the gas phase molecules enter the aqueous (lymph) phase for detection. Simulations of diffusion of molecules indicate that this "forest" of hairs is "designed" to maximize the extraction of the vapor phase molecules. Since typical molecules lose about 4 decades in diffusion constant upon entering the liquid phase, it is important to allow air diffusion to bring the molecule as close to the "sensor" as possible. The moth acts on concentrations as low as 1000 molecules per cubic cm. (one part in 1e16). A 3-D collection system of these dimensions could be fabricated by micromachining techniques available at Sandia. This LDRD addresses the issues involved with extracting molecules from air onto micromachined structures and then delivering those molecules to microsensors for detection.

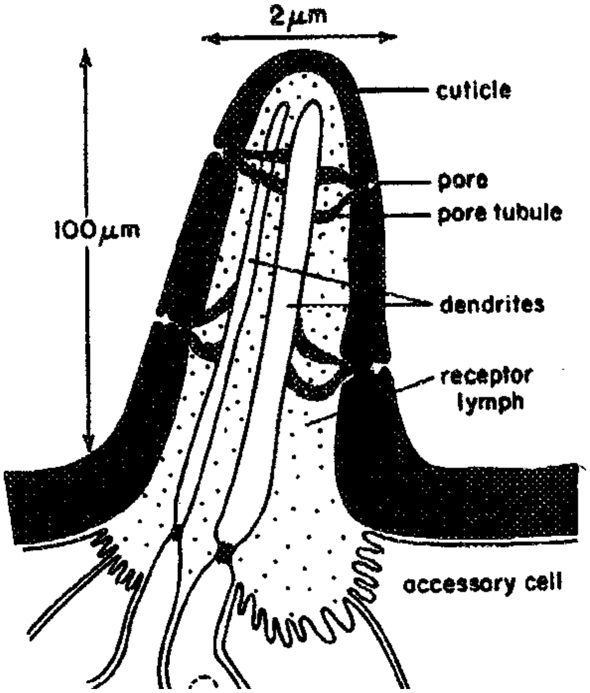
Contents

Acronyms and Abbreviations

DRIE	deep reactive ion etch
LDRD	Laboratory-Directed Research and Development Program
mm	millimeter
ppm	Parts per million
ppb	parts per billion
Si	Silicon
V	Volt
VOC	volatile organic chemical

Introduction

A significant amount of technical effort has recently been expended on fabricating and testing single molecule detectors. For sensors with electrical read-out, protein based ion channels have been deployed in artificial cell membranes like lipid bilayers. Optical microsystems use fluorescent tags that indicate occupation of a site by single analyte molecules. However, in order for these detectors to be useful in the real world for detecting very low concentrations of specific analytes, the molecules must find their way to the detector. This is not always easy, because the detector element, like an ion channel, has a receptor for the analyte molecule that is only 10 nm or less in diameter. Since the ion channels must have aqueous, ionic environments on both sides, the analyte molecule's diffusion constant will be less than 1e-5 cm^2/sec. Experiments with these systems are typically made with high concentrations of analyte, milli to micro Molar. To be useful in many applications, it is desired to detect pico or lower Molar concentrations in the liquid. Also in many applications, the analyte molecule to be detected is in the air, and a transfer from air to liquid phase is required. Present methods of air sampling for low concentrations of chemicals like explosives and bioagents involve noisy and power hungry collectors with mechanical parts for moving large volumes of air (think DustBuster, see for example, Ref. [1]). The sampler captures minor vapor constituents from the air by passing the air in a swirling, highly turbulent motion through a wetted cylindrical tube at a rate of 600–700 L/min. Typically, the collection efficiency for the alkaloid vapors was 40%–60.

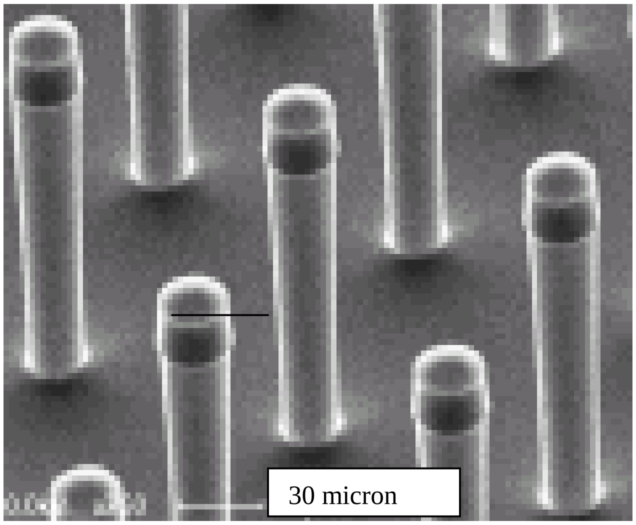


However there are biological systems that are capable of detecting very low concentrations of molecules with no mechanical moving parts. An example is the silkworm moth antenna which is a highly branched structure where each of 100 branches contains about 200 sensory "hairs" which have dimensions of 2 microns wide by 100 microns long. A diagram of one hair is given in the Figure above. The hairs contain about 3000 pores which is where the gas phase molecules enter the aqueous (lymph) phase for detection. Simulations of diffusion of molecules indicate that this "forest" of hairs is "designed" to maximize the extraction of the vapor phase molecules. Since typical molecules lose about 4 decades in diffusion constant upon entering the liquid phase, it is important to allow air diffusion to bring the molecule as close to the "sensor" as possible. The moth acts on concentrations as low as 1000 molecules per cubic cm. (one part in

1e16). The above Fig. 1 and Monte Carlo calculations of analyte molecules interacting with the hairs can be found in Ref. [2].

In Ref. [2], Futrelle uses a Monte Carlo analysis of convective/diffusion motion of the analyte molecule when it enters a “forest” of posts that simulate the moth antenna. He was attempting to explain experimental results which showed how very efficient the detection process is in the bio system. People had incorrectly assumed that the analyte molecules were captured on the surface of the hair and diffused until they found a pore. But Futrelle showed this cannot work because of the analyte particle sticks to the surface, its lateral diffusion constant is decades too slow to explain the effect. The Monte Carlo simulation shows that if the molecules don’t stick, but are reflected, the same molecule can hit a hair up to 250 times in a very short time because of the high velocity of the molecules in the gas phase. Thus the efficiency can be explained by the fact that the pores can get direct hits from almost all the analyte molecules in a very dilute stream (like 1000 per cm^3) even though the pore areas are a very small fraction of the total surface area of the hair. These same diffusion arguments can used to explained how signaling molecules can find receptors on biological cell surfaces when those receptors occupy only a small fraction of the cell surface area. An analysis can be found in Ref [3] This effect has also been exploited in electrochemistry where an array of micro-electrodes can give a higher electrochemical current than a monolithic electrode with the same surface area as the sum of the microelectrodes. Studies of the fluid dynamics of chemical detection in these small structures is ongoing, as seen in Refs. 4 and 5.

In this project we considered conceptual designs of various 3-D micromachined structures like posts and channels, to see if a practical means could be found for both collecting vapor molecules and delivering them to a sensor structure. Fig. 2 shows how Sandia’s Deep Reactive Ion Etch (DRIE) process can be used to make very high aspect ratio structures in Si. These can be of the dimensions of the hairs in the moth antenna. It is also possible to make many other high aspect ratio geometries. It can also been seen that different materials can be introduced in layers which gives us an opportunity to put sensor sites on the walls of the sampler posts through selective etching.



It may turn out that placing the sensor areas on the walls is too hard and it may be productive to coat the walls with absorbant films to create a preconcentrator. The entire structure could be heated to desorb analyte molecules and focus them on a separate sensor structure. This is the path we followed for some preliminary experiments on microstuructures that combine a preconcentrator with a chemiresistor sensor.

Background on the State of the Art of Trace Detection of Chemicals in Air

The chemical analysis industry is very large and important to commerce and health. Trace detection for health protection is a large subset of the industry, often grouped with industrial hygiene. The author recently had the opportunity to serve on a panel for NASA to evaluate the present and future prospects for improved trace gas analysis in the International Space Station (ISS). Although the presentations of the vendors and the deliberations of the panel are proprietary to NASA, some broad conclusions can be made from using the published findings of the previous panel in 2000 (Ref. [6]). The specifications for the trace gas analysis push the state of the art for all present instrumentation. In addition the size, weight and power restrictions, along with ruggedness and reliability requirements mean that no commercial laboratory sized instrument will satisfy the requirements. The instruments tested and reported in the 2001 report are very similar to those proposed to the 2003 panel, including the one already in the ISS; there have been no dramatic breakthroughs in technology. However there are constant improvements in reducing the size and power requirements of these basic instruments.

The “gold standard” for trace gas analysis is the large laboratory model of the combined Gas Chromatograph and Mass Spectrometer (GC-MS). There is often a preconcentrator on some type in front of the GC, which then separates many of the species in a mixture and introduces them, spread in time, to the front end of the MS. The MS further separates and identifies molecular fragments. The requirements call for identifying ppb to ppm levels of molecules in a mixture of perhaps 30 molecules of interest. This is also in a background of O2, N2 and variable CO2. The laboratory GC-MS can do most of the compounds, although the sub-ppb levels of formaldehyde are difficult for everyone. In the past the miniaturized and ruggedized versions of the GC-MS have not won out over the combination of a GC with an ion-mobility spectrometer (IMS). That instrument is now in the ISS and is described in the 2001 report. The MS suffers from requiring a very high quality vacuum (1e-8 Torr or better), which means turbopumps which are power hungry and not so reliable.

The electronic noses being worked on at Sandia and many other labs do not come close to satisfying the NASA requirements for selectivity and sensitivity, although they far surpass the other instruments in size, cost and power requirements. The e-noses fail because they can’t distinguish a low concentration of one molecule in a mixture of 30 other molecules without doing some kind of preconcentration and pre-separation.

In the biological chemical sensing systems, you also do not get the kind of quantitation that is required by NASA. The biological olfactory systems often serve very specific purposes like the pheromone detection of the moths discussed above. Or there may be complex pattern recognition tasks like dogs tracking and identifying specific persons. Tests have shown that the vapor signature of a person will contain 1000’s of volatile organic chemicals (VOCs) and no man-made instrument has been able to perform the pattern recognition of the chemical signals to identify individual persons. The biological systems apparently achieve this performance by the combination of highly efficient air sampling and single molecule chemical detectors. A large number of detectors with different selectivity are required to generate the patterns. System requirements like NASA's exist because the data base for health effects of chemicals on humans is given in terms of exposures to certain concentrations of a chemical and exposure time. Thus the time evolution of exposure to each chemical in the data base must be known to decide if the air is too dangerous to breath for a given length of time.

Biological systems work more in a "smoke alarm" mode where action is taken when, for example, you smell smoke and run away, or don't eat meat because of the way it smells. Industrial hygienists are not ready to abandon their exposure data base for electronic noses that warn of dangerous atmospheres by pattern recognition. However there will be applications for electronic noses in areas like first responders where an alarm mode will be useful in directing action, and specific cases like chemical warfare agent detectors where it may be important to detect very low concentrations of specific molecules.

Results

For this LDRD we studied the structures that insects, particularly moths, use to gather volatile organic chemicals (VOCs) from the air and detect them. The chemical sensors themselves are ion channels in the walls of olfactory nerve cells that are very small in dimension: the individual ion channels have capture areas of only about 10 nm in diameter. However, the structures that extract the VOCs from the air are roughly 2 microns wide and 100 microns long. To begin our simulation of these structures with micromachined components, we designed a three dimensional structure which places a micromachined hot plate with absorbent material on it in close proximity to a chemiresistor which is formed on a planar, photolithographically defined set of electrodes. A more detailed description of the preconcentrator and the chemiresistors can be found in our recent journal article appended to this report. Figs. 1 and 2 in the article show photographs of both the mounted preconcentrator and the chemiresistor array. The absorber on the hotplate has dimensions of 0.04 cm2 with a thickness of about 50 microns. The individual absorber particles are made from commercial Carboxen 1000 and are ground to dimensions of about 25-50 microns. The chemiresistor electrodes are 50 microns apart and the chemiresistor material is about 1 micron thick. The 3-D structure allows the absorber particles to approach within about 1 mm of the chemiresistor material. The air sampling is performed by passing air containing a VOC (xylene in our experiments) across the absorber material for specified lengths of time. The absorbed xylene is then released in a very fast heat pulse provided to the hotplate. The heat driven diffusion of the plume of xylene produces a pulse signal on the chemiresistor, showing that the plume of chemical has been detected. By varying the flow rate of the chemical plume across the absorber material, we showed how the flow rate affects the number of xylene molecules that are absorbed in a given time. By using this form of preconcentration, we were able to enhance the sensitivity of our system by about a factor of 100 over the chemiresistor alone. In future studies we hope to show that by micromachining posts of different dimension and spacing and coating them with the absorber particles we can mimic VOC extraction capabilities of the moth antenna. These natural designs have been shown by fluid flow tests to be highly efficient in extracting VOCs from air.

Conclusions

The insects not only have excellent air sampling efficiency, but the chemical sensors that the molecules are delivered to are capable of detecting almost all the molecules reaching them. The chemiresistors that we used in our air sampling studies are much less sensitive and require concentrations in the ppm level for a good signal to noise. This is compared to the moth detection level of about 1 part in 1e16. In this program we also looked at how micromachined devices might be used to mimic single molecule detection. Jeb Flemming of the CSRL and Jim Fleming of the MDL have been devising ways to extremely small pores in dielectric films based in a planar silicon support structure. In future programs we hope to be able to use these artificial pores as single molecule detectors similar to ion channels. If we are able to make them work, it will be relatively easy to create arrays of these single molecule detectors which then can be coupled to the micromachined air sampling arrays.

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Appendix A

This appendix contains the manuscript entitled “Enhanced Detection of m-Xylene Using a Preconcentrator with a Chemiresistor Sensor”, C.E. Davis , C.K. Ho, R.C. Hughes, and M.L. Thomas, submitted to Sensors and Actuators 6/2003

Enhanced Detection of m-Xylene Using a Preconcentrator with a Chemiresistor Sensor

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Abstract

Chemiresistor chemical microsensors are being investigated as a tool for environmental monitoring. These devices can provide real-time in-situ chemical concentration data for solvent-contaminated sites of interest. Detection limits of an unaided chemiresistor, however, are typically in the range of 1/1000th of the saturated vapor of a given analyte, which may not be sufficient for chemicals with high vapor pressures and low desired detection limits. Tests were conducted in this study to determine the response of a chemiresistor sensor to m-xylene with and with preconcentration. Results showed that by adding a microfabricated preconcentrator to a chemiresistor sensor, detection limits of m-xylene were decreased by more than two orders of magnitude, from 13.5 ppm to 61.8 ppb, without significantly increasing the complexity of the sensing system.

Keywords: chemiresistor, preconcentrator, m-xylene, limit of detection, environmental monitoring

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Introduction and Background

Chemically contaminated sites containing volatile organic compounds (VOCs) exist in virtually every major city throughout the United States. Many of these sites require monitoring to characterize the extent of contamination and to identify changes in the contamination zone over time. In addition, periodic monitoring may be required at these sites to gauge the performance of remediation systems that are intended to prevent the spreading of contaminants to key environmental resources (e.g., groundwater). Traditional monitoring methods rely on manual "grab samples" of soil, gas, and/or water from the site, which are then taken to an off-site laboratory for analysis. These methods can be extremely costly and time consuming. For example, Looney and Falta [1] report that the Department of Energy Savannah River Site requires manual collection of nearly 40,000 groundwater samples per year, which can cost between $100 to $1,000 per sample for off-site analysis. In addition, the integrity of the sample can be compromised during collection, transport, and storage. Clearly, a need exists for reliable, inexpensive, continuous, in-situ analyses using robust sensors that can be remotely operated.

Although a number of chemical sensors are commercially available for field measurements of chemical species (e.g., portable gas chromatographs, surface-wave acoustic sensors, optical instruments, etc.), few have been adapted for use in geologic environments for long-term monitoring or remediation applications. One type of chemical sensor, the chemiresistor, has potential for use in environmental monitoring [2]. Chemiresistors are chemical microsensors that can detect the presence of volatile organic compounds and water in the vapor phase. Our studies have focused on chemiresistors comprised of carbon-particle impregnated insulating polymer films deposited across a set of interdigitated metal electrodes on a silicon substrate. Swelling of the polymeric material due to the presence of an analyte in the vapor phase allows for simple analyte detection by noting the change in electrical resistance measured across the polymer film. Although the polymeric film is insulating, electrical current can be carried through the electrically conductive carbon particles. As the polymer film swells due to chemical exposure, the intra-particle spacing increases, causing a subsequent increase in electrical resistance. Because the polymer swelling process is reversible, removal of the analyte will allow the system to return to approximately the original state, and an individual chemiresistor can be used over and over, or in continuous operation for long-term monitoring.

The chemiresistor is especially well suited for environmental monitoring, not only because it can be reused or used continuously, but also because the fundamental operation of the sensor system is quite simple. Electrical resistance measurements are accomplished with simple DC circuitry, and no moving parts (e.g., pumps, valves) are needed for passive monitoring of environmental conditions.

Our previous work with the chemiresistor in environmental sensing applications has allowed us to demonstrate the sensor's strengths while also protecting it from some potential weaknesses. We have developed a sealed waterproof stainless-steel probe housing with a GORE-TEX® window that allows passage of chemical vapors, while protecting the polymer surface and electrical contacts from undesired exposure to liquid water [2]. Inclusion of a temperature sensor and resistive heater bars on the sensor silicon substrate allow the user to elevate the substrate temperature, if necessary, to prevent condensation of ambient water vapor on the sensor surface.

Despite the apparent usefulness of the chemiresistor for many environmental applications, some concern has been expressed over the sensor's lack of sensitivity for particular analytes in low concentrations. In general, we estimate that a chemiresistor polymer optimally paired with a given analyte of interest can detect approximately 1/1000th (0.1%) of the analyte's saturated vapor pressure at a given temperature. For compounds with high vapor pressures and low desired detection limits, this may not result in favorable detection capabilities for the chemiresistor. For example, carbon tetrachloride, with a saturated vapor pressure of 91.3 mm Hg (12.17 kPa) at 20°C, would be detectable by a chemiresistor at approximately 120 ppm (12.17 Pa); however, the Occupational Safety and Health Administration has a proposed time-weighted average exposure limit for carbon tetrachloride at 2 ppm. Clearly, an improvement in detection limits would be necessary for the chemiresistor to be useful in this application.

To address the issue, work has been performed on coupling a microfabricated planar preconcentrator with the chemiresistor [3]. The preconcentrator consists of a thin film of absorbent material deposited on a resistive wire trace. The absorbent film allows for reversible accumulation of chemical vapors over a period of time until heated by sending current through the wire trace. When the absorbent material is heated to ~200ºC, the absorbed VOCs are thermally desorbed and can be directed as a concentrated plume to a detection system. Thus, the preconcentrator serves as a simple method for collecting and concentrating VOCs in a sensing system for a prescribed period of time. The combination of the sensor response signal and knowledge of the specified integration period allows derivation of an average analyte concentration during the VOC accumulation period. In previous work [3], enhanced detection was demonstrated through the use of the hybrid chemiresistor/preconcentrator, but design issues still needed to be addressed to optimize performance of the hybrid. In this report, we develop a key design improvement made to the hybrid device and demonstrate the signal amplification and detection-limit improvement of a chemiresistor sensor through the use of a preconcentrator to detect m-xylene, an environmental contaminant of interest.

Experimental Approach

Controlled chemical exposures are performed through the use of custom gas cylinders of m-xylene with analytically verified concentrations or gas-washing bottles filled with liquid m-xylene. A range of concentrations are generated by diluting and controlling gas flows through a series of valves (SMC solenoid valve NVZ110 and Nupro/Swagelok stainless bellows valve SS-4BK-1C) and mass flow controllers (Brooks Instrument 5850E mass flow controllers) operated through a LabVIEW interface on a Macintosh computer. Analyte concentration levels are confirmed through the use of a RAE Systems ToxiRAE or ppbRAE photo-ionization detector.

Chemiresistor sensors used in this report are similar to those used in our previous work [3], based on a four-chemiresistor array on a single silicon substrate with integrated onchip platinum-wire temperature sensor and resistive heater bars for temperature control. Arrays are packaged in a 16-pin dual-inline package (DIP) for ease of electrical connections. Chemiresistor polymer solution preparation involves dissolving the polymer in a solvent and adding 40% by weight of 20-30 nm graphitized carbon particles. The polymer solution is subjected to sonication from a point ultrasonic source to enhance ink uniformity, using 15 half-second pulses separated by one-second rest periods. Solution deposition on the sensor silicon substrate is performed with an Asymtek Century Series C-708 automated fluid dispensing system.

Preconcentrator devices are fabricated on a Bosch-etched silicon wafer, with platinum-wire heating elements supported by a thin silicon nitride membrane. A solid analyte-absorbent phase is dispersed in a thin dissolved polymer film used strictly for phase adhesion to the substrate. Individual preconcentrator substrates are also packaged in a 16-pin DIP for ease of electrical connections.

The use of two 16-pin DIPs to separately package the chemiresistor and the preconcentrator is a departure from previous work, where both devices were packaged within a single 32-pin DIP, as shown in Figure 1 and discussed in previous reports [3,4]. Results from this work clearly showed the feasibility and the advantages of using the devices together in a small sensor system. However, as effectiveness of the sensor is directly impacted by the proximity of the analyte source to the sensor itself, we hypothesized that detection limits could be additionally lowered by reducing the distance from the preconcentrator to the sensor. Rather than working with a lateral diffusion distance from the two planar devices, we place the two 16-pin DIPs in a face-to-face orientation to allow only a short vertical distance between the chemiresistor and the preconcentrator. Figure 2 shows a photograph of the custom housing designed for mating the two 16-pin DIPs in the lab.

Chemiresistor signals are monitored using simple two-wire resistance measurements taken by a Hewlett Packard 34970A digital multimeter, and results are logged through the LabVIEW program. Voltage pulses that are applied to heat the preconcentrator are controlled through manual triggering of a Systron Donner Model PLS 50-1 precision power supply.

Results and Discussion

Our work to date on this study has focused on the detection of m-xylene (an aromatic hydrocarbon found in gasoline) as a representative environmental contaminant of interest. We selected poly(ethylene-vinyl acetate) (PEVA) as our chemiresistor polymer, due to past experience with the responsive qualities of PEVA to m-xylene exposures [5]. Commercially available preconcentrator phases were then considered for use in the study based on temperatures of absorption and desorption that would be consistent with environmental monitoring scenarios for analyte loading (~30°C under elevated temperature conditions to prevent moisture condensation on the sensor) and the typical temperature attained by the preconcentrator for analyte thermal desorption (200°C in less than 1 millisecond, due to the small thermal mass of the silicon nitride membrane on the hotplate).

Selection of Preconcentrator Phases

From our initial screening, five preconcentrator phases were identified for further study: Carbosieve, Carbotrap, Carboxen 569, Carboxen 1000, and Tenax GR. Each phase was prepared on an individual preconcentrator device and exposed to a flowing stream of 0.2% saturated vapor pressure of m-xylene (~21 ppm) for a five-minute period. Subsequent to loading the preconcentrator phase with m-xylene, the devices were mated face-to-face with the chemiresistor using the custom housing, and pulsed with five volts for five seconds. The magnitude of response of the chemiresistor sensor to all five phases, represented as an increase in chemiresistor resistance relative to the initial baseline resistance ($\Delta R/R_b$, %), is shown in Figure 3. As clearly shown, the Carboxen 1000 phase outperforms all other preconcentrator phases for preconcentration of m-xylene, with an average $\Delta R/R_b$ of 143%, more than five-times the signal provided by any other preconcentration phase. Carboxen 1000 was therefore selected for continued performance assessment.

Enhancement of Chemiresistor Detection Limits

In order to assess the performance improvement provided by a preconcentrator, a study of the detection limit for the unaided chemiresistor sensor was performed. As mentioned previously, we had predicted the capability of chemiresistors to detect an analyte to be as low as 0.1% of the saturated vapor pressure. As shown in Figure 4, a PEVA chemiresistor appears to be able to detect the m-xylene vapor at 5 ppm. However, as seen in Figure 4, analyte detection through the use of an unaided chemiresistor requires the ability to discriminate a detection signal from the background noise of the sensor. The noise threshold of the sensor was estimated to be equal to three times the standard deviation (σ_{Rb}) of the sensor response during quiescent, unexposed (no chemical), ambient conditions. This value was then divided by the average baseline resistance ($R_{b,avg}$) during the quiescent period to yield the relative change in resistance ($3\sigma_{Rb}/R_{b,avg}$) that corresponds to a minimum detection limit above the noise threshold. For the PEVA chemiresistor used in these experiments, $3\sigma_{Rb}/R_{b,avg} = 0.249\%$. The polynomial fit to calibration data shown in Figure 5 expressing m-xylene concentration as a function of the $\Delta R/R_b$ over a range of concentrations from 4.9 ppm to 587 ppm (with an R-squared value of 0.9983), allows determination of an unequivocal limit of detection of 13.5 ppm (9.3 ppm at two standard deviations above the mean; 5.0 ppm at one standard deviation above the mean) (Figure 6). This detection limit of 13.5 ppm corresponds to slightly less than 0.12% of the saturated vapor pressure of m-xylene (11,600 ppm under our typical laboratory conditions).

To assess the improvement in detection limits provided by preconcentration, the Carboxen 1000 preconcentrator was exposed to a series of low concentration m-xylene streams, with preconcentration capability again measured by the response of the PEVA chemiresistor in the configuration shown in Figure 2. When using the chemiresistor to detect extremely low concentrations of m-xylene through the assistance of a preconcentrator, as in this case, the thermal expansion of the PEVA polymer due to the heating of the preconcentrator device must be taken into consideration to avoid confusion with swelling caused by the presence of the analyte. At the very low concentrations involved in a detection limit study, this is especially important, as the temperature response of the chemiresistor begins to be on the order of the analyte response of the chemiresistor. The necessary correction is accomplished by subtracting the response of the chemiresistor to an average blank heat pulse (no absorbed analyte) from the response of the chemiresistor to a corresponding analyte-loaded pulse. Both the analyte-loaded pulse and the blank heat pulse are calculated as individual $\Delta R/R_b$ values, each with its respective baseline resistance value (to keep consistent with changes in ambient conditions that can impact the baseline), and simple subtraction of one value from the other correctly accounts for the temperature rise associated with the heat pulse.

Applying similar logic to that previously used on the unaided chemiresistor, a detection limit was conceptually defined as a sensor signal that can be differentiated above the signal noise, quantitatively seen as a signal greater than or equal to three standard deviations above the mean noise level. However, in this instance, the sensor signal, an analyte-loaded pulse, must be differentiated from the blank heat pulses, so the mean and standard deviation for the limit of detection are in reference to the set of blank heat pulse $\Delta R/R_b$ values, and not to simple resistance values. As temperature correction must still be applied to remove the influence of the heat pulse, the sensor response corresponding to the limit of detection is calculated as the three standard deviations above the mean blank heat pulse, corrected by the mean blank heat pulse. With cancellation, this simply provides:

$$\left[\left(\frac{\Delta R}{R_b}\right)_{\text{avg heat pulse}} + 3\sigma_{\text{avg heat pulse}}\right] - \left(\frac{\Delta R}{R_b}\right)_{\text{avg heat pulse}} = 3\sigma_{\text{avg heat pulse}} \qquad (1)$$

For the combination of the Carboxen 1000 preconcentrator and the PEVA-40-C chemiresistor, $3\sigma_{\text{avg heat pulse}} = 0.153\%$. Using the polynomial fit to data shown in Figure 7 for preconcentrator exposures over a range of 0 to 2500 ppb (with an R-squared value of 0.9946), the limit of detection at three standard deviations above the mean is 61.8 ppb (47.0 ppb at two standard deviations above the mean; 32.2 ppb at one standard deviation above the mean) (Figure 8)[1]. Comparing both detection limits at three standard deviations above the mean, preconcentration of m-xylene therefore decreased the detection limit to less than 1/200th of the limit without preconcentration, an improvement of more than two orders of magnitude.

Ongoing tests have shown that the Carboxen 1000 preconcentrator is similarly capable of enhancing the chemiresistors' detection limits to other volatile organic compounds such as trichloroethylene and isooctane. Work is currently underway to integrate the preconcentrator and chemiresistor into the same probe that has been developed for in-situ environmental monitoring [2], and to develop the controls and calculations to most effectively take advantage of this performance improvement.

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[1] Note that the plots in both Figures 7 and 8 include data at 0 ppb, where temperature correction was performed on individual blank heat pulses by subtracting the $(\Delta R/R_b)_{\text{avg heat pulse}}$ from each $(\Delta R/R_b)_{\text{heat pulse}}$. These blank heat pulses were also used to determine the value of $3\sigma_{\text{avg heat pulse}}$. Although the data scatter results in some $(\Delta R/R_b)_{\text{heat pulse}}$ values for 0 ppb that are less than zero, while still other individual values are comparable to the one-sigma and two-sigma limits, both artifacts are consistent with typical sensor operation, and simply emphasize the reason for determining a three-sigma detection limit, below which values should be treated with appropriate skepticism.

Conclusions

Addition of a microfabricated preconcentrator to a chemiresistor chemical sensor was shown to improve sensitivity and decrease detection limits for m-xylene. Without the preconcentrator, our PEVA chemiresistor was able to detect concentrations as low as 0.12% of the saturated vapor pressure of m-xylene (at 3σ). Addition of a preconcentrator decreased the detection limit to approximately five one-millionths (0.0005%) of the saturated vapor pressure of m-xylene (at 3σ). This improvement of more than two orders of magnitude may allow the chemiresistor to be used in applications where lower detection limits are required, such as detecting regulated contaminants in geologic media. The preconcentrator also provides the advantage of knowing the precise timing of the heat pulse so that baseline drift of the chemiresistor can be corrected without pumps, valves, and purge gases in the field. The data shown in Figure 4 takes advantage of pumps and valves; it would be more difficult to distinguish the low concentrations if they were varying slowly and unpredictably. The timing of the preconcentrator allows a more definitive detection of low concentrations.

Acknowledgments

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Biographies

C.E. Davis received his BS in Chemical Engineering from The University of Tulsa and his MS in Chemical Engineering Practice from Massachusetts Institute of Technology. As a Member of the Technical Staff at Sandia National Laboratories in Albuquerque, NM, his work has focused on the development and testing of the chemiresistor chemical microsensor. Project work to date has focused on the use of chemiresistors in monitoring solvent-contaminated sites, and in monitoring generated and released gases from radioactive waste. Prior to his arrival at Sandia, he worked with IT Corporation in Albuquerque as a Project Engineer, developing and revising the transportation requirements for transuranic waste shipments to the Waste Isolation Pilot Plant near Carlsbad, NM.

C.K. Ho is a Principal Member of Technical Staff at Sandia National Laboratories. He received a BS in Mechanical Engineering from the University of Wisconsin-Madison (1989), and an MS and PhD in Mechanical Engineering from the University of California at Berkeley (1990, 1993). Dr Ho has performed work as a principal investigator for Yucca Mountain, WIPP, and Hanford in developing models of contaminant flow and transport in porous and fractured media. Dr Ho has also performed experimental and numerical studies for environmental remediation and subsurface contamination problems involving soil vapor extraction, steam injection, and capillary barriers for waste isolation. His current research interests include leading a research project to develop microchemical sensors for continuous, in situ, long-term subsurface monitoring of volatile organic compounds. Dr Ho has published over 30 technical papers in scientific journals and conference proceedings, and serves on the editorial advisory board for the journal Sensors.

R.C. Hughes recently retired from Sandia National Laboratories as a Senior Scientist in the Microsensor Science and Technology Department. He previously managed the Microsensor Division and a number of other groups after joining Sandia in 1966. He received his PhD degree in physical chemistry from Stanford University in 1966. He is currently consulting in the use of silicon microelectronics in both chemical sensing and radiation sensing. He is a Fellow of the American Physical Society.

M.L. Thomas is a Principal Technologist in the Microsensor Science and Technology Department at Sandia National Laboratories in Albuquerque, NM, where he works on fabrication of chemiresistor sensors and testing sensor capabilities. He holds a BA in Chemistry from the University of New Mexico. Mr. Thomas has been at Sandia since 1987 specializing in analytical chemical spectroscopies and development of new techniques. Before joining Sandia he served as technical lead for Delphi Research Inc., also located in Albuquerque, NM.

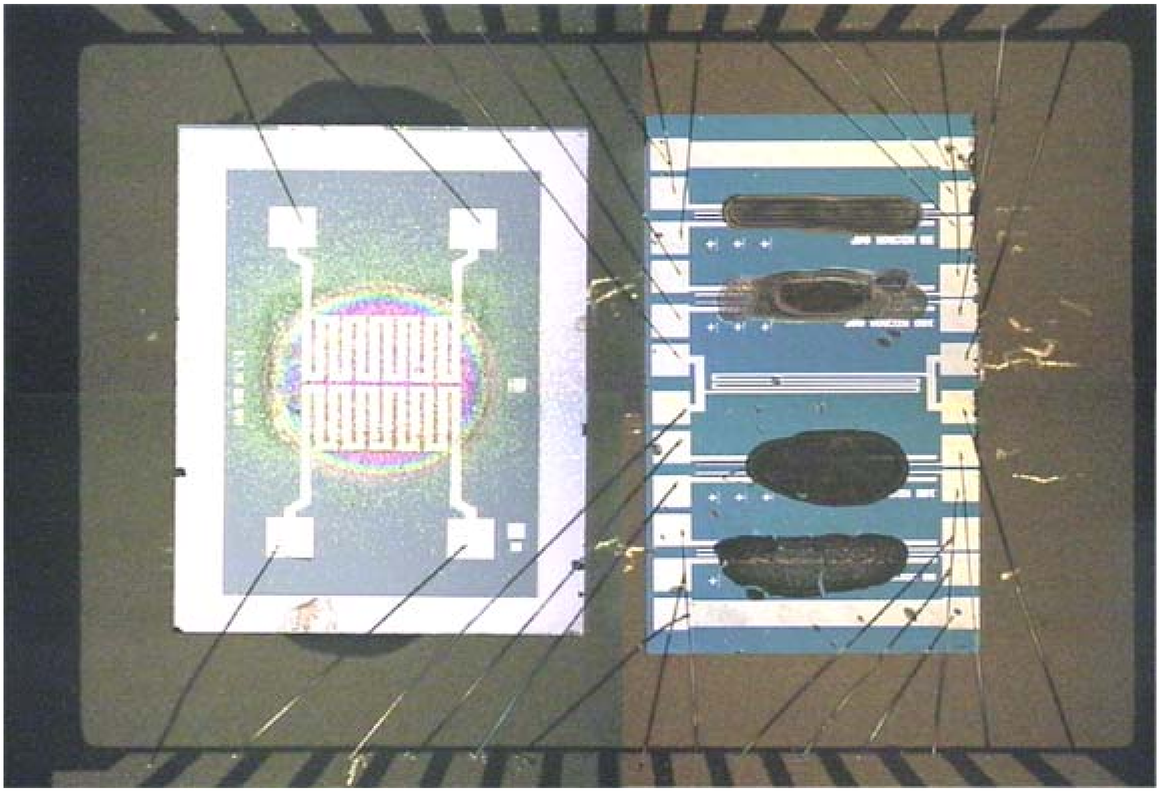

Figure 1: Integrated chemiresistor and preconcentrator packaged in a 32-pin DIP [3]. The chemiresistor die (on the right half of picture) consists of four carbon-particle impregnated polymer films deposited over a set of interdigitated electrodes on a silicon substrate. Heater bars (top and bottom of chemiresistor die) work in conjunction with a temperature sensor (middle of chemiresistor die) for temperature control. The preconcentrator die (on left half of picture) consists of an absorbent phase with a polymer film used for adhesion on a Bosch-etched silicon die. Addition of a preconcentrator to a chemiresistor sensor allows for increased sensitivity to chemical vapors and lower detection limits.

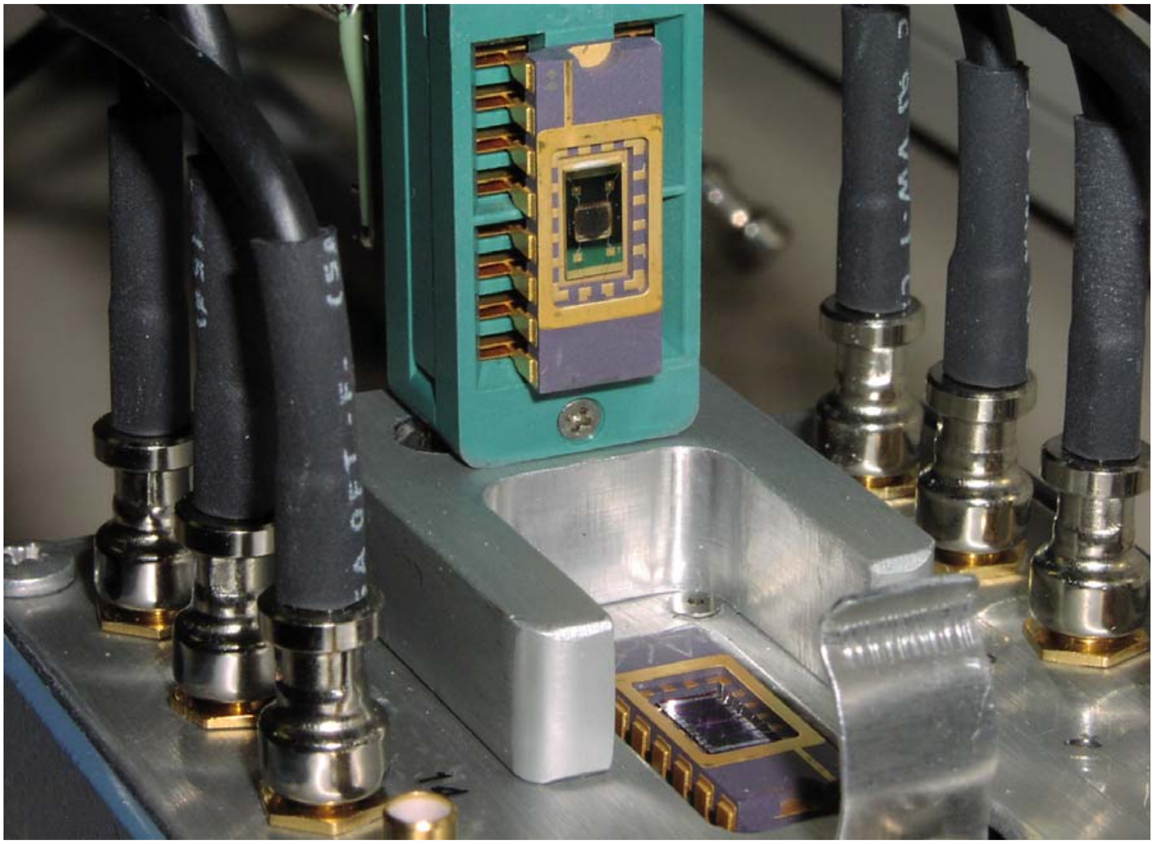

Figure 2: Chemiresistor and preconcentrator dies with custom housing for face-to-face mating. Both the chemiresistor die and preconcentrator die are packaged individually in 16-pin DIPs. The custom housing allows face-to-face mating and a decreased diffusional path length compared to the planar lateral arrangement in a single DIP. Decreased diffusional path length is anticipated to translate directly to more efficient transfer of preconcentrated analyte from the preconcentrator to the chemiresistor sensor, and hence greater response from the sensor and lower detection limits.

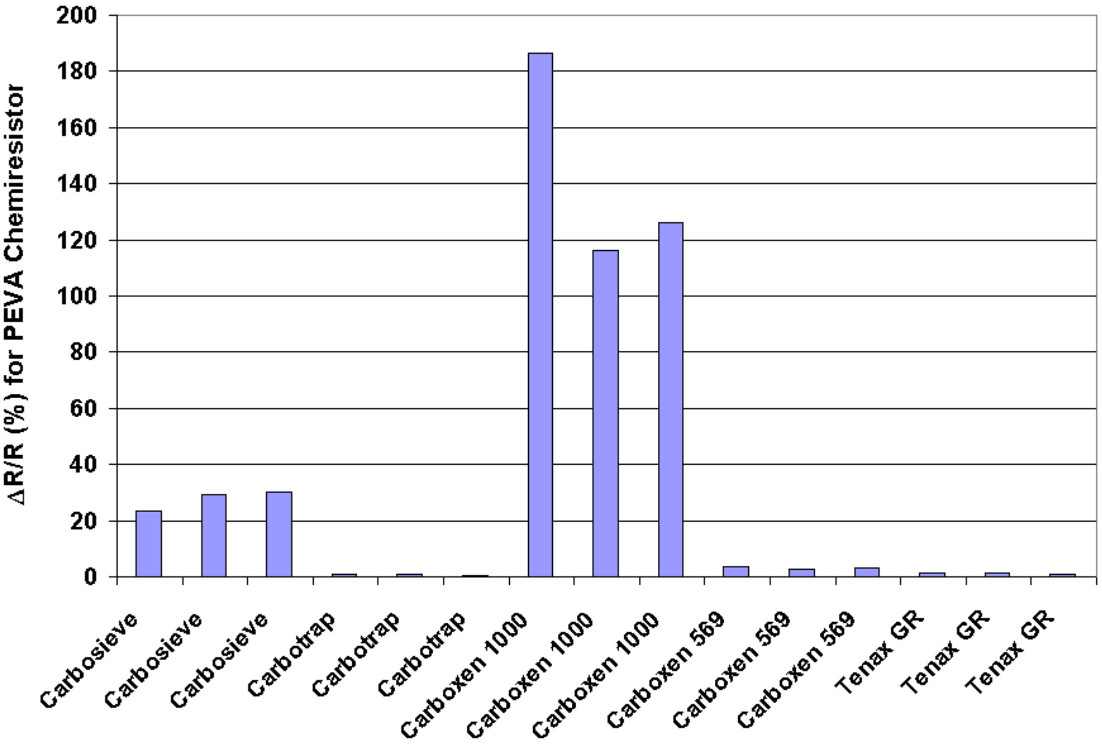

Figure 3: Preconcentrator screening data for PEVA chemiresistor response to m-xylene vapor. Response for the PEVA chemiresistor to m-xylene absorbed onto five preconcentrator candidate phases. Each phase was exposed three times, and all exposures are under five minutes of loading under 0.2% P/Psat m-xylene, followed by a five second-five volt pulse to the preconcentrator. The Carboxen 1000 phase clearly outperforms the other four candidates, with an average DR/R response from the PEVA chemiresistor of 143%, or more than five-times the response from any other candidate phase.

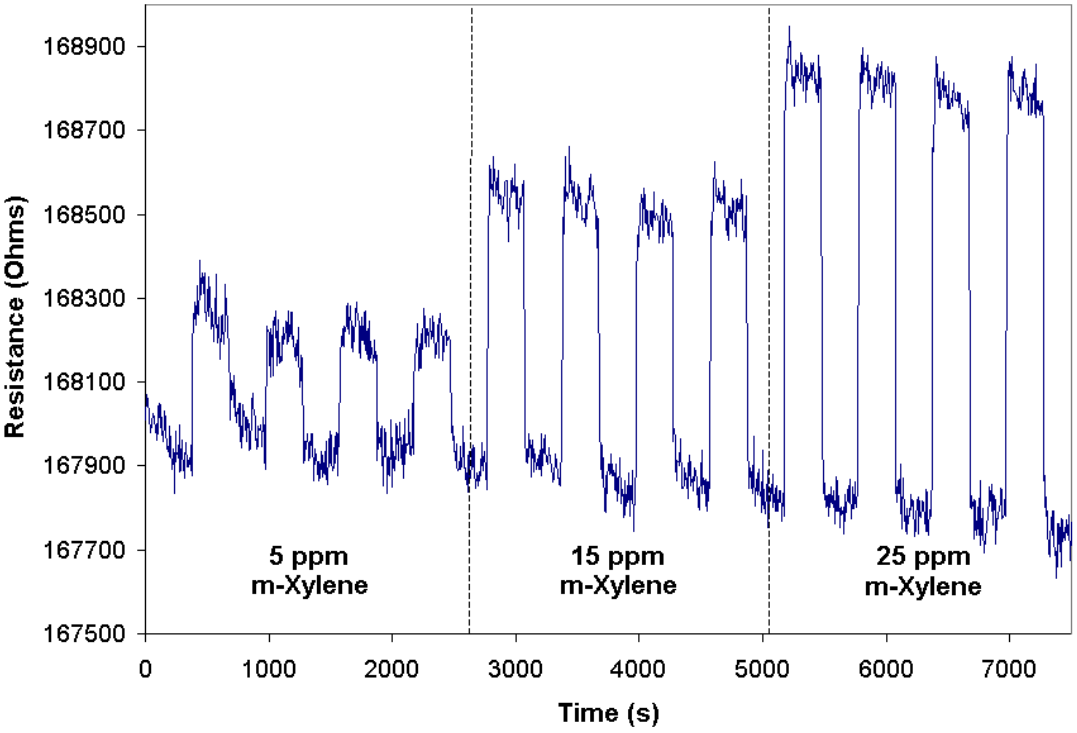

Figure 4: Example resistance plot for a PEVA chemiresistor exposed to m-xylene vapor. The plot shows four exposures each of 5, 15, and 25 ppm m-xylene vapor in balance nitrogen at room temperature. Each exposure is preceded and followed by a purge of 100% nitrogen.

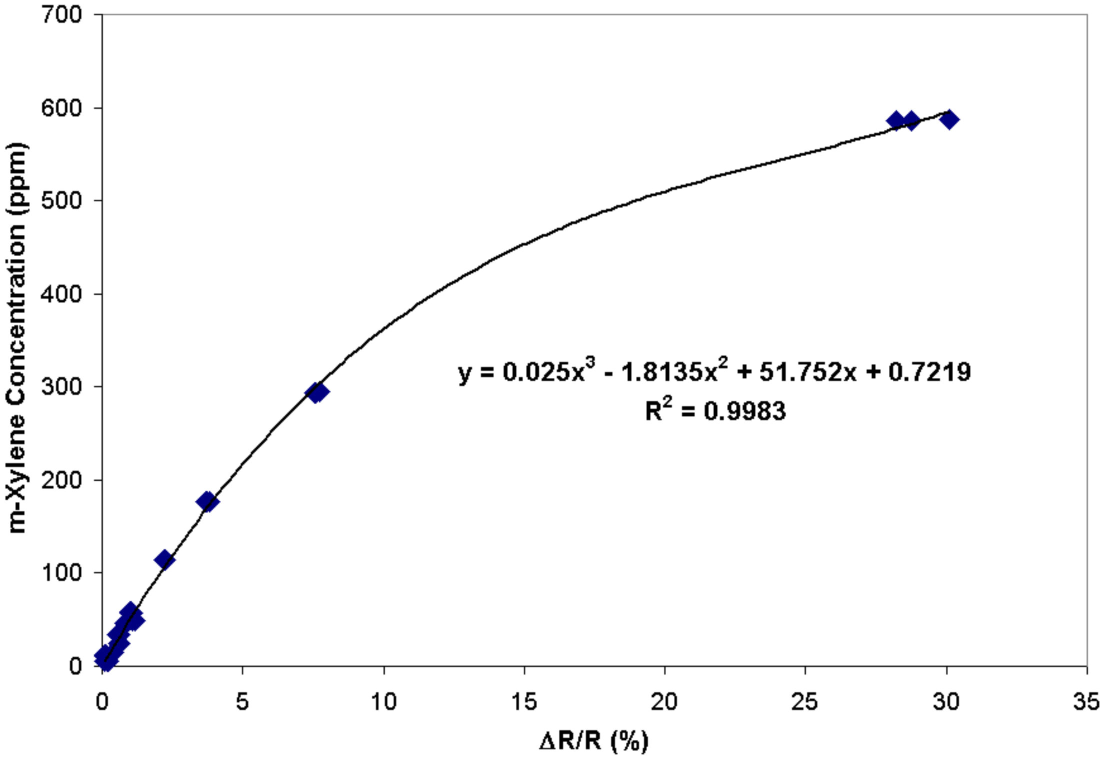

Figure 5: Calibration curve for the unaided (no preconcentrator used) PEVA chemiresistor in response to m-xylene vapor. Chemiresistor response is quantified as the relative increase in resistance (change in resistance/baseline resistance prior to chemical exposure – ΔR/R, expressed as a percentage) due to exposure to a given concentration of m-xylene. The third order polynomial fits the data quite well over the entire concentration range from 4.9 to 587 ppm, with an R-squared value of 0.9983.

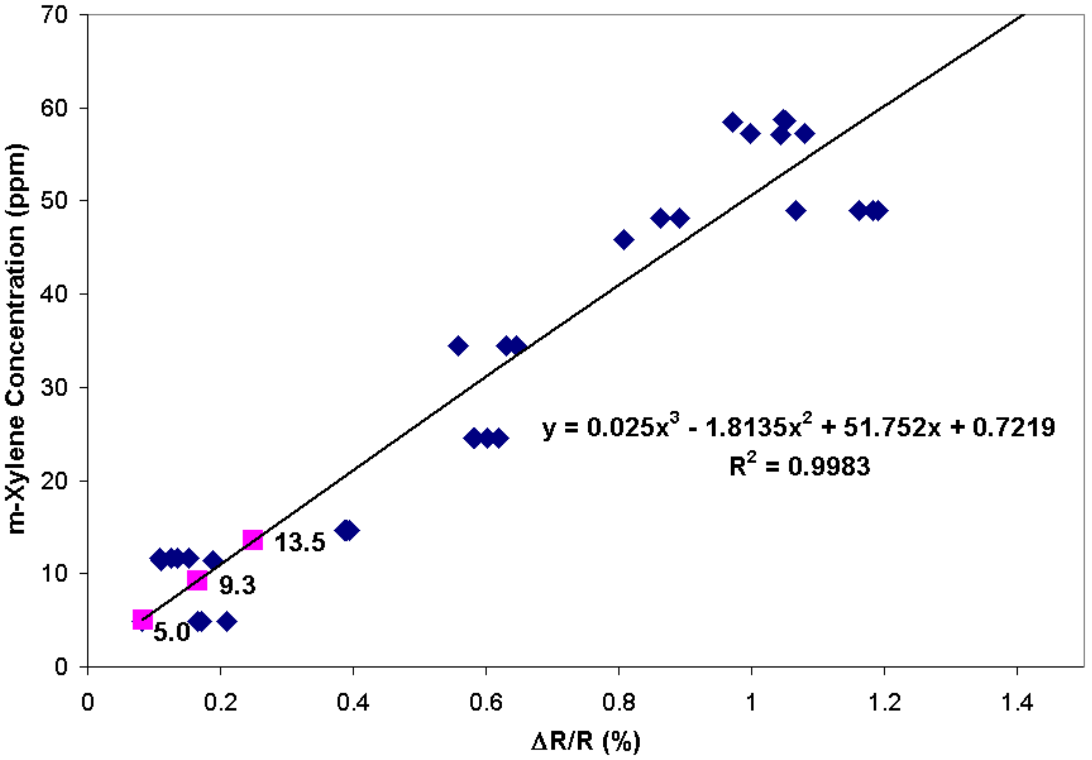

Figure 6: Magnification of the lower concentration region for the unaided PEVA chemiresistor calibration plot, and unaided chemiresistor limit(s) of detection. The magnification of the data presented in Figure 5 provides an opportunity to evaluate the limit(s) of detection for the unaided chemiresistor. The limit of detection was defined as the concentration corresponding to the sensor response that would exceed the inherent sensor signal noise, quantified as a response in excess of three times the standard deviation of the baseline noise ($3\sigma_{Rb}$). Because sensor response is measured as a relative increase in resistance, the limit of detection threshold was taken relative to the average baseline resistance ($3\sigma_{Rb}/R_{b,avg} \sim \Delta R/R$). For a $3\sigma_{Rb}/R_{b,avg}$ value of 0.249%, the calibration curve and polynomial fit provide a limit of detection of 13.5 ppm. Limits of detection corresponding to one and two standard deviations of the baseline noise are also shown, and are 5.0 and 9.3 ppm, respectively.

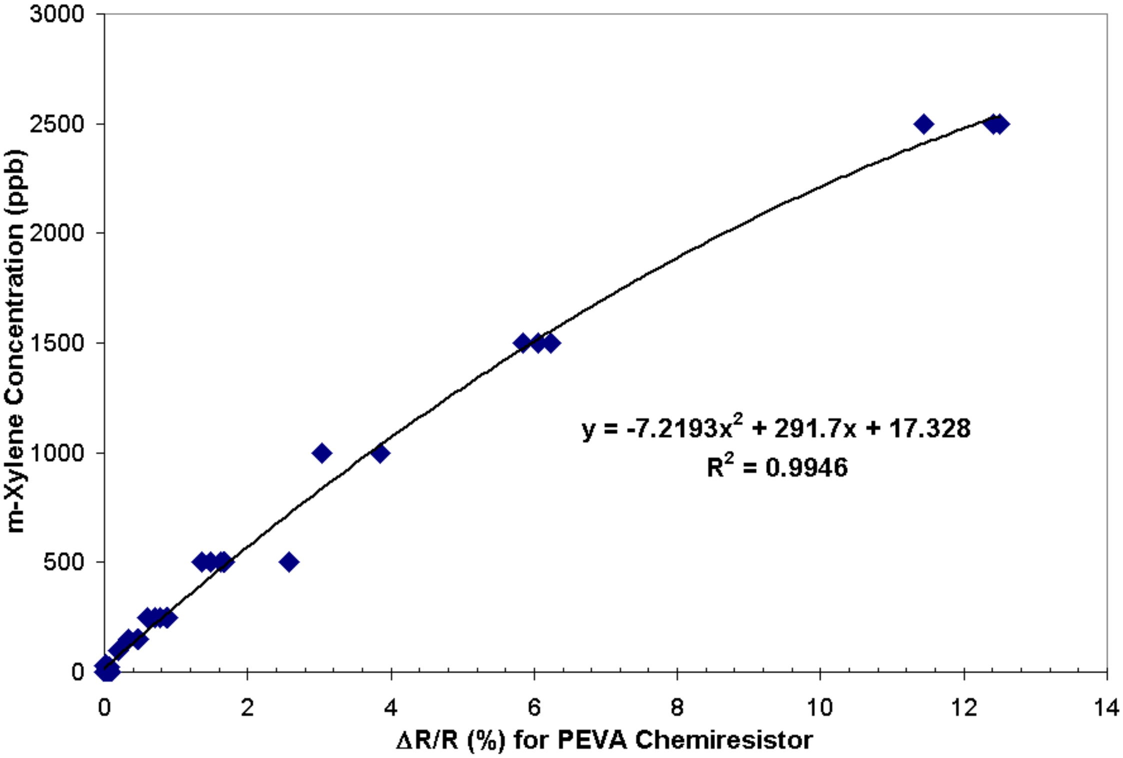

Figure 7: m-Xylene calibration curve for a PEVA chemiresistor coupled with a Carboxen 1000 preconcentrator. Each m-xylene exposure was for five minutes, followed by a five second, five volt pulse to the preconcentrator. The sensor system response is determined by the relative increase in resistance of the PEVA chemiresistor (ΔR/R, %), but the response is corrected for the effects of thermal expansion introduced by the heated preconcentrator through subtraction of a comparable ΔR/R value for a blank heat pulse (no absorbed analyte). The second-order polynomial fits the data quite well over the concentration range from 0 to 2500 ppb, with an R-squared value of 0.9946.

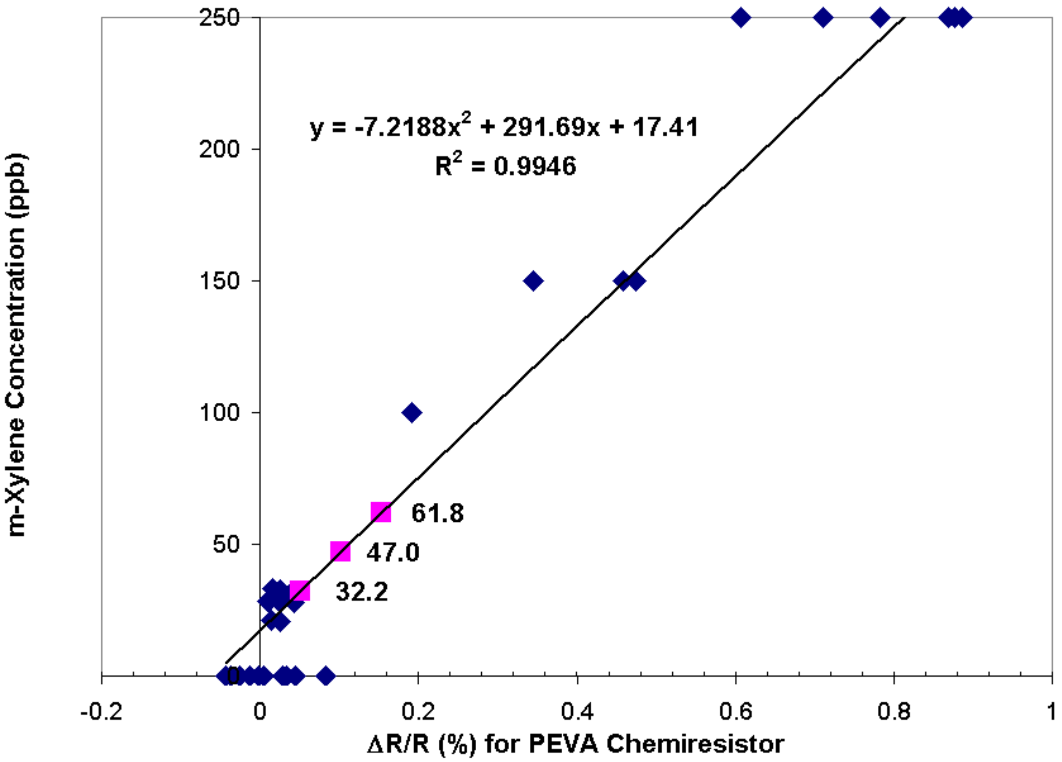

Figure 8: Magnification of the lower concentration region of the m-xylene calibration curve for a PEVA chemiresistor coupled with a Carboxen 1000 preconcentrator, and limit(s) of detection. Magnification of the lower concentration data shown in Figure 7 allows visual examination of the limit(s) of detection for the sensor system. Similar to the logic presented for Figure 6, the limit of detection was established as the concentration corresponding to a sensor signal detectable above the baseline sensor response. For a system using a preconcentrator, however, the baseline is defined by the blank heat pulse used to correct chemiresistor response signals for thermal expansion due to the heating of the preconcentrator. Because the blank heat pulse signal is subtracted from the analyte-exposed heat pulse, the limit of detection was defined as corresponding to three times the standard deviation of the blank heat pulses ($3\sigma_{\text{avg heat pulse}}$) above the average blank heat pulse [$(\Delta R/R_b)_{\text{avg heat pulse}}$]. Correction to eliminate thermal expansion effects, however, simplifies the desired metric for a detection limit to only $3\sigma_{\text{avg heat pulse}}$. For a value of 0.153%, the calibration curve and polynomial fit provide a limit of detection of 61.8 ppb. For one and two standard deviations of the blank heat pulse, the limits of detection are 32.2 and 47.0 ppb, respectively.

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