

Field Test to Demonstrate Real-Time *In-Situ* Detection of Volatile Organic Compounds

Hazmat Spill Center, Nevada Test Site
September 19-25, 2001

Clifford K. Ho
Sandia National Laboratories
Albuquerque, NM 87185
(505) 844-2384
ckho@sandia.gov

Charles F. Lohrstorfer
Bechtel Nevada Corporation
Las Vegas, NV 89193
(702) 295-5681
LohrstCF@nv.doe.gov

Abstract

Traditional methods for monitoring soils and groundwater that may be contaminated with toxic chemicals can be expensive, time consuming, and misrepresentative of *in-situ* conditions. This report presents a demonstration of a real-time *in-situ* monitoring system that can be used to detect volatile organic contaminants in soils and groundwater. A microchemical sensor that is packaged in a waterproof housing is used to detect trichloroethylene (TCE) in a sand-filled 55-gallon drum at the Hazmat Spill Center at the Nevada Test Site.

Background and Objectives

Tens of thousands of sites containing toxic chemical spills, leaking underground storage tanks, and chemical waste dumps require characterization and long-term monitoring to reduce health and environmental risks. Current methods are costly and time-intensive, and limitations in sampling and analytical techniques exist. For example, the Department of Energy (DOE) 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. The integrity of off-site analyses can also be compromised during sample collection, transport, and storage. In addition, newly emerging threats of chemical contamination of our water supplies also requires more frequent (nearly continuous) monitoring that cannot be met by traditional methods. New technologies that provide real-time *in-situ* monitoring and characterization of volatile organic compounds (VOCs) that alleviate the need for manual sampling and off-site analysis may provide cheaper and more reliable information. One such technology is a chemical microsensor (chemiresistor) and monitoring package developed at Sandia National Laboratories that can provide real-time *in-situ* detection of volatile organic compounds. A demonstration was performed at the Hazmat Spill Center at the Nevada Test Site to test this sensor in a sand-filled 55-gallon drum containing trichloroethylene (TCE). Results are reported regarding the response of the sensor during the contaminant emplacement and remediation (air venting) of the sand.

Microchemical Sensor and Packaging

The microchemical sensor, or chemiresistor, used in the test consists of a chemically sensitive absorbent mixed with conductive particles that is deposited onto chip with wire-like electrodes. When chemical vapors come into contact with the absorbent, the chemicals absorb into the polymers, causing them to swell. The swelling changes the resistance of the electrode, which can be measured and recorded. The amount of swelling corresponds to the concentration of the

chemical vapor in contact with the absorbent, and the process is reversible. Two unique features exist regarding the chemiresistors being developed. First, the chips developed at Sandia can house an array of chemiresistors, a temperature sensor, and heater (Figure 1). The array of differing sensors can be used to identify different VOCs by comparing the resulting chemical signatures with calibration (or training) sets. The chemiresistor array has been shown to detect a variety of VOCs including aromatic hydrocarbons (e.g., benzene), chlorinated solvents (e.g., TCE), and aliphatic hydrocarbons (e.g., iso-octane). The temperature sensor and heater can be used to provide temperature control (although this feature was not used in the test). A second unique feature is that a rugged package has been designed and fabricated to house the chemiresistor array (Figure 2). This package is small (< 3 cm diameter) and is constructed of stainless steel. The package is waterproof, but allows vapors to diffuse through a GORE-TEX® membrane. Therefore, if chemicals are dissolved in water, the aqueous-phase contaminants can partition across the membrane and into the gas phase where they can be detected by the chemiresistors. The chemiresistors are situated on a 16-pin dual in-line package that is connected to a weatherproof cable, which can be connected to any data logger.

Experimental Setup

The experiment consisted of a 55-gallon drum that was filled with sand.¹ A slotted PVC tube was placed vertically in the center of the drum to act as a contaminant reservoir. A slotted and screened 3-inch-diameter steel tube was placed 20 cm away from the reservoir to simulate a well (see Figure 3). The sensor package was suspended midway down the steel tube (~36 cm), and the cable was threaded through a port in the drum to an Agilent 34970A data-acquisition unit in a nearby trailer. The data-acquisition unit was connected to a laptop that used the Agilent Benchlink Data Logger software (v. 1.4).

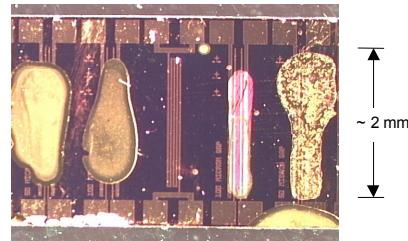


Figure 1. Chemiresistor array developed at Sandia National Laboratories with four different conductive polymer films deposited on different electrodes. A platinum temperature sensor is located in the middle.



Figure 2. Weatherproof chemiresistor package that can be emplaced in a monitoring well or cone penetrometer.

16-pin dual in-line package that is connected to a weatherproof cable, which can be connected to any data logger.



Figure 3. Top view of 55-gallon drum filled with sand. The contaminant reservoir is in the middle of the drum, and the sensor well is towards the outside.

¹ Measured sand properties: grain density=2.3 g/ml; porosity=0.39; saturation=0.18; variable grain size

The experiment consisted of three phases: (1) a period of ambient background data logging for nearly four days to observe the impacts of diurnal temperature variations on the system; (2) emplacement of TCE into the contaminant reservoir; and (3) remediation using compressed air to vent the sand for a brief period. During the ambient logging, the drum was completely sealed (Figure 4). Then, the lid was removed and approximately 60 ml of TCE was emplaced in the contaminant reservoir. Approximately 35 ml was absorbed onto a wick that was placed in the reservoir, and 25 ml was poured into and around the reservoir (see Figure 5). During the simulated remediation process, a compressed air tank was used to blow air (~10 ml/min) through four equally spaced ports around the bottom perimeter of the drum (see Figure 6). The air flowed through the contaminated sand and through the open top of the drum. During all phases, a tarp was draped around the drum to shade the drum from direct sunlight.

Results and Discussion

Figure 7 shows the logged data from the sensor during the ambient data-logging period. Only the temperatures from the temperature sensor and the resistances from chemiresistor 3 are shown in Figure 7 (the response of the other three chemiresistors on the chip were similar to chemiresistor 3, so they were not reported to keep the plots clear). The temperature sensor on the chip indicated that the temperatures oscillated between approximately 20 °C to 30 °C because of the diurnal heating and cooling. The chemiresistor also showed a response that closely resembled the temperature variations. As the temperature increased, the polymers swelled due to thermal expansion, which increased the measured resistance by breaking some of the conductive carbon-particle pathways in the polymer matrix. As the system cooled overnight, the polymers shrunk, and the measured resistances of the chemiresistors decreased as the carbon particles that were separated were brought into contact again. These temperature variations and its affect on the “baseline” chemiresistor resistance pose an issue for calibrations at low chemical concentrations, but at higher concentrations, the magnitude of the increased resistance overwhelms the variations caused by temperature.



Figure 4. View of the sealed 55-gallon drum.



Figure 5. Emplacement of a TCE-soaked wick into the reservoir.

The temperature sensor on the chip indicated that the temperatures oscillated between approximately 20 °C to 30 °C because of the diurnal heating and cooling. The chemiresistor also showed a response that closely resembled the temperature variations.



Figure 6. Air-ventilation system connected to the drum.

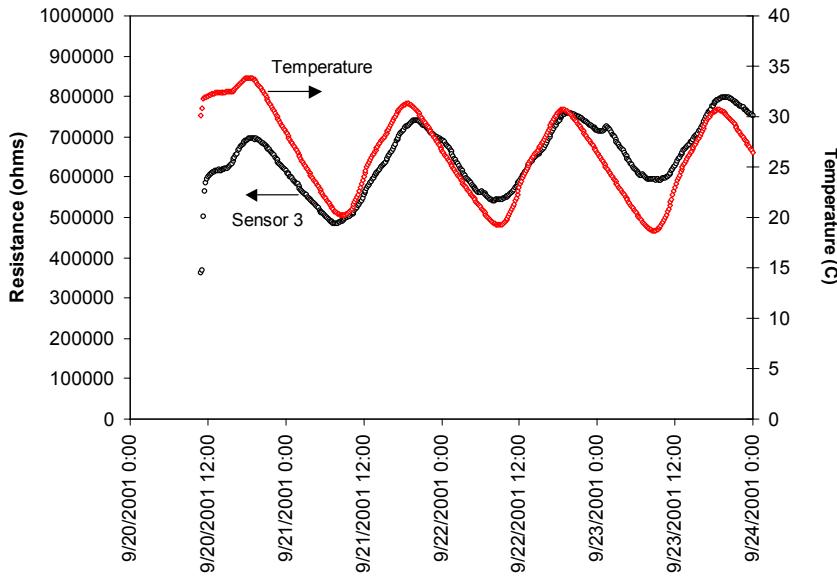


Figure 7. Plot of chemiresistor temperature and resistance during the ambient data-logging period.

Another interesting observation during the ambient period was that significant amounts of water condensed in the drum as the system cooled overnight. The liquid water was observed in large amounts on the lid, along the walls of the steel well (which showed evidence of rusting), and on the sensor package and cable. However, after unscrewing the sensor package, we observed that the chip and chemiresistors inside were dry and did not appear to show any signs of corrosion or mineral precipitation.

Figure 8 shows a plot of the logged data during the TCE emplacement and venting periods. The chemiresistor shows a drastic increase in resistance only a few minutes after the TCE was emplaced. The resistances increased to greater than $100\text{ M}\Omega$, which was the maximum limit on the data acquisition unit. We expected that the response would take longer because the sensor was placed 20 cm away from the contaminant reservoir, and TCE vapors would have to diffuse through the sand. The sooner-than-expected response time may be due to the open headspace between the lid and the top of the sand. TCE could “short-circuit” the sand by diffusing through the open air in the headspace above the reservoir and then down the well to the sensor.

After about four hours, the lid was removed and air was vented through the sand for about 45 minutes. Figure 8 shows that the resistances dropped significantly because of the purging of clean air through the system. After closing the lid and stopping the venting, the resistances began to increase again due to exposure to TCE vapors. It should be noted that the format of the raw data reported (resistances) can be converted to TCE concentrations using calibration curves, but because temperature variations also caused changes to the chemiresistor resistances, we decided to keep the data in its original form.

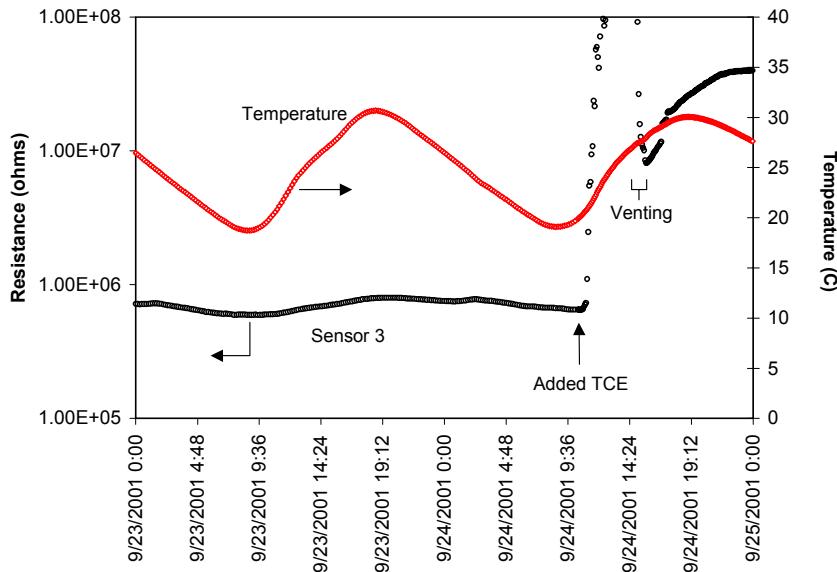


Figure 8. Plot of chemiresistor temperature and resistance during TCE emplacement and venting periods.

Conclusions

The 55-gallon-drum test conducted at the Hazmat Spill Center at the Nevada Test Site provided an opportunity to test the *in-situ* chemiresistor sensor package in harsh environments that included large temperature variations, significant moisture, and large TCE concentrations. The sensor was shown to provide a real-time, continuous response when exposed to TCE emplaced in the sand, and it also recorded a decrease in the TCE vapor concentration as clean air was vented through the system. In addition, the rugged sensor package was shown to prevent condensed liquid water from entering the package. Temperature variations were shown to impact the baseline chemiresistor resistances, but at high TCE concentrations, the temperature-induced resistance variations were overwhelmed by the increase in resistance due to TCE exposure.

Future studies using this apparatus and other *in-situ* configurations are recommended to be performed to test the chemiresistor sensor package and other sensors for use in long-term monitoring applications. Objectives for future tests include maintaining a constant elevated temperature of the chemiresistors via the heater and temperature sensor on the chip. This will aid in providing more accurate calculations of concentration from calibrations, and it will prevent condensation of liquid on the chip. In addition, the integration of the real-time *in-situ* sensor with an air-venting remediation system can be tested. Finally, remote telemetry-based data transmission methods can be added to the existing *in-situ* monitoring system.