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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 pressure 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 without 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

1. 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 and $1000 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 VOCs 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. This type of chemical sensor has received considerable attention recently [3–5]. 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

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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 mmHg (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.

Preconcentrators have been used for many years in analytical chemistry applications for collecting molecules (called analytes) that are present in very low concentrations, often in air or water. The analytical instruments, like gas chromatography, are not able to detect these low concentrations directly, so specialized materials called adsorbent resins were developed to act as room temperature adsorbers of many molecules. These materials are usually high surface area powders and have adsorption properties which are catalogued [http://www.sisweb.com/index/referenc/resins.htm]. The most important property is the ability to adsorb almost all the analyte from a stream of air passing through a packed column and then release all the analyte molecules when the column is heated to a specified high temperature, often a few hundred degrees centigrade. There are no perfect adsorbers for all analyte molecules. The adsorption characteristics of a given resin will depend on the specific analyte. Even at room temperature, most analytes that have been loaded onto the resin will desorb at a low rate when the analyte concentration is zero above the adsorber.

Because of these less-than-perfect features of currently available adsorbent resins, portable systems for doing quantitative analysis of multianalyte, low concentration air samples (in industrial hygiene for example), are fairly complicated. Several high performance portable systems have been described in the literature [6,7]. To get quantitative analysis over wide ranges of concentrations in mixtures of analytes with variable relative humidity, they find they need pumps with well defined pumping volumes through the packed preconcentrator column, chromatographic separation columns which need to be heated, scrubbers and detector arrays, along with the associated plumbing.

Here we report on a much simpler system in which a micromachined, hot plate preconcentrator is coupled to a chemiresistor array. There are no pumps and valves, so preconcentration occurs by analyte diffusion and convection to the resin (or phase) on the microhotplate [8,9]. This simple, low power, system will probably never be able to achieve the kind of quantitative analysis of analyte mixtures of the more complex portable instruments, but we feel there are many applications where the information gathered by a hybrid preconcentrator/chemiresistor array can be valuable.

The preconcentrator consists of a thin film of adsorbent material deposited on a resistive wire trace. The adsorbent film allows for reversible accumulation of chemical vapors over a period of time until heated by sending current through the wire trace. When the adsorbent material is heated to ∼200 °C, the adsorbed 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 [8,9], 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.

Our hybrid concept is closer to solid phase microextraction (SPME) where preconcentration of analyte occurs on a thin fiber coated with adsorbent resin, often a polymer [10]. The loading of the SPME fiber occurs by diffusion and convection which can be in air, water, soil or headspace of a sample bottle. Quantitation of the concentration of analyte is not achieved by complete stripping of the analyte from a measured volume as in the tube preconcentrators discussed above, but by equilibration of the adsorbent phase