Trace chemical detection in air using electronic noses and nano-structured sensing materials

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ABSTRACT
For a variety of application areas, including homeland defense, environmental and health monitoring and emergency response, the detection of gas-phase chemicals is of great interest. One approach to these challenging sensing tasks is to use arrays of broadly selective chemical sensors as an electronic nose. In this presentation, we describe recent research at NIST, which employs multi-element microscale chemiresistor arrays populated with varied (chemically and morphologically) sensing materials. Furthermore, we modulate the operating temperature of the microsensors on millisecond timescales to enable increased selectivity for the detection of several volatile organic compounds in air at varied concentrations less than 100 μmol/mol.

Keywords: gas-phase sensors, e-nose, chemiresistor

1. INTRODUCTION
The detection, identification and quantification of gas-phase chemicals in air is of great interest for a variety of application areas that include health and medicine, process control, homeland security and emergency response and environmental monitoring. Instrumental approaches (e.g., infrared spectroscopy) can be considered the gold standard for these types of measurements, with good specificity and quantification capabilities. However, these types of instruments generally have high costs or high operational requirements, which can make them untenable for wide-spread use. An alternative approach, which can complement instrumental analyses, relies on chemical sensors, which have the potential to be high-performance devices with relatively low cost. In particular, our group is interested in arrays of chemical microsensors, which may be operated as a type of electronic nose.

Our research objective is to elucidate approaches for developing microsensor devices with advanced performance capabilities. The sensor devices are based on a MEMS microscale platform developed at NIST. The sensing approach involves measuring chemiresistive changes produced by gas-phase molecules that adsorb in characteristic ways on chemosensitive materials, such as semiconducting metal oxides of varied chemistry and morphology. The metal oxide sensing materials that we typically employ are broadly selective; that is, they often respond in a qualitatively similar manner to several distinct chemicals. Thus, to achieve selectivity, the chemosensitive films in the array are varied with respect to chemistry and morphology. The sensing material morphology may also offer benefits for improving the response strength of the sensor to low concentrations of the analyte. Furthermore, the microsensors have an embedded resistive heater and short thermal time constants, which enable rapid temperature modulation of the sensing elements. Temperature modulation has been shown to enhance the analytical content of these types of sensors, allowing, in particular, better discrimination of analytes.

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In this paper, we describe some recent work on the use of an e-nose with varied materials in an array, and associated fast temperature modulation, to demonstrate that information is available from the generated data streams to both detect and quantify trace volatile compounds in air. Specifically, we prepare a microsensor array with three different sensing materials: copper oxide, indium oxide and tin oxide. We then characterized the response of the microsensor array, when operated in a pulsed temperature mode, to five different concentrations of three analytes: acetone, toluene and chlorobenzene. The concentrations of the analytes ranged from 1 μmol/mol to 80 μmol/mol, and they are presented in a zero-air background, as well as a background that had ≈ 20% relative humidity.

2. MATERIALS AND METHODS
The sensors used in these studies are based upon multi-element microsensor arrays (Figure 1). Each element (Figure 2) is a square platform, ≈ 100 μm across each side. An embedded polysilicon resistive heater enables temperature control of the microsensor device, with thermal time constants of ≈ 5 ms. Platinum interdigitated electrodes, deposited on the surface of the sensor element, enable electrical resistance measurements of the sensing film. Active layers are isolated from each other using silica. The sensing film is deposited on the microsensor surface using microcapillary pipetting of precursor metal oxide solutions. For these studies, the sensing materials used included tin oxide, copper oxide and indium oxide. After deposition, the materials were thermally processed in air using the embedded heater. Films were characterized by scanning electron microscopy (SEM) and electrical resistance as a function of temperature.

Figure 1. An optical micrograph of a 16-element microsensor array before deposition of sensing films. Each element is individually addressable with respect to temperature control and resistance measurements. A nine-element variant (3 × 3) of the array was also used in these studies.
For sensing studies, analytes were delivered to the microsensor arrays in a zero-air background. For some tests, the background air was humidified by passing a portion of the air flow through a water bubbler. The resultant relative humidity was ≈ 20 % RH. Analytes (acetone, toluene, chlorobenzene) were mixed with the background air from certified, pre-diluted (balanced with zero air) cylinders. By varying the concentration in the cylinder (100 μmol/mol or 500 μmol/mol) and the mixing ratios between the analyte flow and the background flow, analyte concentrations ranging from 1 μmol/mol to 80 μmol/mol were delivered to the microsensor array.

During sensing experiments, the sensors were operated with a temperature-modulated approach. A sample temperature program, shown in Figure 3, was repeated throughout the experimental data collection. The heaters for each microsensor element were calibrated periodically, generally before each experiment, assuming a temperature coefficient of resistance of 1.067 x 10⁻³/°C (determined for a similar device). The uncertainty in temperature was estimated by comparing the calibrations from the sensors over the course of the experiments, which yielded one standard deviation of ≈ 1 % of the temperature value (three sensor elements with four calibrations each). A resistance measurement of the sensing film was acquired for each active sensor element at each temperature step of the program. Linear discriminant analysis (LDA) was employed to evaluate the responses of the sensors to the three analytes, using a custom program, modified for these analytes and operating conditions.

Figure 2. A schematic of a microsensor element showing several of the layers. The sensing films used include tin oxide, indium oxide and copper oxide.
3. RESULTS AND DISCUSSION

Multiple chemiresistive materials can be incorporated into array configurations to gain additional analytical data. Therefore, our platforms include arrays of elements that can be populated with different sensing materials, where each element is individually addressable for resistance measurements as well as temperature control. After deposition and processing, the materials can be characterized on the microsensor platform using SEM (Figure 4), and by their electrical resistance as a function of temperature. The SEM micrographs show the resultant films composed of copper oxide, indium oxide and tin oxide. As seen in Figure 4, the films are quite thin, but they are electrically continuous: the measured resistances, with one standard deviation, of these films at 250 °C are 9.01 kΩ ± 0.03 kΩ (copper oxide), 3.19 kΩ ± 0.01 kΩ (indium oxide) and 137 kΩ ± 1 kΩ (tin oxide).

Figure 4. SEM micrographs of materials deposited onto and processed on microsensor array elements: CuO (left), In₂O₃ (center) and SnO₂ (right).
The initial database of sensing responses to the analytes was acquired with an electronic nose utilizing SnO₂, In₂O₃ and CuO microsensors. In particular, we collected repeated data on their responses to acetone, toluene and chlorobenzene in zero air at five concentrations each. The concentrations of acetone ranged from 5 μmol/mol to 80 μmol/mol, and the concentrations of toluene and chlorobenzene ranged from 1 μmol/mol to 16 μmol/mol. These three analytes were chosen as a subset of common volatile organic compounds that would be of interest for monitoring in several application areas. A small portion of the data is shown in Figure 5. To acquire these dense signal patterns, temperature modulation of the sensing element was used (following the temperature program in Figure 3), enriching the analytical information content from the metal oxide chemiresistor sensing device. We also acquired data from the electronic nose sensors during a mixed-analyte delivery program with background humidity (Figure 6). Within the delivery program, the sensor array was repeatedly exposed to a single, low concentration of each of the three analytes (chlorobenzene, toluene and acetone) in dry and humid backgrounds. During the humid exposures, relative humidity (RH) was maintained at ≈ 20 % as a means to assess the effect of water adsorption on target detection.

Figure 5. Sample resistance data from a copper oxide-based microsensor element during exposure to acetone (left) panel, and from an indium oxide-based microsensor element during exposure to toluene (right). The inset of the left panel shows a larger portion of the data stream, as well as the gross responses of the microsensor to the presence of acetone (red). The blue box in the inset highlights the data plotted in the main panel. The boxes in the main panels highlight single temperature-program cycles.
We performed analysis of the collected data sets at NIST using LDA. Figure 7 shows an example of the separability of the five concentrations of acetone (and background) using data from one microsensor element and from three microsensor elements within the array. The microsensors were all running similar temperature programs (Figure 3). As seen with the separation of the bins by concentration, the single element (left panel) does well in detecting acetone (well separated from the 0 μmol/mol bin), but does not have the capability to distinguish the higher concentrations of acetone. With the data from three sensors (right panel), however, the five concentrations are clearly separated. This demonstrates the utility of the electronic nose concept for this sensing task. This work was conducted to assess the electronic nose performance capabilities and to provide a basis for future testing and associated analyses on 3-gas mixtures. We also examined the data acquired from the sensor array (employing three microsensor elements) during exposure to a 3-target mixture, which included RH effects, using LDA (Figure 8). This analysis also includes an evaluation of whether the background is dry air or humid air (lower right panel). The separation of acetone or chlorobenzene exposures from the background and the other analytes appears to be significant. For toluene, however, there appears to be more overlap between the toluene exposures and the background/other-analyte conditions. Looking at the raw data for one of the sensors (Figure 6), it appears that the humidity is suppressing the response for toluene, interfering with its detection.
4. CONCLUSION
We have prepared a multi-element microsensor array, or electronic nose, using three types of metal oxide materials as the active chemosensing layers. The electronic nose, operating in a temperature-pulsed mode, was exposed to three types of volatile organic compounds under dry and humid background conditions. Using LDA to evaluate the data acquired from the microsensor array, we have demonstrated that the electronic nose has sufficient analytical...
information to detect the analytes in the different backgrounds, and to distinguish the concentrations of the analytes down to 1 μmol/mol. Future research will expand the materials in the microsensor array to solve more challenging sensing tasks. Further efforts will also involve bio-inspired and bio-mimetic approaches to electronic nose development and signal interpretation.

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REFERENCES