Portable electronic nose system with chemiresistor sensors to detect and distinguish chemical warfare agents

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Abstract. An electronic nose (E-Nose) has been studied as a means to realize artificial olfaction. Electronic nose "instruments" are currently relatively large, since the signal manipulation and classification are still done by a personal computer (PC) or a laptop. For this reason, we have developed a portable electronic nose system based on a handheld machine by using a vapor detection array made of carbon-black polymer composites and a sensor circuit. In an effort to make a portable electronic nose, we used thin-film chemical sensors based on the carbon-black polymer nanocomposite to reliably detect chemical warfare agents. To replace the large volume of PCs, we used a field-programmable gate array to perform system control, signal manipulation, and classification. This E-Nose system was exposed to dimethyl-methyl phosphonate (DMMP) and dichloromethane (DCM) in parts per million concentration levels. DMMP and DCM were considered as simulants of the nerve agent sarin and the incapacitating agent BZ gases, respectively. [DOI: 10.1117/1.3466797]

Subject terms: electronic nose; polymer; composite.

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1 Introduction

Gas sensing and identification have found many applications, including indoor air quality monitoring, medical treatment and health care, security, food quality control,[1–3] environment quality control,[4,5] diagnosis,[6–9] medical products, military applications, hazardous gas detection, and so on. Performing these tasks requires an alternative method for gas sensing and recognition other than human beings. Artificial olfaction studies have come a long way, from the earliest mechanical nose by Moncrieff in 1961[10] to today's electronic nose (E-Nose) instruments. Inspired by biology, the electronic nose uses an array of sensors to perform odor sensing and classification tasks. Since 1990, researchers have investigated several different kinds of electronic nose sensors,[11] including conductivity sensors,[12–18] piezoelectric sensors,[19–21] metal-oxide semiconductor field effect transistors (MOSFETs),[22,23] optical sensors,[24,25] and spectrometry-based sensing methods.[26,27] Although several products are currently commercially available, an E-Nose system small enough to be carried or handheld by an individual person[28] is needed. The current project uses carbon-black conducting polymers as the sensors. Sensitivity can reach the parts per million (ppm) range, the interfacing circuitry is relatively simple, and the response time can be as short as within 100 ms depending on the polymer and the odor of interest. The greatest drawback of the conducting polymer sensor may be that it is too sensitive to humidity. For this reason, the interfacing circuitry must include an adaptation circuit capable of adapting to the background odor, responding to quick changes, and tuning out variations with long time constants.

Studies over the past 40 years have attempted to build commercial electronic nose instruments the size of a desktop, laptop, or palm device. One of the reasons these E-Noses are large is to perform odor signal manipulation and classification with demanding CPU computing power due to algorithm complexity. However, an electronic nose in many applications may be responsible for performing a

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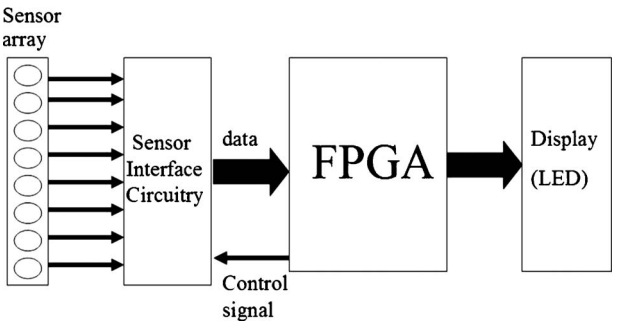

Fig. 1 Block diagram of the FPGA electronic nose system.

relatively simple task, so it does not require a very complicated algorithm, easing the demanding CPU high computing power. Thus, a portable electronic nose may be viable.

Although microcontroller units (MCUs) and advanced reduced instruction set computing (RISC) machine (ARMs) are small and have better computing capability, they require more power and more complicated control scheme than using a simple field-programmable gate array (FPGA). In addition, it is relatively easy to use an FPGA for future development of an integrated gas sensing chip with system-on-chip (SoC) design. Therefore, this study reports using an FPGA instead of a personal computer (PC), an MCU, or an ARM for fabricating the portable E-Nose system, composed of a miniaturized sensor array, electrical and mechanical hardware, and data acquisition and pattern recognition software. This report also includes the test results for the FPGA E-Nose system.

2 Experiment

Figure 1 is the block diagram of the FPGA electronic nose system. The system contains four blocks: the sensor array, the sensor interface circuitry, the FPGA, and the display. The sensor array interacts with the incoming odor; the sensor interface circuitry reads the sensor signal and digitally inputs the sensor data to the FPGA; and the FPGA controls the sensor interface circuitry, receives the sensor data, and performs signal processing and odor classification, and then displays the results.

2.1 *Single Gas Sensor Array Chip*

The sensor chip has 12 independent sensing spots on a single silicon substrate. Ten sensor array chips were fabricated on a 4-in Si wafer through the batch process. Figure 2 shows one sensor array chip obtained by sawing the wafer. The array chip is 100 mm × 30 mm. Eight sensing spots were coated with sensing elements, while the other four sensing spots were reserved for future addition of a humidity sensor, a temperature sensor, and a heating device, in order to further control the stability of the sensing system. Each sensing element contains a square membrane with an area of 10 mm × 10 mm to minimize heat loss to the Si substrate.

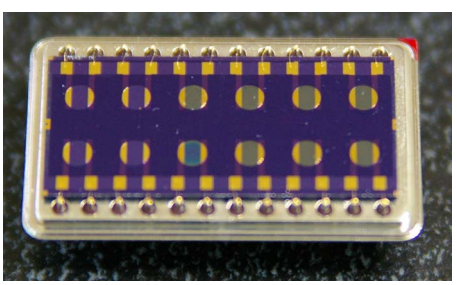

Fig. 2 Photo of sensor array.

Table 1 Polymer materials used in the sensor array.

Sensor no.	Polymer material
1	Poly(ethylene oxide) (PEO)
2	Ethyl cellulose (EC)
3	Poly(4-vinylphenol-co-methyl methacrylate) (PVCMM)
4	Polyethyleneimine (PEI)
5	Poly(vinylpropinoate) (PVPR)
6	Poly(epichlothydrin) (PECH)
7	Poly(isobutylene) (PIB)
8	75%-phenyl-25%-methylpolysiloxane (OV25)

2.2 *Sensor Array*

Table 1 shows the eight polymers, selected according to the linear solvation energy relationship (LSER), to enhance the capability of recognizing different odors. These polymers were mixed with 15 to 20 wt% of carbon black (Pearls 2000, Cabot) to make the composite solutions. Magnetic stir and ultrasonic oscillation achieved uniform dispersion. Next, uniformly mixed composite material was injected with a high-performance liquid chromatography (HPLC) syringe onto the chip. The sensor resistances were controlled to be within the range of 10 kΩ to 1 MΩ by repeating the drop-casting process. The solvent was removed by 24-h baking in a vacuum oven, which formed a composite membrane material.

2.3 *Experimental Setup*

Figure 3 shows the experimental setup used to characterize the sensing volatile organic compound (VOC) properties of the sensor devices. To perform the experiments, the sensor device was placed in a chamber. The gas under test was produced by a standard air generator (AID360). The solvent of the testing gas sat inside the diffusion tube of the standard air generator under room temperature. A constant heater was used to increase the temperature in the tube to cause the organic solvent to evaporate. By the time the whole system reached steady temperature and flow rate for the whole system, a testing gas with stable concentration was achieved. Diffusion rate can be theoretically controlled by the temperature setting, and air concentration can be accurately calculated by measuring the weight loss of the organic solvent. The testing gas was carried out by steady

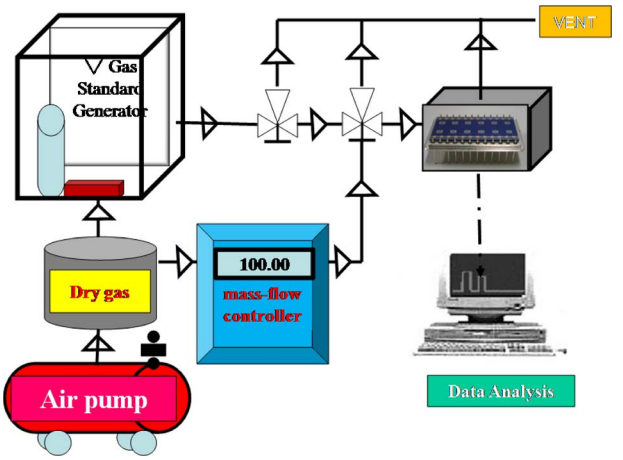

Fig. 3 Experimental setup of the E-Nose system.

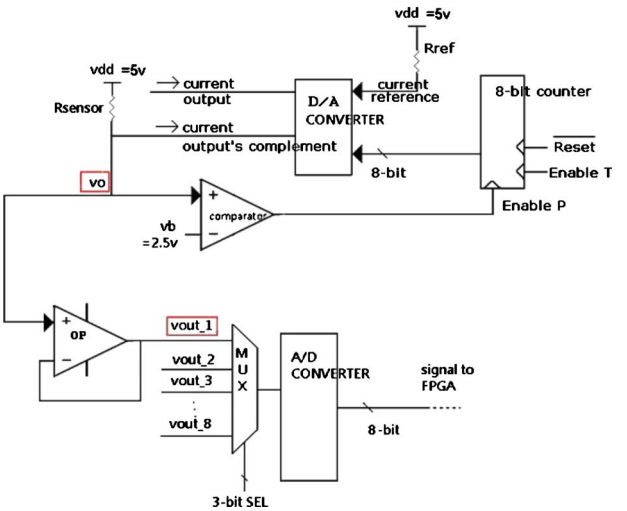

Fig. 4 Circuits implemented in the sensor interface circuitry.

air coming from the air compressor. The gas flow rate was controlled by the mass flow controller. The testing air was then infused into the glass chamber, where the sensor array sat. After completing the experiment, dry air was again used to purge the chamber. The output electric resistances of the sensors were measured by a digital multimeter with signals addressed by a multiplexer switch unit. The sensor array was wired to the remainder of the E-Nose system outside the chamber to perform signal manipulation and odor classification. For each test, the testing air was infused into the chamber for 1800 s (absorption), and then dry air was infused for another 1800 s (desorption).

2.4 *Sensor Interface Circuitry*

Since the sensor fabrication process cannot be easily controlled, sensor resistance may vary from 10 kΩ to more than 1 MΩ. The sensor resistance also drifts with background odor, temperature variation, water vapor, etc. Moreover, the sensor may not come back to the exact baseline after exposure, requiring auto-adjustable biasing for the sensor. Thus, the sensor interface circuitry must respond to quick changes while tuning out long-term constant variation, just like biological nose adaptation. Then, R_{max}/R_b information was extracted and converted to digital statistics through an analog to digital (A/D) converter to an FPGA for further computation, storage, analysis, and recognition. Figure 4 shows the circuit implementation.

3 Results and Discussion

3.1 *Result of Gas Sensing Experiments*

To understand the absorption and desorption phenomenon of gas sensors, this experiment placed a fabricated sensor device inside the sealed chamber filled with chemical vapors of different concentrations produced by a standard gas generator. The device was connected to the digital multimeter outside the sealed chamber through silver wires to continuously monitor resistance variation. Once the resistance value became stable, the current study conducted the gas absorption experiment for 1800 s. Observations showed a rise of resistance due to gas molecule absorption by the polymer sensor membrane during this period. After the gas absorption experiment, dry air was infused into the chamber for 1800 s for the gas desorption experiment. This experiment observed that the resistance dropped to its original baseline. This procedure of gas absorption and desorption experiments was repeated three times. The gas sensors were tested with three kinds of chemical warfare agent simulants: dimethyl-methyl phosphonate (DMMP), dichloromethane (DCM), and acetonitrile (ACN). Figures 5–7 show the radar charts of sensor responses to these three simulants. The radar charts reveal that ethyl cellulose (EC) and poly(epichlorhydrin) (PECH) show greater response for DMMP detection; EC and poly(4-vinylphenol-co-methyl methacrylate) (PVCMM) show greater response for DCM detection; and poly(ethylene oxide) (PEO), EC, and PVCMM show greater response for AN detection. These results show that the eight kinds of polymers selected by the LSER formula are highly capable of distinguishing these three gases. The patterns of these three chemical warfare agents' stimulants on radar charts are also very different from each other. Observations also showed a fast response time: the rise time is 30 s and the fall time is 60 s,

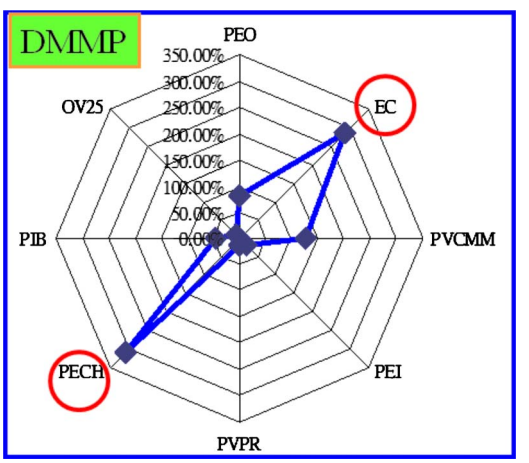

Fig. 5 Radar chart of the chemical warfare agent stimulant DMMP versus the sensitivities of eight different polymer sensor membranes.

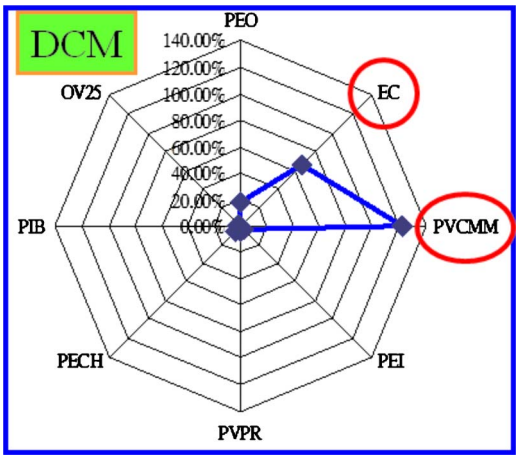

Fig. 6 Radar chart of the chemical warfare agent stimulant DCM versus the sensitivities of eight different polymer sensor membranes.

where the rise and the fall time are defined as the time needed for the signal to reach 90% of the peak maximum and to reduce to 10% of the peak maximum, respectively.

3.2 *Using Principal Component Analysis to Identify All Kinds of Gases*

This research used two major approaches for gas classification. The first approach used principal component analysis (PCA) on a PC or laptop. The second approach used an FPGA for classification to avoid the need for other computer equipment and to reach the goal of reducing the size of the overall sensor system. The principal component analysis method can reduce a large number of correlated channels (variables) to fewer numbers of independent linear combination variables. This maximizes the component variance obtained through linear combination and allows the tested gas to show maximum difference among different component channels. Figure 8 shows that by analyzing the experimental results of three different chemical warfare agent simulants through the principle component analysis

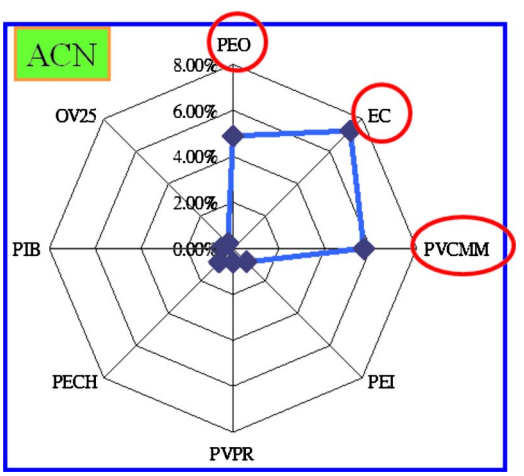

Fig. 7 Radar chart of the chemical warfare agent stimulant ACN versus the sensitivities of eight different polymer sensor membranes.

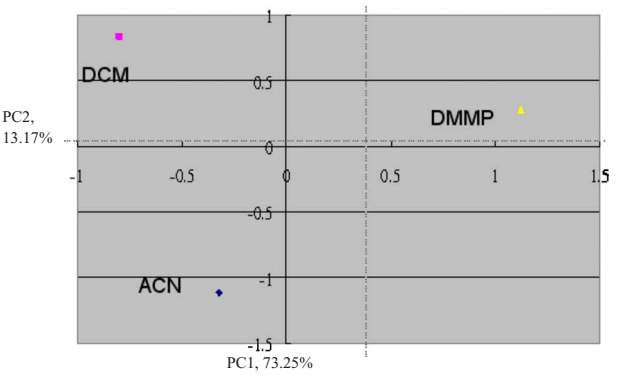

Fig. 8 Analysis of the three chemical warfare agent stimulants using the principle component analysis method.

method, the results fall on different coordinate locations that are far apart. Therefore, simply glancing at the plots obtained by PCA analysis easily confirms successful classification. Figure 8 shows the recognition boundaries of the three simulants in PCA plots displayed with the two main principal PC1 and PC2 axes. They clearly demonstrate that the three simulants have well-defined boundaries.

3.3 *Using the FPGA System*

Forming an array of sensors obtains a signal vector containing odor information. This signal vector is then sent to FPGA for signal processing. The proposed FPGA E-Nose system uses the Altera DE2 Board (Type DK-DE2-2C35N/UN-0A) to perform the designed tasks. Altera DE2 uses Verilog and runs simulation under the ModelSim environment. The FPGA is designed to perform four tasks, as described in the following sections.

3.3.1 *Steady state detection*

The signal vector is constantly sent to the FPGA, and thus the first function of the steady state detection block is to recognize whether an odor is coming in. This is achieved by scanning the sensor signal throughout the array and comparing it with a threshold. As long as one of the channels in the array exceeds the threshold, the system should recognize it as an odor coming in and activate all the circuits. Once the system is activated, the steady state detection block must detect when the sensor responses reach equilibrium. This is done by monitoring the sensor signals throughout the array with respect to its previous state. If no sensor signals change for a fixed time, the system should report steady state and go to the next step.

3.3.2 *Normalization*

The signal vector must be normalized before further processing, since the odor concentration is usually unknown. Studies have reported that the sensor response is linearly proportional to the vapor concentration.[17] Normalization can be performed in a number of ways—for example, Euclidean distance normalization, city-blocks distance normalization, maximum normalization, etc. The proposed FPGA E-Nose system adopts Euclidean distance normalization.

3.3.3 *Learning state*

If the FPGA E-Nose system is in the learning state, the normalized signal vector is stored in the memory as a data vector.

3.3.4 *Classifying state*

If the FPGA E-Nose system is in the classifying state, the normalized signal vector is compared with all the data vectors in memory to perform classification. Many algorithms can perform classification—for example, nearest-neighbor, support vector machine (SVM), PCA, discriminant function analysis (DFA), etc. This study implemented the nearest-neighbor classifier in the FPGA E-Nose because of its simplicity and good performance for odors that do not have very similar patterns. After conducting classification, the FPGA shows the result on the LED display. After the odor signatures of DCM and DMMP were recorded in memory, the E-Nose FPGA system was switched into its classifying state. The experiment tested the system six times. For all six tests, the FPGA E-Nose system was capable of recognizing both DCM and DMMP.

4 Conclusions

Most E-Nose system research has developed gas sensing systems controlled by PC or PDA and are limited in size. This research successfully used FPGA circuits to replace the aforementioned control instruments and successfully completed detection and classification experiments of two special gases. This research can be very helpful for future development of an integrated gas sensing chip with system-on-chip (SoC) design.

Acknowledgments

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