Introduction

The idea of an instrument to detect odors was first published by Hartman (1954) and Wilkens and Hartman (1964). The instrument consisted of eight electrochemical cells that gave different response patterns for different odorants. At the time no attempt was made to decipher the patterns that were generated by the device. Persaud and Dodd (1982) published 20 years later, the concept of an intelligent, chemical sensor array system to detect odors. Gardner coined the term "electronic nose" in 1988 and today defines it as "an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognizing simple or complex odors" (Gardner, 1988; Gardner and Bartlett, 1999). Subsequently, there has been a proliferation of papers as well as an increase in the number of companies working on electronic noses. Currently there are nine sensor types used in these instruments. The principle of operation includes conductivity, piezoelectricity, capacitive charge coupling, fluorescence chemoluminescence, molecular spectrum, atomic mass spectrum and transmitted light spectrum. All of these sensor types have advantages and disadvantages associated with them, and have been described by Nagle et al. (1998).

Unlike conventional chemical sensors, which use a single sensing element for the detection of a single analyte, an electronic nose is composed of sensor arrays of overlapping sensitivity and selectivity. Together with the appropriate pattern recognition algorithms, the e-nose mimics its biological counterpart, the human nose, with up to 100 million receptors of about 1,000 different types. These receptors are not uniquely sensitive to only one odor molecule but to many. It is therefore, the pattern of responses that the brain interprets and recognizes from past training (Gardner et al., 1990). Likewise, the e-nose sensor arrays respond in concert to a given odor to generate a pattern that it is analyzed with appropriate pattern recognition software compared to a stored pattern and recognized.

In this paper we describe sensors based on polymer-carbon black composites. These composites have been used as a sensing medium in electronic noses (Lonergan et al. 1996; Doleman et al., 1998; Ryan et al.,
Sensor arrays composed of a variety of polymers are used to respond to the largest number of analytes possible. The sensor elements are built from films of carbon black particles dispersed in a polymer matrix. The films are deposited across two metal electrodes. The conductivity in these systems arises from the carbon black while the selectivity to different analytes results from the polymer. These composites reversibly swell when exposed to a vapor or analyte, consequently increasing the electrical resistance of the composite (Figure 1). The increase in resistance results from the disruption of conductive paths, naturally present in these composites (Sichel, 1982; Johnson et al., 1997). Each sensor element gives rise to a unique change in resistance. Consequently a pattern of resistance changes is obtained from a given sensor array to a given vapor. Such patterns or fingerprints are unique for each combination of sensor array with the vapor of interest. The swelling mechanism has been probed for a sensor as it was exposed to an analyte using an environmental scanning electron microscope (Figure 2).

Sensor properties

Sensors’ response to analytes
The response of these sensors is expressed as the change in resistance over time (Figure 1). This temporal response signal is obtained by first passing air through the sensor array, followed by exposure to the analyte of interest, followed by purging the sensors again with air. Equilibrium may be reached within seconds or minutes depending on the type of polymer. The average response time varies depending on the sensor’s film thickness and can be as low as tens of milliseconds. A common way of reducing the response data for each sensor is to normalize the data for the base resistance \((R_{\text{max}} - R_0)/R_0\). This feature extraction provides a single number that is plotted for each sensor responding to an analyte, yielding a pattern (Figure 3). Note that the pattern for each analyte is different.

Classification of the analytes in Figure 3 can be better visualized via principal component analysis (PCA). PCA is a supervised pattern recognition technique that reduces the dimensionality of multivariate data sets into two or three dimensions (Beebe, 1998). PCA was applied to the response of the electronic nose to the analytes shown in Figure 3 and it is shown in Figure 4. The data were autoscaled to remove scaling effects and preserve the distances in the configuration space. No normalization was applied to the data. Note that discrimination is obtained even for propylene oxide and ethylene oxide, two compounds, which are chemically related.

Polymer-carbon black sensors can classify, detect and quantify many chemical vapors. The number of chemical vapors that can be detected is almost infinite using a large sensor array with polymers of diverse chemistries. Invariably, some redundancy is present though the polymers are different. The reason is that some polymers share similar properties, such as polarity, dipolar effects, hydrogen bond capability, etc. This is the reason why most polymers in a sensor array respond – however, the magnitude of the response differs.

Sensors’ sensitivity and linearity
Polymer-carbon black sensors are sensitive to a variety of vapors. The degree to which they are sensitive depends on both the analyte and the polymers. The sensitivity of these sensors is related to the vapor pressure of the analyte and it varies from ppb to ppm. The sensors’ response is inversely related to the analyte’s vapor pressure. Low vapor pressure (larger molecular weight) compounds tend to be detectable at very low levels (ppb) while very high vapor pressure compounds are detectable at the high ppm level (Doleman et al., 1998). This trend is due to the partition coefficient of the vapor between the solid
phase of the sensors and the gas phase of the area above the sensors. Low vapor pressure materials have a higher propensity for residing in the polymer, thus leading to a lower detection threshold. Many of these sensors show a linear response over a wide concentration range for many analytes (Figure 5).

**Sensors’ sensitivity to humidity**

Many polymer-carbon black composites respond linearly to relative humidity. Unlike other sensors in the market, these sensors do not degrade upon exposure to humidity. They in fact can discriminate even in the presence of high humidity (Figure 6).
Prototype system

An electronic nose requires the means to collect vapors, analyze the vapors, and report the results. Cyrano Sciences, Inc. has developed the prototype of a hand held electronic nose that contains a 32-polymer composite sensor array. Figure 7 shows a block diagram of the device.

The sampling system comprises a pump and a three-way valve arrangement that delivers air and the sample containing the vapor of interest. The sensors are deposited

Figure 5 The response to methyl ethyl ketone (top) and tetrahydrofuran (bottom) versus concentration

Figure 6 Results of PCA from the response of a 32-sensor array on three vapors in the presence of 66 percent RH

Figure 7 Block diagram of Cyrano’s prototype
on a ceramic substrate containing eight sensor elements as well as a heater and a thermistor, (Figure 8). The sample chamber also contains a humidity sensor and a temperature probe to monitor these variables.

The signals from the sensors are buffered and multiplexed to a 22-bit ADC that converts and feeds the data through the microprocessor to memory or to a serial port for use by a PC. Streaming data to the PC offers the capability to monitor, as well as massaging, the data with a variety of pattern recognition software such as PCA, neural networks, Fisher linear discriminant method, etc. Additionally, the unit microprocessor, memory and a simple built-in algorithm is sufficient for processing data. Hence, the unit can be used to train as well as identify any vapor. Up to seven response patterns can be stored in the unit’s memory. When used with a PC each sensor response can be observed in real time as well as the generated pattern.

The input/output features of the prototype include push-buttons for mode selection and operator control, a display for simple user/instrument communications, a serial port, and an external power supply source for a battery pack or wall transformer supply. The device can acquire data at a user-controlled rate that also determines the resolution of the system. Running the system at more than 30 measurements per second, the resolution is under 10 ppm.

**Applications**

The applications cited for e-noses range from quality control to the detection of disease in humans as well as in animals. Currently, the quality control of products in the flavor and fragrance industries rely on the use of sensory panels. In most instances, the panel is rating a material on a scale of one to four representing very similar, similar, different or very different. This test can be very objective since it does not account for the panel’s adaptation and fatigue, variability between individuals, experience, etc., and it is accurate only when used with a large panel (where averages are taken). Hence, these industries have already begun to benefit from e-nose technology (Johnson et al., 1997). Unpleasant odors from grains, such as ergosterol, and other volatiles given off by bacteria and fungi were detected with an e-nose by Johnson et al. (1997) and Borjesson et al. (1996).

The usefulness of the e-nose has been demonstrated in a number of other applications such as assessing livestock wastes (Hobbs et al., 1995), monitoring airborne pollen levels (Kalman et al., 1997), monitoring waste-gas treatment processes (Homan...
and Fodisch, in press), and many others. In the area of medicine, an e-nose was used to monitor the health of dairy cattle by detecting levels of dimethyl sulfide, methane, 2-butanone, and acetone in the cow nasal breath (Elliot-Martin et al., 1997). The number of applications for the e-nose continues to see an increase and it will not be long before these devices become part of everyday living.

Conclusions

A new type of sensor array used in electronic nose technology was described. These sensor arrays can easily detect, classify and quantify a large number of vapors. These sensors are very reliable, giving repeatable results and can be reproducibly manufactured. They also do not degrade when exposed to humidity or to large temperature fluctuations. They can easily be constructed from mixtures of carbon black and polymer in a solvent. The system performance is similar in response to the human nose and will enable applications as diverse as detection of leaks in petrochemical plants, quality control and detection of disease in humans and animals.

References


