ELECTRONIC NOSES: MULTI-SENSOR ARRAYS

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1. INTRODUCTION

Development of the electronic nose was prompted by the desire for an inexpensive, quick, and portable device capable of quantifying complex mixtures of volatile compounds. Gas chromatography has proven too expensive and time consuming for the widespread use planned for the electronic nose. The realization of the electronic nose was made possible by using the human olfactory system as a paradigm.

The human olfactory system consists of sensory tissue, which is an area of thin epithelium that is located in the upper portion of the nose. The tissue contains approximately fifty million olfactory receptor neurons. Each of these neurons has a dendrite that ends in a bulb, from which cilia extend. G-protein binding receptors are located at the surface of the cilia and act as chemosensory receptors. It is believed that the specificity and sensitivity of the mammalian nose is a result of receptor cells with partially overlapping sensitivities. The olfactory bulb and brain determine patterns in the partially overlapping signals and identifies the odor class or odor compound.

Currently, several sensors are commercially available, where the two most prominent sensors being used are surface acoustic wave (SAW) sensors and tin oxide gas sensors. With the advent of new sensors and new sensor coatings, applications of these multi-sensor arrays have been extensive.

This paper will provide a general overview of electronic noses. Background information on odor molecules, requirements for sensors, system structure, sensor types, and future applications will be detailed.

2. ODOR MOLECULES

Odor molecules are small and hydrophobic organic compounds with molecular masses in the range of 18-300 Daltons.[1] Although there are exceptions, odor molecules usually contain a single polar group. Most molecules with more than one polar group are involatile and the bulk of odorants contain oxygen in the polar group. Shape, size and polar properties of a molecule determine its odor properties. Another trend observed is that the position of functional group is more important than the type of functional group. The threshold value of an odorant is significant since molecules with a low threshold can have a large effect on the perceived odor. The intensity curve of the odorant is also influential. Odorants with a high intensity are less volatile and thus have smaller concentrations in the air.

3. REQUIREMENTS FOR ODOR SENSORS

It is believed that the chemosensory receptors in the human nose are receptive to a wide range of compounds. The brain separates these overlapping signals to classify the nature of the compound. Since the mammalian nose has been used as a model for the electronic nose, it is necessary that an array of sensors with partially overlapping sensitivities be implemented. Sensors that are specific to one compound are not only difficult to produce, but are impractical since it would take thousands of sensors to be able to detect common odors.

It is also necessary that odor interaction with sensor material is reversible, response drift is negligible, training protocols be relatively intuitive, and calibration and sensor preparation are replicable.

Practical considerations for a portable instrument place additional restraints including power consumption, memory requirements, size, and sensor types.

4. TYPES OF SENSORS

A number of different sensors have been developed for multi-sensor arrays. Table 1 shows a list of measurable quantities and type of sensors used to measure these quantities. Surface acoustic wave sensors and tin oxide sensors are predominantly used and are commercially available.

4.1 METAL OXIDE SENSORS

Tin oxide sensors are the most common metal oxide sensors used. These sensors have a high sensitivity to a wide range of organic vapors. A variety of tin oxide sensors are available that have broadly overlapping sensitivities allowing an array to be constructed. Tin oxide sensors are thick film devices made by coating a film of tin oxide onto a tubular ceramic former through which a heater is run.[2] To change sensitivity of the sensor, doping materials such as Pd or Pt are added.

Tin oxide is an intrinsically *n*-type bulk semiconductor.[3] Oxygen is always present in the eluent of tin oxide sensor arrays and upon exposure to oxygen, the oxygen is physi- or chemisorbed onto lattice vacancies in the semiconductor (eq 1), where n is an electron from the conduction band. The loss of the electron results in a decrease in conductance and a depletion layer is formed. When an odorant is present, R, the adsorbed oxygen species reacts and is removed from the surface allowing the electron to flow back into the conduction band thereby increasing the conductance (eq 2). Figures 1 and 2 detail the changes in conduction and valence bands associated with the processes described in equations 1 and 2.

$$n + 1/2\ O_2 \leftrightarrow O(s)^- \qquad (1)$$

$$R(g) + O(s)^- \rightarrow RO(g) + n \qquad (2)$$

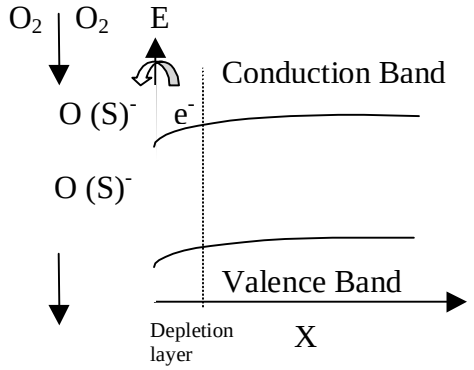

Figure 1. Oxygen is physi- or chemisorbed onto semiconductor surface and an electron from the conduction band is lost creating a depletion layer. This decreases the conductance of the semiconductor.

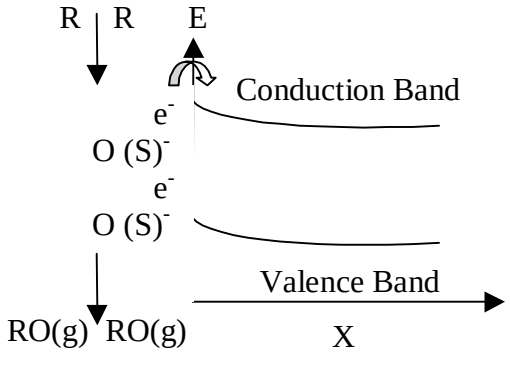

Figure 2. When an odorant molecule, R, is present it reacts with the adsorbed oxygen, is removed from the surface, and releases and electron into the conduction layer. This increases the conductance of the semiconductor.

Tin oxide gas sensors must be operated between 300-500°C since water absorbs strongly to the surface of tin oxide. The response time is only 20 seconds and the adsorption mechanism is repeatable instantly. Concentration dependence of the response in non-linear and is described by equation 3.[4]

$$\Delta G_{\infty}=Ac^{r} \quad (3)$$

Where ΔG_{∞} is the steady state conductance change, A is constant, c is the gas concentration, and r is an index from 0.3-1.0.[4]

4.2 SURFACE ACOUSTIC WAVE (SAW) SENSORS

Work on the combination of SAW arrays with organic polymer films began in the 1980's at the Naval Research Laboratory.[5] *Ricco et al*. describes a library of materials from which sensor coatings can be formed including alkanethiol-based self assembled monolayers(SAMs), plasma-polymerized films (PPFs), Plasma Grafted Films (PGFs), thin film based on dendrimeric polymers, metal thin films, organometallic semiconductors, and porous oxides.[6] *Kellers* describes optimal coating selections for SAWs using a combination of extended disjoint principal components regression (EDPCR) pattern recognition analysis with Monte Carlo simulations.[7] Changes in the mass, pressure, temperature, mass, film mechanical properties, conductivity, or dielectric coefficient affect the concentration dependent frequency shift which is followed using an oscillation circuit loop.[6] Figure 3 shows a picture of the SAW with the chemically sensitive layer covering the piezoelectric substrate.

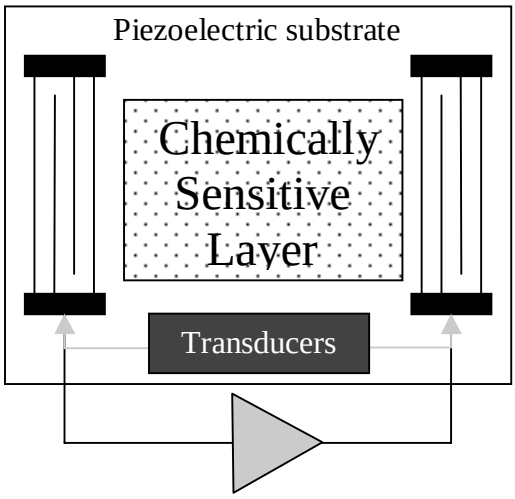

Figure 3. Surface Acoustic Wave (SAW) sensor with oscillator circuit transducers and signal amplifier.

Change in mass measurements can be made to as accurate as 100 pg cm^{-2}.[6] The change in mass is proportional to the change in oscillation frequency as given by equation 4.[6]

$$\Delta f/f_0 = -\kappa c_m f_o \Delta(m/A) \quad (4)$$

Where f_0 is the unperturbed oscillation frequency, κ is the fraction of the center-to-center distance between transducers being perturbed, c_m is the coefficient of mass sensitivity, and $\Delta(m/A)$ is the change of the mass to area ratio.

5. STRUCTURE OF ELECTRONIC NOSES

Figure 1 shows the architecture scheme for most multi sensor arrays. The chemical input typically takes form as a headspace auto sampler or purge and trap instrument for low concentration volatiles. The sensor array consists of two or more sensors with partially overlapping sensitivities. Discrete sensors can also be used if detection of a specific compound is desired.

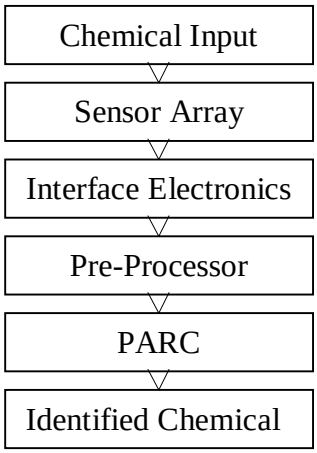

Figure 4. Architecture scheme for an electronic nose.

5.1 Sensor Array.

The sensor array is made up of several sensors whose number depends on the analysis to be performed. With each sensor an additional point in vector space is created. The more points in space, the better the system is able to discriminate between analytes. There is a limit of effectiveness and mathematical calculations can be extremely time consuming with each new addition to the feature space.

There are three concept for sensor array construction:

1) The several sensors, one transducer approach. This approach consists of using the same type of sensor, but with each sensor having a different sensitivity. In this model, only one property of the sensor is measured. For example several tin oxide sensors can be doped with different amounts of Pd or Pt to change selectivity and resistance can be measured for each sensor.
2) The several parameters, one sensor approach. In this method, several independent parameters of the same sensor material are recorded. For instance optical thickness, mass change, conductivity, temperature, etc, can be measured simultaneously.
3) Parameter modulation approach. In this approach either the operation conditions of the sensor are altered or the composition of the gas is changed. Modulation of the operation conditions depends upon the transducer. For example to enhance the

feature space of tin oxide gas sensors the operating temperature can be altered or the potential of the measuring electrodes can be changed.[8] Modulation of the gas composition is achieved by switching between a reference gas and test gas, while observing the dynamic response of the sensor.[8]

5.2 Interface Electronics.

Interface electronics usually consist of an analog to digital converter. The pre-processor is used to alter electrical signals from the sensor array and defines the sensor array parameter that feeds into a pattern recognition (PARC) technique. Parameters are defined by the difference or relative model. In the difference model the difference between resistance or conductance of the analyte relative to air is calculated, while in the relative model, the ratio of resistance or conductance of the analyte to air is calculated.

5.3 PARC.

The PARC technique is the pattern recognition algorithm, which extracts useful information from sensor outputs. Typical PARC techniques include principal component analysis, feature weighting, artificial neural network, cluster analysis, and discriminant function analysis. In a supervised PARC technique input patterns are learned and associated with an odor class. I an unsupervised PARC technique, the multidimensional configuration space from the preprocessor is converted into a feature space. The unknown chemical is identified by comparison to a knowledge base, from a previous learning scheme.[9]

6. PATTERN RECOGNITION TECHNIQUES

Due to the nature of the partially overlapping sensitivity of the sensors in the sensor array, pattern recognition techniques are necessary for analyte discrimination. The most common pattern recognition techniques used are principal component analysis, feature weighting, artificial neural networks, cluster analysis, and discriminant function analysis. Principal component analysis, feature weighting, and artificial neural network techniques will be discussed in further detail since these pattern recognition techniques are most common. Cluster analysis and discriminant function analysis are described in further detail in Gardner and Bartlett.[10]

6.1 PRINCIPAL COMPONENT ANALYSIS.

Principal Component Analysis is a linear data reduction technique, which reduces multivariate data into two dimensions. Assume that the output from a series of sensors, x, is a variable with a mean, μ, and a covariance matrix, Σ, where $x^T = [x_1, x_2, \ldots x_n]$.[8] In PCA a set of new variables are found which are uncorrelated and whose variance decrease. These variables are called the principal components and they are related to the original variables by equation 5.[9] The first principal component, Y_1, is found by setting a_1 so that the variance of Y_1 is maximized. The second principal component, Y_2, if found by choosing a_2 so that the variance of Y_2, is largest for the data uncorrelated to Y_1.[9] Further detail on the mathematical analysis is provided elsewhere.[11] Figure 5 shows a representative PCA plot in which multivariate data was reduced to two dimensions using PCA.

$$Y_n = a_{1n}x_1 + a_{1n}x_1 + \ldots a_{1n}x_1 \quad (5)$$

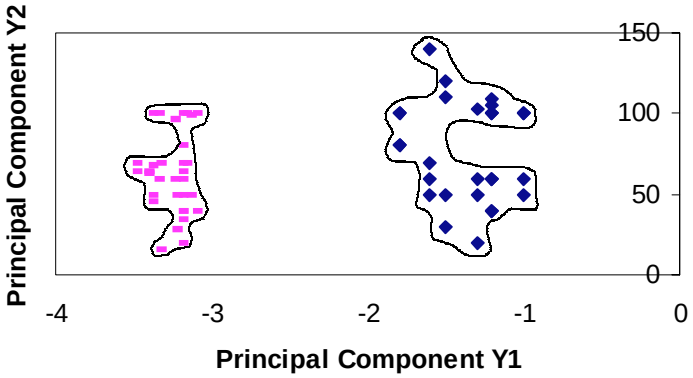

Figure 5. Representative PCA plot for the reduction of multivariate data to two dimensions using principal component analysis.

6.2 FEATURE WEIGHTING.

Feature weighting increases the separation of data in feature space by a simple mathematical transformation. The standard deviation, σ, must be known in the x and y directions for each analyte. Each point on the scattergram is then transformed as described by equation 6. Figure 6 and 7 show a representative scatter gram and feature weighted plot, respectively.

$$(x_1,y_2) \rightarrow (x_1/\sigma_1, y_2/\sigma_2) \quad (6)$$

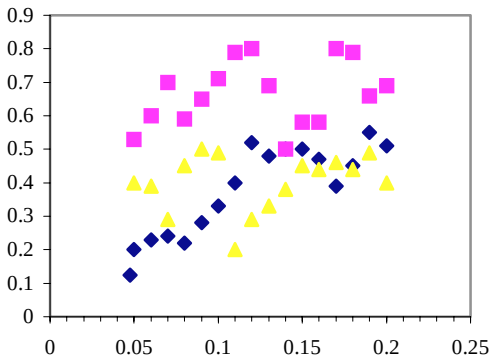

Figure 6. Scattergram for three odor analytes.

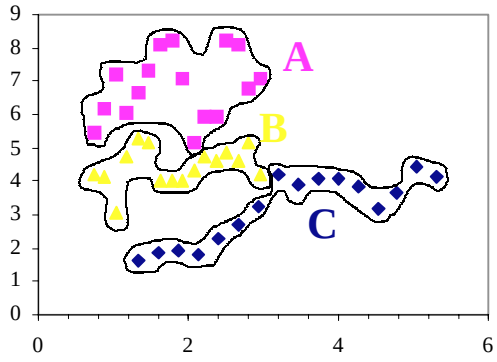

Figure 7. Feature weighting transformed the original data to separate the three odor analytes into three different classes.

6.3 ARTIFICIAL NEURAL NETWORKS

The problem with principal component analysis and feature weighting is that both of these techniques are linear transformations, while the data has a nonlinear response. The understanding of the olfactory bulb and the brain has led to the creation of Artificial Neural Networks (ANNs) that separate complex overlapping signals. In addition to dealing with nonlinear data, ANN can cope with noisy or drifting data. The network consists of several

artificial neurons as shown in Figure 8. Several artificial neurons are connected in the network as shown in Figure 9. Equation 7 describes the weighting and summation of each signal and Equation 8 describes the activation function, F.

$$Y_i = \Sigma\, w_n x_n \qquad (7)$$

$$F:\ O_i = 1/[1+ \exp(-Y_i)] \qquad (8)$$

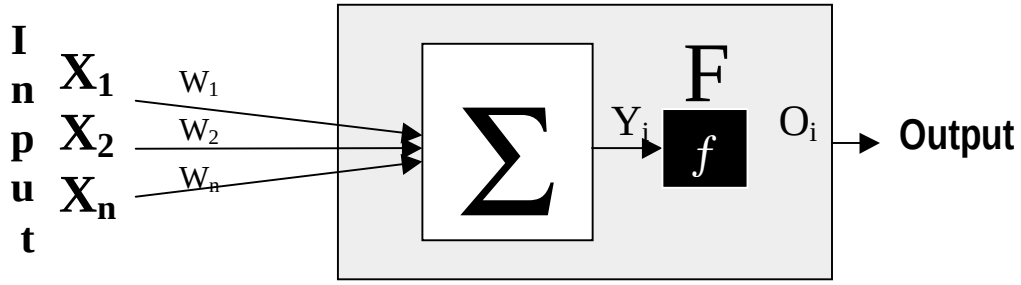

Figure 8. Schematics of an artificial neuron. Input signals, x_n, from n sensors are multiplied by a weighting factor, w_n, and then summed. The activation function, F, squashes the data and sets the output to O_i.

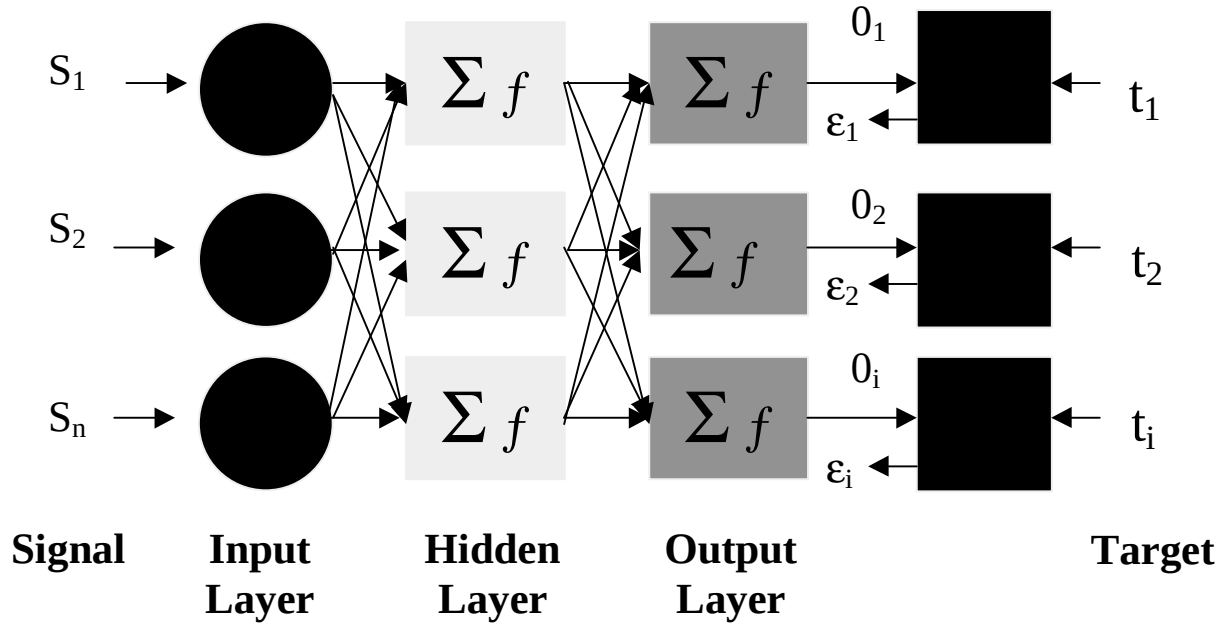

Figure 9. Artificial Neural Network. Structure of a two-layer back-propagation network with n artificial neurons in the hidden layer. The number of artificial neurons in the output layer is equal to the number of odors being analyzed. The network is trained onto a target output.

The two-layer back propagation network shown in Figure 9 is the model proposed by Rumelhart and McClelland.[12] The output from each sensor, S_n, is fed into an input layer, which distributes the pure signal to the first artificial neuron in the hidden layer. The output from the hidden layer is then fed into each of the artificial neurons in the output layer. The number of artificial neurons in the output layer is equal to the number of analytes being evaluated. Identification of the compound or class of compounds is possible based upon the output, O_i, of the Output layer. The network must first be trained with known standards. For example known odor, 1, is trained onto a target output t, e.g. $t_1^T = [1,0,0,0,0]$.[8] The number of components in this vector is equal to the number of outputs from the output layer. The target output, t_i, and the actual output, O_i, are compared using equation 9 and 10,

$$\Delta_i(m) = \eta\delta x_i + \alpha\Delta_i(m) \qquad (9)$$

$$w_n(m+1) = w_n(m) + \Delta_n(m+1) \qquad (10)$$

where δ is the difference between t_1 and O_i, η is the learning rate which determines the magnitude of the change in the weightings, and α is the momentum coefficient which improves the stability of the learning process. This process is performed for thousands of iterations until the error is reduced to less than 0.2. Once the network is trained it requires less than 32K of RAM and a slow 6800 series microprocessor making it ideal to be used for portable analysis.

7 APPLICATIONS OF ELECTRONIC NOSES.

The potential applications for electronic noses are widespread. It is hypothesized that electronic noses will be used in every home to monitor complex mixtures of gases. To date, electronic noses are too expensive and difficult to operate to be used commercially. Several manufacturers have planned to develop commercial instruments in the coming years. Thus far traditional electronic sensor arrays have been shown to monitor fish freshness[13], identify coffee origin[14], identify complex mixtures of alcohols[9], differentiate between mixtures of 39 organic vapors[15] and detect hazardous waste composition[16]. These practical applications have used the techniques described previously in this paper. This section will therefore detail two advances in sensor array analysis. The first uses catalysts to modulate the gas composition of a mixture before it reaches the sensor array. The second is the development of a sensor array system based upon the MOdular SEnsor Systems approach (MOSES).

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