Review

Applications of electronic noses and tongues in food analysis

Anil K. Deisingh,*† David C. Stone & Michael Thompson

Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario M5S 3H6, Canada

(Received 23 June 2003; Accepted in revised form 25 February 2004)

Summary

This review examines the applications of electronic noses and tongues in food analysis. A brief history of the development of sensors is included and this is illustrated by descriptions of the different types of sensors utilized in these devices. As pattern recognition techniques are widely used to analyse the data obtained from these multisensor arrays, a discussion of principal components analysis and artificial neural networks is essential. An introduction to the integration of electronic tongues and noses is also incorporated and the strengths and weaknesses of both are described. Applications described include identification and classification of flavour and aroma and other measurements of quality using the electronic nose. The uses of the electronic tongue in model analyses and other food, beverage and water monitoring applications are discussed.

Keywords

Beverage analysis, biosensor, food analysis, pattern recognition, sensor arrays.

Introduction

In the past decade, many papers have appeared in the literature describing the uses of electronic noses and, more recently, electronic tongues. These devices are typically array of sensors used to characterize complex samples. Arrays of gas sensors are termed ‘electronic noses’ while arrays of liquid sensors are referred to as ‘electronic tongues’ (Stetter & Penrose, 2002). The former group are used in quality control and process operations in the food industry while the latter are widely used in taste studies. In this review, we will discuss the principles behind the design of electronic noses and tongues, describe the senses of taste and smell and evaluate the various uses of these devices.

Development of sensors

The principles of sensor design and technology will be described in this section. This is necessary to both fully understand the subject and to also appreciate their impact upon the development of the electronic noses and tongues.

A chemical sensor is a device which responds to a particular analyte in a selective way by means of a reversible chemical interaction and can be used for the quantitative or qualitative determination of the analyte (Cattrall, 1997). All sensors are composed of two main regions: the first is where the selective chemistry occurs and the second is the transducer. The transducer allows the conversion of one form of energy to another. The chemical reaction produces a signal such as a colour change, fluorescence, production of heat or a change in the oscillator frequency of a crystal (Cattrall, 1997). Other parts of a sensor include the signal processing electronics and a signal display unit. The major regions of a typical sensor are shown in Fig. 1.
Several categories of transducers are available and these include:
1. Electrochemical, such as ion-selective electrodes (ISE), ion-selective field effect transistors (FET), solid electrolyte gas sensors and semiconductor-based gas sensors.
2. Piezoelectric, e.g. surface acoustic wave (SAW) sensors. Piezoelectric materials are sensitive to changes in mass, density or viscosity and, therefore, frequency can be used as a sensitive transduction parameter (Hall, 1990). Quartz is the most widely used piezoelectric material because it can act as a mass-to-frequency transducer.
3. Optical, such as optical fibres, as well as the more traditional absorbance, reflectance, luminescence and surface plasmon resonance (SPR) techniques.
4. Thermal systems, in which the heat of a chemical reaction involving the analyte is monitored with a transducer such as a thermistor.

A subdivision of the sensor grouping is the biosensors. These incorporate a biological sensing element positioned close to the transducer to give a reagentless sensing system specific for the target analyte (Hall, 1990). This ensures specificity of the biological molecules for target species.

What follows is a brief review of the evolution of sensors as this illustrates how developments in the field arose. The first sensor was the glass pH electrode, which appeared in 1930. Initial developments were slow and it was not until 1956 that a significant invention was reported. This was the Clark oxygen electrode, which spurred research in biomedical areas (Thompson & Stone, 1997). The piezoelectric mass deposition sensor (quartz crystal microbalance, QCM) was produced in 1959. In 1961, a solid electrolyte sensor was reported while in 1962, the first biosensor (an enzyme electrode) was described by Clark & Lyons (1962). In this case, glucose oxidase was held between membranes and the concentration of oxygen in an internal solution was measured. The platinum electrode responded to the peroxide produced by the reaction of the enzyme with its substrate:

\[
glucose + oxygen \rightarrow \text{gluconic acid} + \text{hydrogen peroxide}
\]

This investigation led to the production of the first glucose analyzer for measuring glucose in blood.

Also in 1962, a metal oxide semiconductor gas sensor (the Taguchi sensor) was reported and this was followed, in 1964, by the piezoelectric bulk acoustic wave (BAW) chemical vapour sensor. In 1966, the first glucose sensor and a fluoride ISE were reported in the literature. Many ISEs are available and they are very popular as the basis of electronic tongues. The advantages of ISEs include the linear response that they show and the ability to obtain direct potentiometric measurements. They also measure ion activity of the ions rather than the total content.

The 1970s and 1980s saw many developments including the ion-selective FET (1970), a fibre optic gas sensor (1970), a palladium gate FET hydrogen sensor (a metal oxide semiconductor FET or MOSFET, 1975), an enzyme FET biosensor (1977) and the SAW vapour/thin film sensor (1979). In 1980, a liquid-phase BAW operation was described while in 1982 the SPR sensor made its debut. An evanescent wave fibre optic sensor was developed in 1984 and in 1986 there was the production of a BAW liquid-phase immunosensor. Further details of these systems are given in the succeeding sections.

Since then, there has been the refinement of the various device technologies leading to the production of arrays of sensors (as used in electronic noses and tongues), microarrays and the development of micro-Total Analytical Systems (µm-TAS). The last category is also known as lab-on-a-chip or as...

integrated systems as they incorporate all analytical operations on a single chip.

Sensor arrays

Four major categories have been involved in the development of electronic noses and each will be briefly described.

1 Catalytic or tin oxide sensor: A commercially available Taguchi Gas Sensor (TGS) can be and is widely used as the core-sensing element in array-based odour detectors. This consists of an electrically heated ceramic pellet upon which a thin film of tin (II) oxide doped with precious metals is deposited (Persaud & Travers, 1997). Tin (II) oxide is an n-type semiconductor and when oxygen adsorbs on the surface, one of the negatively charged oxygen species is generated depending on the temperature. This results in the surface potential becoming increasingly negative and the electron donors within the material become positively charged. When an oxidizable material comes into contact with the sensor surfaces the adsorbed oxygen is consumed in the resulting chemical reaction. This reduces the surface potential and increases the conductivity of the film. Several recent developments with tin oxide detectors have led to further advantages over the Taguchi sensor, which generally requires high power consumption and high temperatures. These include the fabrication of thin-film tin (II) oxide arrays using planar microelectronic technology leading to reduced size and lower power use, the production of thin-film sensors by chemical vapour deposition and the use of screen printing to make thick-film sensors (Persaud & Travers, 1997).

2 Conducting polymer sensors: Many other materials are conducting (or semiconducting) and show a variation in conductivity with sorption of different gases and vapours. Conducting polymers are very popular in the development of gas- and liquid-phase sensors with polypyrrole and polyaniline being the favoured choices. Materials used to make conducting polymers tend to have some common features, including the ability to form them through either chemical or electrochemical polymerization and the ability to change their conductivity through oxidation or reduction. Conducting polymers are widely used as odour-sensing devices, the major reasons for this being (Persaud & Travers, 1997):
(a) the sensors display rapid adsorption and desorption phenomena at room temperature;
(b) power consumption is low;
(c) specificity can be achieved by modifying the structure of the polymer;
(d) they are not easily inactivated by contaminants;
(e) they are very sensitive to humidity.

3 Acoustic wave sensors: AT-cut quartz crystals (+35° 15’ orientation of the plate with respect to the crystal plane) are favoured as piezoelectric sensors because of their excellent temperature coefficients. The type of acoustic wave generated in piezoelectric materials is determined by the crystal cut, thickness of the material used and by the geometry and configuration of the metal electrodes employed to produce the electric field (Thompson & Stone, 1997). One of the first sensors to be introduced was the thickness-shear mode (TSM) sensor, which, if the substrate is quartz, may commonly be termed the QCM or BAW sensor. A typical TSM sensor is shown in Fig. 2. The sensor consists of overlapping metal electrodes at the top and bottom and the device is normally 1.56 mm thick and 12.5 mm in diameter. This type can be used with up to 10 MHz fundamental resonance frequency with a standing resonant wave being generated where the wavelengths are related to the thickness. As the thickness increases (for example, due to added mass by deposition on the surface), the wavelength increases and the frequency decreases. Thus, the TSM can act as a mass-sensitive device. A major advance on the TSM sensor was the SAW version consisting of interdigitated electrodes fabricated on to quartz containing a thin film of material (Fig. 3). When a potential is applied across the two halves of the interdigital transducer (IDT), a surface Rayleigh wave is launched in both directions across the surface from the IDT. Adsorption of odours to the coating results in a change in mass and the acoustic wave is perturbed leading to a frequency shift (Persaud & Travers, 1997). SAW sensors can be operated at higher frequencies than QCM sensors thereby leading to better sensitivities. Acoustic wave sensors can also be operated in the liquid-phase.

4 MOSFET technology: In the 1970s, improvements in semiconductor technology led to the devel-
Development of a FET. This is a very high impedance transistor and the most sensitive measurements of small potentials requiring very low current flows are made using this technology. In the FET, current flows along a semiconductor path called the channel, at one end of which is a source electrode. At the opposite end is the drain electrode. The effective electrical diameter of the channel can be varied by application of a voltage to a control or gate electrode. The conductivity of the FET depends on the electrical diameter of the channel. A small change in gate voltage leads to a large variation in current from the source to the drain. This allows the signal to be amplified. For the MOSFET, the thermal oxidation process used to form the silicon dioxide layer on the silicon surface of the device also forms a double layer, which can induce a conducting channel in the silicon substrate. In the MOSFET, the conducting channel is insulated from the gate terminal by a layer of oxide. Thus, there is no conduction even if a reverse voltage is applied to the gate. FET sensors can be operated both with and without a reference electrode. Other chemical principles are being applied to vapour-sensing devices and these include:

5 Ion mobility spectrometry (IMS) which has the ability to separate ionic species at atmospheric pressure. However, there is also research underway to develop low-pressure IMS systems. This latter technique can be used to detect and characterize organic vapours in air. This involves the ionization of molecules and their subsequent drift through an electric field. Analysis is based on analyte separations resulting from ionic mobilities rather than ionic masses. A major advantage of operation at atmospheric pressure is that it is possible to have smaller analytical units, lower power requirements, lighter weight and easier use (Graseby Ionics, 2002).

6 Other mass spectrometric (MS) techniques that are in commercial development. Two recent developments in MS are atomic pressure ionization (API) and proton transfer reaction (PTR). Both are rapid, sensitive and specific and allow measurements in real-time. Additionally, they do not suffer the drift or calibration problems currently experienced by electronic noses. With API-MS, ionization takes place at atmospheric pressure, which allows nebulization and ionization to be independent of each other. The solute and the solvent elute from a capillary, which is surrounded by the nebulizing gas, usually nitrogen. The capillary and gas are contained in a probe which can be heated up to 700 °C depending on the analyte being investigated. The combination of nebulizer gas and heat convert the solvent flow into an aerosol, which evaporates rapidly. Inside the heated source is a corona discharge needle, which ionizes the solvent molecules. In the atmospheric region around the corona pin, a combination of collisions and charge transfer reaction produces a chemical ionization reagent known as gas plasma. Sample molecules which elute and pass through this region can be ionized by the transfer of a proton to produce (M + H)⁺ or
ions (Ashcroft, 1997). The impact of volatile organic compounds (VOCs) on the environment has led to a growing demand for devices to detect these compounds. One of the most promising uses the proton transfer reaction (PTR)-MS, with the first instruments just appearing on the market (Ellis, 2003). As a result of the advantages listed above, these may play an increased role in the future development of electronic noses and tongues. However, a limitation is the use of quadrupole MS, which has a modest mass resolution and can only monitor a single mass channel at any moment (Ellis, 2003). Research is currently underway to replace the quadrupole system by a time-of-flight MS, which will allow more rapid data acquisition.

Optical/spectroscopic techniques are being currently employed, the most popular being the use of fibre optics and fluorescence.

For the electronic tongue, classical electrochemical principles such as potentiometry, amperometry and voltammetry have been utilized. When designing potentiometric devices, ion-selective and redox electrodes are commonly used. Additionally, ISFET technology has been incorporated into commercially available electronic tongues. Many of the available electronic tongues are based on ISEs and a brief discussion of the principles behind this technique will now be given.

Otto & Thomas (1985) reported the first application of ISE arrays for multicomponent analysis. Eight sensors were used for the simultaneous determination of sodium, potassium, calcium and magnesium at concentrations typical of biological fluids. However, there was insufficient selectivity for magnesium and sodium. Since then, multisensor arrays have become much improved with greater selectivities being reported.

Potentiometry generally assumes a linear dependence between an ISE output and the logarithm of activity of the primary ion in a solution. The electrode response should obey the Nernst equation:

\[ E = E^0 + (RT/Z_i F) \ln a_i, \]  

where \( E \) is the potential difference of the electrochemical cell comprising an ion-selective and a reference electrode, \( E^0 \) is the standard potential, \( R \) is the gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday constant, \( Z_i \) is the electrical charge of the primary ion and \( a_i \) is the activity of the primary ion. The term \( RT/Z_i F \) is the sensitivity of the ISE (Legin et al., 2002a).

If there are interfering ions on the ISE response, the Nikolsky eqn 2 is used:

\[ E = E^0 + (RT/Z_i F) \ln a_i + \Sigma K_{ij}(a_j)Z_j/Z_i, \]  

where \( K_{ij} \) is the selectivity coefficient of the ISE to the primary ion \( i \) in the presence of an interfering ion, \( j \), and \( Z_i \) and \( Z_j \) are the charges of the primary and interfering ions, respectively (Legin et al., 2002a).

### Sensations of taste and smell

#### Taste

The taste buds, of which there are around 10 000, are found mainly on the tongue with a few on the soft palate, inner surface of the cheek, pharynx and epiglottis of the larynx (Marieb, 1998). Taste sensations can be classified into five basic categories: sweet, sour, salty, bitter and umami. Table 1 gives examples of each of these.

A single taste bud contains 50–100 taste cells representing all five taste sensations. Each taste cell has receptors which bind to the molecules and ions which result in the different taste sensations (Kimball, 2002). Also, some materials change in flavour as they move through the mouth, e.g. saccharin is initially sweet but has a bitter aftertaste at the back of the tongue (Marieb, 1998). Each of the basic taste sensations has a different threshold level with bitter substances having the lowest. This is probably a protective function as many poisonous substances are bitter (Tortora & Grabowski, 1996). Sour substances have an intermediate threshold limit while sweet and salty

<table>
<thead>
<tr>
<th>Sensation</th>
<th>Elicited by these compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweet</td>
<td>Sugars, amino acids, alcohols</td>
</tr>
<tr>
<td>Sour</td>
<td>Acids, e.g. acetic, citric</td>
</tr>
<tr>
<td>Salty</td>
<td>Table salt</td>
</tr>
<tr>
<td>Bitter</td>
<td>Quinine, caffeine, aspirin, nicotine</td>
</tr>
<tr>
<td>Umami</td>
<td>Monosodium glutamate (MSG), disodium inosinate in meat and fish disodium guanylate in mushrooms</td>
</tr>
</tbody>
</table>

Table 1 Taste sensations (Marieb, 1998)
materials have the highest threshold values. Partial adaptation to a taste occurs in about 3–5 s with complete adaptation in 1–5 min.

Smell

The human sense of smell can recognize and discriminate volatile compounds with high sensitivity and accuracy. Some odours are detected at the parts per trillion level and even stereoisomers are differentiated (Breer, 1997). Between 10 and 100 million receptors for olfaction lie in the nasal epithelium in an area of about 5 cm².

Unlike taste, smell cannot be easily classified into different groups. Humans can distinguish around 10 000 chemicals with the olfactory receptors being stimulated by different combinations of a limited number of primary odours. Different researchers have suggested that this number can vary between 7 and 50. Recently, it has been proposed that there may be 1000 ‘smell genes’, which are actively transcribed only in the nose (Marieb, 1998). Odours (or, scientifically, odorant molecules) are generally light (molecular mass up to 300 Da), small, polar and often hydrophobic (Craven et al., 1996). Simple odours, e.g. an alcohol, will have only one chemical component while complex odours may have up to several thousands.

The need for electronic noses and tongues

Gardner & Bartlett (1994) have defined the electronic nose as ‘an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition (PR) system, capable of recognizing simple or complex odours’. Electronic tongues, on the contrary, are ‘multisensor systems for liquid analysis based on chemical sensor arrays and PR’ (Legin et al., 2002a).

Why, then, is there any need for these multisensor systems to be designed for use with PR? The human olfactory system can detect thousands of different compounds with high specificity and research on artificial olfaction has led to significant advances in odour quality in the food and beverage industries (Craven et al., 1996). There is a relationship between the electronic and human noses. Each nose consists of three major regions. The human nose has an array of olfactory receptor cells, the olfactory bulb and the brain. The equivalent of these regions in the electronic nose are the odour sensor array, data pre-processor and PR system.

Meanwhile, the electronic tongue can have better sensitivity and detection limits than the human tongue. This is because the taste system in humans is not as highly developed as the olfactory system. As Legin et al. (2002a) have pointed out, ‘the electronic tongue can be thought of as analogous to both olfaction and taste and it can be used for the detection of all types of dissolved compounds, including volatile compounds [which] give odours after evaporation’. This device can be used for the recognition, classification and quantitative determination of multiple component concentrations.

Data processing

A generalized structure of an electronic nose is shown in Fig. 4. This could just as easily be applied to the electronic tongue except that liquids are studied. As seen in this diagram and as mentioned in the previous section, PR techniques are used for data processing. The sensor array may be either acoustic wave (e.g. TSM), conducting polymer (e.g. polypyrroles, metal phthalocyanines) stannic oxide catalytic or semiconducting in nature. The data generated by each sensor are processed by a PR algorithm and the results are then analysed. The potential advantages of such an approach include the reduction in complexity of the sensor coating selection, the ability to characterize complex mixtures without the need to identify and quantify individual components and that it can be exploited for structure–activity relationship studies. In this section, we will briefly review the concepts behind this method.

Pattern recognition is a decision vector used to classify a species based on a series of measurements (a pattern) on that species. Generally, a matrix is formed from the patterns for a number of species and then a decision vector which divides the pattern into an assigned binary classification is calculated based on standard experiments. This is then used to classify unknown patterns. The success of PR techniques can be enhanced or simplified by suitable prior treatment of the data.
such that feature selection and feature extraction are important approaches (Adams, 1995). The former identifies and selects those features present in the analytical data, which may be important to calibration. Feature extraction changes the dimensionality of the data and generally refers to processes combining original variables to provide new and better ones. A widely used method is principal component analysis (PCA) (Adams, 1995).

The PR methods may be divided into supervised and non-supervised methods although a combination of both can be used. In this discussion, we will consider both, as each type is widely used for electronic noses and tongues. The major unsupervised technique is PCA while artificial neural network (ANN) is the best-known supervised technique.

PCA is a linear PR technique which reduces multidimensional, partly correlated data to two- or three-dimensions. It makes the assumption that, if there is a large number of a variable obtained from a number of cases, then a smaller set of derived variables, which retain most of the original information, can be obtained. The main aim of PCA is to reduce dimensionality with a minimum loss of information. This is achieved by projecting the data onto fewer dimensions and these are chosen to exploit the relationships between the variables. Projections are chosen so that the maximum amount of information is retained in the smallest number of dimensions (Fielding, 2000). It also measures qualitative associations between variables. To analyse the results, a line of best fit through a system of points in space is obtained. This technique allows the similarities and differences between objects and samples to be better assessed (Adams, 1995). For a full discussion of PCA, the reader is referred to the book by Beebe et al. (1998).

The ANNs are programs used to simulate biological nervous systems and they are based on simulated neurones, which are joined together to form networks. They are computer programs based on a simplified model of the brain; they do not attempt to copy the minute details of how the brain works but reproduces its logical operation using a collection of neurone-like entities to perform processing (Cartwright, 1993). ANN programs are multipurpose and with suitable training, a single program could solve several problems (Cartwright, 1993).

An artificial neurone with simple characteristics is called an elementary perceptron. This is a simple feed forward system from which artificial networks are constructed (Cartwright, 1993). An ANN, including the perceptron, starts from a position of complete ignorance and so a training period is required before it can be used for real problems. A training set consists of two parts: a training stimulus, a collection of inputs to the perceptron and a training target, the desired output for each stimulus. An example is training of the ANN to be able to distinguish between two or more odorous molecules with different structures. A structure from the training set is shown
and the perceptron is allowed to identify it. This decision is compared with the training target and adjustments are made as necessary. Another structure is shown and the process is repeated until the perceptron becomes proficient at identifying the structures (Cartwright, 1993).

Several different types of ANN are available and the most popular is the back propagation approach (Fig. 5). The diagram shows a simple three layer feed forward network incorporating input, hidden and output layers. In this procedure, input patterns presented to the input layer, e.g. signals from an array of chemical sensors, generate a flow of activation to the output layer. Errors in the output are then fed back to the input layer to modify the weights of the interconnects. It should be emphasized that back-propagation does not describe a network but represents a learning algorithm. In this way, the network can be trained with known parameters, such as sensor array responses to sets of known chemicals. The network can then ‘recognize’ an unknown chemical composition when the sensor array is challenged with such a cocktail. This type excels at prediction and classification jobs. In a back-propagation system, extra hidden layers (in addition to the input and output layers) are added. Connections are allowed from the input layer to the hidden layer and then from the hidden layer to the output later (Computer Science, Stirling University, 2001).

Advantages of ANNs include the ability to handle noisy or missing data, no equations are involved, a network can deal with previously unseen data once training has been completed, large number of variables can be handled and they provide general solutions with good accuracy.

Data analysis should include calibration, modelling and PR. Many of these procedures are based on multivariate numerical data processing and before the methods can be successfully applied, it is usual to perform pre-processing of the data (Adams, 1995). The main aims of this stage are:

1 to reduce the amount of data which are irrelevant to the study;
2 to enhance sufficient information within the data to achieve the desired goal;
3 to extract the information in, or transform the data to, a form suitable for further analysis.

Probably the most common method of preprocessing spectral data is normalization. This may involve either scaling each spectrum in a collection so that the most intense band in each spectrum is a constant value or the spectra may be normalized to constant area under the absorption or emission curve. More complex approaches involve developing a covariance matrix between variables and extracting the eigenvectors and eigenvalues. Eigen analysis will provide a set of variables, which are linear combinations of the original variables. This has the effect of reducing...
the dimensionality of the data and making the analysis simpler (Adams, 1995).

An important consideration is the statistical design of experiments (DOE) to ensure that data obtained are valid. This is largely because of the use of too few samples with very different characteristics. One-at-a-time experiments, i.e. those where only one variable is changed at a time, are inefficient. Thus, the statistical DOE is of paramount importance, especially when many variables are involved. DOE techniques allow the experimenter to identify the input variables which affect the output of any process (Connecticut Quality Council, 2003). DOE can speed up process and product development as well as improve existing processes and products. Furthermore, DOE can also be used to reduce the amount of effort needed in an experiment by eliminating redundant observations (Burrows, 2003). Thus, the main advantages of DOE are (Burrows, 2003):

1. fewer experiments are needed because several factors are varied simultaneously;
2. the judicious choice of factor settings reduces the number of experimental runs;
3. more information per experiment is generated.

Applications of electronic noses

A search of the relevant literature shows that there are three major categories of use for electronic noses. These are (i) flavour and aroma, (ii) identification and classification and (iii) other quality areas. Examples of each of these will be described.

Flavour and aroma

The monitoring of flavour and/or aroma components is probably the area where electronic noses have been most widely utilized. One of the earliest reports of an electronic nose to detect complex vapours appeared in 1995 when researchers at Neotronics (Cambridge, UK) used it to detect chemicals in the parts per billion range (Hodgins & Simmonds, 1995). The system used here was the Neotronics Olfactory Sensing Equipment (NOSE). In this subsection, we will mention several examples of different foods which have been analysed by this approach.

Aroma production during wine-must fermentation has been monitored during bioconversion (Pinheiro et al., 2002). In this study, the muscatel aroma was chosen because the profile formed as a result of yeast metabolism is complex, being composed of many compounds. These differ from each other in concentration, chemical and organoleptic properties and contribute to the overall muscatel aroma (Liden et al., 2000). This, therefore, was a challenging project. A commercially available electronic nose (A32S Aroma Scan, Osmetech, UK) consisting of 32 organic conducting polymer-based sensors was used. Data analysis was by PCA. The authors found that without sample pretreatment, the nose could only detect ethanol production, while for small quantities of muscatel a selective enrichment step was needed. Once this was done, the electronic nose was able to discriminate samples based on aroma content. However, enrichment increases the time and effort required for analysis, which could prove to be a major disadvantage to this approach. Additionally, there is the problem that there is competition between the aroma compounds and ethanol for detection by the sensor. As ethanol is present in higher concentration, it will be detected preferentially to the aroma.

A further complication is that ethanol may also interfere during the headspace sampling. Ethanol acts as a co-solvent in the aqueous wine-must matrix and so the activity coefficient of the hydrophobic aroma compounds in the aqueous-phase is lowered, resulting in a decreased partitioning into the sample headspace (Pinheiro et al., 2002). This can lead to erroneous results with the electronic nose.

Similarly, an electronic nose was used for on-line gas-phase monitoring of major metabolites in the cultivation of Saccharomyces cerevisiae (Liden et al., 2000). The metabolites were either non-volatile or present in low concentration and so were not detected by the sensors in the electronic nose. However, it was possible to make predictions by using the off-gas emissions. This was achieved by training ANN with data acquired from the gas sensors and reference data from on-line HPLC analyses. Glucose, glycerol, acetate and acetaldehyde were monitored but the problems indicated above will have a decisive effect in
determining if electronic noses can be successfully used for routine analyses of this type.

An electronic nose based on arrays of differently coated quartz microbalances (QMB) has been used to discriminate between VOCs formed during the post-harvest ripening of apples (Herrmann et al., 2002). The compounds monitored were aldehydes and esters. The relative ratios of these compounds change during post-harvest ripening and this allows them to be analysed by PR methods. This is due to the formation of characteristic patterns of sensor responses. During the ripening of apples, \textit{trans}-2-hexenal can serve as an indicator compound because its concentration increases significantly. It was found that the detection limit of \textit{trans}-2-hexenal was 20 mL m$^{-3}$. Both qualitative (type of apple) and quantitative identification were possible. However, the correlation between the vapour concentration and sensor response is linear within a limited concentration range. It was found that the shape of the curve is similar to the Langmuir adsorption model, thereby limiting the range, which could be used.

An interesting example of the use of an electronic nose involves the development of sol–gel metal oxide sensors for the analysis of vapours and foods (Capone et al., 2000). Thin films produced by sol–gel methodology were used to make a metal oxide gas sensor array. Arrays consisting of tin (II) oxide sensing layers and chemically modified tin (II) oxide thin films were used to analyse air pollutants such as carbon monoxide, nitrogen dioxide, methane and ethanol as well as foods such as oil, milk, tomato and wine. PCA was used to recognize contaminants and food aroma.

Meat flavour can also be analysed by these devices. In one example, warmed-over flavour (WOF) in beef was evaluated by 32 conducting polymer sensors (Grigioni et al., 2000). The meat was processed by vacuum cook-in-bag/tray technology (VCT) and stored in a refrigerator. The VCT process involves treatment at 50 °C for 390 min. The study indicated that an electronic nose can be used for WOF odour identification in beef and may be a complementary approach for current sensory analysis. In another case, flavour differences in dry-cured and other ham products were investigated by a conducting polymer electronic nose (Spanier et al., 1997). The salt and nitrate used for curing can develop and stabilize flavour. The ham-drying process involves several time-temperature interactions and these lead to variation in flavour. Use of an Aroma Scan A32/50S (AromaScan plc, Crewe, UK) electronic nose (32 sensors) allowed the differentiation of Spanish Serrano dry-cured hams processed for 7 or 12 month periods. Prosciutto, Country, Virginia and Deli hams can also be successfully analysed. It should be noted that these examples do not directly refer to the meat itself but to the relative humidity (RH) above the meat. Volatile compounds from the samples were not used and, thus, the differentiation may be based on a flawed assumption.

**Identification and classification**

It is probably safe to claim that, in terms of identification, alcoholic beverages provide the best known example of electronic noses. However, other foods, which have been analysed for identification purposes, include olive oil, cheese, vegetable oil and pig products.

French researchers have coupled gas chromatography (GC) with an electronic nose to identify alcoholic beverages (Ragazzo et al., 2001). As discussed previously, high concentrations of ethanol tend to affect the detection of aroma compounds by an electronic nose. However, pretreatment of samples before GC by dehydration and de-alcoholization solved this problem. A semi-dynamic headspace at controlled temperature was used for pretreatment of samples and also to standardize aroma composition. Tequila, whisky, vodka and red wine were analysed and four compounds responsible for off-flavour in red wine were detected. PCA allowed discrimination between the four types of beverages and wines from different regions of France were also distinguished. German workers have also reported on the analysis of alcoholic beverages, again with a selective enrichment procedure before using the electronic nose (Walte & Munchmeyer, 2000). They have indicated that enrichment allows better correlation to human taste. A major problem with the sensors employed in the electronic noses is drift in the signals. To overcome this effect, researchers have used a zero-gas and a differential...
measuring technique. Another possible drawback is that the selectivity can be increased by adsorbing only the aromatic compounds with boiling points higher than the solvent. As mentioned previously, electronic noses give more accurate results for these analyses once an enrichment procedure is incorporated. However, analysis of alcoholic beverages by electronic noses can be problematic as the composition of the headspace is monitored rather than the sample itself. The concentration of the headspace of a particular substance is related to the vapour pressure and to the liquid-phase concentration of the substance. It is also directly related to the temperature (especially important for the analysis of red wines). This means that the more volatile compounds are present in greater quantities in the headspace and may not be a true reflection of the composition of the sample itself.

Electronic noses have been used in the discrimination of extra virgin olive oils by identifying the geographical origin of these products (Gardini et al., 2000). The authors indicated that a hybrid electronic nose consisting of different types of sensors such as MOS and QCM allowed a wider range of analyses to be achieved. Similarly, vegetable oils can be classified by chemometric treatment of the data obtained from a gas sensor array (Gonzalez-Martin et al., 1999). In this case, the nose consisted of six metal oxide semiconductor arrays, which were used to generate a pattern of the volatile compounds present in the samples. Linear discriminant analysis allowed classification capabilities better than 95%. As with all new technologies, caution is required before assuming that the instrumentation is perfect. For example, the detection of defects in virgin olive oil by electronic nose technology coupled with static headspace analysis has proved impossible (Lacoste et al., 2001).

Products derived from Iberian breed pigs and different types of Italian cheeses have been classified by this method. In the former, chemometric analysis of the data obtained from a gas sensor array was used to differentiate products from the pigs (Gonzalez-Martin et al., 2000). These products are expensive because the animals have been reared in a unique ecosystem where the diet plays an important role. The electronic nose approach was found to be rapid and simple, allowing the classification of the products based on diet, e.g. feed, feed + acorn and acorn alone.

This last example allows us to examine many of the problems which affect the operation and sensitivity of electronic noses. First, calibration is very important as it reduces the influence of variations in RH, changes in temperature and sensor drift over time. Secondly, there must be optimization of the measuring process as signal intensity is a function of the composition of the carrier gas, temperature and RH. Water vapour leads to competition between the oxygen and water on the surface of the sensor. This can lead to the sensor response being adversely affected. In this example, humidity was controlled by using an air-conditioned chamber.

The reproducibility of the signal depends on the recovery of the baseline between injections (optimized at about 7 min), the injection time (90 s optimization) and the flow rate (300 mL min$^{-1}$) of the carrier gas. It also depends on the sample size (0.5 g) and waiting time in the chamber before the injection is made (Gonzalez-Martin et al., 2000). Thus, there must be detailed optimization to ensure the accuracy of the results. In this particular case, it was necessary to ensure that the baseline had recovered and that sufficient volatiles had entered the headspace before injecting a new sample. The percentage of correctly identified samples ranged from 96 to 100%.

Finally, the signal was influenced by the speed with which the volatile compounds entered the sensor chamber. For low flow rates, the signal was small and the recovery times of the sensors were long while for high flow rates, the signals were increased. However, at these high rates the sensor was destabilized, leading to poor reproducibility (Gonzalez-Martin et al., 2000).

Other quality aspects

In this section, we will consider quality aspects other than those which were covered in the preceding sections. These will include aspects which cannot be easily included in either identification/classification or aroma and flavour.

Several investigations with electronic noses have involved studies with fish and fish products. In one of these, a quality assessment of salmon fillets under various storage conditions was reported by Du et al. (2002). The fillets were stored at $-20, 4$ and $10{^\circ}\text{C}$ for 14 days and examined by the
Aroma Scan electronic nose for changes in bacteria and histamine over time. Comparison with sensory panel evaluations showed that this approach might be valuable in evaluating fish quality. A gas sensor consisting of 10 MOSFET’s was used to assess the freshness of shrimp and cod roe, amongst other products, while stored in a refrigerator (Winquist et al., 1998). The sensor also contained four Taguchi sensors and a carbon dioxide monitor based on infrared absorption. The assumption was made that the composition of volatile compounds evolved from the food reflects the activity and type of micro-organisms present and can be related to the quality of the food. Gas samples were directed to the sensor array and the signals obtained were analysed by PR software based on an ANN. This study showed that the storage time for shrimp and cod roe could be estimated while, in some instances, it was also possible to determine if samples had been allowed to warm to room temperature before being refrigerated. However, the researchers have indicated that the predictions for cod roe were better than for shrimp. Furthermore, the predictions in both cases improved as storage time increased. This is probably due to a greater evolution of gas over time leading to increased response of the sensor. The signals for cod roe were higher than for shrimp, which explains the higher degree of accurate predictions for the fish. Once again it is clear that sample size is important in sensor response and this could be a major drawback if only small volumes are available.

The quality of fruit and vegetables has also been studied by electronic noses. Post-harvest quality, e.g. detection of defects of apples and oranges, was investigated by a TSM quartz resonator-based electronic nose (DiNatale et al., 2001). Defects such as mealiness (due to over-ripening), skin damage and infections can lead to changes in aroma. It was found that the electronic nose was sensitive enough to correctly predict the number of defects in these fruit. Early detection of soft rot in stored potato tubers was obtained by a sensor array in a prototype device (DeLacy Costello et al., 2000). The device was capable of detecting one tuber with soft rot in 100 kg of good tubers in a simulated storage crate while it was also able to detect a tuber inoculated with Erwinia carotovora (the bacterium responsible for soft rot), but with no external signs of soft rot from 10 kg of good tubers.

Finally, the effects of different colouring agents (‘taints’) on the sensory properties of packaging materials were determined (Heino & Ahvenainen, 2002). These taints were studied in unprinted solid board, lacquered board, offset printed solid board with 14 different colours and offset printed, lacquered solid board with four colours. The electronic nose was efficient in grouping these materials depending on colouring agents or lacquering. However, there was slight overlapping of replicates, which could pose problems in accurately determining the effects of the taints. Further testing with respect to this application is needed.

Tainted-water samples were also monitored by semiconducting oxide gas sensors (Singh et al., 1996). In this instance, a fuzzy neural network (FNN) was used to discriminate the signals generated. The FNN is claimed to be superior to an ANN as the latter does not handle vagueness (fuzziness) of data. This leads to poorly trained networks where the problem becomes more significant when the uncertainty in the data increases and the size of the training set decreases. As its name implies, FNNs use fuzzy logic to model data. Six different types of water were investigated viz. two vegetable-smelling waters, a musty one, a bakery water, a grassy and a plastic water. The FNN produced significantly fewer misclassifications compared with ANN. The former gave 85% accuracy while the latter produced an accuracy of 75%.

Concluding remarks

Several applications of electronic noses have been described in this paper. However, most of these represent limited feasibility studies with concurrent poor validation especially in terms of reproducibility and predictive ability. There are very few long-term studies, which indicate excellent reproducibility without the need for extensive calibration and mathematical analyses of the sensor readings. Furthermore, the successful use of electronic noses is application-specific which may limit their use. Also, electronic noses as commonly employed do not allow for chemical differentiation.
A major issue with gas sensors is their sensitivity to humidity. It is well-documented that water vapour affects measurements by electronic noses and manufacturers of these instruments have been forced to issue specific operating procedures. However, electronic noses using conductive polymers are more sensitive to differences in moisture in samples than other gas sensors. The use of non-gas sensor systems such as MS in combination with multivariate analysis can replace those now widely used.

Electronic noses have been proposed as fantastic instruments which could solve almost any problem concerned with odour. However, the reality is that there is much research still to be done especially with interpretation of the results. Although differences can be measured by these devices, they are rarely related to sensory testing or they may only apply to one set of samples, which cannot be extrapolated to other samples. More emphasis will need to be placed on the method of obtaining headspace samples as each method will have a different mix of volatile components.

There are also a few disadvantages associated with the data processing techniques. For example, one of the main problems with using an ANN is knowing when optimal network parameters have been found. As data sets become less well-behaved, the training becomes more difficult and the class prediction becomes unsatisfactory (Singh et al., 1996). PCA is also sensitive to drift in data. In this respect, it should be mentioned that there is also instrumental drift and, thus, a stable calibrating standard is essential.

Applications of electronic tongues

Although the development of electronic tongues is still in the early stages, several applications have already been described. These include model analyses, food and beverage analysis and water monitoring.

Model experiments

Model experiments are those which are not done directly on food samples but, rather, they involve the use of individual constituents of foods. Several investigations of this type have been reported and some of these will be described in this subsection.

Legin et al. (2000) tested organic compounds such as alcohols, carboxylic acids, aldehydes and terpenes in addition to quinine, urea and glutamate. They reported that the electronic tongue was capable of distinguishing different tastes in both individual and binary solutions. It was also possible to estimate the taste intensity of each substance in the mixture. However, there was no correlation between the electronic tongue and human perception only for coffee and soft drinks, suggesting that further testing is required before there is widespread use of this device.

Brazilian researchers have recently shown that an artificial hand-held tongue of four sensors made from ultrathin films deposited on gold interdigitated electrodes was able to distinguish the four basic tastes (Riul et al., 2002). Some of the samples, e.g. 5 mM NaCl and sucrose, were detected below the human threshold level and suppression of quinine by sucrose was also observed. The high sensitivity was attributed to the ultrathin nature of the films. By using four sensors for the different tastes, an electronic fingerprint of the taste is obtained. These responses are combined into a single data point on a PCA chart, which allows the team to predict the taste of a particular solution.

Toko’s group in Japan have used an electronic tongue to detect the suppression of saltiness by umami substances (Nagamori et al., 1999). The transducer was composed of lipid/polymer membranes each with different characteristics. The umami substance chosen for study was monosodium glutamate (MSG) and PCA was used to determine the levels of saltiness. Saltiness was expressed on the taste scale, the relationship between the salt strength perceived by humans and NaCl concentration. This research has shown that the saltiness of NaCl is reduced by the presence of MSG. Similarly, this same group has reported on the suppression of bitterness with the same electronic tongue (Takagi et al., 2001). Phospholipids, which suppress bitter taste, were measured with respect to their effects on quinine and l-tryptophan taste, both of which are bitter. It was found that the change of bitter intensity caused by the phospholipids was easily quantified by PCA and the taste scale.

A micromachined sensor array has been developed for the rapid characterization of
multicomponent mixtures in aqueous media (Lavigne et al., 2000). Synthetic taste buds consisting of beads were used to incorporate receptors such as small molecules, nucleic acids and antibodies. The buds were deposited on an array of micromachined wells on silicon wafers, which in turn was interfaced to a charge-coupled device. This allowed the acquisition of colorimetric data from the individual buds. Data streams of red, green and blue patterns were used for the analysis.

In these examples, it was claimed that the electronic tongue was able to distinguish various tastes but it must be emphasized that tests were not reported on food samples. The technique measures indirectly the chemical or physical properties of the sample. The sensors utilized in these instruments will not specifically measure taste compounds, mainly due to their lack of sensitivity and selectivity. Furthermore, they tend to respond to major analytes in the liquid-phase and minor analytes tend to be ignored.

**Beverages and foods**

Many beverages have been analysed by electronic tongues and these include fruit juices, milk, mineral water, coffee, tea and wine. Flesh foods and tomatoes have also been characterized in this way.

Winquist and co-workers used an electronic tongue based on voltammetric principles to analyse fruit juices, still drinks and milk (Winquist et al., 1997). Voltammetry offers several advantages including high sensitivity, versatility, robustness and the availability of different techniques such as cyclic, stripping or pulse voltammetry. Measurement by potentiometry, on the contrary, is based on the charging of the membrane. This will limit the range of detectable compounds to charged species. Also, potentiometry is sensitive to electronic noise. PCA was used to treat the data generated. It was also possible to classify orange juice and milk but samples of the former presented some problems as they contained fruit fibres. These attach to the working electrodes and alter their properties leading to variation in the results. In addition, it was possible to follow the ageing processes of these liquids when they were stored at room temperature. It was determined, however, that the changes for orange juice were largest at the beginning of the experiment and they became very small after 8 h. These plots were difficult to explain by PCA mainly because of the problem of determining the principal components. Also, different samples undergo different ageing processes. Orange juice samples show large changes at the beginning due to evaporation of volatile compounds followed by a slow oxidation of ascorbic acid. Milk ageing follows a different process with not much change at the beginning. After 9 h, the differences increase to reach a maximum between 17 to 19 h. In this case, oxidation at the beginning is followed by microbiological activity. Another problem with these experiments is that the electrodes are not mechanically cleaned between measurements. Thus, protein adsorption on the electrode will influence the results (Winquist et al., 1997).

An electronic tongue consisting of 30 potentiometric chemical sensors and PR data analysis were used to analyse mineral water, coffee and soft drinks (Legin et al., 2002b). The device was able to distinguish between natural and artificial mineral waters, between commercial and individual brands of coffee and between commercial and experimental samples of soft drinks containing different sweeteners. To calibrate the tongue, taste parameter assessments obtained by a professional taste panel were used.

A hybrid electronic tongue based on a combination of potentiometry, voltammetry and conductimetry has been described for the classification of six different types of fermented milk (Winquist et al., 2000). Parameters measured were pH, carbon dioxide and chloride ion concentrations, which were determined by ISEs. The voltammetric tongue was made up of six working electrodes of different metals (gold, iridium, platinum, palladium, rhenium and rhodium) with an Ag/AgCl reference electrode. Pulse voltammetry was used to measure changes in current and the data was analysed by PCA and ANN. It was determined that all samples were differentiated from each other. Along with this, the micro-organisms involved in the different fermentations could be determined by PCA.

Russian and Italian researchers have described a sensor array of 29 different chemical sensors for the analysis of mineral water and wine (Legin et al., 1999). During data processing, however, smaller subarrays of sensors were used. This reduced the size of data sets without any loss of
analytical information. Sensors with chalcogenide glass and PVC membranes with enhanced cross-reactivity were incorporated into the sensor array. Measurements were performed on six types of Italian mineral water, tap water from Rome and 20 red wine samples (Barbera from Piemonte). The electronic tongue was able to distinguish all water and wine samples. Both qualitative and quantitative data were obtained.

Water analysis

The quality of drinking water varies due to the origin and quality of raw water, untreated surface or ground water and to differences in the water treatment processes (Krantz-Rulcker et al., 2001). Variations in water quality can be monitored by electronic tongues and a few examples are described in this section.

A multielectrode sensor system based on voltammetric analysis of water samples has been described. This electronic tongue was able to perform a total water quality estimate based on predetermined constraints extracted from pattern structures (Lindquist & Wide, 2001). Experiments were conducted to virtually monitor the drinking water quality, measured from the raw water in a river to the tap water of the consumer. The researchers claim that the electronic tongue was able to detect changes in the water quality by use of statistical multivariate methods to analyse the signal responses.

DiNatale et al. (1997) have analysed polluted water by using an electronic tongue composed of ISEs. Techniques based on chemometrics, non-linear least squares and neural networks were required. The best results, however, were obtained by the use of molecular models, which utilize both qualitative and quantitative information.

A microbial sensor that lays the foundation for a new electronic tongue has been described (Konig et al., 2000). Two microbial strains with different substrate spectra were immobilized on to a biosensor chip composed of four platinum electrodes. The biosensor was incorporated into a flow-through system to measure oxygen consumption of the microbes in the presence of nutrients. A yeast strain was used to determine biochemical oxygen demand (BOD) while another strain was used to degrade polycyclic aromatic hydrocarbons (PAH). It has been reported that the sensor could measure wastewater samples contaminated with PAH.

Concluding remarks

Electronic tongues are starting to prove useful as quality control devices in the food industry along with a few other applications such as process monitoring and clinical analysis. However, several issues remain before these instruments can be easily obtained commercially. Research is needed in several sectors including (Vlasov et al., 2002):

1. experimental evaluation of sensor mechanisms and the theoretical basis of the operation of the electronic tongue;
2. further testing of the various suggested applications;
3. development of new sensor arrays.

Once these issues have been addresses, then it will be possible to consider commercialization.

Integration of electronic noses and tongues

Recently, there have been attempts to integrate electronic noses and tongues to obtain improved classifications and/or detection of foods. Winquist et al. (1999) described the combination of these two devices to discriminate between experimental samples. The nose was comprised of an array of gas sensors with different selectivity patterns while the tongue was based on pulse voltammetry. PCA was used to analyse data from both devices. A combination of the nose and tongue was found to markedly improve classification properties.

Taguchi’s group in Japan has attempted to use an integrated system for the detection of gases and volatile liquids (Talaie et al., 2000). The detection is based on changes in the electrical resistance, which occur when polymer-coated microelectrodes are exposed to the different samples. For this preliminary investigation, detection of pH and sodium chloride was reported. The authors also claim that this integrated approach can be developed to detect colour for display device applications. This will lead to further development of an electronic eye. Finally, sensors operating in both liquid and headspace environments were developed based on the use of metalloporphyrins (DiNatale et al., 2000). The
combined system was tested in both clinical and food analyses and there was an increase in the amount of information obtained.

Conclusions
In this review, we examine applications of both electronic noses and tongues in food analysis. Each technique is still being developed but the advantages are already clear. Strengths of the electronic nose include high sensitivity and correlation with data from human sensory panels for several applications (Harper, 2001). An electronic tongue can perform as an ‘intelligent sensor to reproduce the taste sense which is a complex, comprehensive sense’ (Toko, 1998). It is, therefore, able to transform molecular information into taste qualities.

However, there are several problems with the technology and these were described in the preceding sections. In both devices, sensor drift is a major problem, which leads to the inability to provide proper calibration. This will be of concern in quality control laboratories and is one of the reasons for the general absence of these instruments from these establishments. For the electronic nose, in particular, there is loss of sensitivity in the presence of water vapour and high concentrations of single components (Harper, 2001). Even with the integrated electronic nose–tongue systems, there is the major issue of combining data of different origins (Legin et al., 2002a). For each approach there is also the requirement for considerable method development for each application (Harper, 2001). This was clearly described with alcohol analyses where it was shown that ethanol has a strong effect on both sampling method and detection. Finally, sensor arrays and PR tend to predict the quality of a sample without providing hard data with respect to composition and concentration (Krantz-Rulcker et al., 2001).

Regardless of these concerns, the future for both the electronic nose and tongue appears to be promising as they can fulfil niche analyses. This is because research and development activities are continuing apace in several laboratories around the world. Even the early instruments have performed well for some applications and it is believed that the newer prototypes will advance the field further. Some of these exciting developments include:

1 A MS-based electronic nose for headspace characterization. This has been tested at Leatherhead Food Research Association in Surrey for several applications such as the detection of taints in packaging, meat spoilage and benzene at trace levels in water (Shiers et al., 1999). Another similar approach, which holds promise in the area of aroma differentiation, has been recently reported (Drake et al., 2003). Tentative identification of compounds is based on theory and these are then confirmed by development of a NCI mass library.

2 The use of QCM sensors in the development of an electronic tongue. This approach allows even more information to be derived (Hauptmann et al., 2000).

3 The development of pulse spectroscopy by Bloodhound Sensors Ltd (Leeds, UK), which uses a single sensor to give a response similar to GC–MS but in a much shorter time (Gibson et al., 2000).

4 The use of rapid gas chromatographic methods in combination with multivariate analysis holds promise but will depend on the method used to obtain volatile components. Solid-phase micro-extraction (SPME) may be the preferred method.

References


