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Research Paper :

Application of electronic nose in food analysis

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ABSTRACT

Electronic nose is mostly used for different applications in food and beverage industries: identification, quantification, quality control. In each application, the principal goal is that this instrument could discriminate different organoleptic properties of different samples. Those properties could be qualities, origins, defects, and concentration of pollutants. As pattern recognition techniques are widely used to analyse the data obtained from these multisensor arrays, Applications described include identification and classification of flavour and aroma and other measurements of quality using the electronic nose.

Key words : Electronic noses, Biosensor, Food analysis, Pattern recognition, Sensor arrays.

An electronic nose is an instrument, which generally consists of an array of cross-sensitive electronic chemical sensors and an appropriate pattern recognition method (PARC), to automatically detect and discriminate simple or complex odors. Arrays of gas sensors are termed as "electronic noses" while arrays of liquid sensors are referred to as "electronic tongues" (Stetter and 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. 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,vfluorescence, 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.

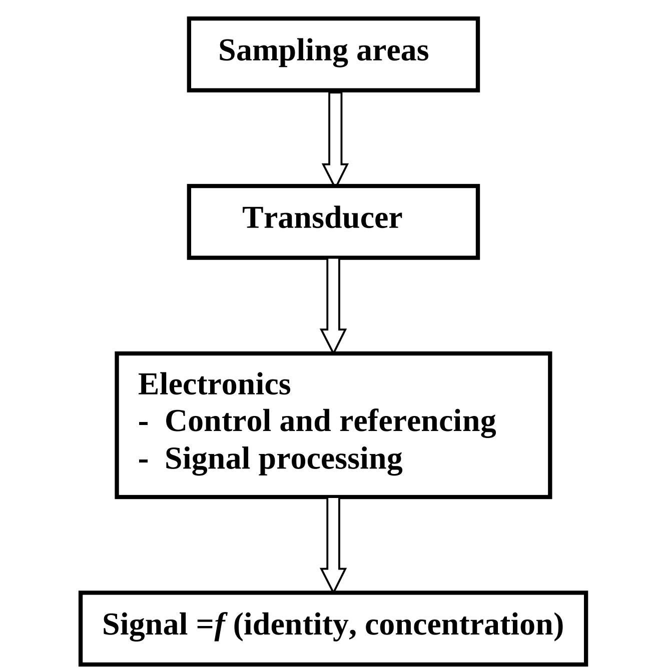

Fig. 1 : The main parts of typical sensor

The electronic nose is an instrument that begins to bridge the gap between analytical techniques such as gas chromatography (GC) and sensory analysis. Monitoring the level of retained solvents is the primary method of quality control of packaging after printing. Current quality assurance techniques use sensory analysis, GC, GC-olfactory, and GCmass spectroscopy. Among these, the popular method is the 'sniff test' using trained panel members. While these methods are useful research tools, they require extensive time and preparatory measures, and also expertise in understanding the results. In addition, the analytical methods (GC, GC-MS) analyze the individual volatiles that comprise an aroma, and not the overall aroma itself. If an electronic nose could be demonstrated to be effective in this application, it could become a complementary tool in quality assurance (Van Deventer and Mallikarjunan, 2002).

METHODOLOGY

Several categories of transducers are available and these include:

Electrochemical, such as ion-selective electrodes (ISE), ion-selective field effect transistors (FET), solid electrolyte gas sensors and semiconductorbased gas sensors.

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.

Optical, such as optical fibres, as well as the more traditional absorbance, reflectance, luminescence and surface plasmon resonance (SPR) techniques.

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.

Sensor arrays:

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

***Catalytic or tin oxide sensor*:**

A commercially available Taguchi Gas Sensor (TGS) can be and is widely used as the core-sensing element in arraybased 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 and 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 detectorshave 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 and Travers, 1997).

***Conducting polymer sensors*:**

Many other materials are conducting (or semiconducting) and showa 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 and 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.

***Acoustic wave sensors*:**

AT-cut quartz crystals (+35^{0}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 and Stone, 1997).

A typical TSM (Thickness-shear mode)sensor is shown in Fig. 2. The sensor consists of overlapping metal

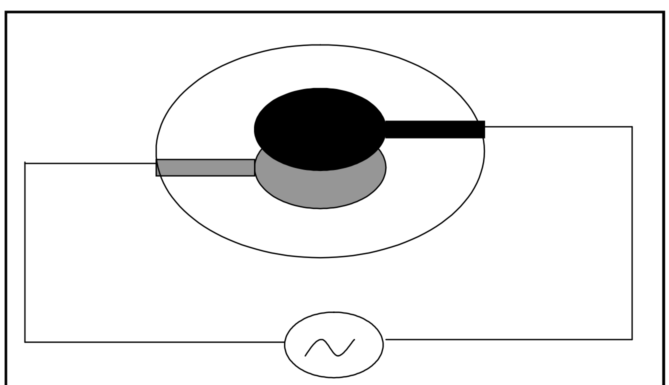

Fig. 2 : Typical thickness-shear mode (TSM) sensor with electrode connections

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.

***MOSFET technology*:**

FET 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. 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.

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).

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.

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

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 *viz.*, 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 and Grabowski, 1996). Sour substances have an intermediate threshold limit while sweet and salty. materials have the highest threshold values. Partial adaptation to a taste occurs in about 3–5 s with complete adaptation in 1–5 min.

Table 1 : Taste sensations (Marib, 1998)

Sensation	Representative components
Sweet	Sugars, amino acids, alcohols
Sour	Acids, e.g. acetic, citric
Salty	Table salt
Bitter	Quinine, caffeine, aspirin, nicotine
Umami	Monosodium glutamate (MSG), disodium inositate in meat and fish disodium guanylate in mushrooms

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 cm^2.

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).

A generalized structure of an electronic nose is shown in Fig. 3. As seen in this diagram, PR (pattern recognition (PR) system), techniques are used for data processing. 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

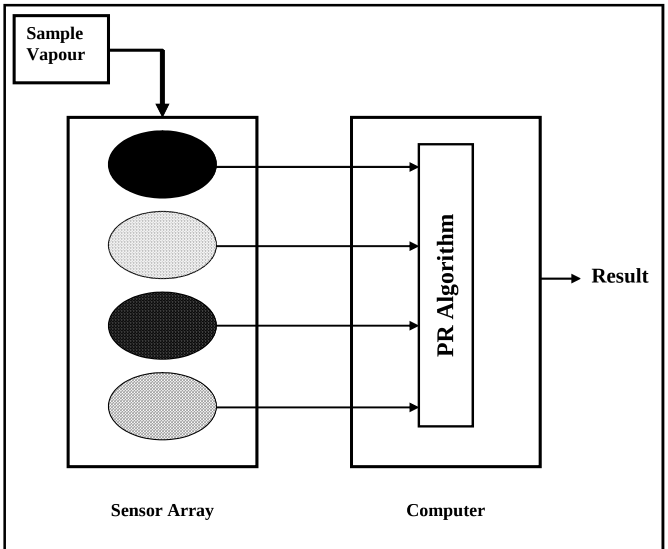

Fig. 3 : Ageneric electronic nose

classification is calculated based on standard experiments. This is then used to classify unknown patterns.

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.

RESULTS AND DISCUSSION

The findings of the present study have been discussed under following heads:

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 have been described.

Flavour and aroma:

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). A commercially available electronic nose (A32S Aroma Scan, Osmetech, UK) consisting of 32 organic conducting polymer-based sensors was used.

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.

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.

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.

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).

French researchers have coupled gas chromatography (GC) with an electronic nose to identify alcoholic beverages (Ragazzo *et al.*, 2001).

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.

Other quality aspects:

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^{0}C for 14 days and examined by the Aroma Scan electronic nose for changes in bacteria and histamine over time

Conclusion:

Strengths of the electronic nose include high sensitivity and correlation with data from human sensory panels for several applications. The future for electronic nose appears to be promising as they can fulfill 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 aroma differentiation etc.

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