Intelligent Sensing and Packaging of Foods for Enhancement of Shelf life: Concepts and Applications

Anamika Bagchi

Abstract—India is the world's second largest producer of food next to China, and has the potential of being the biggest with the food and agricultural sector. The food processing industry is one of the largest industries in India-it is ranked fifth in terms of production, consumption, export and expected growth. The Indian food processing industry stands at $135 billion and is estimated to grow with a CAGR of 10 percent to reach $200 billion by 2015. The food processing industry contributed 7 percent to India's GDP.The Confederation of Indian Industry(CII) has estimated that the foods processing sector has the potential of attracting US$ 33 billion of investment in 10 years and generate employment of 9 million person-days. So, ensuring the safety of food is of great importance. The present review paper introduces about intelligent sensing, electronic nose and tongue, their development and application in the food processing sector. In this review the real time detection of food safety problems such as microbial hazards, chemical hazards and toxins into the food supply ,by the intelligent sensors are also depicted.

Index Terms— Aflatoxins, Amperometric , Chronoamperometric , Electronic Nose, Electronic Tongue ,Intelligent Sensing, Sensors.

1: Introduction

THE food sector is one of the fastest growing sectors in our world. For fresh products the quality of the product can vary considerably during shelf life. The deterioration of foods that occurs progressively during storage may result from physical or chemical changes in the food itself, or from the activity of micro-organisms growing in or on the product. Eventually, the cumulative effect of the changes reaches a point at which the consumer rejects the product. Rejection is based on the sensory expectations and perceptions of consumers. Shelf life depends on a multiplicity of variables and their changes, including the product, the environmental conditions, and the packaging. Depending on the product and its intended application, shelf life may be dictated by microbiology, enzymology, and/or physical effects (Singh and Singh, 2005). Monitoring the quality during transport and storage in the production chain gives additional information for better predicting the product quality and can give important information for logistic control of the chain. This is done by the use of intelligent packaging system and intelligent sensing. The method has been developed so as to reduce the destruction of food samples for its analysis and to modify the approach to a new dimension of food analysis.

Intelligent packaging is defined as a packaging system that is capable of carrying out intelligent functions (such as detecting, sensing, recording, tracing, communicating, and applying scientific logic) to facilitate decision making to extend shelf life, enhance safety, improve quality, provide information, and warn about possible problems. For example, an intelligent package is one that can monitor the quality/safety condition of a food product and provide early warning to the consumer or food manufacturer. According to Kit et al. (2005) Smart package devices are defined here as small, inexpensive labels or tags that are attached onto primary packaging (for example, pouches, trays, and bottles), or more often onto secondary packaging (for example, shipping containers), to facilitate communication throughout the supply chain so that appropriate actions may be taken to achieve desired benefits in food quality and safety enhancement. There are two basic types of smart package devices: data carriers (such as barcode labels and radio frequency identification [RFID] tags) that are used to store and transmit data, and package indicators (such as time-temperature indicators, gas indicators, biosensors) that are used to monitor the external environment and, whenever appropriate, issue warnings.

Sensors incorporated with dedicated signal processing functions are called intelligent sensors or smart sensors. The roles of the dedicated signal processing functions are to enhance design flexibility of sensing devices and realize new sensing functions (Yamasaki, 1996).Electronic nose and tongues are examples of such. Electronic noses (e-noses) are instruments which mimic the sense of smell. These devices are typically array of sensors used to detect and distinguish odors precisely in complex samples and at low cost. These

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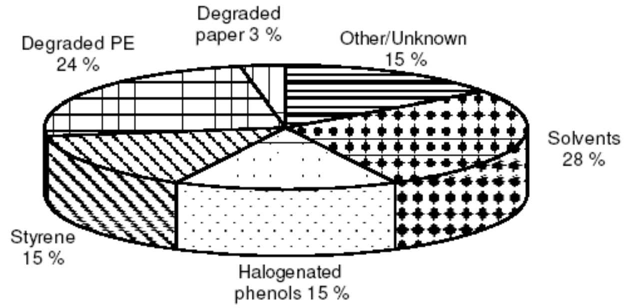
features make e-noses very useful for diverse applications in the food, cosmetic and pharmaceutical industry as well as in environmental control or clinical diagnostics. Applications described include process monitoring, shelf-life investigation, freshness evaluation, authenticity assessment, as well as other general aspects of the utilization of electronic noses in food control (Peris and Escuder-Gilabert, 2009).

A multichannel taste sensor, namely an electronic tongue, with global selectivity is composed of several kinds of lipid/polymer membranes for transforming information about substances producing taste into electrical signals, which are input to a computer (Kiyoshi Toko1998). Electronic tongues for liquid analysis, based on the organizational principles of biological sensory systems, developed rapidly during the last decade (Vlasov et al., 2002). Applications of voltammetric electronic tongue are described, such as in the food industry, environmental analysis, paper and pulp industry, household appliances and agriculture (Winquist, 2007).

The aim of this report is to present the development of intelligent packaging and intelligent sensing concepts that can monitor and predict food quality and/or safety within the supply chain.

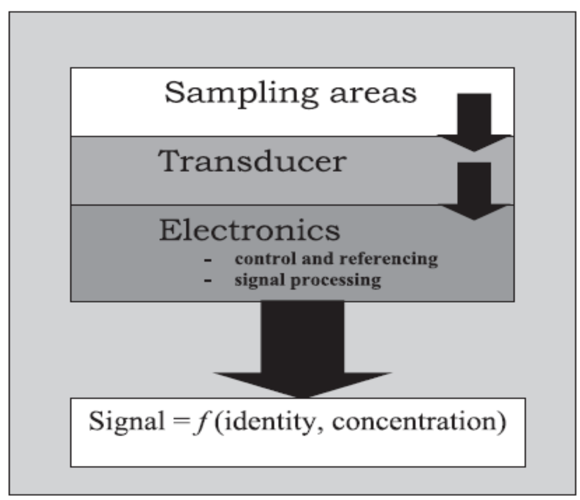
2: Review of Literature

Off-flavors in packed food are causes for consumer complaints. Often, they are related to packaging materials. For food companies, this represents not only costs related to production, but also a possible loss of brand confidence and market share. The origin of packaging-related off-odours is many sided. Odors derive from the degradation of base packaging materials and their converting processes, including printing, coating and lamination as well as the interaction between food and packaging. Many substances and groups of substances have been identified so far. In spite of the fact that the quality of packaging materials is clearly defined in the specifications (e.g. limit for residual solvents, standardized odor and taste transfer tests), off-flavor cases still do occur(Huber et al.2002).Due to the above and various other reasons electronic nose and tongue along with intelligent packaging system came into play.
Fig 1.Shows the packing related off flavor production analyzed at the Central Packing Laboratory (1996-2000).



2.1 Development of Sensors

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 color 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. 2.



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 appropriate pattern recognition (PR) system, capable of recognizing simple or complex odors. 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? The human olfactory system can detect thousands of different compounds with high specificity and research on artificial olfaction has led to significant advances in odor 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 is the odor 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 odors after evaporation. This device can be used for the recognition, classification and quantitative determination of multiple component concentrations (Deisingh et al, 2004).

2.1.1. Electronic Nose

An electronic nose is a machine that is designed to detect and discriminate among complex odors using a sensor array. The sensor array consists of broadly tuned (non-specific) sensors that are treated with a variety of odor-sensitive biological or chemical materials. An odor stimulus generates a characteristic fingerprint (or smell print) from the sensor array. Patterns or fingerprints from known odors are used to construct a database and train a pattern recognition system so that unknown odors can subsequently be classified and identified. This is the classical concept of an e-nose; however, in recent years, as discussed below, the classical sensor types used for e-noses have been enhanced and complemented by other technologies introduced in this field. Nevertheless and in a broader sense, electronic nose instruments are composed of three elements, namely: (i) a sample handling system, (ii) a detection system, and (iii) a data processing system. Fig. 1 below shows the basic architecture of a data processing system for an electronic nose.

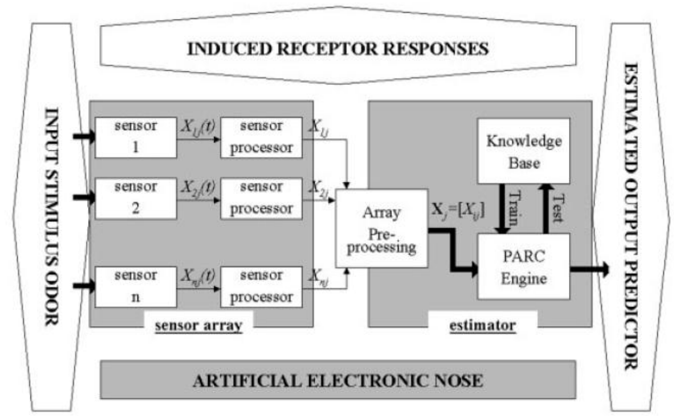


Fig. 3. Basic architecture of a data processing system for an electronic nose

The complexity of most food aromas make them difficult to be characterized with conventional flavor analysis techniques such as gas chromatography or gas chromatography olfactometry. Nevertheless, sensory analysis by a panel of experts is a costly process since it requires trained people who can work for only relatively short periods of time; additional problems such as the subjectivity of human response to odors and the variability between individuals are also to be considered. Hence, the need of an instrument such as the electronic nose, whose strengths include high sensitivity and correlation with data from human sensory panels for several specific applications in food control. Because they are easy to build, cost-effective and as they provide a short time of analysis, electronic noses are becoming more and more popular as objective automated non-destructive techniques to characterize food flavors (Peris and Escuder-Gilabert 2009).

The sensor array in an electronic nose performs very similar functions to the olfactory nerves in the human olfactory system. Thus, the sensor array may be considered the heart and most important component of the electronic nose. A good sensor should fulfill a number of criteria. First, the sensor should have highest sensitivity to the target group of chemical compound(s) intended for detection and with a threshold of detection similar to that of the human nose, down to about 10-12 g mL-1. Sensors should be capable of operating at relatively low temperatures when necessary, have short calibration and training requirements, fast recovery time between runs and maintenance procedures to maintain low operating costs. They must also have short recording and analysis times, particularly when used as on-line systems, and high sensor array stability. As most applied markets and industries tend to move more toward miniaturization of analytical instrumentation, the sensor array must ultimately be very portable and small for convenient diverse operations and with built-in recording and analysis capabilities. There are a variety of advantages

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and disadvantages of using various e-nose sensors based on their response and recovery times, sensitivities, detection range, operating limitations, physical size, inactivation by certain poisoning agents, and other limitations that are specific to individual sensor types. The types and categories of advantages and limitations associated with individual e-nose sensor types are closely linked with the nature of the technology that determines the principle for detection and the types of gas analytes that may be detected with each sensor type. Fig. 4 shows the diagram of sensors MOSFET, SAW and MOS.

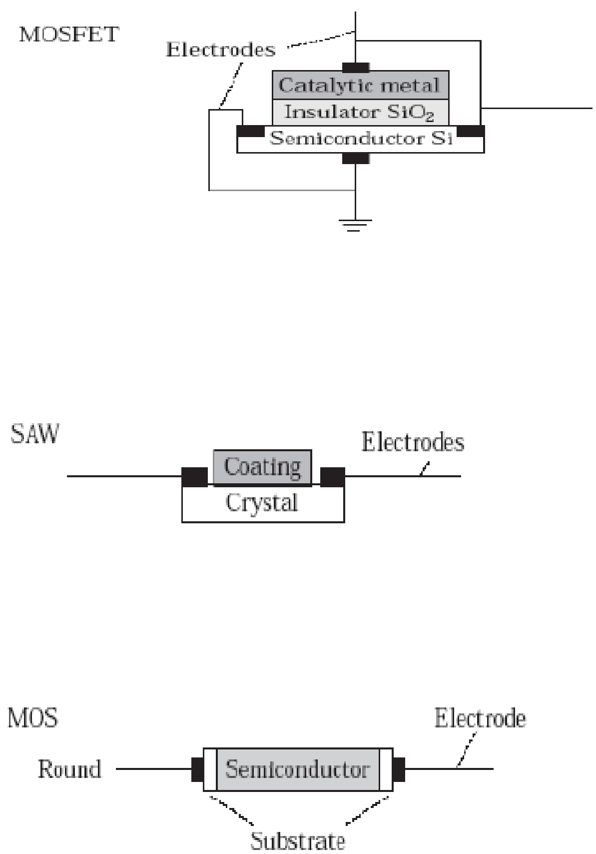


Table 1 represents the overall advantages and disadvantages of different sensors used.

Summary of advantages and disadvantages of e-nose sensor types.

Sensor type	Advantages	Disadvantages
Calorimetric or catalytic bead (CB)	Fast response and recovery time, high specificity for oxidized compounds	High temperature operation, only sensitive to oxygen-containing compounds
Catalytic field-effect sensors (MOSFET)	Small sensor size, inexpensive operating costs	Requires environmental control, baseline drift, low sensitivity to ammonia and carbon dioxide
Conducting polymer sensors	Ambient temperature operation, sensitive to many VOCs, short response time, diverse sensor coatings, inexpensive, resistance to sensor poisoning	Sensitive to humidity and temperature, sensors can be overloaded by certain analytes, sensor life is limited
Electrochemical sensors (EC)	Ambient temperature operation, low power consumption, very sensitive to diverse VOCs	Bulky size, limited sensitivity to simple or low mol. wt. gases
Metal oxides semi-conducting (MOS)	Very high sensitivity, limited sensing range, rapid response and recovery times for low mol. wt. compounds (not high)	High temperature operation, high power consumption, sulfur & weak acid poisoning, limited sensor coatings, sensitive to humidity, poor precision
Optical sensors	Very high sensitivity, capable of identifications of individual compounds in mixtures, multi-parameter detection capabilities	Complex sensor-array systems, more expensive to operate, low portability due to delicate optics and electrical components
Quartz crystal microbalance (QMB)	Good precision, diverse range of sensor coatings, high sensitivity	Complex circuitry, poor signal-to-noise ratio, sensitive to humidity and temperature
Surface acoustic wave (SAW)	High sensitivity, good response time, diverse sensor coatings, small, inexpensive, sensitive to virtually all gases	Complex circuitry, temperature sensitive, specificity to analyte groups affected by polymeric- film sensor coating

Electronic Nose Instrumentation

Gardner and Bartlett provided a basic requisite definition of an electronic-nose device with a list of necessary components (as follows):

- an aroma delivery system, which transfers the volatile aromatic molecules from the source material to the sensor array system.
- a chamber where sensors are housed: this has usually fixed temperature and humidity, which otherwise would affect the aroma molecules adsorption.
- an electronic transistor which converts the chemical signal into an electrical signal, amplifies and conditions it.
- digital converter that converts the signal from electrical (analog) to digital
- a computer microprocessor which reads the digital signal and displays the output after which the statistical analysis for sample classification or recognition is done (Wilson and Baietto, 2009)

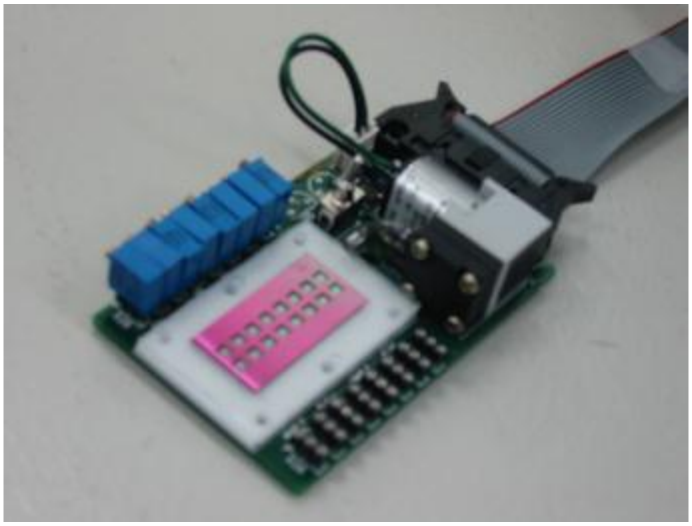


Fig 5 above shows electronic interface circuits for vapor sensing as minimized module for portable system

Data Analysis for Electronic Noses

Instrumental methods of determining volatiles, such as gas chromatography – mass spectrometry (GC-MS), are expensive and require trained personnel. As a result there has been a drive to establish a device for rapid, inexpensive analysis of volatile organic compounds (VOC) that do not require specialist technicians.

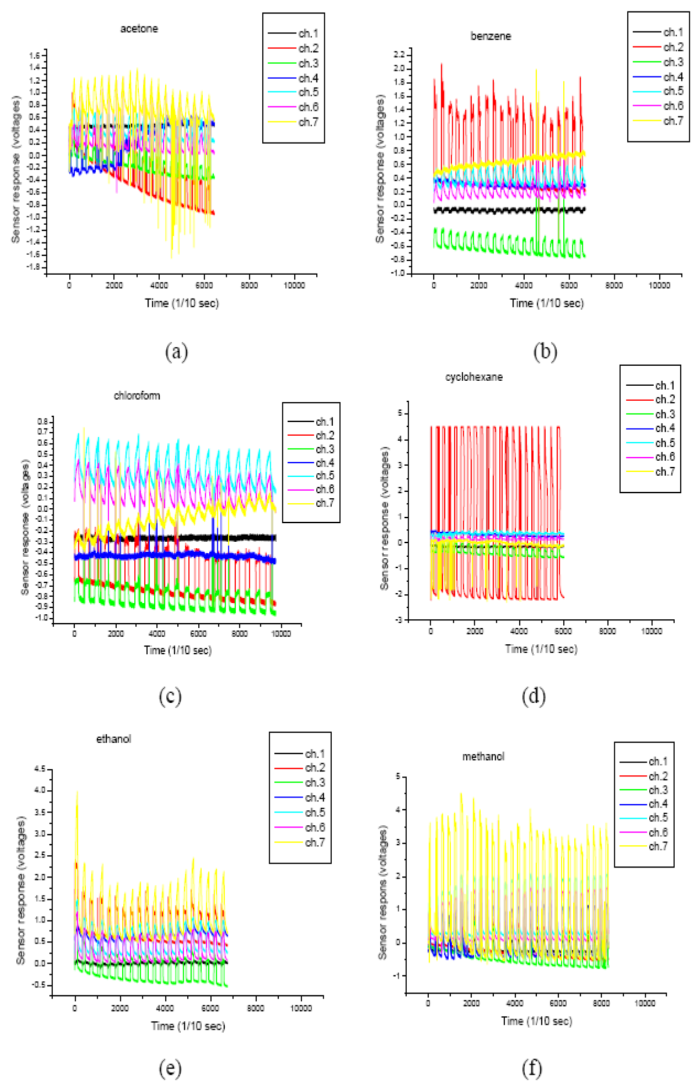
Data acquisition is the first step for data analysis; sensors collect the data and convert it into an electrical signal pattern that is more suitable for computer analysis. This step often causes the difficulty in the classification problem as the characteristics and limitations of the transducer may limit or distort the available information. The output is a pattern vector, in pattern space. The pattern vector is passed into the second stage, the feature extractor. Feature extraction is the use of one or more transformations of the input features to produce new salient features. Feature extraction may be regarded as a dimensionality reduction process; data is converted from pattern space into feature space. Features should be easily evaluated, there are two kinds, the first have a clear physical meaning, the second have not and are called mapping features. In the context of e-noses the features that are usually considered are the maximum sensor responses, but some groups have used temporal data or mapping features such as constructs of gradient information. Data pre-processing can affect the classifier, there are no general guidelines to determine the appropriate data pre-processing technique. Concentration may have a scaling effect on the patterns of the sensors. While a pattern recognition algorithm normally examines the differences between the patterns, a scaling effect may mask the interrelations between them. Normalization is normally used to remove this effect.

Sensor arrays may generate a large volume of high dimensional data; it is often a challenge to extract useful information from the data to solve the problem under investigation. Graphical methods are a simple exploratory way of analyzing data, some methods may plot the high-dimensions produced, whilst others reduce the data to two or three dimensions for visual Analysis (Scott et al., 2006). Bar charts, Polar plots, Hierarchical cluster analysis (HCA) and Sammon mapping are some of the methods used to do so

Headspace Analysis by Electronic Nose

A semiconductor electronic nose with a sensor array of 15 elements has been fabricated by magnetron radio frequency sputtering technique for detecting various volatile organic compounds (VOCs) in a low concentration range from 50 to 250 ppm in air at 300°C. The main components of the array have been titanium oxide and tin oxide (the latter has been doped with different Pt doses) semiconductor oxides with different thicknesses. A good single classification for six tested VOCs (propanal, methyl ethyl ketone, octane, benzene, toluene, and chloroform) has been obtained from this electronic nose through the technique of principal component analysis. In general, good response times, sensitivity and reproducibility values have been obtained for all sensors, but it is interesting to underline the sensitivity increases to these gases from sensors in which titanium oxide is used for their preparation.

E-noses employ an array of chemical gas sensors, a sample handling system and a pattern recognition system. Pattern recognition provides a higher degree of selectivity and reversibility to the system leading to an extensive range of applications. These ranges from the food and medical industries to environmental monitoring and process control. Many other types of different gas sensors available. These include conducting polymers (CP), metal oxide semiconductors (MOS), piezoelectric, optical fluorescence, quartz crystal microbalance (QCM) and amperometric gas sensors. The ideal gas sensor would exhibit reliability, robustness, sensitivity, selectivity and reversibility. High selectivity with high reversibility is difficult to attain. After signal processing and feature extraction the output of the sensors provide a unique smell print for that substances which can be used to classify, measure concentration, or verify quality. The present paper illustrates the function of electronic nose, its application and investigates the effective use of e-nose in detecting gases that have some smell developed by the volatile organic compounds (VOC) like ethanol, acetone and benzene at different concentrations. The response and characteristics prove that the Electronic nose is a reliable instrument which can be used for environment control (air quality, pollutants, and gas emission levels), medical science (urine, skin and breath odour etc.), food industry (coffee, milk, soft drink fish, meat etc.), pharmaceutics, chemical industry, Defence and security industries (detecting humanitarian land mines etc.) and semiconductor industrial processes. . Fig 6 describes a typical response signals for each odor obtained by the PDA-based e-nose. a) acetone, b) benzene, c) chloroform, d)cyclohexane, e) ethanol, f) methanol (Yang et al. ,2006)



Electronic-Nose Applications

Electronic-nose systems have been designed specifically to be used for numerous applications in many different industrial production processes. A wide variety of industries based on specific product types and categories, such as the automobile, food, packaging, cosmetic, drug, analytical chemistry and biomedical industries utilize e-noses for a broad and diverse range of applications including quality control of raw and manufactured products, process design, freshness and maturity (ripeness) monitoring, shelf-life investigations, authenticity assessments of premium products, classification of scents and perfumes, microbial pathogen detection and environmental assessment studies (Wilson and Baietto, 2009).The monitoring of flavour and/or aroma components is probably the area where electronic noses have been most widely utilized.Some of the applications are as follows.

1: During the winemaking process, unpleasant organoleptic taints arise from Brettanomyces yeasts spoilage. The two main components of the taint are 4-ethylphenol (4EP) and 4-ethylguaiacol (4EG). The existing procedures to monitor spoilage due to Brettanomyces Dekkera sp. are time-consuming and expensive, making it difficult for winemakers to monitor their wines at all stages of production. Consequently, there is a need for a rapid and cost-effective screening method to monitor the levels of 4EP and 4EG in wine.

In this way, Cynkar et al. used a MS-based e-nose (HP4440) together with PCA and stepwise linear discriminant analysis (SLDA). On the other hand, Berna et al. compared the performance of a MOS sensor based e-nose (FOX 3000) and a MS-based e-nose. GC–MS was used for quantification and prediction purposes. Following ethanol removal and SPME sample handling, the limits of detection of a MOS based e-nose were determined as 44gL−1 for 4EP and 91gL−1 for 4EG (values significantly lower than the reported human sensory thresholds). Partial least squares (PLS) regression of MOS based e-nose signals against known levels of 4EP and 4EG in 46 Australian red wines showed that such devicewas unable to identify Brettanomyces spoilage reliably because of the response of the gas sensors to inter-sample variation in VOCs other than 4EP and 4EG.

Conversely, the MS-based e-nose (SHS sample handling without ethanol removal but selecting a window scan excluding ethanol derived ions) was capable of reliably estimating concentrations of 4EP higher than 20gL−1 and good PLS correlations were obtained between estimates of 4EP and 4EG concentrations with the concentrations determined by conventional GC–MS.(Peris and Escuder-Gilabert,2009)

2: During black tea manufacturing, tea leaves pass through a fermentation in which the grassy smell is transformed into a floral smell. Optimum fermentation is extremely crucial in deciding the final quality of finished tea and it is very important to terminate the fermentation process at the right time. Bhattacharya et al. (2008) presented a study on real-time smell monitoring of black tea during the fermentation process using an e-nose (8 MOS sensors array) as well as prediction of the correct fermentation time. Different time-delay neural networks (TDNNs) and self-organizing map (SOM) methods for the prediction of optimum fermentation were used and both the methods appear to be suitable for the purpose. However, the combined SOM and TDNN-based prediction algorithm proved to be the better alternative as the computational complexity is relatively less. The results showed excellent promise for the instrument to be used for the on-line prediction of optimum fermentation time by the industry (Peris and Escuder-Gilabert, 2009).

3: 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, concentration of pollutants. One of the usefulness of this instrument is when it induces, on the analyzed products, the same structure as the one induced by a human sensory panel allowing instrumental measurement of sensory properties.

In this case, mathematical methods are used to exploit this correlation in order to bring in line the sensory panel capabilities. Sensory panel knowledge and capabilities are transferred to the production shop floor for routine analysis. Electronic Nose has been used to determine the shelf life of milk. To do this, milk was stored at ambient temperature and at constant temperature of 5°C. Samples of each of the stored milk have been analyzed by electronic nose at different times. In parallel to the instrumental analysis, milk changes have been investigated by estimation of the microbial count by using the 3MTM Petri film TM test. The microbial count evolution will be detected by the electronic nose results. The growth of total bacteria in the milk was measured at two temperatures: ambient temperature and 5 ◦C during 52 days (8 July 2003 to 28 August 2003). During this period, samples of the milk have been analyzed by electronic nose. The electronic nose used for this study was a Fox 4000 (ALPHA MOS, Toulouse FR) with three Metal Oxide Sensors chambers equipped with 18 sensors.

The results showed that measurement generated by the electronic nose can be used to detect both bacteria growth in milk and shelf life. The time-events suggested by the mathematical method can be associated to significant dates in the milk evolution. So this instrument can be easily used to date products and to control their freshness (Labreche et al., 2005).

4: Meat, especially beef, reaches an acceptable state for consumption after a long period of storage at low temperature, a storage procedure known as aging. During storage, not only aging but also bacterial spoilage can occur. Consequently, to obtain appropriately aged meat, it is desirable to monitor the progress of aging and bacterial spoilage simultaneously.

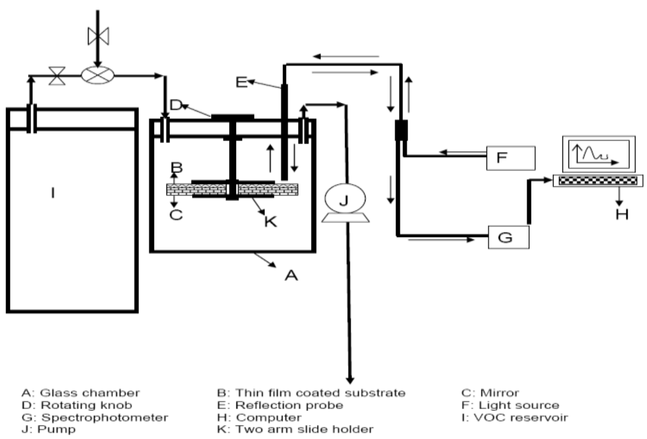
For this, a method was developed a direct sensing method for monitoring meat quality. The sensor is composed of an Ag/AgCl electrode and a platinum electrode on which putrescine oxidase or xanthine oxidase were immobilized to estimate bacterial spoilage or the progress of aging, respectively. A potential-step chronoamperometric method was applied in which the potential was stepped from 300 mV to 600 mV. A linear relationship was obtained between 5 and 60 nmol g-1 for putrescine (Put) and 0.05 and 1.0 µmol g-1 for hypoxanthine (Hx). The coefficient of variation was 0.75% for 20 nmol mL-1. Put solution and 2.2 for a meat sample using the putrescine sensor, and 1.09% for 0.25 µmol mL-1. Hx solution and 2.6% for a meat sample using the xanthine sensor. The pH requirements and substrate selectivity were suitable for the direct measurement of substrates on the surface of meat.

From the results of practical experiments, the direct sensing method was indicated to be useful with some modifications for the estimation of meat quality during aging. This method is capable of comparison with the electronic nose method (gas-sensor array). In principle, the results obtained from a gas-sensor array represent qualitative and quantitative information of the composition of the headspace gas mixture of a sample. The technique should therefore have a great potential in a number of applications related to meat.

Quality control is of great importance within the meat industry and with this technique it would be possible to monitor the meat from the raw material throughout the process and to the final product by analyzing volatile compounds released from the meat matrix. There are several aspects of quality control that may be the issue in the context of meat; Sensory quality, shelf life, spoilage, off-flavor and taints and authenticity. In addition, the electronic nose may have a potential in product development when it comes to the design of a product with certain flavor characteristics.

Electronic noses have been widely used to distinguish between "spoiled" and "unspoiled" meat products. Electronic nose techniques have also been used on several applications concerned with classification of meat samples. The electronic nose system could identify meat samples contaminated with Salnonella typhimurium at a population concentration level of 0.7–2.6 log10 cfu/g. Boothe and Arnold also employed an electronic nose technique to analyze the volatile compounds emitted from poultry meat samples. Their sensor used MOS based sensors. Their study revealed that the electronic nose was able to detect changes in the volatile compounds associated with chicken meat based on the storage time and temperature. Their technique was also found to give reproducible results even after 6 months, indicating that the electronic nose was reliable. They had performed a Principal Component Analysis technique (PCA) on the data they obtained from their electronic nose. They reported that the PCA maps they obtained were able to differentiate (classify) the smell patterns obtained from different poultry meat samples (fresh and stored) and also between the samples stored at different temperatures.

Fig7: The schematic diagram of opto-electronic nose system for detection of VOC.



Modified atmosphere packaging is commonly applied to various fresh products including poultry meat to extend the shelf-life of the product. Inhibition of microbial growth is achieved by elevated carbon dioxide level and/or by minimized oxygen level in the package headspace (Varnamkhasti et al., 2009)

5: An electronic nose based on acoustic wave sensors has been developed to detect spoilt fruit. Different varieties of fruits, edible and rotten, were analyzed. Starting from six sensors, the minimum number of sensors capable of discriminating between spoiled and unspoiled fruit was found. The discrimination capability of the sensor array was studied separately for each fruit variety, as well as for the whole set. Mathematical models were built to classify the fruits within a fruit variety, in an objective and clear way. The models were able to distinguish between edible and rotten fruits with 100% success for New Hall oranges, Golden apples, Kiwis and William pears, and with 97.2% of success for the Starking apples. Without forming fruit variety subsets, discrimination between edible and rotten fruit was achieved with 95% success.

The main purpose of these studies was to monitor the ripeness of fruit in order to find the optimum timing for harvest Fruit aroma is a complex mixture of alcohols, aldehydes, terpenes and mainly C1–C6 esters, and ethylene Acoustic wave sensors are inexpensive highly sensitive mass sensors. In order to detect volatile compounds, a sensitive layer must be applied onto the electrodes. This sensitive layer must be carefully chosen as it must be very stable and interact reversibly and selectively with the compound to be detected. The sensor signal is caused by adsorption of aroma compounds on the sensor coating which produces a frequency change that is proportional to the adsorbed mass.

This adsorption is ruled by physicochemical parameters of the volatile compounds and the applied film. The interaction between aroma compounds and coatings can be of several types, ranging from Van der Waals to hydrogen bonding, and depends upon polarity, steric hindrance and electron density. However, a covalent bond cannot be present because it would impair the reversibility of the sensor. The major goal in this study was to evaluate the potential of an electronic nose to detect spoiled fruit (Fernandes et al., 2008)

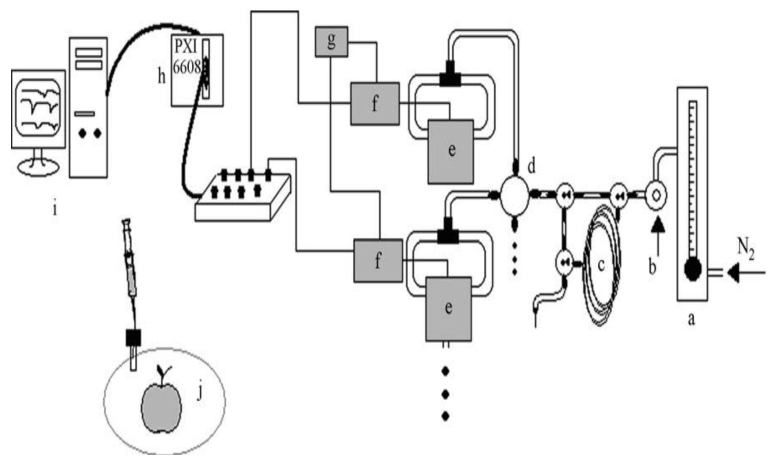


Fig 8:Experimental layout: (a) flow meter; (b) injection port; (c) sample loop; (d) distribution valve; (e) crystal cell; (f) oscillators; (g) power supply; (h) Counter/Timer PXI 6608; (i) computer; (j) sample bag with a septum to withdraw the sample

6: Aflatoxins are a group of toxic compounds produced by the secondary metabolism of toxigenic fungi, mainly of the Aspergillus genus. The occurrence of these toxins is frequent in food commodities, including cereals for human and animal consumption. Because of the highly heterogeneous distribution of aflatoxins in contaminated alimentary matrices, the availability of rapid and cost-effective analytical methods, which enable high sample throughput from the same lot, is urgently needed. From this point of view, the electronic nose appears to be a promising technology characterized by the required features. The ELISA test applied to the corn samples demonstrated the presence of aflatoxins at the concentrations of 90, 60, 50 ppb respectively, in three samples, while two samples showed contamination levels below the detection limit (3 ppb) of the ELISA assay.

Data generated by the electronic nose of corn samples previously analyzed by ELISA, were submitted to PCA. The statistical model revealed a clear separation of the samples into two groups, according to the presence and absence of total aflatoxins. The results from electronic nose analysis clearly indicated that it was possible to differentiate between samples that had been contaminated and those that were not contaminated with aflatoxins. These results were evident both in the case of naturally contaminated ground corn meal and in solutions fortified with synthetic aflatoxins. The results allowed assuming that in the case of aflatoxins, the electronic nose was able to detect contamination by both the direct detection of toxins and indirect recognition based on detection of volatile fungi metabolites associated to aflatoxins. (Campagnoli et al, 2009)

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7: An E-nose has been developed in a briefcase form factor (19.5cm×29.5cm×10 cm).The clean air produced from a pump carries aroma molecules of sample into a sensor chamber at flow rate 2 l/min. Four electrical solenoid valves were used to avoid mixing of gas from the reference and the sample. It is necessary for this type of measurement to switch between a reference and a sample glass in order to reduce the humidity effects. The sensor array consisting of three gas sensors: SnO_2, 0.5 wt% CNT–SnO_2 and 1 wt% CNT–SnO_2 was symmetrically embedded at the bottom of a Teflon chamber. A simple linear circuit, called as voltage divider, was employed for measuring the resistance of each gas sensor. The load resistance is 20k_±1% while the resistance of each gas sensor lies within the range 20–40 k_. The voltage input is fixed at 5V. The data were collected every second by a notebook computer using a data acquisition card (NI-DAQ 6008) under LabVIEW software for subsequent analyses (Wongchoosuka et al., 2010)

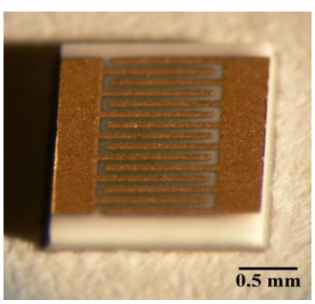
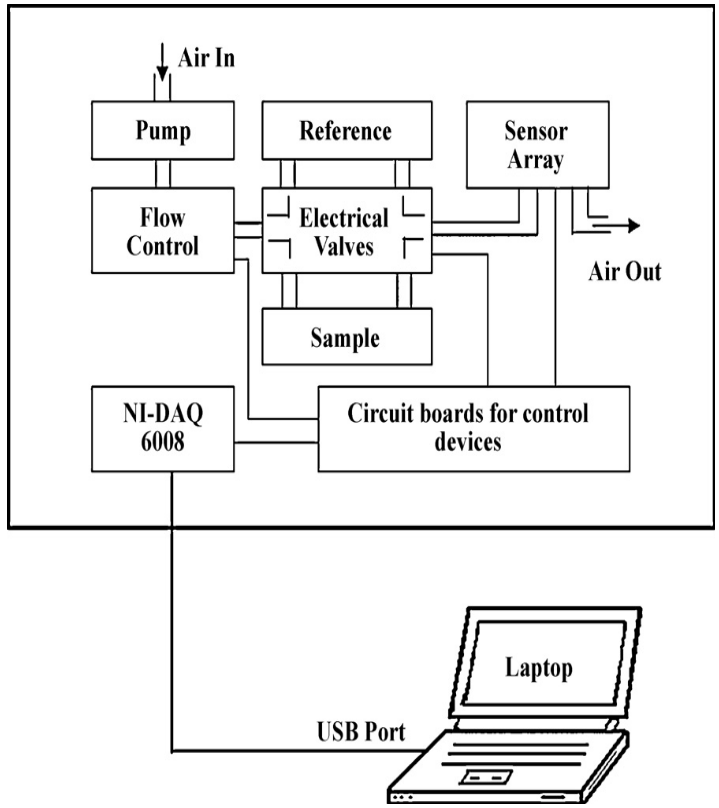


Fig 9: Schematic diagram of the portable E-nose system

Fig 10 shows Schematic diagram of the portable E-nose system



8: The aroma of grains is the primary criterion of fitness for consumption in many countries. However, the sniffing of grain lots for quality grading is potentially hazardous to humans and should be avoided because of inhalation of toxic or pathogenic mold spores such as from Aspergillus species.

Electronic nose was used with three different complementary sensors (ten gas sensitive metal-oxide-semiconductor field effect transistors, four tin dioxide-based sensors and a CO_2 sensor to test samples of oats, rye and barley with different aromas, and wheat with different levels of ergosterol, fungal and bacterial contamination. The ANN could predict the aroma classes of good, moldy, weakly and strongly musty oats with a high degree of accuracy. The ANN also indicated the percentage of moldy barley or rye grains in mixtures with fresh grains. In wheat, a high degree of correlation between ANN predictions and measured ergosterol as well as fungal and bacterial colony forming units (CFUs) was observed. (Wilson and Baietto, 2009).

9: An electronic nose was applied to the detection of adulteration of virgin coconut oil. The system, which is based on a surface acoustic wave sensor, was used to generate a pattern of volatile compounds present in the samples. Virgin coconut oil was mixed with refined, bleached and deodorized palm kernel olein at a level of adulteration from 1 to 20% (wt/wt). Adulterant peaks were identified from the chromatogram profile and fitted to a curve using linear regression. The best relationship (R 2 = 0.91) was obtained between the peak tentatively identified as methyl dodecanoate and the percentage of palm kernel olein added. Pearson's correlation coefficients (r) of 0.92 and 0.89 were obtained between adulterant peak methyl dodecanoate and of the iodine and peroxide values, respectively. Principal component analysis (PCA) was used to differentiate between pure and adulterated samples. The PCA provided good differentiation of samples with 74% of the variation accounted for by PC 1 and 17% accounted for by PC 2. Pure samples formed a separate cluster from all of the adulterated samples (Marina et al., 2010).

10: The application of an electronic nose equipped with a Metal Oxide Semiconductor sensor array for the detection of Alicyclobacillus acidoterrestris and A. acidocaldarius artificially inoculated in peach, orange and apple fruit juices was done. Overall the system was able to detect the presence of Alicyclobacillus sp. in all the tested fruit juices at 24 h from inoculation. The electronic nose could detect bacterial concentration as low as <102 colony forming unit/ml and it was also able to classify bacterial contamination independently of the Alicyclobacillus species. The gas chromatography–mass spectrometry characterization of the volatile profile of orange juices confirmed the existence of quantitatively different patterns between contaminated and uncontaminated samples (Gobbia et al., 2010).

Nowadays, electronic nose (E-nose) has become a powerful tool to evaluate the aroma compounds during the quality control process of foods and beverages. Besides, E-noses have also been employed for public safety, environment protection, disease diagnostics etc. E-nose is composed of an array of gas sensors made from various materials that display distinct gas-sensing behaviors of which differentiation can be combined and interpreted via pattern recognition techniques. Among the available sensing materials, metal oxide semiconductors (MOS), such as SnO2 and WO3, have been the most popular due to their high sensitivity to a rich set of volatile compounds. In this work, we report on an E-nose based on hybridized CNT–SnO2 gas sensors prepared by electron beam (E-beam) evaporation, which is inexpensive, fast, portable, reliable and suitable for use for the detection and classification of both solid and liquid samples. In addition, feature extraction techniques including integral and primary derivative are proposed for improving classification performance by principal component analysis (PCA). This E-nose was tested in a real-world application, i.e., for detecting methanol (MeOH) contaminant in whiskeys. This system will be a useful tool for quality assurance of whiskey produced by village industries.

2.1.2. ELECTRONIC TONGUE

Taste is comprised of five basic taste qualities: sourness produced by hydrogen ions of HCl, acetic acid,
citric acid and so on; saltiness produced mainly by NaCl; bitterness produced by quinine, caffeine, L-tryptophan and MgCl2; sweetness due to sucrose, fructose, glucose, L-alanine and so on; and umami, which is the Japanese term implying 'deliciousness', produced by monosodium glutamate (MSG) contained mainly in seaweeds, disodium inosinate (IMP) in meat and fish and disodium guanylate (GMP) in mushrooms. In biological taste reception, substances producing taste are received by the biological membrane of gustatory cells in taste buds on the tongue. Then information on the taste substances is transformed into electrical signals, which are transmitted along the nerve fibre to the brain, where the taste is perceived. One of the goals of a sensor is to reproduce the five kinds of senses of humans or surpass their abilities. In this case, the abilities required of sensors are the following. The first is high sensitivity, the second is stability and the third is high selectivity. The first two items seem to be fairly reasonable. However, the last is not always true. Surely, light is received in the case of the sense of sight. A sound wave is received in the sense of hearing. Pressure or temperature is experienced in the sense of touch. In these kinds of senses, only each physical quantity such as light and sound waves must be detected with high sensitivity and selectivity. A taste sensor should be able to measure those effects; discrimination of each chemical substance is not important here, but recognition of the taste itself is; and its quantitative expression is necessary. The taste sensor using lipid/polymer membranes embodies concept of global selectivity which implies the ability to classify a great variety of chemical substances into several groups, such as is really found in the taste reception in biological systems.

A multichannel taste sensor, namely an electronic tongue, with global selectivity is composed of several kinds of lipid/polymer membranes for transforming information about substances producing taste into electrical signals, which are input to a computer. The sensor output exhibits different patterns for chemical substances which have different taste qualities such as saltiness, sourness and bitterness, whereas it exhibits similar patterns for chemical substances with similar tastes. The sensor responds to the taste itself, as can be understood from the fact that taste interactions such as the suppression effect, which appears for mixtures of sweet and bitter substances, can be reproduced well. The suppression of the bitterness of quinine and a drug substance by sucrose can be quantified. Amino acids can be classified into several groups according to their own tastes on the basis of sensor outputs. The tastes of foodstuffs such as beer, coffee, mineral water, milk, sake, rice, soybean paste and vegetables can be discussed quantitatively using the taste sensor, which provides the objective scale for the human sensory expression. The flavour of a wine is also discriminated using the taste–odour sensory fusion conducted by combining the taste sensor and an odor-sensor array using conducting polymer elements. The taste sensor can also be applied to measurements of water pollution. Use of the taste sensor will lead to a new era of food and environmental sciences (Toko, 1998).

Measurement principle and data analysis

In voltammetric measurements a current is measured between the metal working electrode and the counter-electrode when a voltage pulse is applied over the working electrode and the reference electrode.
A set of pulses can be put together to form a pulse train in order to extract as much information as possible from the solution. When the potential is applied, electro-active compounds that react to that potential will be reduced or oxidized and a current, that can be measured, will arise. In measurements with the voltammetric electronic tongue, data are collected over the whole pulse and not only at the end of the
pulse, as in traditional electrochemistry. This is done since it has been found that extra information is also found at the beginning of the pulse (mainly conductivity and mobility). The electronic tongue creates a data matrix that is treated with MVDA, e.g. principal component analysis (PCA). PCA explains the variance in the experimental data and reduces the large data set to plots that can be easily surveyed. PCA produces a 'score plot' that visualizes differences between the experiments. This can be used for
classification or grouping of the experiments.

The electronic tongue consists typically of four working electrodes made of the metals gold, iridium, platinum and rhodium, an Ag/AgCl reference electrode and a stainless steel counter electrode. A relay box is used, enabling the working electrodes to be connected consecutively to form four standard three-electrode configurations. The potential pulses/steps are applied by a potentiostat which is controlled by a PC. The PC is used to set and control the pulses, measure and store current responses and to operate the relay box.

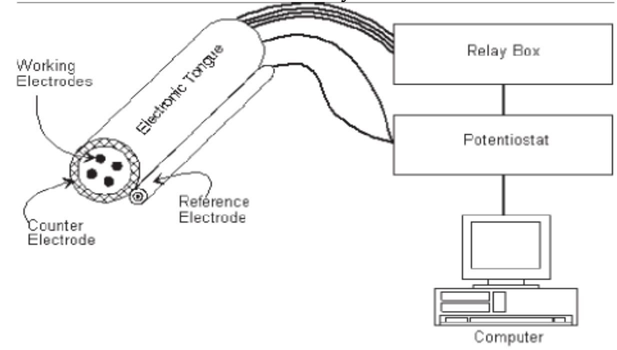


Fig 11 shows the schematic diagram of a Volta metric electronic tongue (Ivarsson et al., 2005)

Electronic tongue applications

There is an urgent need in the food industry for rapid, low-cost and simple methods of analysis and quality assessment of raw components, intermediate products during processing and final food-stuffs during storage. High performance liquid and gas chromatography, NIR (near infrared) spectroscopy and other methods are widely used now for this purpose (Kirk & Sawyer, 1991). These methods allow the determination of numerous compounds in many food-stuffs. However, the expensive laboratory equipment and highly qualified manpower needed to perform the analysis are significant drawbacks. On the other hand, analysis related to food flavor characteristics is not done by analytical instruments but by specially trained professional tasters. In spite of intensive studies during recent decades the correlations between the chemical composition of food and its flavor are often not well established or are highly complicated (Rudnitskaya et al., 2001).

1: An electronic tongue comprising thirty potentiometer chemical sensors and pattern recognition tools for data processing was used for the analysis of mineral waters, coffee, soft drinks and flesh food, namely fish. The electronic tongue appeared to be capable of distinguishing between different sorts of beverages: natural and artificial mineral waters, individual and commercial brands of coffee, and commercial and experimental samples of soft drinks containing different sweeteners. A quantitative correlation between human perception and 'electronic tongue' output was obtained. Taste parameter assessments produced by a professional taste panel were used for 'electronic tongue' calibration. It was found that the 'electronic tongue' is capable of distinguishing sea water and freshwater fish and monitoring their spoilage (Rudnitskaya et al.,2001).

2: Dutch scientists have developed a new methodology to mimic the actions of the tongue which could enhance the formulation of low-fat versions with the texture of their high fat originals. Developed within the research programme Top Institute Food & Nutrition (TIFN), scientists led by NIZO Food Research Harold Bult developed a methodology to provide information into the the pressures and shear forces that a food undergoes into the mouth. Differences in the observed mouth feel of foods can thus be related to the way a food product reacts to pressure and shear. Reduction of fat in products is of growing interest to food manufacturers and this new methodology appears to address these issues, by providing some spatial profiles of oral behavior based on the movement of tongue and cheeks during consumption.

3: An electronic tongue based on pulsed voltammetry over an array of electrodes with different sensitivity and selectivity patterns was used to recognize six different microorganisms: one yeast, two bacterias , three molds. Measurements were performed during the whole growth period from lag phase to the stationary phase. The electrode array was dipped into the malt extract growth medium and voltage was applied over the electrode in pulses of different amplitude and the resulting data was evaluated through principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA). After further growth however all the included microbial species could be recognized from each other (Soderstrom et al., 2002)

4: An important industrial application for electronic tongues is as a monitoring device in drinking water production plants. The quality of drinking water varies due to the origin and quality of the raw water and with efficiency variations in the drinking water purification process. A Volta metric electronic tongue was thus used for quality estimations of water samples from three parallel sand filters in a drinking water production plant. The raw water samples are well separated from the treated water samples in the plot. Samples were collected and measured each week and the drifts in the filters were clearly observed. Shortly afterwards, this filter was taken out of use for regeneration. The Volta metric electronic tongue has also been used in the dairy industry. One application has been to follow the fermentation process in yoghurt fabrication (Winquist, 2008).

Electronic tongues are an emerging and promising field in modern chemical sensor science. Electronic tongue systems seem to be very useful for process monitoring and as a quality-control tool in the food industry, in clinical analysis, and in environmental control in research laboratories, etc. Although it has already been suggested that some electronic tongues should be marketed as commercial instruments, this direction of analytical chemistry and sensor science is quite young and research in the area remains substantially semi-empirical. Significant efforts are needed and expected in the following fields: experimental evaluation of sensor mechanisms and theoretical consideration of electronic tongue operation;

- development of new sensors and new sensor arrays; and
- development of the application approaches to numerous practical tasks.

The value of research and development of electronic tongues and related prospects for the liquid sensing seems to have been seriously underestimated in the recent past, although this situation is now changing for the better. An increase in research and commercial interest in this area expected in the near future (Vlasov et al., 2002)

3: Conclusion

Innovative food companies have shown an increased interest in developing fast analytical techniques to characterize the flavor/aroma of food products that compare well with sensory analysis by human taste panels. Fast sensory-directed techniques can rely on electronic nose (e-nose) or electronic tongue (e-tongue) technology. Both technologies have been developed by research laboratories and commercial companies during the past 10 years, but still have a long way to go before they are applied in an industrial environment. As the human nose is involved in 80–90% of the total flavor perception, digital odor characterization using electronic nose technology can be used for fast classification of food products in good accordance with sensory analysis.

Although there may be few problems associated with the development of electronic nose and tongue such as improper calibration, sensor drift, relatively short shelf life of few sensors, necessity to do some considerable amount of developmental work according to the specific needs. Regardless of this concerns both the electronic nose and the electronic tongue can provide help for analyzing a variety of food products and determine their shelf life in a more concise and appropriate manner than the earlier methods of analysis. This new era of nanotechnology will help in improvising food quality to a newer level that could guarantee the product quality up till its consumption.

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