Electronic noses and electronic tongues

THE TASTE OR SMELL OF END-PRODUCTS MANUFACTURED IN THE FOOD, BEVERAGE, PHARMACEUTICAL AND COSMETIC INDUSTRIES CAN BE OF VITAL IMPORTANCE TO THE COMMERCIAL SUCCESS OF THE PRODUCT. IDEALLY TASTE ANALYSIS, BOTH IN THE DEVELOPMENT OF NEW PRODUCTS AND THEIR ROUTINE PRODUCTION, SHOULD BE CARRIED OUT BY TASTING PANELS COMPOSED OF HUMAN EXPERTS. IN PRACTICE SUCH PANELS ARE EXTREMELY EXPENSIVE AND ESPECIALLY PROBLEMATIC WHEN USED FOR PRODUCTION CONTROL PURPOSES. ELECTRONIC NOSES AND TONGUES HAVE BEEN DEVELOPED THAT ARE BASED ON A POWERFUL COMBINATION OF SENSITIVE SENSORS AND SOPHISTICATED SOFTWARE. OPERATING IN A MANNER THAT IS ANALOGOUS TO THE WAY HUMANS PERCEIVE ODOURS AND TASTES, SUCH E-NOSES AND E-TONGUES ARE PROVIDING SOLUTIONS TO THE PROBLEM OF RELIABLE TASTE AND ODOUR MEASUREMENT.

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Odour and taste are, of course, very important in the food, beverage, pharmaceutical and personal care industries. The expectations of consumers regarding the quality of products in these fields are continually increasing as a result of greater range of choices in the marketplace together with targeted advertising, which emphasises product quality. Competition for market share and the added emphasis on quality have increased pressure on product development and rigorous QA/QC to meet consumer expectations.

TASTING PANELS

For manufacturers, the quality of in-coming raw materials and finished products are of the upmost importance to achieve maximum consumer satisfaction.

The organoleptic characteristics of these products are typically assured by human sensory panels such as consumer panels and expert sensory panels that are widely used for product development, product optimisation and product matching in the food and beverage industry. The members of the expert panels have very special skills for describing products, both qualitatively and quantitatively, for odour, taste, mouth-feel, texture and many other attributes. Panel selection, training and re-training is part of the process of maintenance of an expert sensory panel. Tasting panels are however a resource that must be used sparingly since the members' senses fatigue and their efficiency decreases with increasing panel session times so that, typically, sessions are limited to 1 hour duration. Special environments are also necessary to ensure that there is no bias during preparation of samples, tasting and smelling of samples. For odour/taste and texture tests, standardised lighting must be used to ensure that no bias is introduced via the taster's perception of the product's colour. After product development, it is the responsibility of the manufacturing department to ensure that the end-product respects the specifications and is identical to the product defined in R&D.

Processing methods that are similar to those used in development should be used in manufacturing together with tight QC of raw materials, ingredients and additives. The final verification that the manufactured product is identical to that defined in R&D ideally lies in using the same final testing methods in both R&D and manufacturing, i.e. the use of tasting panels.

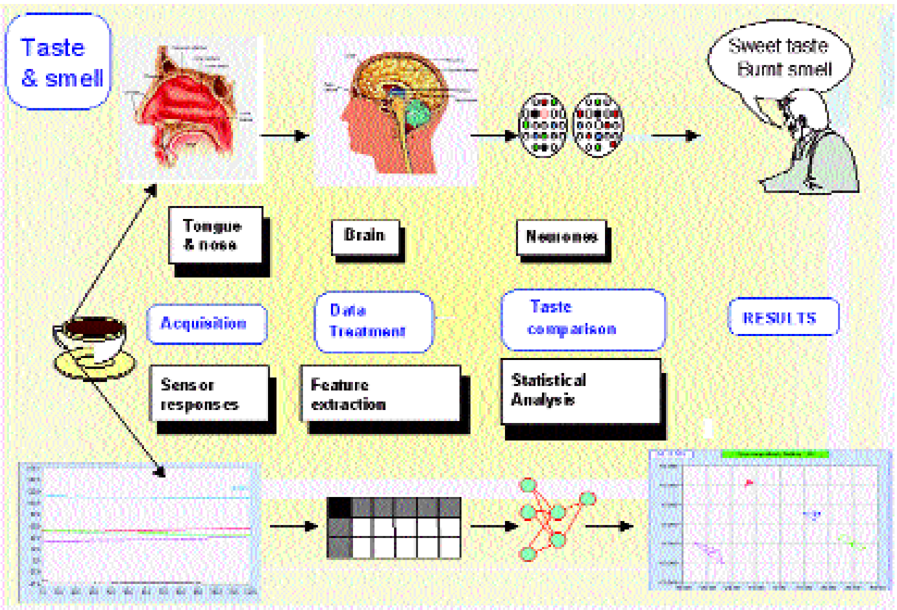

Figure 1. Schematic representations of electronic nose and tongues. Like human beings such systems require training with an appropriately selected set of samples to ensure both good taste recognition and reproducibility. Use of electronic nose and tongues involve the same training, model building and validation procedures

The use of sensory panels in manufacturing plants is however significantly more difficult than within a R&D environment. Typically, sensory panelists in the factory are staff with other main responsibilities so that their availability can be limited. In addition, the production environment is very hostile to sensory analysis with the noise, odours and pressure making it difficult to get objective and reproducible results. Unlike the typical sensory panelist in R&D, a panelist in a manufacturing environment needs continual motivation when faced with for repetitive QC tasks for evaluating new production batches.

In practice, therefore, such problems make the sensory panel method of QC difficult to implement and maintain in terms of routine operation and costs. However, given that the end-consumer will judge the product on the basis of taste, it is vital that the QC process of verifying taste be maintained. Such conflicting pressures are the impetus behind the current trend to improve current sensory QC/QA methods by the introduction of alternative or complementary methods.

Such methods must be fast, accurate and cost effective and of course must correlate with the results of sensory panel analyses.

SENSOR ARRAY SYSTEMS

Nowadays, odour, aroma and taste control evaluation can be performed by gas and liquid sensor array system - the so-called electronic nose and electronic tongues. Due to their simplicity, rapidity and objectivity, they have started to be extensively used by major food, cosmetic and packaging companies in various applications such as quality control, product matching, origin identification, spoilage detection, and flavour quantification. Without needing any prior fractionation, electronic noses and tongues can determine the fingerprint of a complex volatile or dissolved compound mixture by an array of semi-specific sensors coupled to a pattern recognition system. Just as humans do, an electronic nose operates by recognising the overall pattern of components. In addition, the "odour/aroma and taste fingerprints" could then be stored in a data base in a way analogous to the memorisation of olfaction perception in the human brain.

PRINCIPLES OF OPERATION

E-noses are comprised of four basic elements, namely a sampling system, an array of sensors, an electronic data acquisition and control system and a pattern recognition software

In the E-nose, the sampling system is used to introduce the odour or headspace sample to the chemical sensors and is designed to do this in a reproducible manner.

SENSORS

The chemical sensors are basically detectors whose conductance changes when volatile chemical compounds come into contact with the surface of the sensor and reacts with its sensitive material. There are several types of sensors, of whom the most commonly used are Metal Oxide Sensors (MOS), Conductive Polymer Sensors (CP) and Quartz Crystal Micro-balance sensors(QCM). Recently E noses based on mass spectrometry have been produced.

MOS sensors are the most commonly-used and are based on doped metal oxide and undoped complex metals. Comprising a thin layer (50µm) of an oxide film deposited on a ceramic tube or plate, they operate at temperatures between 175°C and 450°C. The selectivity of the sensors is related to different catalytic amounts of a doping metal (such as Pd in tin oxide sensors) introduced as a trace impurity on the sensor surface. Very sensitive(ppm or in some cases ppb) and with a rapid response rate, these sensors react to a broad range of chemical compounds. The use of arrays of such sensors with different characteristics can however give rise to a specific selectivity, i.e. a pattern or "fingerprint" of several sensors.

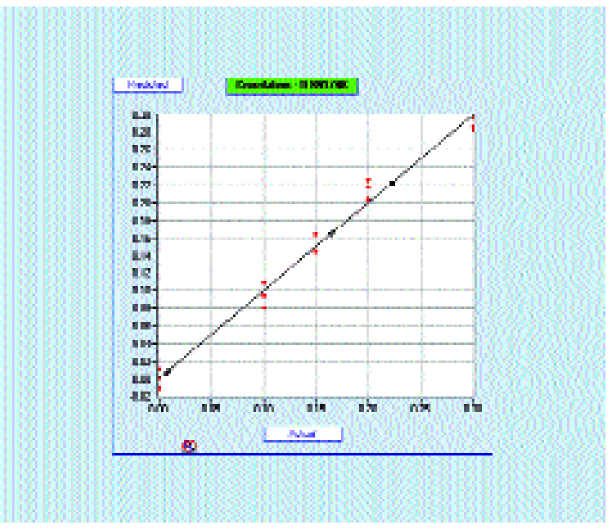

Figure 2. Linearity of response of estimations of peppermint flavour in toothpaste. Correlation coefficient, r^2, was >0.997 Determinations carried using an 18 sensor E-nose, Fox 4000, Alpha MOS, France

CP sensors consist of a silicon substrate on which conducting polymers have been electrochemically deposited. The conducting polymers electrochemically polymerised in situ from pyrrole, indole, thiophenes and aniline monomers and their derivatives. Each individual device has a distinctive response characteristic to various odours. The polymers are very responsive to vapours from polar molecular species but have very little or no response to alkanes and non-polar species, thus making them complementary to MOS sensors. In contrast to MOS sensors, CP sensors are more sensitive to variations in humidity.

In QCM sensors, the sensing element is a coated resonator. A thin coating of silicone or polyglycols is deposited onto a quartz support. When the sensor is exposed to gas molecules, both absorption within and adsorption onto the coating will occur to an extent which depends on the solubility of the gas in the particular coating.

The result is a change in the mass of the crystal which affects the frequency at which the crystal oscillates. This change in frequency is detected electronically and results in an output signal for further amplification.

The combination of several sensors, of different basic types, but also of sensors of the same type but with different response characteristics, enables a wide range of chemicals and odours to be detected. The particular choice of sensors depends on the individual application. Advice on choice of sensors is generally provided by the manufacturer. Frequently, the development and validation of a method in a particular application is first carried out with a research type e-nose containing a large range of sensors. Depending on the different responses of individual sensors, a more restricted choice can then be made of a smaller number of sensors which nevertheless can satisfactorily carry out the analysis. These latter systems are frequently used for routine production monitoring and QC purposes.

Pattern recognition software

Since all e-noses comprise arrays of electronic chemical sensors, all of which provide a time-dependent output signal in response to an odour. The dynamic sensor signal depends on several physical parameters, such as the speed of the flow that carries the odour from the source to the sensor array, the chemical nature of the odour itself, the diffusion and reaction of the odour within the active sensing material and the ambient conditions such as pressure, temperature and humidity.

Sophisticated software is necessary to be able to handle such complex information. In general, such software is based on powerful algorithms for pattern recognition.

The most well established algorithm is that for static pattern recognition and includes techniques such as principal components analysis, discriminant function analysis, cluster analysis and multilayer perception based neural networks. (Ref 1)

More recently algorithms have been developed to process signals from sensor arrays dynamically.

Such dynamic processing techniques include traditional parametric and non-parametric methods as used traditionally in the field of system identification, as well as linear filters, time series neural networks. In addition to being able to cope with the dynamic nature of the response of the sensor array, such dynamic signal processing techniques are also particularly suited to handle factors such as sensor drift.

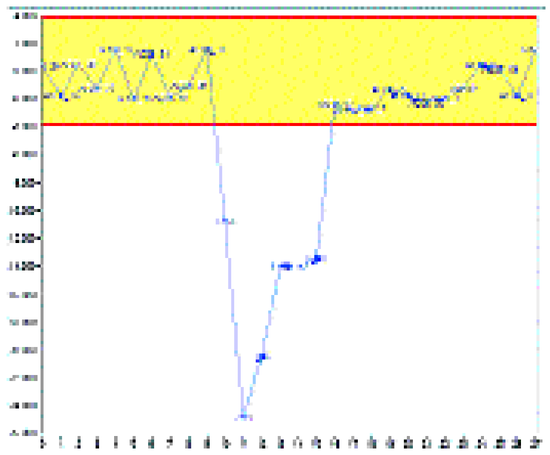

Figure 3. Use of an E-nose for quality control of a production process (estimation of peppermint flavour in different batches of toothpaste). Acceptable product limits are indicated by the yellow band. Data generated by a 6 sensor Gemini Plant QC E-nose, Alpha MOS, France

Electronic Noses and Electronic Tongues: A comparison.

Electronic nose and electronic tongues instruments analyse different aspects of the sensory perception. The electronic nose (E-nose) measures volatile components of aroma/odour in the sample headspace while the electronic tongue measures dissolved organic and inorganic components (i.e. non-volatile molecules, DOC) that remain in the food/beverage.

For electronic noses, the final response can be described as R = f (SG, H (P)), where SG represents the sensitivity and selectivity of the gas sensor array sensitivity and selectivity and H (P) is a variable representing the properties of the sample headspace. Typically, E-noses measure attributes like flo-

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ral, estery, hoppy, acetaldehyde, mouldy as well as many others. These attributes are typically very different for different applications.

Electronic tongue (E-tongue) sensors detect all chemical species present directly in the liquid samples. Only some of these species can be observed in the sample headspace generated. The response R can be described as R = f (SL, P), where SL represents the sensitivity and selectivity of the liquid sensors and P represents the properties of the liquid sample. Typically, E-tongue systems measure attributes like saltiness, sweetness, bitterness, sourness and metallic taste. In general, these attributes are fairly similar for each application area.

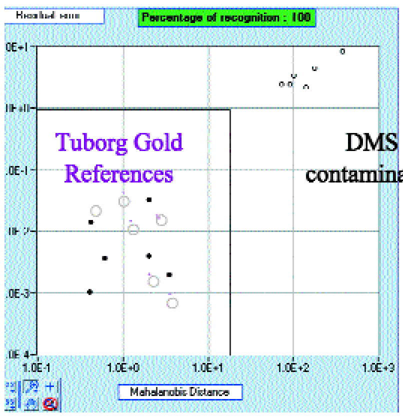

Figure 4. E-tongue evaluations of beer for off-flavour caused by high levels of Dimethyl sulphide. Data obtained via soft independent model class analogy (SIMCA) analysis of beer using an Astree e-tongue

The two instruments are thus complementary in most applications.

Benefits of E-nose and E-Tongue

E-Tongues and E-Noses have the ability to perform sensory based analyses like odour/aroma and taste rapidly and in a cost-efficient manner. Not only are the systems more rapid and objective than human-based tasting panels but they are much more amenable to routine use for example in production QC applications. Since they correlate well with human sensory panels, the instruments can be described as a 'consumer based instrumental test'.

E-noses and tongues also correlate well with more classical analytical methods such as HPLC and GC/GC-MS instruments which measure a specific analyte or group of analytes. E-noses and e-tongues are however much more rapid. For example the HPLC analysis of caffeine levels in a carbonated soft drink generally takes about 15 minutes. An E-tongue will give the result in approximately 3 minutes.

Applications

Both the E-nose and the E-tongue can be used for a wide variety of analytical applications including quality control and product matching. Just like a human taster and odour controller, E- noses and E- tongues can be used for both quantitative and qualitative applications. Quantitative applications include sensory score correlation and the measurement of the concentration of flavours or fragrances within a food or cosmetic product. Qualitative sensory applications include the determination of the origin and quality of raw materials, consistency of finished products, and taint-free products. Other applications of the technologies include shelf life measurements and the evaluation of any interactions between packaging and the product. The following examples illustrate typical applications of the techniques.

Quantification of peppermint flavour in toothpaste

In this example, a preliminary evaluation of a method employing an E-nose was carried out in an R&D environment. After successful validation of the method it was transferred to a more simple E-nose for routine use in a production QC capacity.

For the initial development work, a Fox 4000 Electronic nose equipped with 18 sensors was used (Alpha MOS, France) Samples with fragrance concentration from 0.1% to 1.0% were prepared and analysed on the system. 0.5 g of each sample was introduced in a 10 ml vial. After an equilibrium period of 5 minutes at 40°C, 1 ml of the gas phase was injected in the E nose.

A calibration curve was constructed using partial least squares (PLS) regression analysis. Figure 2 shows the linearity of the response. Additional samples with intermediate concentrations were prepared and analysed. The experimentally-derived values of these samples were found to correlate precisely with their expected value (Figure 2)

When the method development process was completed, the system was set-up in a production environment as part of the QC evaluation of the production process. For this a Gemini QC/QA instrument was used. This E-nose has a throughput time of 5 minutes and incorporates 6 sensors. These were chosen from the optimised sensors used in the preliminary 18 sensor development work. Figure 3 shows typical results from several production batches. The data were treated using statistical quality control (SQC) analysis; the acceptable range of concentrations was fixed as between 0.2% and and 0.5% and is shown within the yellow band. All unacceptable samples are outside this range. The SPC data allow realistic production limits to be set and controlled taking into account intrinsic manufacturing variabilities but also the important QC characteristics of the product defining customer acceptability. In practice, alarms would be triggered whenever a an out-of-specification result or trend is detected, allowing prompt adjustment of the production process.

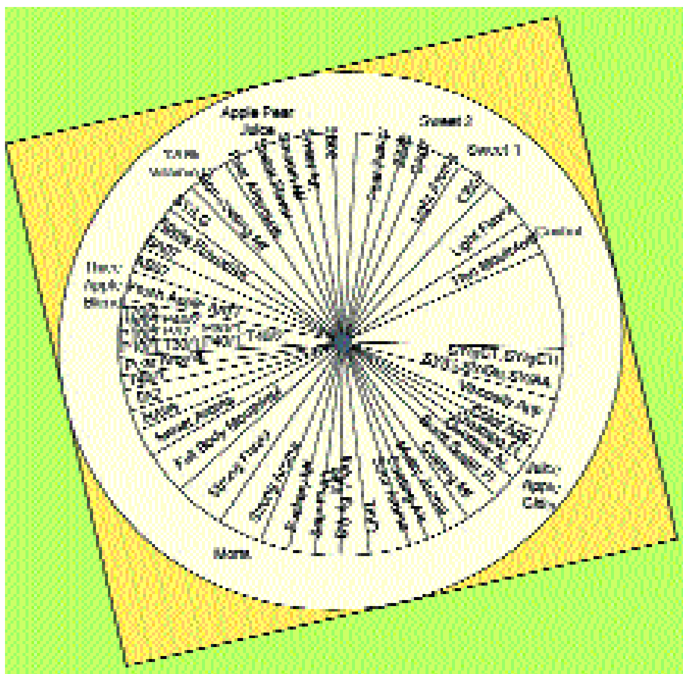

Figure 5 Schematic representation of the results of analyses of apple juices obtained by a sensory testing panel, e-tongue instruments and e-noses.. This method of presenting taste data enables connections to be established between the results of individual sensors and the descriptions of taste perceptions given by the tasting panel

Flavours in Beer

E-tongues can be used for general batch analysis of beers but are also being used to detect off-flavour in beer such as is produced if the beer contains too high a concentration of dimethyl sulphide (DMS). This can be formed from a malt-derived precursor during wort production or can result from bacterial contaminant during fermentation. Acceptable DMS concentration in beer is 0.01 - 0.25 mg/l. Figure 4 shows experimentally derived E-tongue data on various beers containing different levels of DMS The samples outside the rectangular box have been correctly detected as having a high level of DMS. Samples within the box are considered acceptable variations of good beer containing the usual amount of DMS and other flavour and taste compounds. These experimental data were generated by the E-tongue within several minutes; a classical chemical determination of DMS in beers involves prior extraction of the beer and is tedious and time-consuming.

Bitterness in beer

An extremely important taste attribute of beer is its bitterness. Typical American style beers have low bitterness characteristics (in the order of 6-8 Bitterness Units, BU) while in general European beers are typically more bitter in character (10 - 50 BU)and in general contain more flavours. The industry uses an internationally accepted method to measure bitterness units where bitterness is calculated through spectrophotometric determination of iso-octane at 275 nm. Classical chemical analysis of iso-octane in beer is however tedious to carry out, and involves prior extraction sample. Using e-tongues, the bitterness of beers can be evaluated out in minutes. Data generated by e-tongues correlate well with the reference chemical method and show a linear response over bitterness range up to 60 BU.

Apple juice quality

A broad range of apple juices,including a three-apple blend, vitamin C- fortified apple juice, apple pear juice, and an apple cider was analysed in order to compare the results generated by the e-tongue system with the results of a complete sensory testing panels

Figure 5 shows the full analyses that were carried out and shows the relationship between the sensory and instrumental measurements that were made. The results show that certain E-tongue sensors like the ZZ36 and the CA07 are more correlated to the sweetness attribute while BA07 and AB07 are more correlated with apple flavour and fresh apple attribute.

Food Ingredients

The analysis of food ingredients is an important field of application of e-nose technology and many systems are used on a routine basis throughout the food industry.

The Cerestar Research and Development Centre, Vilvoorde Belgium, is using e-nose technology as a powerful tool to complement the expensive and subjective sensory panels that the centre uses for sensory evaluation and assessment of the quality of a variety of food ingredients. Using an e-nose (Model E5000, Marconi, UK) as well as GC-MS methods, a comprehensive method development study has been carried out for food ingredients such as starches, maltodextrins, glucose syrups as well as oils, lecithins and feed products.

It was found that, for all these food ingredients, MOS sensors discriminated best between good and off-flavoured samples. For all these ingredients a good correlation was found between the e-nose results and those from the sensory analysis. It was found that, because of their relative lack of sensitivity, CP sensors were not suitable for this application.

All-in-all, Cerestar have concluded that e-nose technology can provide objective and rapid characterisation of overall flavour quality, and fills the gap between taste panel and specific analytical techniques such as GC-MS.

On the basis of their studies, Cerestar recommend that in situ evaluation of cheap, robust QC-scale e-nose instruments (including hand-held instruments) be carried out when food ingredient analysis is to be carried out.

Industrial packaging.

In the manufacture of plastic containers of drinking water, it is important that the plastic used be tested rigorously to ensure that there is no plastic taste imparted to the water. Traditionally, the pellets of the plastic raw material, typically polyethylene, PE, are tested for this by lengthy soaking in water. This is then diluted serially until no odour or taste is detected. Such tests are generally carried out by a number of sensory panelists and are consequently extremely expensive and time-consuming.

A leading German manufacturer (Basell Polyolefine GmbH, Frankfurt) of PE for use in the manufacture of drinking water bottles has installed an electronic nose to carry out such analyses. Over a period of time now stretching to 2 years, such electonic noses have performed well and reliably, and generate results much quicker than with a standard QC sensory panel. Periodic replacement of the e-nose sensors has not affected the performance of the system over this time period.

Summary

Electronic Noses and Electronic tongues are particularly suitable for the carrying out, mainly within a QC/QA environment, of rapid and objective sensory measurements, that are important in the food, beverage, pharmaceutical and personal care industries. Systems exist for either quantitative and qualitative analyses and have been shown to be useful in a wide variety of applications.

When operated correctly, and calibration, validation and training process, the technology has been shown to be able to contribute significantly to the maintenance or improvement of quality for products destined for both the consumer market and the industrial market and to improve quality for both consumer and industrial products in these domains. In several sites e-nose and e-tongue systems have by now clocked up several years of satisfactory operation.

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Further reading

www.nose.uia.ac.be

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