Olfative Sensor Systems for the Wine-Producing Industry

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ABSTRACT

The quality of wine is influenced by different sensory characteristics. The most important is aroma. This attribute has a 70% weight in sensory panels with respect to texture and taste. Usually, the determination of volatile compounds is carried out through expensive techniques such as gas chromatography-mass spectrometry (GC-MS) which require complicated extraction methods and in addition are very expensive. The most important drawback, however, is that these techniques are not able to measure in real time and in an on-line process. Olfactive sensor systems (electronic noses) technology has emerged as a possibility for aroma profile analysis. The electronic nose consists of an array of gas sensors with different selectivity, a signal collecting unit, and a pattern recognition software (PCA, ANNs, etc). Different types of sensors have been used to detect wine aroma, such as electrochemical sensors, resistive sensors (mainly type MOS), and gravimetric sensors (type SAW) allowing for the distinguishing of wines elaborated with diverse grape varieties and ageing processes. It has also been possible to determine the detection and recognition threshold values of typical compounds of the wine and to compare them with the values obtained by a sensory panel, as well as to discriminate defects in order to detect adulterations or to identify ageing times and barrel type in order to avoid frauds. Portable systems are being developed for measuring in situ the wine evolution process, which is of great interest to the wine-producing industry.

Keywords: sensor, wine, electronic noses

INTRODUCTION

Among the numerous applications of electronic nose technology, the analysis of foodstuff is one of the most promising and also the most travelled road towards industrial applications. On the other hand, since human senses are strongly involved in the interaction with foods the analysis of food provides an excellent field to compare the performance of natural and artificial olfaction systems. The electronic nose, being non-destructive and, in principle, directly correlated with the consumer perceptions, is a good candidate to develop quality evaluation tools for quality assessment (reviewed by Lozano Rogado 2006).

Olfactory systems

The human nose is much more complicated than other human senses like the ear and the eye, at least regarding the mechanisms responsible for the primary reaction to an external stimulus. Therefore it has been much simpler to mimic the auditory and the visual senses. In olfaction hundreds of different classes of biological receptors are involved. Although several interesting developments have been made regarding so called electronic noses, their performance is far from that of our olfactory sense. They are not as sensitive as our nose to many odorous compounds. The human nose contains approximately 50 million cells in the olfactory epithelium that act as primary receptors to odorous molecules. There are about 10,000 primary neurons associated with these primary receptors that synaptically link into a single secondary neuron which in turn feeds the olfactory cortex of the brain (Persaud 1982). This parallel architecture suggests an arrangement that could lead to an analogous instrument capable of mimicking the biological system. In Fig. 1 the analogy between the biological and the electronic nose is shown. Despite this difference, chemical sensor arrays combined with pattern recognition methods are very useful in many practical applications such as monotonous tasks in quality control. Electronic noses are thus emerging as new instrumentation, which can be used to measure the quality or identify an aroma of a product (reviewed by Lozano Rogado 2006). They work in a similar way and have, in that respect, a large similarity with the human nose (Gardner 1999; Pearce 2003).
The electronic nose is an electronic system that tries to imitate the structure of the human nose, so the first step in both is the interaction between volatile compounds (usually a complex mixture) with the appropriate receptors: olfactory receptors in the biological nose and a sensor array in the case of the electronic nose. One odorant receptor is sensible to multiple odorants and one odorant is detected by multiple odorant receptors. The next step is the storage of the signal generated by the receptors in the brain or in a pattern recognition database (learning stage) and later the identification of one of the odour stored (classification stage).

Wine aromas

Wine is one of the most complex alcoholic beverages with more than 1000 of volatile components identified in its headspace ranging from a few ppm to a few percents in weight, mainly alcohols, esters, ketones, acids, ethers, aldehydes, terpenes, lactones, sulphur-, nitrogen-, carbonyl-, phenolic-compounds. Hence, the features extraction procedure results elaborated to qualitatively and quantitatively assess the wine aroma profile. Due to high economic value of the wine-product for some worldwide typical geographical areas and annexed socio-cultural reasons, the development of analytical methods and pattern recognition systems for wines classification is extremely important, mainly for the assignment of a trade mark such as protected designation of origin (PDO), controlled denomination of origin (CDO), protected geographic indication (PGI) for quality wines. In this context, useful analytical systems coupled to pattern recognition methods serve to wines identification and, consequently, to protect the trade-marked quality wines and to prevent their illegal adulteration.

Traditional methods of analysis of wine aroma

The detection of aroma and the quality control of foodstuffs and beverages can be assessed by different analytical methods for the identification of the organoleptic properties of the products. In fact, the classical methods of chemical analysis such as gas and liquid chromatography, mass spectrometry, nuclear magnetic resonance and spectrophotometry are highly reliable and suitable for these purposes, but these analytical techniques are of high cost, long processability and low in situ and on-line measurableness.

The human nose is currently used commercially to test a diverse range of products. Highly skilled, trained human panels have been used to evaluate the odours produced from food products such as wines, grains, tea and cheeses in order to determine their quality and freshness. In the medical profession, the sense of smell is also used for the diagnosis of common disorders such as pneumonia and diabetes, as these disorders produce distinguishing odours that can be recognised by a trained human nose.

Chromatography is a method for the separation and analysis of complex mixtures of volatile organic and inorganic compounds. A chromatograph is essentially a highly efficient apparatus for separating a complex mixture into individual components. When a mixture of components is injected into a chromatograph equipped with an appropriate column, the components travel down the column at different rates and therefore reach the end of the column at different times. A detector is positioned at the end of the column to quantify the concentrations of individual components of the mixture being eluted from the column. Several different types of detectors can be used with chromatographic separation.

ELECTRONIC NOSES

An accepted definition of an electronic nose is: “an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognizing simple or complex odours” (Gardner 1999) and tries to characterise different gas mixtures. This definition restricts the term electronic nose to those types of sensor array systems that are specifically used to sense odorous molecules in an analogous manner to the human nose. However, the architecture of an electronic nose has much in common with multisensor systems designed for the detection and quantification of individual components in a simple gas or vapour mixture. A simple flow chart of the typical structure of an electronic nose is shown in Fig. 2. It consists of an aroma extraction technique or air flow system which switches the reference air
and the tested air; an array of chemical sensors which transform the aroma into electrical signals; an instrumentation and control system to measure the sensors signal and a pattern recognition system to identify and classify the aroma of the measured samples in the classes previously learned when using supervised learning or perform by itself the classification in unknown classes.

It uses currently a number of individual sensors (typically 5-100) whose selectivities towards different molecules overlap. The response from a chemical sensor is usually measured as the change of some physical parameter, e.g. conductivity, frequency or current. The response times for these devices range from seconds up to a few minutes. By teaching a computer (or hardware) to recognise different patterns, it should now be able to classify the wine aroma belonging to the different classes of learned aromas or patterns. A very important part of the electronic nose is thus an efficient technique for pattern recognition.

Extraction systems

The aroma extraction system or sampling method carries the aromatic compounds from the food to the sensor chamber. Several aroma extraction techniques are usually used for electronic noses: static headspace (HS) (Penza 2004), purge and trap (P&T) (Pillonel 2002) and solid phase micro extraction (SPME) (Guadarrama 2001) are most common techniques used in wine applications.

In static headspace a thermodynamic equilibrium is allowed between the liquid sample and its vapour phase and then this vapour is extracted for analysis. Usually the vapour is transferred to the sensors by a constant flow of an inert gas. Static headspace is widely used for its simplicity and reproducibility. The main drawback of this method is the extraction of high amount of water and ethanol that can interfere with sensor response.

The purge and trap method is based on the transport of volatiles compound to a trap by means of an inert gas. Static headspace is widely used for its simplicity and reproducibility. The main drawback of this method is the extraction of high amount of water and ethanol that can interfere with sensor response.

SPME consists of the extraction of analytes from the matrix through the adsorption on a silica fibre covered by a sorbent material. Sorbent material is usually a polymer. For example, polydimethylsiloxane/divinylbenzene (PDMS/DVB) has been used for the discrimination of different types of wine from Madrid region and polyacrylate (PA), a non polar material, has been used to discriminate Spanish red wines varieties (Villanueva 2006). Desorption is achieved by temperature or by organic solvents.

There are three operation modes for SPME: direct, headspace and membrane protected. Related to SPME there are other techniques as headspace sorptive extraction (HSSE) and stir bar sorptive extraction (SBSE). Main advantage of SPME is that selectivity is achieved through the sorbent.

Sensors

The core of an e-nose is the array of gas sensors for the analysis of the head space of liquid or solid food samples. A gas sensor is a device that is capable of converting a chemical change into an electric signal and respond to the concentration of specific molecules in gases. Gas sensors can be based on electrical, thermal, mass or optical principles. The most common gas sensors used in electronic noses are: conducting polymers (Guadarrama 2000), quartz resonators (di Natale 1997), surface acoustic wave sensors (SAW) (Santos 2005) and semiconductor devices (Santos 2004).

Conducting polymer gas sensors exhibit interesting properties that make them useful for gas sensors: room temperature operation, easy to prepare and quick response among others. They experiment changes in their electrical resistance when exposed to different volatile species. In spite of some promising perspectives, these sensors lack specificity, show a limited reproducibility and display a marked cross-sensitivity to water vapour.

Quartz crystal microbalance sensors essentially weigh the amount of gas or vapour interacting with a sensing layer coated onto a microbalance. If a quartz crystal oscillator is coated with a material such as a gas chromatographic stationary phase the resonance frequency decreases at a rate quantified by the Sauerbrey equation provided the acoustic impedance of the coating material does not change and is similar to that of quartz.

The Sauerbrey equation (Sauerbrey 1959) is used in quartz crystal microbalance measurements. It gives the change $\Delta f$ in the oscillation frequency of a piezoelectric quartz crystal as a function of the mass $\Delta m$ added to the crystal:

$$\Delta f = \frac{-2\Delta m f_0^2}{A \sqrt{\rho_q \mu_q}} = -2 f_0^2 A \rho_q \nu_q^3 \Delta m.$$

Here, $f_0$ is the resonant frequency of the crystal, $A$ is the active area of the crystal (between electrodes), $\rho_q$ is the density of quartz, $\mu_q$ is the shear modulus of quartz, and $\nu_q$ is the shear wave velocity in quartz.

The process is essentially a single step sensing mechanism followed by a separate transduction step - direct weighing of the interacting analyte. This feature has the ad-
and rubber polymers as polyetherurethane (PEUT), polybutadiene (PBD) and polydimethylsiloxane (PDMS). Rubber polymers coated SAW sensors have been used in the discrimination of different wines from the same producer and from different grape variety and ageing processes (Santos 2005).

Semiconductor metal-oxide based gas sensors have been studied for many years, despite of this further research is ongoing mainly to improve their sensitivity, selectivity and stability. Several commercial available e-noses based on this technology are now available as PEN-3 for Airsense Analytics and Fox 4000 from AlphaMos. Sputtering, thermal vacuum deposition, chemical vapour deposition (CVD) and sol-gel process are the most widely used deposition techniques for the sensitive layers. They are deposited either as a thick or thin film over different types of substrates mainly ceramic or silicon (Fig. 4).

The basic principle of SAW sensors is the reversible sorption of vapours by a sorbent coating which is sensitive to the vapour to be detected. The vapour is sorbed by the surface wave velocity in the device. The velocity changes due to the vapour sorption. Quartz is usually used as substrate for the device as the resonant element in a delay line (DL) oscillators are measured indirectly with good precision using the surface wave velocity in the device. The velocity change of the sorbed layer resulting in a mass increase which modifies the surface wave velocity in the device. The velocity changes are measured indirectly with good precision using the resonator as the resonant element in a delay line (DL) oscillator circuit and measuring the frequency shifts due to the vapour sorption. Quartz is usually used as substrate for the deposition of the sensitive layer but other piezoelectric materials as zinc oxide are used as well. In Fig. 3 an array of quartz based SAW sensors is shown. Several materials are used as sensitive layers. The most used are polymers like phthalocyanines, cyclodextrins, organometallic compounds and rubber polymers as polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), polyetherurethane (PEUT), polybutadiene (PBD) and polydimethylsiloxane (PDMS). Rubber polymers coated SAW sensors have been used in the discrimination of different wines from the same producer and from different grape variety and ageing processes (Santos 2005).

Instrumentation

The instrumentation system of an electronic nose is one of the basic elements since it measures the sensor chemical signals and converts them in electrical signals amplifying and conditioning them if is necessary. This can be done using conventional analogue electronic circuit (e.g. operational amplifiers) and the output is then a set of n analogue outputs, such as 0 to 5 V d.c., although a 4 to 20 mA d.c. current output is preferable if using a long cable. The signal must be converted into a digital format to be processed by a computer, and this is carried out by an analogue to digital converter (e.g. a 12-bit converter) followed by a multiplexer to produce a digital signal which either interfaces to a serial port on the micro processor (e.g. RS-232) or a digital bus (e.g. GPIB).

The microprocessor (e.g. an Intel 486, Motorola 68HC11, etc.) is programmed to carry out a number of tasks. These include the pre-processing of the time-dependent sensor signals to compute the input vectors and classify them against known vectors stored in memory for later training the pattern recognition methods (e.g. Principal Component Analysis or Artificial Neural Networks). Finally, the output of the sensor array and the odour classification can be displayed (e.g. display LCD). All system is carried out by a control programme realized in any language (e.g. C++, Labview, Testpoint, etc.) (Gardner 1999).

Pattern recognition methods

The multivariate information obtained by the sensor array can be sent to a display so a human can read that information and do an action or an analysis. Also that information that is an electronic fingerprint of the volatile compound measured, can be sent to a computer to perform an automated analysis and emulate the human nose. These automated analysis that comes from methods of statistical pattern recognition, neural networks and chemometrics, is a key part in the development of a gas sensor array capable to detect, identify or quantify different volatile compounds.

All these pattern recognition methods are composed by several stages of processing multivariate data. In the first stage the sensor data is pre-processed, usually the data curves are smoothed, drift compensated, outliers eliminated and also extracting of descriptive parameters can be done in this phase. In the second stage an extraction or selection of the features that will be used by the pattern recognizing method is done. Some of these techniques are extraction of the steady data of the response, Principal Components Analysis of the responses, Fourier analysis of the response curve. In the third part a classifier is used to decide to which class the
measured sample belongs to. The classifier usually are neural networks trained with data coming from measured know samples but also fuzzy logic systems, linear and non-linear regression algorithms, Bayesian classifiers or other statistical methods. The final stage is to validate the model with additional data to estimate its accuracy. Now we will review with more detail the different stages.

In the pre-processing stage the raw data from the sensors is gathered and it is processed in order to extract parameters that are descriptive of the response of those sensors. A good processing in this phase is essential to the performance of the subsequent stages of the pattern recognition method (Gardner 1998). Usually this can be arranged in three steps (Gutiérrez-Osuna 2002). In the first one there is a baseline manipulation that transforms the sensor response according with its baseline. In the second step various descriptive characteristics from the transient and steady state of the response are extracted by different methods. Finally a normalization procedure prepares that feature vector so the next procedures work on a local or a global fashion.

The second stage performs a dimensionality reduction. Feature vectors with a great number of components are not suitable to the processing in the next stage due to the well known problem of the “curse of dimensionality”. This term is used to the difficulties that arise when using with dimensionality and redundant data to predict classification or quantification. So usually there is a reduction of this feature vectors to a smaller size by a feature selection or extraction. With feature extraction we transform the feature vector so we reduce the number of components preserving most of the information in the original feature vector. Techniques as PCA or LDA are used (Fukunaga 1991; Duda 2000). With feature subset selection we try to find an “optimal” subset of features preserving also most of the information. In both cases we try to maximize the information contained in the new feature vector (Doak 1992).

The third part is the prediction part that can be a classification, quantification or clustering. The classification method aims to assign an unclassified feature vector to one class from a previously learned discrete set of labels. There are several methods such as the quadratic classifiers, kNN and neural networks (Haykin 1999). The quadratic classifier is one of the simpler ones, in this method we assume that the probability function of each class is a unimodal Gaussian density so we can calculate the class separation in the feature vector space. The kNN finds the closest samples but also fuzzy logic systems, linear and non-linear artificial neural networks trained with data coming from measured know samples but also fuzzy logic systems, linear and non-linear regression algorithms, Bayesian classifiers or other statistical methods. The final stage is to validate the model with additional data to estimate its accuracy. Now we will review with more detail the different stages.

APPLICATIONS OF ELECTRONIC NOSES

Since the seminal paper by Persaud and Dodds (Persaud 1982) electronic noses have been developed for qualitative classification of various kinds of environments. Among the many applications of electronic noses (Gardner 1994) food analysis have been perhaps the topic taken into consideration more than any other else. There are many reasons to develop electronic noses for applications in the field of food control; the monitoring of quality of foods is of primary importance due to a general rise of the level of pollution. Furthermore food aroma analysis represents an opportunity to compare the electronic nose performances with those of natural olfaction. From the chemical point of view foods are characterized by the presence of a large number of different species, many of them are responsible of the qualitative differences existing in terms of taste and aroma and in terms of edibility as well.

In the past electronic noses have been developed for the classification and recognition of a large variety of foods, such as coffees (Gardner 1992), meats (Bourrounet 1995), fishes (Schweizer-Berberich 1994), cheese (Winquist 1995), spirits (Nakamoto 1990) and wines (di Natale 1995; Sayago et al. 2000). With regard to wine applications, olfactive artificial systems started to develop in 1995 applied to the recognition of different vintage years of the same kind of wine (di Natale et al. 1995). A sensor array formed by a number of metal-oxide semiconductor (MOS) gas sensors was utilized for the recognition. The principal-component-analysis technique has been proved to be suitable for the extraction of the pattern features from the array’s data set. The same authors used also a sensor array of metal-oxide based gas sensors for the recognition of two wines, having the same denomination (Groppello red wine) but coming from different vineyards (di Natale et al. 1995). One of the most common methods used for the classification is the principal component analysis (PCA). This method is useful when the sensor signals are more or less independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small. The PCA method is based on a mathematical transformation that is performed on the sensor signals to make them more independent of each other and when the amount of noise is small.
With an electronic nose based on a SAW array were identified four kinds of liquors (beer, spirit, samshu, wine) (Yang et al. 2000). Three white and two red Spanish wines produced in different locations were discriminated using an array of conducting polymer sensors in combination with the technique of solid-phase micro-extraction (SPME). This sampling method permits a better discrimination of the samples by increasing the concentration of the minority compounds responsible for the specific aroma of the wines (Guadarrama et al. 2001).

An electronic nose containing eight, thickness-shear mode resonators coated with various films of metalloporphyrins was used to distinguish 36 different wines produced in the 2001 vintage. Wines of different denomination came from the Lombardia region in the north of Italy. In particular, these systems have been shown to be able to be trained to provide the same evaluation (qualitative and quantitative) of the sensorial analysis (di Natale et al. 2004). Comparative studies between sensor array and GC-MS applied to wine discrimination have been also realized obtaining coincident results by both techniques (Santos et al. 2004). Comparisons between an electronic nose and a human sensory panel for wine compounds detection have been also carried out, being for some compounds better the electronic nose than human panel (Santos et al. 2004). In another majority compounds of wine, the system could discriminate correctly the aromatic compounds added to the wine with a minimum accuracy of 97.2% (Lozano et al. 2005).

In the same way aromatic compounds of red wines have been characterized and classified four types of red wines of the same variety of grapes which come from the same cellar (García et al. 2006). In addition these authors have also discriminated these same wines with another type of nose electronic constituted by seven surface acoustic wave sensors realized in quartz (García et al. 2006). Besides by first time a SAW sensor array, using Si technology to realize a SAW structure on-SiO$_2$ structure has been applied for the discrimination of wines from different grape varieties and ageing processes (Lozano et al. 2006). A solid phase micro-extraction (SPME) system coupled to an array of MOS sensors has allowed the discrimination of five red wines elaborated using the same vinification and ageing methods being the only the variety of grape modified variable (Villanueva et al. 2006). Finally an electronic nose, an electronic tongue and photometric measurements have been used to predict sensorial descriptors of Italian red dry wines of different denominations of origin (Buratti et al. 2007).

Lozano (2005) developed an artificial olfactory system to measure the on line and in situ (experimental wine cellar in Madrid) evolution of two different wines. The system was also able to differentiate both wines and to detect the controlled alterations produced in the same ones (correction of volatilities, pH, etc.). A small and portable e-nose has been developed to measure different wine samples (Lozano 2007). This system is composed of two parts, a laptop and a central control unit. The device was prepared to work with headspace extraction but an external portable concentrator can be couple with it as well. The system is also capable of real-time training and recognition.

**FUTURE OUTLOOK**

The quality of foods and beverages is certainly among the most explored area of applications of electronic noses. In many cases the results are certainly interesting for the improvement of the field, but only rarely do they constitute a basis for immediate industrial exploitation. The field requires more basic research. However the results achieved so far are a sound basis for continuing towards reliable and industrially applicable quality measurement systems. The cooperation of electronic nose researchers and food scientists is necessary in order to customize a general purpose technology like the electronic nose to the specific requirements of food and beverage industries.

All the participants in the food chain (producers, processors, and consumers) are potential users of electronic noses. Each step of the chain has peculiar needs that an electronic nose approach can satisfy in principle. As an example, at producer level the increment of quality and yield, at processor level the screening of quality of incoming products to optimize the processing and to sort processed food, and finally at consumer level the control of quality and safety both on the market and at home. All these applications require instruments that work on-site. By acting on the sense systems it is possible to form a full judgement over a particular food sample. This suggest that, to fully reproduce the perceptions of humans with artificial sensors, the electronic nose has to be compared and integrated with instruments providing information about visual aspects, texture and firmness. This opens a further novel investigates direction involving researchers from different areas, confirming that the interdisciplinary nature is the most strong added value for food analysis (Pearce 2003).

With regard to specifically the wine it would be interesting to carry out the following research in the future:

- To typify wines from different Origin Denominations.
- To miniaturize the existent systems through the integration of the electronics in the Si substrate.
- To use networks of wireless sensors to establish control of the processes of elaboration, ageing and conservation of wine in wine cellar.

**REFERENCES**


