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Electronic Noses Applications in Beer Technology

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Abstract

This chapter describes and explains in detail the electronic noses (e-noses) as devices composed of an array of sensors that measure chemical volatile compounds and apply classification or regression algorithms. Then, it reviews the most significant applications of such devices in beer technology, with examples about defect detection, hop classification, or beer classification, among others. After the review, the chapter illustrates two applications from the authors, one about beer classification and another about beer defect detection. Finally, after a comparison with other analytical techniques, the chapter ends with a summary, conclusions, and the compelling future of the e-noses applied to beer technology.

Keywords: beer, electronic noses, gas sensor, pattern recognition, beer discrimination, defect detection

1. Introduction

Among the alcoholic beverages, beer is one of the most consumed in the world [1]. Because of such a big market, beer safety and the repeatability of its organoleptic qualities are very important for the manufacturers. For this reason, several techniques are used in the beer industry; they assess these aspects by analyzing the chemical composition or by human panels. One of the most difficult analyses is the chemical species of the beer headspace (HS). The headspace contains multitude of volatile organic compounds (VOC) that determine the organoleptic qualities or VOCs that are markers of spoilage, toxins, or flavor instability. For example, beer evolution can be marked by the presence of oxidative species such as aldehydes produced from alcohol oxidation [2]; contamination by bacteria can be marked by the presence of diketones such as diacetyl [3]; or toxic species such as nitrosamines [4] that can

be generated during the malt production. Furthermore, the analysis is hindered by the high amount of CO_2 in the beer so usually, there is a required degasification process. The analysis of the volatile chemical species not only applies to the final product but also to the ingredients (hops, malt, etc) as the quality and characteristics of the components have a determinant effect on the final product. All these analyses (human and chemical) are complex so they are done in batches and are costly in time and money. However, an early detection or continuous monitoring by means of a fast analysis can avoid wastage and save money and time. An e-nose is a technology that could able to analyze and extract the chemical information of the beer organic volatile compounds and correlate their organoleptic qualities. The aim of this chapter is to bring in the innovative and promising technology of e-noses in the traditional beer industry. With this intention, there is, first, an introduction to e-nose technology where the different parts are described in detail. Then, several examples of its use are enumerated and some of them are explained. In addition, there is a brief comparison with other techniques to highlight the advantages and the scope of its use. Finally, there are the conclusions and future trends.

2. Electronic noses

An e-nose is a device that tries to imitate the structure and functionality of the human nose, and both of them are intended to be used in similar applications. **Figure 1** shows this similarity in the way they work: 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 e-nose. There is an overlapping in sensitivities so one odorant receptor responds to multiple odorants and one odorant can be detected by

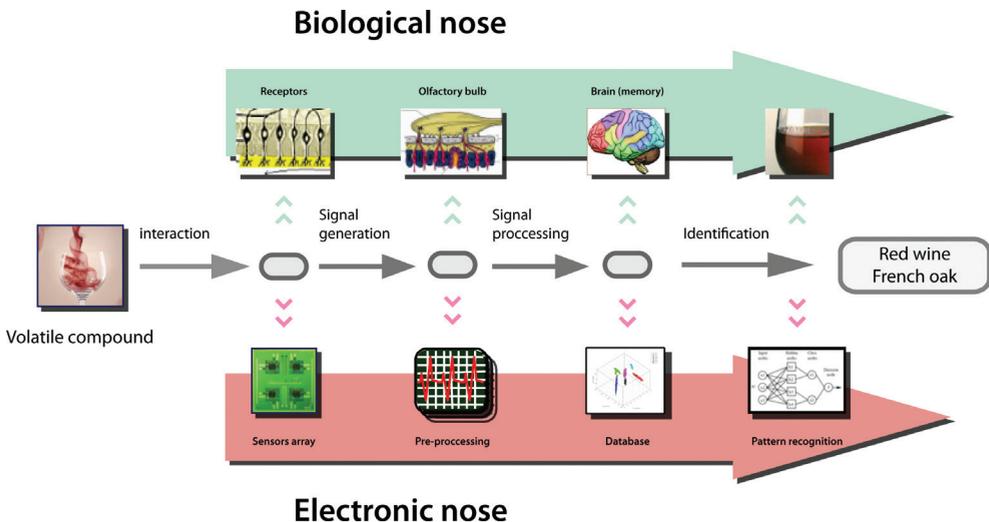


Figure 1. Similarity between the biological olfactory system and an e-nose.

several odorant receptors. The next step in both is the storage of these signals in the brain or in a database of a pattern recognition machine (learning stage) for further identification of one of the odors that is learned (classification stage).

Pre-1920 work on machine olfaction was prevented by the absence of any suitable electronic instrumentation. In 1920, Zwaardemaker and Hogewind suggested that odors could be detected by measuring the electrical charge developed on a fine spray of water that contained the odorant in solution, but they were unable to develop this into a useful instrument [5].

The first real report of an experimental instrument was published by Hartman and colleagues who described an electrochemical sensor consisting of a polished metal wire microelectrode in contact with the surface of a porous rod saturated with a dilute electrolyte [6, 7]. By using various combinations of metal electrodes, electrolytes, and applied potentials, a system of several sensors was made to operate simultaneously. In essence, the sensors used in this work were examples of amperometric electrochemical gas sensors. The instrument they developed comprised an array of eight different electrochemical cells and gave different patterns of response for different odorant samples, although in this work, they made no serious attempt to process the patterns which they generated even though computers were becoming available.

At about the same time, Moncrieff was working on the same problem but using a different approach. He employed a single thermistor (temperature-sensitive resistor) coated with a number of different materials, including poly(vinyl chloride), gelatin, and vegetable fat, to monitor odors [8]. He recognized that the coatings he used were non-specific, and he postulated that if an array of six thermistors with six different coatings were constructed, then the resulting instrument would be able to discriminate between a large number of different smells. In 1965, two other groups published early studies of e-noses: Buck et al. made use of the modulation of conductivity [9], while Drawnieks and Trotter used the modulation of the contact potential to monitor odors [10]. However, the concept of an e-nose as an intelligent system composed of an array of chemical sensors for odor identification did not emerge until nearly 20 years later, following publications by Persaud and Dodd in 1982 at Warwick University, UK [11] and by Ikegami in 1985 and 1987 at the Hitachi Research Laboratory in Japan [12, 13]. By this time, developments in electronics, sensors, and computing came together to reach a stage where an e-nose had become a genuine possibility. The term "e-nose" first appeared in the literature around the late 1980s [14]. Then, in 1991, a session of a NATO advanced workshop on chemosensory information processing was dedicated to the topic of artificial olfaction.

An accepted definition of an e-nose given by Gardner in 1994 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" [15]. This definition restricts the term e-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 e-nose has much in common with multi-sensor systems designed for the detection and quantification of individual components in a simple gas or vapor mixture [16]. An e-nose generally consists of an aroma extraction system, a sensor array, a control and measurement system, and a pattern recognition method [17]. A block diagram of the typical structure of an e-nose can be observed in **Figure 2**.

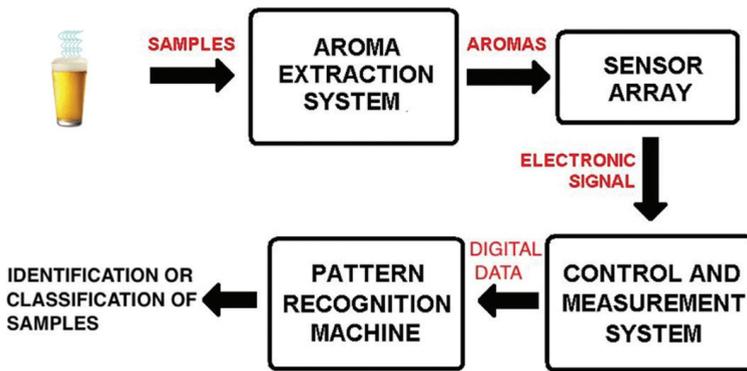


Figure 2. Block diagram of an e-nose system.

The sampling method or aroma extraction system carries the aromatic volatile compounds from the samples to the sensor cell. Different sampling techniques can be used in e-noses [18]: static or dynamic HS, purge and trap (P&T), and solid-phase micro-extraction (SPME) are the most common techniques.

A gas sensor is a device that is capable of converting the concentration of chemical compounds into electric signals and responds to the concentration of specific particles in gases or liquids [19]. Chemical sensors can be based on electrical, thermal, mass, or optical transducer principles. Several examples of chemical sensors used in e-noses are conducting polymers [20], quartz resonators [21], and surface acoustic wave (SAW) [22] and semiconductor devices [23]. The e-nose device has the advantage of low cost and portability for making in situ and online measurements.

The instrumentation and control system includes the electronic circuits needed for the measurements of sensors signals (e.g., interface circuits, signal conditioning, and analog-to-digital (A/D) or digital-to-analog (D/A) converters).

The goal of an e-nose is to identify an odorant sample and perhaps to estimate its concentration by means of a signal processing and pattern recognition system. However, those two steps may be subdivided into the following steps [24]: preprocessing, feature extraction, prediction or classification, and decision-making.

It is necessary to create a database of expected odorants by presenting the samples to the sensors. Preprocessing techniques try to compensate sensor drift, compress the transient response of the sensors, and reduce variations from sample to sample. Typical techniques include manipulation of baselines, response normalization, and compression of sensor transients.

Feature extraction has two different purposes: first, to reduce the dimensionality of the measurement space and second, to extract information relevant for pattern recognition. It is generally performed with linear transformations such as the classical principal component analysis (PCA) and linear discriminant analysis (LDA). PCA is a powerful, linear, unsupervised, and non-parametric pattern recognition technique that has been used by many researchers to

reduce the dimensionality of the pattern space leading to better visualization of data clustering. This method expresses the response vectors by using linear combinations of orthogonal vectors along a new set of axes and is sometimes referred to as vector decomposition, and it usually helps to display multivariate data in a plot of two or three dimensions. PCA finds projection of maximum variance and is the most widely used linear feature-extraction technique [24]. But it is not optimized for classification tasks since it ignores the identity (class label) of the odor examples in the database. LDA, on the contrary, tries to find projections that maximize the distance between examples from different odorants and minimize the distance between examples of the same class [25, 26].

Finally, the classification task is usually performed by artificial neural networks (ANNs). An ANN is a mathematical algorithm that has the same function as that of the human brain in the biological sense of smell. The typical structure of an ANN is a network with two or more layers of neurons that are connected with synaptic weights—real number multipliers that connect the output of neurons to the inputs of neurons in the next layer [25–27]. During training, the ANN tries to learn the patterns of the different odorants by adapting the weights in order to obtain the desired output. After training, when an unidentified sample is presented, the ANN calculates the output of each layer and assigns the class label that provides the best response. In some cases, an undetermined class is used to determine the unknown sample that does not belong to any of the learned classes in the database [28].

The application of the human sense of smell as an odorant instrument is limited for different reasons: it is strongly subjective, gets tired easily, and in some cases, it is difficult to interpret. Consequently, there is considerable need for an instrument that could mimic the human sense of smell but without those limitations in order to be used as industrial applications. In this sense, e-noses could be used in areas like food, automobile, environmental industry, and medicine for different tasks like: pollution control and air-quality monitoring, control of industrial processes, detection of illnesses by exhaled breath, and safety aspects.

E-nose instruments are attractive in different fields due to several reasons: the fast assessment of samples, a qualitative and quantitative representation, and the use of low-cost and small-size sensors, appropriate for production processes. A considerable number of applications of e-noses have been reported for sensing applications. A broad list of e-nose reviews can be found in the literature that are structured and focused on mass spectrometry-based e-noses [29], biomedical and health care applications [30], agriculture and forestry applications [31], microbial quality control of food products [32] and food industry [33], pharmaceutical applications [34] developing chemical sensor arrays [35], etc.

3. E-nose applications in beer

E-noses have been applied to the whole production chain of beer, from the main ingredients (barley, hops, and yeasts) going through the different processes (mainly fermentation) to the final product. In this sense, the discrimination between beers and other beverages is the one that has more applications with enoses. In the following lines, an overview of the different

applications of e-noses in breweries is given although it does not pretend to be exhaustive. A brief review of the applications of e-nose technology in breweries can be found in Ref. [36].

A classification of beer ingredients has been studied with these systems. Hops classification was performed in Ref. [37]. Using a commercial e-nose (FOX 2000), discrimination of different malt types could be done [38].

Fermentation monitoring, usually by measuring alcohol content, has been addressed by some authors [39, 40]. A recent review of e-nose applications on alcoholic beverage fermentation is found in Ref. [40].

Other common applications are detection of defects such as dimethyl sulfide detection [41] and 1-hexanol, ethyl acetate, oct-1-en-3-ol and diacetyl [42]. Related to this is the work in Ref. [43] that studies the influence of the fungicide triadimefon on the quality of beer using an e-nose, e-tongue, high-performance liquid chromatography (HPLC), and a sensory panel. Other authors [44] used a hand-held e-nose to detect different amounts of intentionally added ethyl acetate and acetaldehyde to commercial beer. In Ref. [45], discrimination among beers with some defects (diacetyl or dimethylsulfide) was performed using an MOS-based e-nose.

But by far the most common application is beer discrimination among other beers or among other alcoholic beverages. The first work about e-nose applied to beer is the paper by Aishima [46]. He used an e-nose composed of six Taguchi metal-oxide (MOX) gas sensors to discriminate among several alcoholic beverages. Also, in the 1990s, an e-nose based on conducting polymers was used to classify different types of beers and identify certain off-flavors [47]. In Ref. [48], an e-nose based on quartz crystal balance (QCB) and MOSX sensors was used in conjunction with a chromatographic column to discriminate among eight brands of beer. Other authors used an MOX-based e-nose to classify several alcoholic beverages and studied the ethanol influence in the response to the system [49]. In Ref. [50], an MOX-based e-nose was also used to differentiate among beverages, including beer, and in Refs. [51, 52], an MOX-based e-nose was used to classify commercial beers. Li [53] used an MS-based e-nose to discriminate among beers with different characteristics. Zhou discriminated among 12 commercial beers and other products with a 3 MOX sensor-based e-nose [54]. Siadat used an MOX-based e-nose to differentiate among alcoholic and non-alcoholic beer [55]. Vera [56] used an MS e-nose to discriminate among several beers from different breweries. Recently, Liu used a combined e-nose and electronic tongue system to correlate the information with a sensory panel for five commercial beers [57]. A SAW-based e-nose to discriminate volatile compounds, liquors, and perfumes can be found in [58].

Beer-aging experiments in commercial (lager and ale beers) industries under different storage conditions are shown in Refs. [59, 63, 64]. A review of e-noses with some information for beer classification and ageing is shown in Ref. [60].

Another application, far from the above cited, is the example of Thepudom et al. [61], who employed an optical e-nose to investigate alcohol decay in breath after drinking beer.

Table 1 summarizes the applications of e-noses in beer with information about the technology, number of sensors, and data processing algorithms.

Application	Sensor technology	Number of sensors	Data processing algorithm	References
Malt classification	MOX	6	PCA, CLA	[38]
Hops classification	MOX	6	PCA, SOM	[37]
Classification	CP	12	CLA	[47]
	SAW	8	PCA	[58]
	GC-MOS	14	PCA	[49]
	MOX	3	ANN	[50]
	MOX	8	PCA	[46]
	QCB, MOX	8,8	PCA	[48]
	MOX	5	PCA, LDA, PNN,	[51]
	MS	1	PLS-DA, SIMCA	[53]
	MOX	5	PCA	[52]
	MOX	3	PCA	[54]
	MOX	5	PCA, ANN	[55]
Off defects	MS	1	PCA, ANN	[56]
	CP	?	ANN	[45]
	MS	1	?	[41]
	GC-MOS	14	PCA, DFA	[42]
Fermentation	MOS	4	ANN	[44]
	Catalytic	1	?	[39]
Flavor assessment	MOX	7	PCA	[62]
	MOS	8	ANN	[57]
Aging	MS	1	PCA, LDA, PLS	[59]
	MOX	12	PCA	[63]
	MOX	5	PCA, LDA, ANN	[64]
Other (pesticides)	MOX	10	PCA	[43]
Breath	OPT	2	PCA	[61]

Table 1. E-noses and their beer applications.

4. Detailed examples of applications in the beer field

In this part of the chapter, the development of a portable e-nose designed and optimized for beer discrimination is presented. The device is validated by doing two different measurements: draft beer discrimination and off-odor detection. The main features of the designed e-nose [65] are portable, low size, autonomous, low cost, and easy to use. The designed e-nose (**Figure 3a**) is equipped with wireless communication capable of forming a network of e-noses for distributed measurements [66] (**Figure 3b**). It has been designed to work with resistive sensors, headspace as the sampling method, and a portable instrumentation and control system; it includes rechargeable batteries, touch screen, and IEEE 802.11 transceiver for wireless communication (**Figure 4**).

It consists of two gas inlets that are switched through a three-way electrovalve whose output is connected to the sensors cell that contains the micro-sensor array. One of the gas inlets has a carbon filter and is intended to provide clean air as the reference baseline. Downstream are located

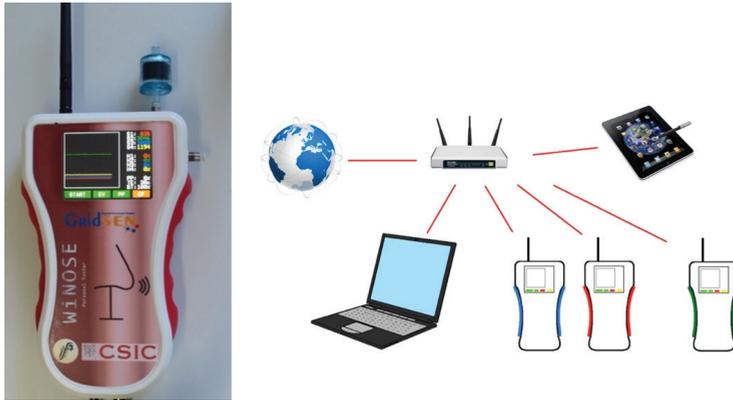


Figure 3. Portable e-nose (left) and configuration of the e-nose in the network (right).

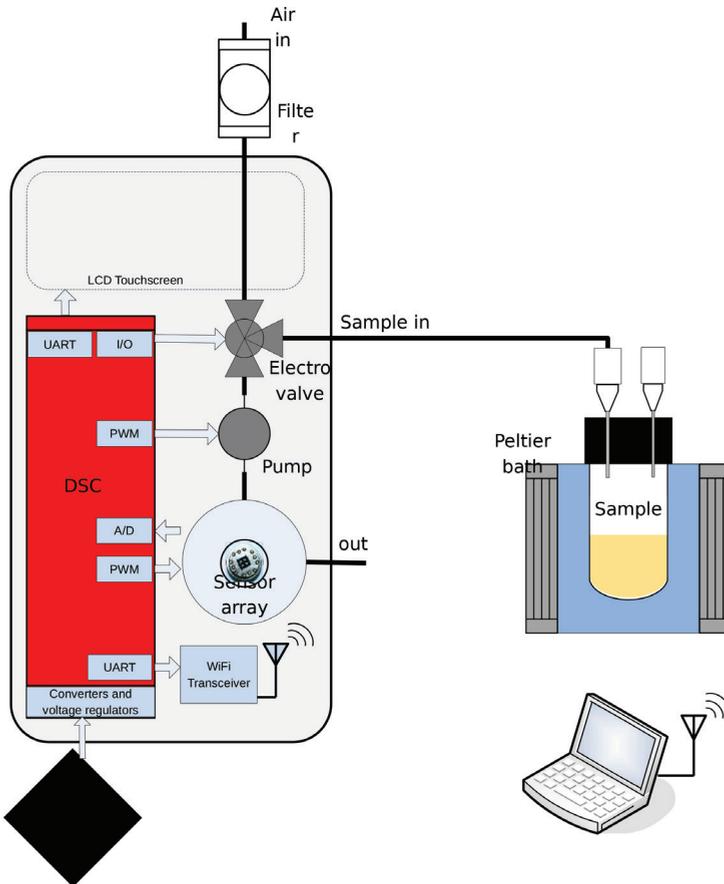


Figure 4. Schematics of the e-nose and measurement system.

the temperature sensor and the pump. The whole system is controlled by a digital signal controller (**Figure 5**). The sensor resistances are measured by A/D circuits, and their heating consists of pulse width modulation (PWM) outputs. An LCD touchscreen shows the measurements that allow the manual control of parameters such as pump, heater, power, or the electrovalve. Rechargeable batteries give about 8 h of autonomy to the e-nose. Wireless communications are provided by a Wifi transceiver. A network could be established with a host computer for remote operation. The sensors cell and board are designed for micro-sensors in a TO-5 or TO-8 12 leads package but it is easily adaptable to other packages and sensors. The system can measure up to four resistive sensors and provides independent heating for each one. The instrument is controlled by a program developed in Labview™. The program displays and controls the measurement parameters and generates the response database. Algorithms for both online and off-line pattern recognition techniques have been developed in Matlab™ and integrated in the program through Mathscrypts. External classification using a web server can also be performed [67].

The control program displays and controls the main measurement parameters (temperature, sensor resistance, temperature, valve status, battery status, and pump power) and automatically generates the response database. The program user interface is shown in **Figure 6**.

After measurements are made, data processing methods are applied to the data. PCA and ANN have been implemented in Matlab™ for data processing. PCA applies a linear transformation to the data, and this results in a new space of variables called principal components [24]. The number of variables is reduced from the number of sensors 4 to 2 or 3 variables in order to show it in a plot and see the discrimination capability of the array. Next, a classifier is used to give a response to a typical problem of prediction of unknown samples. The most used classifiers are based in ANN. In these experiments, two types of ANNs were used for

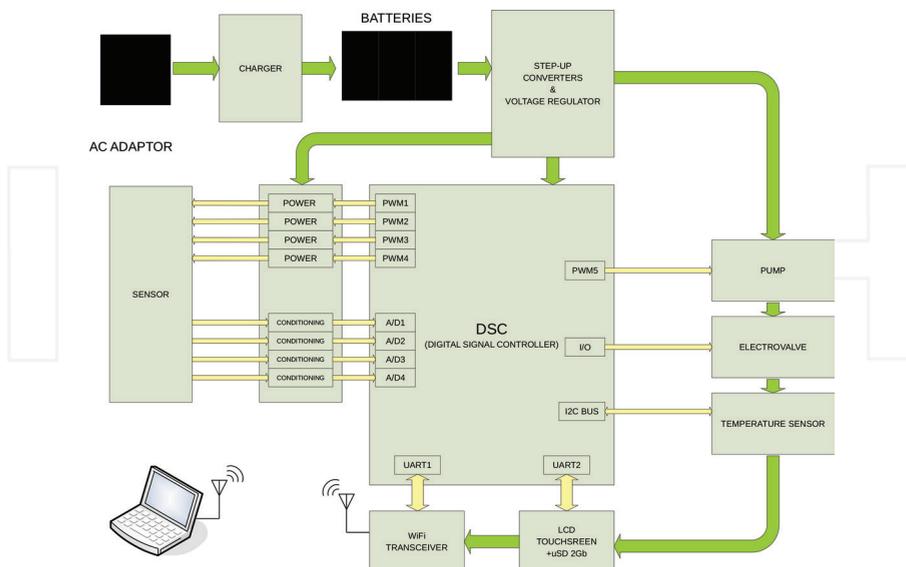


Figure 5. Block diagram of the main components of the developed portable e-nose.



Figure 6. Control program user interface.

classification purposes: feedforward network with backpropagation learning algorithm (FF-BP) and probabilistic neural networks (PNN).

The FF-BP networks had three layers, an input layer with a number of neurons equal to the sensors of the e-nose (four), a hidden layer with a variable number of neurons that went from 10 to 25, and finally an output layer with a neuron for each class of the classification problem.

The PNN were also composed of three layers [26], the input layer with a number of neurons equal to the sensors of the e-nose (four), a hidden layer of neurons with radial basis transfer functions that had neurons equal to the training set, and finally an output competitive layer with a neuron for each class of the classification problem. The structure of this type of neural network can be seen in Figure 7.

To validate the performance of the network [26], leave one out (LOO) cross-validation was applied to the networks. In LOO, the network is trained with all the data except one data point and then the data left out is used to evaluate the performance of the network. This is repeated for each data point, leaving, in each iteration, one data point out. The performance is the assembled errors that are made [68, 27].

4.1. Beer discrimination

The main aim of this experiment was to check the discrimination capability of the proposed system. In this sense, the task of classifying different draft beers was attempted. Different

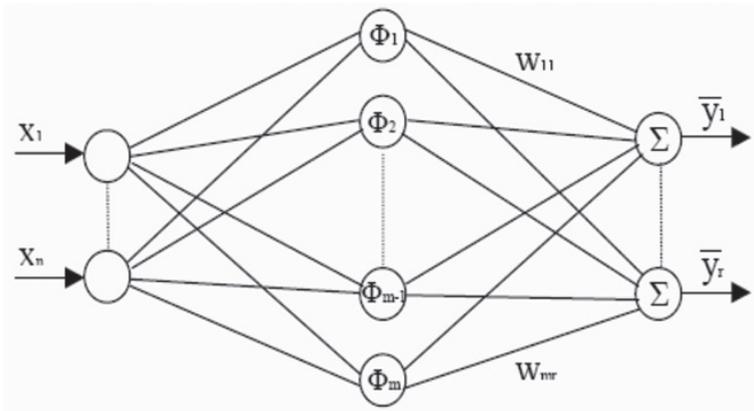


Figure 7. Scheme of the probabilistic neural network classifier.

commercial draft beers (Blomberg Blanca, Blomberg Rubia, Blomberg Dubbel, Marwan, Cerex, Jacha Jigo Jiguera, Ballut Rubia, and Ballut Negra) were purchased in specialized shops and kept to the moment of measurements. Before that, a degasification process based on magnetic agitation for 20 min was performed. Next, 10 mL of each sample was taken and kept at 12°C with a thermal bath in order to generate a stable headspace for each sample. A total number of 128 measurements (16 replicates per beer) were performed. The measurement cycle was for a duration of 10 min: 1 min of adsorption (air passes through the samples) and 9 min of desorption (air directly passes through the sensors). The air rate flow was 150 mL/min, constant in every measurement. Once a second, measurements of the parameters (sensors resistance, relative humidity, ambient temperature, air rate flow, and battery voltage) were taken and stored in a file. Commercial sensors of e2V SGX sensortech based on tin oxide MOS sensors were used. The operation temperatures of the sensors were optimized for beer discrimination, and its range was among 350 and 450°C. Once the measurements were performed, data were stored in a hard disk for data processing. A periodic calibration made with 10% of Ethanol in water is usually performed for compensating sensor drift. In this case, it is not necessary because of the short time spent doing the measurements. No variation in the sensors response to reference air is observed during the measurement period.

Data obtained from measurements were processed using PCA. The first three principal components were shown in **Figure 8**. This plot shows an almost complete separation among the eight classes of beer. The ellipses show 80% of the variance of the classes, some partial overlapping between Marwan and Cerex, and other neighbor classes can be observed. The variance explained by each principal component is in brackets.

To confirm these results, a classification with three different classifiers based on artificial intelligence was performed. Three different classifiers were used: feedforward neural network with backpropagation algorithm, probabilistic neural networks, and fuzzy logic (FL) classifiers. Both FF-BP and PNN employed eight neurons at the output layer corresponding with the eight brands of craft beers. In the case of the fuzzy logic-based classifier, a total of eight

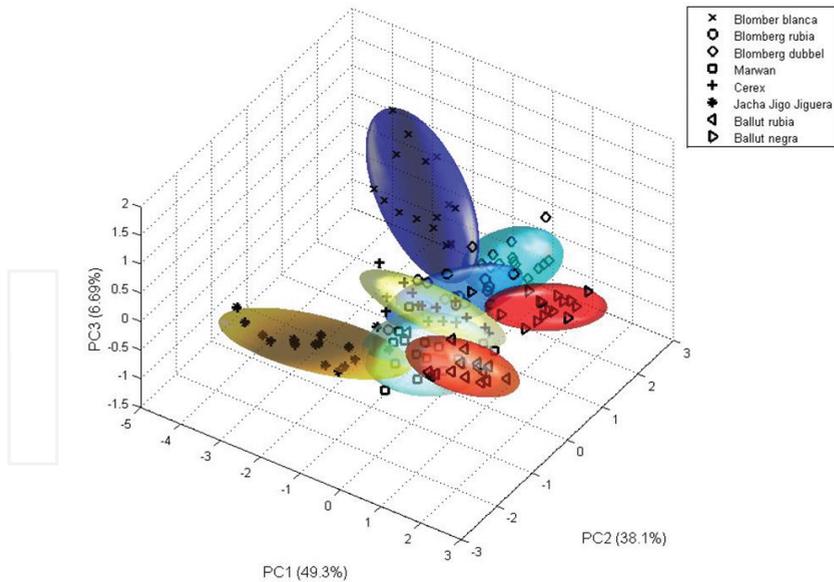


Figure 8. PCA score plot of the measurements of different draft beers.

fuzzy rules (corresponding with the eight brands of beers) is built over each sensor output on the 128-sample knowledge database. Each of these rules is optimized in the training stage to maximize both acceptance and rejection scores of the unknown samples. First-order cross-validation (leave one out) was used for validation because a great number of measurements were not available.

The confusion matrix obtained in the validation of the classifiers is shown in **Table 2**, in which the system classifies (in columns) the real samples (rows). The success rate obtained in the classification, defined as the rate between the number of samples correctly classified over the total number of measurements, was 87.5% for FF-BP network, 92.96% for the PNN, and 89.84% for FL-based classifier. Results confirm that the PNN classifier presents the best performance in the classification of these beer samples.

4.2. Beer defects detection

Another experiment was made with the same prototype. In this case, two aromatic defects in beer (acetaldehyde and ethyl acetate), at a level between the organoleptic threshold and five times this quantity, were measured. Acetaldehyde threshold is 25 ppm and ethyl acetate is 21 ppm [69, 70]. The lager beer from cans was magnetically stirred (350 rpm, 20 min) to degas before the measurement procedure. Glass vials of 22 mL were filled with 10 mL of the sample and they were kept at $18 \pm 1^\circ\text{C}$. A minimum of 10 replicates for each compound were measured.

Predicted real	Blomberg Blanca	Blomberg Rubia	Blomberg Dubbel	Marwan	Cerex	Jacha Jigo Jiguera	Ballut Rubia	Ballut Negra
Blomberg Blanca	16 15		1					
Blomberg Rubia	14	15 13	1		1 1 2	1		1
Blomberg Dubbel	1		16 15 15					1
Marwan				15 11 13	1 6 2			1
Cerex	4	1		2	14 12 14	1		
Jacha Jigo Jiguera				2 2 1		14 14 15		
Ballut Rubia				1 1 1			15 15 15	
Ballut Negra		1			1 1 2			15 14 15

Table 2. Confusion matrix with three classifiers: FF-BP, PNN, and FL.

Once the measurements have been made and the raw data is stored, data processing is performed. **Figures 9 and 10** show the 3D plot of a PCA made to the measurements for the ethyl acetate and acetaldehyde samples. The blank samples are clearly separated from the samples with the two compounds but the two defective types of samples (with the different compounds) seem to overlap a bit.

Results are confirmed with a non-linear classification method. PNN networks, which obtained the best performance in previous experiments, were trained to classify samples according to their defects. The percentages of cases correctly classified in the LOO validation were 83 and 91% for ethyl acetate and acetaldehyde, respectively. While all the samples at five times the threshold concentration values were correctly classified, there were some errors in the lower concentration samples; for ethyl acetate, the network confounded some blank samples with concentration of 1 T and also concentrations of 1 T with concentrations of 2 T; for acetaldehyde, only 2 samples of T concentrations and 5 T concentrations were confounded by the PNN.

A qualitative classification of the beers according to the defect (at all the concentrations levels) can be seen in **Figure 11**. The PCA shows that the beer samples with ethyl acetate, the beer samples with acetaldehyde, and the beer samples without defects (blank) are separated with only a small overlap among the classes.

For this qualitative classification problem, the PNN analysis gave a 94% success rate in the validation, regardless of the overlap seen in the PCA plot.

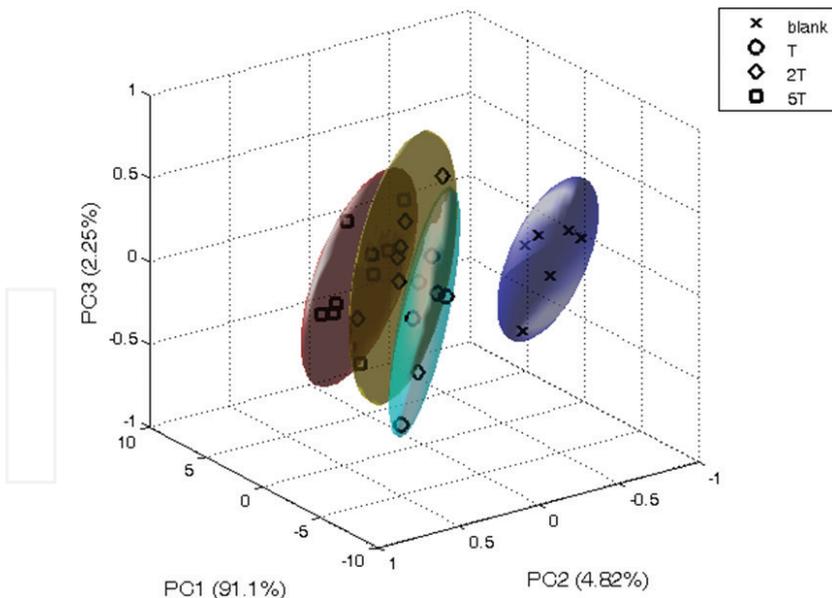


Figure 9. PCA plot for the ethyl acetate measurements in beer.

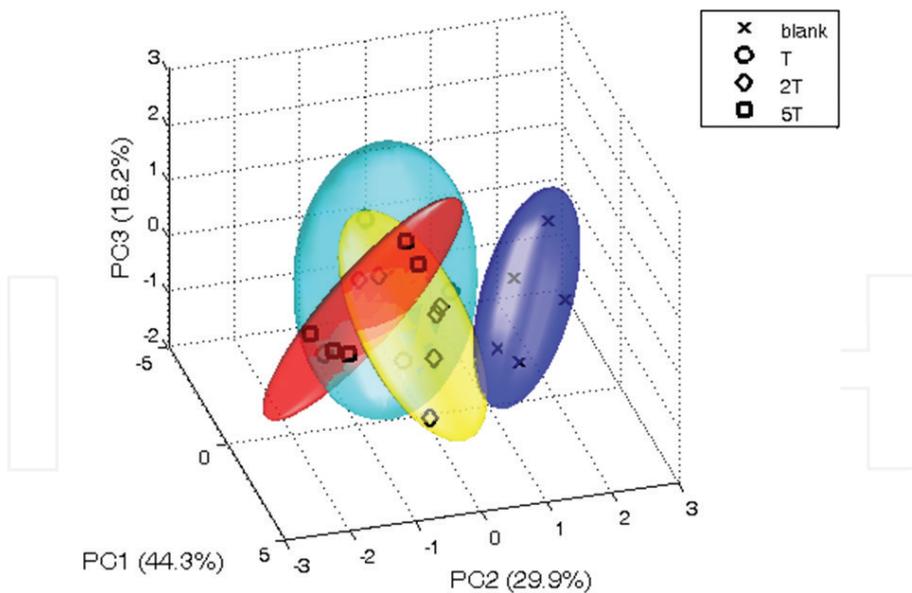


Figure 10. PCA plot for the acetaldehyde measurements in beer.

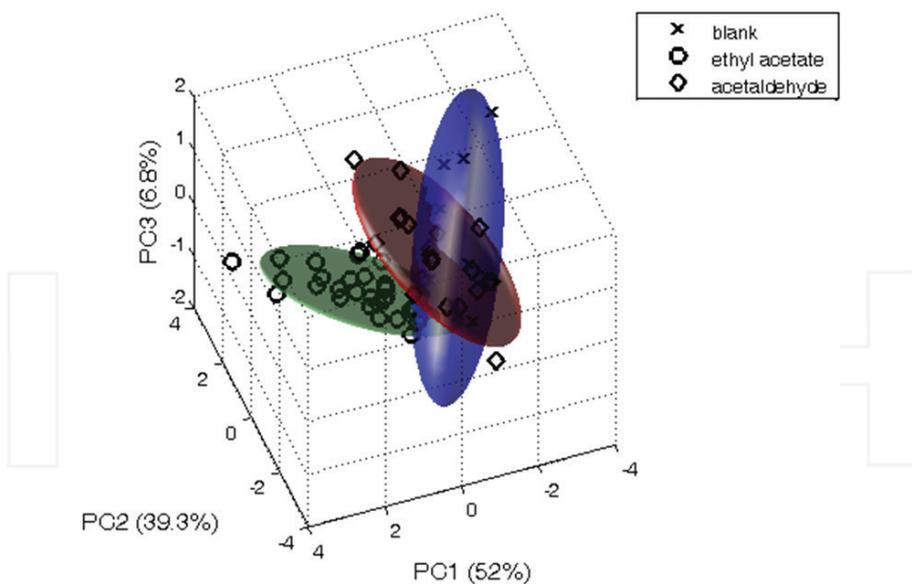


Figure 11. PCA plot for the defect measurements in beer.

These classification results could be improved by several strategies. Better classification algorithms could be applied to the data. Also, the data could be less noisy by using better systems that keep temperature or flows more controlled.

5. Comparison with other techniques

There are several traditional chemical methods like titration, gravimetric analysis, international bitterness units (IBUs), alcohol measurement, extract, calories, pH, high-performance liquid chromatography, or new methods like capillary electrophoretic method [70] to characterize the beer but few methods are used to analyze the volatile compounds of its headspace as the e-nose does. Techniques such as gas chromatography (GC), soft ionization techniques, or human sensory panels are among them. Each one has its own characteristics and when deciding what method to use, one should select the one more appropriate for its interest and the task at hand.

Human panels record the experience of beer tasting by several senses, and they use the most complex of them, the scent, to detect the volatile organic compounds that emanate from beer [71]. However, human panels are subject to variability not only within different panels but also with itself over time. They need to be trained to become experts which is time-consuming and expensive. Due to VOCs matrix interaction and physiological singularities, the correlation between the chemical analysis and the scents is not clear and not always straightforward [72] so human panelists are usually mandatory.

Traditional gas chromatography has been widely used for beer analysis, detecting singular VOCs. There are very different ways to gather, separate, and detect the volatile compounds [73]. GC has been used successfully to detect diacetyl, pentanedione, acetoin, and acetaldehyde during the fermentation process, showing the evolution of these VOCs [74]. GC monitors the concentration of singular compounds and requires time-consuming analysis to extend the analysis to the many volatile compounds that the beer headspace has. The process is slower, more expensive, and more complex, making it very difficult to operate in a continuous way.

GC-olfactometry combines both the human panel and gas chromatography by placing a human panel as a detector at the end of the chromatograph. In this way, the system can detect individual aromas and correlate them with the physiological sensation they provide. In [75], the compounds from Challenger and Saaz hops were analyzed and correlated with several olfactory descriptors in pellets and they analyzed the evolution after the brewing process. This technique allows the evaluation of the scent as perceived by humans but the analysis is costly and time-consuming.

Soft ionization techniques, selected ion flow tube mass spectrometry (SIFT-MS), or proton transfer reaction time-of-flight (PTR-ToF) allow fast analysis of the samples in a continuous fashion. For example, PTR-ToF has been used to monitor the fermentation process of different yeasts pointing to the different VOCs released [76], and SIFT-MS has been used to determine the aldehyde content of malt as a biomarker to identify each variety [77]. PTR-ToF usually lacks on precision in identifying the individual VOCs, and SIFT-MS has lower sensitivity.

Both methods are fast and can be used as online monitoring devices but they are cumbersome and expensive compared to the potential of e-noses.

6. Conclusions and future trends

Monitoring or fast analysis of the chemical composition of the beers in all steps of the production and consumption chain is of capital importance for the beer industry. Rapid detection of problems like contamination, spoiled ingredients, or flavor instability can save time, money, or prevent health problems. The traditional chemical beer analyses are done in batches; in contrast, the e-noses are a good instrument to use in online analyses. Although e-noses are not as accurate as traditional analysis, they work very well in controlled environments like the ones of the beer industry or in laboratory. In these controlled environments, differential analysis can be easily made and interesting results can be obtained like the ones presented in this chapter.

For more complex applications or scenarios, there is still a need for better sensors with better characteristics such as reproducibility, repeatability, and selectivity. There is also a need for the standardization of these sensors and methods to increase reproducibility of analysis so studies can easily be transferred from one device to another. But the sensor technology is blooming and multitude of research groups and enterprises are working on their improvement. New materials like carbon nanotubes, nanostructured metal oxides, or graphene materials are offering very interesting and improved sensor capabilities. To complement the sensor, new algorithms are being developed in deep learning or semi-supervised learning that would reach soon the e-nose technology and take advantage of those improved sensor characteristics. New commercial sensors are being miniaturized more and more and will be able to be deployed in small power consumption devices as wearables or mobile devices that will integrate in the Internet of things.

There are a multitude of possible applications, from the analysis of the ingredients to mobile applications for the final consumer. To name a few, there are several interesting possibilities that could be used in the analysis of ingredients, to detect spoilage, or to store scent profiles year after year. They could be used for the online monitoring of the fermentation process and by applying closed loop control to it. They could be used as storage monitoring, ensuring that the product reaches the final consumer in optimal conditions. The final consumer could use these new small sensors in wearable devices and apply them in food safety, detecting contaminants before consuming them. The e-nose presents endless and very interesting potential applications.

Abbreviations

ANN	Artificial neural network
CA	Correlation analysis
CDA	Canonical discriminant analysis

CP	Conducting polymers
CLA	Cluster analysis
DA	Discriminant analysis
DFA	Discriminant factorial analysis
FL	Fuzzy logic
GA	Genetic algorithms
GC	Gas chromatography
LR	Linear regression
LDA	Linear discriminant analysis
MOX	Metal oxide semiconductor sensor
MS	Mass spectrometry
OPT	Optical projection tomography
PCA	Principal component analysis
PLS	Partial least squares
QCB	Quartz crystal balance
SAW	Surface acoustic wave
SIMCA	Soft independent modeling by class analogy
SOM	Self-organizing maps

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References

- [1] World Health Organisation. Global Status Report on Alcohol and Health 2014. Global Status Report Alcohol [Internet]. 2014. pp. 1-392. Available from: http://www.who.int/substance_abuse/publications/global_alcohol_report/msbgsruprofiles.pdf
- [2] Vanderhaegen B, Neven H, Verachtert H, Derdelinckx G. The chemistry of beer aging—a critical review. *Food Chemistry*. 2006;**95**(3):357-381

- [3] Wainwright T. Diacetyl—a review: Part I—analytical and biochemical considerations: Part II—brewing experience. *Journal of the Institute of Brewing* [Internet]. 1973;**79**(6):451-470. Available from: <http://doi.wiley.com/10.1002/j.2050-0416.1973.tb03567.x>. [Accessed: March 1, 2017]
- [4] Izquierdo-Pulido M, Barbour JF, Scanlan RA. N-nitrosodimethylamine in Spanish beers. *Food and Chemical Toxicology* (Internet). 1996;**34**(3):297-299. Available from: <http://linkinghub.elsevier.com/retrieve/pii/0278691595001166>. [Accessed: March 1, 2017]
- [5] Zwaardemaker H, Hogewind F. On spray-electricity and waterfall-electricity. *Proceedings of the Royal Academy of Sciences at Amsterdam*. 1920;**22**
- [6] Hartman JD. A possible objective method for the rapid estimation of flavors in vegetables. *Proceedings of the American Society for Horticultural Science*. 1954;**64**
- [7] Wilkens WF, Hartman JD. An electronic analogue for the olfactory process. *Annals of the New York Academy of Sciences*. 1964;**116**
- [8] Moncrieff RW. An instrument for measuring and classifying odours. *Journal of Applied Physiology*. 1961;**16**
- [9] Buck TM, Allan FG, Dalton M. Detection of chemical species by surface effects on metals and semiconductors. In: Bregman JI, Dravnieks A, editors. *Surface Effects in Detection*. London: Macmillan; 1965
- [10] Dravnieks A, Trotter PJ. Polar vapour detection based on thermal modulation of contact potentials. *Journal of Scientific Instruments*. 1965;**42**
- [11] Persaud KC, Dodd GH. Analysis of discrimination mechanisms of the mammalian olfactory system using a model nose. *Nature*. 1982;**299**
- [12] Ikegami A, Kaneyasu M. Olfactory detection using integrated sensors. In: *Proceedings of the 3rd International Conference on Solid-State Sensors and Actuators (Transducers 85)*. New York: IEEE Press; 1985. pp. 136-139
- [13] Kaneyasu M, Ikegami A, Arima H, Iwanga S. Smell identification using a thick-film hybrid gas sensor. *IEEE Transactions on Components, Packaging, and Manufacturing Technology, CHMT-10*. 1987;**10**
- [14] Gardner JW. Pattern recognition in the Warwick electronic nose. In: *8th International Congress of the European Chemoreception Research Organisation*; Coventry, UK. 1988. p. 9
- [15] Gardner JW. A brief history of electronic noses. *Sensors and Actuators B: Chemical*. 1994;**1818-19**
- [16] Gardner JW, Bartlett PN. *Electronic Noses: Principles and Applications*. Vol. 233. New York: Oxford University Press; 1999
- [17] Lozano-Rogado J. , *New Technology in Sensing Odours: From Human to Artificial Noses*. In *Floriculture, Ornamental and Plant Biotechnology*, vol. IV, Global Science Books, UK, pp. 152-161, 2006

- [18] Lozano J, Santos JP, Gutiérrez J, Horrillo MC. Comparative study of sampling systems combined with gas sensors for wine discrimination. *Sensors and Actuators B: Chemical*. 2007;**126**(2)
- [19] Pearce T C, Schiffman S S, Nagle H T & Gardner J W. *Handbook of machine olfaction: electronic nose technology*. 2006. John Wiley & Sons, Weinheim (Germany)
- [20] Guadarrama A, Fernandez JA, Iniguez M, Souto J, De Saja JA. Array of conducting polymer sensors for the characterisation of wines. *Analytica Chimica Acta*. 2000;**411**(1)
- [21] Sharma, P., Ghosh, A., Tudu, B., Sabhapondit, S., Baruah, B. D., Tamuly, P. & Bandyopadhyay, R. (2015). Monitoring the fermentation process of black tea using QCM sensor based electronic nose. *Sensors and Actuators B: Chemical*, 219, 146-157
- [22] Lozano J, Fernández MJ, Fontecha JL, Aleixandre M, Santos JP, Sayago I, Horrillo MC. Wine classification with a zinc oxide SAW sensor array. *Sensors and Actuators B: Chemical*. 2006;**120**(1)
- [23] Di Natale C, Macagnano A, Nardis S, Paolesse R, Falconi C, Proietti E, D'Amico A. Comparison and integration of arrays of quartz resonators and metal-oxide semiconductor chemoresistors in the quality evaluation of olive oils. *Sensors and Actuators B: Chemical*. 2001;**78**(1)
- [24] Gutierrez-Osuna R. Pattern analysis for machine olfaction: A review. *IEEE Sensors Journal*. 2002;**2**(3)
- [25] Waldemark, J. T., Roppel, T. A., Wilson, D. M., Dunman, K. L., Padgett, M. L., & Lindblad, T. (1999, March). Neural networks and PCA for determining region of interest in sensory data preprocessing. In *Ninth Workshop on Virtual Intelligence/Dynamic Neural Networks: Neural Networks Fuzzy Systems, Evolutionary Systems and Virtual Re* (pp. 396-405). International Society for Optics and Photonics
- [26] Duda, R O, Hart, P E, & Stork, D. G. *Pattern classification*. 2nd. Edition. Wiley & Sons. New York. 2001
- [27] Bishop CM. *Neural Networks for Pattern Recognition*. Oxford: Oxford University Press; 1999
- [28] Nagle HT, Gutierrez-Osuna R, Schiffman SS. The how and why of electronic noses. *IEEE Spectrum*. 1998;**35**(9)
- [29] Peris M, Escuder-Gilabert L. A 21st century technique for food control: Electronic noses. *Analytica Chimica Acta*. 2009;**638**
- [30] Wilson AD, Baietto M. *Advances in electronic-nose technologies developed for biomedical applications*. Sensors (Basel). 2011;**11**
- [31] Wilson AD. *Diverse applications of electronic-nose technologies in agriculture and forestry*. Sensors (Basel). 2013;**13**
- [32] Falasconi M, Concina I, Gobb E, Sberveglieri V, Pulvirenti A, Sberveglieri G. Electronic nose for microbiological quality control of food products. *International Journal of Electrochemical Science*. 2012;**2012**

- [33] Loutfi A, Coradeschi S, Mani GK, Shankar P, Rayappan JBB. Electronic noses for food quality: A review. *Journal of Food Engineering*. 2015;**144**:103-111
- [34] Alam H, Saeed SH, Engg C. Electronic nose in food and health applications: A review. *International Journal of Computing and Corporate Research*. 2012;**2**
- [35] James D, Scott SM, Ali Z, O'Hare WT. Chemical sensors for electronic nose systems. *Microchimica Acta*. 2005;**149**
- [36] Ghasemi-Varnamkhasti M, Mohtasebi SS, Rodriguez-Mendez ML, Lozano J, Razavi SH, Ahmadi H. Potential application of electronic nose technology in brewery. *Trends in Food Science & Technology*. 2011;**22**(4)
- [37] Lamagna A, Reich S, Rodriguez D, Scoccola NN. Performance of an e-nose in hops classification. *Sensors and Actuators B: Chemical*. 2004;**102**(2)
- [38] Zimmermann D, Leclercq C. Electronic nose for monitoring the flavour of special malts. In: *2nd International Symposium on Olfaction and Electronic Nose.*; Toulouse. 1995
- [39] Austin GD, Russell I, Meiering AG, Subden RE. A gas-sensor-based on-line ethanol meter for Breweries. *Journal of the American Society of Brewing Chemists*. 1996;**54**(4)
- [40] Buratti S, Benedetti S. Alcoholic Fermentation Using Electronic Nose and Electronic Tongue, In *Electronic Noses and Tongues in Food Science* (pp. 291-299). Academic Press, San Diego, 2016
- [41] Kojima H, Araki S, Kaneda H, Takashio M. Application of a new electronic nose with fingerprint mass spectrometry to brewing. *Journal of the American Society of Brewing Chemists*. 2005;**63**(4)
- [42] Ragazzo-Sanchez JA, Chalier P, Chevalier-Lucia D, Calderon-Santoyo M, Ghommidh C. Off-flavours detection in alcoholic beverages by electronic nose coupled to GC. *Sensors and Actuators B: Chemical*. 2009;**140**(1)
- [43] Kong Z, Li M, An J, Chen J, Bao Y, Francis F, et al. The fungicide triadimefon affects beer flavor and composition by influencing *Saccharomyces cerevisiae* metabolism. *Scientific Reports*. 2016;**6**
- [44] Santos, J. P., & Lozano, J. (2015, February). Real time detection of beer defects with a hand held electronic nose. In *Electron Devices (CDE), 2015 10th Spanish Conference on* (pp. 1-4). IEEE.
- [45] Bailey TP, Hammond RV, and Persaud KC. Application for an electronic aroma detector in the analysis of beer and raw materials. *Journal of the American Society of Brewing Chemists*. 1995;**53**
- [46] Aishima T. Discrimination of liquor aromas by pattern recognition analysis of responses from a gas sensor array. *Analytica Chimica Acta (Internet)*. 1991;**243**:293-300. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0003267000825738>. [Accessed: February 20, 2017]

- [47] Pearce TC, Gardner JW, Friel S, Bartlett PN, Blair N. Electronic nose for monitoring the flavour of beers. *Analyst*. 1993;4(118)
- [48] Heberle I, Liebming A, Weimar U, Göpel W. Optimised sensor arrays with chromatographic preparation: Characterisation of alcoholic beverages. *Sensors and Actuators B: Chemical*. 2000;68(1):53-57
- [49] Ragazzo-Sanchez JA, Chalier P, Chevalier D, Ghommidh C. Electronic nose discrimination of aroma compounds in alcoholised solutions. *Sensors and Actuators B: Chemical*. 2006;114(2)
- [50] Tao, Z., Lei, W., & Teng, J. (2008, December). Pattern recognition of the universal electronic nose. In *Intelligent Information Technology Application, 2008. IITA'08. Second International Symposium on* (Vol. 3, pp. 249-253). IEEE.
- [51] Pornpanomchai, C., & Suthamsmai, N. (2008, August). Beer classification by electronic nose. In *Wavelet Analysis and Pattern Recognition, 2008. ICWAPR'08. International Conference on* (Vol. 1, pp. 333-338). IEEE.
- [52] Ghasemi-Varnamkhasti M, Mohtasebi SS, Siadat M, Ahmadi H, Razavi SH. From simple classification methods to machine learning for the binary discrimination of beers using electronic nose data. *Engineering in Agriculture, Environment and Food*. 2015;8(1)
- [53] Li W, Pickard MD, Beta T. Evaluation of antioxidant activity and electronic taste and aroma properties of antho-beers from purple wheat grain. *Journal of Agricultural and Food Chemistry*. 2007;55(22)
- [54] Zhou, J., Lei, W., Teng, J., & Tao, Z. (2010, July). Research on the recognition of chemical odour information based on probabilistic neural networks. In *Environmental Science and Information Application Technology (ESIAT), 2010 International Conference on* (Vol. 1, pp. 825-828). IEEE.
- [55] Siadat, M., Losson, E., Ghasemi-Varnamkhasti, M., & Mohtasebi, S. S. (2014, November). Application of electronic nose to beer recognition using supervised artificial neural networks. In *Control, Decision and Information Technologies (CoDIT), 2014 International Conference on* (pp. 640-645). IEEE.
- [56] Vera L, Aceña L, Guasch J, Boqué R, Mestres M, Busto O. Characterization and classification of the aroma of beer samples by means of an MS e-nose and chemometric tools. *Analytical and Bioanalytical Chemistry*. 2011;399(6)
- [57] Liu J, Yang J, Wang W, Fu S, Shi Y, Men H. Automatic evaluation of sensory information for beer at a fuzzy level using electronic tongue and electronic nose. *Sensors and Materials*. 2016;28(7)
- [58] Yang YM, Yang PY, Wang XR. Electronic nose based on SAWS array and its odor identification capability. *Sensors and Actuators B: Chemical*. 2000;66(1):167-170
- [59] Sikorska E, Chmielewski J, Górecki T, Khmelinskii I, Sikorski M, De Keukeleire D. Discrimination of beer flavours by analysis of volatiles using the mass spectrometer as an electronic nose. *Journal of the Institute of Brewing*. 2007;113(1)

- [60] Berna A. Metal oxide sensors for electronic noses and their application to food analysis. *Sensors (Basel)* (Internet). 2010;**10**(4):3882-3910. Available from: <http://www.ncbi.nlm.nih.gov/pubmed/22319332>. [Accessed: February 13, 2017]
- [61] Thepudom, T., Kerdcharoen, T., Tuantranont, A., & Pogfay, T. (2012, December). Health-care electronic nose to detect beer odor in breath after drinking. In *Biomedical Engineering International Conference (BMEiCON), 2012* (pp. 1-4). IEEE.
- [62] Phetchakul T, Sutthinet C. Monitoring of draft beer fermentation process by electronic nose. *Advanced Materials Research*. 2014;**911**
- [63] Mckellar RC, Young JC, Johnston A, Knight KP, Lu X, Battenham S. Use of the electronic nose and gas chromatography-mass spectrometry to determine the optimum time for aging of beer. *Technical Quarterly—Master Brewers Association Amsterdam* [Internet]. 2002;**39**(2):99-105. Available from: <http://cat.inist.fr/?aModele=afficheN&cpsid=13842154>. [Accessed: February 20, 2017]
- [64] Ghasemi-Varnamkhasti M, Mohtasebi SS, Siadat M, Lozano J, Ahmadi H, Razavi SH, et al. Aging fingerprint characterization of beer using electronic nose. *Sensors and Actuators B: Chemical*. 2011;**159**(1)
- [65] Lozano J, Santos JP, Suárez JI, Arroyo P, Herrero JL, Martín A. Detection of pollutants in water samples with a wireless hand-held E-nose. *Procedia Engineering*. 2014;**87**
- [66] Santos JP, Lozano, J, Suárez JI, Aleixandre M. Electronic Nose Network For Detection Of TATP Precursors. *Proceedings of International Symposium on Olfaction and Electronic Nose 2013*. Daegu (South Korea). 2013
- [67] Herrero JL, Lozano J, Santos JP, Suárez JI. On-line classification of pollutants in water using wireless portable electronic noses. *Chemosphere*. 2016;**152**:107-116
- [68] Derks EP, Beckers ML, Melssen WJ, Buydens LM. Parallel processing of chemical information in a local area network—II. A parallel cross-validation procedure for artificial neural networks. *Computers & Chemistry*. 1996;**20**(4):439-448
- [69] Blanco CA, Andrés-Iglesias C, Montero O. Low-alcohol beers: Flavor compounds, defects, and improvement strategies. *Critical Reviews in Food Science and Nutrition*. 2016;**56**(8)
- [70] Cortacero-Ramírez S, de Castro MH-B, Segura-Carretero A, Cruces-Blanco C, Fernández-Gutiérrez A. Analysis of beer components by capillary electrophoretic methods. *TrAC Trends in Analytical Chemistry* (Internet). 2003;**22**(7):440-455. Available from: <http://www.sciencedirect.com/science/article/pii/S0165993603007040>
- [71] Stucky GJ, Mcdaniel MR. Raw hop aroma qualities by trained panel free-choice profiling. *Journal of the American Society of Brewing Chemists* (Internet). **55**(2):65-72. Available from: <http://cat.inist.fr/?aModele=afficheN&cpsid=2677437>. [Accessed: March 1, 2017]
- [72] Lozano J, Santos JP, Aleixandre M, Sayago I, Gutiérrez J, Horrillo MC. Identification of typical wine aromas by means of an electronic nose. *IEEE Sensors Journal*. 2006;**6**(1)

- [73] Andrés-Iglesias C, Montero O, Sancho D, Blanco CA. New trends in beer flavour compound analysis. *Journal of the Science of Food and Agriculture* (Internet). 2015;**95**(8):1571-1576. Available from: <http://dx.doi.org/10.1002/jsfa.6905>
- [74] Tian J. Determination of several flavours in beer with headspace sampling–gas chromatography. *Food Chemistry* (Internet). 2010;**123**(4):1318-1321. Available from: <http://www.sciencedirect.com/science/article/pii/S0308814610007235>
- [75] Lermusieau G, Bulens M, Collin S. Use of GC-olfactometry to identify the hop aromatic compounds in beer. *Journal of Agricultural and Food Chemistry*(Internet). 2001;**49**(8):3867-3874. Available from: <http://dx.doi.org/10.1021/jf0101509>
- [76] Capozzi V, Makhoul S, Aprea E, Romano A, Cappellin L, Sanchez Jimena A, et al. PTR-MS characterization of VOCs associated with commercial aromatic bakery yeasts of wine and beer origin. *Molecules*. 2016;**21**(4)
- [77] De Clippeleer J, Van Opstaele F, Vercaemmen J, Francis GJ, De Cooman L, Aerts G. Real-time profiling of volatile malt aldehydes using selected ion flow tube mass spectrometry. *LC GC North America* [Internet]. 2016:67-74. Available from: http://cat.inist.fr/?aM_odele=afficheN&cpsid=23239175. [Accessed: March 1, 2017]

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