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Classification of white wine aromas with an electronic nose

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Abstract

This paper reports the use of a tin dioxide multisensor array based electronic nose for recognition of 29 typical aromas in white wine. Headspace technique has been used to extract aroma of the wine. Multivariate analysis, including principal component analysis (PCA) as well as probabilistic neural networks (PNNs), has been used to identify the main aroma added to the wine. The results showed that in spite of the strong influence of ethanol and other majority compounds of wine, the system could discriminate correctly the aromatic compounds added to the wine with a minimum accuracy of 97.2%.

Keywords: Aromatic compound; Thin film sensor; Pattern recognition techniques

1. Introduction

1.1. Biological and electronic noses

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. Despite this difference, chemical sensor arrays combined with pattern recognition methods are very useful in many practical applications like 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. They work in a similar way and have, in that aspect, a large similarity with the human nose [1,2].

The human olfactory system is very complex, and has been recently successfully investigated and recognized with the Nobel Prize [2–4]. Each olfactory receptor cell possesses only one type of odorant receptor, and each receptor can detect a limited number of odorant substances. The electronic nose is an electronic system that tries to imitate the structure of the human nose. Both systems are based on non specific receptors (cells and sensors) followed by a posterior signal processing.

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" [5] and tries to characterise different gas mixtures [3,6,7]. 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 or current. The response times for these devices range from seconds up to a few minutes. This is a significant drawback for these devices, and thus one of the main research topics in this field is to reduce the response time. A simple flow chart of the typical structure of an electronic nose is shown in Fig. 1.

By teaching a computer (or hardware) to recognise those patterns we have used to train the electronic nose, it should

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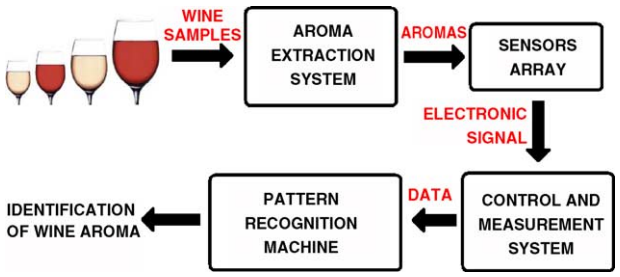

Fig. 1. Typical block diagram of an electronic nose.

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. Several methods are used, some statistical which determine the clusters of data representing different classes of odours and some based on different forms of artificial neural networks (ANNs) for classification and quantification of aromatic compounds and gas mixtures. The development of efficient pattern recognition algorithms is, therefore, one of the most important issues in the field of electronic noses. One common method for pattern recognition is principal component analysis (PCA) [8,9]. 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 a better visualization of data clustering. If we use, for instance, 16 sensors for our measurements (one measurement can thus be represented as a point in a 16-dimensional space), some of them probably respond in a similar (but not identical) way. This means that the number of dimensions in the data set can be reduced without any loss of information. This method consists of expressing the response vectors in terms of linear combinations of orthogonal vectors along a new set of coordinate axes, and is sometimes referred to vector decomposition and thus helps to display multivariate data in two or three dimensions. A loading plot of a PCA shows to what degree the different sensors contribute to the principal components. In this plot, sensors with similar contributions (i.e. that contain similar information) will be close together. Sensors that are close to the origin have comparably small variance, and therefore, probably contain little information.

One of the most popular supervised methods to handle electronic nose data is the artificial neural network (ANN), which bears a certain resemblance to the function of the human brain. In principle, an ANN is constituted of many (in the order of 50–100) artificial neurons. The artificial neurons are organised in different layers, often three, together forming a network (see Fig. 2). An artificial neuron is a simple processing element, which in resemblance to biological neurons uses signals from several inputs to produce one output. A linear combination is taken of all the inputs, giving a single value. This value is then used in a transfer function, which could have arbitrary shape.

An alternative for classical neural networks are Radial Basis Function Networks (RBFs). They may require more neurons than standard feed-forward backpropagation networks, but often they can be designed in a fraction of the time it takes to train standard feed-forward networks. They work best when many training vectors are available.

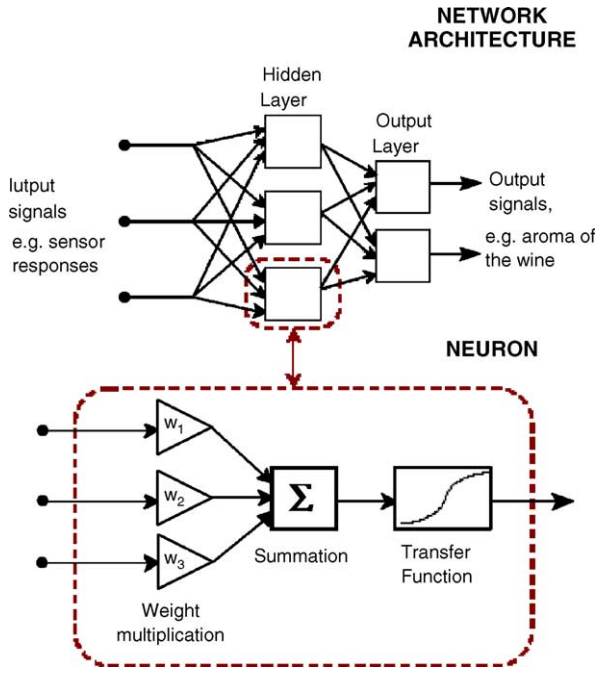

Fig. 2. Schematic of an artificial neural network. It consists of a multilayered (often three) interconnected layers of neurons. The computing neurons (hidden and output layers) have a non-linear transfer function. The parameters of the neurons are chosen through a minimisation of the output error for a given training set.

The learning in an ANN is performed by changing the parameters in the linear combination. By feeding data from known odours into the network, the parameters can be adapted to recognise the sensor signals from these odours. In order to adapt the parameters, the training data has to be used many times. This is very similar to training of odour recognition for humans. After being exposed to an odour only once we seldom remember it very well, while odours we have often experienced in youth can be recognised a long time afterwards. It is important to note that an ANN, just like the human nose, cannot identify odours it has never experienced before. When confronted with the sensor signals from a new odour, the ANN can only say which of the known odours the signals are most similar to, or that it does not recognise the odour. A human can easily say if it considers an unknown odour to be pleasant or not, while an electronic nose cannot make any subjective judgement of that type.

2. Experimental

2.1. Electronic nose

An electronic nose based on tin oxide array has been used for headspace analysis of the samples. The electronic nose

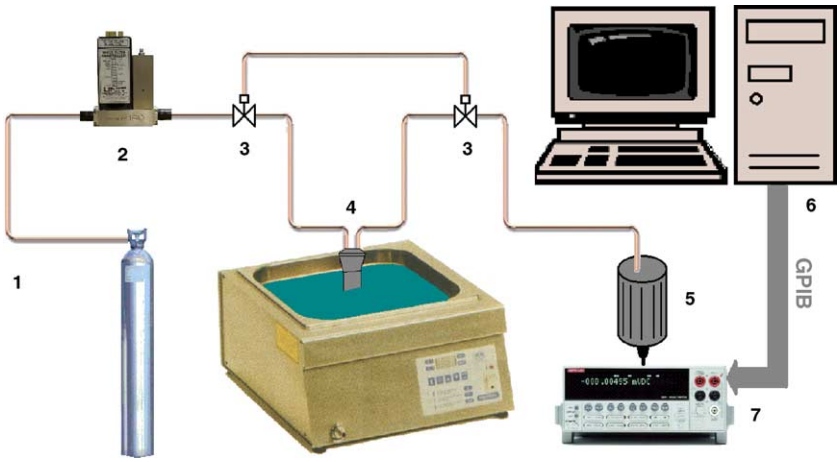

Fig. 3. Measurement set-up: (1) nitrogen bottle; (2) mass flowmeter controller; (3) electrovalves; (4) Dreschell bottle with sample in a thermostatic bath; (5) sensors cell; (6) PC; and (7) DMM with multiplexer.

used has been home-fabricated and home-developed for wine aroma purposes [10]. The sensor array was prepared by RF sputtering onto an alumina substrate. The array is formed by 16 thin film sensors with thicknesses between 200 and 800 nm. Some sensors were doped with chromium and indium either as surface or intermediate layer. The operation temperature of the sensors is controlled at 250 °C with a PID regulator. The array was placed in a 24 cm^3 stainless steel cell with a heater and a thermocouple. The carrier used gas was 99.998% purity nitrogen in order to preserve the wine. Gas line tubes were of stainless steel covered with fused silica in order to minimize gas adsorption in the line. The sampling method employed was static headspace followed by a dynamic injection because of its sensitivity to highly or medium volatile compounds present in wine. The way of carrier gas and volatile compounds is selected with the control program using two electrovalves. The main components of the measurement set-up are shown in Fig. 3.

The resistance of the sensors was measured with a Keithley 2700 7 1/2 digits digital multimeter (DMM) with a 40-channels multiplexer, connected to a personal computer using a GPIB interface. The measurement system was fully automated and controlled with a program developed in Testpoint ®.

Responses of the individual sensors are defined respect to the minimum resistance to 12% (v/v) of ethanol for all the measurements:

$$r = \frac{R_{\text{wine}}}{R_{\text{calibration}}}$$

where R_{wine} is the minimum resistance of the sensor in the measurement of wine and $R_{\text{calibration}}$ is the minimum resistance of the sensor exposed to a solution of 12% of ethanol.

The data collected were analyzed using a commercial software package (Matlab 6.1) for programming the feature extraction and the pattern recognition techniques (PCA and ANNs).

The principal component analysis applies a linear transformation to the data and result in a new space of variables called principal components [11]. A probabilistic neural network (PNN) was used for classification purposes. The PNN was composed by three layers: the input one had three neurons, corresponding with the three principal components; the hidden layer, with radial basis transfer functions, had the same number of neurons that number of training vectors and a competitive layer in the output [11], leave one out (LOO) cross validation method was applied in order to check the performance of the network [12]. LOO consists of training N distinct nets (in this case, N is the number of measurements) by using $N-1$ training vectors; while the validation of the trained net is carried out by using the remaining vector, excluded from the training set. This procedure is repeated N times until all vectors are validated [13].

2.2. Wine samples and protocols

A total of 29 aromas have been analyzed. The measured aromas are the most common ones in white wines. The chemical compounds responsible of these aromas are dissolved in the same wine at concentrations from two to eight times the threshold concentration the humans can smell [14,15]. The chemical compounds are responsible of typical aromas found in white wines and correspond to several descriptors such as fruity, floral, microbiological, herbaceous and chemical. The aromatic compounds measured and descriptors of the aroma added to the wine are shown in Table 1.

The base wine comes from Malvar variety and has been elaborated in the “Instituto Madrileño de Investigaciones Agroalimentarias (IMIA)” with grapes of Madrid region. All compounds were of analytical quality and were provided by Merck and Sigma–Aldrich. The samples are frozen at the moment of preparation and stored at −20 °C in a freeze until the moment of measurement. Each sample is measured during a day. A total of 9–10 measurements per day are performed. The sampling method was headspace, so 10 ml of solution

Table 1
Aromatic compounds and aroma measured

Chemical compound	Aroma	Group
Geraniol	Geranium	Floral
2-Phenylethanol	Rose	Floral
β-Ionone	Violet	Floral
Linalool	Rose, citric	Floral
Phenyl ethyl acetate	Pollen, rose	Floral
Ethyl octanoate	Apple	Fruity
Isoamyl acetate	Banana	Fruity
Ethyl isobutirate	Pear	Fruity
Ethyl hexanoate	Fruit	Fruity
Hexyl acetate	Pear 2	Fruity
Ethyl cinnamate	Strawberry	Fruity
Ethyl 2-methylbutyrate	Blueberry	Fruity
Ethyl isovalerate	Mulberry	Fruity
1-Hexanol	Green grass	Microbiological
Diacetyl	Butter	Microbiological
Isovaleric acid	Cheese	Microbiological
Isoamyl alcohol	Soap, oil	Herbaceous, Vegetative
Butyric acid	Cheese 2	Microbiological
Acetoin	Cream, milky	Microbiological
C-3-hexen-1-ol	Cut green grass	Herbaceous, vegetative
Benzaldehyde	Almond	Herbaceous, vegetative
Acetic acid	Vinegar	Chemical pungent
Decanoic acid	Natural soap	Chemical
Sulphur dioxide	Sulphur	Chemical pungent
Ethyl acetate	Gum	Chemical pungent
Octanoic acid	Rancid	Chemical
Acetaldehyde	Sherry	Chemical oxidized
Guaiacol	Wood	Chemical
P-cresol	Stable, horses	Chemical

are kept in a 50 ml Dreschel bottle at 30 °C for 30 min in order to generate a vapour phase in equilibrium with the liquid. The electrovalves are switched and nitrogen fluxes for 20 min carrying the aromatic compounds to the sensor cell. Then the electrovalves are switched again to allow the sensors to desorb. This procedure is repeated several at least eight times for each compound. Sensors are calibrated once a week with a blank solution (12% (v/v) ethanol in deionised water) in order to reduce the drift of the sensors [5]. All measurements are carried out at a total gas flow of 200 ml/min.

3. Results and discussion

Fig. 4 shows the typical transient responses of four chemoresistive sensors, operating at 250 °C, exposed towards the headspace of the blank wine. The response of the sensors corresponds to several pulses of 20 min of exposition to the tested wine flavour followed by a pure nitrogen purge for 40 min.

A polar plot of the average signals of the sensors for the wine samples is shown in Fig. 5 in terms of relative resistance changes respect to ethanol 12%. The contour of these polar plots differs from one aroma to another, illustrating the discrimination capabilities of the array. The standard deviation ($n = 8$ samples) for the 16 sensors ranged between 0.5 and 12%.

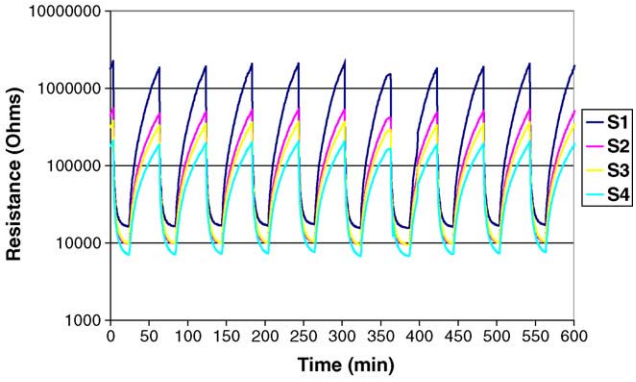

Fig. 4. Typical transient response of four sensors of the array.

The data obtained from sensor array, after feature extraction and calibration with ethanol measurements, have been processed by the PCA pattern recognition technique to investigate the discrimination capability of the present system. Nevertheless, to process uniform and homogeneous data in the PCA study, the sensor response to the first exposure of each wine flavour was eliminated. Usually the first two components carry the most information of the old variables.

Fig. 6 illustrates the principal components plot which shows separate clusters for geranium, rose, violet, citric and pollen aromas in white wine. In Fig. 7 is shown the PCA plot for apple, banana, pear, fruits, pear 2, strawberry, blueberry and mulberry aromas. There is some partial overlapping between "banana" and "fruits" aromas, however, the other classes are well separated. Fig. 8 shows the PCA plot for green grass, butter, cheese, soap, cheese 2, cream, milky, cut green grass and almond aromas. This figure shows an overlapping between two very similar aromas: "green grass" and "just cutted grass". Looking Fig. 9, it can be concluded that there isn't overlapping in chemical aromas added to blank wine and shows separate clusters for vinegar, natural soap, sulphur, gum, rancid, sherry, wood and stable aromas. In Figs. 6–9, the percentage of variance explained by each principal component is in brackets.

A pattern classifier based on a probabilistic neural network has been employed for recognition of the aroma added to the blank wine. The leave one out (LOO) method has been used for validation. Table 2 defines several parameters used for measuring the classification performance: sensitivity, selectivity and accuracy.

Table 2
Parameters used to evaluate the performance of the network in classification of class *i*

Real	Predicted	
	Class *i*	Class *j*
Class *i*	True positive (TP)	False negative (FN)
Class *j*	False positive (FP)	True negative (TN)

Sensitivity = TP/(TP + FN); selectivity = TN/(FP + TN); accuracy = (TP + TN)/(TP + TN + FP + FN).

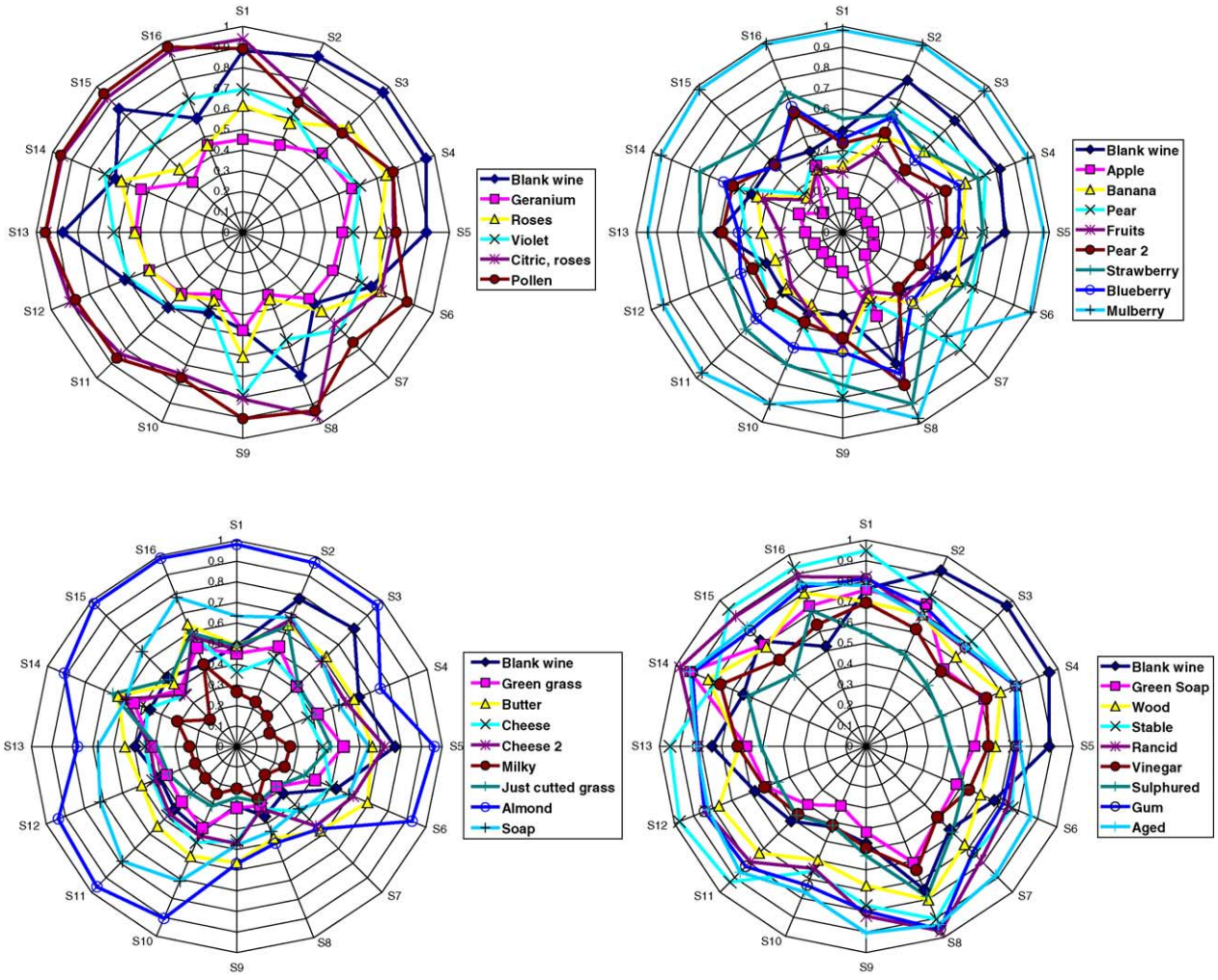

Fig. 5. Polar plot of the average signals of the sensors for wine samples grouped by families: floral, fruity, herbaceous and microbiological and chemical aromas.

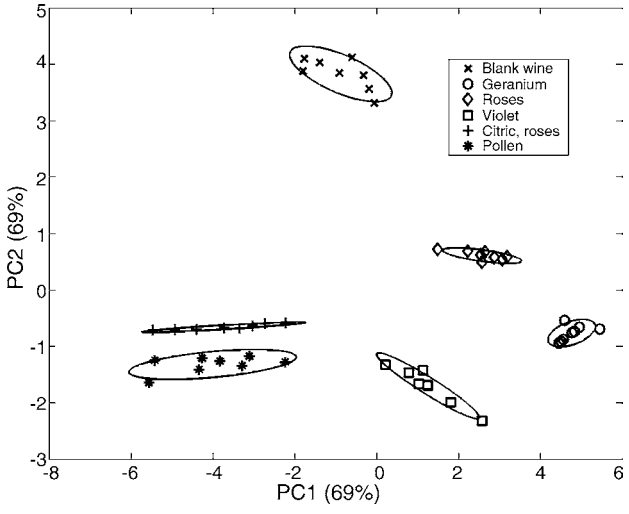

Fig. 6. PCA plot of the measurements of floral aromas in white wine.

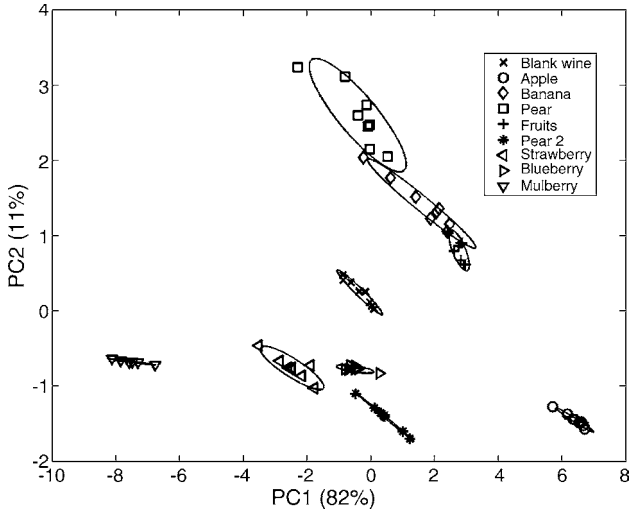

Fig. 7. PCA plot of the measurements of fruity aromas in white wine.

Table 3
Confusion matrix of the probabilistic neural network for the chemical aromatic compounds in wine

	Blank wine	Green soap	Wood	Stable	Rancid	Vinegar	Sulphured	Gum	Aged
Blank wine	8	0	0	0	0	0	0	0	0
Green soap	0	8	0	0	0	0	0	0	0
Wood	0	0	8	0	0	0	0	0	0
Stable	0	0	0	8	0	0	0	0	0
Rancid	0	0	0	0	8	0	0	0	0
Vinegar	0	0	1	0	0	7	0	0	0
Sulphured	0	0	0	0	0	0	8	0	0
Gum	0	0	0	0	0	0	0	7	1
Aged	0	0	0	0	1	0	0	0	7

Table 4
Neural networks results for chemical compounds in wine

	Blank wine (%)	Green soap (%)	Wood (%)	Stable (%)	Rancid (%)	Vinegar (%)	Sulphured (%)	Gum (%)	Aged (%)
Sensitivity	100	100	100	100	100	87.5	100	87.5	87.5
Selectivity	100	100	98.4	100	98.4	100	100	100	98.4
Accuracy	100	100	98.6	100	98.6	98.6	100	98.6	97.2

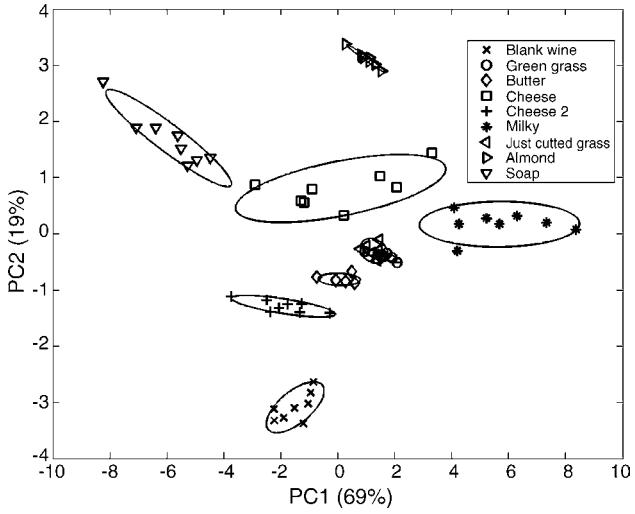

Fig. 8. PCA plot of the measurements of herbaceous and microbiological aromas in white wine.

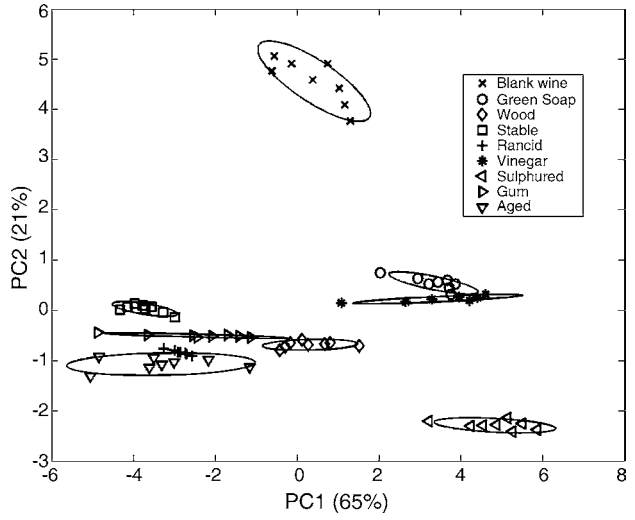

Fig. 9. PCA plot of the measurements of chemical aromas in white wine.

In floral, fruity, herbaceous and microbiological aromas, the probabilistic neural network has obtained 100% in sensitivity, selectivity and accuracy. In the case of chemical aromas, the pattern classifier has confussed several aromas. The confusion matrix for this case is shown in Table 3, and sensitivity, selectivity and accuracy calculated for chemical aromas in Table 4.

4. Conclusions

Discrimination of several aromatic compounds from different families of main aromas of white wine has been performed by a semiconductor sensor array based electronic nose.

A 100% in sensitivity, selectivity and accuracy has been obtained with the probabilistic neural network trained for the following aromas: floral, fruity, herbaceous and microbiological. For chemical aromas the minimum sensitivity, selectivity and accuracy obtained has been 87.5, 98.4 and 97.2%, respectively.

In conclusion, as wines from different areas and grape varieties exhibit different aromatic profiles, the developed system could be useful for the typification (identification of origin and grape variety) of white wines.

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