A neural approach for improving the measurement capability of an electronic nose

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Abstract
Electronic noses, instruments for automatic recognition of odours, are typically composed of an array of partially selective sensors, a sampling system, a data acquisition device and a data processing system. For the purpose of evaluating the quality of olive oil, an electronic nose based on an array of conducting polymer sensors capable of discriminating olive oil aromas was developed. The selection of suitable pattern recognition techniques for a particular application can enhance the performance of electronic noses. Therefore, an advanced neural recognition algorithm for improving the measurement capability of the device was designed and implemented. This method combines multivariate statistical analysis and a hierarchical neural-network architecture based on self-organizing maps and error back-propagation. The complete system was tested using samples composed of characteristic olive oil aromatic components in refined olive oil. The results obtained have shown that this approach is effective in grouping aromas into different categories representative of their chemical structure.

Keywords: electronic nose, sensors, odour recognition, hierarchical neural networks, olive oil

1. Introduction

In many industries, including food and beverage, cosmetics or car component manufacturing, the qualitative evaluation of products is strictly related to human perception of odours. Traditional analytical techniques often fail to give an accurate representation of the quality of products, since in most cases it is impossible or too expensive to determine the exact aroma composition and there is no way to recover the synthetic human judgement from the analytic outputs. Often large companies are equipped with human panels, but this solution suffers many drawbacks (cost, low throughput, limited accuracy and reproducibility). Hence, the advantages expected from an automated system capable of detecting and classifying odours, vapours and gases has stimulated scientific interest in development of artificial olfactory systems [1], also called electronic noses. These instruments are expected to have significant application in fields such as food analysis (freshness and aroma of some aliments and beverages [2]), environmental and industrial monitoring [3], safety and medical diagnosis [4].

In general, an electronic nose is composed of an odour sampling system, an array of chemical sensors, an electronic front-end and a data processing unit. The sampling system conveys the odour sample to the array of sensors, which convert the chemical information into the variation of a

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Table 1. Polymers, dopants and the molar ratios used for each sensor.

Sensor	Polymer	Dopant salt	Molar ratio
2DI2	3, 3′-Dipentoxy-2, 2′bithiophene	Iodine	2
5TCR1	3, 3″-Dipentoxy-2, 2′:5′, 2″-terthiophene	Cupric chloride	5
3DPR2	3, 3′-Dipentoxy-2, 2′bithiophene	Cupric perchlorate	3
3TPR3	3, 3″-Dipentoxy-2, 2′:5′, 2″-terthiophene	Cupric perchlorate	3
3DCF1	3, 3′-Dipentoxy-2, 2′bithiophene	Iron chloride	3
3TI1	3, 3″-Dipentoxy-2, 2′:5′, 2″-terthiophene	Iodine	3
5DPR3	3, 3′-Dipentoxy-2, 2′bithiophene	Cupric perchlorate	5
3DPF2	3, 3′-Dipentoxy-2, 2′bithiophene	Iron perchlorate	3

physical quantity. By means of generation and measurement of electric signals, the electronic front-end allows the acquisition of these data, which are then analysed by the processing unit for the classification of the odours tested. The whole measurement process is automated to enhance repeatability.

In spite of the many potential applications, electronic noses are not as widespread as might be expected. There are two main reasons for this apparent paradox, cost and the very aggressive market policy companies adopted in the past for a product while it was still in a research and development phase. In many cases enthusiastic users were unable to obtain the results they were promised because of inappropriate choice and treatment of samples, incorrect use of the instruments, instability and non-reproducibility of sensors. Some of these problems can be solved by tailoring devices to a specific application and developing specific pattern recognition techniques [5].

In this work, an artificial olfactory system based on the combination of conducting polymer sensors and an advanced neural recognition algorithm was set up with the ultimate aim of developing an instrument capable of monitoring olive processing and evaluating the quality of olive oils. The system was tested on samples of refined oil containing some of the main components of olive oil headspace. Data were analysed by a hierarchical neural network [6], based on both self organizing maps (SOM) [7] and error back-propagation (EBP) [8] modules.

Data analysis was performed by a three-step procedure, i.e. selective extraction of features from the data, preclassification of features by SOMs on a topological basis, final classification by the EBP module.

Since the headspace of real olive oils is much more complex than our samples, results are not immediately applicable to olive oils. Nevertheless, the advantages obtainable by the computational model presented here are much more general, and could make the difference even in other application areas.

The characteristics of the sensors, sampling system and data acquisition unit are presented together with a detailed description of the recognition algorithm and results obtained by the preliminary testing of olive oil aroma components.

2. Materials and methods

2.1. The electronic nose

The electronic nose is based on an array of eight conducting polymer sensors. Sensor supports were prepared by vacuum evaporating four gold tracks on 4 mm × 7 mm alumina plates, a material chosen for its porosity, which permits good adhesion of the polymeric film, its insulating properties and its low degree of chemical reactivity. After depositing the conducting polymers, four pins were glued to the alumina by means of an epoxy resin in order to be able to insert the sensor in a standard socket.

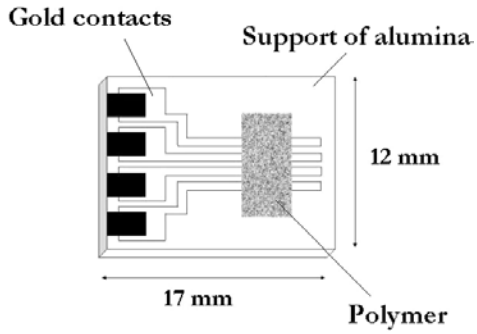

Figure 1. Structure of a conducting polymer sensor.

The conducting polymers were synthesized as a colloidal microsuspension obtained via chemical polymerization by substituted dimers and trimers of thiophenic units with alkoxy groups as substituents [9, 10]. Doping reactions with salts that act both as a catalyst and a doping agent were performed in order to give differentiated resistance characteristics to the polymers. The salts used were cupric and ferric perchlorates, cupric and ferric chlorides, hydrated gold chloride and iodine. The deposition of the different doped microsuspensions on supports was performed by means of a micropipette. A schematic representation of a sensor is depicted in figure 1, while polymers, dopants and their molar ratios are reported in table 1 for each sensor.

The conducting polymer sensors exhibit a variation of the electric resistance when exposed to volatiles, which can be measured by forcing a current between the two external pins by means of an electronic interface and measuring the voltage drop across the polymeric film by a high-impedance multimeter (Keithley 2700). The resistance values are calculated from the ratio between the output voltage and the input current; the sensor response consists of a time sequence of resistance values that depends on the type of odorant.

The array of sensors was housed in a stainless steel measuring chamber. The accurate design of the chamber allowed creation of a homogeneous flow with a low speed gradient, no recirculating zones or stagnant regions and the same local concentration of volatiles over each sensor [11].

A block diagram describing the experimental set-up is shown in figure 2. The sampling system, which conveyed

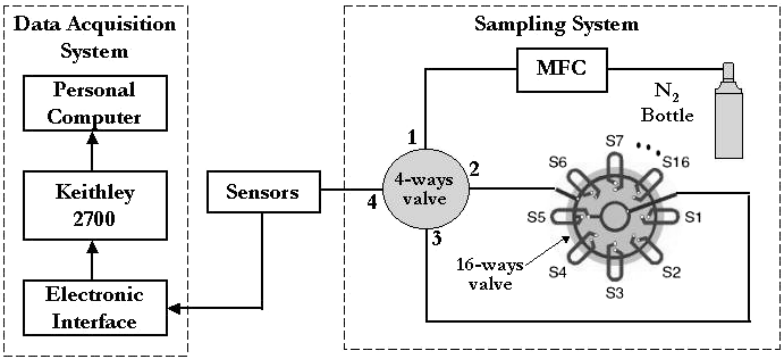

Figure 2. Scheme of the experimental set-up. MFC is the mass flow controller and S1 . . . S16 are the glass vials, connected to the 16-way valve, containing the samples.

Table 2. Olive oil aroma components analysed.

Aroma number	Compound	Structural formula
1	*trans*-2-Hexen-1-al	$CH_3–CH_2–CH_2$ H C=C H C O H
2	1-Pentanol	$CH_3–CH_2–CH_2–CH_2–CH_2–OH$
3	1-Hexanol	$CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–OH$
4	3-Pentanone	$CH_3–CH_2–C(=O)–CH_2–CH_3$
5	Ethanol	$CH_3–CH_2–OH$

the odour from the vials to the sensors, was composed of a bottle of ultra-pure nitrogen, a mass flow controller (MFC), a four-way valve (model 0011522, Omnifit Ltd) and a 16-way valve (model EMT4ST16MWE, Valco Instruments Co. Inc.) connected to sixteen 125 ml glass vials containing the samples. Inert PTFE tubing and fittings were used for the connections. Vials were kept at a constant temperature of 25 °C by means of a thermostatic bath.

Each sampling consisted of an eight-data vector obtained by sequentially scanning all the sensors of the array in 4.5 s. The measurement protocol consisted of three phases for each experiment:

- baseline acquisition: sensors flushed with nitrogen and 15 samplings acquired in 67.5 s;
- exposure: sensors exposed to the sample headspace, 7 samplings acquired in 31.5 s;
- desorption and cleaning: odours flushed away by nitrogen to restore baseline conditions, 98 samplings acquired in 441 s.

The 16-way valve allowed the selection of the sample to be analysed, while the four-way valve was used to switch the system between state 1 (sensors flushed with nitrogen, baseline acquisition and cleaning, figure 3(a)) and state 2 (exposure of sensors to odorant, figure 3(b)). The whole system was controlled by a personal computer with dedicated software to prevent the skill of the operator from playing a role in the reproducibility of measurements.

Samples comprised 10 ml of solution (2.5 μl ml^{-1}) of different olive oil aroma components (table 2) in refined olive oil.

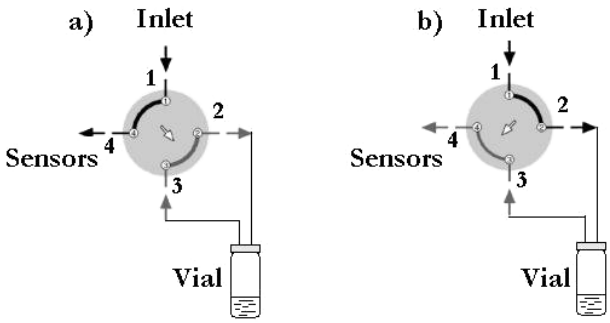

Figure 3. Positions of the four-way valve during (a) baseline and desorption and (b) exposure phases.

2.2. The processing unit

The recognition of samples is based on a multistep approach [12]. Recognition and classification are performed by a neural network having a hierarchical architecture comprising two different modules of parallel classifiers. The first module, comprising several SOM-based units, receives the input data acquired by the electronic front-end, i.e. the resistance values versus time. The analysis of these data permits extraction of characteristic features which are then preclassified, i.e. a unique position that identifies the winning neuron in the SOM topology for each input. The outputs of this preclassification step are sent to the second module of the network, defined by the EBP, whose task is to combine the inputs properly and perform the final classification. Each SOM of the first module acts to separate the input data into crisp classes. This preclassification is performed without any

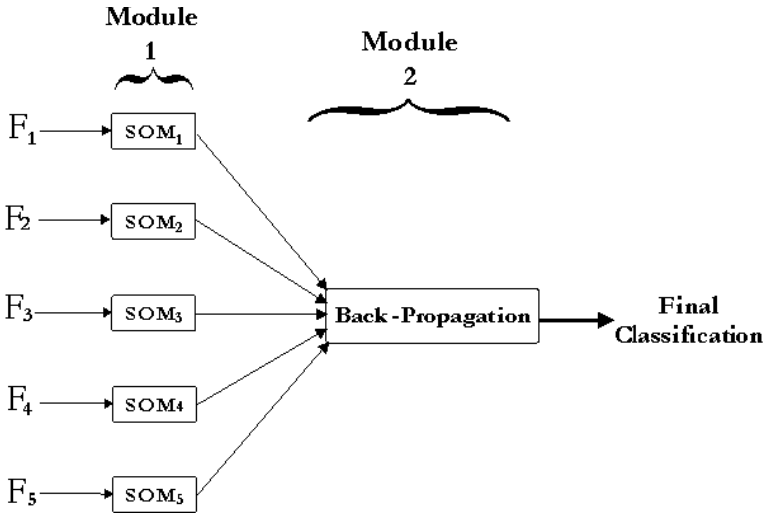

Figure 4. Hierarchical classification architecture with five features selected.

information on the odour to be recognized (i.e. unsupervised learning), but using only the appropriate feature for each of the SOMs. The outputs of this module are used to form the input pattern for the second module, which refines the classification and gives the group to which the odour belongs as a final response.

In the approach followed in this work, two main characteristics were pursued:

- to exploit the differences among the extracted features to improve the classification capability;
- to be able to change the number of features easily, for better tuning of the network.

To achieve this end, a hierarchical neural network was designed as shown in figure 4, so that implementation by means of two independent modules implies rapid and efficient training.

The first module is composed of a set of various units (or *preclassifiers*). Each unit is trained with the purpose of clustering each input value into specific classes of characteristics, without using any information related to the aroma component to which the input belongs. Each specific feature is the input to only one classifier of the first module; in this way, each SOM can be individually optimized without affecting the other modules of the global neural-network architecture, in order to reduce the computational complexity locally and, at the same time, to implement a flexible system.

In the SOM units, the weights w_j of a generic neuron j at time t, for the input $F_k(I)$ are modified as follows:

$$w_j(t+1) = \begin{cases} w_j(t) + \alpha(t)[F_k(I) - w_i(t)] & \text{if } j \in N_i(t) \\ w_j(t) & \text{if } j \notin N_i(t) \end{cases}$$

where w_i represents the weight at time t of the neuron i most excited by the input signal; $\alpha(t) = (1 - \frac{t-1}{T}) \in]0 \ldots 1[$ is the learning coefficient, which depends on t and
on the f i xed
maximum number of iterations T; $F_k(I)$ is the value of the feature k computed for the signal I (i.e. an aroma component); and $N_i(t)$ is the set of neurons in a fixed neighbourhood of given radius and centred around i, inf l uenced by the modification of $w_i(t)$.

Each SOM acts as an independent classification unit, giving a classification value for each input sample of the data set without taking into account the output of the other SOMs. The input is different for each SOM: every unit is trained and then used for the classification of a specific feature and, therefore, its input is only one of the processed features.

The preclassifications performed by the first module are the input to the EBP, which is able to train itself by propagating the resulting error $\delta_l(I)$ backward. $\delta_l(I)$ is calculated as follows:

$$\delta_l(I) = \begin{cases} f_l'(net_l(I)) \\ \quad \times (C_{I,T} - O_l(I)) & \text{if } l \in \text{output neurons} \\ f_l'(net_l(I)) \\ \quad \times \sum_{m \in \text{output neurons}} (\delta_m(I) \cdot w_{l,m}) & \text{if } l \notin \text{output neurons} \end{cases}$$

where $net_l(I)$ is the weighted sum of the inputs to the neuron l for the input I; $f'(net_l(I))$ is the derivative of an activation function f used to compute the output; $C_{I,T}$ represents the correct classification value of the input I; $O_l(I)$ is the output value of the neuron l for the input I; and $w_{l,m}$ is the weight of the connection between neurons l and m.

The architecture of the second module is shown in figure 5. For each sample to be classified, the input is a one-dimensional array containing the response given by each SOM unit of the first module to the specific feature extracted (see also figure 4).

The algorithm implemented has the following parameters:

- The network used is a feed-forward EBP network
- The training function updates weights according to a resilient back-propagation algorithm [8]
- The input dimension corresponds to the number of different features taken into account
- The input layer is composed of 25 neurons
- The output layer is composed of a number of neurons that correspond to the number of odours to be recognized.

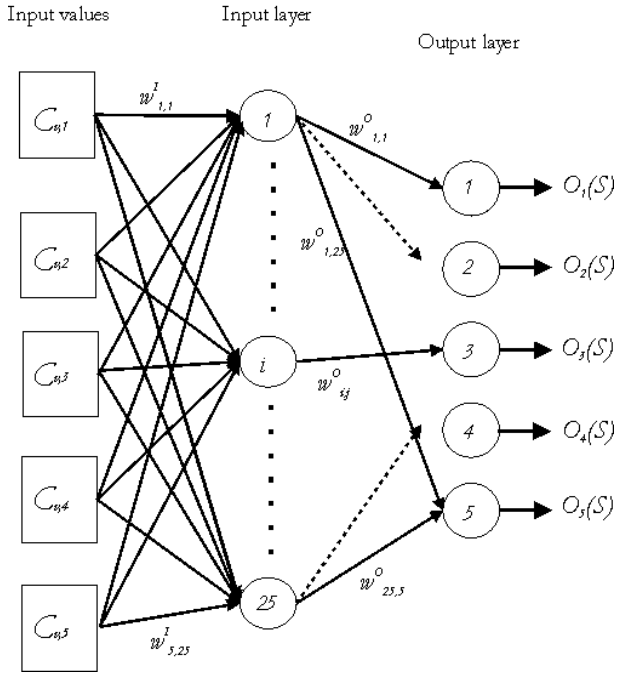

Figure 5. Back-propagation architecture with five features selected. $C_{v,1} \ldots C_{v,5}$: input stimulus corresponding to the output of the SOMs; $w^O_{l,m}$, $w^I_{k,j}$: weights; 25-neuron input layer; 5-neuron output layer; $O_j(S)$: final classification of the input sample S.

3. Results and discussion

Measurements were carried out in four different sessions; six series of measurements were performed during each of the first two sessions and three in the last two. Each series consisted of 15 measurements (three for each type of sample), so the overall number of measurements was 270 (54 for each type of sample). The data set was segmented to provide training and test sets of 90 and 180 measurements respectively.

A typical response of the array of sensors is reported in figure 6. The sensor responses are processed to extract a set of features that can be used to characterize the input data. The function $x_n(t)$, which defines the resistance of the sensor at time t, is normalized over the time interval $L = (t_1, t_2)$ during which the polymer is in contact with the gas; the result is a function $x'_n(t) = (x_n(t)/x_m - 1)$, where x_m represents the minimum value of $x_n(t)$ in the time interval L.

For each experiment, the behaviour of the normalized function $x'_n(t)$ is studied to extract a number of statistical parameters (features) and to obtain a characteristic fingerprint for each aroma.

The features selected are the following:

- $E = \sum_{i \in L} x'_n(t)^2$, energy
- $t_{\max}$, abscissa of the maximum value x_n
- S_c, angular coefficient of the line connecting $x'_n(t_1)$ and $x'_n(t_{\max})$
- D_c, angular coefficient of the line connecting $x'_n(t_{\max})$ and $x'_n(t_2)$
- N_z, number of zeros of the second derivative of $x'_n(t)$ with respect to t.

The set of features represents the output of the sensor array to the stimulus of a particular sample and is used as input to the SOM units composing the first module of the hierarchical neural network in such a way that each SOM is devoted to the preclassification of just one specific feature.

Table 3. Results of aromatic component recognition at the different time intervals.

Aroma	Success percentage interval = 90 s	Success percentage interval = 202.5 s
1	85.7	80.5
2	60.0	74.1
3	80.7	79.2
4	86.5	40.0
5	100	100
Average	82.2	79.3

Training is preceded by an *initialization* subphase obtained by inputting each SOM with a subset of values randomly selected from the features.

Subsequently, the SOMs generate a set of outputs that are the input to the second module of the network (i.e. the EBP).

Each of the SOMs is composed of 16 neurons, disposed in a 4×4 grid. The EBP-based module has no hidden layer and a number of outputs equal to the number of odours to be recognized (in our case five, see table 2). The format of the input to the EBP is a five-dimensional array containing, for each odour to be analysed, the five features preclassified by the SOM module. Each input array is sent to all 25 neurons comprising the input layer of the EBP module.

Once the training process is completed, the network is ready for odour recognition. It can then be evaluated for its accuracy, which is assessed by presenting input samples (belonging to known classes) to the net and then comparing the output classification obtained with the expected result. Because of SOM characteristics, the disposition of the nodes and the topological order can be checked after the preclassification.

Sensors were exposed to samples for 31.5 s, then they were allowed to recover initial conditions for 441 s. Only part of the sensor response was used for feature extraction, namely the whole exposure time and the initial 90 (or 202.5) s of the desorption phase. Results are shown in table 3.

The analysis of the topological maps resulting from the SOMs shows the existence of overlapping zones causing aromatic components 1 and 4 and 2 and 3 to be occasionally mistaken for one another. Grouping these aromas together gives a remarkable increase in correct recognitions, as shown in table 4. The chemical structure of the compounds suggests a possible explanation for this fact. Aromas 2, 3 and 5 belong to the same chemical class (alcohols) and their structures differ only in the number of CH_2 groups (table 2). In particular, 1-pentanol and 1-hexanol are very similar, while ethanol has a shorter chain. Since the hydroxyl group of the odorant molecule is largely responsible for interaction with the sensitive layer, and to a lesser extent its chain length, these results are coherent. Similar considerations apply for components 1 and 4. Chemical similarity is less evident, but in both cases the interaction with the sensitive material occurs at the same carbonyl group C=O and molecules only differ by one carbon atom.

Even if it there is not an unambiguous correlation between a single compound and an organoleptic attribute (many

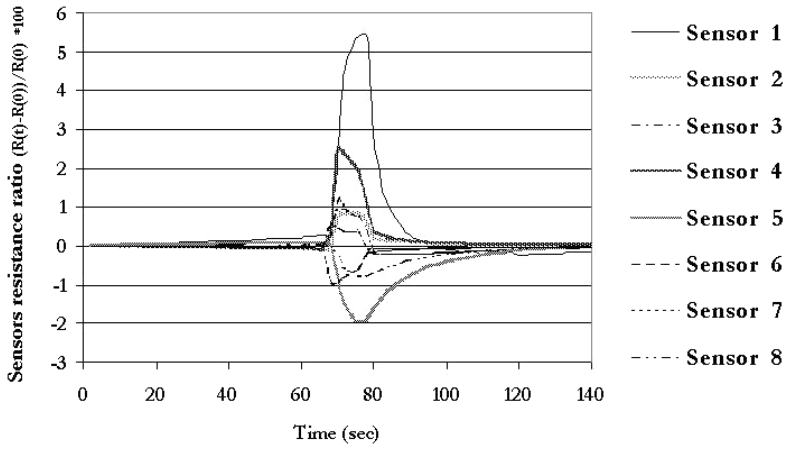

Figure 6. A typical response of the array of sensors.

Table 4. Results of grouped aroma recognition at 90 s time interval.

Grouped aromas	Success percentage interval = 90 s
1 and 4	91.2
2 and 3	95.6
5	100
Average	94.8

Table 5. Comparison of the results obtained using the MLP, LVQ and HNN networks.

Network	Average performance on five different aromas interval = 90 s	Average performance on grouped aromas interval = 90 s
MLP	48.9	61.2
LVQ	62.0	84.2
HNN	82.2	94.8

compounds are usually involved, the reciprocal concentration is important; there is no unanimous agreement in the literature on these points), it may be stated that odours 1 and 4 contribute to giving fruity and sweet characteristics to olive oils, while odours 2 and 3 contribute a pungent flavour. In this last case, the distinction between organoleptic quality and defect is subtler and highly dependent on the concentration. The high recognition rate of ethanol is particularly promising, since this compound is the main interferer in the headspace. More precise considerations will be possible after the system has been tested on olive oil samples.

The success rate of the implemented network has been assessed by comparing our results with the results obtained by means of the most frequently used pattern recognition methods adopted by electronic nose researchers [13, 14]. In particular, we used both a learning vector quantization (LVQ) and a multilayer perceptron (MLP) network on the same training and test sets of our experiments. The best performance of the LVQ network was obtained using an architecture composed of a first layer of 15 competitive neurons (corresponding to the number of measurements for each series) and a second layer of five linear neurons (corresponding to the number of different aromas); while the best MLP network was composed of three layers with 30, 15 and five perceptron neurons, respectively. As shown in table 5, the HNN approach gives better results both in the case of the recognition of a single component and the case of grouped aromas with chemical similarity.

The LVQ network required longer training and still gave a lower performance than HNN; the requirement that the number of competitive neurons be fixed *a priori* requires the whole network to be reconstructed if features need to be changed or added.

4. Conclusions

An olive oil aroma recognition system using hierarchical neural networks is presented. In particular, a SOM-based module was used for its ability to utilize typical characteristics of input data to create a topological order over the input stimulus space in an automated manner.

This latter feature proved to be effective in investigating aroma–sensor interaction mechanisms and, in particular, in grouping different aromas into categories which are in accordance with the chemical structure of the compounds. For this task, the recognition system achieved a high performance. The agreement between the chemistry of the molecules and the results of the data analysis is also promising for applications to olive oil sample analysis.

It seems that our algorithm has been satisfactorily trained with a limited number of measurements. This is important because the availability of large data sets is usually a key issue when dealing with neural networks, but problems due to sensor drift arise in the time required to obtain large data sets. The use of both recognition algorithms that need limited data sets to be trained and dynamic measurement databases, periodically updated by the addition of new calibration measurements and the removal of the oldest, is in the authors' opinion the most promising approach to tackle the drift problem of electronic noses. Further experiments will enable us to verify to what extent a higher selectivity can be obtained by increasing the number of measurements before drift effects become so important as to cancel the improvements in the recognition percentages.

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