ANEXO A

Congresos

Contribuciones

"Fast detection of rancidity in potato crisps using e-noses based on MS or gas sensors", The 10th International symposium on olfaction and electronic nose (ISOEN'03), Riga, Latvia, pp: 105 -108, (2003).

Fast detection of rancidity in potato crisps using e-noses based on MS or gas sensors

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Abstract
We show that it is possible to reliably assess rancidity in potato crisps by either an MS or a gas sensor based electronic nose. The two approaches are presented and their performance compared in the framework of this application.

1. Introduction
In the last years, consumers show a growing concern about quality and safety of food and foodstuffs. The food industry needs the development of equipment and techniques to trace the quality of raw materials and finished products not only in the production plant, but also during storage and vending. A very important aspect for the potato crisps producers is the detection of rancidity and shelf-life estimation. During the process of deep-frying, vegetable fat oil is under temperature stress. This can induce degradation and oxidation processes that generate a wide range of products (aldehyde, ketones, acid, lactones, etc) that generally have unpleasant odor and may conduce to rancidity. Monitoring flavors and off-flavors during various processing steps should be conducted to ensure the processes are operating correctly. Finished products should also be monitored to ensure that no off-flavors have developed. Exposure to light, heat, pro-oxidant metals, or oxygen can degrade unsaturated fatty acids in fat triglycerides and produce hexanal and other adehydes.
Nowadays, there is not a reliable, easy to use and fast method to determine rancidity in potato crisps. The most well established methods for the evaluation of rancidity are:

- -Evaluation of samples by a trained panel of experts. This is a slow and expensive method. Furthermore, expert’s opinion is always somewhat subjective.
- -Chemistry-based methods that can quantify the products resulting from fat and oil spoilage like the peroxide value. Other methods are based on IR and UV band absorption of some products formed by oxidation like hexanal, pentanal and pentane. An alternative test is to quantify by HPLC the products responsible for rancidity. All these methods require the use of reagents and do not work on-line.
- -One of the most used method in quality control laboratories is the Rancimat test. This method is based on the increase of the electrical conductivity of oil during its oxidation in an air flow of 20 l/h at 120 °C. When oxidation is induced, a sharp change in the conductivity is observed (results are expressed in hours to induce oxidation). In the specific case of potato crisps this method needs to previously extract oil from the crisps. This is again a time-consuming process that cannot provide on-line results.

In this context, the use of e-nose technologies would be of help to develop faster and simpler techniques to assess rancidity from the off-odours of potato crisps.
In this work we report on the design and use of two different electronic noses (one based on a mass spectrometer and the other on an array of semiconductor gas sensors) to assess rancidity in potato crisps. In the next section, details on the e-noses, sample preparation and measurements run are given. Section 3 shows and discusses the results and the usefulness of the methods for the application considered.

2. Experimental

Crisp samples

Four boxes (labelled *A*, *B*, *C* and *D*) with twelve 200g packs each of potato crisps were prepared by Frit Ravich, S.L.. These crisps belonged to the same frying batch but they undergo different rancidity accelerating treatments:

- Crisps in box *A* were stored in a dry and dark conservation chamber, where their temperature was kept around 20°C.
- Crisps in box *B*, *C* and *D* were kept during 6, 12 and 18 days, respectively in a rancidity accelerating chamber. The chamber was kept at high temperature (around 40°C) and UV light was used to promote oxidation.

After sample preparation, crisps *A* were not oxidised and crisps *B*, *C* and *D* had increasing rancidity levels, as revealed by a Rancimat test (Rancimat time for the different samples (in hours) *A*: 5.36 h; *B*: 2.63 h; *C*: 1.61 h; *D*: 0.01 h). During the analysis with e-nose, all the boxes were kept in darkness and under controlled atmosphere.

GC/MS profiles

The system used to obtain chromatographic profiles of the crips consisted of a Shimadzu QP 5000 GC/MS. Crisps were crushed and 4±0.2 g were inserted in 20 ml vials. The vials to be measured were placed inside a thermostatic bath (50ºC) to promote volatile to headspace. SPME was performed by introducing fibre into the vial and exposed to the headspace of the crisps for 20 minutes. The sample adsorbed on the SPME fibre was then introduced into the injection port and thermally desorbed for 5 min at 250ºC onto an Equity-5 poly (5%diphenyl/95% dimethylsiloxane) (30m x 0.25mm x 0.25μm) capillary column purchased from Supelco. The injector port was equipped with a 0.75-mm i.d. liner to optimize SPME desorption and sample delivery onto the column. The GC oven was held at 45ºC during 1.5 min, after the oven was programmed to increase its temperature to a final value of 250ºC at a 6ºC/min rate, and helium 1.2 mL/min column flow was the carrier gas. Mass spectrometry analysis was carried out using a Shimadzu mass detector, he operated in the electron impact ionization mode (70 eV) with a scan range of 35 to 290 amu. The ion source temperature was kept at 250ºC.

MS-based electronic nose

This method allows the direct analysis of the components in the headspace of a sample without chromatographic separation, and the resulting mass spectra gives a fingerprint specific to each aroma. Marsili and co-workers have demonstrated the capacity of SPME (Solid Phase Microextraction)-MS (Mass spectrometry)-MVA (Multivariate Analysis) as an e-nose system. The separation column was replaced by a 5 m deactivated fused silica column to co-elute all volatile components achieving one single signal for all the components in the headspace of the crisps. The column was kept isothermal at 250ºC and the helium flow was set to 1.4 ml/min. The samples were prepared and adsorbed onto the SPME (75-μm Carboxen/PDMS) fibre as described above. Thermal desorption of the analytes trapped on the fibre was conducted for 3 minutes in the cromatograph injector port at 300ºC. The split valve was closed during this time. The quadrupole mass spectrometer acquired in scan mode, the mass range used was m/z 35 to m/z 390 at 0.5 scan/sec. The fibre remains 5 minutes more in the injector port to ensure all the fibre is cleaned.

Metal oxide sensors based electronic nose

An electronic nose system based on 12 commercially available gas sensors (TGS-type) and a dynamic headspace sampling system to collect volatiles from the samples. The system consists in two heating vessels with temperature control, one sensor chamber, four electrovalves, a flow meter and one pump. Each measurement with the systems implies three different phases to be completed. These are sample concentration, measurement and cleaning. 60±1 g of chips were weighed and placed on an aluminium tray, then the tray was inserted in heater vessel 1 (sample vessel). The concentration phase lasted for 30 minutes. During this phase the headspace from the crisps is concentrated in vessel 1, while a continuous flow of clean air passes trough the heating vessel no. 2 (reference vessel) and the sensor chamber. During the measurement phase (10 minutes) air from the sample unit is circulated to the sensor chamber and the resistance of the sensors is monitored. Finally all the system is cleaned with air before a new measurement is performed. The use of sample and reference vessels is to make sure that the sensor response is only due to the headspace of the crisps.

3. Results and discussion

Typical results of the GC/MS analysis are shown in figure 1 where the differences in the chromatographic profiles between rancid (class D) and fresh (class A) are revealed.

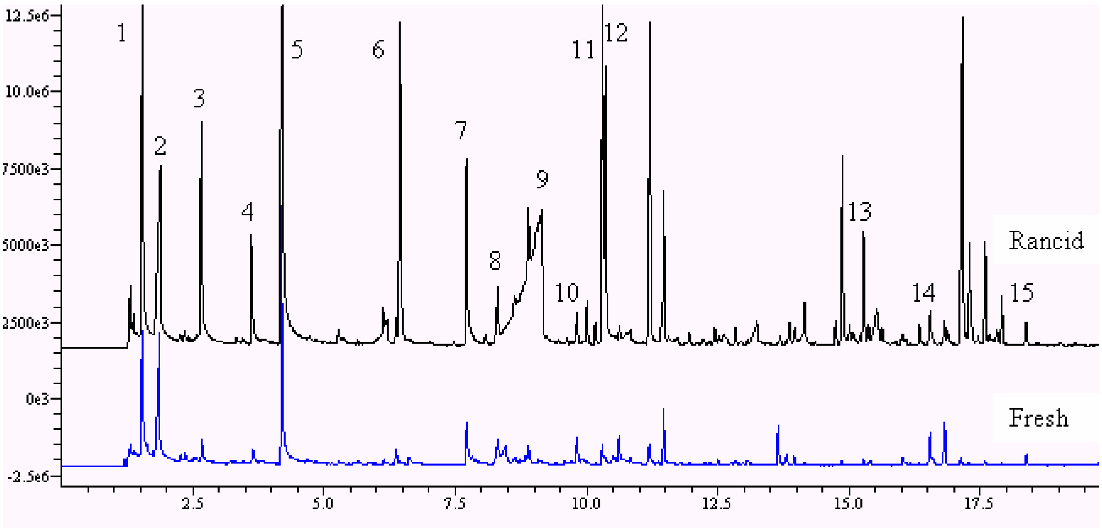

Fig. 1. Chromatographic profiles identified by GC/MS 1: Acetone, 2: Acetic acid, 3: Pentanal, 4: Pentanol, 5: Hexanal, 6: Hepatnal, 7: 2-Heptenal, 8: 1-octen-2-ol, 9: Hexanoic acid, 10: 3-octen-2-one, 11:2-octenal, 12: 2,3-octanedione, 13: 2-decenal, 14: 2,4-decadienal, 15:Undecane.

The content of each potato pack was split to perform consistent measurements with the MS-based e-nose and the gas sensor based e-nose. The mass spectra were acquired by averaging mass intensity along the detected peak (just a single peak since there was no separation column). A mass intensity table was obtained for every sample measured. For the gas sensor based e-nose, the resistance of the 12 sensing elements was monitored and the sensor conductance change was the parameter used for further processing. With the sensor-based e-nose, calibration measurements (non-rancid crisps from a different brand) were performed to ensure that the differences observed were not due to sensor drift. Either with the MS or the gas sensor based e-noses, a measurement took 35 minutes to complete.

Figure 2 shows the results of a linear discriminant analysis (LDA) performed with the data from the two different e-noses. The data were mean-centred prior to perform the analysis. The first 2 discriminant factors accounted for more than 99% of variance in the data. From figure 2, it can be derived that both instruments can easily separate the fresh crisps (*A*) from those that have undergo rancidity-promoting processes (*B*, *C* and *D*). A slightly better separation between classes *B*, *C* and *D* is visible for the MS-based e-nose.

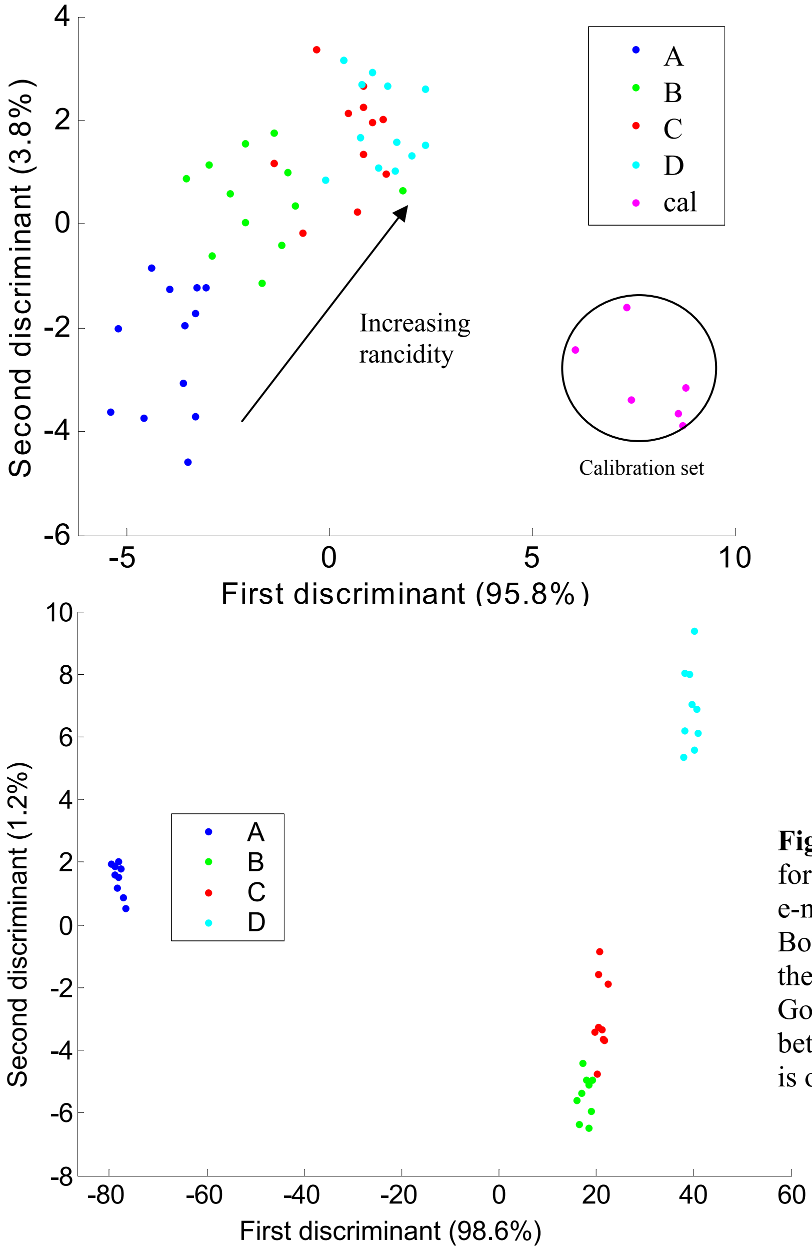

Fig.2. Top: DFA results for the gas-sensor based e-nose.
Bottom: DFA results for the MS-based e-nose.
Good separation between fresh crisps (A) is obtained.

A fuzzy ARTMAP neural network was used to classify the samples within the four categories of rancidity (*A* to *D*). A leave one out cross-validation method was implemented to estimate the success rate in classification reached by the two different e-noses. On the first step a two-category classification was attempted. Class 1 was for fresh potato crisps (*A*) and class 2 was for rancid potato crisps (*B*, *C* and *D*). Both e-noses were able to separate the two classes with a 100% success rate. On the second step, a 4-class category classification was attempted. This classification aimed at identifying rancidity in a semi-quantitative way. While with the MS based e-nose, a 100% success rate in this classification task was reached, with the gas sensor based e-nose, success rate fell to 56%.
We have shown that e-nose technology can provide a simple and fast method (compared to traditional techniques) to detect rancidity in potato crisps. In particular, the MS-based e-nose is suitable for a semi-quantitative analysis of rancidity in the application discussed here.

"Concatenation of a Fuzzy ARTMAP Neural Network to Different Variable Selection Techniques to Enhance E-Nose Performance", The 11th International symposium on olfaction and electronic nose (ISOEN'05), Barcelona, (España), (2005).

Concatenation of a Fuzzy ARTMAP Neural Network to Different Variable Selection Techniques to Enhance E-Nose Performance

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Abstract

This work compares the coupling of different variable selection techniques to a Fuzzy ARTMAP neural network in order to enhance Electronic Nose performance. Based on a matrix of metal oxide gas sensors (TGS and FIS), we designed an instrument to identify and classify different fungi species (from *Eurotium, Aspergillus*, and *penecillium* genres) that contaminate industrial bakery products. In this paper we present the classification results obtained for 7 fungal species using Fuzzy Artmap paradigms coupled to DFA, PCA, Genetic, Forward selection and intra-inter variance variable selection algorithms. Results show a boost in performance from a 43% (when no variable selection techniques are used) to a 75% using the combination of DFA and Fuzzy ARTMAP.

1. Introduction

Many microbial problems in bakery products are produced by fungal infections. The growth of these micro-organisms during storage are especially important in three different genres: *Eurotium*, *Aspergillus* and *Penicillium*. Microbial spoilage is a problem since it can induce nutritional losses, off-flavors and formation of mycotoxins or potentially allergenic spores. Therefore, besides being an economic problem, unwanted fungal growth can cause some serious health hazards that have to be monitored carefully. Nowadays researchers look for a method to conveniently assess the degree of fungal growth in bakery products at a very early stage and well in advance to becoming visible [1, 2, 3]. The electronic nose (EN) promises to be one alternative for this case.

In these systems sensor noise and drift are well known problems that interfere in the results that can be obtained. For that reason, it is very important to choose those variables (parameters and/or sensors) that contain the most useful and relevant information to the classification problem envisaged. It is even more important to eliminate those variables with noisy or meaningless information that generate erroneous answer [4]. There are several variable selection techniques that can improve the performance of an EN. Moreover, in the analysis of data sets with a large number of descriptors (variables) for each measurement, a frequent aim is to reduce the dimensionality of the data set preserving meaningful information and discarding noisy descriptors.

The goal of this paper is to improve the response of an EN, enhancing the performance in the classification of seven fungal species. To do so, we have coupled different variable selection algorithms to pattern recognition methods.

2. Variable selection techniques

A traditional way to reduce dimensionality is through Principal Component Analysis (PCA). PCA is a method that uses principal components based on the variance of each original parameter. The may be used to extract the most relevant information from the entire data set. A sensor that has loading values near zero for the retained principal components contributes little to the overall model and can be eliminated. If two sensors have similar loadings they are highly collinear and one can be removed. However, PCA is a linear method that does not work very well in non-linear conditions [5].

Another classical method is Discriminant Function Analysis (DFA), which is used to discriminate a set of measurements using the coefficients of the canonical variables. Like in PCA, the loadings (eigenvectors) are used to determine whether there are irrelevant or redundant sensors than can be removed. The main difference to PCA is that DFA is a supervised method that determines the variables to choose from the results expected in a training stage.

GAs (Genetic Algorithms) are optimization methods inspired on natural evolution. They have been shown as a successful method when selecting variables [6]. When this algorithm is applied for variable selection, a population of *n* subsets or chromosomes is created, each containing a random combination of variables. Chromosomes are binary strings where the occurrence of a bit equal to 1 (or 0) in position *i*-th implies that variable *i*-th is present (or absent). A cost function for each subset is then evaluated in turn and, using techniques loosely based on biological genetics and evolution, a new population is created. During the variable selection process, the cost function being optimized by the GA is, for example, the prediction error of a fuzzy ARTMAP based classifier [7-12]. In comparison to many other search techniques, GA's are not constrained by initial assumptions about the search space such as continuity and smoothness and, therefore, apply generally.

Another variable reduction method is through a ranking according to a figure of merit. The best option in this approach is to define a relationship between the average variance between measurements of the same category (internal variance, related to the repetitivity of the variable) and the average distance between centroids of different categories (external variance, related to the selectivity of the variable). The criterion is defined to select an optimal subset of parameters, i.e., those showing a small internal variance combined with a high external variance [13]. This translates into selecting those variables with the highest discrimination power in the categorization problem under study.

Heuristic algorithms such as forward selection are widely used in linear regression [14]. Forward selection is quite simple and fast. Its main approach is to choose one variable at each iteration. Once the variable that gives the best prediction is selected, the process starts again trying to find the second variable that, with the first one, gives the best prediction ability to the system. The process ends when the prediction error increases adding any of the remaining variables.

3. Experimental

For the development of the EN we used an array of 12 metal oxide sensors (SP series from FIS and 8-series from Figaro). A methacrylate chamber was designed to house these sensors. Table 1 describes each sensor used and its target vapours and figure 1 shows a picture of the EN designed.

Table 1. Sensors array description

Sensor	**Target vapours**
TGS 800	Air contaminants
TGS 813	Combustible gas
TGS 822	Alcohol, toluene, *o*-xylene, etc
TGS 825	Hydrogen sulphide
TGS 826	Ammonia
TGS 831	R-21-R-22
TGS 832	R-134a, R-22
TGS 842	Methane, butane, propane
TGS 880	Volatile species from food
TGS 882	Alcohol vapours from food
FIS SP-31-00	Organic solvents
FIS SP-32-00	Alcohol

A HeadSpace AutoSampler (Hewlett Packard model 7694) was used to deliver the sample to the sensor chamber, so that a good reproducibility could be obtained. All sensor responses were acquired using a PCI-NI6023E data acquisition card. The control of the hardware, sampling equipment, data acquisition and signal processing was executed by a written-in-house software under the Matlab 6.5 environment, through the use of a GUI. This software allowed to monitor sensor output in real time and to obtain processed results very fast. The PARC algorithms used were PCA, DFA and the fuzzy ARTMAP neural network.

Figure 1. Electronic Nose designed

After ten days of incubation, a total of 19 vials (20 ml volume) were prepared. 14 contained 2 replicates of 7 fungal species and 2 contained empty cultivation mids. Finally, 3 vials of ethanol were used for sensor calibration. Table 2 describes the different samples used and the number of replicates. It also classifies each specie with its genre according to the different background color. The acquisition time for each sample was 10 minutes. For sample delivery, the following parameters in the sampling system were introduced: oven temperature between 70^{o}C-80^{o}C, 50 min vial heating time, 1 min vial pressurisation time, 1 min of loop fill time, 0.05 min of loop equilibration time, and 10 minutes of injection time. The carrier gas was regulated at a flow rate of 50 ml/min.

Table 2. Fungal Species measured

Genre/specie	Replicates
Eurotium Repens	2
Eurotium Herbariorum	2
Eurotium Amstelodami	2
Eurotium Rubrum	2
Aspergillus flavus	2
Aspergillus Niger	2
Penicillium Corylophilum	2

4. Results and discussion

As mentioned earlier, measured data was processed coupling Fuzzy ARTMAP neural networks to different variable selection algorithms. In all cases, a leave-one-out approach was used to estimate the performance of the network in the classification of fungi species.

This iterative validation approach generates N evaluation procedures (1 for each measurement). For each iteration, a different measurement is left out, while the remaining ones are used to build the model (PCA, DFA, etc) and train the network. The remaining measurement (the one not used for training) is then projected onto the model and classified using the already trained network. This is repeated N times (one for each measurement) so that the final result is the average success of entire iterative process (Figure.2).

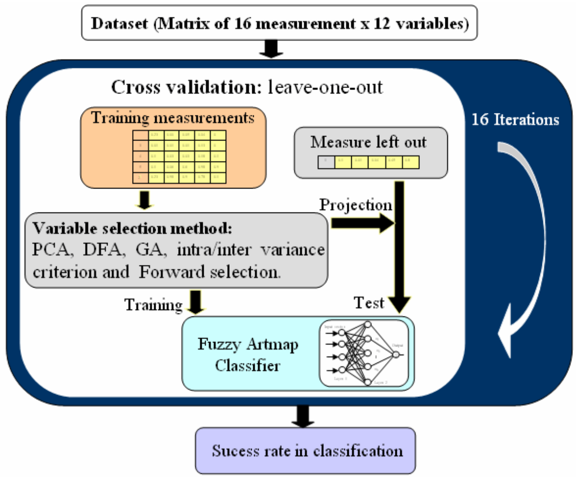

Figure 2. Block diagram of the validation approach

4.1. Fuzzy ARTMAP classifier

First, in order to compare the results, a fuzzy ARTMAP neural network was used to classify the samples from 7 fungi species using all the sensors (12 variables). The classification success rate into seven categories reached a 43 % using the leave-one-out approach. Once this classification rate was obtained, the goal was to couple different variable selection techniques to the fuzzy ARTMAP paradigm to see whether this approach improved these results.

4.2. Using DFA as a variable selection technique

For each iteration, a DFA model was built with the training measurements. Then, the coordinates of the training samples in the DFA projection were used to train a Fuzzy ARTMAP neural network. The evaluation measurement was projected onto the DFA model and its coordinates fed to the neural network. Eigenvectors were used to classify samples. A 75% success rate was achieved using only 2 eigenvectors. These results were expected due to the clusters of fungal genres and species that the DFA graphic shows in figures 3 and 4. It is important to note that when using a leave-one-out cross-validation method, the over-fitting risk is eliminated since the evaluation measurement has not been used to build the DFA model.

DFA can be used in supervised and in unsupervised mode. In unsupervised mode it can give interesting information about the clustering of the dataset. Anyway, for serious benchmarking, a supervised mode has to be used where the training measurements should be different from the test data set, which is the way we have performed our leave-one-out approach.

4.3. PCA used as a variable selection method coupled to fuzzy ARTMAP

In each iteration, a PCA model was calculated with the training measurements and the scores were fed to a fuzzy ARTMAP for training purposes; then, with the PCs calculated and the weights from the Fuzzy ARTMAP, the validation measurement was projected and evaluated. Results with different number of principal components were tested. The best results were achieved with just 2 PC's, where a classification rate of 63 % was achieved.

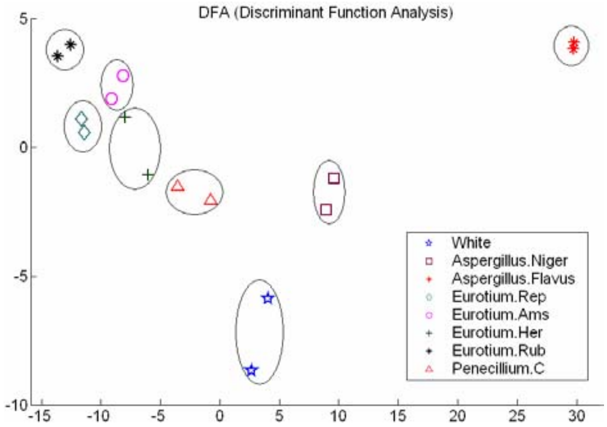

Figure 3. DFA clustering of fungal species.

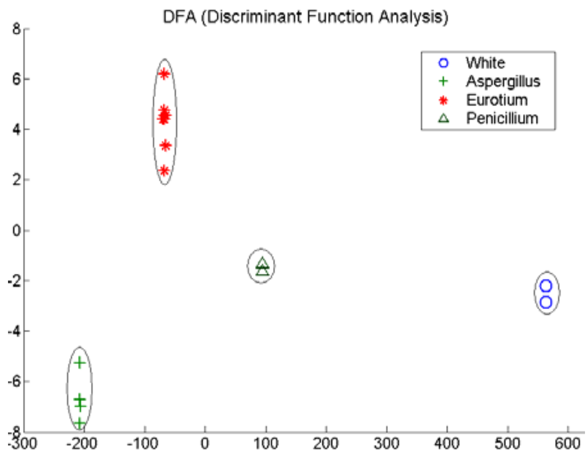

Figure 4. DFA clustering of fungal genres.

4.4. Results coupling Genetic Algorithms and fuzzy ARTMAP:

A genetic algorithm coupled to the fuzzy ARTMAP classifier selected 5 out of 12 variables. The fitness was evaluated as the PER (Predictor Error Rate) and the cross-validation of order one (leave-one-out) with 16 measurements was applied. The PER was 0.3556 and the algorithm converged after 33 generations. The success rate was 63 %.

4.5. Variable selection using the intra/inter variance criterion

A variance criterion was defined in order to reduce the number of variables. Equation 1 shows this criterion, which somehow measures the resolution power of each variable related to the differentiation between the 7 fungal species. A higher value for Vr means a better discrimination capability for a given variable.

Fuzzy ARTMAP was applied to evaluate the variable subset selected. The best results where obtained when selecting the 7 variables with the highest *Vr*. The success rate peaked at 63 %.

$$Vr = \frac{External Variance}{Internal Variance} \quad (1)$$

4.6. Forward selection

The forward selection algorithm used in linear regression was applied in our case to select a subset of the 12 original variables. In the end, only 2 variables were selected. Using these variables, the success rate achieved was 70 %.

Table 3 summarises the results obtained, comparing the coupling of different variable selection techniques to a fuzzy ARTMAP classifier. We can observe that applying any of the variable selection methods leads to better results than using the Fuzzy ARTMAP alone.

As it can be seen, the best results are achieved coupling Fuzzy Artmap algorithms with DFA, 75% of success rate when classifying samples in 8 categories (seven fungi species and a control vial without fungal contamination). Anyhow, it is interesting to note the performance of the forward selection method (70%), since it gives very good results and the variables selected come from the original sensor array, giving a straightforward interpretation (sensor selection) that can be used to reduce the sensor array for a given application. That is why this method should be studied in greater detail for each application sought for an electronic nose.

Table 3. Results and number of variables selected.

Method	Results	Variables selected
Fuzzy ARTMAP alone	43%	12
DFA+ Fuzzy ARTMAP	**75%**	**2**
PCA+ Fuzzy ARTMAP	63%	2
GA+ Fuzzy ARTMAP	63%	5
Variance + Fuzzy ARTMAP	63%	7
Forward + Fuzzy ARTMAP	70%	2

5. Conclusions

The results of this paper demonstrate that coupling variable selection techniques (e.g., GA, DFA, PCA and heuristic algorithms) to a Fuzzy ARTMAP neuronal network can improve significantly the performance of an EN classifier system for fungi detection and identification. Best results were obtained coupling DFA to a Fuzzy ARTMAP neural network using only 2 variables (factors) instead of 12.

The manufacture of electronic noses equipped with variables selection algorithms could increase the industrial interest of these instruments in food applications.

Acknowledgements

Work funded by INIA. Project CAL01 - 037- C3 – 1.

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"Enhancing sensor selectivity via flow modulation", IEEE Sensors, California, EEUU, October, (2005).

Enhancing sensor selectivity via flow modulation

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Summary

In the last ten years, considerable efforts have been made to use sensor dynamics as a source of multivariate information leading to an enhancement in the discriminating ability of poorly-selective metal oxide gas sensor arrays. Many authors have reported on strategies based on modulating either the sensors' operating temperatures or the analytes' concentration. Here we introduce and demonstrate, for the first time, a simple method that, combining simultaneously both effects, has the potential of increasing the resolving power of metal oxide sensors. Furthermore, its simplicity makes it especially suited for low-cost applications. Small-sized, hand-held gas analyzers and e-noses (i.e., the so-called sniffers) use simple sample-delivery systems based on pumps (e.g. peristaltic) rather than mass-flow controllers. The new method presented here consists of applying a modulated control signal to the peristaltic pump of a sniffer, which results in the gas flow being modulated. The effect of this flow modulation is twofold: First, the concentration of analytes at the surface of sensors is modulated and second, fast periodical flow changes result in periodical cooling and heating of sensors' surface. Therefore, specific response patterns, which are characteristic of the analytes present, develop. The method can be easily adapted to both static and dynamic headspace sampling strategies. Here we show that it is possible to easily discriminate among methanol, toluene and o-xylene (all reducing species) in a broad concentration range, using a single sensor.

Motivation

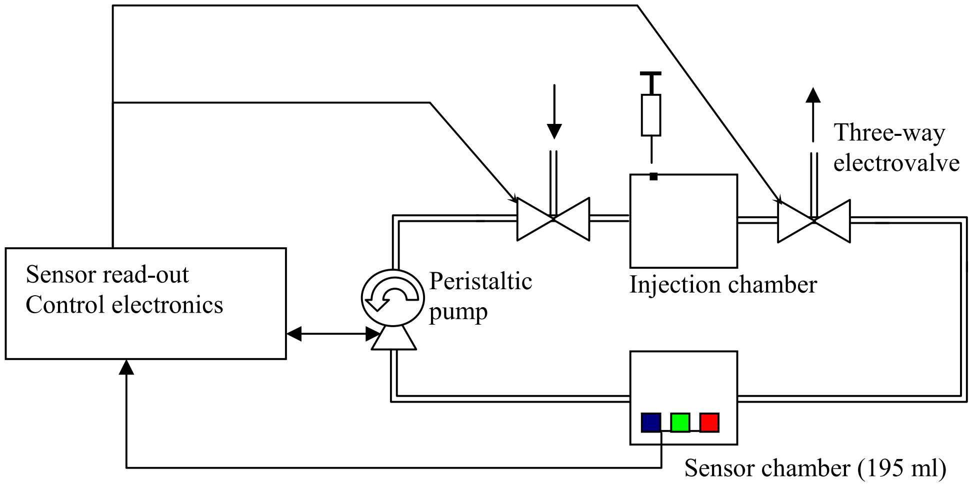
Hand-held 'sniffers' make use of simple sample delivery units based on pumps rather than mass-flow controllers. Because it is well known that sensor dynamics can be of help to increase the selectivity of metal oxide sensors[1], there is a need for developing uncomplicated methods to use transient information in such analyzers.

Results

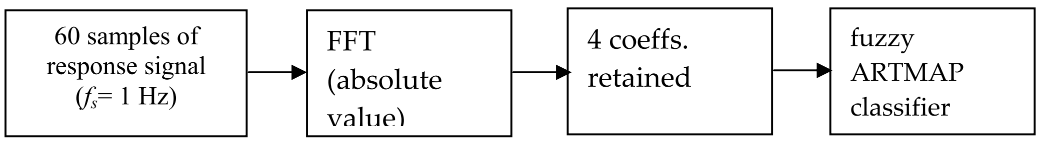
The sniffer consisted of three metal oxide gas sensors kept in a sensor chamber, two three-way electrovalves, a peristaltic pump and a sampling chamber: dynamic headspace sampling (see fig. 1). Different concentrations (ranging from 20 to 320 ppm) of methanol, toluene and *o*-xylene were measured. These concentrations were chosen for the static sensor responses to be similar, which prevented correct discrimination using the static sensor response only. The system was operated by applying a stepwise voltage to the pump, which resulted in a stepwise flow through sensor chamber (10 mHz). This resulted in a sensor response where dynamic patterns developed (see fig. 2). Sensor signals were standardized to eliminate offset and concentration effects and response features were extracted by performing a FFT. By keeping a few coefficients (up to 4) of the absolute value of the FFT, it was possible to discriminate among the different substances (100% success rate) using one sensor only (result reached with any of the sensors studied). The discrimination ability was assessed using a fuzzy ARTMAP classifier and the leave one out cross-validation method.

[1] A. Vergara, E. Llobet, J. Brezmes, X. Vilanova, et. al, IEEE Sensors 2004, Book of Abstracts.

Figures



a)



b)

Fig. 1: (a) Experimental set up for the flow-modulation experiment. Flow: 200 ml ± 100 ml @ 10 mHz (b) Block diagram of the feature extraction/ PARC method.

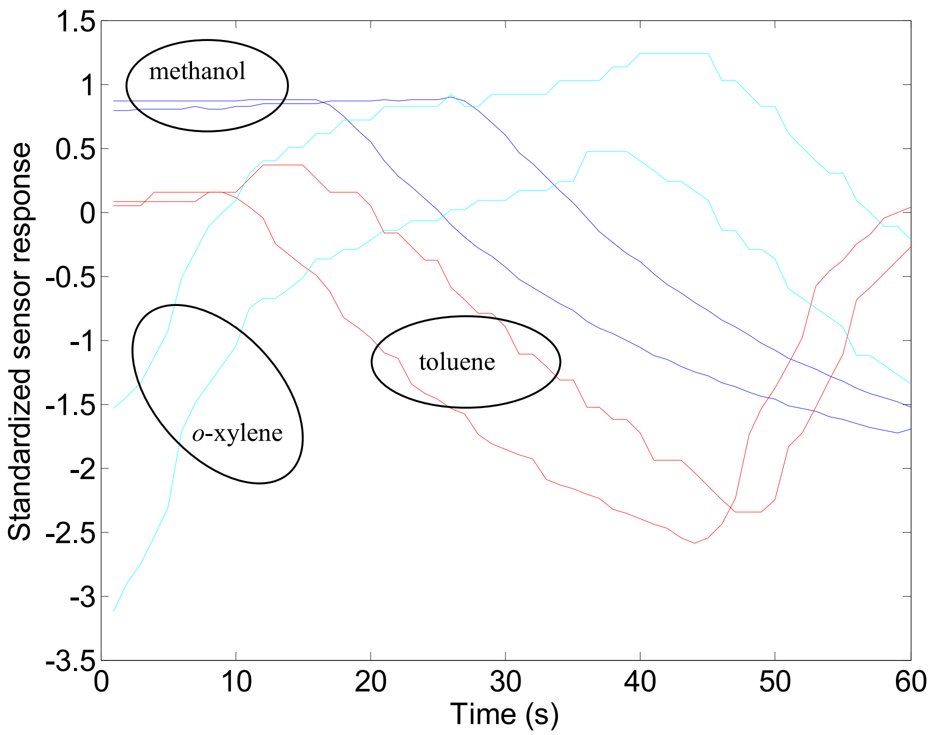


Fig. 2: Standardized sensor responses (TGS800) for methanol, toluene and *o*-xylene when flow modulation was applied. The two curves/species show the responses at lower and higher concentrations.

"Electronic Nose to Guarantee the Microbiological Quality of Bakery Product Manufacturing". Ph.D Students Meeting on Electron Devices and Microelectronics, Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, ETSE, Universitat Rovira i Virgili, (2003).

Electronic Nose To Guarantee The Microbiological Quality Of Bakery Product Manufacturing

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Abstract

This paper describes an Electronic Nose (EN) based on a Headspace Sampler and an array of gas sensors developed with the aim to guarantee the quality of products of industrial bakery. The experimental application for the EN is the identification and classification of different fungi species. The different species have been identified with processing algorithms, basically PCA, DFA and the Fuzzy Artmap Neuronal Network. This device consists of an array of chemical sensors (gas sensors), software developed in Matlab 6.1 and the associated hardware, which allows a fast data acquisition, and effective recognition of patterns. This system is easy to use and appropriate for applications in the food industry.

Keywords – Electronic Nose, Pattern recognition,fungi detection.

1. Introduction

An Electronic Nose (EN) is an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropiate pattern recognition system, capable of recognising simple or complex odours [1]. Gas sensors tend to have very broad sensibility, responding to many different substances.

Food companies can use the Electronic Nose as a quality control tool (e.g., to check raw materials, to check product deterioration during shelf life studies, to monitor product during transport to retailers, to ensure that packaging odors do not contaminate products, etc) and as a tool for process control (e.g., to monitor food odors during critical stages of production to ensure that optimum processing conditions are being maintained).

In recent years, the use of arrays of gas sensors in these devices for the detection and classification of odors has created the field of Electronic Noses (EN). The EN recognizes a global information (fingerprint) of the volatile compounds in contrast to classical techniques such as gas chromatography in which the single components are identified. They consist of a sampling system, electronic circuit, an array of sensors and data analysis (pattern recognition) software.

2. Experimental

For the development of the EN, an already made Electronic Nose at the laboratory was used with the goal to make preliminary tests with fungi and to evaluate the quality of responses of its Metal Oxide Sensors (MOS). The goal was to develop a more portable system, suitable to be used in nutritional product analysis, investigations and others applications.

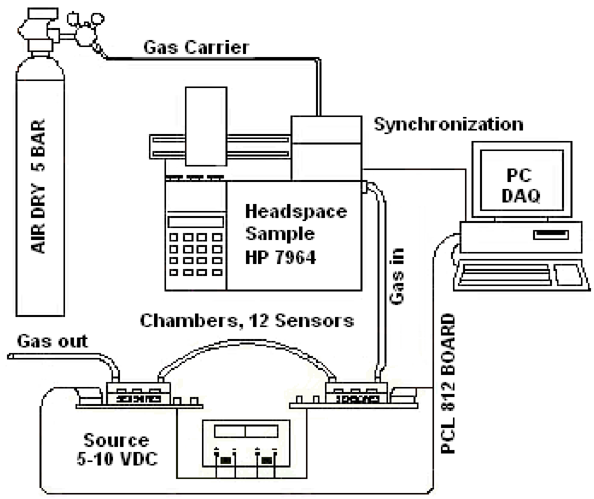

Fig.1. Scheme of the Electronic Nose developed in the Gas Sensor Lab (dynamic head space sampling).

The laboratory EN

The initial prototype of electronic nose consists of: (see scheme in Fig.1).

- Hewlett Packard 7694 Headspace Sampler. This device is useful to prepare the sample and has a high reproducibility [2]. It is made up of a movable deposit where the vials take the scent, an oven where the sample is pre-conditioned and a manual flow meter to regulate the carrier gas flow (synthetic air dry).

- Two chambers of methacrylate, containing 12 gas sensors (FIS SP and TGS Models), in 2 arrays of 6 sensors each one.
- Data acquisition board (PCL 812) Via PC.

Sample Preparation

It was done using the headspace sampler: The temperature of the Oven was 70°C-80°C, Vial heating time 50 min, Vial pressurization time 1 min, loop fill time 1 min, loop equilibration time 0.05 min, Injection time 10 min. The carrier gas was regulated at flow rate 25-50 ml/min.
In two test with the Headspace, a group of 27 and later 19 vials of 20 ml closed samples were filled with 7 fungi, 1 cultivation mid (substance to cultivate fungi) and ethanol (for the calibration of sensors). In the table.1 we can see the fungi species with the number of vials used by each specie.

#Fungi	Name	1st Round	2nd Round
1	Eurotium Repens	3	2
2	Aspergillius flavus	2	2
3	Eurotium Rubrum	3	2
4	Aspergillius Niger	3	2
5	Penicillium Corylophilum	3	2
6	Eurotium Herbariorum	3	2
7	Eurotium Amstelodani	3	2

Table1. Fungi groups for each round

Measurement and Data Aquisition

The third and fourth column contain the number of vials used in the two tests for each specie. In order to obtain a an appropriate number of measures a PC was used, with the DOS operating system and software written in house. The acquisition time for each sample was 10 minutes. In the first tests, a group of 20 vials with fungi, 4 vials ethanol and 3 vials of cultivation, the data aquisition was made with 12 sensors. A total of 27 measures were acquired, to check the operation of the system and especially the response of the sensors. The responses were highly sensitive in the presence of volatiles, but had a poor resolution. The second test was made with another group of 14 fungis, 3 ethanol and 2 vials of cultivation with the same number of sensors, 19 measures were acquired, the same sensitivity was obtained and the operation of the system was satisfying.
In Fig.2 the change of the sensor resistance Rs is observed, which is variable due to the presence of the odors emitted by fungi, and where Ro is the baseline reading, the reference gas being the ambient room air [1], [3]. The signals were obtained measuring Aspergillius Niger.

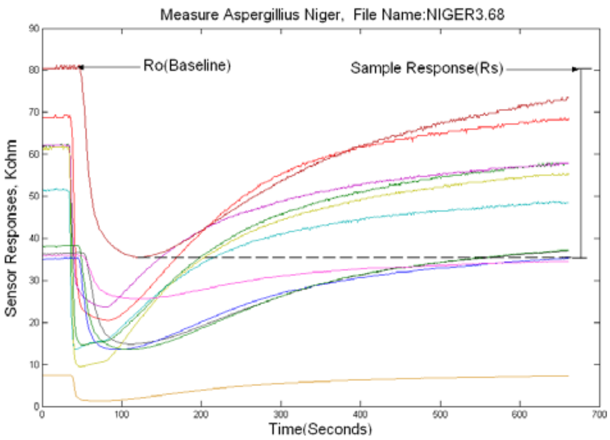

Fig.2. Gas sensor Response as a function of time.

Data pre-processing

A pre-processing algorithm written in Matlab 6.1. was used to extract features from the data in terms of the static change in sensor resistance. In order to optimise the performance of that specific type of odour sensor the parameter used in this case was:

$$x_{ij} = (y_{ij} - y_i) \qquad (1)$$

Where y_i or baseline signal is the steady-state response or the conductance (resistance inverse) of the sensors i in air, and y_{ij} is the conductance of the sensor i in the presence of odour j [3].

Data processing

The pattern recognition (PARC) applied two tecniques often used in applications with electronic noses, based on Multivariate analysis (PCA) and Neuronal networks (Fuzzy Artmap).

- ***Principal Component Analysis (PCA):*** Is an effective linear unsupervised method to project data from several sensors to a two-dimensional plane [4], [5], [6].

- ***Fuzzy Artmap:*** Algorithm of artificial intelligence with supervised learning [7], [8]. In the training phase the network needs a set of measures (array of data). Each measurement must contain a vector of inputs (Parameters measured in each experience) and a vector of output data that codifies categories that have to be assigned. In the evaluation phase the input vector is provided and the network classifies this measurement following the criteria that has learnt in the training phase.

3. Results

A set of Matlab 6.1 functions (toolbox) or algorithms has been developed and applied to analyze the data.

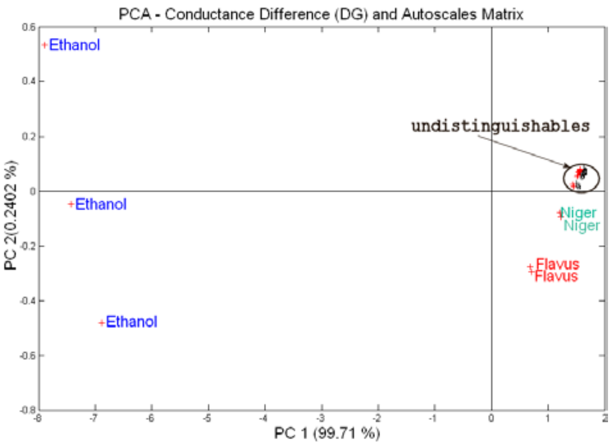

Fig.3. Result of the PCA of the gas sensor array for 19 gas samples.

The results were the following:

1) With PCA Analysis and previous pre-processing (Autoscales)**,** the obtained result can be seen in the Fig.3. The goal was to classify the 7 species of fungi corresponding to 19 measures; therefore the data was separated according to the variance captured by each PC (Principal Component). Most of the fungi could not be distinguished but 3 different kinds could be told apart; this verifies the performance of the EN in classifying between different kinds of organic components.

2) The Fuzzy Artmap verifies the previous result. This neural network was used to classify the samples of 9 species. A cross-validation technique called leave one out of order one, was implemented to estimate the success rate in classification The success rate was 9 with an average of 47.368 %.

4. Optimized EN

The following step was to design an electronic nose system using the experience obtained with the laboratory EN. The main components used to improve the system were: A board from National Instruments (6023E Model) [9], a chamber of methacrylate with an array of 12 gas sensors (The same as the laboratory's EN), an interface board (Electronic Control for Headspace sampler and the board data acquisition) Via PC, See Figs. 4 and 5. The processing and acquisition software was written in Matlab 6.1[10], having added Graphical User Interface (GUI).

Its compact design makes it more portable and facilitates the tests in the laboratory with less errors. It also improves the stability when dealing with the headspace sampler.

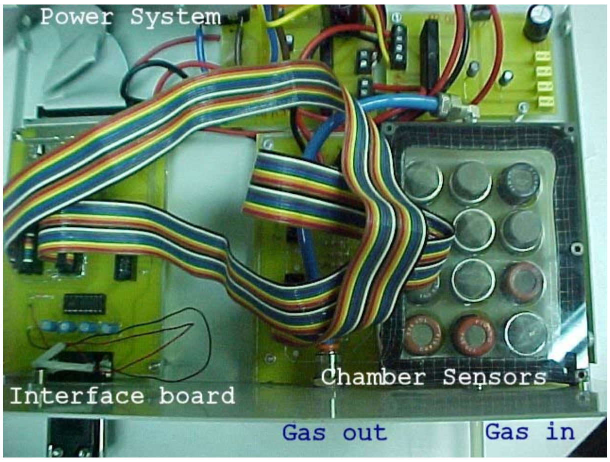

Fig.4. Photograph 1, components of the optimized Electronic Nose.

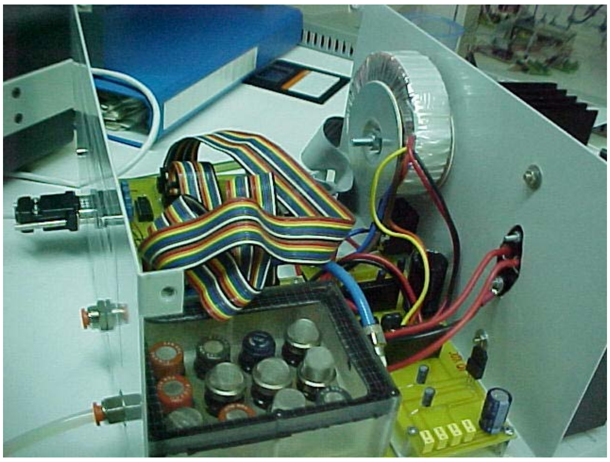

Fig.5. Photograph 2, components of the optimized Electronic Nose.

The Fig.6 shows the software developed with a group of windows or GUIs, that make the synchronization tasks with the headspace sampler, data acquisition and processing much simpler. In contrast to the previous EN system, the fast processing is a great advantage and allows a suitable and significant time gain.

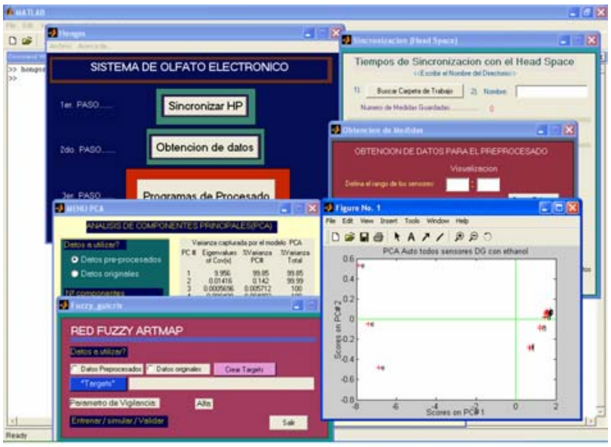

Fig.6. GUIs for data acquisition and processing.

Final tests

In order to evaluate the behavior of the new system, several tests with 9 vials (3 Ethanol, 3 Ammonia and 3 Acetone) were executed.
The GUIs of synchronization, pre-processing and PARC techniques were used to improve the system. The system operated suitably. Fig.7 shows the response with a PCA.

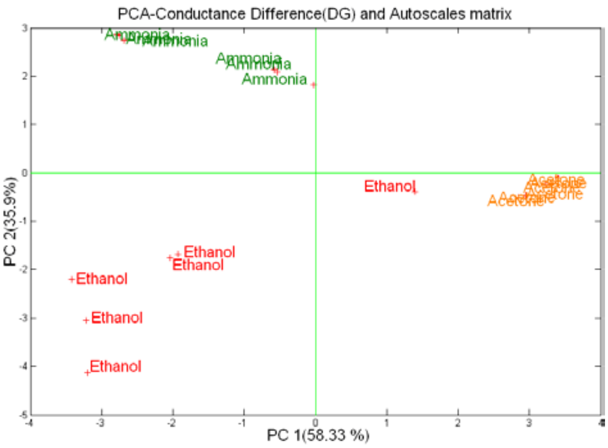

Fig.7. PCA plots drawn with 18 measures and 12 sensors.

A separation of contaminants could be observed but with one error with a measurement of ethanol, which lays very close to the cluster of acetone. The captured variance was a 95 % in the 2 first PC (Principal Components).
With the fuzzy Artmap and the cross-validation technique (leave one out) the results of the PCA, have been verified, with a success rate in classification of 94.4 %.

Fig.8. Photograh of the electronic nose system

5. Conclusions

In this paper we have presented an EN system designed to classify between different fungi species, as shown in Fig.8. With preliminary laboratory tests the gas sensors achieve broad sensitivity and selectivity, responding to each one of the samples, while the Matlab toolbox permits to make pre-processing and data analysis with PARC methods, PCA and Fuzzy Artmap. These results show that is possible to use the Electronic Nose for food quality analysis. By means of adequate selection of materials, conditions of operation and better PARC, better results are expected with a new version of this device.

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"Concatenation of a Fuzzy ARTMAP Neural Network to Different Variable Selection Techniques to Enhance E-Nose Performance", Nanoelectronics and photonics system Workshop, ETSE, Universitat Rovira I Virgili, (2004).

Concatenation of a Fuzzy Artmap neural network to different variable selection techniques to enhance E-nose performance

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Summary: *This work compares the coupling of different variable selection techniques to a Fuzzy Artmap neural network in order to enhance Electronic Nose performance. The study was applied to the classification of 7 fungal species, boosting classification performance from 43% to a 75% using the combination of DFA and Fuzzy Artmap.*

Keywords: *Electronic nose; Fuzzy Artmap; Variable selection.*

1 Introduction

Many microbial problems in bakery products are produced by fungal infections. The growth of these micro-organisms in bakery products during storage are specially important in three different genres: *Eurotium*, *Aspergillus* and *Penicillium,* [1].
The goal of this paper is to improve the performance of an electronic nose in the classification of seven fungal species coupling a Fuzzy Artmap neural network to different variable selection techniques [2, 3].

2 Experimental

2.1. Materials and methods

An application specific electronic nose was built using 12 metal oxide commercial gas sensors, (FIS SP-series and TGS 8-series). A Headspace Autosampler (Hewlett Packard 7694) was used to heat each vial and the volatiles emitted were driven to the sensor chamber.
Sensor responses were acquired through a PCI-NI6023E data-acquisition card via PC. The control of the hardware, sampling equipment and data acquisition was done using written-in-house software under Matlab 6.1. Pattern recognition was performed using Fuzzy Artmap coupled to different variable selection techniques based on PCA, DFA, Genetic Algorithms (GAs), Forward selection and intra/inter variance criteria.

Table 1. Fungal Species measured

Genres	Replicates
Eurotium Repens	2
Eurotium Herbariorum	2
Eurotium Amstelodami	2
Eurotium Rubrum	2
Aspergillus flavus	2
Aspergillus Niger	2
Penicillium Corylophilum	2

2.2. Sample preparation

A total of 19 vials (20 ml) were prepared. 14 contained 2 replicates of 7 fungal species and 2 contained empty cultivation mids (substance to cultivate fungi). Finally, 3 vials of ethanol were used for sensor calibration. Table 1 shows the seven different species measured. Note that each shadow denotes a different fungal genre.

3 Results and discussion

As mentioned earlier, measured data was processed coupling Fuzzy Artmap neural networks to different variable selection approaches. In all cases, a leave-one-out approach was used.
This iterative validation procedure generates N evaluation procedures (1 for each measurement). In each iteration, a different measurement is left out, while the remaining ones are used to build the model (PCA, DFA, etc) and train the network.
The remaining measurement (the one not used for training) is then projected onto the model and classified using the already trained network. This is repeated N times (one for each measurement) so that the final result is the average success of the entire iterative process.

3.1. Fuzzy Artmap classifier

First, in order to compare results, a Fuzzy Artmap neural network was used to classify the samples from 7 fungal using all the sensors (12 variables). The classification success rate into seven categories reached a 43 %.
Once this classification was obtained, the goal was to couple different variable selection techniques to the fuzzy paradigm to see whether this approach improved results.

3.2. Using DFA as a variable selection technique

In each iteration, a DFA model was built with the training measurements. Then, the coordinates of the training samples in the DFA projection were used to train a Fuzzy Artmap neural network. The evaluation measurement was projected onto the DFA and the coordinates fed to the neural network. Eigenvectors (the coefficients for canonical variables) were used to classify samples.

A 75% success rate was achieved using only 2 eigenvectors. These results were expected due to the clusters of fungal genres that the DFA graphic shows in figure 1. It has to be noted that, since DFA is a supervised method, overfitting results can be obtained in the training measurement set. Anyway, when using a cross validation method, the overfitting risk is eliminated since the evaluation measurement has not been used to build the DFA model.

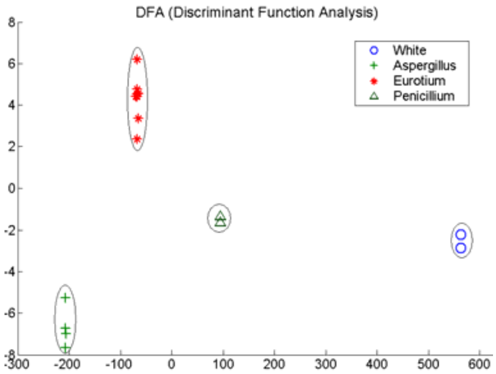

Fig.1. DFA clustering of fungal genres.

3.3. PCA used as a variable selection method coupled to Fuzzy Artmap

In each iteration, a PCA model was calculated with the training measurements and the coordinates fed to a fuzzy Artmap for training purposes; then, with the PCs calculated and the weights from the Fuzzy Artmap, the validation measurement was projected and evaluated.

Results with different number of principal components were tested. Best results were achieved with just 2 PC's, where a classification rate of 63 % was achieved.

3.4. Results coupling Genetic Algorithms and Fuzzy Artmap:

The GA coupled to the Fuzzy Artmap classifier selected 5 out of 12 variables. The fitness was evaluated as the PER (Predictor Error Rate) and the cross-validation of order one with 16 measurements was applied. The PER was 0.3556 and the algorithm converged after 33 generations. The success rate was 63 %.

3.5. Variable selection using intra/inter variance

A variance criterion was defined in order to reduce the number of variables. Equation 1 shows this criteria, which somehow measures the resolution of each variable related to the differentiation between the 8 fungal species. *External variance* was calculated as the variance between the 8 average (centroid) values obtained for each fungal sample (plus blank vials). *Internal variance* was defined as the average of the 8 distances calculated for the 2 repetitions performed on each sample. A higher value for Vr means a better resolution capability for a given variable.

$$Vr = \frac{External Variance}{Internal Variance} \qquad (1)$$

Fuzzy ARTMAP was applied to evaluate the selection. Best results where obtained when selecting the 7 variables with the highest Vr. The success rate topped at 63 %.

3.6. Forward selection

The forward selection algorithm used in linear regression was applied in our case to select a subset of the 12 original variables. In the end, only 2 variables were selected. These variables were used as the input to a Fuzzy Artmap model The neural model was cross-validated using 16 measurements. The success rate achieved was 70 % with the selected variables.

4 Conclusions

Table 2 summarises the results obtained, comparing the coupling of different variable selection techniques to a Fuzzy Artmap. The number of variables that give best results is also specified. We can observe that applying any of the methods leads to better results than using the Fuzzy Artmap alone. The best results were obtained coupling DFA to a Fuzzy Artmap neural network using only 2 variables (factors) instead of 12.

Table 2. Variables selected.

Methods	Results	Subset selected
Fuzzy ARTMAP alone	43%	12
DFA+ Fuzzy ARTMAP	75%	2
PCA+ Fuzzy ARTMAP	63%	2
GA+ Fuzzy ARTMAP	63%	5
Variance Criterion	63%	7
Forward + Fuzzy ARTMAP	70%	2

As it can be seen the forward selection method gives very good results and the variables selected come from the original sensor array, giving a straightforward interpretation (sensor selection) that can be used to reduce the sensor array for a given application. That is why this method should be studied in greater detail.

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Enhancing sensor selectivity through flow modulation

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Abstract

In this paper, a new method to enhance sensor selectivity is described. A flow modulation system, driven by a PC-controlled peristaltic pump, has been designed to feed a sensor chamber with different vapors. 45 measurements where performed comprising five different species (benzene, toluene, o-xylene, methanol and para-xylene) in three different concentrations (20, 200, 2000 ppm). Using frequency domain techniques and neural networks, the system was able to reach a 92% classification success rate when identifying all five vapors despite concentration was not constant and a single sensor was used.

1. Introduction

In the last ten years, considerable efforts have been made to use sensor dynamics as a source of multivariate information leading to an enhancement in the discriminating ability of poorly-selective metal oxide gas sensor arrays. Many authors have reported on strategies based on modulating either the sensor operating temperature [1] or the analyte concentration [2,3]. Here we introduce and demonstrate, for the first time, a simple method that, combining simultaneously both effects, has the potential of increasing the resolving power of metal oxide sensors. Furthermore, its simplicity makes it especially suited for low-cost applications.

The approach involves a flow modulation of contaminated air through the sensor chamber. In this manner temperature and concentration modulations are achieved indirectly. By changing flow rate periodically, local differences in the concentration of the species being measured are generated. Moreover, surface temperature changes as the refrigeration effect of air flow is proportional to the flow rate applied.

Section 2 describes the experimental set-up, while section 3 describes the measurements performed and discusses the results obtained. Finally, section 4 outlines the conclusions and describes future work in this direction.

2. Experimental set-up

To achieve a flow-modulation capable electronic nose, we designed a closed loop system, based on a PC controlled peristaltic pump. Figure 1 shows the configuration devised.

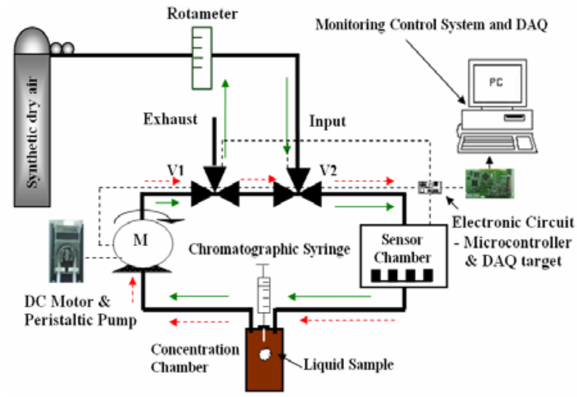

Figure.1. Schematic diagram of the flow modulation system.

The system has two operating modes. In the cleaning configuration, synthetic dry air enters the system through the first electro-valve and cleans the peristaltic pump, the sensor chamber and the evaporation chamber. Solid arrows mark the flow of clean air in this mode.
In measuring mode, air re-circulates around a closed circuit. Once the modulation is initiated, a chromatographic syringe sprays a calculated quantity of liquid contaminants into the evaporation chamber. Clean air inside the circuit becomes contaminated when forced to re-circulate around the evaporation chamber thanks to the peristaltic pump. Dashed arrows show this circuit.
A microcontroller commands the speed of the peristaltic pump which directly translates into different flow rates. A PC programmed with a written-in-house user friendly program communicates with the microcontroller so that the user can select the frequency and flow rate waveform that has to be applied. Moreover, through this program, the PC commands the microcontroller to open or close the electro-valves to change the configuration of the system depending upon the operating mode desired.
Moreover, the PC records the sensor response (in terms of conductivity) and applies signal pre- and post-processing algorithms to identify the vapor sample measured.

Liquid quantities of the contaminants measured were calculated and sprayed into the contaminants chamber using a chromatographic syringe. A total of 45 measurements were performed. The measurements comprised five different vapors (benzene, toluene, methanol, *o*-xylene and para-xylene) at three different concentrations (20,200,2000 ppm) with three replicates for each type of measurement.

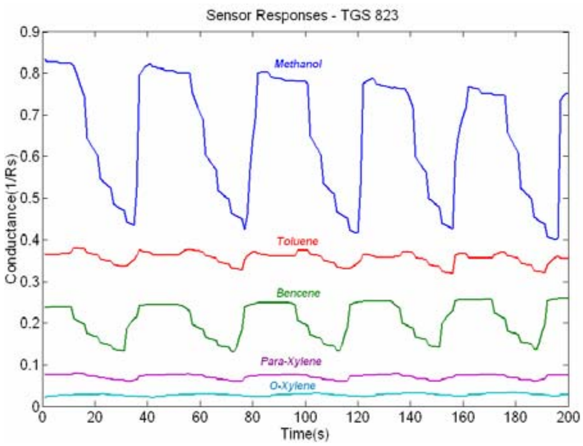

Figure.2. Typical responses with 5 contaminants.

Then, a periodic pulse modulation with a frequency of 10 mHz and an amplitude of 250 sscms was applied. Figure 2 shows a typical response from a sensor to five different contaminants when flow is pulsed as described above.

Sensor	Main application
TGS 800	Air Quality control
TGS 822	Alcohol detection
TGS 823	Organic Dissolvent

Table1. Sensors used and their main applications

Three different sensors were used for the measurements. Table 1 lists their designation and main applications. Their information was never combined to obtain better results, since the main goal of the experiment was to determine how selective each single sensor could get by itself using the flow modulation approach.

An FFT was applied to the periodic response and its amplitude value was considered. Values for the fundamental and harmonic frequencies were used as output data from the sensors and fed a Fuzzy Artmap pattern recognition algorithm.

3. Results and discussion

All results obtained and listed in Table 2 were performed using a cross-validation of order 1 (the so-called leave-one-out approach). The goal was to classify measurements in five different categories, one for each contaminant , with the added difficulty of variable concentration (20, 200 and 2000 ppm).

Pre-processing	TGS 800	TGS 822	TGS 823
None	84.44%	93.33%	91.11%
Mean centring	82.22%	82.22%	80.00%
Auto-scaling	53.33%	62.22%	55.55%

Table2. Classification rate for normalization strategy

Different preprocessing strategies were used to determine how much the mean amplitude, variance and waveform from each sensor response contributed to the classification of the 45 measurements.

From the results exposed in table 2 it is clear that best results are obtained when the evolution of sensor conductance through time is not preprocessed.

Anyhow, considering that classifying samples into 5 categories at random would yield a 20% success rate, it is clear that sensor response without mean value or even unbiased and scaled by its variance still retain useful information since classification rates never fail below a 53%.

4. Conclusions

A new modulation method has been tested to increase sensor selectivity. A wide range of concentrations and contaminants have been tested confirming that flow modulation allows for a reliable identification of different vapor species.

Additional work has to be done to optimize the system and test the approach under tougher conditions like binary or tertiary vapor mixtures.

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POSTER

UNIVERSITAT ROVIRA I VIRGILI

University of Pamplona

Concatenation of a Fuzzy Artmap neural network to different variable selection techniques to enhance E-nose performance

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1. Goal

To improve the performance of an electronic nose in the classification of seven fungal species coupling a Fuzzy Artmap neural network to different variable selection techniques.

2. Experimental

Species	Replicates
Eurotium Repens	2
Eurotium Herbariorum	2
Eurotium Amstelodami	2
Eurotium Rubrum	2
Aspergillus flavus	2
Aspergillus Niger	2
Penicillium Corylophilum	2
Cultivation Mid	2

Table 1. Fungal Species measured

Materials and Methods

- 12 metal oxide commercial gas sensors, (FIS SP-series and TGS 8-series) were used with the Electronic Nose.
- A total of 16 vials (20 ml) were prepared

3. Results and discussion

Measured data was processed coupling Fuzzy Artmap neural networks to different variable selection approaches. In all cases, a leave-one-out approach was used.

Dataset (Matrix of 16 measures x 12 variables)

Cross validation: leave-one-out

Training measurements

16 Iteractions

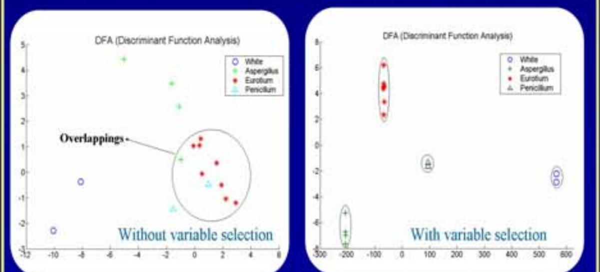
Measure left out

Measurement projection

Variable selection method:
PCA, DFA, GA, intra/inter variance criterion and Forward selection.

Fuzzy Artmap Classifier

Sucess rate in classification



DFA clustering of fungal genres.
A 75% success rate was achieved using only 2 eigenvectors.

4. Conclusions

Methods	Results	Subset selected
Fuzzy ARTMAP alone	43%	12
DFA+ Fuzzy ARTMAP	**75%**	**2**
PCA+ Fuzzy ARTMAP	63%	2
GA+ Fuzzy ARTMAP	63%	5
Variance Criterion	63%	7
Forward + Fuzzy ARTMAP	70%	2

Table 2. Variables selected

- The best results were obtained coupling DFA (75% success rate) to a Fuzzy Artmap neural network using only 2 variables (factors) instead of 12.
- The forward selection method gives very good results and the variables selected come from the original sensor array.
- These results indicate that is possible to optimize a EN using a suitable variable selection and to use it as food quality analysis.

Nanoelectronics and Photonics Systems Workshop, June 21, 22, 2004.

Acknowledgments: This work was funded by the redes temáticas de investigación cooperativa: "RED DE CENTROS EN METABOLISMO Y NUTRICIÓN C03/08"

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Enhancing sensor selectivity via flow modulation

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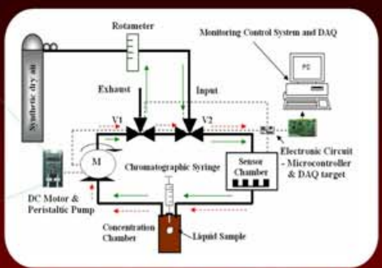
1. Goal

- To improve electronic nose performance, through the enhancement of sensor selectivity using a flow modulation system.
- Application of the designed system to the identification and classification of different contaminants agents.

2. Experimental Set-up

To achieved a flow-modulation capable e-nose, we designed a closed loop system, based on PC controlled peristaltic pump. The system has two operating modes: Cleaning Configuration (Green arrows) and measuring mode (Red arrows) using flow modulation.



Low cost Peristaltic Pump with mechanical parts and Silicone tubes

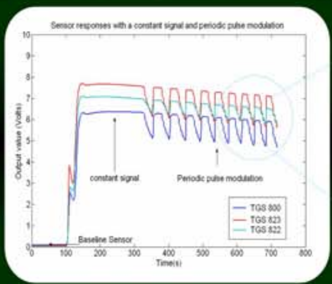
A microcontroller commands the electro-valves and the speed of the peristaltic pump, which directy translates into different flow rates. The system is controlled by a PC and a written-in -house program.

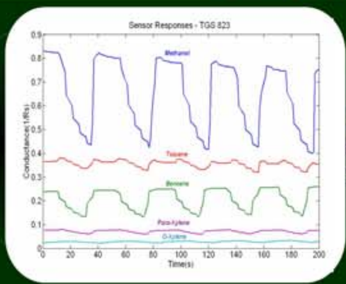
A total of 45 measurements were performed using five different vapors (benzene, toluene, methanol, *o*-xylene and para-xylene) at three different concentrations (20,200,2000 ppm) with three replicates for each type of measurement.

Sensor	Main applications
TGS 800	Air Quality
TGS 822	Alcohol detection
TGS 823	Organic dissolvents

Three different sensors were used for the measurements with their main applications

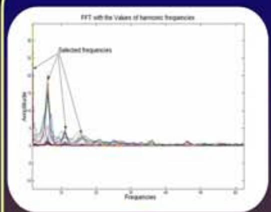
A periodic pulse modulation with a frequency of 10 mHz and an amplitude of 250 sscm (ml/min) was applied to the sensors.





The signals acquired were the conductivity of each sensor

3. Results and discussion



Fuzzy Artmap Classifier

Absolute values of the FFT were used to feed a Fuzzy Artmap pattern recognition algorithm.
All results were obtained using a leave one out approach. Different preprocessing strategies were used to determine the classification of the 45 measurements.

Pre-processing	TGS 800	TGS 822	TGS 823
None	88.44 %	93.33 %	91.11 %
Mean centring	82.22 %	82.22 %	80.00 %
Auto-scaling	53.33 %	62.22 %	55.55 %

4. Conclusions

✓ A new modulation method designed to increase sensor selectivity has been tested. A wide range of concentrations and contaminants have been measured confirming that flow modulation allows for a reliable identification of different vapor species.

✓ Additional work has to be done to optimize the system and test the approach under tougher conditions like binary or tertiary vapor mixtures.

MinoS microsystems nanotechnologies for chemical analysis

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IEEE SENSORS 2005
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Electronic Nose To Guarantee The Microbiological Quality Of Bakery Product Manufacturing

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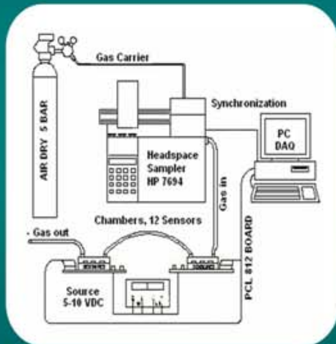
1. Goals

- To identify and classify the different fungi species.
- To design an electronic nose system using the experience obtained with the laboratory EN.
- To develop an EN with software and associated hardware, which allows a fast data acquisition, and an effective recognition of patterns (with PCA and the Neuronal Network Fuzzy Artmap Neuronal Network).

2. Experimental

With an already made Electronic Nose from the laboratory, two test with the Headspace sampler, were executed a group of 27 and later of 19 vials of 20 ml closed samples were filled with 7 fungi, 1 cultivation mid (substance to cultivate fungi) and ethanol (for the calibration of sensors).

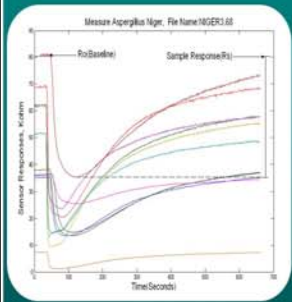
#Fungi	Name	1st Round	2nd Round
1	Eurotium Repens	3	2
2	Aspergillius flavus	2	2
3	Eurotium Rubrum	3	2
4	Aspergillius Niger	3	2
5	Penicillium Corylophilum	3	2
6	Eurotium Herbariorum	3	2
7	Eurotium Amstelodani	3	2



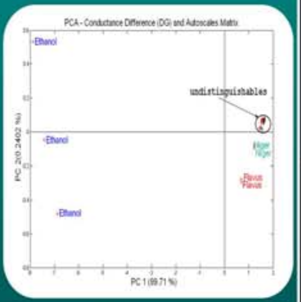
The carrier gas was regulated at flow rate of 25 - 50 ml/min. The acquisition time for each sample was 10 minutes with 12 sensors.

3. Results with the laboratory EN

A set functions or algorithms have been developed and applied to analyse the data. Most of the fungi could not be distinguished but 3 different species could be told apart.



Gas sensor Response as a function of time.



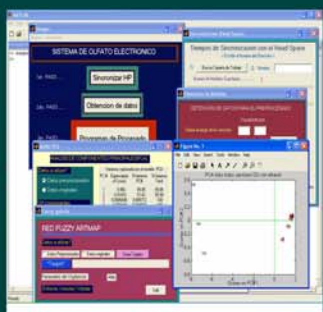
Result of the PCA with the gas sensor array for 19 gas samples.

The Neuronal Network Fuzzy Artmap and a cross-validation technique (leave one out) of order one, was implemented to estimate the success rate in classification The success rate was 9 with an average of 47.368 %.

4. Optimized EN

The following step was to design an electronic nose system using the experience obtained with the laboratory EN . Its compact design makes it more portable and facilitates the tests in the laboratory with less errors. It also improves the stability when dealing with the headspace sampler.

Components of the optimised Electronic Nose.

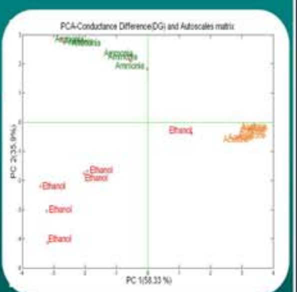


GUIs for data acquisition and processing.

5. Final tests

In order to evaluate the behavior of the new system, several tests with 9 vials (3 Ethanol, 3 Ammonia and 3 Acetone) were executed.

Electronic nose system.



With the fuzzy Artmap, the results of the PCA have been verified, with a success rate of 94.4 %.

6. Conclusions

- With preliminary laboratory tests the gas sensors achieve broad sensitivity and selectivity, responding to each one of the samples
- These results show that is possible to use the Electronic Nose for food quality analysis. By means of adequate selection of materials, conditions of operation and better PARC, better results are expected with a new version of this device.

Acknowledgments: To R. Calavia for his helpful work during the realisation of this project.

This works was supported by: CAL01 – 037 – C3 – 2