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Hand Held Electronic Nose for VOC Detection

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In this work we present a novel hand held electronic nose. This electronic nose is a lightweight instrument with wireless communications capable of stand alone operation. It has been designed to accept and work with several types of resistive microchemical sensors. The electronic nose can be operated stand alone or controlled externally by a personal computer.
The external measurement and control program has been developed in Labview. Although this device has been developed for indoor applications it is versatile enough to be used as a general purpose low cost electronic nose. A low volume microsensor chamber has been designed to accept several sensor packages. The device has been tested in laboratory with volatile organic compounds (VOCs) such as acetic acid, acetone, ethanol, propanol, hexanal, ethyl acetate, acetaldehyde, butanediol, toluene and xylenes. The external program that controls the measurements performs real time data processing through linear pattern recognition techniques such as principal component analysis (PCA). Non linear pattern recognition techniques such as neural networks have been developed in Matlab for identification and classification purposes. Comparison between these methods is accomplished.

1. Introduction

Although there are a wide range of commercial available electronic noses few of them are really portable (Wilson et al., 2009). Moreover, few of them are designed for remote operation. In the past years we have developed several prototypes of portable, wireless electronic noses under a generic name of WiNOSE (Santos et al., 2010; Santos et al., 2011). The first two prototypes were intended to be operated outdoors. For this reason they included solar cells and several rechargeable batteries allowing continuous operation for long time periods. The model presented here is smaller, designed to perform indoors, hand held and capable of stand alone operation.

2. Instrument description

2.1 Hardware

A schematic of the new WiNOSE is shown in Figure 1. It consists of two gas inlets that are switched through a three way electrovalve (SMC S70_ES) whose output is connected to the sensors cell that contains the microsensor array. A photograph of the electronic nose used is shown in Figure 2. The low volume microsensor cell, the pump, the electrovalve and the antenna are placed on the left board. The electronics is placed in the right board inside the case.
One of the gas inlets has a carbon filter and is intended to provide clean air as reference baseline. Downstream are located the temperature sensor and the pump (Rietschle Thomas model 2002).
The whole system is controlled by a digital signal controller (DSC Microchip model dsPIC33FJ128GP306). It is a 16 bit microcontroller with 16 Kb of Ram and 128 Kb of FLASH memory.

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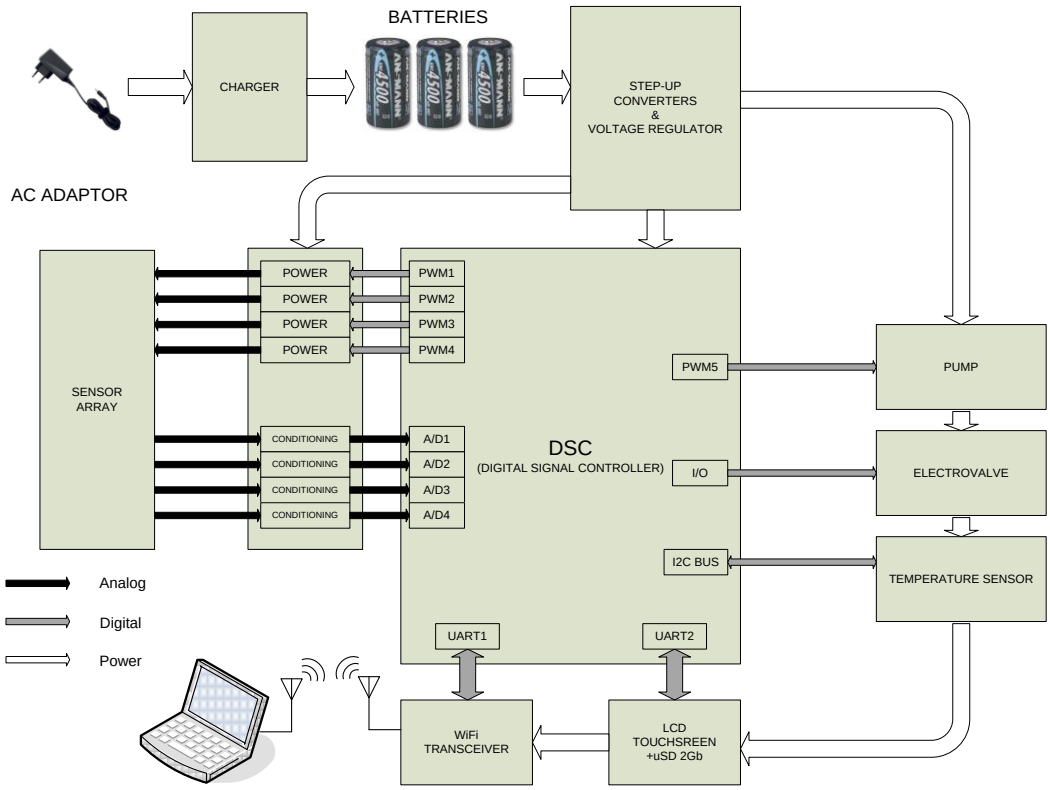

Figure 1: Schematic diagram of the electronic nose

It has several analog to digital converters (A/D) inputs for sensor measurements and several pulse width modulation (PWM) outputs for sensor heating. Main measurement parameters are shown in a LCD (Figure 3). The LCD is a touch screen that allows the introduction of several measurement parameters, as pump and heaters power, as well as electrovalve switching.

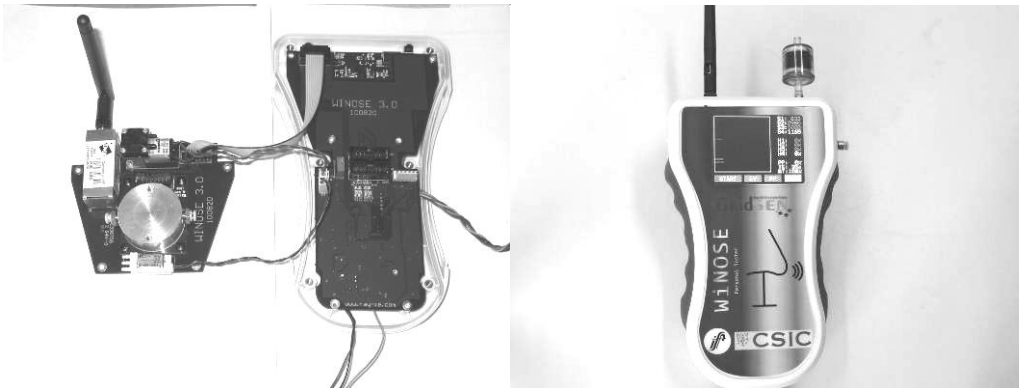

Figure 2: Photographs of the electronic nose. Left: without the cover showing the antenna, sensors cell, pump and electrovalve in one board and the main electronic board in the case. Right: the electronic nose with the cover taking measurements.

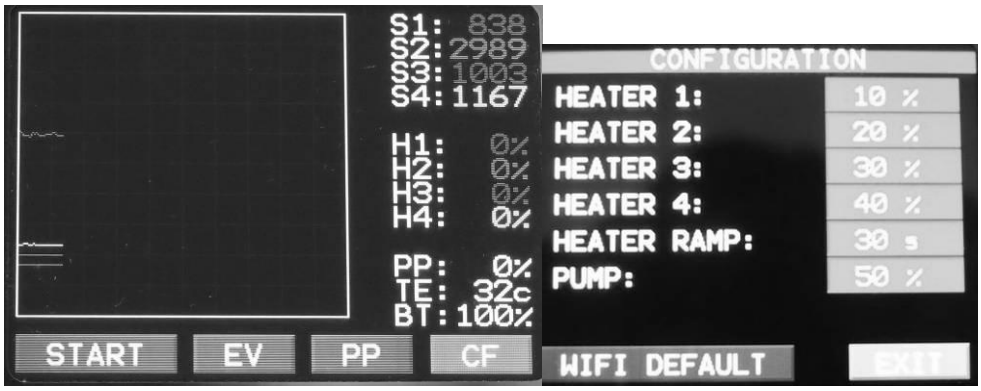

Figure 3: LCD screen. Left: measurement screen (Si, sensors resistance; Hi, heater power; PP, pump power; TE, temperature; BT, battery charge). Right: configuration screen with the initial heater and pump power and heater ramp value.

It has an internal 2 Gb SD memory card for data storing. It gives the electronic nose an autonomous capacity. However in this operation mode there is no data analysis. Several rechargeable batteries give about 8 hours of autonomy to the e-nose.
Wireless communications are provided by a Wifi transceiver. A point to point communication is established with a host computer for remote operation.
The sensors cell and board are designed to interface to microsensors in a TO-5 12 leads package but it is easily adaptable to other packages. The system can measure up to 4 resistive sensors and provides independent heating for each one. The tests performed in this work have been done with a commercial microsensor (SILSENS MSGS-4000). It is made of four thin nanocrystalline tin oxide layers deposited over micromechanized silicon hot plate. One of the sensors is doped with palladium.
As this model has no flowmeter a calibration of the pump is necessary.

2.2 Software
The instrument is controlled by a program developed in LabVIEW. It has two main operation modes: training and classification. In training mode a series of known chemicals is presented to the e-nose and the results are stored in a database. In classification mode an existing database is loaded and the measurements are classified in real time in one of the classes previously defined.
The program displays and controls the measurement parameters (temperature, flow, sensor resistance, temperature, valve status, battery status, pump power). It automatically generates the response database. Several programs developed in Matlab have been integrated in LabVIEW through mathscript to perform pattern recognition. Real time classification is based in principal component analysis from the response database. The algorithm calculates normal distribution parameters of each different training class in the PCA space and then calculates the probability corresponding to the unknown measurement. The sample is classified as the class with higher probability.
The results were compared with a previously developed non linear pattern recognition method based on probabilistic neural networks (PNN) a special case of radial basis function classifiers (Gutierrez-Osuna, 2002).

3. Results

Two groups of measurements have been done in order to create two different response databases. In the first one eight different VOCs have been measured: acetic acid, acetone, ethanol, propanol, hexanal, ethyl acetate, acetaldehyde and butanediol. In the second group four similar VOCs have been tested: toluene, o-xylene, m-xylene and p-xylene.
The sensors operating temperatures in all tests were 150, 200, 250 and 300 ºC. Flowrates were set to 70 mL/min for adsorption and 115 mL/min for desorption. Adsorption time was 20 s and desorption

time was 160 s. These times were too short for equilibrium measurements but allowed fast and reproducible responses. However, due to the lower volume of the new sensors cell design, the response was faster than in the previous models.

One mL of each compound was placed in a 20 mL vial and kept at 16 ± 1 ºC by a Peltier system. The measurements were repeated a minimum of 10 times. The response was calculated as the ratio between the sensor resistance in filtered air to the sensor resistance at the end of the sampling time and store in a file. In training mode the program also stored the compound name.

Figure 4 shows the PCA score plot of the responses for VOCs. Each response is a point in the plot and each compound is represented by a different symbol. The ellipses represent the estimated normal distribution of each gas calculated by estimating the covariance matrix of their responses. The ellipses drawn in the figure correspond to the equiprobability surface that encompasses the 90% of the probability of that given normal distribution. The PCA with three components shows a very good separation among the different gases.

The same graphic for toluene and xylenes is plotted on Figure 5. In this case the system does not separate well m- and p-xylenes, but shows a better separation of toluene and o-xylene from the other two.

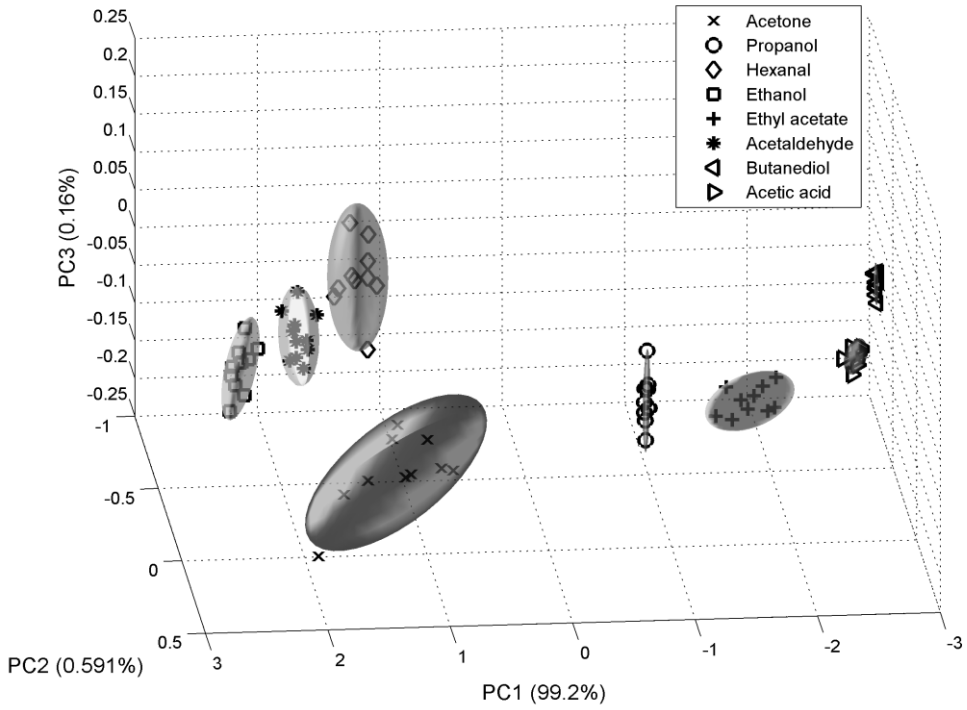

Figure 4: PCA score plot for VOCs

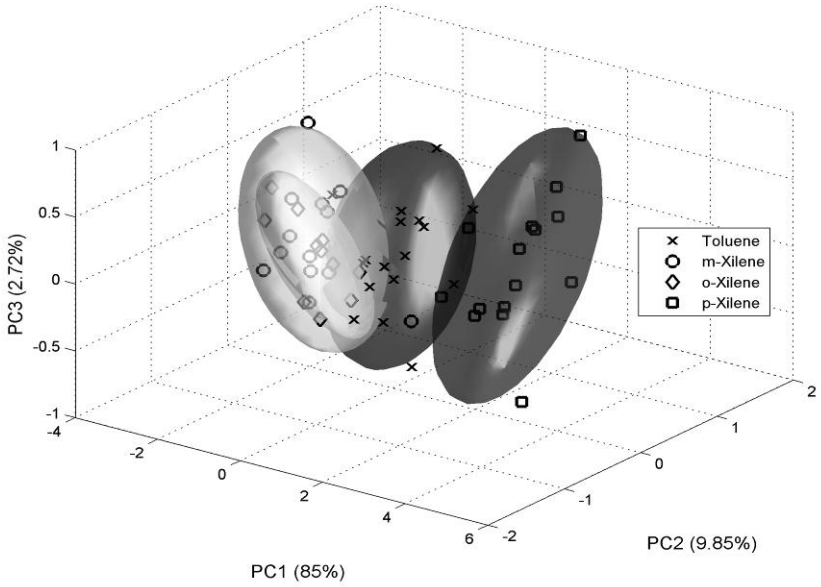

Figure 5: PCA score plot for toluene and xylenes.

As online classification we use a probabilistic approach (centroid method) that supposes that the measurements form a normal distribution. We assign the test sample to the gas witch probability of its estimated normal distribution at that measurement point is higher. This method is equivalent to a quadratic discriminant analysis (Hastie et al., 2008) but not only gives the classification result but also a quantification of the probability. Example of classification results output for one measurement (that corresponds to an acetone response) is shown in Table 1. Since this method has the advantage of giving different probabilities for the different gases a list can be given in each measurement allowing the assessment of uncertainties as shown in Table 1.

Table 1: Classification results of an acetone measurement

Rank	Gas	Probability
1	Acetone	61.4
2	Hexanal	41.8
3	Acetaldehyde	24.0
4	Propanol	12.0
5	Ethanol	8.9
6	Ethyl acetate	1.5
7	Acetic acid	0.1
8	Butanediol	0.0

To validate the method of classification we use leave one out cross validation, leaving one sample out and performing the whole analysis for each sample taken. This method allows us to asses the whole classification with a small number of samples. Figure 6 shows the classification results for toluene and xylenes with an overall performance of 71.9 %. For VOCs the performance is 97.5 % as only two of the acetone measurements are not correctly classified. In the previous e-nose models a probabilistic neural network was used to classify the measurements off-line. The validation of those analyses gave 98.8 % accuracy for generic VOCs and 73.6 % for toluene and xylenes, very close to the performance of the centroids method. For small datasets the centroid method is easier to program and faster than the probabilistic neural network method.

Compared with the previous developments this e-nose is lighter, faster and performs classification tasks in real time. Future work will focused in two fields. The first one is the study of high sensitivity low power sensors based on nanomaterials, mainly semiconductor nanowires and nanofibers. The other one is the software improvement for real time quantification.

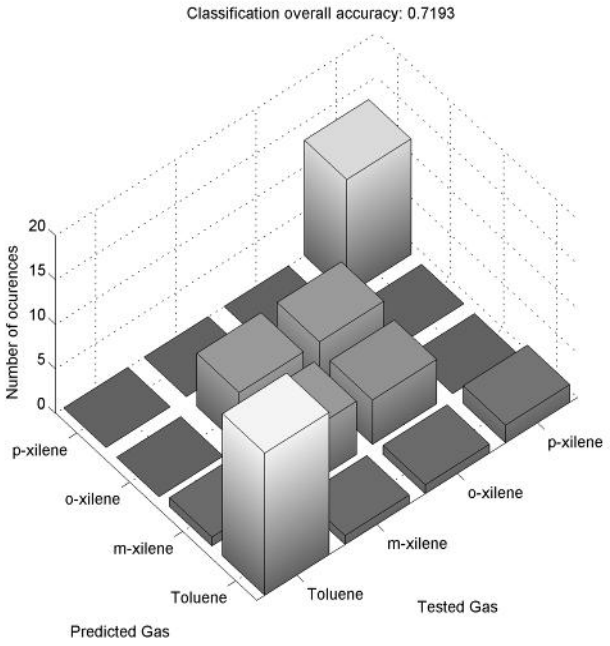

Figure 6: Classification results for toluene and xylenes by centroid method.

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