Detection of Pollutants in Water Using a Wireless Network of Electronic Noses

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We present here a network of hand-held wireless electronic noses (e-noses) for the detection of solutions of different chemicals such as ammonia, ethanol, toluene and ethyl acetate in water. The network is formed by two identical e-noses based on resistive microchemical sensors. Data processing techniques are based in Principal Component Analysis for dimensionality reduction for 3D representation and Neural Network for classification of the samples. The proposed system can be used for sensor optimization since different sensors with different temperatures of operation could be tested in several devices in order to select the optimal array for a particular detection or application. Result show that, depending on the parameters of the sensor array, the discrimination of the pollutants can be achieved with different success rate in classification.

1. Introduction

Detection of volatile organic compounds (VOCs) in aqueous media has many potential applications. VOCs are a class of highly toxic contaminants commonly found in groundwater, which may pose a substantial threat to human health (Van Leeuwen and Vermeire, 2007). On the other hand human breath contains VOCs biomarkers that can be used to identify numerous diseases. For example it is known that the presence of certain level of acetone is an indication of diabetes (Minh et al, 2011). Abnormal ethanol levels are as well used for the same purpose (Daneshkhah et al., 2015). Grab sample collection followed by off-line laboratory analysis is usually used for current environmental monitoring programs. Nowadays there exist several portable sensing technologies that can be used for in situ measurements. Most of them, however, are based on mass spectroscopy which is still expensive and difficult to operate (Bell et al., 2015). Although not as sensitive nor selective of the above methods chemical sensors are a good alternative due to their rapid response time and low cost. New materials such as molecular imprinted polymers (Cho et al, 2011) and graphene (Tung et al, 2014) are being developed for the new generation of sensors. To overcome their lack of selectivity the sensors are grouped in arrays which with appropriate sampling and signal analysis methods form the electronic nose. Among the e-noses there are few examples of portable ones, see for example (Zhang et al, 2014) and our earlier work (Santos et al 2010).. For environmental applications it is advisable to have a network of e-noses in order to make a pollutant map.

The objective of this work is to identify several VOCs in water by means of an electronic nose network.

2. Experimental

2.1 Samples

Solutions of 5 % v/v of acetone, ethanol and ethyl acetate and 1 % v/v of ammonia and toluene in pure water were prepared. Ten mL of each solution were placed in a 22 mL vial inside a Peltier thermostatic bath kept at 16 ºC. All chemicals were purchased at Sigma Aldrich (St. Louis, MO, USA).

2.2 Electronic nose network

A network is configured with several e-noses (described in the next paragraph). Each device has a unique IP address and it allows to access to each device from any device connected to the network or through the

Internet. The network could be configured and used for a double purpose: first, a network with identical devices and parameters configured to perform distributed measurements and second, a network with different sensors or parameters and the same samples in order to increase the number of sensors or optimize the composition of the array.
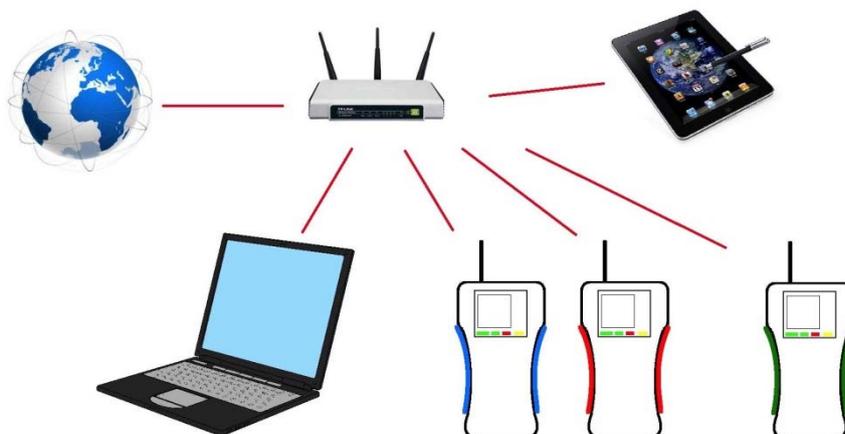

Figure 1: Schematics of the network.

The network is composed by two e-noses as it is shown in figure 2. The computer can access to the data and control the parameters of each e-nose through a Labview program, although each device can also be controlled through the touch panel.
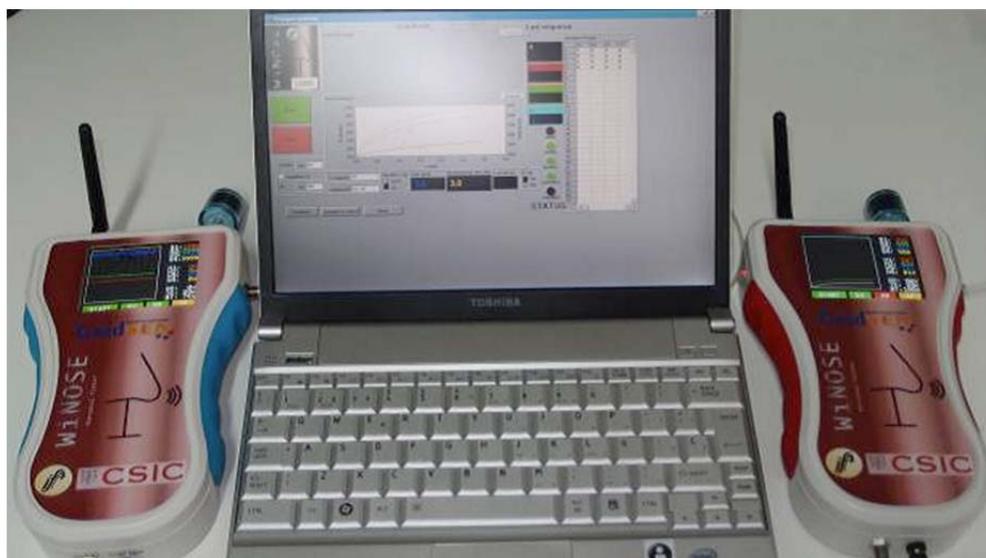

Figure 2: The two e-noses used in this work.

2.3 Electronic nose

Each node of the e-nose network is a home-made and home-developed e- nose with wireless communication. They were developed and presented in this paper for water pollutants discrimination. The main blocks of the e-noses are shown in figure 3. Each e-nose consists of two gas inlets that are switched through a three way electrovalve whose output is connected to the sensors cell that contains the sensor array (set of several micromechanized sensors). 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. A digital signal controller controls the whole system. 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. The LCD is a touchscreen that allows the introduction of several measurement parameters as pump and heaters power as well as electrovalve switching. Rechargeable batteries give about 8 hours of autonomy to the e-nose. Wireless communications are provided by a Wifi transceiver. The system can measure up to 4 resistive sensors and provides independent heating for each one. Tests have been made with commercial microsensors for the e-noses, SILSENS MSGS-4000 and MSGS-6000 respectively. Both sensors have similar principle of working and sensing materials, but different geometry and temperature of operation. More details can be found in (Santos et al., 2012).
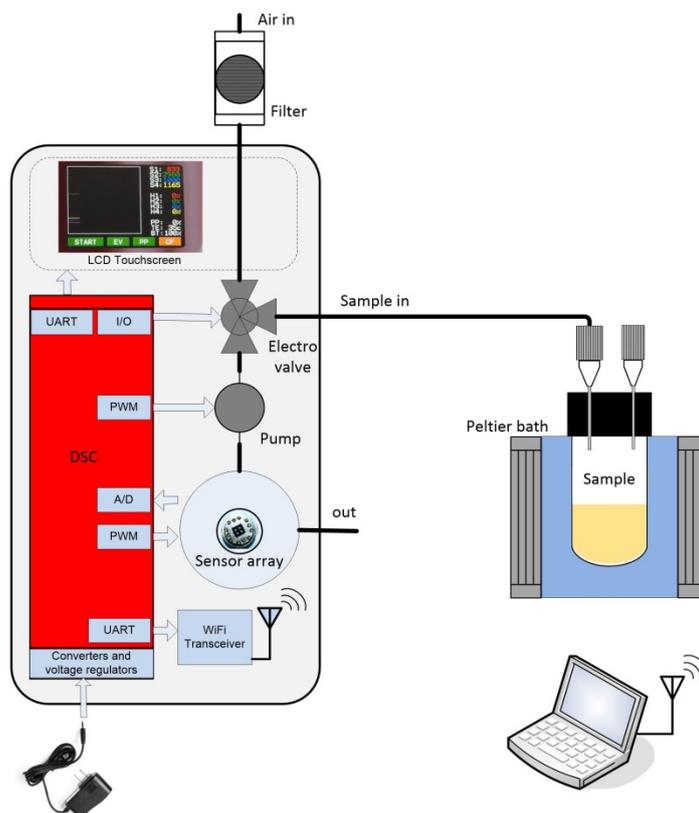

Figure 3: Schematics of the e-nose and the measurement setup.

2.4 Measurement setup

A schematics of the e-nose and the measurement system is shown in figure 3. Parameters in the measurements were as follows: the sensors operating temperatures in all tests were in the range of 150 to 350 ºC. Sensors usually operate at different temperature in order to increase the response spectrum. Flowrates were set to 70 mL/min for adsorption and 115 mL/min for desorption. Adsorption time was 60 s and desorption time was 840s. These times were short for equilibrium measurements but allowed fast and reproducible responses. At least 18 adsorption desorption cycles were performed for each sample.

2.5 Data processing

The data processing of the e-nose network consists of several stages: preprocessing, feature extraction, reduction of dimensionality, learning and classification. First, the data was preprocessed (centered and scaled), and after feature extraction (relative response baseline manipulation and sensor normalization), Principal Component Analysis (PCA) was performed on the data to reduce data dimension and show it in a plot. After PCA processing, classification of unknown samples into the classes previously learned is performed. In this task, two commonly used Artificial Neural Networks (ANN) have been used: Probabilistic Neural Network with Radial Basis Functions (RBF) and Feed Forward Neural Network with Backpropagation (BP) learning algorithm. Leave One Out crossvalidation is used for performance estimation.
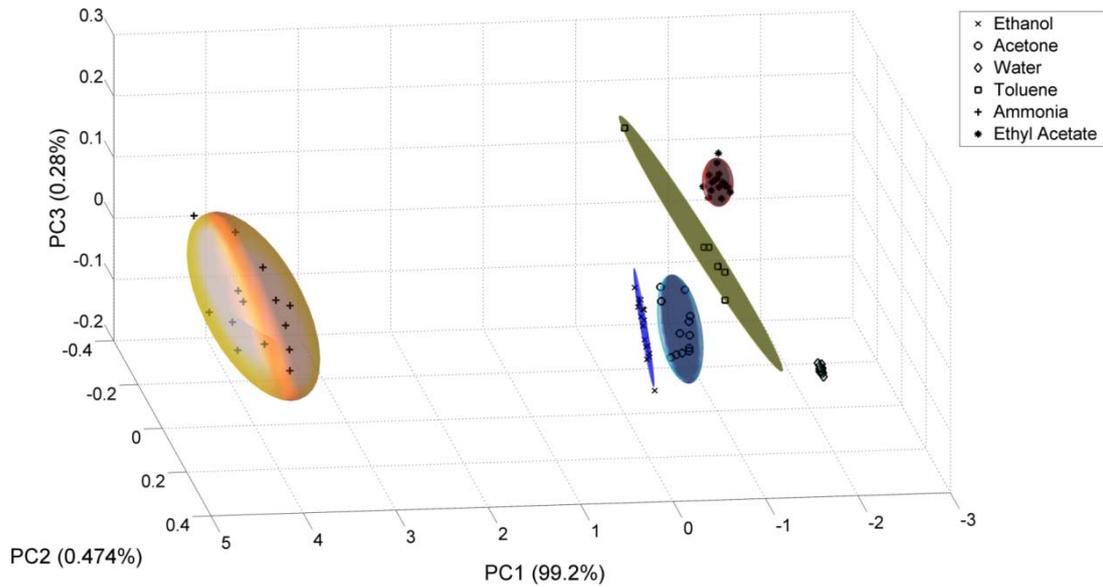
Figure 4: PCA plot for e-nose 1

3. Results

This work shows the viability of a network of wireless e-nose to detect several pollutants in water and a comparison of the discrimination capability of the different nodes of the network in order to optimize the composition of the array. Both prototypes use headspace sampling system: the headspace of samples stored in 22 ml vials is carried to the sensors cell by using an integrated pump. The measurement setup includes at least 20 cycles of adsorption and desorption. The raw data were stored in disk for further analysis.

Once the measurement of the samples was performed, the data was preprocessed, and the sensor response was calculated as the ratio between the sensor resistance in filtered air to the sensor resistance at the end of the sampling time. PCA was made to the sensors response of each e-nose node, plots of three first principal components of node 1 and 2 responses are shown in figures 4 and 5 respectively. Node 1 shows a complete separation of the clusters corresponding to the different classes of samples. Node 2 shows separate zones for Ammonia and Ethyl Acetate, but some partial overlappings among the other classes can be found. Since the observation of the PCA plots, it can be observed that Node 1 could have a better discrimination capability than Node 2.
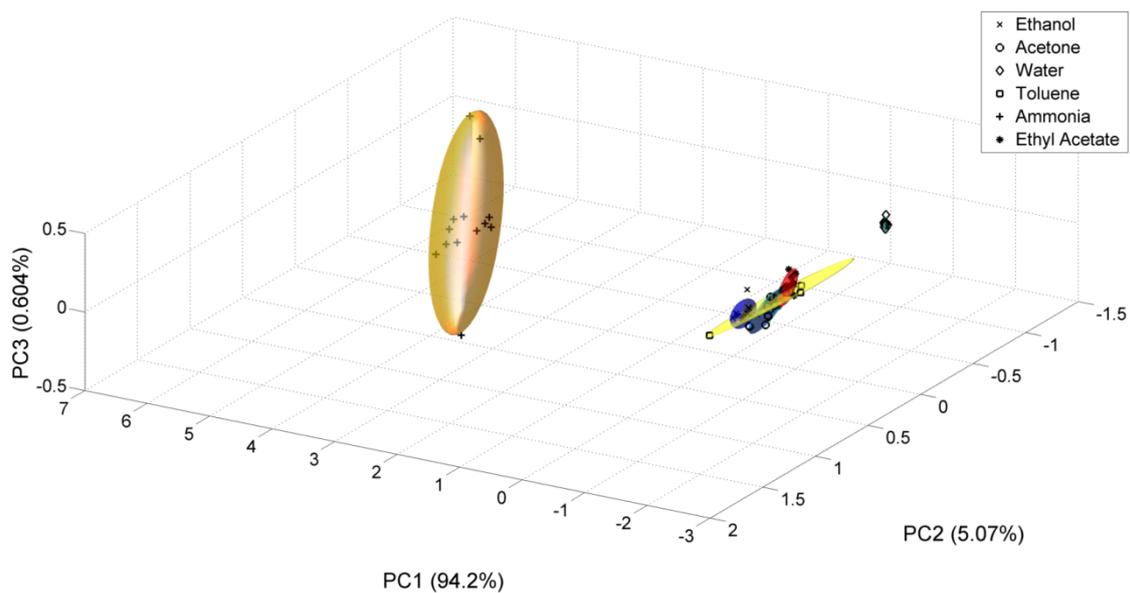

Figure 5: PCA plot for e-nose 2

The results obtained in PCA are confirmed with classification with ANNs. Classification rates for the e-noses are shown in tables 1 and 2 as a confusion matrix of Probabilistic Neural Network with Radial Basis Functions (RBF), in which real values are explained in rows and predicted values in columns.

Table 1: PNN classification matrix for Node 1

	Ethanol	Acetone	Water	Toluene	Ammonia	Ethyl Acetate
Ethanol	17	0	0	0	0	0
Acetone	0	12	0	0	0	0
Water	0	0	11	0	0	0
Toluene	1	0	0	5	0	0
Ammonia	0	0	0	0	13	0
Ethyl Acetate	0	0	0	0	0	17

Table 2: PNN classification matrix for Node 2

	Ethanol	Acetone	Water	Toluene	Ammonia	Ethyl Acetate
Ethanol	9	0	1	1	0	6
Acetone	0	11	0	0	0	1
Water	1	0	9	0	0	1
Toluene	4	0	0	0	0	2
Ammonia	0	0	1	0	12	0
Ethyl Acetate	5	0	0	1	0	11

Tables 1 and 2 shown that Node 1 obtains higher classification rates than Node 2. The success rate (% samples well classified over total number of samples) was 85.1% for the Node 1 and 58.5% for the Node 2. In order to explain these values for the nodes, the loadings for the different sensors in the PCA is calculated and shown in figure 6. As it can be seen the loadings of the sensors for the Node 2 show a wider dispersion, that could be due to a higher noise level. Additional tests for different combination of sensors have been made. Different groups of four sensors (within the 8 sensors of the two nodes) have been chosen and the discrimination capability as success rate in classification has been calculated. Results show that the 4 sensors of the Node 1 are the most useful for an array, and offer the highest success rate.
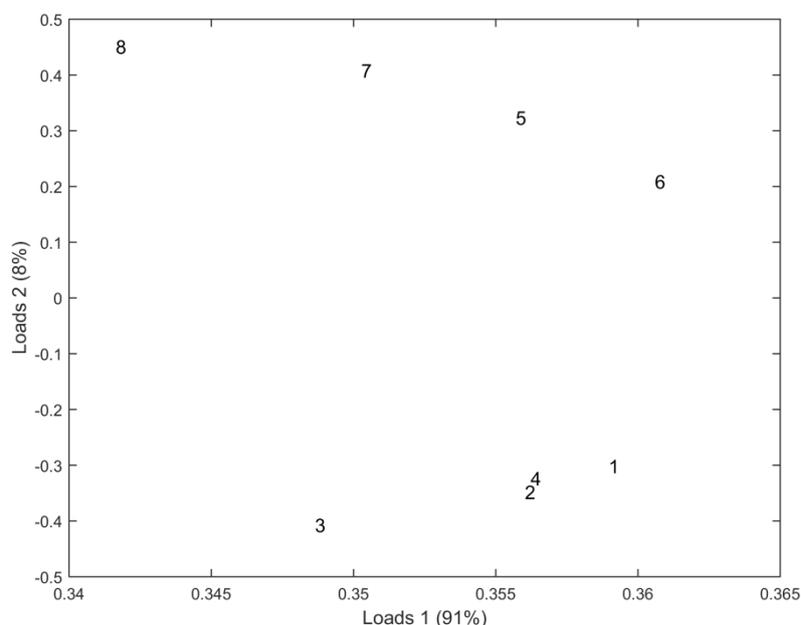

Figure 6: Loading plots of PCA for the 8 sensors of the network.

4. Conclusions

A portable e-nose has been developed in order to create a distributed wireless network for VOC detection. A comparison of the discrimination capability of two different sensor arrays has been made. Measurements with 5 different pollutants in water have been performed with two nodes of the network. Results have been shown that the system is capable of discriminate among the different classes since a success rate near to 100% has been obtained in validation. Results show that the composition of the array determine the discrimination capability of the e-nose: composition of Node 1 have better results than Node 2. Although a single e-nose is capable to identify the tested pollutants, a network of e-noses can be used to perform distributed measurements in different locations or in the same place in order to increase the number of sensors.

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