An Advanced Hand Held Electronic Nose for Ambient Air Applications

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Ambient air carries hundreds of volatile compounds that can provide information about the toxicity and quality of our immediate environment. This paper presents a prototype of an advanced electronic nose (e-nose) based on resistive microsensors for the measurements of volatile organic compounds (VOCs) and inorganic pollutants in ambient air. It integrates an array of chemical sensors into the embedded system to detect volatile compounds in the ambient air. The e-nose is the sixth prototype of the WiNOSE series developed by the Spanish National Research Council (CSIC) and the University of Extremadura (UEx). The main features of the e-nose are its compact size and low weight and it includes eight chemical sensors, completed with humidity and temperature sensors. It was tested with several samples and the results show that the system can detect and discriminate them with a high degree of accuracy. The system development, testing methodologies, and results analysis are presented and discussed.

1. Introduction

Some gases and odours require continuous measurement over some weeks, months or years. These measurements can be taken by installing specific sensors which detect certain gases or dusts, or by using an electronic nose. Electronic noses (Gardner, 1994) are promising devices that are able to detect and quantify gases and volatile compounds. They are composed by gas sensors, sampling hardware that extracts the gases and leads them to the sensors, and algorithms that classify or quantify the gases. One of the fundamental parts of an electronic nose is the cluster of gas sensors. Electronic noses usually have resistive sensors (Berna, 2010) but may have other kind of sensors like gravimetric (Alizadeh et al. 2008) or electrochemical (Collier et al. 2003). In electronic noses prototypes the sensors can be custom made or commercial versions. The commercial sensors are incorporating some of the advances published in the literature (Neri, 2015) and are becoming more and more sensible with lower power consumption and smaller in size (Schneider et al. 2018).

In the past years a series of electronic noses for environmental applications has been developed by two research groups of the Spanish Council for Scientific Research (CSIC) and University of Extremadura (UEx). They have been applied both to air (Santos et al. 2012) and water (Lozano et al. 2016, Herrero et al. 2016) pollution. This paper presents the last prototype designed by both research groups. The electronic nose developed uses some of the latest resistive commercial sensors. The electronic nose is tested in this work with the ambient air pollutant NO\textsubscript{2} that is regulated by the European directives (Air Quality European Directive, 2008) and with a series of pollutant VOCs common in indoor environments.

2. Experimental

2.1 Samples

To test the performance of the e-nose we have measured low concentration of inorganic pollutants such as nitrogen dioxide and several VOCs responsible of different odours in the environment. The NO\textsubscript{2} came from calibrated cylinders (Praxair, Madrid, Spain) using a gas mixer provided with mass flow controllers for
generating the gas mixtures. The measurements of VOCs were made using headspace sampling methods from water solutions (blank water, acetone, ammonia, dichloromethane, dimethylacetamide, ethyl acetate and xylene) at 5% in volume. Chemical compounds were supplied by Sigma–Aldrich, and Milli-Q water was used for solutions. One mL of each compound was placed in a 20 mL vial and kept at 30 ± 0.1 °C by a Thermostatic bath.

2.2 Electronic nose

A photograph of the e-nose developed is shown in Figure 1. The e-nose is a compact size and light instrument that has the possibility to measure up to eight microsensors. It has a micropump to create a flow through the sensor chamber and an electrovalve to choose the sampling path. It also has an internal temperature and humidity sensor and the possibility to connect and measure an external temperature sensor.

![Figure 1: Photograph of the e-nose](image)

Different arrays of sensors are available to be used with this prototype. For this work, we used two different arrays. Table 1 shows the composition of the arrays of sensors used in the experiments. The first one consists of an 8-sensor array made by ultra-low power, state of the art commercial microsensors using CC801 (AMS, 2017) and CC803 (Cambridge 2015) operating at different temperatures. The second one is based on eight different tin oxide sensors from AMS (AMS, 2017), Cambridge (Cambridge 2015) and Sgx sensortech (SGX 2018), with integrated heaters, SMT encapsulated, capable of reaching 500 °C with tenths of mW power consumption.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Manufacturer</th>
<th>Sensor model</th>
<th>Manufacturer</th>
<th>Sensor model</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Cambridge</td>
<td>CCS-801</td>
<td>AMS</td>
<td>CCS-801</td>
</tr>
<tr>
<td>S2</td>
<td>Cambridge</td>
<td>CCS-801</td>
<td>Cambridge</td>
<td>CCS-803</td>
</tr>
<tr>
<td>S3</td>
<td>Cambridge</td>
<td>CCS-801</td>
<td>Sgx sensortech</td>
<td>MICS-4514 - OX</td>
</tr>
<tr>
<td>S4</td>
<td>Cambridge</td>
<td>CCS-801</td>
<td>Sgx sensortech</td>
<td>MICS-4514 - RED</td>
</tr>
<tr>
<td>S5</td>
<td>Cambridge</td>
<td>CCS-803</td>
<td>Figaro</td>
<td>TGS-8100</td>
</tr>
<tr>
<td>S6</td>
<td>Cambridge</td>
<td>CCS-803</td>
<td>Sgx sensortech</td>
<td>MICS-6814 - OX</td>
</tr>
<tr>
<td>S7</td>
<td>Cambridge</td>
<td>CCS-803</td>
<td>Sgx sensortech</td>
<td>MICS-6814 - RED</td>
</tr>
<tr>
<td>S8</td>
<td>Cambridge</td>
<td>CCS-803</td>
<td>Sgx sensortech</td>
<td>MICS-6814 - NH3</td>
</tr>
</tbody>
</table>

The fluidics inside the e-nose is formed by 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 micropump (Rietschle Thomas model 2002) is located downstream. One of the gas inlets has a carbon filter and is intended to provide clean air as reference baseline.
The core of the electronics (Figure 2) is a microcontroller Atmel, ATmega2560 with the following main features: an eight-channel, 24 bits analog to digital converter for the acquisition of the sensor resistance values; an eight-channel, 12 bits digital to analog converter that provide heating voltage to the microsensors; a pulse width modulation port for controlling the micropump; an input/output port for activating the electrovalve; four Universal Asynchronous Receiver-Transmitter ports control the communications and the LCD display. It includes local data storage capacity through a uSD card and local data analysis (classification and quantification). Communication to a PC can be done wired through an USB port or wireless through WiFi or Bluetooth. A 3000mAh Li-Po battery provides up to eight hours of continuous operation.

Figure 2: Schematics of the e-nose

The instrument can be controlled using the touch screen or remotely by a software tool developed in LabVIEW (version 12, National Instruments). The control software has two main operation modes: training and classification. In the training mode, a series of known chemicals is presented to the e-nose and the results are stored in a database. In classification mode, the existing database is loaded and the measurements are classified in real time in one of the previously defined classes. The program also displays and controls the measurement parameters (sensor resistance and heater values, ambient temperature and humidity, valve status, battery status, pump power).

2.3 Measurement setup

Two different tests were done in order to check the performance of the developed e-nose: measurements of NO$_2$ were made in order to calculate the limit of detection and the linearity of the response to this pollutant at increasing concentrations and to test the quantification capability. The second tests are related with the discrimination capability of the device.

The measurements of NO$_2$ were made in laboratory conditions. Nitrogen dioxide measurements were made at a constant flow of 200 mL/min. Adsorption time was 20 min and desorption time 60 min to ensure total recovery. Nitrogen dioxide concentrations from 0.1 to 1 ppm were generated through a gas-mixing unit (GMU-06, Ray IE, Mirabel, Spain) from calibrated cylinders (Praxair, Madrid, Spain).
In case of VOCs, headspace with transfer effluent was used as sampling method. In this sense, 10 ml of each sample was prepared and kept in glass vials in a thermostated bath at 30 °C. Once the response of the e-nose sensors was stabilized and the temperature of the samples reached the setpoint, the measurements cycles were programmed. Each measurement cycle consists of two different stages: adsorption and desorption: 60 s of exposition to the sample, followed by a clean air purge for 540 s. These stages are controlled with the status of the electrovalve, when it is switched on, sample headspace is carried to the sensors cell (adsorption) and the resistance of the sensors decreases to a steady value. When electrovalve is switched off (desorption) the response increase to the equilibrium values. A total of 20 cycles of measurements (replicates) were made with the samples of different compounds (Sigma–Aldrich, Spain) in water: acetone, ammonia, dichloromethane, dimethylacetamide, Ethyl Acetate and xylene.

In both experiments, raw data was being stored in disk and feature extraction was made once each measurement cycle was completed. The sensor response is defined as follows:

\[ r = \frac{R}{R_a}, \]  

where \( R \) is the maximum resistance of the device when exposed to each sample and \( R_a \) is the baseline resistance in air.

The data collected were analyzed using a commercial software package (Matlab ®) for programming the feature extraction and the pattern recognition techniques: principal component analysis (PCA) and artificial neural networks (ANNs). The PCA applies a linear transformation to the data and this results in a new space of variables called principal components. A probabilistic neural network (PNN) was used for classification purposes. The PNN was composed by three layers: the input one had three neurons, corresponding to the three principal components; the hidden layer (with radial basis transfer functions) had the same number of neurons as the number of training vectors and a competitive layer in the output (Duda et al., 2001). Leave one out (LOO) cross validation method was applied to the network in order to check its performance. LOO consists of training N distinct nets (in this case, N is number of measurements) by using N−1 training vectors, while the validation of the trained net is carried out by using the remaining vector, excluded from the training set. This procedure is repeated N times until all vectors are validated (Bishop, 1999).

3. Results

3.1 NO\textsubscript{2} measurements

Figure 3 shows the response of 4 commercial microsensors to low NO\textsubscript{2} concentrations at 285 ºC and 350 ºC. A clear trend can be seen in the response, so that the sensors have a better response to NO\textsubscript{2} at the lower temperature tested. The sensors show a small deviation from linearity.

![Figure 3. Response of four commercial microsensors to low NO\textsubscript{2} concentrations at two operating temperatures.](image-url)
3.2 VOCs measurements

Once the responses were stored in the database, Principal Component Analysis (PCA) was made to the data for visualization in a 2D-plot, which is shown in Figure 4. It shows the distribution of the measurements, the clusters corresponding to some compounds (water, acetone, ammonia, dichloromethane, ethyl acetate and xylene) are well separated and only some partial overlapping between water and dimethylacetamide can be observed.

![PCA score plot (variance of each principal component is in brackets)](image)

**Figure 4.** PCA score plot (variance of each principal component is in brackets)

PCA results are confirmed with Artificial Neural Networks classification. Once it was trained, it was validated by leave one out cross validation and the results, as a confusion matrix, can be seen in table 2. The only confusion found was a dimethylacetamide sample classified as water.

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Water</th>
<th>Ammonia</th>
<th>Dichloromethane</th>
<th>Dimethylacetamide</th>
<th>Ethyl acetate</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Dichloromethane</td>
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<td>0</td>
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<td>0</td>
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<tr>
<td>Dimethylacetamide</td>
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<td>0</td>
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<tr>
<td>Ethyl acetate</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>Xylene</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 2: Confusion matrix**

4. Conclusions

A compact versatile e-nose has been home-made and home-developed for environmental applications. It has been tested with NO\(_2\), showing that can detect concentrations of NO\(_2\) as low as 100 ppbv. Also it has been tested with different VOCs showing that it can differentiate among them with a success rate near to 100% in validation.

**Acknowledgments**

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