Identification of pollutant gases and its concentrations with a multisensor array

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Abstract

We have modeled the performance of an electronic nose, composed by tin dioxide commercial sensors, addressed to identify gases of relevance in polluted atmospheres. We analyze the possibilities of determining both the concentration and composition of a mixture of gases containing carbon monoxide, ethanol, methane or isobutane. We have modeled the theoretical response function of the array when sensing a mixture of gases, based on data from these commercial sensors, and designed an appropriate pattern recognition scheme for the simultaneous identification of a given gas and its concentration in the mixture. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electronic nose; Pattern recognition; Tin dioxide sensors; Environmental relevant gases

1. Introduction

A multisensor array of non-specific gas sensors, like the electronic nose device, is an appropriated approach for identifying the presence of a particular gaseous mixture in air. This task relies on the ability of pattern recognition techniques to recognize a characteristic pattern between a limited number of possibilities. This approach has been widely used in numerous applications [1].

A further step is to determine also the concentration of some of the compounds that are present in the mixture. Although the concentration dependence of the response signal of every sensor can be measured for a given gas in the absence of others, it is much more difficult to know the concentration dependence of the responses in the presence of other chemicals.

This is an open question and so it is worth modeling the overall nose response, as accurately as possible to analyze several aspects about the identification of a target gas and its concentration in the presence of interfering chemicals [1–5]. In a previous work, Gardner and Bartlett [6] have used an empirical linear model to simulate the response of semiconductor sensors to a mixture. The concentration dependence of a sensor signal in a gas mixture of N components of concentrations \(c_1, \ldots, c_N\) was calculated as the arithmetic sum of the sensors response to every individual gas in a pure system.

The aim of this work is to analyze the ability of an electronic nose, based on commercial sensors to identify gases of relevance in polluted atmospheres, mainly CO, when the measured sample also contains other interfering chemicals. It is relevant also to identify organic reducing gases emitted in a variety of different processes [7], represented here by isobutane (ISBU). We also analyze the case where the air sample contains gases, which although not pollutants, modify each sensor response and thus masking the correct identification of a given gas. This is the case of the well known tin dioxide (SnO₂) sensors which are sensitive to alcohols, mainly ethanol (EtOH) [8], and methane (CH₄). The last mentioned CH₄ is usually present in urban atmospheres due to emissions from natural gas vehicles, gas stations, residential cooking or natural fermentation processes.

For these reasons we have modeled the overall response of an electronic nose composed by a few number of commercial tin dioxide sensors (Taguchi). We investigate the ability of these arrays to identify the presence of CO, ISBU, CH₄ and EtOH and to determine its concentrations. In this case, the gas concentration ranges between few hundred to thousand parts per million, which is the characteristic range for the Taguchi sensors. The concentration dependence of each sensor resistivity to pure gases diluted in synthetic air was
taken from available Figaros, Inc. data. We analyze the performance of the pattern recognition scheme in determining the concentration of a given analyte in the absence and presence of other active gases.

2. Definition of a theoretical multisensor response

We built a theoretical array of tin dioxide sensors whose response to specific chemical components was taken from the corresponding vendor data sheet. The sensors are labeled with the index “i” (1 < i ≤ M) and the gases with “k” (1 < k ≤ N). It is known [9,10] that for SnO_2 sensors the dependence of the i-sensor’s resistance, R_k^i, with the concentration of the k gas c_k, in the absence of the other gases has been described by

\[ R_k^i = \frac{R_0^i A_k^i}{1 + B_k^i c_k^{m_k^i}} \]  

where R_0^i is the resistance in the presence of a reference gas, A_k^i is specific for each sensor and B_k^i and m_k^i depend on the sensor and the target gas.

We used four Figaros sensors (M = 4). For each sensor, the concentration dependence of R_k^i for CO, ISBU, EtOH and CH_4 was fitted according to Eq. (1). Excellent fits were obtained for all cases and the recovered values of the fitting parameters are quoted in Table 1. The reported uncertainties are those given by the fitting program.

The first task was to determine the ability of the adopted pattern recognition algorithm to identify a particular gas (from the four above mentioned) and its concentration. The combined response of the four-sensor system was reduced by the principal component analysis (PCA) technique to the first two principal components (p_1, p_2), which take into account almost 95% of the total response. The results are shown in Fig. 1. Fig. 2 shows the correspondence between the gas concentration (in ppm) and the absolute value of the first principal component. The main conclusion of the analysis shown in both figures is that identification of the corresponding gas is obtained from its position in the p_1-p_2 plane and its concentration can be obtained from Fig. 2.

Individual sensor drifts, random changes in material properties and noisy signal recording, may affect the response of each sensor. This was modeled by introducing noise in the following way. A set of blurred sensor vectors was constructed varying each sensor resistivity, for a given gaseous component, with concentration according to

\[ R_k = \frac{A_k^i (1 + \varepsilon_k A_k^{\prime})}{1 + B_k^{\prime} (1 + \varepsilon_k A_k^{\prime}) c_k^{m_k^i(1+\varepsilon_m A_m)}} \]  

where A_k^i, A_k^{\prime} and A_m (that are dependent on the sensor i and the gas k, indeed) are given in Table 1 and \varepsilon_k, \varepsilon_k^{\prime} and \varepsilon_m are random numbers in the interval [−1, 1]. Almost 200 sensor vectors, corresponding to varying concentrations of the gases were generated with this procedure. They were afterward projected onto their principal axis space. The resulting first two principal components are shown in Fig. 3. Noise appears as a blurring in the PCA space. Although identification of the different gases is still possible by its position in the p_1-p_2 plane, since the corresponding regions do not significantly overlap, the assignment of the correct concentration needs further mathematical treatment since it does not depend monotonically with the value of any single principal coordinate. Therefore, a neural network approach was used for the overall identification task (both gas identification and concentration). A two-step feed forward neural arrangement was adopted.

The first two principal components (p_1, p_2) of the sensor response vector are first broadcast to a perceptron type arrangement whose output unit gives the gas identification. The same principal (p_1, p_2) components together with the perceptron output enter the second network with three input

<table>
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<tr>
<th>Name</th>
<th>Gas</th>
<th>A</th>
<th>A_k</th>
<th>B</th>
<th>A_k</th>
<th>m</th>
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<td>0.01</td>
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neurons that are then fully connected with a five neuron hidden layer and one output unit. Then, the two final outputs of the arrangement give the normalized response vector that allows the identification of the particular gas and its concentration. The details of implementing a back-propagation definition of the network synapses by minimizing the learning of a given set of examples can be found elsewhere [11].

The results for a set of 600 simulated response vectors under noisy conditions show a 100% efficiency for gas identification. For the concentration assignment the performance is shown in Fig. 4 where the average absolute value of the relative error, defined as the absolute value of the “real concentration” minus the recovered one divided by the latest, is plotted as a function of the percentile (the percentage of the total number of cases). It can be seen that for almost 90% of the “measurements” the concentrations were correctly identified with less than 15% of uncertainty.

Fig. 1. First two principal components for the modeled sensor response accounting 95% of the total response vector.

Fig. 2. Plot of the absolute value of the first principal component vs. gas concentration (in ppm) for the pure gases detected.
3. Simulation of a mixture of gases

We have modeled the overall nose response vector to a given sample when two or more gases, for which each sensor has a non-negligible response, are simultaneously present.

The approach followed in this paper is not linearly additive. For a sample consisting of $N$ gases the total concentration of the mixture is

$$c = \sum_{k=1}^{N} c_k$$  \hspace{1cm} (3)

Fig. 4. Average absolute value of the relative error, define as the absolute value of the “real concentration” minus the recovered one divided by the latest, is plotted as a function of the percentile (the percentage of the total number of cases). Almost 90% of the “measured concentrations” are correctly identified with less than 15% of error.
The relative proportions, $z_k$, are defined as

$$z_k = \frac{c_k}{c}$$  \hspace{1cm} (4)

with

$$\sum_{k=1}^{N} z_k = 1$$  \hspace{1cm} (5)

The particular case when the response of the $i$ sensor is equal to $\tilde{R}_k$ corresponds to ($z_k = 1, c = c_i$).

In order to establish the sensor response for a mixture a recursive procedure is used. For a two-gas mixture that has a given total concentration $c$, and with proportional fractions $z_1$ and $z_2$, the response of sensor $i$ measured by its relative resistance is

$$F^i(c_1, c_2) = \tilde{R}_1(c) + (\tilde{R}_2(c) - \tilde{R}_1(c))g(z_1)$$  \hspace{1cm} (6)

where $\tilde{R}_k$ corresponds to gas $k$ with concentration $c$ measured by sensor $i$ and $g(x)$ is any function that interpolates the modeled value such that $g(0) = 1$ and $g(1) = 0$. In the above formula all $\tilde{R}_k$ are evaluated for a given value of $c$ and the varying parameter is the concentration fraction $z_k$ of each component. This approach is equivalent to that of [6] when the extrapolation function is linear and the sensor response for each gas is also linearly dependent with concentration.

Generalizing, if a third gas is present in the mixture with fraction $z_3$ and such that the total mixture concentration is also $c$, then the relative resistivity of sensor $i$ is assumed to be given by

$$F^i(c_1, c_2, c_3) = \tilde{R}_1(c) + (\tilde{R}_2(c) - \tilde{R}_1(c))g(z_1) + (\tilde{R}_3(c) - \tilde{R}_2(c))g(z_1)g(z_2)$$  \hspace{1cm} (7)

Thus, a simple recursion formula can be implemented for an arbitrary number of active gases.

From the wide variety of scenarios of samples and modeled responses, we have chosen the identification of CO and its concentration when it is sampled in combination either with CH$_4$ or with EtOH. The modeled nose consists of the same four sensors used before.

The sample contains CO with significant mixture of either CH$_4$ or EtOH. Total concentrations were varied between 500 and 2500 ppm, and with $z_k$ covering all ranges between 0

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**Fig. 5.** First two principal components, accounting 93% of the overall projection, for the nose response function to mixtures generated as specified in the text. The overlapping region corresponds to mixtures where the $z_k$ of CO is above 0.8.

**Fig. 6.** Pattern recognition scheme. The response of each sensor $i$ ($F^i$) is first broadcast to a network (A) with an architecture 4–2–1 that identifies the particular mixture between the two possibilities (mixture with CH$_4$ or EtOH). Then, the $F^i$ of each sensor is input to a second 4–5–2 network (B) together with the first output. This second network (B) is separately trained for each of the two combination of gases.
and 1 in steps of 0.1. A linear function for \( g(z) \) was chosen for the sake of simplicity but of course more complex options can be adopted. We generated about 450 samples for each mixture using the above procedure and with noisy responses simulated by fluctuations of the order of the errors of Table 1. Principal components, with 93\% of the overall projection concentrated in the first two components are shown in Fig. 5. The corresponding graph exhibits an overlapping region. This region corresponds to mixtures where \( z_k \) corresponding to CO is above 0.8.

The best strategy found for identification of a particular gas, its proportion in the mixture and the total concentration of the mixture is sketched in Fig. 6. The response of each sensor \( i \) (\( F^i \)) is first broadcasted to a network (A) with two neurons in a hidden layer and one output unit (4–2–1 architecture) that identifies the particular mixture between the two possibilities (mixture with CH\(_4\) or EtOH). Then, the \( F^i \) of each sensor are input to a second network (B) with an architecture 4–5–2 together with the first output. This second network (B) is separately trained for each gas mixture.

![Graph](image1.png)

**Fig. 7.** Average absolute value of the relative error, defined as the absolute value of the “real concentration” minus the recovered one divided by the latest, is plotted as a function of the percentile (the percentage of the total number of cases). Almost 85\% of the “measured concentrations” are correctly identified with less than 10\% of error.

![Graph](image2.png)

**Fig. 8.** Retrieved (network response) relative proportional fraction \( z \) vs. the “real” ones. The trendline and the \( R^2 \) of the adjustment are displayed in the plot.
This approach gave a better performance for concentration identification than the dimensional reduction via principal component analysis. A 20% of the generated response vectors were randomly chosen for the training set. The generalization is done with the rest (80%) of the samples.

With respect to the performance for gas identification, the network (4-2-1) has a 100% of efficiency if the gas other than CO was present with a molar fraction grater than 0.1. In the case of the other gas predominant with more than 89%, the first network has a percentage of confidence of about 60%, consistent with a random election between the two possibilities.

Results for concentration and composition are shown in Figs. 7 and 8. In Fig. 7, we plotted the percentile for the absolute values of the relative error of the adjustment between the network identification of the concentration of the mixture and the “real” ones. It indicates that 85% of the times the concentration is estimated with less than 10% of relative error. Fig. 8 shows, for the relative proportional fraction \( z \), the retrieved values versus the real ones. As it can be observed the adjustment is fairly good. The trend line and the \( R^2 \) of it are displayed in the plot making evident the adequate fitness.

4. Conclusions

We have shown that it is possible to determine the concentration of a given gas of environmental concern when detected in the presence of other sensible gases. This was based on the response of specific sensors (SnO₂) for which information from calibration data sheets were available. A procedure to construct a modeled response when two or more of the sensible gases are simultaneously present was proposed. Although only a few scenarios were chosen, we have verified the ability of the designed pattern recognition scheme to perform the proposed task.

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