Enhanced Selectivity of Sensors Array for Brazilian Brandy Classification

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Abstract: In this paper, we describe solutions to reduce the analysis time and to simplify the pattern recognition of a system designed to discriminate alcoholic substances. An electronic nose was built with that system including five sensors altogether. The sensors are usually used to detect general combustible gases like ammonia, chlorofluorocarbons and vapors from food. The used methodology considers all sensors in a variable regime of operation temperature as a way to increase the number of parameters to reduce the response time. The sensor responses analyzed with fast Fourier transform (FFT) allows to make a discrimination of substances with the first six harmonics. Measures of chemical compounds were made in two different series. The first series as representative of ethyl alcohol family were composed by Brazilian sugar cane commercial brandy and Chilean grape brandy. In the second series we included rice alcohol, Peruvian anise alcohol and a mixture of rice alcohol with two types of herbs identified as "Pimpinella anisum" and "Foeniculum vulgare". The obtained results show a reduction in the analysis time and a direction in the future characterizations to be carried out to select the most efficient attributes to accomplish substance discrimination. The results presented here include the comparison between the average value (DC) and the alternate component rms (AC rms) of sensor responses. To improve the reliability of the electronic nose a system composed by a multilayer perceptron was included to work recovering the signal of each sensor if its polarization voltage changes or if one sensor is switched off. The perceptron was trained with the backpropagation algorithm using the voltages of sensor in steady state condition, before and after injection of the sample to be recognized, as training patterns.

Key-Word:- Electronic Nose, Gas Sensors, Pattern recognition, Neural network.

1 Introduction

Research on the development of gas sensors has been directed towards systems with the ability to recognize several multiple-component chemicals, in order to avoid expensive and non-portable laboratory instrumentation systems [1,2].

Commercial gas recognition systems have been developed and are available. These systems usually use thick-film tin dioxide based sensors. These sensors have their conductive characteristics altered due to the interaction of tin dioxide molecules with gas form compounds [3,4]. That interaction is what defines the sensitive capabilities of this material.

The pioneer work using tin dioxide to detect reducing gases and vapors was carried out independently by Taguchi [5] and Seiyama [6] in 1962. In the past three decades, a great deal of research effort has been devoted to modeling the properties of tin dioxide materials [7-9]. Today, metal-oxide gas sensors, mostly tin dioxide gas sensors, have become the most commonly used types of chemical sensors [10, 11].

Application of metal-oxide sensors is greatly diversified, ranging from environmental monitoring and disaster prediction to industrial process control. However, in spite of these research efforts and a wide variety of applications, the major technical difficulty of this type of sensor is its lack of selectivity, which restricts its further applications in areas where multiple gases are present and need to be distinguished. On the other hand, two new trends were developed in the mid 1980s. The first is the concept and practice of sensor array instrumentation [12-14]. The purpose of a sensor array is to discriminate multiple components of a mixture with the aid of multivariate regression algorithms with a minimized penalty of accuracy. Most of the previous and current work on chemical-sensors arrays have concentrated on application of multivariate regression algorithms while using commercial and discrete gas sensors. The second is the use of silicon-based micro-manufacturing techniques to fabricate micro-sensors [15].

The aim of our work is to present the results obtained to identify gaseous substances, controlling
the operation temperature of sensors in dynamics condition. Different periodic wave forms were applied to the heater of sensors. Response patterns were analyzed with fast Fourier transform. Besides that it was included a study with mean value (DC) and rms value (AC) as an option to simplify the signal processing. To increase the confiability of the system we present a system to recover the electrical response of a sensor if the normal operation fails.

1.1 Tin Oxide Sensors

Over the past few decades solid-state gas sensors based on SnO₂ have become the predominant devices for gas alarms used in domestic, commercial and industrial ambient. These sensors require high operational temperatures to allow a greater number of carriers to reach the SnO₂ conduction band. Modulation of the sensor element temperature serves as a new control parameter to define the quantity of free electrons in the composite; this new parameter is then capable of enhancing the selectivity of these kinds of sensors [16, 17].

2 Experimental

Two series of measures were accomplished in order to recognize gaseous samples. In the first series of measures, with operation temperature of the sensor in constant regime, four types of commercial Brazilian sugarcane brandy (commercial name: "3 Fazendas", "Pirassununga 51", "Pitu" and "Chave de ouro") and Chilean grape brandy ("Pisco") were used.

The volume of each sample was varied in the range 5 - 25 ml. In the second series, with operation temperature of the sensor in variable regime, four types of Brazilian sugarcane brandy ("3 Fazendas", "Pirassununga 51", "Pitu" and "Chave de ouro"), Chilean grape brandy ("Pisco"), Peruvian anise alcohol (commercial name "Anis Najar", distillation of anise in grain with neater alcohol), mixture of rice alcohol with "Pimpinella anisum" and mixture of rice alcohol with "Foeniculum vulgare" were used. The mixture of rice alcohol with herbs was: 50ml rice alcohol with 9gr "Pimpinella anisum" in grain and 50ml rice alcohol with "Foeniculum vulgare" in grain. These mixtures were softened during two months.

2.1 Sensors and experimental set-up.

In this study the sensors used are usually specified to detect general combustible gases. Table 1 shows the sensitivity of sensors used in this array. These sensors require temperatures around 350°C to be operational. In order to achieve these temperatures, each unit has a heating resistance associated to the sensor element.

<table>
<thead>
<tr>
<th>Sensors*</th>
<th>Higher sensitivity to</th>
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</thead>
<tbody>
<tr>
<td>TGS-813</td>
<td>General combustible gases (methane, ethanol, isobutane, hydrogen). 500–1000 ppm</td>
</tr>
<tr>
<td>TGS-822</td>
<td>Organic solvents (alcohol, toluene, xylene). 50–5000 ppm</td>
</tr>
<tr>
<td>TGS-824</td>
<td>Toxic Gases (ammonia). 30–300 ppm</td>
</tr>
<tr>
<td>TGS-832</td>
<td>Chlorofluorocarbons (R-134a, R-22). 100–3000 ppm</td>
</tr>
<tr>
<td>TGS-881</td>
<td>Volatile Gases</td>
</tr>
</tbody>
</table>

* Sensors of SnO₂ from Figaro Engineering Inc.

Tab. 1. Types of sensors used and their sensitivity.

The sensors were set into a gas chamber jointly with both a temperature and a relative humidity sensors. A full power supply structure as well as a data acquisition system had to be developed in order to allow experimentation. A specific virtual instrument was designed to facilitate the definition of sensor operating parameters such as the sensor element and heating resistance polarization levels. Another virtual panel was used to view and store, on hard disk, the measured data as it is acquired [18].

A series of measurements were conducted with different kinds of samples present in liquors. The first step, before the compound injection into the gas chamber is cleaned with synthetic dry air. The next step after the cleaning procedure is to use a medical syringe to extract a volume of air saturated with the sample from its bottle, and subsequently inject a volume of sample into the gas chamber. The data acquisition system has to be switched on before the gas is injected into the chamber so that the dynamic sensor response can be recorded.

3 Feature Extraction and Pattern Recognition

Improving the sensor selectivity has been the goal of a great deal of work over the last few years. One strategy consists of using non-selective sensor arrays and appropriate pattern recognition system capable of recognising simple or complex odours. The term 'Electronic Nose' has been widely accepted to refer to this kind of system. In this case, measurements of the steady-state sensor response are used to train an artificial neural network [13-15]. Other approaches rely on dynamically characterising the sensor response, so obtaining a new set of parameters to improve the sensor selectivity.

3.1 Constant operation temperature

An array of non selective tin oxide gas sensors and a pattern recognition system, artificial neural networks, were used in order to recognize gaseous compounds (four types of commercial Brazilian brandy, Chilean grape brandy and rice alcohol). In
this case steady-state sensor response and operation temperature of the sensor in constant regime were used, Figure 1, [19].

Fig. 1 Sensor responses for constant operation temperature.

3.1.1 Recognition error versus time

In order to classify the studied patterns, an artificial neural network multilayer perceptron (MLP), trained with a backpropagation algorithm was used to recognize the substances. MLP was formed with 5 neurons in its input layer, 8 neurons in the hidden layer and 6 neurons in the output layer. A first methodology used sensors in constant operation temperature condition (heater voltage 5V DC). The data, obtained in steady-state condition, as that of Figure 1, considers the conductance ratio \( G_1/G_0 \) as input data to the network; \( G_0 \) is the steady-state conductance before the sample injection and \( G_1(t_1) \) the steady-state conductance after the injection [19]. This last value is defined if the sensors conductance remain inside of a variation minor than 5% during 10 minutes. \( T_1 \) is the delay time to measure \( G_1 \), it is used as parameter to evaluate the recognition error of studied substances, as shown in Figure 2. Independently the quality of result, to recognize a substance, a response time of 800 seconds is required, this value is a very long time for a instrument with preferential application on line.

3.1.2 Signal reconstruction

A multilayer perceptron was used to reconstruct the signal of a sensor array. It was chosen an artificial neural network by the complexity of the problem and by no existence of a model that take in consideration all the involved variables. For the reconstruction of sensor signal, a multilayer perceptron was used, with 4 neurons in the input layer and 4 neurons in the output layer. The number of neurons in input layer is the same of sensors number. The training set was built using as input patterns the voltage on sensors extracted in steady state experiments.

Results from that simulations are presented in graph of rms error of output network against number of presentations, as shown in Figure 3. It is observed that using 3 or more neurons in hidden layer doesn't alter the error on output network significantly. However, observing the output of net, is not appreciable a difference on response with 2, 3 or more neurons into hidden layer.

Using hidden layer with two neurons the rms error increases. However, as the objective of this layer is to correct the signal of sensors, the use of two neurons is a commitment among a low value of rms error of output network and its generalization. As the number of neurons in hidden layer is smaller than the number of sensor, the network seeks a representation that minimizes the error.

The use of a network to reconstruct the sensor signal is approximately 25%. However, signals on other sensors are also altered. If the number of sensors is sufficiently large, a better reconstruction of signal of inactive sensor is expected. To verify this hypothesis, a simulation was accomplished with synthetic patterns.

The number of sensors was altered from 4 to 64. The number of neurons in hidden layer was chosen as being the half of neurons number in input layer. Training sets were generated with 120 patterns and 6
hypothetical samples. The rms error in network was calculated being held all the sensors active or inactive one per time. Simulations results can be observed in Figure 4. It is observed that rms error decreased when number of sensor increased. The rms error when one of them is maintained inactive is about 100 times greater than when all the sensors are in activity. In agreement with these simulations, the number of different sensors suitable to an experiment is approximately 16, when the number of species is of the order of 6.

3.2 Cyclic operation temperature
To reduce the response time, a second methodology was implemented, controlling the operation temperature of sensors in dynamics condition. Aiming at this, periodic waveforms were applied to the heater of the sensors, including rectangular, triangular, positive slope and negative slope as current polarization, for period of 22s, 44s and 68s. The experiments were made with compounds of the second series. Sensor responses to rice alcohol corresponding to rectangular waveform are shown in Figure 5.

Sudden changes which result from the gas introduction disappear rapidly at the change of heater voltage after the first 3 or 4 period with a clear trend to stay almost uniform and periodic patterns. This means that the data obtained after the gas introduction, forming a periodic wave can be utilized for pattern matching and therefore, fast discrimination can be expected from the periodic operation of sensor.

3.2.1 Discrimination for periodic response patterns using FFT
As a method for classifying response patterns, fast Fourier transform (FFT) was utilized in order to analyze the first 3 periods after the sample injection.

The six data from 1st to 6th harmonic of the amplitude spectrum obtained were used in order to classify the substances. Figures 6 and 7 show the harmonics magnitude versus sensors TGS813 (1), TGS832 (2), TGS824 (3), TGS822 (4) and TGS881 (5). In Figure 6, the discrimination for brandy samples, with 3rd harmonic of sensor responses are shown. In Figure 7, the discrimination for herb samples with 3rd and 4th harmonic of sensor responses, are shown.

3.2.2 Observed value DC and AC rms
Differences between responses either for DC voltage or concerning the forms of response waves can be observed in Figure 5. Analysis is accomplished by mean of characterization of average and AC rms value. This analysis was carried out by implementing a LabVIEW...
program which makes the calculation of average and AC rms value [20].

AC value is obtained by subtracting the DC value from the input signal before the rms value calculation. The analysis that follows, takes into account the differences between the initial DC value and AC rms value in the initial 350 seconds, that is, before sample injection and the final value DC and AC rms after 600 seconds, after sample injection.

Figure 8 shows the result for distilled alcoholic drinks for heater period of 22 seconds. The average and standard deviation for several experiments for a same substance is presented. For the herb samples the results are presented in Figure 9, where the average value and standard deviation for several experiments with the same samples are shown. The values presented correspond to a period of 22 seconds applied to the heater resistor.

**Fig. 8.** Variation of DC and AC rms values for the distilled alcoholic drink samples with period in the heater resistor of 22s.

**Fig. 9.** DC and AC rms values for herb samples with period in the heater resistor of 22s.

### 4 Discussion and conclusions

A multilayer perceptron reconstructs partially the response of a sensor array, when the polarization voltage on sensor is altered or when one sensor is inactive.

In the training, the perceptron is made auto-associative and voltage in steady state on sensor array, before and after the injection of the sample, are used as patterns. Perceptron is capable of reproducing with reasonable fidelity both response in steady state and transient response of sensor. The perceptron can have only 1 hidden layer. A larger number of hidden layers don’t produce better results. The number of neurons in the input and output layer of perceptron is equivalent to number of sensors. As rule of the thumb the number of neurons in hidden layer can be made half of total sensors number.

The capacity of the artificial neural network to reconstruct the signal increase with the number of sensor up to value above which the gain is small. For six samples the optimum number of sensors is approximately 16.

The signal reconstruction using the method of this work allowing to suggest the use of neural network for signal compression in application such as here presented. Fails on the array are detected by comparison measured voltage on sensor with values obtained from artificial neural network.

Periodic operation temperature of gas sensors allows to get much information as well as to reduce the measure time of sensor response. Samples of equivalent chemical composition were discriminated, having a major fraction of similar component with a minor quantity of herb. Forms of heating voltage: rectangular wave, negative slope and positive slope presented better results. First six harmonics of magnitude spectrum allow making discrimination of the studied substances. To classify aromas was necessary 66s approximately, time corresponding to the first three periods of sensor responses after sample injection.

Measures were accomplished in order to recognize gaseous samples belonging to two different series of chemical compounds. One characterized as alcohol and other as a mixture of pharmaceutical alcohol and herbs. In first series, four types of commercial Brazilian brandy and Chilean grape brandy as representative samples of ethyl alcohol family were used. In second series of measures, rice alcohol, Peruvian anise alcohol and two type of herbs identified as *Pimpinella anisum* and *Foeniculum vulgare* were used and recognized.

The DC and AC rms values, present a discrimination capacity to classify brandy samples. As it is an extremely simple method, is very important that it could be implemented either as electronic circuit (hardware) or software tool.

The AC rms value presents lower dispersion than the DC value as shown in Figure 8. DC and AC rms values present higher sensitivity for larger periods applied to the heater resistor. This is shown in Figure 10, where average values and standard deviations are
presented for all samples. Another verification is that for herb samples, such as rice alcohol, *Foeniculum Vulgare*, *Pinpinella Anisium* and *Peruviam anise* alcohol, this method does not present enough sensitivity because the dispersion is higher than the difference between the samples (See Figure 9).

This method presents a pretty high potential if used together with artificial neural network, once it increases the discrimination level and reduces the analysis time.

![DC and AC rms value variations for all the samples](image)

Fig. 10. Sensitivity for the two heater periods T=22 and T=68 seconds

It is also evident that using variable operation temperature the potentialities in gaseous compounds analysis is increased conform similar results obtained by Kunt [21].

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**5.0 References**


