Quantification of volatile compounds present in organophosphorus compounds, through the variation of the electrostatic potential in chemical-resistive sensors

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Abstract. In the present work is presented a method capable of quantifying a pesticide (organophosphate) or an organic product (Prunus persica), by means of a matrix of chemical-resistive sensors, which are part of a multisensory system called electronic nose. The sample is placed in a concentration cabin, where a time is established where the amount of volatiles emitted increases, after the fixed period, a flow of these volatiles is generated towards the chamber where the matrix of sensors is arranged, where the volatiles generate enough force for the free electrons of the semiconductor material to react, allowing a constant flow of electric current, this output signal is captured by means of an acquisition card, once all the data is recorded and by means of a pattern recognition system, analysis of main components, the variation of the electrostatic potential provided by the sensors was related to the amount of volatiles present in the sample. The sensors showed a high change in the electrostatic potential, corroborating the capacity of detecting the number of volatiles thrown by the sample, this response accompanied by the statistical analysis has the capacity of creating groupings, one of them is the pure organic product and another is this one, with the presence of the selected chemical compound. With this, a methodology was established that is capable of detecting a change in the electrostatic potential and relate to the number of volatiles emitted by the sample of study, through a matrix of sensors, coupled to a multisensory system.

1. Introduction

Metal oxide semiconductor (MOS) gas sensors are widely used nowadays, due to their electrical conductivity, which is regulated by the reaction that the semiconductor has with the gases present in the control space. As they are formed by dielectric materials, they have different physical and electrical properties: conductivity, dielectric loss, polarization, among others. These properties give them the ability to detect, amplify and modulate electrical and optical signals [1].

The MOS have a very wide applicability, which include, the environmental field, with the control of air quality, industrial process safety, with the detection of toxic and explosive gases, in health applications, where it can be given advances of a medical diagnosis through breathing, in the quality of agricultural products, such as the presence of pesticides in excess, with which they violate the minimum limits allowed. This widespread use of MOS for various applications is due to its low cost, simplicity, high sensitivity, flexibility in manufacturing and excellent compatibility with modern electronic devices [2].
One of these electronic devices is the electronic nose (E-Nose), which is a multisensorial method, that shows advantage over other traditional analytical methods, being friendly with the samples, since it has the capacity to detect the emitted volatiles, without carrying out pre-treatment to the sample and therefore it does not destroy it. A variety of these devices contain MOS sensors, which generate a change in electrical resistance as a result of the chemical reaction. Based on these changes in electrical resistance, the data can be used to predict concentrations or other characteristics of an identified compound [3].

The E-Nose is an instrument which is designed to distinguish complex odors, resembling the human nose, through a series of sensors. A common configuration of this device consists of a series of gas sensors, which detect the volatiles emitted by the samples, also has a converter from analog to digital, coupled to a computer that has a pattern recognition algorithm. This method has a very wide range of application, compared to traditional methods, given its low cost, the rapid detection that presents and being a friendly method with the sample [4]. Once the sensors of the electronic nose collect the data of the volatiles emitted by the sample it is necessary to have pattern recognition algorithms capable of analyzing them, and thus have a qualitative or quantitative classification, depending on the objective of the research, which have been widely used in various works include, artificial neural network (ANN), convolutional neural network (CNN), principal components analysis (PCA), partial least squares regression (PLS) and support vector machine (SVM) [5].

The electronic nose is a multisensory system that has been used in research work in the branch of agriculture and food products, which several with respect to the characteristics of the volatiles that detect the sensors, you can determine the maturity of different products (banana, guava), quality (apple), battery detection (cheese), contamination detection (wheat), adulteration and shelf life determination (milk), which shows the good performance of this analysis method when working with fruits or vegetables to provide a quality inspection, a fast and more consistent procedure [4,6].

Colombia is a country that has most of its economy revolving around agricultural processes, due to the great variety of thermal floors that different regions have, these are raw materials for products with added value, or simply for daily consumption. One of the major disadvantages of these processes is the indiscriminate use of pesticides, which are used to manage pests and diseases, which do not have the side effects that this produces, food contamination, environmental degradation by contaminating water sources and wages, long-term diseases in animals and humans, who consume them and those who are responsible for their cultivation [7,8]. In this work, several sensors will be implemented in the electronic nose to see its electrical response with respect to the volatiles emitted by a fruit of the region (*Peach-Prunus persica*). In addition, the response will be analyzed if a characteristic pesticide is added in its cultivation process, with the data obtained using a pattern recognition algorithm to demonstrate if a respective classification can be made [9].

2. Materials and methods
The variation of the electrical potential in the chemical-resistive sensors was carried out in the peach (*Prunus persica*), first pure and then with the addition of different concentrations of pesticides, according to the amount of volatiles emitted by each one of the samples, the sensors react or not, and based on these, the capacity that the multisensory system has to quantify the presence of pesticides was evaluated. The following explains where the samples were taken from, how the samples were prepared, the sensors used in the electronic nose and the data processing system used.

2.1. Sample preparation
For the tests carried out, fruits were taken from the surroundings of Pamplona, Norte de Santander, Colombia. The peaches were added a pesticide selected by a professional, who made the choice of a pesticide that has the active component organophosphate, since this is one of the most toxic in the crop and can present long-term health problems for consumers and farmers. The samples were prepared with volumetric material in the laboratory to guarantee precision in the measurements, all the tests were made in triplicate.
2.2. Electronic nose
For the detection of the volatiles in pure samples and those containing a controlled amount of pesticide, an electronic nose was used which was manufactured at the Universidad de Pamplona, Colombia, (Figure 1). The sample cabin is observed, where the emitted volatiles are concentrated, then an internal pump transports these volatiles to the cabin where the chemical-resistive sensors are located, where these show a variation in the electrostatic potential depending on the volatiles present.

![Figure 1. Electronic nose Universidad de Pamplona, Colombia.](image)

The choice of these sensors was based on the information collected from the volatiles normally emitted by the study fruit (peach). The sensors used are highly sensitive to these volatiles and have a long-life span. Table 1 describes each of the gas sensors used in the electronic nose. The eight gas sensors used for the development of the equipment were TGS (Taguchis) semiconductor type from the Japanese company Figaro Inc. [10].

| Table 1. Sensors used in the electronic nose. |
|---------------------------------------------|
| **Figaro gas sensor** | **Type of gas**      |
| TGS-821       | Hydrogen             |
| TGS-813       | Combustible gases    |
| TGS-832       | CFC                  |
| TGS-825       | Hydrogen sulphate    |
| TGS-880       | Food odors           |
| TGS-822       | Organic vapors       |
| TGS-800       | Air pollutants       |

The process of analysis of the fruits through the electronic nose has three steps, which have characteristic times that allow an optimal sampling, this process was made based on previous research work, conducted by the research group:

- The sampling stage where the volatile compounds of the fruit are concentrated in a chamber for subsequent data collection, in this stage the samples are hermetically sealed (4 minutes).
- A second stage that counts on the measurement through the chemical-resistive sensors where they respond to the presence of the volatile compounds of the sample, taking into account their manufacture and principle of operation, so that the sensors take a temperature suitable for an adequate reaction to the exposed volatiles (5 minutes).
- Finally, the acquisition and processing stage of the electrical signals coming from the sensor matrix, for their subsequent analysis (4 minutes).
2.3. Data processing
The pattern recognition process is a primordial phase in the analysis done by the electronic nose, a good result goes hand in hand with a good reaction of the sensors to the volatiles present in the sample. Based on the electrical differences presented, the data collected are organized in an X matrix, with \( n \times m \) dimensions where each column (m) shows the information collected by the sensors and each row (n) represents each of the samples analyzed, first without the presence of pesticides and then with a certain concentration.

These methods are also characterized by dividing the samples, in a set with which the prediction is made, which is used to observe the generalization capacity of the model and another with the calibration set, with which the model is adjusted.

2.3.1. Principal component analysis. PCA is an unsupervised method of pattern recognition where the \( X \) matrix is broken down into a product of two other matrices: scores (T) and loads (Pt). Having these two matrices calculate the principal components (PC) using the corresponding algorithms through MATLAB. Generally, but not always the first PC, contains the maximum explained variance of the data set of interest. The next PC, the second one contains an explained variance lower than PC1 and higher than PC3, and so on [11].

The results of the decomposition of matrix \( X \) into scores and loads can be interpreted graphically: the score matrix provides information about the sample (lines of matrix \( X \)), while the loads provide information regarding the variables (columns \( X \)). To interpret these graphs, it is necessary to observe the negative and positive parts of each PC chosen during the development of the PCA model.

3. Results and discussion
The main objective of the research is to observe the capacity that the metal oxide semiconductor gas (MOS) sensors have, to capture the intensity generated by the volatiles present in the sample, these generate the reaction of the electrons present in the semiconductor material, giving a signal with which the electronic nose can create the sample footprint, as seen in Figure 2, a satisfactory response is shown, since a change in the representative electrostatic potential is evident, in most of the chemical-resistive sensors present in the E-nose. This response shows the correct choice of sensors, which are suitable for determining the volatiles present in the sample (peach). These results are consistent with previous work done on peaches, which shows an electrostatic change of the chemical-resistive sensors coupled to the electronic nose, to detect the stages of ripening fruit, in turn to respond to the presence of different fungi that generate decomposition in the peach [12,13].

![Figure 2. Sensor response to pesticide-free fruit.](image)
Based on this satisfactory response of the chemical-resistive sensors, we proceeded to take the samples, adding different concentrations of the chemical compound and thus observing if the electronic nose coupled to the system of pattern re-command has the capacity to group the samples, depending on the intensity in the signal due to the electrostatic change generated in the sensors. The PCA analysis showed the good performance of the multisensorial system (Figure 3), grouping according to the characteristics of the samples, the pure fruits (blue box) and with the presence of the chemical compound (red box), which evidences that the implementation of the MOS sensors, coupled to the E-Nose and the pattern recognition system, to group the samples according to the variation of the electrostatic potential, characteristic of each one of them. This result was expected compared to those shown by previous works, in one of them they group different types of rice, according to the signal from the sensors, in another one given the intensity emitted by the volatiles present in the peach and captured by the sensors, they monitor and group the fruit, according to its growth cycle [14,15].

![Figure 3. PCA pure fruits (blue) and with pesticide (red).](image)

**4. Conclusion**
The metal oxide semiconductor gas sensors (MOS), showed that they have the capacity to detect the volatiles present in the fruit (peach), due to the change of the electrostatic potential in the samples, both in pure fruits, and in those containing a known concentration of pesticide, this evidences two important aspects, the first the appropriate choice of MOS sensors, based on the known information of the volatiles emitted by the fruit, and the second the possibility of further studies, based on the dielectric differences shown by the sensors due to a chemical reaction carried out inside.

Once observed the satisfactory response of the MOS sensors, which are coupled to the E-Nose, it was proceeded to implement a principal component analysis (PCA), this evidence that, having a variation of the electrostatic potential of the chemical-resistive sensors, which represents the presence of the emitted volatiles, it is possible to make an appropriate classification of the fruits (peach) without pesticides or pure, with respect to the fruits to which a known concentration of the chemical compound was added, grouping them in different classes.

The next step for this study is to evaluate the capacity of the MOS sensors, together with the electronic nose and a pattern recognition algorithm, to have an optimal detection and classification of the fruits with presence of pesticide with an approximate concentration to the limits allowed by the national and international regulations.

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