Detection of deltamethrin remains in mint with an electronic device coupled to chemometric methods

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Abstract. This article describes the possibility of an electronic device coupled with chemometric methods to detect and discriminate between mint treated with an insecticide containing deltamethrin and the untreated mint. A multi-sensor system is designed and realized mainly by a commercial metal oxide (MOS) gas sensors array, a data acquisition board, and a personal computer coupled with chemometric methods to achieve the objective. In each experiment, data were collected for 510 s using the multi-sensor system. Then, the principal component analysis (PCA) statistical data projection method and the support vector machine (SVM) machine learning method were exploited to prove the ability of our laboratory prototype to differentiate untreated mint from deltamethrin mint treated. The data projection with principal component analysis algorithm indicates that this method can classify the data with 98% of the variance by the first three main components (PC1, PC2, and PC3) with remarkable separation between mint groups while that the machine support vector (SVM) method was able to distinguish samples with a success rate of 95%. As such, this work offers the ability to identify the mint treated from untreated one using a simple, fast, and inexpensive multi-sensor system.

1 Introduction

Recognized by its various uses, mint (Mentha Spicata L.) [1] is an aromatic herb very widespread and consumed throughout the world and in particular in Morocco (mint tea), recognized since antiquity as a medicinal plant; it is also used in the preparation of cosmetic products due to the benefits of its essential oils.

To assess the quality of grown foods, traditional techniques are used, such as gas chromatography coupled with mass spectrometry (CPG-MS) [2], analysis by gas chromatography coupled with olfactometry [3], or ion mobility spectrometry (IMS) [4] … etc. These techniques are expensive and require a trip to the laboratory, hence the idea of simplifying the quality control process. Lately, an electronic nondestructive tool is very widely used to assess the quality of food; it is the electronic nose or multi-sensor system. This tool has been used by several researchers in the food industry for the control of the quality and to identify counterfeits. This study comes to facilitates the process of controlling pesticides in the mint after knowing that the National Office of Sanitary Safety of Moroccan Food Products (ONSSA) found that Moroccan mint intended for consumption is poisoned by pesticides. The analysis of the samples taken has demonstrated very high non-compliance rates, either because of the use by operators of unauthorized products or to excessively elevated residue levels of homologous products.

To facilitate the control mission, a measurement prototype based on gas sensors was designed and produced. Second, the principal component analysis and carrier vector machine algorithms were applied to select the processed mint from the untreated mint.

2 Materials and methods

2.1. Mint preparation and sampling

In this work, the mint (Mentha Spicata L.) used is collected from a local mint field planted in our school located in the city of Khouribga, Morocco. A part of the field is kept without treatment while a part has been treated with the product decis fluxx. The last contains 25g/l of deltamethrin, a highly hazardous insecticide used against insects or snakes that is effective in touch and ingestion, chemically recognized under the formula: $C_{22}H_{19}Br_2NO_3$.

By respecting the rate subscribed in its instructions, a mixture for the spraying was prepared, including 2 ml in a liter of potable water. In this case, only 1 liter of the solution was prepared and utilized to spray the treated area once.

For the sampling, a sample of 5g ± 0.1g of fresh and carefully picked mint of each type (treated and untreated) was taken for the experiment five times during the first four days after treatment.

2.2 Experimental setup

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 https://doi.org/10.1051/e3sconf/202235101023

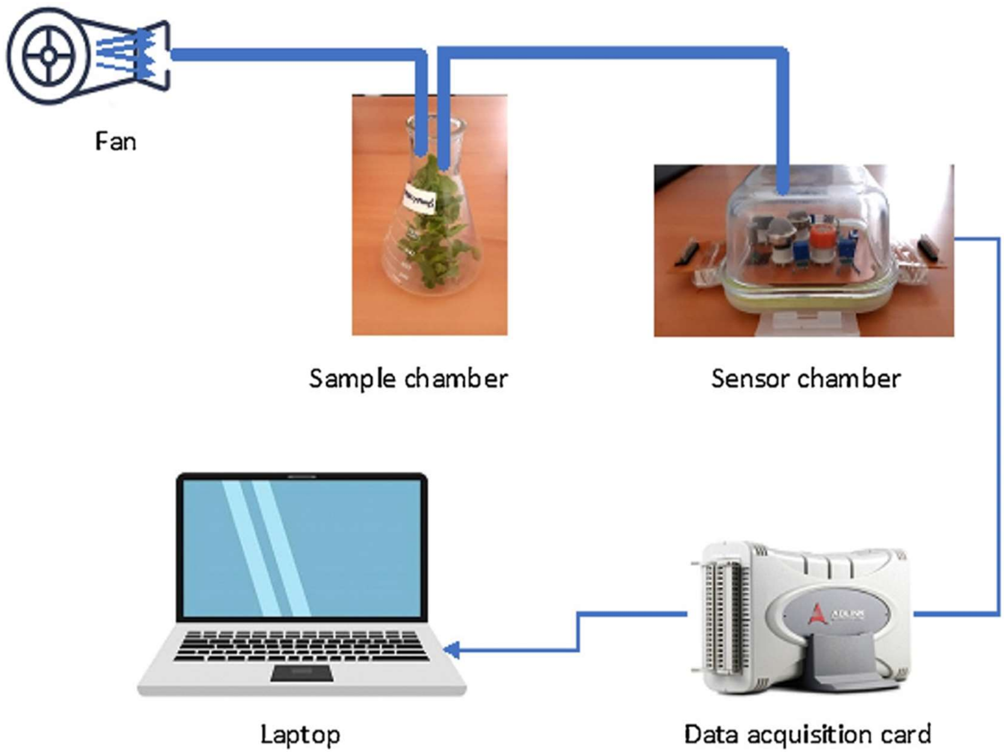

Fig. 1 Schematically representation of the portable system utilized.

A multi-sensor system is a device inspired by the human nose used to detect and recognize odors [5], it generally consists of the hardware part of a sensors network that plays the role of a receiver and a software part that uses the pattern recognition algorithms.

Our tool is composed of a ventilator, a sampling chamber, a chamber that contains the sensors network, a conversion and protection circuit, a data acquisition card (ADLINK USB 1901 DAQ), and a laptop. Figure 1 represents the tool designed; it was used in a previous study [6] also carried out on mint but with another insecticide which is malathion.

For metal oxide sensors, the key element is the sensitive material that reacts to a change in the surrounding environment. Changing the environment around it modifies the characteristic of the sensitive element reflected by a signal. Consequently, each sensor generates a signal of its own. Table 1 list the sensors that make up the sensor array.

Table 1. Sensors make up the network.

Sensor	Target gas
TGS-822	Vapors of organic solvents such as ethanol
TGS-2620	Volatile organic vapors
MQ-136	Hydrogen sulfide, ammonia, Air, and carbon monoxide

The part sensitive to the variation of odors is the sensors array; it is mainly made of three metal-oxide-semiconductor (MOS) gas sensors: two manufactured by a Japanese company, namely Figaro Engineering, and one by a Chinese company MQ. Preliminary tests were carried out with a matrix of 12 sensors to arrive at the choice of these three, which reacted well in the presence of mint.

A handicap was observed during data acquisition, and by consulting the documentation relating to the acquisition card, it was found that the latter is conserved by a high impedance in its analog inputs so as not to damage it, which pushed us to design a conversion and protection circuit, it is composed of an amplifier in buffer mode for impedance matching namely TL082CP, and for protection, a simple electronic diagram used in we find a resistor, a capacitor, and a Zener diode.

Also, a stabilized power supply was designed, equipped with six outputs for powering the different components of the system: three outputs of 5V for the matrix of the sensors, a + 15V output, and one other of -15V for the conversion and the protection card and a 12V output for the ventilator.

2.3 Data processing

After the mint samples (deltamethrin treated or untreated) were subjected to the process of our study, that is, it was ventilated, and the sensors interacted with the headspace of the samples, the different responses from the sensors were recorded, and these raw data were observed as part of pretreatment in order to extract the characteristics that will benefit us in accessing to the desired goal, which is to distinguish between the two categories of mint. But before that, the accumulated raw data needs to be prepared. To achieve this, the data were normalized, and as this can go through several methods, it was chosen in this study to normalize them by column,

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meaning that by dividing each column by its maximum value according to the following equation:

$$Xij = Xij / (Max\ (Xi)) \quad (1)$$

Xij is the ith sample of the jth sensor, Xi contains all the p responses for the sensors of the ith sample.

The principal components analysis (PCA) method was exploited to form an idea of the data sets resulting from the sensor matrix. Invented by Karl Pearson in 1901 and integrated into mathematical statistics by Harold Hoteling in 1933[7], principal component analysis (PCA) is one of the furthermost often utilized methods in signal processing to diminish the dimensions of large-dimension matrices to two or three dimensions only.

The lack of a decision rule in the principal components analysis allowing us to recognize the unidentified samples prompted us to use the support vector machine (SVM) method. The latter was created by Vladimir Vapnik in the 1990s [8]; the support vector machines (SVM) method, is a method of supervised classification that consists in carrying out a separation between the data groups with a hyperplane that maximizes the margin which dissociates them.

3 Results and discussion

3.1. Sensor's responses and features extraction

The first step after acquiring the data by the acquisition card and LabVIEW software is to consult the signals from the sensors' responses and to extract the main characteristics that allow distinguishing between the signals and through them between samples.

Initially, a remarkable change in the sensor's responses intensities in the presence of mint was recorded, which proves the capacity of our device to detect mint. Then, by bringing together the different signals in the existence of the deltamethrin treated mint and the untreated one, it's noticed a remarkable change in the sensors responses intensities according to the sample's nature, thus demonstrating the capacity of the sensors array to sense the variation in the composition of the mint odor. The response intensities for the treated mint are very high compared to the intensities of the untreated ones, which allowed us to take the following main characteristics:

- The maximum signal value.
- The average signal stabilization value in the time interval from 450s to 500s.
- The signal area of each sensor between the 40s and 240s.

Knowing that it took 5 samples per day during the first 4 days after the application of the insecticide, the resulting data set is therefore made up of nine columns (3 responses from the three sensors * 3 main features) and forty rows (5 samples * 2 mint types (treated or not) * 4 days).

The new data set composed of the characteristics extracted from the sensors' response signals will subsequently be utilized in machine learning algorithms.

Figure 2 represents an example of responses to the treated mint and to untreated one collected from the TGS822 sensor for a day.

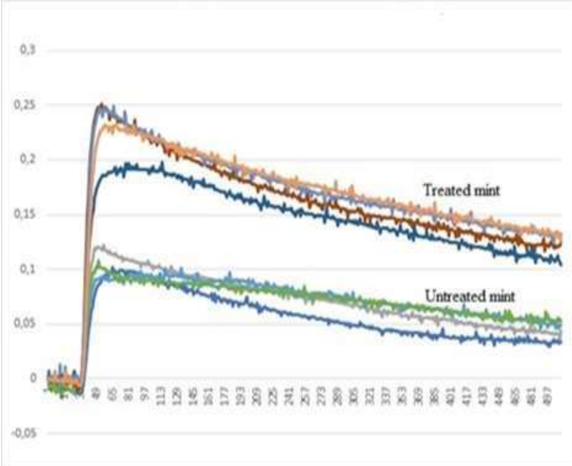

Fig. 2. Example of responses collected from TGS822 sensor for a day.

2.2 Principal component analysis (PCA) results

Principal Component Analysis (PCA) is a method commonly used with multi-sensor systems and electronic noses, in this study its objective is to move from a nine-dimensional data space to a data space reduced with just three dimensions (PC1, PC2, and PC3), which will allow us to view the data properly and to judge the ability of our tool to differentiate between mint treated with deltamethrin and untreated mint. The results of the PCA algorithm are shown in figure 3.

This method achieved a very good contribution rate of about 97.5% with the first (PC1) contributing with 64.57%, the second (PC2) with 19.59%, and the third (PC3) with 13, 30%, best than our first study where it has been used just two principal components, and the cumulative contribution was 85% [8]. The graph plot explains that the groups of untreated mint and those of treated were comparatively separate and somewhat overlapped, consequently, it's therefore simple to rank them with a good success rate.

2.3 Support vector machines (SVM) results

In the support vector machines (SVM) method, the training data groups choice is made beforehand since it is a supervised method. The classification was created using the linear SVM classifier with five-fold cross-validation, 80% for training and 20% for the test.

In the objective of looking for the maximum margin hyperplane, linear SVM was utilized. The support vector machines algorithm was carried out to the dataset obtained from different mint types. Figure 4 represents a visualization of the result using the maximum value of the MQ-136 sensor and the mean value of the TGS822 sensor.

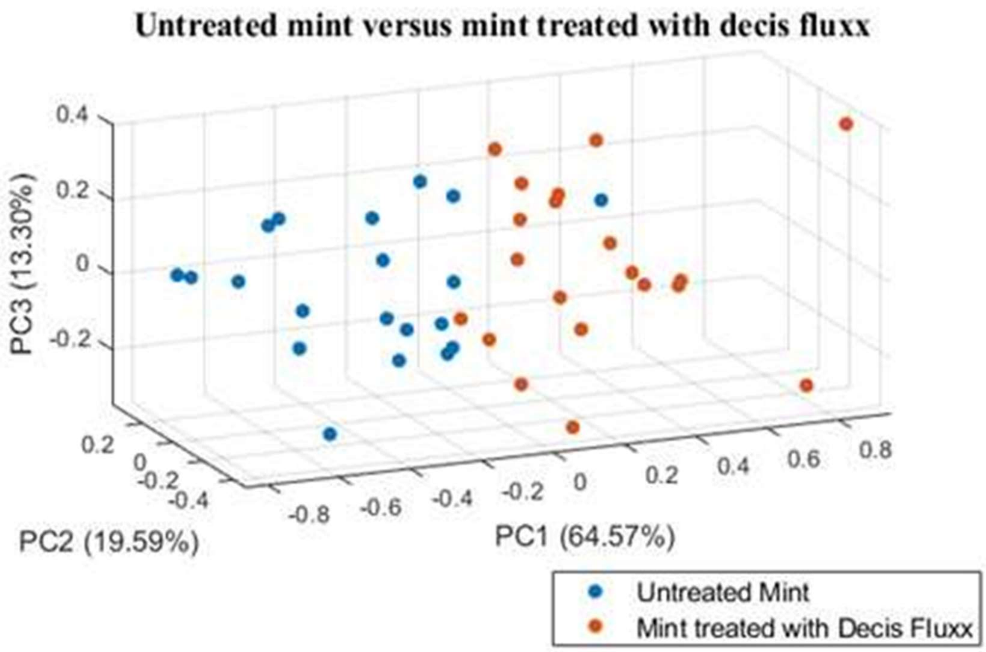

Fig. 3. PCA results for the treated mint and the untreated one.

By examining the figure, we notice that the samples have been correctly assigned to their data classes, with the exception of one sample relating to untreated mint and two samples relating to that treated which were misclassified. A very encouraging result was achieved with a success rate of 95% for the discrimination between untreated mint and the treated one.

Those promising results prove that our simple and inexpensive tool is useful to distinguish mint treated with deltamethrin from the untreated one.

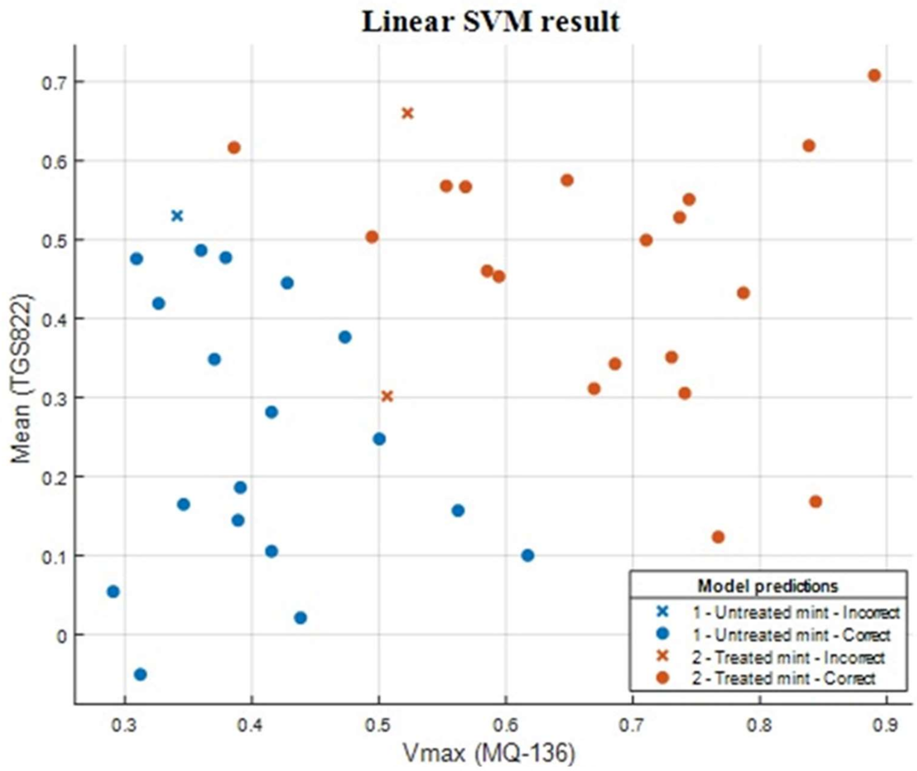

Fig. 4. PCA results for the treated mint and the untreated one.

3 Conclusion

The problem of quality control of marketed foods has become a big headache for the authorities responsible for promoting public health security. In this paper, the possibility of exploiting a simple multi-sensor system manufactured essentially from metal oxide gas sensors commercialized to differentiate between the deltamethrin treated mint from the untreated one is demonstrated. The statistical principal component analysis (PCA) method and the machine learning support vector machines (SVM) algorithm were used and archived good results with a cumulative contribution rate of the first three principal components of 97.46% for the PCA and a success rate of 95% for the SVM.

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