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Identification and detection of organophosphorus pesticides using artificial neural networks based on spectra obtained in gas chromatography

[1]Angélica Palacios, [1]Olga Ramos, [1]Darío Amaya

[1]*Engineering in mechatronics, Faculty of Engineering, Nueva Granada Military University, Bogotá D. C., Colombia.*

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Address For Correspondence:
Dario Amaya, Engineering in mechatronics, Faculty of Engineering, Nueva Granada Military University, Bogotá D. C., Colombia.

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ABSTRACT

Background: The analysis associated with detection of compounds from spectra is a process in which the results tend to be a tentative identification of compounds. Different factors as including technical, methodology, environmental and climatic effects processes affect the detection method in its precision, separation, quantification and characterization of compounds. This process can be tedious and complex due to the number of existing compounds on existing databases. ***Objective***: Training an artificial neural network to identify three main organophosphate pesticides, based on different chromatographic graphs obtained in a preliminary study. ***Conclusions:*** In training, the algorithm corrects the worst error converging on the optimal solution from the fourth iteration with final error of 0.0218 in 10th iteration. The total error of the test was 0.0212, even lower than the value obtained in the training. The algorithm developed in this paper decreased by up to 65% the initial error, obtaining as total mean squared error of 0.0218 value in its execution for 10 iterations. The development of this study identified three types of pesticides organofosfarados with a total error test 0.0212, from parameters such as retention time, intensity and concentration.

KEY WORDS

Artificial intelligence, artificial neural networks, organophosphate pesticides, gas chromatography.

INTRODUCTION

Pesticides are part of a different category of chemicals, manufactured specifically for the control of diseases, pests, weeds and other biological organisms that can affect growth and crop quality [1], [2]. Its use is because so far is the most effective technique for pest protection, increased productivity and performance in agriculture. [3]

Organophosphorus compounds are part of a group of organic substances from the chemical structure of phosphorus are implemented primarily as insecticides in crop protection,[4] their chemical properties tend to be similar to each other, and inhibit the enzyme acetylcholinesterase, as consequence the functioning of nerve impulses is disrupted. [5], [6].

Most such compounds are metabolized substances, which can be identified and measured for further characterization of the same, [7]. However, these decompose more easily and are not bio-accumulate in the body.

The toxicity associated with organophosphorus compounds derived from the effects caused to the central nervous system, [8] being the type of pesticide that most often causes damage to humans. [9] These mainly penetrate the skin, the absorption at low temperatures tends to be slow, while at high temperatures accelerates; constant contact and inhalation gradually increases the intoxication [10].

The impact and affected by exposure and consumption of these chemicals it become necessary to have control measures and study. Currently, it requires reliable and efficient analytical methods for the detection, identification and quantification of pesticide residues in food [11].

Features like simultaneous determination of pesticides (multi-residue methods), high sensitivity and selectivity, confirmation of identity, quantification of any detected residue and obtaining results in the shortest time possible, should be present in these analytical methods [12].

Chromatographic techniques are highly used in the analysis of pesticide detection and identification, because of its ability to resolve complex samples [13]. For a reliable identification regardless of concentration levels, whether high or low, correct separation of compounds is critical.

Have been developed many studies related to the detection and identification of pesticides in food, from chromatographic techniques and mass spectrometry. In [14], a method developed for the determination of different plant samples as carbamates (cucumber) and water from different sources is described. Through capillary liquid chromatography and different detection techniques such as mass spectrometry coupling. Resulting in the chromatographic separation of components effectively and in the shortest time possible.

By liquid chromatography mass of high pressure, [15]the characterization and quantification of pesticides are developed, samples of fruits as blueberries, strawberries, raspberries, and vegetables such as peas, corn and beans. Pesticide residues found in 68.4% of the samples, and some of them exceeding the maximum residue limits. It is emphasized that the breach in regulations in the use and handling of these products represents a latent consumer health threat.

This paper aims at training an artificial neural network to identify three main organophosphate pesticides, based on different chromatographic graphs obtained in a preliminary study, where the quantification of these chemicals in soil was conducted.

Methods:

For the development of this work an artificial neural network trained with data related to the spectra obtained by gas chromatography in the study, [16] was implemented. Made in Colombian soil for the characterization of organochlorine and organophosphorus pesticides.

The main variables for identification of pesticides in chromatographic techniques are the retention time and intensity detected for a specified concentration analysis. Next, the information relevant to the network training presented.

Table ***1***, shown spectral data for a concentration of 0.05 ppm.

Table 1: Chromatograph data for 0.5 ppm.

	Methyl-parathion	Chlorpyrifos	Phenthoate
ppm	0.5	0.5	0.5
RT	16.901	17.537	18.683
Intensity	750	1400	1500

Fig. ***1*** illustrates the chromatogram for a concentration of 0.5 ppm.

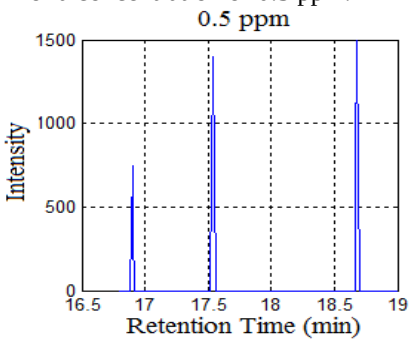

Fig. 1: Chromatogram for0.5 ppm.

Table ***2***, present the spectral data for a concentration of 1 ppm.

Table 2: Chromatograph data for 1 ppm.

	Methyl-parathion	Chlorpyrifos	Phenthoate
ppm	1	1	1
RT	16,901	17,537	18,683

Intensity	800	2100	2000

The chromatogram for a concentration of 1 ppm shownin Fig. ***2***.

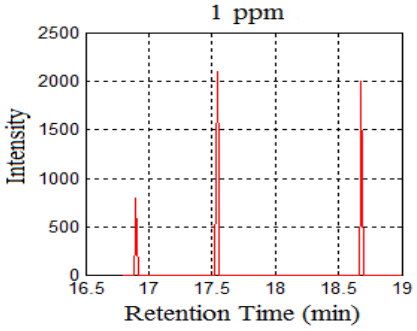

Fig. 2: Chromatogram for 1 ppm.

Spectral data for a concentration of 5 ppm shown in

Table ***3***.

Table 3: Chromatograph data for 5 ppm.

	Methyl-parathion	Chlorpyrifos	Phenthoate
ppm	5	5	5
RT	16,901	17,539	18,683
Intensity	3100	5000	4500

The chromatogram to a concentration of 5 ppm illustrated in Fig. **3**.

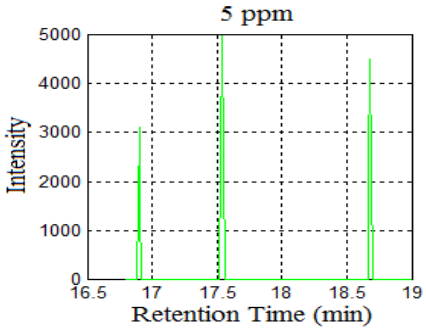

Fig. 3: Chromatogram for 5 ppm.

Spectral data for a concentration of 7 ppm shown in

Table ***4***.

Table 4: Chromatograph data for 7 ppm.

	Methyl-parathion	Chlorpyrifos	Phenthoate
ppm	7	7	7
RT	16,901	17,538	18,682
Intensity	4400	6900	5500

Fig. ***4***present the chromatogram for a concentration of 7 ppm.

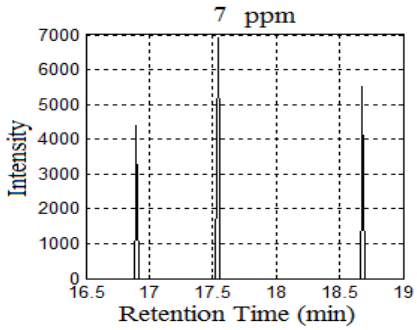

Fig. 4: Chromatogram for7 ppm.

Chromatogram data implemented in the test algorithm presented in

Table 5.

Table 5: Chromatograph data for 10 ppm.

	Methyl-parathion	Chlorpyrifos	Phenthoate
ppm	10	10	10
RT	16,9	17,537	18,681
Intensity	5400	9500	6500

The chromatogram for the test algorithm to a concentration of 10 ppm shown in Fig. ***5***.

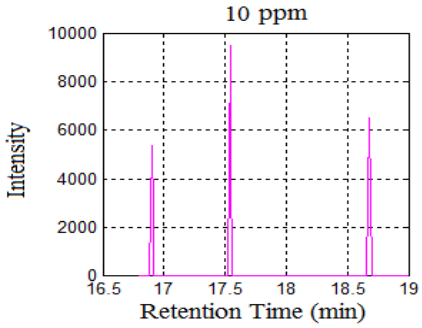

Fig. 5: Chromatogram for 10 ppm.

Training algorithm begins with reading a text file that contained information regarding retention time and intensity for each concentration of the different chromatograms. After the reading, the algorithm executes normalization corresponding data if necessary.

Then comes the training of the network, obtaining the error and better weights. From the above it is performed the test with the selected chromatogram obtained error and graphical identification of pesticides (methyl parathion, Chlorpyrifos, Phenthoate), corresponding to the output of the network according to the weights obtained in training

Analysis of Results:

The results obtained in the development and implementation of the proposed algorithm, are shown below.

The network characteristics obtained for the proper implementation and convergence of optimal solution depends mainly on the amount of data to be processed, and the relationship between them.

The final parameters of the network in this algorithm shown in Table 6.

Table 6: Developed algorithm parameters.

No. Input Variables	2
No. Inputs Training Network	412
No. Inputs Network Test	103

No. Hidden layer neurons	140
No. Outputs	1
Minimum value Weights	-1.8
Maximum Value Weights	1
Minimum Error	0.03
Maximum iterations	10

The results obtained in the test are presented in

Table *7*.

Table 7: Errors obtained in training.

Initial Error		0.0624	
worse Error	0.0278	Epoch	3
best Error	0.0218	Epoch	10

The initial error obtained by the preliminary search random, was 0.0624 above parameter set to 0.03, an expected result due to the randomness of the initial values. However, the correction of it is during execution of the algorithm reducing it approximately 63% in the first iteration and the maximum iteration a decrease of 65%.

This shows that the algorithm approaches a possible solution from the first iteration of its execution, despite this, the worst error occurred in the third iteration with a value of 0.0278 increased in value from the previous iteration 0.006. With this small increase never comes to exceed the minimum error set in the parameters, the algorithm corrects this worst mistake converging on the optimal solution from the fourth iteration with final error of 0.0218 for the 10th iteration, where it meets the parameter maximum number iterations.

In Figure 6, the error obtained in each iteration after initial error optimization with random values is illustrated.

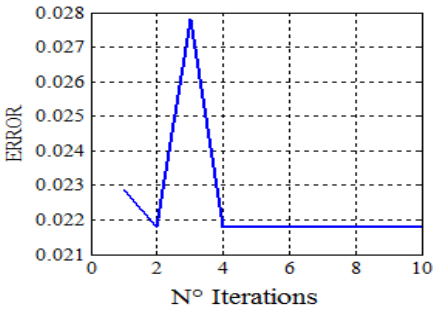

Fig. 6: Training Error.

As the weights obtained in the training, testing obtained the results presented in Table 8.

Table 8: Tests Results.

Error	0.0212
Pesticide 1	11
Pesticide 2	36
Pesticide 3	71

The total error of the test was 0.0212, even lower than the value obtained in the test. Resulting in the identification of the pesticide 1 (methyl parathion) in the dataset 11, the pesticide two (Chlorpyrifos) in 36 and the pesticide 3 (Phenthoate) at 71.

Identified data sets are shown in Fig. *7* shows the graph associated with chromatography to 10-ppm spectrum.

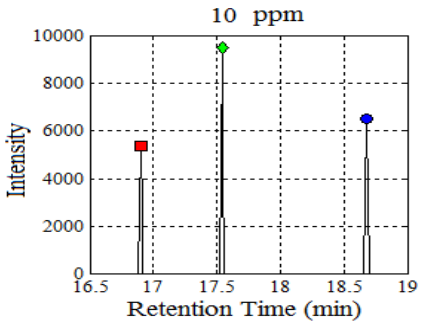

Fig. 7: Identification of pesticides in test chromatogram.

The red square identify the first pesticide, the green diamond the second one and the last blue circlethe last one, as illustrated in the figure above. Thus, the output coincides with the corresponding test pesticides to the retention time and intensity in the spectra obtained in the study by gas chromatography.

Conclusions:

The algorithm developed in this paper decreased by up to 65% the initial error, obtaining as total mean squared error of 0.0218 value in its execution for 10 iterations. Thus validating the parameters implemented in the network as well as the values of the weights and Biaseachieved.

The development of this study identified three types of pesticides organofosfarados with a total error test 0.0212, from parameters such as retention time, intensity and concentration, mainly related chromatographic analysis for quantification of these chemical compounds in the environment . So the algorithm presented can be implemented in different applications to facilitate these types of analyzes.

Using tools in artifical intelligence for the detection, identification and prediction parameters are a valid resource for the application of biological models, because of their behavior and its multiple variations, their analysis is affected by the high costs and long times in adquición, management and implementation of the technology necessary to perform the various analysis with which one can conclude about it.

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