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Design And Implementation Of A Neural Network Trained By Particle Swarm To Estimate Retention Times Frequently Used Chemicals In Pesticides

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ABSTRACT

Analysis of pesticide residues in food has increased in recent years due to the damages that have occurred in humans and other living beings in the ecosystem. This analysis can be performed under different methods as (liquid chromatography linked to mass spectrometry, gas chromatography, solid phase extraction etc.).However to perform a consistent analysis, it requires multiple and expensive equipment. Therefore, it has been developed and implemented algorithms parameter estimation, in order to reduce time and costs of analysis through simulation of spectra of compounds. In this paper the results obtained in the development of a neural network trained by particle swarm is exposed to estimate the retention time of pesticides from related parameters associated with liquid chromatography mass spectrometry. Using as a simulation tool spectra, the ACD / LAB software specialized in the analysis of structures of chemical compounds.

KEY WORDS

Pesticides, Retention time, Neural Network

INTRODUCTION

The constant threat for adverse effects on human health due to the use, handling and use of pesticides on food crops, [8,10,15], has created an alert in most countries and consumer societies, so, it is necessary to have a better control over this activity, [4].

For that, it has encouraged the scientific community to produce developments, in order to detect, quantify and analyze different types of toxic chemicals to humans, [11,12] and [17]. This contributes to the monitoring and control agencies, (SIVIGILA) to regulate the quality of products and processes.

Various methods currently exist for the analysis and detection of components such as gas and liquid chromatography, mass spectrometry, matrix dispersion, solid phase extraction, among others, [21,19]. These methods require equipment like (adsorbent polymer, gas chromatograph, liquid chromatograph detectors μ-ECD and NPD, ultrasonic, centrifugal, etc.) [9,13]. However, these technologies are very costly, so it has been necessary to develop models that try to represent the behavior of a system.

The accuracy of these depends on the parameters that characterize it. Generally, there is a difficulty in obtaining these experimental. Using computational techniques, time and cost of testing in laboratories is reduced, [3].

Local optimization methods based on iterative algorithm, Newton Raphson type or least squares remapping weights are generally used to estimate the coefficients of a linear model [13].

The nonlinearity in biochemical processes, presents a challenge to the development of many of the classical optimization algorithms. These processes usually not convex, can converge to a local solution and can obtain a better solution at a specific distance, so the optimization method fails, [3]. Learning algorithms as (Particle Swarm, Genetic algorithm and differential evolution) to neural networks are techniques that can solve these problems.

Liquid chromatography with mass spectrometry it has been greatly used, for the detection of pesticides in food and the environment, [5]. It's not the only technique for the analysis of pesticides, is the most recommended and optimal for analysis. This provides more benefits than gas chromatography with mass spectrometry, related to increased coverage, increased selectivity and sensitivity [6].

Estimating model parameters of a chromatography was performed in [20], which was applied as a learning algorithm to a genetic process protein. For a similar process, in [22], a method was developed to determine parameters difficultto estimate, with a protein chromatography process by the aim of reducing time and cost of design evolved.

In [18], the analysis of growth of P. pulmonarius in corncob was performed, using artificial neural networks and logistic model in order to determine the fermentation kinetics of this model. The results conclude that the logistic model and artificial neural networks are useful tools for modeling solid fermentation.

The improving to, the predictive power of models for the dimensionless retention time (DRT) and the partition coefficient (K) protein, it was presented in [14], with the following clustering algorithms: Growing Neural Gas, based on grids, clustering hierarchical, bisection method of k-neighbors search algorithm, Markov Clustering and Genetic algorithms.

The design and development of a neural network trained by particle swarm, is presented in this paper to estimate retention times for the main chemical components of pesticides, from, of chromatographic parameters such as, detection limit, Ion quantification and concentration of fortification.

Methods:

This work is based on the study *"Comparison of two methods for multi-residue analysis of pesticides in pollen"*, [1]. In which, a comparative study between a conventional method for detecting residues of pesticides in pollen and a modified method was performed in order to conclude which is the most suitable method.

In the work mentioned, 58 pesticides were analyzed using liquid chromatography coupled with mass spectrometry, chromatography was carried out in a liquid chromatograph UFLC ultra-fast (Ultra-Fast Liquid Chromatograph) Shimadzu Prominence (Maryland, CA, USA), coupled to a mass selective detector LCMS-2020.

Obtaining parameters of a model as chromatographic (quantified ions, retention times, concentrations of fortification and Levene test results) for each compound. These were selected based on international law, the level of involvement and use in Colombia.

The estimation algorithm retention time, requires 3 model parameters characteristic of liquid chromatography, for this application the inputs to the neural network are relevant to the detection limit, quantitation ion concentration and fortification data.

Database for training and testing of the network, are illustrated in Table 1.

Table 1: Data obtained in the comparative study.

Component	Limit D	Ion T	Concentration F	Time R
Acephate	2,53	201	9,79	2,56
Monocrotophos	1,84	241	12,94	2,78
Oxamyl	2,78	237	5,74	2,91
Methomyl	3,02	163	9,69	3,06
Carbendazim	3,58	192	17,07	3,15
Dimethoate	2,22	230	6,1	3,63
Thiabendazole	1,78	202	14,33	3,24
Cimoxanil	2,15	197	5,18	3,86
Tiodicarb	4,68	355	4,44	4,83
Carbofuran	0,96	222	5,66	4,81
Atrazine	5,22	216	6,44	5,19
Metalaxil	2,05	280	5,55	5,34
Pirimicarb	2,32	239	10,19	4,81
Imazalil	2,24	297	5,94	4,66
Tebuconazole	7,13	308	4,38	6,79
Hexaconazole	1,85	358	5,97	7
Spinosad A	9,39	733	3,76	6,33
Benalaxyl	4,61	326	5,7	7,73
Methamidophos	3,23	142	5,75	2,54
Propamocarb	1,74	189	7,95	2,63
Dinotefuran	0,45	203	17,03	2,7

Linuron	1,07	247	6,44	2,7
Nitenpyram	3,34	271	17,17	2,79
Thiametoxan	1,62	292	6,11	2,99
Dazomet	3,8	163	14,78	3,03
Mevinphos	2,09	225	7,08	3,17
Acetamiprid	4,87	223	19,08	3,3
Thiacloprid	0,96	297	6,93	3,71
Simazine	1,21	202	11,62	4,08
Carbaryl	3,19	219	9,48	4,57
Lufenuron	4,19	509	1,19	9,41

In Table 2, the characteristics of the network appears.

Table 2: Characteristics of Red.

Number of Inputs	*3*
Number of neurons in the hidden layer	*Variable*
Number of Outputs	*1*

The structure of the neural network is presented in Fig. ***1***.

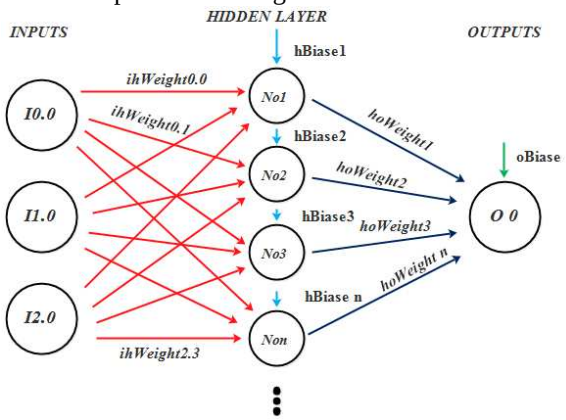

Fig. 1: Structure of the neural network.

The program starts with importing the Excel database, this data is stored in an array to be standardized. The algorithm normalizes the data value from 0 to 1. It is essential data normalization in training a neural network, of this process will depend, the accuracy of the algorithm in turn ensure that the obtained solution is optimal.

Subsequently, the normalized matrix is organized randomly and 80% of data for training and the remaining 20% for the test of the optimum solution algorithm is selected.

In Fig. ***2***, the normalized data for training, is displayed.

```
TrainData =

    0.1725    0.3984    0.3202    0.3177
    0.3557    0.3697    0.8999    0.2965
    0.3440    0.1937    0.3014    0.2699
    0.1140    0.3370    0.3375    0.2869
    0.4984    0.4843    0.2327    0.5133
    0.4909    0.4447    0.2987    0.8215
    0.2364    0.3138    0.3197    0.3858
    0.2226    0.3070    0.3711    0.3369
    0.2290    0.2688    0.2715    0.4102
    0.2386    0.4052    0.3113    0.4952
    0.1960    0.3288    0.6782    0.2954
    0.4047    0.2224    0.7746    0.3220
    0.1853    0.2578    0.4167    0.2795
    0.7593    0.4202    0.2296    0.7216
    0.3813    0.2619    0.8947    0.3348
    0.2471    0.3261    0.5341    0.5112
    0.5186    0.3042    1.0000    0.3507
    0.5559    0.2947    0.3375    0.5515
    1.0000    1.0000    0.1971    0.6727
    0.3397    0.2988    0.4969    0.4857
    0.1022    0.3029    0.2966    0.5112
    0.2961    0.3233    0.3008    0.3092
    0.1289    0.2756    0.6090    0.4336
    0.1970    0.4884    0.3129    0.7439
    0.2694    0.2742    0.5131    0.2721
```

Fig. 2: Training Data.

The test data are illustrated in, Fig. ***3***.

DTest =

0.1022	0.4052	0.3632	0.3943
0.0479	0.2769	0.8926	0.2869
0.2183	0.3820	0.2909	0.5675
0.3216	0.2224	0.5079	0.3252
0.4462	0.6944	0.0624	1.0000
0.1896	0.2756	0.7510	0.3443

Fig. 3: Test Data.

Particle swarm optimization (PSO):

In the optimization, the search is performed using a population of particles corresponding to individuals, each represents a candidate solution. The particles change their state to explore, through the search space until it has found a relatively stable state, [16].

Algorithm

A. Definition of parameters:

The parameters in are global values, and depend on the creation and structure of the neural network.

Table 3: Network Parameters.

Network Parameter	N° Inputs. N° Hidden. N° Outputs. N° Particles. Max Epoch. Best Global Error.

Table 4 contains the parameters required by the PSO, these are used for correcting the speed of each particle swarm.

Table 4: PSO Parameters.

PSO Parameters	Inertia weight. Cognitive weight. Social weight.

B. Creating the initial population and the swarm.

$P^0 = [x_1^0, e_1, v_1^0]$;

$x_i^0 = [x_i1, x_i2, x_in]$ And$v_i^0 = [v_i1, v_i2, v_in]$.

The position and initial velocity is defined randomly.

$$E = \begin{bmatrix} P^0 \\ P^1 \\ P^n \end{bmatrix}$$

C. Objective function calculation, error, and choosing the best position for each particle.

$x_{p,i} \leftarrow x_i \leftarrow$ Best current position.

D. Selecting the best position and best overall error.

$x_G \leftarrow$ Best Global Position.

While the stop condition is not met, calculate new speed and position for each particle swarm, as shown in 1 and 2.

$$v_i^j = \left(w \times v_i^{j-1}\right) + (c1 \times r1 \times \left(x_{p,i} - x_i^{j-1}\right) + (c2 \times r2 \times (x_G - x_i^{j-1})$$

R1 and r2 are random values between 0 and 1.

$$x_i^j = x_i^{j-1} + v_i^j \qquad 2$$

E. Calculate objective function, error, and select best current global position. Get as best particle solution. Finally the final weights are the best vector of the particle.

The diagram shows the flowchart of the algorithm performed is shown, Fig. ***4***.

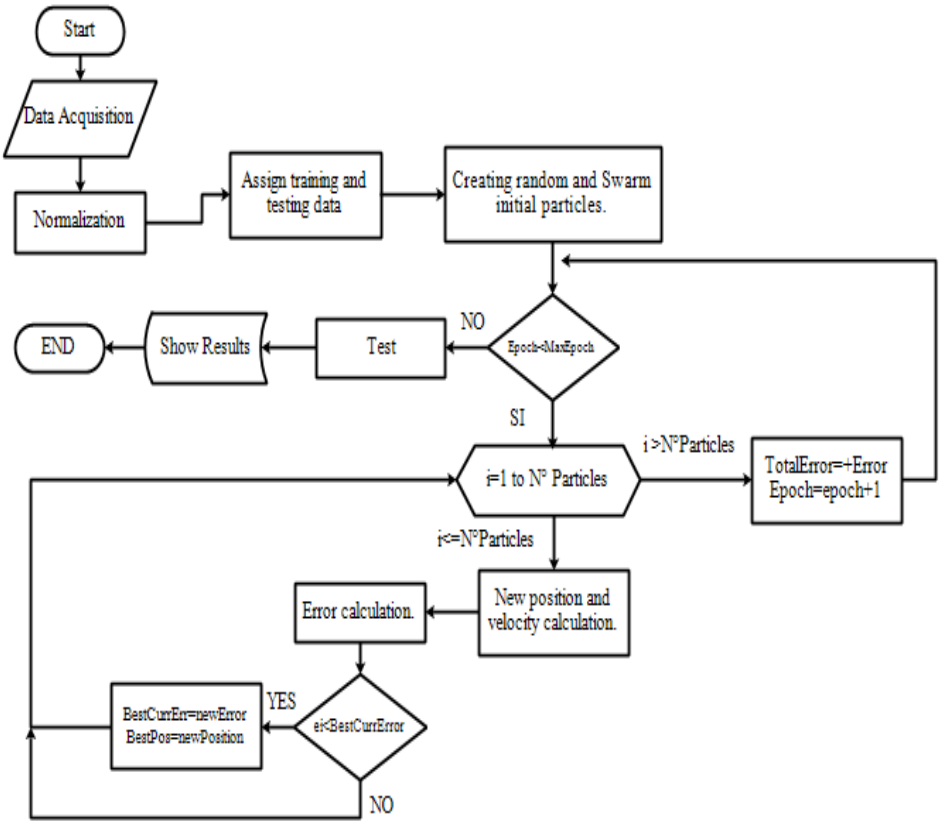

Fig. 4: Flowchart of the algorithm.

Results:

The algorithm was developed, taking into account the parameters presented in Table 5

Table 5: Parameters of the neural network.

Network Parameters	
N° Inputs.	3
N° Hidden.	6
N° Outputs.	1
N° Particles.	10
Max Epoch.	90
PSO Parameters	
Inertia weight.	0.729
Cognitive weight.	1.4944
Social weight.	1.4944

The parameters of the particle swarm optimization was taken from, [7].
For the training phase, the results obtained are shown below:
In

Table ***6***, you can see the corresponding weights of the entrances to the hidden layer.

Table 6: IhWeight obtained in training.

ihWeight					
ih0.0	ih0.1	ih0.2	ih0.3	ih0.4	ih0.5
4.7	-5.5	-5.5	4.7	0.9512	1.8578
ih1.0	ih1.1	ih1.2	ih1.3	ih1.4	ih1.5
2.23	-5.23	-2.49	4.7	-5.5	4.7
ih2.0	ih2.1	ih2.2	ih2.3	ih2.4	ih2.5
3.43	-5.11	-4.27	4.7	-5.19	-5.5

The value of bias for each neuron in the hidden layer, are presented in Table 7

Table 7: Results for hBiase of the hidden layer.

hBiase	
h1	-5.5
h2	4.7
h3	1.2622
h4	4.1376
h5	-5.5
h6	0.7442

As a result of the weights of the hidden layer to the output, the values in

Table ***8***, was obtained.

Table 8: Output weights network.

hoWeights	
hoWeight1	2.7614
hoWeight2	4.7
hoWeight3	1.7787
hoWeight4	4.0869
hoWeight5	2.2356
hoWeight6	1.9881

Finally Bias output is illustrated in Table 9

Table 9. Output oBiase Network.

oBiase	1.3402

The mean square error per iteration in the training phase is illustrated in Fig. ***5***.

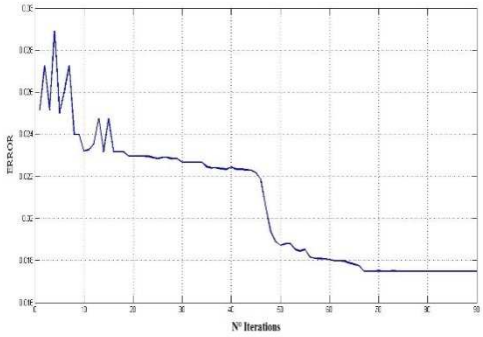

Fig. 5: Error.

In the graph of error it can be seen that for the first 15 iterations, particle swarm roamed the search space, where possible solutions represent an alternating error.

From iteration 20, the swarm begins to find a relatively stable area search, so the error is gradually decreasing, to completely secure a stable area where a better solution is obtained.

The best global error delivered by the algorithm shown in

Table ***10***.

Table 10: Best Global Error.

BestGlobalError	0.0175

The results of the test phase are shown in Table 11

Table 11: Test Results.

I0.0	I1.0	I2.0	Y
0.1022	0.4052	0.3632	0.4138
0.0479	0.2769	0.8926	0.3437
0.2183	0.3820	0.2909	0.4901
0.3216	0.2224	0.5079	0.3582
0.4462	0.6944	0.024	0.9187
0.1896	0.2756	0.7510	0.3445

The mean square error obtained in the test phase is presented in Table 12

Table 12. Mean Squared Error Test.

Test Error	5.944e-9

The error value shows that the estimated retention time for the following compounds (Tiaclorprid, Methomyl, Lufenuron, dinotefuran, Metalaxyl, Thiabendazole) is a good approximation of the values obtained by liquid chromatography coupled to spectrometry masses.

Application ACD/LAB:

For this application Famaxadona compound was simulated, through the ACD / LAB software obtaining this spectrum, as illustrated in Fig. ***6***.

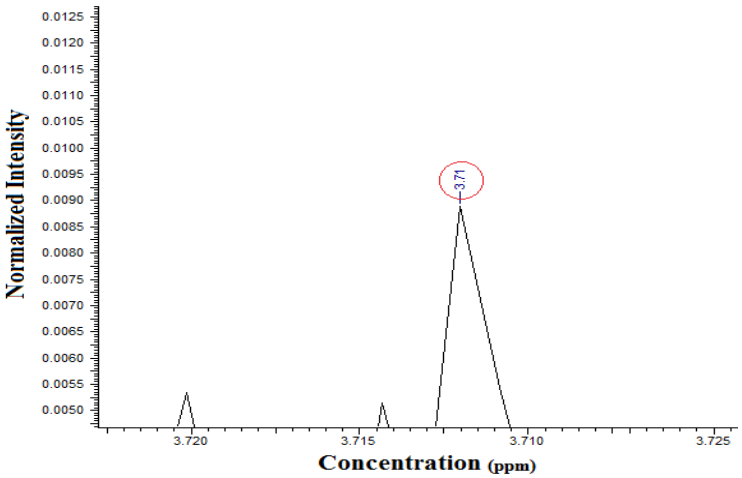

Fig. 6: Famoxadone spectrum.

The software allows exporting information concerning the spectrum of each compound, in this case the concentration in ppm and normalized intensity was used.

This information is imported into Matlab where reconstruction of the spectrum becomes as shown in the graph of Fig. ***7***.

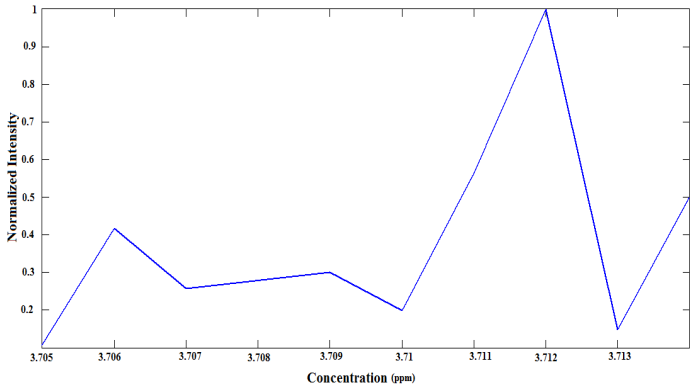

Fig. 7: Spectrum in Matlab.

To estimate the retention time of the compound, the concentration was taken as the retention time and the parameters as Ion T and concentration of fortification were taken from, (Ahumada & Zamudio, ANÁLISIS DE RESIDUOS DE PLAGUICIDAS EN TOMATE MEDIANTE EL USO DE QuEChERS Y CROMATOGRAFÍA LÍQUIDA ULTRARRÁPIDA ACOPLADA A ESPECTROMETRÍA DE MASAS, 2011).

The input parameters for the estimation algorithm is shown in Table 13

Table 13: Parameters for estimation.

Famaxadone Parameters		
Detection limit	Ion T Quantification	Concentration Fortification
3.71	373	22.5

The results for the compound are presented in Table 14

Table 14: Results Retention time estimate.

Results Retention time	
Normalized Retention T.	0.3435
Retention T.	3.2320

Conclusions:

The algorithm presented in this paper, we can estimate the retention time of compounds found in essential pesticides, most used in food crops. With a low rate of error in the estimation of 5.944e-9, which can be considered as a very good approximation.

The development of computational techniques, estimation, prediction and detection parameters through the representation of models, can get effective results, reducing time and costs of laboratory equipment, and encouraging research in this area.

The neural network calculates the value of the retention time of a compound, through the Ion quantification limit of detection and the concentration of fortification. However it is an algorithm that can work as a parameter estimator, used as input variables related to different processes, either liquid chromatography, gas, ..., among others, and the output of the algorithm is the unknown process variable.

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