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Displacement Analysis Of Pesticides In Strawberry Crops From The Savannah Of Bogotá (*Fragaria Vesca*) Through The Simulation Of A Liquid Chromatography Column

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ABSTRACT

The strawberry is a fruit widely marketed. In Colombia is grown mainly in the variety of *Fragaria Vesca*. This species is characterized by its low carbohydrate content, as well as being an important source of vitamins and minerals essential for humans. Because of his high nutritional value, this fruit is often attacked by different pests such as mites, fungi in the roots, leaves añublo, among others. For a proper harvesting and preservation of fruits, the use of chemical pesticides is necessary, mainly Tetradifon, Iprodione, Propargite and Profenofos. The properties of these compounds depend on the purity, generally it seeks to obtain the highest possible purity in compounds for optimal performance in crops of *Fragaria Vesca*. One method of purification of these compounds is the preparative chromatography. Which it is a specific separation technique in which the property of chemical affinity is used. To isolate the different components of a sample, to determine his retention time in the column. Therefore, the analysis of the displacement of the main pesticides used in *Fragaria Vesca* at the inside within a column through simulation thereof is necessary. With the mathematical model it can make a comparison, in the elution rate in separation. In this work, the results of the mathematical model and the prediction of retention times for liquid chromatography (LC) were presented, which was applied in the purification of pesticide. It was found that Tetradifon, has little elution for a tao of 1 in the column used, the peak concentration was at a standard length of 0,41. The maximum peak for Iprodione was 0.14, while for Propargite and Profenofos, peaks were 0.63 and 0.82 respectively. The latter three compounds are similar and cause adverse effects when applied simultaneously on *Fragaria Vesca*, which was made more complex the separation.

KEYWORDS: *Fragaria Vesca*, Liquid chromatography, Pesticide, Chromatography column.

INTRODUCTION

The *Fragaria Vesca*, is commonly known as wild strawberry, because their size is smaller relative with *Fragaria x ananassa* that is the variety of strawberry more marketed by its high content of meat. However the variety Vesca is very sought after in Latin America, due to his high content of vitamins and minerals. Besides, their pleasant aroma and flavor [12,15]. These characteristics cause this plant suffer the attack of various pests, such as mites, fungus in the roots, leaves añublo, etc. [4,7]. Currently, to combat this phenomenon, chemical pesticides were used, which directly combat organisms harmful to the plant and the fruit.

To combat these pests, chemical pesticides were used, such as Tetradifon, iprodione, propargite and Profenofos. These compounds are classified as averagely toxic to human health by the Environmental Protection Agency of the United States (US-EPA). However, mixing these compounds can even cause a resulting mixture

which have a greater toxicity [13]. This mixture can be given due to incorrect synthesis, purification poor or for an inadequate enforcement in the crops.

For the preparation and purification of some pesticides, separation techniques such as chromatography were implemented. This technique is widely used in industry to carry out the separation of reactants and products in the industry. Among the main mixtures to be purified are some contaminants in crops such as pesticides natural compounds, enzymes, proteins, etc. [3,6,10]. This dissociation occurs due to the physicochemical properties of each compound. This occurs by the interaction between the chromatography column and the compound [2]. Different types of chromatography are characterized by the state in which phases, for the case of liquid chromatography (LC), the mobile phase is liquid and the stationary phase is in solid state [8,9,14]. The degree of migration and separation of compounds is given by the chemical interactions between the compound and each of the phases.

This technique is very expensive due to the lack of specific experiments for each compound. Because of this arises the need to develop models that predict the behavior of this technique. Wicke in 1939, develop the ideal model for liquid chromatography, which was improved by Wilson a year later [17,18]. This mathematical modeling was performed for determining the behavior of a single compound based on the Langmuir isotherm. Gu Tingyue in 1995 based on the balance of matter and energy proposed a model, adding differents dimensionless numbers as the Biot and the Peclet, who were affected in a liquid chromatography column (Tingyue, n.d.). Because of the importance of this technique, Buitrago S. et al in 2015 developed a model for liquid pesticides chromatography [5].

Therefore, it is given the need to analyze the displacement of the most widely used pesticides in *Fragaria Vesca*, to determine their behavior through a liquid chromatography column. This seeks to observe the relationship of these pesticides, choosing the appropriate column and the elution pattern of the compound through the same.

MATERIAL AND METHODS

Pesticides:

To preserve the *Fragaria Vesca*some chemical pesticides were used (

Fig. 1). Of these pesticides the Iprodione is a fungicide, which is solid at room temperature, for use on crops, this was dissolved in water. The Tetradifon, the Propargite and the Profenofos, are compounds used as acaricides. The Profenofos is an organophosphorus compound. The main toxic feature of these compounds, is when entering the human system can produce muscular atrophy.

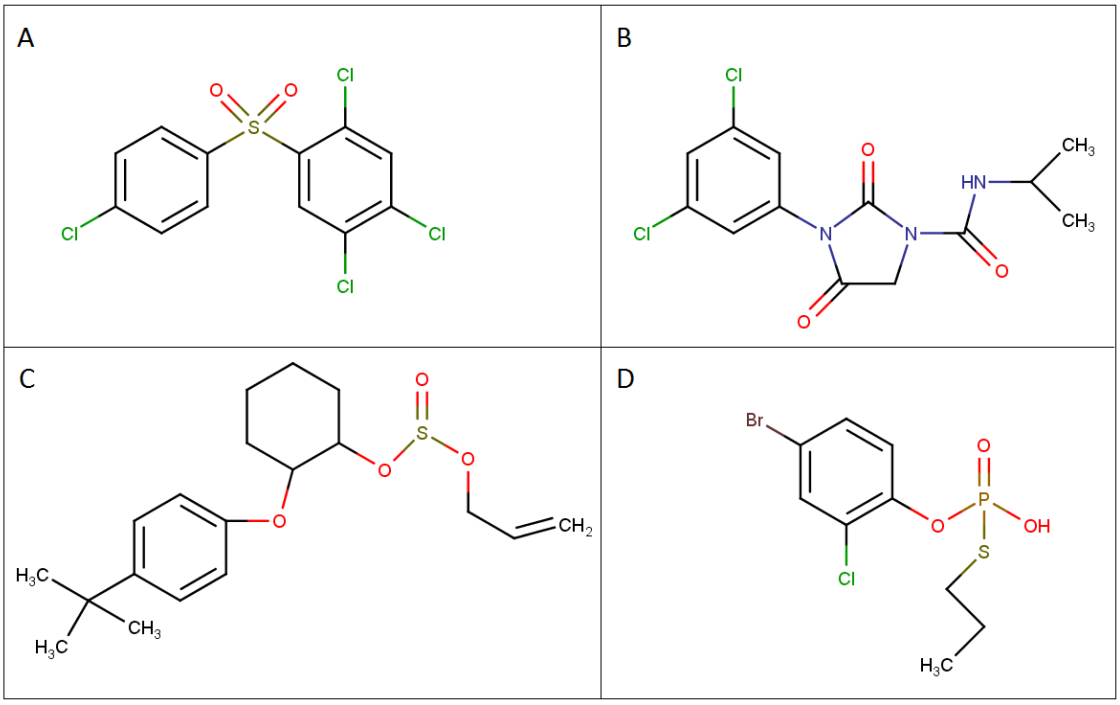

Fig. 1: Pesticides used on crops of *Fragaria Vesca* in Colombia. A. Tetradifon, B. Iprodione, C. Propargite, D. Profenofos.

Mathematical model:

The simulation of the movement of pesticides through liquid chromatography was carried out on the basis of the model developed by Buitrago Salazar et al in 2015 [5] In the work developed, the displacement was determined by varying the physical conditions of a column and properties of the compounds. The material balances for the particle (Eq. 1) and the fluid passing through the column (Eq. 2) were taken.

$$-\frac{1}{Pe_L}\frac{\delta^2 c_b}{\delta z^2}+\frac{\delta c_b}{\delta z}+\frac{\delta c_b}{\delta \tau}+\xi*\left(c_b-c_{p,r=1}\right)=0 \quad (1)$$

$$\frac{\delta}{\delta \tau}\left[\left(1-\epsilon_p\right)c_p^*+\epsilon_p c_p\right]-\eta\left[\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta c_p}{\delta r}\right)\right]=0 \quad (2)$$

The following boundary conditions (BC) were used:

$$z=0 \qquad \frac{\delta C_b}{\delta z}=Pe_L\left[c_b-\frac{c_f(\tau)}{c_0}\right] \quad (3)$$

$$z=L \qquad \frac{\delta C_b}{\delta z}=0 \quad (4)$$

$$R=0 \qquad \frac{\delta C_p}{\delta r}=0 \quad (5)$$

$$r=1 \qquad \frac{\delta C_p}{\delta r}=Bi(c_b-c_{p,r=1}) \quad (6)$$

To the solution of the model the data of an ideal column was taken (

Table 1), with which the initial values were obtained for each case of change of the compound, according to the points made in the article [5].

Table 1: Initial values for calculating the parameters in the ideal column.

Parameter	Value	Units
MW	10000	g/mol
Q	1,0000	mL/min
L	10,000	cm
d_c	1,0000	cm
R_p	0,0113	cm
ϵ_b	0,4000	
τ_{cor}	4,0000	
d_p	300,00	Å
ϵ_p	0,5000	

To calculate the error in the equalization of the equations to zero, the mean, median and standard deviation were calculated. This procedure was made for each of the compounds studied to verify the performance versus time.

Obtaining parameters for each compound:

Table 2: Properties of pesticides in *Fragaria Vesca.*

Property	Value for Tetradifon	Value for Iprodione	Value for Propargite	Value for Profenofos	Units
MW	356,05	330,17	350,47	373,63	$\frac{g}{mol}$
μ	1,00E-03	2,08E-03	3,50E-01	2,00E-01	$Pa\ s$
Vm	0,2342	0,3302	0,3149	0,2559	$\frac{m^3}{kgmol}$
ρ	1,52	1,00	1,11	1,46	$\frac{g}{cm^3}$

For the model solution, physical properties of each molecule were required (

Table 2) and specific data of the column used (

Table 1). The remaining parameters required for solving equations 1 and 2, were calculated taking into account the development of the model proposed by Buitrago Salazar in 2015 [5].

Solution of the equation system:

For the system solution, 20 points were defined for the variables "z" and"r", using a step size of 0.0526. While the variable"τ", 6 points were defined, with a step size of 0.200. With these data, the corresponding matrix was constructed using an operating temperature of 120 °C, temperature at which work much of the chromatographic columns.

In the solution of the system, the equalization sought the zero for all points of the matrix. These equations were solved with the help of Microsoft Excel 2013 Solver function.

The error in the solution of equations was calculated by determining the mean, median and standard deviation. This solution was repeated for each of the compounds tested, taking into account the properties of each molecule.

RESULTS AND DISCUSSION

Pesticides:

In crops of Fragaria *Vesca*, chemical pesticides were used to control pests, as shown in

Table 3. Of the pesticides analyzed the Profenofos and the iprodione have the highest toxicity, however the degradation of the Profenofos in fat matrices is carried out in about 7 days, while the concentration of iprodione decreases in 36.2 days. The Tetradifon, the compound was less toxic in the rats measured, it requires a higher dose of 14.7 g/kg, however, that compound take approximately 112 days to degrade in adipose tissue, reason why this compound is bioaccumulate in some species.

Table 3: Toxicological properties of pesticides used (Ahmed et al., 2010; Lewis, Tzilivakis, Warner, & Green, 2016).

Compound	Formula	Number CAS	Toxicity (Oral LD50 Rat)	Soil degradation (DT50)
Tetradifon	$C_{12}H_6Cl_4O_2S$	116-29-0	> 14700 mg/kg	112,0 days
Iprodione	$C_{13}H_{13}Cl_2N_3O_3$	36734-19-7	> 200 mg/kg	36,2 days
Propargite	$C_{19}H_{26}O_4S$	2312-35-8	2639 mg/kg	56,0 days
Profenofos	$C_{11}H_{15}BrClO_3PS$	41198-08-7	358 mg/kg	7,0 days

The main change in the compounds analyzed (

Table 2) were the density and the viscosity. These parameters directly affect the calculation of the Peclet number, due to is the relationship between the advection of the fluid and the diffusion rate. To big values of the number, indicates that the system was mainly governed by fluid displacement. For the compounds studied, density was higher than water, thus, these compounds tend to remain in adipose tissue more time.

The atomic volume is a measure of the flow of molecules through the pores of the column. The Propargite and the Iprodione have the larger values, thus these compounds will have less dispersion in the matrix of the stationary phase, which would hinder the preparation of these compounds.

Mathematical model:

For solving the system of equations, steps of h 0.0526 were taken, this size was defined for the change in the variables of length "z" and radio"r", because they were the main variables on which the studio was located and on which the main analysis was performed. The step size for each of the variables is modifiable, and sizes of high step, the system loses accuracy, while sizes low pass, the error at each step builds up, thus the system behaved so oscillatory.

The mathematical model was solved by following the steps in Buitrago Salazar et al [5]. To verify the system solution through the proposed method, was determined the average, median, and standard deviation (Table 4) for each column. These values were calculated using the data obtained from each point of the matrix, in total 240 points.

Table 4: Error calculated in the solution of the system of equations.

Parameter	Tetradifon	Iprodione	Propargite	Profenofos
Avergae	0,311	0,085	0,438	0,258
Median	9,282,E-05	4,168,E-05	5,178,E-06	1,048,E-07
Standard deviation	0,796	1,382	1,332	0,811

For all the solutions found through the proposed method, it was found, that there was no significant error in the solution of the equations. The average data approaches the ideal value, which was zero. This value was

confirmed by the standard deviation of the results which was lower than 1.5 for all the cases. Whereupon the 240 equations that make up each matrix for each pesticide had a mathematically appropriate value.

Solution of the equation system:

The system of equations (Equation 1 and 2) for each column respectively was resolved, as proposed by Buitrago Salazar. With these solutions the displacement of the maximum concentration of the pesticide through column length was determined (

Fig. 2). Of the compounds tested, which presents greater variation in the data was the Profenofos. This compound had a higher molecular weight, whereby his movement through the column was slow. This behavior was due to the phosphate group of the molecule, which produces an interaction with the stationary phase of the column, which was composed primarily of polymers. The Tetradifon and Propargite also had some ripples in the chromatographic response, this was primarily due to sulfur-containing group.

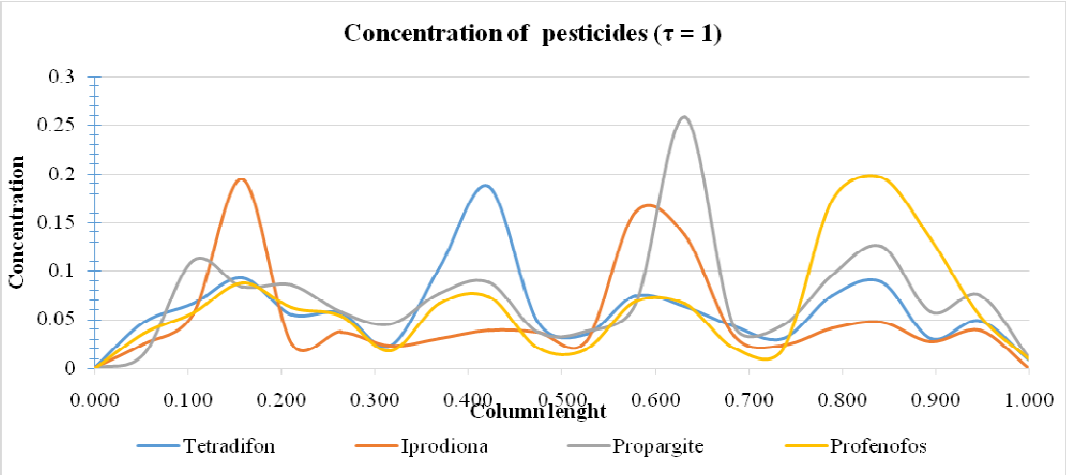

Fig. 2: Concentration profiles for a tao of 1 in the column for the selected pesticedes.

The Tetradifon can be obtained in a length of approximately 0.4 of the column, place where his concentration was maximized, whereby this compound will have a high recovery and purification in this length. The Iprodione presented two prominent peaks at approximately 0.15 and 0.6. However, in the second peak extraction was not recommended because this interferes with the principal peak of Propargite, besides of being a broad peak, with this, cannot be obtained the desired effectiveness in the separation of this compound. The Propargite had a well-defined peak at 0.63. The more defined than the peak separation will be more effective and take less time, however the sample obtained will have significant traces of Iprodione, it was recommended to use a second method of extraction for proper separation of the compounds.

The profenofos have their highest peak at 0.82, however this peak was very wide, and thereby for obtaining the pure compound was difficult. This behavior was due to the molecule, because his high molecular weight require a greater drag force to pass through the column. The increase in this force, causes the column had to work at a higher pressure, whereby the column will have increased wear in the operation. This leads to increased system maintenance costs.

The diffusion in the column had as one of his main factors the intraparticle diffusion in the stationary phase. This diffusion for the different compounds tested are shown in

Fig. 3. The Tetradifon had a big intraparticle diffusion, reason why his peak was well-defined and was obtained with short length of the column used. However, their distribution was not uniform throughout the radius of the particle. This was because the interaction between the rest of the compounds.

Other pesticides had a little diffusion compared to Tetradifon, however, the spread of these compounds was uniform throughout the particle studied.

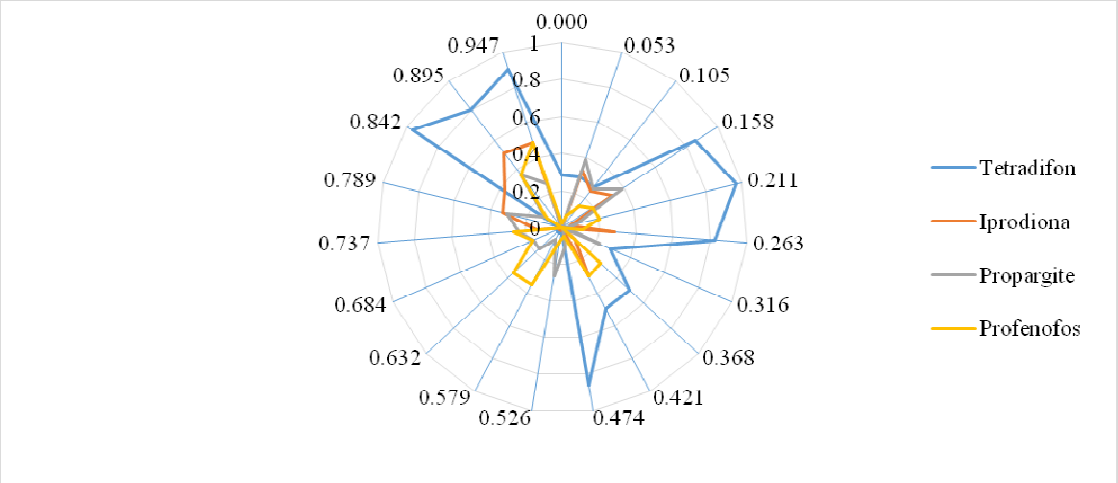

Fig. 3: Concentration profiles intraparticle for a tao of 1.

This article was interesting and contribute to the knowledge, due to they contribute to the development of a technique for analysis of pesticides for *Fragaria Vesca* in a liquid chromatography separation. His best objective, was made easier the industrial implementation, besides being a base for developing future models for predicting the displacement inside a column of liquid chromatography.

Conclusions:

The displacement of the compounds analyzed through the model solution was determined, which was based on the material balances in liquid chromatography. The accuracy in the solution of the matrix was corroborated by determining the average and median of points in the matrix, for the 4 cases were found to be less than 0.5 and 0.001 respectively. The model adequately describes the behavior of the pesticides studied.

The physical and chemical properties of each compound directly affect the dispersion in the stationary phase and the diffusion through the column, for the same configuration in the column used. A column with ideal characteristics, with which a better reading of peak separation of each compound was obtained.

The separation was efficient for the Tetradifon and the Propargite, which were separated at a standard length of 0.42 and 0.63. Iprodione presents problems for long lengths of column due to peak overlaps with the peak of Propargite, whereby separation was recommended to a length of 0.16. The Profenofos were separated at a length of 0.84, but his peak was not well defined, whereby the separation will not be efficient and have a higher chance of contamination with other samples.

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