



Method for determining the parameters ΔH_s and ΔS , to simulate the retention time in gas chromatography for Malathion, Fenitrothion and Clorpirifos

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Abstract: Gas chromatography (GC), is consider as one of the best analytical techniques due to their speed and effectiveness in the identification and quantification of pesticides in food. These parameters depend on the type of column, the pressure and temperature programmed inside the system. The relationship between these is not linear. Due to this, it is requires the development of a model for predicting the retention time (RT), with the aim of optimizing the process and thus spend fewer resources in the trial. To carry out this prediction, it was determined the parameters ΔH_s and ΔS . It was taken in account the results obtained in other studies and they were adjusted to the predictive model. It were developed the parameters of the predictive model in a DB-5 column. Parameters were obtained (ΔH_s [KJ / mol]; ΔS [J / mol K]) with values (-106, -170) (-72.7, -100) and (-107, 171.1) for Malathion, Fenitrothion and Clorpirifos respectively. It was found that these values depend on the polarity of the compound given by it is chemical structure.

Keywords– Chemical pesticide, Liquid chromatography, Retention time.

Introduction

Gas chromatography (GC) coupled with mass spectrometry, it is the technique most used for the analysis of pesticides in any matrix. Due to it high efficiency in the separation and identification of compounds. The scientific basis of this analytical method is the competition between the mobile phase and the stationary phase, for drag and hold the analyte¹.

E The retention time (RT) of a compound in a chromatographic column, depends on the conditions under which the assay was performed, such operation mode (constant pressure or constant flow) and the temperature programming² Furthermore it must take into account, the physical and chemical parameters of the column, such as length, diameter, chemical interactions between the mobile phase, stationary phase and the solute. These parameters make the analyte take more or less time to reach the detector^{3,4}.

For prediction of the RT of a solute in gas chromatography, Gonzalez and Nardillo in 1997 developed a mathematical model for simulating RTs, of five alkanes and three aromatics. For which, they obtained a maximum relative error of 1.15%⁵. This work, had become in the basis of several studies conducted from 1997. In most of the studies, the RT was optimized for chromatographic assays and the time machine to solve the equations of the model^{6,7,8}.

Gonzales certified the results obtained with the model, by performing chromatographic assays, where the parameters $-\frac{\Delta H_s}{R}$ and $\frac{\alpha}{\beta}$ were determined and reported for the solutes in his work⁵. These parameters are directly related with the constants ΔH_s and ΔS required in the model.

Other studies on simulation of the RTs in gas chromatography, where the constants ΔH_s and ΔS were determined for different substances from the used in the work of González et al. One of them was optimizing the retention time for ninety-three volatile compounds, where they can be estimated by graphing the values reported for 21 solutes, of which five are tabulated (C9, C10, C11, C12 and C14)⁹.

Thewalin et al in 2011 reported values for some long-chain alkanes, aromatic compounds and esters [10]. Where change of these parameters was assessed on different chromatographic columns. Also they simulated the separation of a mixture of pesticides in a DB-5 column.

Based on the study by Thewalin and results of measurements made in the agricultural and medical fields, the objective of this work is to determine the constants ΔH_s and ΔS for Malathion, Fenitrothion and Clorpirifos by adjusting the model to the RT reports in^{11,12,13}.

Materials and Methods

Model Description

Model development for simulation of the retention time, consider the equations of Darcy's and the ideal gas, to describe the dynamics of the gas inside the column. Axial variable which indicated the peak position (x) was replaced by $z = \frac{x}{L}$ obtaining the equation (1).

$$\frac{dz}{dt} = \frac{1}{t_0 \frac{3P^2 - 1}{2P^2 - 1} \sqrt{P^2 - z(P^2 - 1)}(1 + k)} \quad (1)$$

Where P was the relationship between the input and the output pressure of the column. t_0 Was the holdup time of the carrier gas and k was the factor of capacity, defined as showed in equation (2).

$$k = \frac{\alpha}{\beta} e^{-\frac{\Delta H_s}{R}} \quad (2)$$

$$\alpha = e^{\frac{\Delta S}{R}} \quad (3)$$

$$\beta = \frac{r}{2d_f} \quad (4)$$

Chromatographic assays are not isothermal processes, so, the t_0 was calculated with the equation (5).

$$t_0 = t_0^j \frac{j^0 P^0 - 1}{j P^2 - 1} \left(\frac{T}{T_0} \right)^N \quad (5)$$

Where the superscript 0, indicates the initial conditions, T was the temperature and N was a constant that depend on the carrier gas (0,725 for nitrogen). j was the factor of James-Martin, which is calculated through the equation (6).

$$j = \frac{3P^2 - 1}{2P^2 - 1} \quad (6)$$

Due to the chromatographic assays were performed at constant flow, the pressure was included in the model through the equation (7).

$$P = \sqrt{1 + \left(\frac{T}{T_0}\right)^N (P_0^2 - 1)} \quad (7)$$

Determination of the parameters ΔH_s and ΔS

Chromatographic test results of various studies were taken as basis, for Malathion, Fenitrothion and Clorpirifos in a chromatographic column DB-5 or similar column such as HP-5ms.

The retention time of each substance was taken, further, were taken the physical characteristics of the column as the length, the diameter and thickness of the film. It was also considered the temperature programming that was used in the chromatographic assay.

From the study realized for Thewalim in 2011, the retention times for Malathion, Fenitrothion and Clorpirifos were determined in the same chromatographic column and under the same temperature program. These values are designated as Malathion 1 Fenitrothion 1 and Clorpirifos 1.

The information for Malathion 2 and Clorpirifos 2 reported in Table 1 were obtained from the study realized by Borrás in 2013¹³, wherein the quantification of pesticides were developed in atmospheric residues. The data for Fenitrothion 2 are from an analysis of the molecule and its metabolites found in the Alamo¹⁴.

To solve the system, was use an Excel Spreadsheet, where carried out the model solution for the simulation of the RT (Equation 1) by Euler's method, with a step of 0,05 min¹⁵.

After, with two chromatographic results for each pesticide, in the spreadsheet were estimated the values for ΔH_s and ΔS , that adjusted the RT reported in each study, under the conditions where chromatographic assays performed.

Results and Discussion

Table 1 shows the characteristics of the chromatographic columns selected for determining the values ΔH_s and ΔS of Malathion, Fenitrothion and Clorpirifos. The retention time was showed for each one in their respective studies.

Table 1. Parameters of the column and the retention time reported in the chromatographic results for calculating the ΔH_s and ΔS .

Solute	Column	Length (m)	Diameter (mm)	Film Diameter (μ m)	RT (min)
Malathion 1 [10]	DB-5	26,2	0,25	0,25	10,35
Malathion 2 [13]	TR-5MS	30	0,25	0,25	37,08
Fenitrothion 1 [10]	DB-5	26,2	0,25	0,25	10,27
Fenitrothion 2 [14]	HP-5MS	30	0,25	0,2	5,5
Clorpirifos 1 [10]	DB-5	26,2	0,25	0,25	10,55
Clorpirifos 2 [13]	TR-5MS	30	0,25	0,25	37,41

Table 2. Temperature program used in the chromatographic assays to calculate the ΔH_s and ΔS .

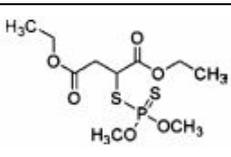
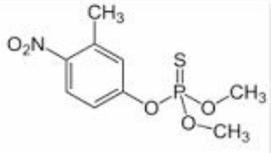
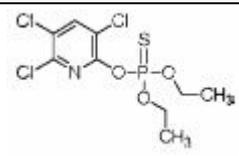
Solute	Temperature program	Operation mode
Malathion 1	60°C [I:1 min] --> 30°C/min until 120°C --> 15°C/min until 295°C [I: 5min]	Flow constant
Malathion 2	60°C [I:1 min] --> 5°C/min until 170°C --> 1°C/min until 200°C --> 15°C/min until 280°C [I:5min]	Flow constant
Fenitrothion 1	60°C [I:1 min] --> 30°C/min until 120°C --> 15°C/min until 295°C [I: 5min]	Flow constant
Fenitrothion 2	70°C --> 40°C/min until 280°C [I:10 min]	Flow constant
Clorpirifos 1	60°C [I:1 min] --> 30°C/min until 120°C --> 15°C/min until 295°C [I: 5min]	Flow constant
Clorpirifos 2	60°C [I:1 min] --> 5°C/min until 170°C --> 1°C/min until 200°C --> 15°C/min until 280°C [I:5min]	Flow constant

e (5% phenyl) methylpolysiloxane 95%.

Table 2 shows the temperature program and the operating mode used at each chromatographic assay. All assays operate at constant mass flow, which was due to the increased gas density, which causes a greater pressure drop through the column and thus a reduction in the axial velocity, which means more time in to obtaining the signal desired of the solute.

Table 3 shows the results obtained for ΔH_s and ΔS for Malathion, Fenitrothion and Clorpirifos with their respective values of retention index (RI) or Kovats index, molecular weight and chemical structure that each substance.

Table 3. Values of ΔH_s and ΔS calculated to Malathion, Fenitrothion and Clorpirifos [13]

Solute	RI	MW	Structure	$-\Delta H_s$ (kJ/mol)	$-\Delta S$ (J/mol K)
Malathion	1917 (SE-30)[16][17]	330		106	170
Fenitrothion	1944 (SE-30)[16][17]	277,23		72,7	100
Clorpirifos	1866 (SE-30)[16][17]	351		107	171,1

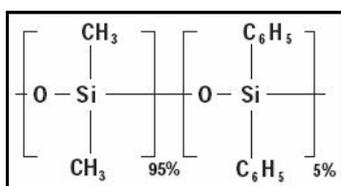


Figure 1.(5% phenyl) methylpolysiloxane 95%

The chromatographic column DB-5 consists of 95% methylpolysiloxane and 5% of the phenyl group inside his structure, so it is a non-polar medium which will retain non-polar substances on its surface. The structure of this compound is shown in Figure 1.

The RT of each pesticide (Table 1) shows that Fenitrothion was the first compound to emerge from the column, followed by Malathion and then by the Clorpirifos with a retention time of 10.27, 10.35 and 10.55 min respectively. It indicate that the substance less polar was the Clorpirifos, followed by Malathion and finally Fenitrothion which was the more polar. Due to this the Fenitrothion did not have much affinity with th

The chemical affinity between the solute and the stationary phase was directly relate with their signal received in the detector. This is because the adsorption phenomenon, which occurs on the surface of the stationary phase, where there an energy exchange system represented by ΔH_s , which was negative for a small loss.

For the solute reached the detector, must be presented inside the chromatographic column a continuous adsorption and desorption of the solute. For that the second phenomenon occurs, the mobile phase must provide the same energy lost. Thus, a substance with a high value of ΔH_s must have a higher RT.

In Table 3, this phenomenon was observed when comparing the ΔH_s of three pesticides, where the largest value was represented by the Clorpirifos, follow by Malathion and finally Fenitrothion, in the same order they had the retention time of high to low.

ΔH_s Represents the required energy to separate the solute in the mobile phase. ΔS Was a thermodynamic property that indicates the "degree of disorder" of a substance and it was the measure of irreversibility of the system. Thus, to higher values of irreversibility, it was required more resources the medium for this return to its initial state.

Table 3 shows that the higher irreversibility occurs in Clorpirifos adsorption on the surface, followed by adsorption of Malathion and Fenitrothion because they exhibit the same order for the ΔS . Thus, it requires more energy to separate from the stationary phase, causing a longer retention.

Finally in Table 3 shows the chemical structures of the pesticides of interest in this work, where it can be seen that the Clorpirifos has the lowest number of oxygen which makes this molecule less polar. Also, these oxygens were in a difficult position to access. Thus, this substance had high affinity with (5% phenyl) methylpolysiloxane 95%.

Conclusions

It were determined the values of ΔH_s and ΔS for malathion, Clorpirifos and Fenitrothion, where a greater magnitude of these parameters, the solute takes longer to display a signal in the detector and had a longer retention time (RT)..

The RT of a substance inside a DB-5 column or similar, depends on how nonpolar was this, because to higher values was presented a more chemical affinity between solute and the stationary phase, increasing the values of ΔH_s and ΔS . This implies a greater energy expenditure of the mobile phase to separate, when was done the adsorption phenomenon.

Finally, the amount of oxygen involved and his localization in the Clorpirifos molecule was analyzed. To explain how affect the polarity and its chemical affinity with the stationary phase. The Clorpirifos had less oxygen and presents greater difficulty to access them, so it was the less polar species with a highest retention time on a DB-5 column.

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