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Research Article

Organochlorine Pesticides Detection in Blacberry (*Rubus* sp.,) by Electronic Nose

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Abstract: The objective of the present investigation was to detect the organochlorine pesticides presence in Blackberry (*Rubus* sp.,) by means of the Electronic Nose, generating in the future an alternative tool for the early detection of these types of pollutants. The studied samples were randomly collected in the main market of the city of Pamplona, Norte de Santander (Colombia), followed by physical (surface area, color and firmness) and chemical (moisture, pH, soluble solids and titratable acidity) analysis to establish the appropriate maturity index. Organochlorine pesticide residues were detected (Aldrin, Beta-BHC, Delta-BHC, Gamma-BHC, Endosulfan I, Endosulfan II, 4, 4-DDE) by the coupled Gas Chromatography-Electroantennographic Detection recording (GC-EAD) and finally the measurement and validation of the method were made with the Electronic Nose. It was determined that the multisensory system is able to detect organochlorine pesticides in concentrations of 0.5; 0.7 and 1 ppm. The Electronic Nose application has potential as an alternative method for the early detection of traces of organochlorines and therefore for the innocuity of the agricultural products.

Keywords: Blackberry, chromatography, maturity index, multisensory system, organochlorine pesticides

INTRODUCTION

Pesticides are substances or mixtures used by farmers throughout the world to prevent, destroy, repel or mitigate pests and diseases in order to conserve agricultural products, as well as to increase production and ensure that there is no possibility of crop loss by unwanted organisms (Zhang *et al*., 2011; Bempah *et al*., 2012). The most commonly used pesticides for pest control are insecticides and herbicides following fungicides, acaricides, nematicides, molluscicides and rodenticides (EPA, 2009). Pesticides can be chemically classified as:

- Organochlorines (OCs)
- Organophosphates
- Carbamates
- Urea substitutes

Among them, OCs are the most dangerous and persistent organic pollutants in the environment (Choi *et al*., 2016; Barron *et al*., 2017).

In recent years, the use and quantity of pesticides in agriculture is high, therefore an increase is expected in the coming decades to meet the growing demand for food (Liu *et al*., 2002; Bempah and Donkor, 2011). Its use is due to the biocidal properties and the selectivity that they possess (Cooper and Dobson, 2007; Cortes *et al*., 2006). However, inadequate use at erroneous times and levels of toxicity have led these substances to represent a potential risk to human health (de Albuquerque *et al*., 2017; Saeed *et al*., 2017) and for the general environment, affecting the soil (Andreu and Picó, 2004; Mahugija *et al*., 2014; Sánchez-Osorio *et al*., 2017), water (Mekonen *et al*., 2016; Kafilzadeh, 2015), air and some agricultural products (Bempah *et al*., 2016; Liu *et al*., 2016; Skretteberg *et al*., 2015); becoming contaminating waste in the final product that goes to the consumer and a negative impact on its commercialization (Guerrero, 2003; Francisand Betancour, 2007; Yadav *et al*., 2015); Then, carrying out monitoring and control is a primary activity in determining the quality and safety of food because most of the human population is exposed to pesticides, with babies being a specific vulnerable subgroup because their processes metabolites are immature and consume more fruits than adults (Lozowicka, 2015; Colosio *et al*., 2017).

Nowadays, foods are analyzed by different specific techniques, such as chromatography (Masiá *et al*.,

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2014; Hou *et al*., 2016; Villaverde *et al*., 2016) with the objective of establishing the residuality of the pesticides present in the product and the environment (López *et al*., 2017). However, these analyzes are expensive, which has motivated scientists to investigate other fields, such as nanotechnology, obtaining results equal to or better than chromatography in shorter times and with lower costs. The use of the electronic nose has very interesting advantages (Quicazan *et al*., 2011; Costa *et al*., 2016; Ortiz *et al*., 2016; Maldonado *et al*., 2016).

The development of technology has allowed the electronic nose to become a valuable tool to solve problems in the world (Lundström *et al*., 2007; Guo *et al*., 2015; Fitzgerald *et al*., 2017) and in different areas of knowledge (Jiang *et al*., 2015) as the quality assessment and detection adulteration in food (Abbasi *et al*., 2015; Herrero *et al*., 2016).

To establish if chemical residues exist, the present investigation was proposed in the cultivation of blackberry (*Rubus* sp.,) in the region of Pamplona (Norte de Santander) of the 31 producers of the 35 localities of the Municipality (La Opinión, 2015) generating another alternative for reduce the time of detection of pesticides in fresh fruit and facilitate the acceptance or rejection of the product.

MATERIALS AND METHODS

Raw material characterization: In the selection and classification of the samples of blackberries (*Rubus* sp.,) the state of maturity contemplated in the norm NTC 04106 (Table 1).

Subsequently, physical characteristics (surface area, color and firmness) and chemical (moisture, soluble solids, pH and titratable acidity) of raw materials were analyzed in triplicate for each sample using the methods defined in the AOAC (1994) for food analysis.

Chromatographic analysis: The QuEchERS method was used for the extraction of organochlorine pesticide residues in the samples, using the certified mixture of organochlorine pesticides Part. No. M-8081-SC (AccuStandard, Inc., 125 Market Street, New Haven, CT 06513). Chromatographic analysis was performed on an HP 6890 Series PLUS gas chromatograph (Hewlett-Packard, Palo Alto, California, USA), equipped with an Electron Capture Detector (ECD). The column used in the analysis was DB-5 {5%-phenyl-polo (methylsiloxane), 30 m×0.25 mm×0.25 µm. The injection was performed in Splitless mode (Viny = 1 µL). To assess the sensitivity method, detection limit and pesticides quantification limit were determined. The pesticides analyzed in the fruit samples were Aldrin, Beta-BHC, Delta-BHC, Gamma-BHC, Heptachlor, Endosulfan I, Endosulfan II, 4, 4-DDE.

Table 1: State of maturity of the fruit (*Rubus* sp.,)

Maturity state	Description
5	Fruit with a half-red area and a half purple area
6	Dark purple fruit

Table 2: Matrix sensors used in E-nose 2.0

Sensor reference	Specific use
FS1	Sensor reference
FS2	Hydrogen and fuels
FS3	Combustible gases
FS4	CFC
FS5	Hydrogen sulfate
FS6	Food odors, volatile gases, water vapor in food
FS7	Organic vapors, alcohol, toluene, xylene

Electronic nose system: For the analysis of the prepared samples the Electronic Nose was used which is a prototype designed by the Electronic Engineering Program of the University of Pamplona called E-nose 2.0 (Ortiz, 2016) composed by a matrix of seven Metal Oxide Semiconductor Sensors (MOS) (Figaro Engineering, Osaka, Japan) (Table 2).

The organochlorine pesticides standard solutions were prepared using different solvents according to the pesticides characteristics: for Aldrin, Endosulfan I and II, Beta-BHC acetone was used and for Delta-BHC, Gamma-BHC, Heptachlor and 4, 4-DDE; Methanol. Samples were doped in the two maturity stages established with the POCs at three different concentrations (0.5, 0.7 and 1 ppm, respectively) for a total of 85 samples including the control sample. With the prepared solutions, the multisensory system was trained in order to capture and record the signals and patterns corresponding to each chemical, which were subsequently recorded and evaluated. In order to carry out the training of the Electronic Nose, rest time between each concentration (30 min) and the characteristics of the sensors were taken into account.

Statistical analysis of data: For the physicochemical analysis of the fruit samples was applied the Analysis of Variance (ANOVA). The statistical significance of the maturity stages was determined using the Tukey and DMS comparison test ($p \leq 0.05$). The physical-chemical analysis correlation, the chromatographic profile, the training, the measurement and the validation of data with Electronic Nose were realized through the Principal Components Analysis (PCA) and the Support Vector Machines (SVM), allowing the separation of non-linear data. The transformation was obtained with functions called cores processed in SPSS v 22.0.

RESULTS AND DISCUSSION

Physicochemical characteristics: Figure 1 shows that there are significant statistical differences in L, a, b parameters between the 2 states of maturity of the blackberry. This is because anthocyanins and carotenoids increase as the fruit develops (Ayala *et al*., 2013). The state of maturity 5 presents an intense red color with little purple drupes and the 6, has a dark purple coloration (NTC 4106, 1997). In the case of length, width and thickness for the 2º of maturity analyzed, the analysis of variance established

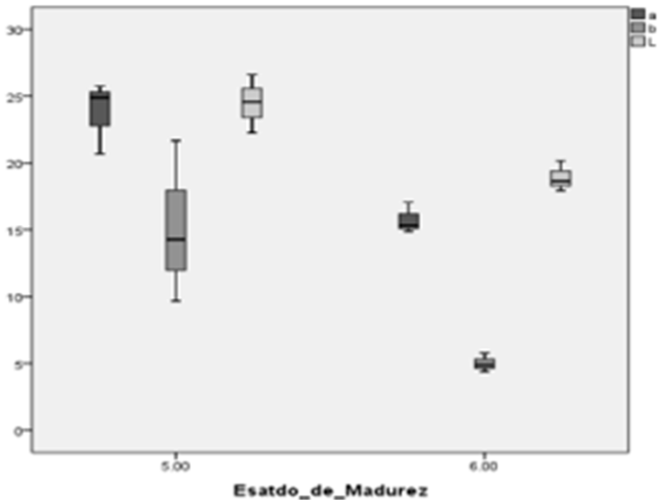

Fig. 1: Box plot of the color, length, width and thickness parameters with respect to the state of maturity of the blackberry

Table 3: ANOVA of the weight, moisture and ºbrix of the two maturity stages of the blackberry

Parameter	S.V.	df	M.S.	F	p* value
Weight	Between groups	1	3.082	7.793	0.049
	Within groups	4	0.395		
	Total	5			
Moisture	Between groups	1	0.749	0.241	0.649
	Within groups	4	3.113		
	Total	5			
Brix	Between groups	1	0.107	0.299	0.614
	Within groups	4	0.357		
	Total	5			

S.V.: Source of variation; M.S.: Mean square; *: $p<0.05$ indicates significant difference

Table 4: Analysis of Variance (ANOVA) of pH and acidity of the two maturity stages of the blackberry

Parameter	Source	df	M.S.	F	p* value
pH	Between groups	1	3.286	172.623	0.00
	Within groups	4	0.190		
	Total	5			
Acidity	Between groups	1	62.727	55.923	0.02
	Within groups	4	1.122		
	Total	5			

M.S.: Mean square; *: $p<0.05$ indicates significant difference

that there are no significant differences between the measures analyzed.

Table 3 shows that weight had statistically significant differences, observing a downward behavior between the maturity stage 5 and 6 of 7.65 to 7.58 g respectively. This can be due to the importance of the harvest, transfer, packing, storage and transport conditions of the fruit, since these can influence that the harvested blackberry does not reach the structural changes in the protopectin, generating softening of the tissues, releasing water and other compounds causing weight reduction. Regarding to the TSS content and moisture, the variance analysis established that there were no significant statistical differences between the two maturity stages, obtaining average values corresponding to 6.4-6.67 for brix and 82.85-83.56 for moisture.

In general, the fruit moisture content presented an upward trend attributable to the fulfillment of the biological cycle of the fruits in the phases of growth and maturation, as well as respiration (Alvarez-Herrera *et al*., 2009). ANOVA showed that there is no statistically significant difference (p = 0.649) between the moisture means for the evaluated maturity states, results that are similar to those obtained by Ayala *et al*. (2013).

Regarding to the total soluble solids content, an directly proportional increase to the maturity degree was presented; behavior attributable to the conversion of the organic acids into sugars (Soledad *et al*., 2012) or to the carbohydrate reserve of the plant due to the low fruit´s photosynthetic capacity (Ayala *et al*., 2013). The values obtained by SS variable differ from those reported in the standard NTC 4106 (7.2-7.7 for MD 5 and 7.9-8.5 for MD 6), but are similar to those obtained by Alzate-Quintero *et al*. (2010), who found in the evaluated blackberries of two zones of the Caldas department, that the average °Brix content obtained was of 6.948 and 6.432 respectively.

The above may be due to the fruits respiration that is classified as non-climacteric, characteristic that affect the soluble solids content, the sugars synthesis and other compounds during the fruit development and maturation, even when changes in coloration occur. Other factors that be taken into account are the variety of the fruit, the assimilative yield of the leaves, the leaf/fruit ratio, the weather conditions during its development and its storage conditions (Ayala *et al*., 2013). Likewise, the positive correlation between the maturity stage and the increase of TSS attributed to the conversion of organic acids into sugars or the translocation of reserve carbohydrates to simple saccharides due to the low fruit´s photosynthetic capacity (Llácer, 2008). Table 4 shows that exist statistically significant differences between the pH and the acidity in the evaluated maturity stages.

These results are similar to those obtained by Ayala *et al*. (2013), Alzate-Quintero *et al*. (2010) and Bernal-Roa *et al*. (2014); who found significant

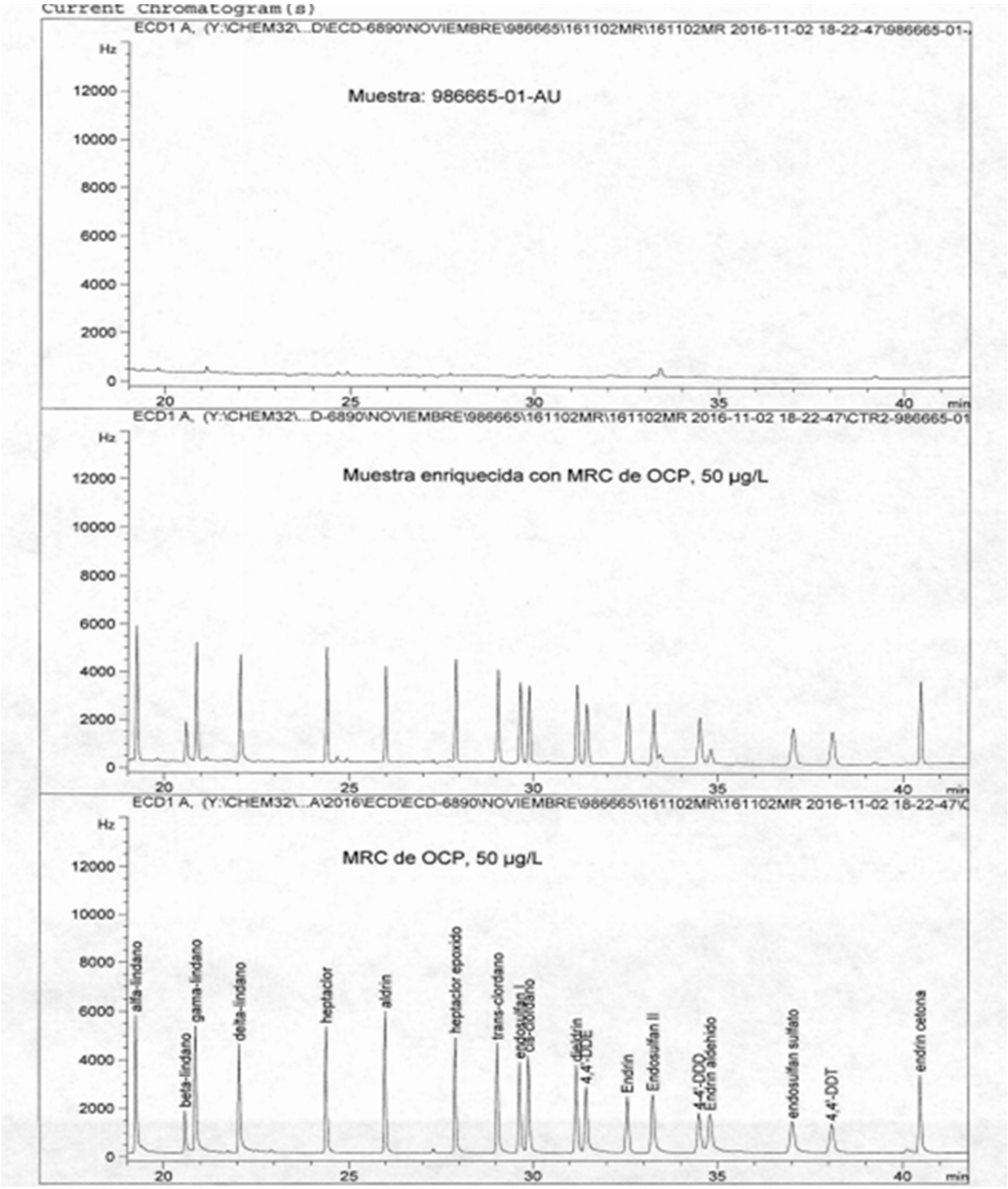

Fig. 2: Organochlorine pesticides residues in blackberry (*Rubus* sp.,)

differences in the pH and the decrease of the acidity percentage of different maturity stages of the Castilla blackberry. According to Jaramillo *et al*. (2000), the pH and the soluble solids of the materials increase at the end of the maturation stage while the acidity percentage decrease.

Montalvo (2010) reports that this behavior is due to the natural biochemical changes in the fruit that occur in the first stages of the maturation process, where the organic acids concentration or other contributing hydrogen compounds increase, resulting from the activity of specific enzymes that promote the accumulation of sucrose and glucose during the fruit filling, causing the pH increase and the acid concentration decrease during the last maturation stages. In the same way, Ligia *et al*. (2010) concluded that the variable behavior of this parameter in the final maturity stages (5 and 6) is considered to be related to the increase in the respiratory rate and the content of sugars and pigments during the maturation and senescence. In the case of firmness, there were no significant differences between the evaluated fruit for the two maturity stages, with averaged values between 7.6-7.7 N respectively, values similar to reported by Moreno and Deaquiz Oyola (2016).

Chromatographic analysis: In the fresh fruit samples *Rubus* sp., analyzed no pesticide residues were found that exceeded the standard allowed limit (0.001 mg/mL) (Fig. 2). A similar case occurred with the results

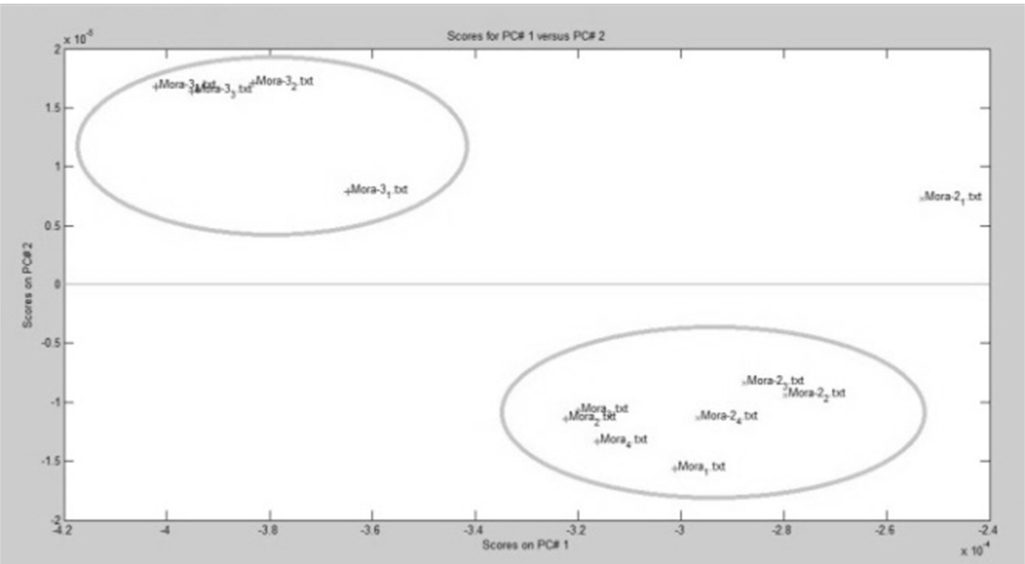

Fig. 3: PCA of fresh fruit without pesticide using the electronic nose

obtained by Guerrero (2003) who did not find residues that exceeded the Maximum Residue Limits (MRLs) in 95.4% of the fruit samples evaluated in different departments of Colombia.

Other similar results were obtained by Bempah *et al*. (2016) where data revealed that 80% of the fruit and vegetable samples analyzed contained pesticide residues below the Maximum Residue Limit (MRL) approved by the Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) of the Codex Alimentarius Commission (CAC).

Electronic nose: First, the PCA analysis was performed to establish if the electronic nose would recognize the fresh fruit without pesticide in its two states of maturity, as shown in Fig. 3, where was clear that there was a 100% of positive response of recognition of the sensors where the electronic nose separated the natural fruit from the pesticide contaminated fruit, result also obtained by Ortiz (2016).

Subsequently, analysis was performed to the pesticides under study in order to determine if the electronic nose differentiated the concentrations of 0.5; 0.7 and 1 ppm, obtaining that the Electronic Nose sensors classified the different pesticides concentrations under study (Fig. 4).

After analyzing the principals components in the pesticide contaminated fruit under study, the training of the Support Vector Machine (SVM) was performed with the SMO algorithm (Sequential Minimal Optimization) for the binary SVM using a RBF kernel (Radial Basis Function) or Gaussian with σ = 1 and C = 100. Seven generalized signals of each pesticide with an average concentration of 0.5-0.7 and 1 ppm were used and then the classification was performed using random signals (concentrations of pesticides different from those previously established) that were not used for the training of the machine and allowed to establish the robustness and reliability of the training. In addition, the percentages of detection of the pesticides by the sensors were established (Fig. 5) the sensors that have the best detection response to the pesticides present in the blackberry (*Rubus* sp.,)

The sensors that detected the signals were FS2, FS4 and FS5, relating an electrochemical energy that oscillates between 0.8 and 1.5×1011 respectively; standing out a signal or electrochemical pattern of greater intensity (2 to 3.5 1.5×1011) in the blackberry detection with Endosulfan II.

Taking into account the detection factors analyzed above, it can be inferred that the sensors selected for the detection of pesticides in the blackberry vary in comparison to the strawberry because of the characteristics of the volatile compounds of the fruit and the specificity of the sensors. In the blackberry, there are secondary metabolites that give the aroma, color and the characteristic flavor (Balasundram *et al*., 2006). These compounds are flavonoids especially anthocyanins, with antioxidant capacity that promote the formation of products with a low toxicity like phenols, production of alcohols, aldehydes, esters and ketones and influence the red, blue and violet colors of the fruit (Magalhães *et al*., 2008; Perkins-Veazie *et al*., 2000) during storage.

The FS2, FS4 and FS5 sensors respond to aromatic compounds of short-chain organic substances such as combustible gases, Chlorofluorocarbons (CFCs) and organic vapors, alcohol, hydrogen and methane respectively (Table 2), with a recognition of 85.71% in general. Similar results were reported in the research conducted by Bernal-Roa *et al*. (2014), who stated that

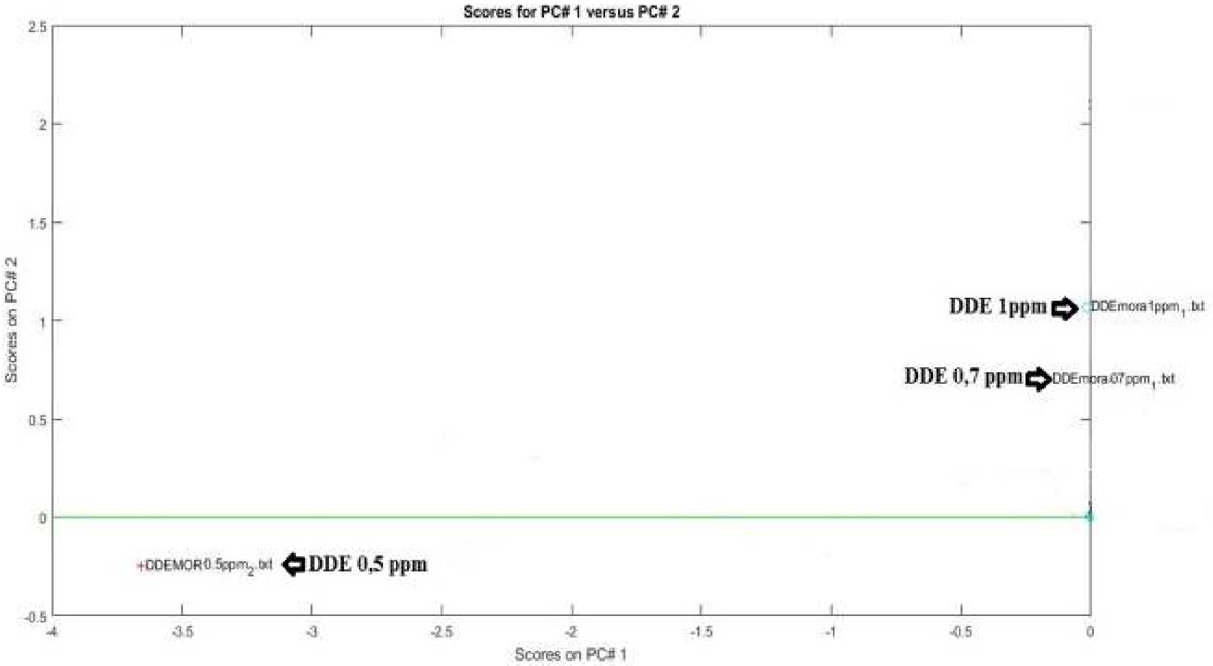

Fig. 4: PCA in blackberry (*Rubus* sp.,) contaminated with three different pesticide concentrations 4,4-DDE using electronic nose

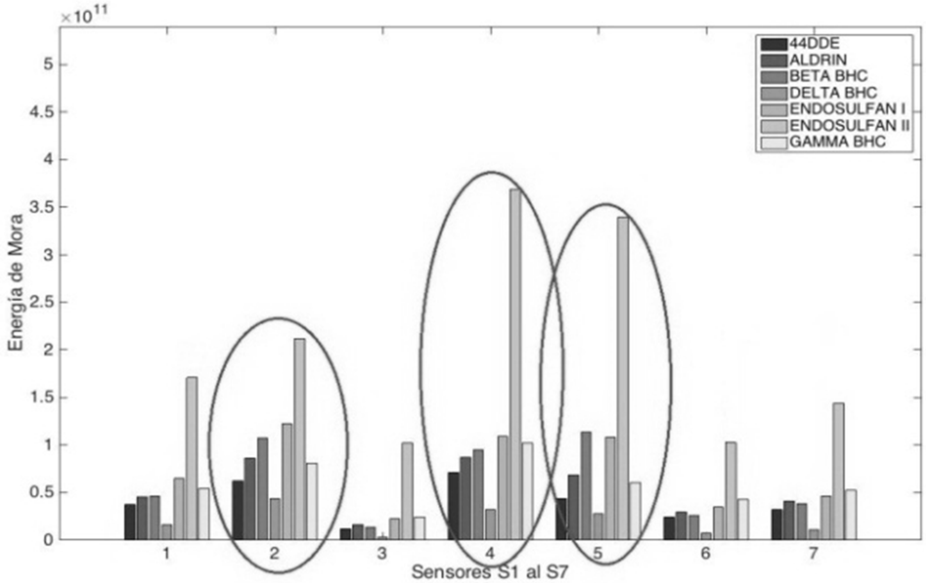

Fig. 5: Sensors response in the pesticides detection by electronic nose in blackberry (*Rubus* sp.,)

the state of harvest can be distinguished by the evaluation of the aromatic profile and the content of anthocyanins showing the total phenol content and the antioxidant capacity between different stages of maturity of the fruit. In the same way, they obtained that the volatile compounds released by the blackberry in maturity different states were detected by the sensors that recognized the following compounds: Hydrogen, methane, sulfur compounds and terpenes, alcohols and organic compounds; characteristics that are in line with those sensors used in the present investigation.

CONCLUSION

The Electronic Nose is an alternative analytical instrument to detect traces of pesticides in different concentrations (0, 5; 0, 7 and 1 ppm, respectively) in the blackberry. Sensors FS2, FS4 and FS5 were identified as the most suitable for detecting aromatic compounds of blackberry with a recognition level of 85.71%. This allows us to propose this multisensory system as a monitoring and monitoring tool for chemical contaminants in the agro-food sector, obtaining real-time results and other multiple advantages that provide a positive impact on food science and technology.

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CONFLICT OF INTEREST

The authors state that there is no commercial or associative interest that represents a conflict of interest with the results of the article.

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