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ORIGINAL ARTICLE

Use of the SPME-GC/MS/FID Technique as Effective Alternative for the Determination of Organophosphorus Pesticide Residues

Empleo de la técnica SPME-GC/MSD/FID como alternativas efectivas para la determinación de residuos de pesticidas organofosforados

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ABSTRACT. Organophosphorus pesticides (OPs) widely used in agriculture, can cause toxic effects to humans and animals. The indiscriminate use of pesticides has generated numerous environmental problems. Especially, in the long term, they can cause serious harm in ecosystems and their associated individuals. The purpose of this investigation was to determine if the milk that is commercialized in the city of Cartagena de Indias has residual concentrations of organophosphorus pesticides. Seven milk samples were analyzed: six types of pasteurized milk of different brands and one type of raw milk obtained from a herd of Maria la Baja Municipality, Bolívar, Colombia. The extraction technique used was solid phase microextraction (SPME) in headspace (HS) mode and the methods employed for separation and identification of the compounds were gas chromatography (GC) with flame ionization detector (FID) and mass spectrometry detector (MSD). These methods proved to be advantageous in its application because of their environmental relevance and proficiency in obtaining confirmed accurate results. Organophosphorus compounds were not detected in the milk samples.

Keywords: Milk, organophosphorus Pesticides, Extraction, Identification, Quantification.

RESUMEN. Los pesticidas organofosforados (OPs) están siendo ampliamente usados en la agricultura, ellos pueden causar efectos tóxicos en humanos y animales, generando numerosos problemas ambientales. Especialmente, a largo plazo, puede causar daños graves en los ecosistemas y sus personas asociadas. El objetivo de esta investigación fue determinar si la leche que se comercializa en la ciudad de Cartagena de Indias tiene concentraciones residuales de plaguicidas organofosforados. Se analizaron siete muestras de leche, seis tipos de leche pasteurizada de diferentes marcas y un tipo de leche cruda obtenida de una piara del municipio de María la Baja, Bolívar, Colombia. La técnica de extracción utilizada fue microextracción en fase sólida (SPME) en modo headspace (HS) y los métodos empleados para la separación e identificación de los compuestos fueron cromatografía de gases (GC) con detector de ionización de llama (FID) y detector de espectrometría de masas (MSD). Estos métodos reflejaron ser ventajosos debido a su solidez ambiental y facilidad en sus resultados precisos confirmados. Los compuestos organofosforados no se detectaron en las muestras de leche**.**

Palabras clave: leche, plaguicidas organofosforados, extracción, identificación, cuantificación.

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INTRODUCTION

Within the agricultural industry, synthetic chemicals are used to increase the quality and yield of crops. One type of synthetic chemicals are organophosphorus pesticides (PO) that help to keep food in excellent conditions by attacking crop-damaging pests. After discovering that these types of pesticides are easily degradable, they are considered as a more environmentally friendly solution compared to organochlorine pesticides that are more persistent despite the fact that PO possess greater acute toxicity (Rodrigues *et al.*, 2011). Organophosphates are characterized as phosphoric acid esters, and are used as broad-spectrum insecticides in various crops (Pagliuca *et al.*, 2004). Additionally, organophosphates can act as neurotoxic compounds, because they are inhibitors of the cholinesterase enzyme, an enzyme, which is responsible for the proper functioning of the nervous system (Fenik *et al.*, 2011). The indiscriminate use of pesticides has generated numerous environmental problems, especially in the long term. The health of all species is put at risk when they are exposed daily to unknown doses of these potential aggressors. Considering this major problem, organizations such as Codex Alimentarius Commission (CODEX), have been responsible for regulating the use of various pesticides in foods such as milk. One method of control is to establish maximum residue levels (MRLs) of pesticides for each product in order to define suitable levels for human consumption. In this way, CODEX hopes to mitigate the effect of these pesticides. To enforce these restrictions, officials must have the means to assess the levels of organophosphates in crops. This was the point of departure for analytical scientists to create and search new detection methods for products containing pesticides. (Sang *et al.*, 2013).

Standard consumable milk can be contaminated by pesticides through various routes of exposure. Either prior to processing through the cow's consumption of pesticide-contaminated food, grazing on soils that have been affected by these contaminants, or direct application to animals in stables. Alternatively, it can also occur during processing in the milk producing industries, where pesticides are applied to eliminate insects in order to guarantee the hygiene of the product (Santaeufemia *et al.*, 2006).

Milk-producing animals exposed to high pesticides conditions are able to transfer a significant load of pesticides to their metabolic process, where these pesticides accumulate in lipids and lipoproteins (Dagnac *et al.*, 2009). Thus, the main causes of organophosphate residues presence in milk are the excessive and poorly regulated use of these compounds in agricultural practices for pest control, and their particular physicochemical property of liposolubility.

Different methods of sample preparation were employed over time such as liquid liquid extraction (LLE), solid phase extraction (SPE), dispersive solid phase extraction (DSPE), matrix solid phase dispersion (MSPD) and solid phase micro extraction (SPME), among others. (González *et al.*, 2005; Xu *et al.*, 2016). The different analysis methods were developed with the objective to quantify pesticide residues in milk, mainly based on chromatographic techniques (Nunez *et al.*, 2005; Gomes *et al.*, 2013).

Standard analytical procedures to detect PO residues in samples consist of the use of highly toxic chemical compounds or very volatile solvents for the sample treatment (Tobiszewski *et al.*, 2009; Armenta y de la Guardia, 2016). Gas Chromatography -Headspace (GC-HS) is considered a 'green' analytical technique, since it is somewhat environmentally friendly. The advantages of its use are: (i) reduction of analytical plates, (ii) elimination of solvents and reagents, (iii) use of relatively low temperatures, (iv) easy and rapid analysis, and (v) application to both liquid and solid samples. Dynamic and static systems can be used in conjunction with desorption techniques such as solid phase microextraction (SPME). This sample preparation technique is advantageous, compared to others because it does not require any kind of solvents and it allows combining sampling, analyte isolation and enrichment in one-step. It is composed of a fiber coated with a solid sorbent or a liquid polymer depending on the exposure format of the sample. (Dagnac *et al.*, 2009; Armenta y de la Guardia, 2016; Xu *et al.*, 2016). By means of the SPME technique, it is possible to analyze several complex matrices, including environmental, biological and food samples as confirmed by Lin *et al.* (2016). In the analysis of pesticide residues, SPME also allowed the determination of different classes of pesticides, such as organophosphorus, organochlorine and pyrethroid, in numerous types of matrices such as wine urine, serum, samples of environmental liquids and milk, (Rodrigues *et al.*, 2011; Gomes *et al.*, 2013).

The purpose of this research was to identify and determine organophosphorus pesticide residues in processed cow's milk commercialized in the city of Cartagena de Indias. The analysis was performed with the help of solid phase microextraction (SPME) in headspace and chromatography (GC) with a flame ionization detector (FID) and a mass spectrometry detector (MSD).

METHODS

Reagents. The standard solutions disulfoton, chlorpyrifos and diazinon were purchased from Fluka Analytical (Germany). The solvents Acetone and n-Hexane were analytical grade (Panreac, USA). A solution of 500 µg / mL dissolved in acetone was used: Hexane (2:8), for each of the evaluated pesticides. All organophosphorus compounds' solutions were protected from light and stored at low temperatures prior to use.

Chromatographic Conditions: Analyzes were performed using a GC / FID (Agilent 4890) chromatographic system, in splitless mode, and a capillary column. (HP-5 30m x 0.32mm ID x 0.25 µm). Helium was used as entrainment gas. The initial temperature was 60°C for 2 minutes, with a heating rate of 15°C / min until 160°C, held for 6 minutes, and a heating rate of 20°C / min to 280°C, held for 10 minutes. The temperature of the detector was 300 ° C.

The solid phase microextraction procedure (HS-SPME) was carried out using a 65 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB) fiber, Supelco brand (North Harrison road, Bellefonte PA).

Qualitative and quantitative analyses were performed using standard patterns of organophosphorus compounds.

GC- MS analysis were carried out using a gas chromatograph *Agilent Technologies* 7890A Network GC (Palo Alto, California, USA) coupled to a mass selective detector (MSD) *Agilent Technologies* 5975 inert GC−MS system, equipped with an automatic injector *Agilent* 4513A. The column used was a capillary column HP-5MS (30m x0.2 5mm id) coated with 5% diphenyl-95% polydimethylsiloxane (0.25 µm phase thickness) (J&W Scientific, USA), the carrier gas was helium (quality grade 5.0, 99.99%) at 87 kPa (1.17 mL/min); the injection mode was splitless and the sample volume injected was 1 µL. The mass spectra were obtained by electron-impact ionization (EI, 70 eV). The temperatures of the ionization chamber and transfer line were 230°C and 300°C, respectively, and the acquisition mass range was 50-500 m/z.

Samples of Milk. Samples were collected from bags of pasteurized milk, which were purchased in chain supermarkets in the city in February 2016 and stored at low temperatures (4°C) until analyzed. Untreated milk samples were also taken from the farms of María la Baja Municipality, which were stored in glass bottles and placed in iceboxes, and then transported to the laboratory for later analysis.

Fiber Exposure Time. In order to optimize the adequate time for the extraction of the pesticides, a validation of the exposure time of the polydimethylsiloxane-divinylbenzene fiber was carried out, with times of 15, 30, 45, and 60 minutes (Rodrigues *et al.*, 2011).

Solid Phase Mircroextraction Procedure. The extraction step was performed by placing 12 mL of milk in an amber vial with a screw cap, and a 20 mL silicone septum. The milk sample was subsequently heated to 90°C with stirring at 600 rpm. Then the previously activated polydimethylsiloxane-divinylbenzene fiber was transferred through the septum of the vial, in the headspace, to be exposed to the milk sample for 45 minutes. After this time, the fiber was removed from the vial and the compounds extracted on the fiber were desorbed thermally in the port of injection of the gas chromatograph for 5 minutes (Rodrigues *et al.*, 2011).

Preparation of the Samples for Validation: As a reference for the validation of the analytical method, the validation guides for the Ministry of Health of Costa Rica were followed (Ministerio de Salud Pública de Costa Rica, 1998).

To evaluate the parameters of linearity, precision and accuracy, 9 concentrations of diazinon were prepared in duplicate in the range of 50 to 200 mg / kg. The linearity of the method was performed by linear regression. Three dilutions of the standard were analyzed in triplicate for calculation. External standards were used for the quantification of the different milk samples.

RESULTS AND DISCUSSION

After the data analysis by means of method validation, a linear response in the range of 50 to 200 mg / kg was demonstrated. The correlation coefficient was higher than 0.99 (Figure 1).

Precision was assessed by twelve determinations with four levels of concentration 50, 100, 150 and 200 mg / kg. The results obtained are shown in Table 1. The values of relative standard deviation were less than 2%, confirming the accuracy of the analytical method.

The test results are shown in Table 2. The percentages of recovery are within the standard limits of 86.02 - 95.32, as defined in the agreement of the European Commission Regulation, which establishes recovery values between 70% and 120% (FAO/OMS, 2010).

In Table 3, Minimum Detection Level (NMD) and Minimum Level of Quantification (NMC) for organophosphorus pesticides evaluated in milk are shown.

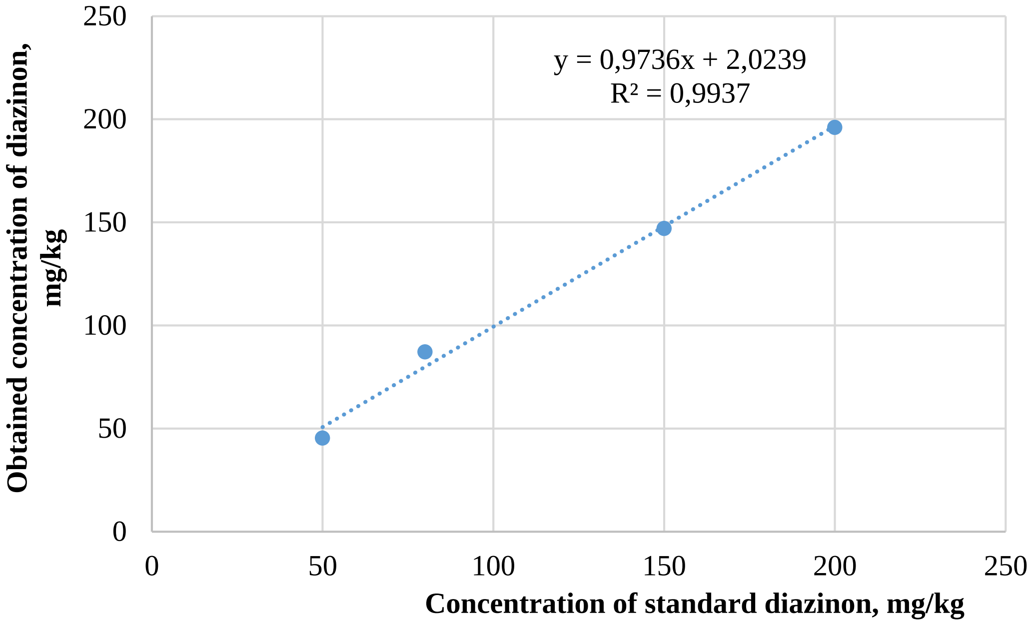

FIGURE 1. Graph of the accuracy study.

TABLE 1. Results of the Study of the Validation of the Analytical Method for the Determination of Pesticides in Milk

Concentration (mg/kg)	Day	x̄	Standard Deviation	Relative Standard Deviation
50	1 2 3	45,3	1.94	2.75%
100	1 2 3	87.10	0.66697	0.77%
150	1 2 3	139.55	0.7207	0.52%
200	1 2 3	184.41	1.7271	0.93%

TABLE 2. Results of Method Accuracy

Concentration Diazinon (mg/kg)	Recovery Percent (%)
87.10	89.00
139.55	93.03
184.41	92.47

TABLE 3. Results of NMD and NMC

Pesticides	NMD mg/kg fat	NMC mg/kg fat
Diazinon	0.0004	0.0016
Disulfoton	0.004	0.016
Chlorpyrifos	0.004	0.016

In Figure 2, total areas for each POs are shown. In addition, the exposure time is shown in which the areas had the maximum increase to 45 minutes. Thereby, this time was chosen to carry out the solid phase microextraction process.

The calibration curves were obtained with three concentrations of the standards (Disulfoton, Diazinon, Chlorpyrifos). These curves are presented in Figure 3.

In Figure 4, a chromatographic profile of the organophosphorus pesticides dissolved in the Acetone: Hexane solution is shown. In Figure 5, the chromatographic profile of the milk enriched with the diazinon, chlorpyrifos and disulfoton compounds, is illustrated.

The results of this analysis suggest that there was no detectable presence of organophosphorus pesticides (Table 4). The method developed in this research was gas chromatography coupled to a flame ionization detector (FID) and confirmation with mass spectrometry detector (MSD).

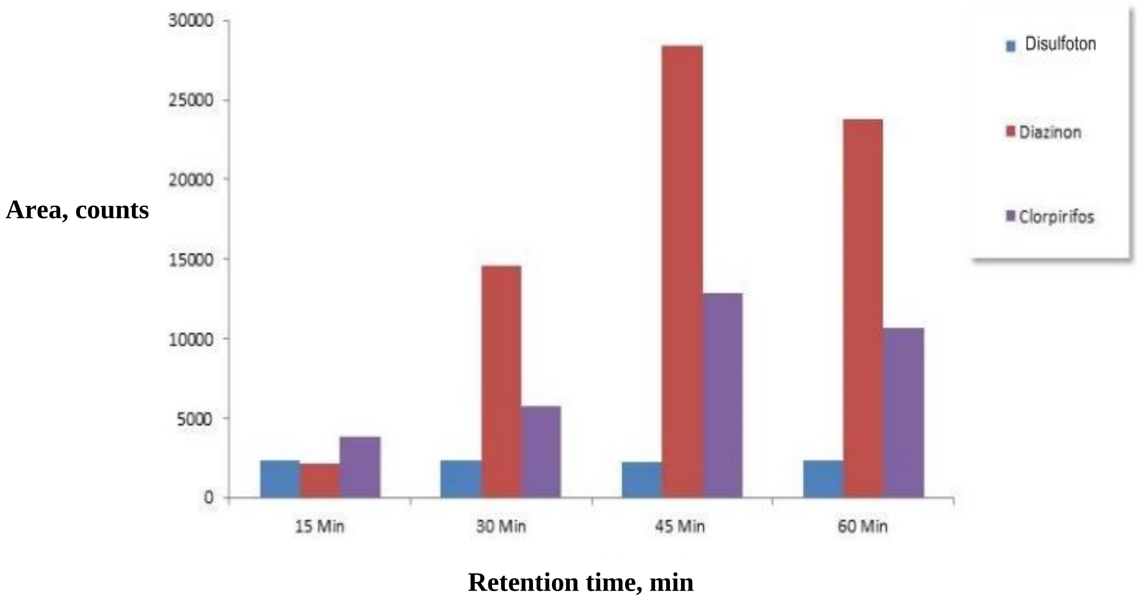

FIGURE 2. Evaluation of exposure time for microextraction.

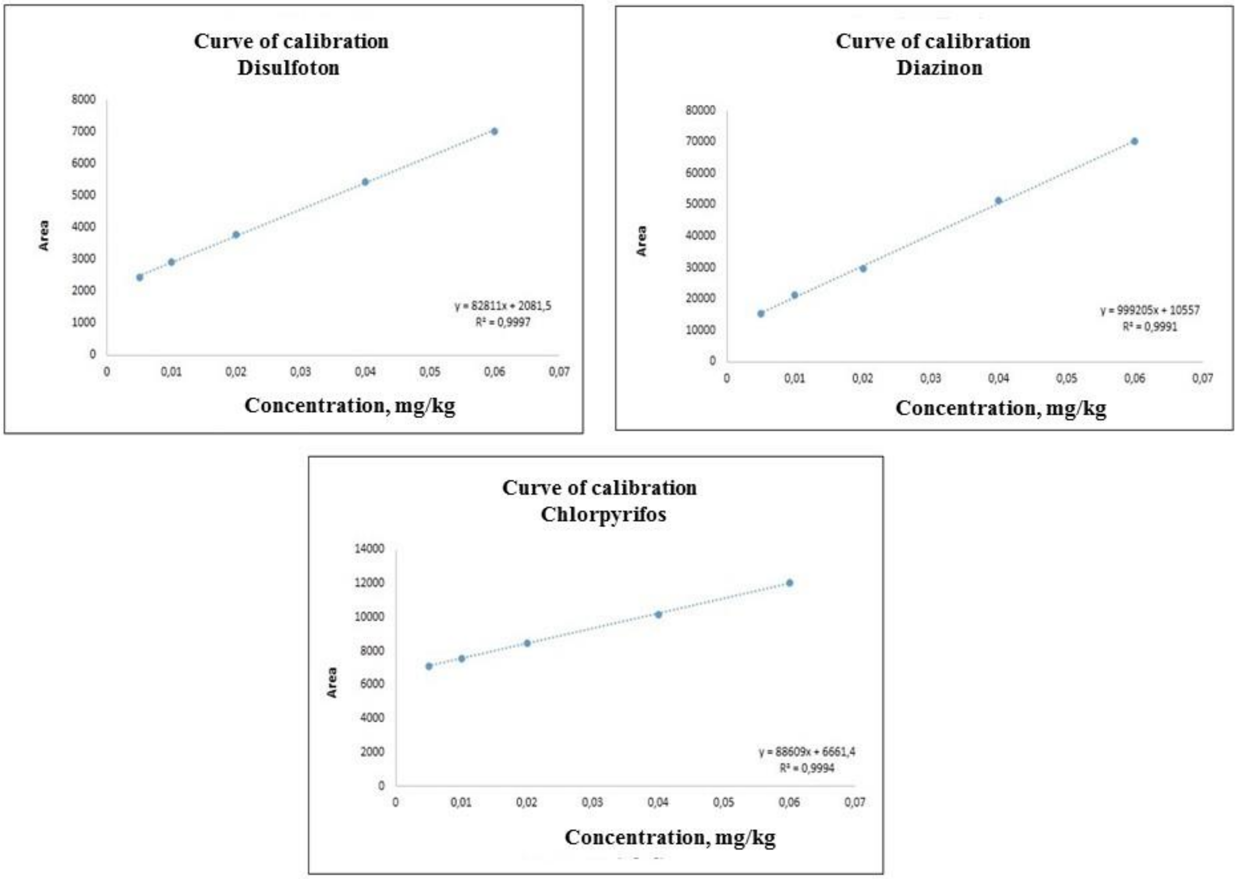

FIGURE 3. Calibration curves for the organophosphates used.

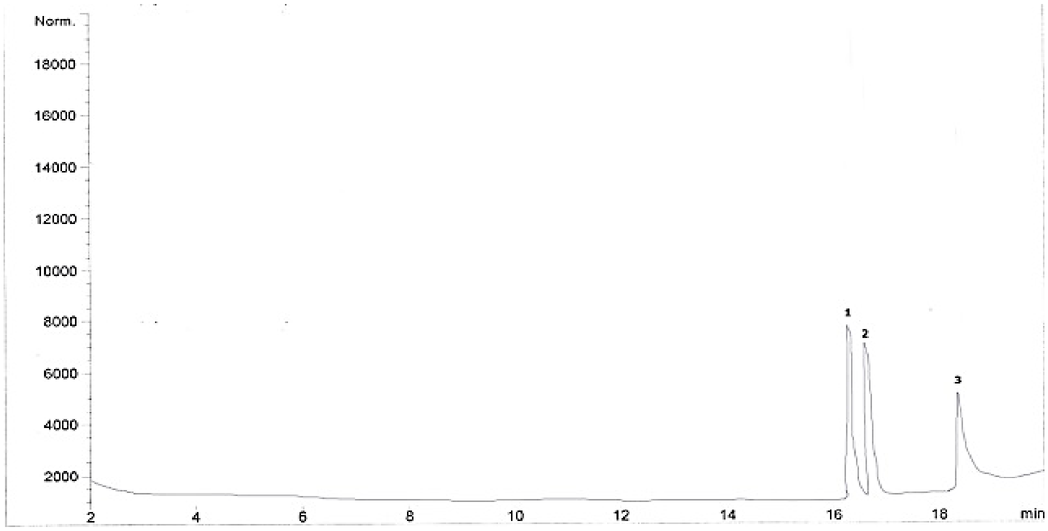

FIGURE 4. Chromatographic profile of the mixture of the three organophosphorous patterns. Peak #1 corresponds to diazinon, peak #2 to disulfoton, and peak #3 to chlorpyrifos.

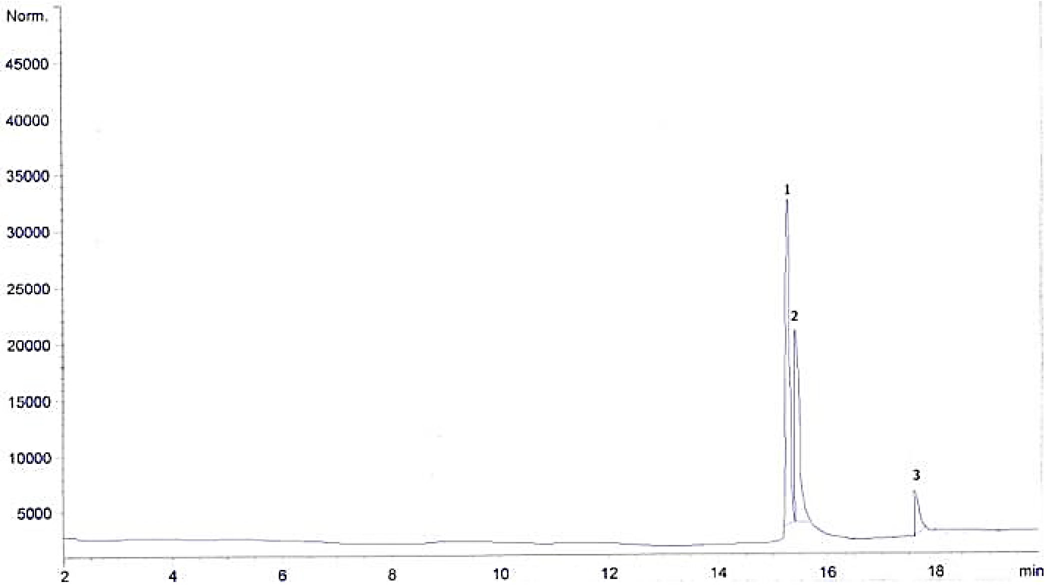

FIGURE 5. Chromatographic profile of milk doped with organophosphate patterns. Peak #1 corresponds to diazinon, peak #2 to disulfoton, and peak #3 to chlorpyrifos.

TABLE 4. Results of Analyzed Samples

	Diazinon	Disulfoton	Chlorpyrifos
Marca A	N.D	N.D	N.D
Marca B	N.D	N.D	N.D
Marca C	N.D	N.D	N.D
Marca D	N.D	N.D	N.D
Marca E	N.D	N.D	N.D
Marca F	N.D	N.D	N.D
Marca G	N.D	N.D	N.D
LMR (mg/kg)	0,02	0,01	0,02

Diverse analyses have worked the presence of organophosphorus compound pesticides in the foods being obtained as a result, the detection of residuals in high and low concentrations. Among them, there is the study on the presence of pesticide residues in the feed chain of cattle milk that have mainly focused on the presence of organochlorine pesticides because of their high persistence and liposolubility (Selvi *et al.*, 2012). However, their progressive disuse in favor of organophosphorus compounds has led to studies being done on the residual content of organophosphorus compounds (Santaeufemia *et al.*, 2006; Rodrigues *et al.*, 2011).

It has generated the necessity of chemical analysis methodologies to detect the presence of certain pollutants. When considering the low levels that characterize the allowed maximum concentrations reported for organophosphorus pesticides in milk, it should be emphasized that methodologies of chemical analysis directed to the detection and quantification of these pesticides should be able to provide high recovery rates and low detection limits (LeDoux, 2011).

Methodologies like those of HS-SPME, allow analyzing residuals of OPs in cow milk, giving as results, in conditions standardized, detection limits and quantification oscillated among 2.16 µg/ L and 6.55 µg/ L for etion, 10.9 µg/ L and 32.9 µg/ L for Methyl Paration. After the use of the outlined method, chlorpyrifos and ethion residuals were detected in samples of not processed milk. This procedure also demonstrated to be good for the determination of pesticides that it is at low cost and it avoids the use of solvents in the course of the extraction of the sample, becoming a friendly alternative with the atmosphere (Rodrigues *et al.*, 2011).

In the research have presented the clear need to establish control and monitoring mechanisms, after carrying out the pertinent analyses to each of the samples, no traces of any type of pesticides were found. Due to that, a doped with three organophosphorus pesticides was carried out (Diazinon, Disulfoton and Clorpirifos) to the samples of milk to check the efficiency of the technical microextraction in solid phase (SPME) in way headspace (HS) and of the methods of gas chromatography (GC) with detector of flame ionization (FID) and detector of mass spectrometry (MSD). They showed excellent results proven by means of the validation of the method and for the chromatographic profile generated by the equipment making visible the presence of the used patterns.

The main cause of the presence of organophosphorus pesticide residues in milk is their physicochemical property of liposolubility. In addition, the excessive and poorly regulated use of these compounds in agricultural practices for the control of animal diseases, transmitted by insects and parasites.

Studies analyzing 242 samples of milk, carried out in Galicia Spain, found the presence of dichlorvos, coumafos and methyl parathion below the residual maximum limit (MRL) established by FAO (Santaeufemia *et al.*, 2006; FAO/OMS, 2010).

The toxicity of these compounds, even in small amounts, may trigger a range of acute to chronic effects. Several effects have been confirmed by different studies (Pagliuca *et al.*, 2004; Gazzotti *et al.*, 2009). Researchers have presented the clear need to establish control and monitoring mechanisms regarding organophosphorus contamination present in milk for human consumption (Vallecilla *et al.*, 2010; Shaker y Elsharkawy, 2015). The need for chemical analysis methodologies to detect the presence of these pollutants is a fundamental part of these mechanisms. When considering the low levels that characterize the maximum allowed concentrations reported for organophosphorus pesticides in milk, it should be emphasized that the chemical analysis methodologies aimed at the detection and quantification of these pesticides should be capable of providing high recovery rates and low detection limits (LeDoux, 2011).

CONCLUSIONS

The analytical method developed in this research could not detect the presence of organophosphorus compounds (diazinon, dichlorvos, chlorpyrifos) in any of the evaluated milk samples in the city of Cartagena de Indias

The developed method proved to be viable for its low cost, besides being fast and environmentally friendly, since it does not use a solvent in the extraction stage.

The accuracy of the method is adequate and it is below that specified as acceptance criterion (relative standard deviation ≤ 2%). Based on the results obtained from the validation, it is concluded that this analytical method used for the determination of organophosphates in milk is a reliable method.

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