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Development, validation and application of a SDME/GC-FID methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water

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ABSTRACT

A single-drop microextraction (SDME) procedure was developed for the analysis of organophosphorus and pyrethroid pesticides in water by gas chromatography (GC) with flame ionization detection (GC-FID). The significant parameters that affect SDME performance, such as the selection of microextraction solvent, solvent volume, extraction time, and stirring rate, were studied and optimized using a tool screening factorial design. The limits of detection (LODs) in water for the four investigated compounds were between 0.3 and 3.0 $\mu g\,L^{-1}$, with relative standard deviations ranging from 7.7 to 18.8%. Linear response data were obtained in the concentration range of 0.9–6.0 $\mu g\,L^{-1}$ (λ-cyhalothrin), 3.0–60.0 $\mu g\,L^{-1}$ (methyl parathion), 9.0–60.0 $\mu g\,L^{-1}$ (ethion), and 9.0–30.0 $\mu g\,L^{-1}$ (permethrin), with correlation coefficients ranging from 0.9337 to 0.9977. The relative recoveries for the spiked water ranged from 73.0 to 104%. Environmental water samples ($n = 26$) were successfully analyzed using the proposed method and methyl parathion presented concentration up to 2.74 $\mu g\,L^{-1}$. The SDME method, coupled with GC-FID analysis, provided good precision, accuracy, and reproducibility over a wide linear range. Other highlights of the method include its ease of use and its requirement of only small volumes of both organic solvent and sample.

1. Introduction

Over the years, several different strategies have been used in the attempt to control the microorganisms, weeds, insects, and rodents that threaten food supplies and human health. Among these strategies is the use of pesticides. Currently, synthetic organic pesticides (e.g., organophosphates, organochlorines, carbamates, dithiocarbamates, pyrethroids, and nitrogen containing heterocyclic compounds) are the most widely used. In Brazil, the pesticide market in 2004 was over 4.5 billion US dollars. This is of great concern because only 0.1% of the amount of pesticides used in the field reaches the specific target, while the remaining 99.9% has the potential to affect different environmental systems, such as air, soil, surface water, and groundwater [1].

Some of the undesirable consequences of pesticide use include the presence of residues in the soil, water, and air; residues in plant and animal tissues; the destruction of soil microorganisms; harmful effects in non-target organisms; mortality of beneficial insects; and the presence of residues in food [2,3]. The presence of pesticide residues in food, air, and water has also been identified as a probable cause of increasing cancer rates and the incidence of other serious diseases that affect the human population [4].

The toxicity of pesticides and their harmful environmental effects, especially in water, is increasingly evident. Thus, it is of paramount importance to develop faster and more selective analytical methodologies, with higher cost–benefit ratios, that are less harmful to the environment and more sensitive to trace levels of pesticide residues in natural and drinking waters.

The increasing demand for analytical methods for the analysis of pesticides has driven efforts in two directions: the adaptation of existing methods and the development of new techniques with increasingly improved performance [5,6]. In the latter case, one of the trends has been the solvent microextraction method, which is a miniaturization of traditional liquid–liquid extraction (LLE).

The solvent microextraction, now called single-drop microextraction (SDME), is also known as liquid–liquid microextraction (LLME) [5,6] or liquid phase microextraction (LPME) [6]. This method is based on the principle of a distribution of analytes between a microdrop of an organic solvent and an aqueous phase.

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The SDME procedure uses a microsyringe, whose needle is immersed into the water sample (containing the analytes). The needle then hangs up a 1 μL drop of the solvent under stirring. After extraction, the drop is aspirated into a microsyringe and then injected into a gas chromatograph (GC) [7] or liquid chromatograph (LC) [8,9]. An important requirement for efficient extraction is that the extraction solvent must be immiscible in the aqueous sample.

The disadvantages of SDME include drop volume variation during the process of extraction, which affects parameters such as: the precision [10]; drop stability; drop solvent dissolution when using extreme conditions of extraction, such as a high stirring speed, long extraction time, and high temperature; and operator experience, which may affect SDME linearity and precision [6,11].

SDME has several advantages compared to other extraction/preconcentration techniques: it is not exhaustive, uses a negligible amount of organic solvent (minimum volume of solvent, which also minimizes analyst contact with potentially toxic fumes and environmental contamination) [11,12], offers the freedom to select the most suitable solvent for the target analytes [11], requires only a short time for analysis, has a high sensitivity and low cost when compared to SPME and SPE, and uses simple equipment [13–15]. Additionally, SDME combines the pre-concentration and sample introduction into a single-step extraction [9]. Indeed, SDME procedures have been widely used in the determination of both organic [16,17] and inorganic species [18–20].

The development of miniaturized methodologies that combine high throughput analysis, low cost, and environmental sustainability, is of great current concern. Therefore, this study aims to optimize, validate, and apply an SDME methodology to measure methyl parathion (organophosphate), ethion (organophosphate), permethrin (pyrethroid), and λ-cyhalothrin (pyrethroid) in aqueous samples by GC-FID.

2. Experimental

2.1. Reagents and solutions

Chromatographic grade methanol was purchased from Merck (Darmstadt, Germany). Pesticide standards of λ-cyhalothrin (99.6%), methyl parathion (99.6%), permethrin (99%), and ethion were all purchased from AccuStandard (New Haven, USA). Stock standard solutions were prepared in methanol at a concentration of 200 μg mL^{-1}. Analytical standard solutions were prepared at different concentrations, according to the response of each pesticide in a flame ionization detector: methyl parathion (10 μg mL^{-1}), permethrin (30 μg mL^{-1}), ethion (30 μg mL^{-1}), and λ-cyhalothrin (20 μg mL^{-1}).

2.2. Optimization of the SDME procedure

The efficiency of SDME depends on parameters such as temperature, extraction time interval, stirring speed, type of solvent, and sample size. The optimization of the microextraction conditions is thus a multiparameter evaluation task that may be overcame by multivariate techniques.

In order to identify the relevant parameters that could contribute to the sensitivity of the proposed method, two screening 2^3 full factorial designs were carried out, both with three replicates in the central body being in this way, able to quantify the experimental error [21]. Regarding the solvents, cyclohexane was placed at the central point since it is an intermediate polar compound, in relation to isooctane and toluene. In the first factorial design, the investigated factors and their levels were selected after preliminary experimental studies. In turn, the second factorial design aimed to better optimize the initial parameters to reach the best possible working conditions. The response evaluated during all experiments was the sum of all the peak areas obtained in the GC-FID analysis. The statistical experimental designs and optimization calculations were carried out using the Statistica 7.0 software (Statsoft, USA) [21–24].

Table 1
Scores of sampling used in the first factorial design.

Factors	Levels of sampling		
	−1	Center point	1
Extraction time (min)	10	30	50
Stirring speed (rpm)	200	300	600
Extraction solvent	Isooctane	Cyclohexane	Toluène

In the first 2^3 full factorial design study, 10 mL of ultrapure water was spiked with 50 μL standard solutions of λ-cyhalothrin (4 μg mL^{-1}) and ethion, permethrin and methyl parathion (10 μg mL^{-1}), with final concentrations of 0.02 μg mL^{-1} for λ-cyhalothrin and 0.05 μg mL for ethion, methyl parathion, and permethrin. Table 1 shows the factors studied as well as their respective scores. In the second 2^3 full factorial design study, 10 mL of ultra-pure water was spiked with a 5 μL standard solution (2 μg mL^{-1} of λ-cyhalothrin and 4 μg mL^{-1} of ethion, permethrin, and methyl parathion), with final concentrations of 0.001 μg mL^{-1} (λ-cyhalothrin) and 0.002 μg mL^{-1} (ethion, methyl parathion, and permethrin). Table 2 shows the factors studied, as well as their respective scores.

2.3. The adopted SDME procedure

In the SDME procedure, a 10 μL microsyringe was used to measure and introduce the microdrop of solvent (1 μL of toluene) to the glass vial (equipped with magnetic stir bar and silicone septum) with water sample. The needle of the microsyringe was inserted through the septum and directly immersed into the water sample (10 mL) that contained the analytes, under stirring (300 rpm). The microsyringe plunger was depressed to expose the toluene drop to the sample to occur the transferring the analytes from the aqueous phase to the drop. After microextraction (30 min), the organic drop (1 μL) was drawn back into the syringe and the needle removed off the vial and immediately injected into the gas chromatograph equipped with flame ionization detector (total run time of 23.33 min).

2.4. Chromatographic analysis

The chromatographic analyses were performed using a Varian Star 3400 GC (Walnut Creek, CA, USA) equipped with a flame ionization detector (FID). The capillary column used was a DB-5 (30 m × 0.25 mm i.d. × 0.25 μm film thickness) supplied by J&W Scientific. The injector and detector temperatures were both 250 °C. The temperature program was the following: the temperature was initially set to 60 °C and held for 1 min, then increased to 150 °C at a rate of 30 °C min^{-1} and held for 4 min, and finally increased to 290 °C at a rate of 15 °C min^{-1} and held at this temperature for 5 min, for a total analysis time of 23.33 min.

Helium was used as carrier gas and the injection was split/splitless with a purge time of 0.75 min and split of 1:50. The

Table 2
Scores of sampling used in the second factorial design.

Factors	Levels of sampling		
	−1	Center point	1
Extraction time (min)	10	20	30
Stirring speed (rpm)	100	200	300
Drop volume (μL)	0.5	0.7	1.0

flame ionization detector was fed by synthetic air (300 mL min^{-1}) and hydrogen (30 mL min^{-1}). The injection volume of the samples was 1 μL.

2.5. Sampling

First, ten water samples were collected in the irrigation project "Platô de Neópolis," located in the city of Neópolis (State of Sergipe, Brazil: 10°19′12″S, 36°34′46″W) from the right border of the San Francisco River where locally cultivated crops include mango, acerola, pineapple, papaya, passion fruit, banana, grapes, fig, date, kiwi fruit, coconut-dwarf, cashews, and citrus. Then, 16 water samples were collected from the irrigation project "Perimetro Irrigado Propriá," located in the city of Propriá (State of Sergipe, Brazil: 10°12′40″S, 36°50′25″W) also from the San Francisco River, where the cultivation is mainly rice.

3. Results and discussion

3.1. Multivariate optimization of the SDME procedure

3.1.1. First factorial design

The results obtained from the evaluation of significant parameters by the first screening factorial design are summarized in the Pareto chart shown in Fig. 1. As can be seen from this figure, the extraction time, stirring speed, and solvent type are important in SDME. The solvent is the most significant variable. The extraction time is also highly significant, which reinforces the assertion of Bagheri and Khalilian [12], that the extraction time is the main parameter that affects the efficiency of extraction. The extraction efficiency depends on the mass transfer of the analytes from the aqueous phase to the drop of organic solvent, and the mass transfer is dependent on the extraction time [6].

The graphical determination of the best levels for the three factors studied can be seen in Fig. 2, which shows a marginal means chart. The best extraction efficiency (best signal) was achieved when the solvent was toluene, the extraction time 50 min, and the stirring speed 600 rpm. In regards to the solvent, toluene is one of the most frequently used solvents in the analysis of pesticides by SDME, mainly because it produces stable drops. The toluene stands out in this study because the signals obtained from the analytes in this solvent are approximately two times higher than the signals obtained with isooctane, when the extraction time was fixed and increased up the stirring from 200 to 600 rpm. This is in agreement with the results obtained elsewhere [8,25–27]. Additionally, toluene has the advantage of being more stable and less toxic than cyclohexane and hexane, and is considered the most suitable solvent for injections in GC.

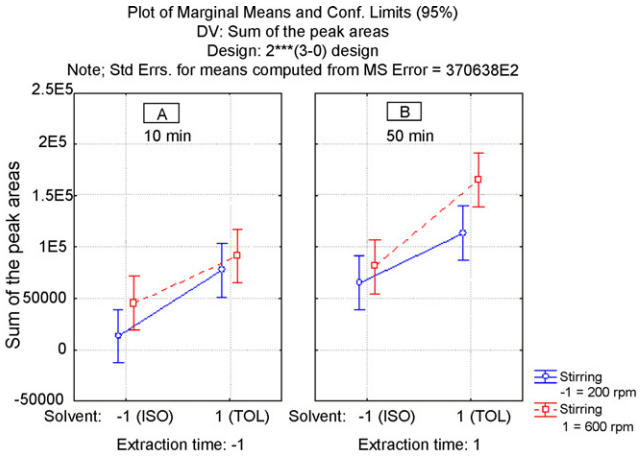

Fig. 2. Marginal means for the first factorial design (in the *x*-axis "1" means toluene and "−1" means isooctane. Straight line means 200 rpm and dashed line means 600 rpm). ISO = isooctane and TOL = toluene.

The response surface charts shown in Figs. 3 and 4 compare the performance and extraction efficiency of toluene to that of isooctane as function of increasing stirring speed and extraction time.

The normal probability plot shown in Fig. 5 is used to verify the assumption of normality errors. The closer points are to the continuous experimental line, the more valid is the assumption of normality residues. The residues, in this case, follow a normal distribution.

Statistical analyses have shown that the extraction time, stirring speed, and solvent choice influence the efficiency of extraction. For this first experiment, within the range of proposed variables, the best performances were obtained with an extraction time of 50 min, a stirring speed of 600 rpm, and toluene as the extraction solvent, resulting in an analytical response (total peak area) of more than 1.4×10^5, thus reinforcing the previous results that pointed to toluene as the best extraction solvent for the proposed method (SDME-GC-FID).

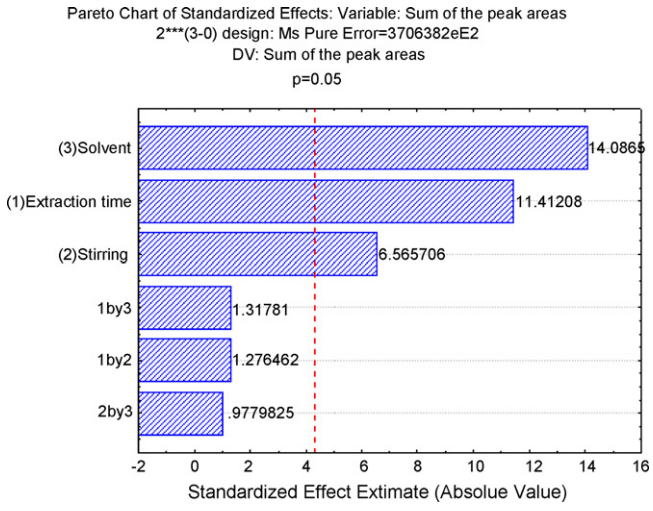

Fig. 1. Pareto chart (first factorial design).

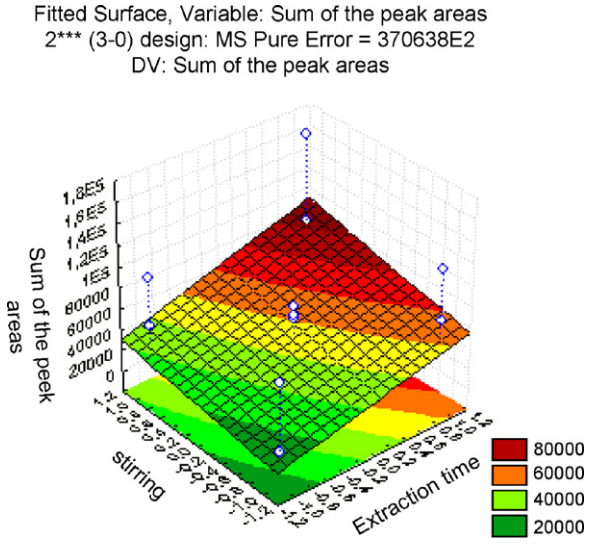

Fig. 3. Response surface (isooctane).

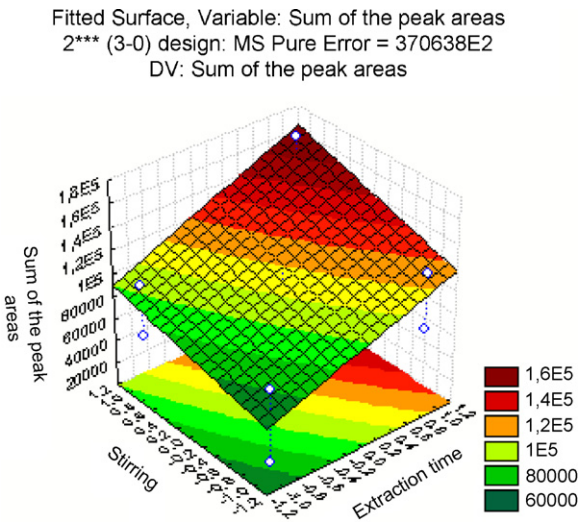

Fig. 4. Response surface (toluene).

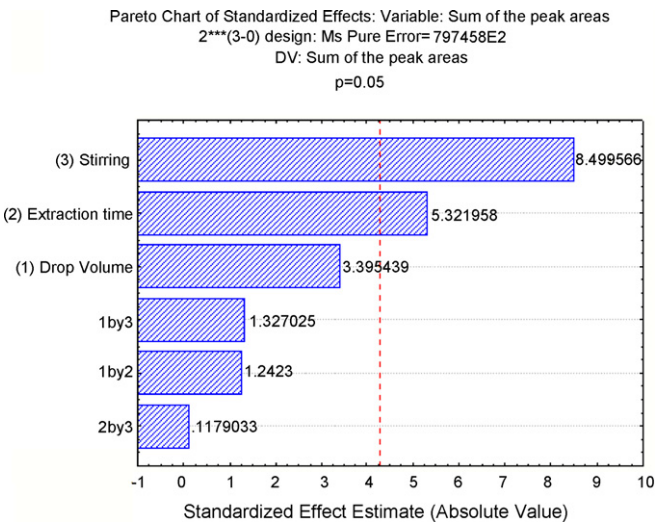

Fig. 6. Pareto chart (second factorial design).

Since one of the goals of SDME is a short analytical time requirement, the 50 min extraction time is too long and can affect the precision and reproducibility of extraction [9]. Thus, the second factorial design was employed to optimize the extraction time, stirring speed, and also a new variable, the drop volume, was introduced in order to check whether 1 μL is the most appropriate for the methodology used.

3.1.2. Second factorial design

The results obtained from the evaluation of the significant parameters by the second screening factorial design are summarized in the Pareto chart of effects shown in Fig. 6. As can be seen from this figure, the stirring speed and extraction time, in this order, are the most important variables in this experiment, indicating that their highest levels yield the best analytical responses.

Fig. 7 shows a marginal means chart, wherein it appears that the best efficiency of extraction (best signal) was achieved with a drop volume of 1 μL, in an extraction time of 30 min, and at a stirring speed of 300 rpm.

It is worth to mentioning that the volume of the drop, although not significant at a 95% confidence interval, showed a positive effect, suggesting that a larger volume (1 μL) is ideal for better analytical responses. The increase in the drop volume results in an increased extraction efficiency [9,28,29]. In the analysis of pesticides by SDME, it is common to use 1 μL organic solvent drop volumes because they form stable drops, and thus, allow the use of high stirring rates. On the other hand, a drop volume of 1 μL is consistent with the instruments of GC [6] and as drop volumes exceed 1 μL, they become unstable [28].

Another way to view the performance of each drop volume, together with stirring rate and extraction time, is shown in the response surface plots shown in Figs. 8 and 9. As can again be seen from these figures, a drop volume of 1 μL provides the best extraction efficiency.

The normal probability plot shown in Fig. 10, used to verify the assumption of normality errors, shows that the residues follow a normal distribution. Thus, the conditions for the best performance of the method, namely high precision, short chromatogram running time (23.33 min), and good analytical responses are: toluene as the extraction solvent, an extraction time of 30 min, a stirring speed of 300 rpm, and a drop volume of 1 μL of the extraction solvent.

3.2. Validation of the analytical method SDME

The parameters used in this study for the validation of the developed analytical method were as follows: linearity, precision,

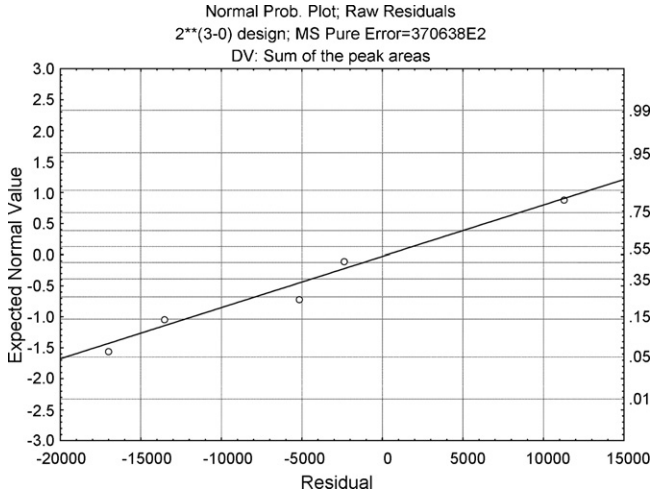

Fig. 5. Diagram of normal probability residues.

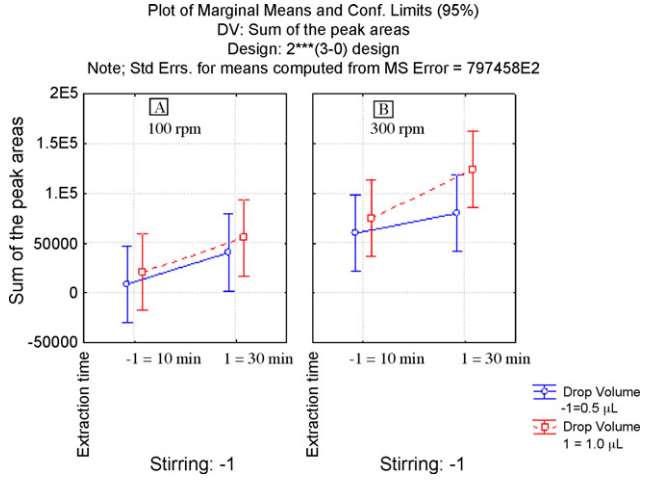

Fig. 7. Marginal means for the second factorial design (in the *x*-axis "1" is 30 min of extraction time and "−1" is 10 min of extraction time. Straight line is 1.0 μL of drop volume and dashed line is 0.5 μL of drop volume).

Table 3
Parameters for validation of the method.

Pesticide	Linear range ($\mu g\,L^{-1}$)	r^2	CV (%) ($n=3$)	EF	R (%)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
λ-Cyhalothrin	0.9–6.0	0.9977	15.8	284	104.0	0.3	0.9
Methyl parathion	3.0–60.0	0.9965	7.7	221	91.3	1.0	3.0
Ethion	9.0–60.0	0.9941	18.8	170	73.0	3.0	9.0
Permethrin	9.0–30.0	0.9337	11.7	26	82.2	3.0	9.0

CV: coefficient of variation; EF: enrichment factor; R: relative recovery; LOD: limit of détection; LOQ: limit of quantification.

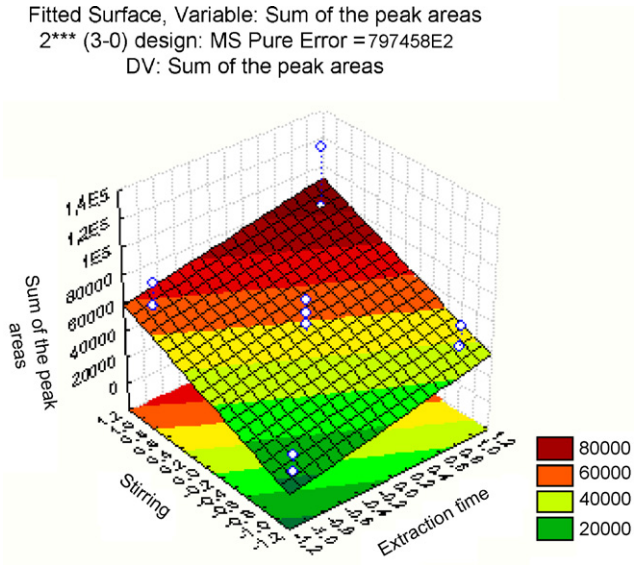

Fig. 8. Response surface (second factorial design—drop volume 0.5 μL).

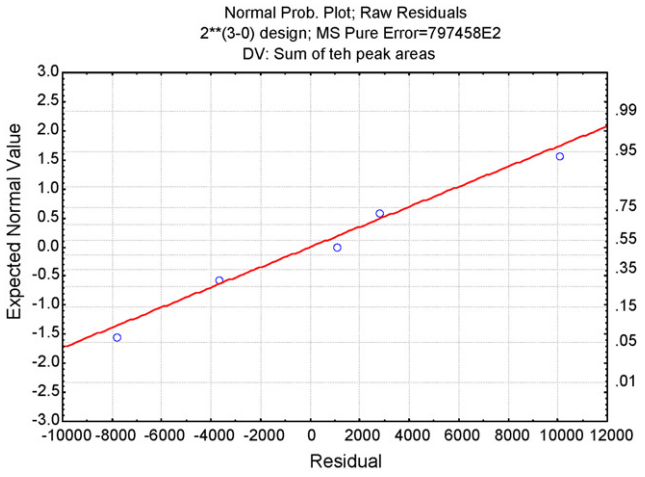

Fig. 10. Diagram of normal probability residues (second factorial design).

accuracy, limit of detection (LOD), limit of quantification (LOQ), and enrichment factor. Table 3 presents these parameters for each one of the pesticides studied.

Linearity was studied using a pre-concentration of 10 mL of ultra-pure water fortified with a standard solution of pesticides in the concentration ranges 0.9–6.0 $\mu g\,L^{-1}$ for λ-cyhalothrin, 3.0–60.0 $\mu g\,L^{-1}$ for methyl parathion, and 9.0–60.0 $\mu g\,L^{-1}$ for other pesticides (ethion and permethrin), which is a range similar to that used by Tor [30]. Our results of r^2 (determination coefficient) were better than those reported elsewhere [11] in a methodology developed for the SDME-GC-MS measurement of nitroaromatic explosives in water, whose correlation coefficients were in the range of 0.94–0.97 for most compounds, and also those from another study aimed at the identification of herbicides in water [12]. In Brazil, the ANVISA [31] and INMETRO [32] have recommended correlation coefficients greater than 0.99 and 0.90, respectively, as indicators of good linearity of the analytical curve.

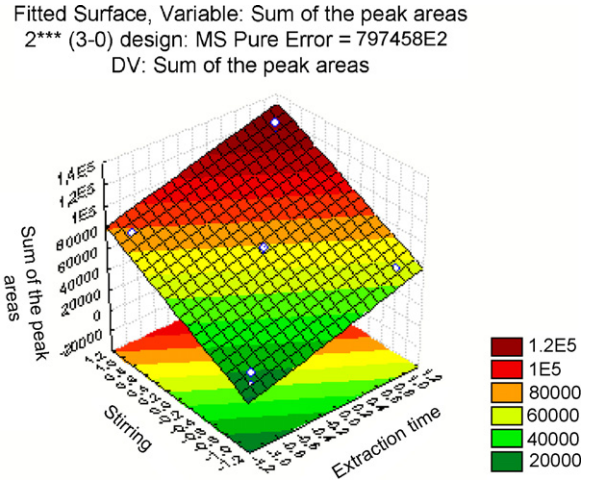

Fig. 9. Response surface (second factorial design—drop volume 1.0 μL).

The result for the coefficient of variation (CV) was obtained with triplicates ($n=3$) [13], using a sample of ultra-pure water that had been spiked to a concentration of 5 $\mu g\,L^{-1}$ (λ-cyhalothrin) and 20 $\mu g\,L^{-1}$ (methyl parathion, ethion, and permethrin). The calculated values of CV were in the range of 7.7–18.8%, thus indicating that the developed method is precise. Similar results of CV (3.5–16, 5–13, and 9–14%) were obtained in other studies using SDME-GC-FID, SDME-GC-NPD, and SDME-GC-MS [15,33], respectively. Additionaly, the total time analysis of 53.33 min is shorter than those obtained in other studies that used SDME-GC-MS (82 min) [16] and SDME-GC-FPD (75 min) [34] for determination of pesticides.

The enrichment factors (EF) obtained in this study were calculated using the ratios of the concentrations of the analytes in the drop before SDME to the concentrations of analytes after the application of SDME to the spiked water samples (under optimized conditions). The EF were higher than those obtained elsewhere [13,26,35], and close to that obtained by Bagheri and Khalilian (38–189) [12]. A high EF is indicative of good extraction efficiency [34].

The LOD and LOQ were established by an analysis of samples of ultra-pure water, spiked with decreasing concentrations of the analytes to the lowest detectable concentration (a concentration that is three times the signal-to-noise ratio), and lowest quantifiable concentration (a concentration that is ten times the signal-to-noise ratio), respectively. The found values of LOD and LOQ (0.3–3.0 $\mu g\,L^{-1}$) and (0.9–9.0 $\mu g\,L^{-1}$), respectively, are either comparable to or better than those reported elsewhere [15,27,36,37] which demonstrates the high sensitivity of the method. In fact, the present method is capable of detecting and quantifying permethrin and methyl parathion concentrations below the maximum permitted residue level, according to the Brazilian Norms 518/04

Table 4
Results of real samples analyses using the optimized method.

Sample	*n*	Pesticide methyl parathion
		Range of concentration ($\mu g\,L^{-1}$)
PLATÔ DE NEÔPOLIS	10	nd–2.65
PERIMETRO IRRIGADO PROPRIÀ	16	nd–2.74

Note: in all of the samples, the pesticides λ-cyhalothrin, permethrin, and ethion were not detected; nd = not detected; *n* = number of samples collected.

[38] (20 $\mu g\,L^{-1}$ for permethrin) and 357/2005 [39] (35 $\mu g\,L^{-1}$ for methyl parathion).

The evaluation of percentage of recovery was made using a sample without the analytes which was then contaminated in the laboratory with a high-purity standard of each analyte. A sample of ultra-pure water and tap water, spiked to a concentration of 5 $\mu g\,L^{-1}$ (λ-cyhalothrin) and 20 $\mu g\,L^{-1}$ (methyl parathion, ethion, and permethrin), was used in this analysis. In order to be considered sufficiently accurate for the analysis of pesticide residues in water, the obtained recovery must be in the range of 70.0–120% [40]. The developed method proved to be accurate, as the achieved recovery was in the range of 73.0–104% (Table 3) [8,40].

Tap water and river water were spiked with 5 $\mu g\,L^{-1}$ λ-cyhalothrin analytical solution and 20 $\mu g\,L^{-1}$ methyl parathion, ethion, and permethrin analytical solution in order to assess possible matrix effects. The relative recoveries of λ-cyhalothrin, methyl parathion, ethion, and permethrin from tap water were 104, 91.3, 73.0 and 82.2%, respectively, and from river water were 112.9, 97.6, 76.2 and 83.8%, respectively. The results demonstrate that tap water and river water matrices have little effect on SDME analysis of the studied pesticides [9].

3.3. Application of the developed method

Table 4 summarizes the results of real samples analyses using the optimized method. Among the analyzed pesticides (λ-cyhalothrin, methyl parathion, ethion, and permethrin), only methyl parathion was found above LOD, and was present in 30% of the samples.

4. Conclusions

The developed SDME method coupled with GC-FID analysis provided good precision, accuracy, and reproducibility over a wide linear range. Other highlights of the developed method include its ease of use and its requirement of only small volumes of both organic solvent and sample, which makes it suitable for the measurement of λ-cyhalothrin, methyl parathion, permethrin, and ethion levels in water samples.

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References

[1] D.A. Belluck, S.L. Benjamin, T. Dawson, in: L. Somasundaram, J.R. Coats (Eds.), Groundwater Contamination by Atrazine and Its Metabolites in Pesticide Transformation Products, Fate and Significance in the Environment, American Chemical Society, Washington, DC, 1991, p. 254.
[2] J.H.A. Ruzicka, D.C. Abbott, Talanta 20 (1973) 1261.
[3] W.H. Lara, G.C. Batista, Quim. Nova 2 (1992) 161.
[4] C. Baird, Quimica Ambiental, 2nd edition, Bookman, Porto Alegre, 2002, p. 622.
[5] L. Ramos, J.J. Ramos, U.A.Th. Brinkman, Anal. Bioanal. Chem. 381 (2005) 119.
[6] D.A. Lambropoulou, T.A. Albanis, J. Biochem. Biophys. Methods 70 (2007) 195.
[7] J. Zhang, H.K. Lee, J. Chromatogr. A 1114 (2006) 269.
[8] E. Zhao, L. Han, S. Jiang, Q. Wang, Z. Zhou, J. Chromatogr. A 1114 (2006) 269.
[9] P. Liang, L. Guo, Y. Liu, S. Liu, T. Zhang, Microchem. J. 80 (2005) 19.
[10] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.
[11] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 938 (2001) 113.
[12] H. Bagheri, F. Khalilian, Anal. Chim. Acta 537 (2005) 81.
[13] Y. He, H.K. Lee, J. Chromatogr. A 1122 (2006) 7.
[14] M.C. Lopez Blanco, S. Branco-Cid, B. Cancho-Grande, J. Simal-Gándara, J. Chromatogr. A 984 (2003) 245.
[15] M. Palit, D. Pardasani, A.K. Gupta, D.K. Dubey, Anal. Chem. 77 (2005) 711.
[16] M. Zhang, J. Huang, C. Wei, B. Yu, X. Yang, X. Chen, Talanta 74 (2008) 599.
[17] Y. Wu, L. Xia, R. Chen, B. Hu, Talanta 74 (2008) 470.
[18] H.F. Maltez, D.L.G. Borges, E. Carasek, B. Welz, A.J. Curtius, Talanta 74 (2008) 800.
[19] J.L. Manzoori, M. Amjadi, J. Abulhassani, Talanta 77 (2009) 1539.
[20] D. Verma, S.K. Verma, M.K. Deb, Talanta 78 (2009) 270.
[21] E.T. Souza, F.M. Rodrigues, C.C. Martins, F.S. Oliveira, P.A.P. Pereira, J.B. de Andrade, Microchem. J. 82 (2006) 142.
[22] N.M. Aragão, M.C.C. Veloso, M.S. Bispo, S.L.C. Ferreira, J.B. de Andrade, Talanta 67 (2005) 1007.
[23] S.L.C. Ferreira, R.E. Bruns, E.G.P. Silva, W.N.L. Santos, C.M. Quintella, J.M. David, J.B. de Andrade, M.C. Breitkreitz, I.C.S.F. Jardim, B. Barros Neto, J. Chromatogr. A 1158 (2007) 2.
[24] L.S. Oliveira, F.M. Rodrigues, F.S. Oliveira, P.R.R. Mesquita, D.C. Leal, A.C. Alcântara, B.M. Souza, C.R. Franke, P.A.P. Pereira, J.B. de Andrade, J. Chromatogr. B 875 (2008) 392.
[25] E. Zhao, W. Shan, S. Jiang, Y. Liu, Z. Zhou, Microchem. J. 83 (2006) 105.
[26] Q. Xiao, B. Hu, C. Yu, L. Xia, Z. Jiang, Talanta 69 (2006) 848.
[27] C.B.M. Rahul, P. Roy, Res. J. Chem. Environ. 10 (2006) 1.
[28] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[29] D.A. Lambropoulou, T.A. Albanis, J. Chromatogr. A 1049 (2004) 17.
[30] A. Tor, J. Chromatogr. A 1125 (2006) 129.
[31] ANVISA. Agência Nacional de Vigilância Sanitária. Resolução RE no 475 de 19 de março de 2002. "Guia para Validação de Métodos Analíticos". Available on: http://www.anvisa.gov.br/hotsite/genericos/legis/resolucoes/2002/475_02re.htm (accessed: 15/04/2007).
[32] INMETRO. Orientações sobre validação de métodos de ensaio químicos. 2003. Available on: http://www.farmacia.ufmg.br/lato/downloads/validacao_inmetro.pdf (accessed: 23/11/2008).
[33] R. Batlle, C. Nerín, J. Chromatogr. A 1045 (2004) 29.
[34] F. Ahmadi, Y. Assadi, S.M.R. Milani, M. Hosseine, M. Rezaee, J. Chromatogr. A 1101 (2006) 307.
[35] L. Zhao, H.K. Lee, J. Chromatogr. A 919 (2001) 381.
[36] C. López-Blanco, S. Gómez-Alvarez, M. Rey-Garrote, B. Cancho-Grande, Simal-Gándara, Anal. Bioanal. Chem. 383 (2005) 557.
[37] L. Guo, P. Liang, T. Zhang, Y. Liu, S. Liu, Chromatographia 61 (2005) 523.
[38] BRASIL. Portaria 518, de 25 de março de 2004. Controle e vigilância da qualidade da água para consumo humano. Available on: http://www.agrolab.com.br/portaria%20518_04.pdf (accessed: 15/10/2005).
[39] BRASIL. Resolução CONAMA no 357, de 18 de Junho de 2005. Classificação das água doces, salobras e salinas do Território Nacional. Available on: http://www.mma.gov.br/port/conama/res/res86/res2086.html (accessed: 15/10/2005).
[40] CODEX ALIMENTARIUS, Pesticide Residues in Food: Methods of Analysis and Sampling, 2nd edition, part 1, CODEX ALIMENTARIUS, Roma, 2000.