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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

Anselmo de Souza Pinheiro [a,b,c], Jailson B. de Andrade [a,b,c,*]

[a] Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, 40170-290, Salvador, BA, Brazil
[b] Centro Interdisciplinar de Energia e Ambiente (CIEnAm), Universidade Federal da Bahia, Canela, 40110-040, Salvador, BA, Brazil
[c] INCT de Energia e Ambiente, UFBA, 40170-290, Salvador, BA, Brazil

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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.

* Corresponding author at: Universidade Federal da Bahia, Centro Interdisciplinar de Energia e Ambiente (CIEnAm), Instituto de Quimica, UFBA, Campus Universitario de Ondina, 40110-040, Salvador, BA, Brazil. Tel.: +55 71 32375524; fax: +55 71 32375524.
E-mail address: jailsong@ufba.br (J.B. de Andrade).

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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 $\mu g\,mL^{-1}$. Analytical standard solutions were prepared at different concentrations, according to the response of each pesticide in a flame ionization detector: methyl parathion (10 $\mu g\,mL^{-1}$), permethrin (30 $\mu g\,mL^{-1}$), ethion (30 $\mu g\,mL^{-1}$), and λ-cyhalothrin (20 $\mu g\,mL^{-1}$).

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 $\mu g\,mL^{-1}$) and ethion, permethrin and methyl parathion (10 $\mu g\,mL^{-1}$), with final concentrations of 0.02 $\mu g\,mL^{-1}$ 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 $\mu g\,mL^{-1}$ of λ-cyhalothrin and 4 $\mu g\,mL^{-1}$ of ethion, permethrin, and methyl parathion), with final concentrations of 0.001 $\mu g\,mL^{-1}$ (λ-cyhalothrin) and 0.002 $\mu g\,mL^{-1}$ (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