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ENVIRONMENTAL ANALYSIS

Fast Screening Determination of Some Ubiquitous Pesticides with SPME in Water Samples

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ABSTRACT

A simple multiresidue direct solid phase microextraction (SPME) method with PA fiber is described for determination of pesticides in water samples. The residues were determined by gas chromatography with mass spectrometry detection (GC/MS). The recovery obtained for the proposed method ranged from 94% to 110% and the sensitivity of the method was determined by calculating the limit of detection (DL) that ranged from 0.004 to 0.1 $\mu g\,L^{-1}$. The results obtained with spiked real sample, at three concentration levels, showed acceptable agreement with the expected values.

Key Words: Pesticides; SPME; GC/MS; Water.

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INTRODUCTION

Pesticides are organic compounds intensely employed in agricultural activities to increase their productivity by protecting plants from weed, fungus, and insects.[1] They have high toxicity and cause many damages to the human health, to the flora, and to the fauna.[2]

According to EPA pesticides are substances or mixture of substances with capacity to prevent, to destroy, to repel, or to lessen any plague. The pesticides can be classified in accordance to the plague type such as algaecides, fungicides, herbicides, insecticides, acaricides, moluscidas, nematicidas, ovicidas, among others. Besides, substances defoliants, desiccants, regulators of the growth of insects and plants can be considered as well.

Pesticides can also be classified in agreement with the chemical structure. The choice of the pesticides studied in this work was based mainly on the major use in world scale, xenobiotic potential, and ubiquity.[3] Their general characteristics are presented in Table 1.

Due to the persistence, pesticides can be found in the different environmental compartments.[4–6] In air they are found in aerosols form due to the pulverization procedures. In superficial waters they are found due to runoff effect, by spilling or applications to eradicate insect-borne or endemic diseases.[7] In the soil they are found due to spilling or inadequate discards and by percolation they can reach subterraneous waters.[8]

In environmental water samples, extraction and preconcentration steps usually precede the determination of pesticides. The extraction techniques[3,9] more employed are extraction liquid–liquid (LLE) and extraction in solid phase (SPE). Gas chromatography (GC) and high performance liquid chromatography (HPLC) are the most useful techniques employed for quantification.[3] Besides the extraction procedures mentioned, other powerful technique[10–12] in ascension is the solid phase microextraction (SPME).

Table 1. Characteristics of studied pesticides.

Pesticide	CAS n°	Formula	Class	Type[a]
Trifluralin	1582-09-8	$C_{13}H_{16}F_3N_3O_4$	Dinitroaniline	H
Simazine	122-34-9	$C_7H_{12}ClN_5$	Triazines	H
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	Triazines	H
Pentachlorophenol	131-52-2	C_6Cl_5NaO	Organochlorine	H; I; F
Bifenthrin	82,657-04-3	$C_{23}H_{22}CF_3O_2$	Pyrethroide	I; A
Permethrin	52,645-53-1	$C_{21}H_2OCl_2O_3$	Pyrethroide	I

[a] A, Acaricide; F, fungicide; H, herbicide; I, insecticide.

This consists in two basic stages: adsorption and desorption of the analyte in a silica fiber covered with a polymeric material. The adsorption stage is accomplished by exposing the fiber directly in the sample or in the headspace. Desorption stage usually occurs directly in the chromatograph with little or no modifications to existing injector.

SPME differs from the other extraction techniques for aqueous samples, due to lesser time of analysis and is a solventless technique minimizing the generation of discards and the occupational exhibition. In comparison to the other techniques it is simple, fast, and easy handling with the advantage of the use of small sample amount. The SPME have been applied in several samples such as: pharmaceutical, environmental, nutrition, flavor, forensic, and toxicological.[13–15]

Although SPME is a versatile technique, the extraction conditions should be optimized for each sample type.[16,17] In this case the main optimized parameters are: extraction type (headspace or direct immersion in the liquid sample), fiber type, pH, agitation speed, ionic concentration, temperature, and sample volume.

In this work, an analytical procedure based on direct SPME coupled to GC/mass spectrometry (GC/MS) for fast screening and determination of low concentration of trifluralin, simazine, atrazine, pentachlorophenol, bifenthrin, *cis*-permethrin, and *trans*-permethrin is proposed and applied to real water samples.

EXPERIMENTAL

Chemicals and Materials

The pesticide standards were purchased from Supelco and Riedel-de-Häen. Sodium sulfate (purity grade >99%), hydrochloric acid (purity grade >99%), sodium hydroxide (purity grade >99%), and acetonitrile (grade HPLC) were purchased from Merck. Deionized water was obtained from a Nanopure water purification system (Barnsted). Stock solutions at a concentration of 1000 $\mu g\,mL^{-1}$ in acetonitrile of the following individual standards: trifluralin, simazine, atrazine, pentachlorophenol, bifenthrin, *cis*-permethrin, and *trans*-permethrin, were prepared and stored in freezer at 4°C. Mixtures containing appropriate amounts of each pesticide standard, were prepared by dilution of the stock solutions with acetonitrile. The water sample was collected in the municipal district of Cananéia, in Itapitangui River, with collection point before the water station treatment. The recovery studied was made by adding the appropriated amount of pesticide stock solutions in deionized water and in the real sample.

Sample Preparation and SPME Procedures

The SPME extractions were performed in 4.0 mL of water sample with 20% w/v of sodium sulfate, pH adjusted to 3 into amber vials with magnetic stirring at 900 rpm and capped with PTFE coated septa. The extraction was made during 30 min with a polyacrylate (PA) fiber, from Supelco, with 85 μm of film thickness. After extraction, the fiber was thermally desorbed for 5.0 min into the glass liner of the gas chromatograph injector at 260°C in split less mode.

The fiber was conditioned before use by heating in a gas chromatograph injection port at 300°C for 2 hr.

GC/MS Analysis

A gas chromatograph (Model GC-17A, Shimadzu) coupled with a mass spectrometry detector (Model QP5000, Shimadzu) was used for the experiments to determine the optimized SPME conditions. A 30 m × 0.25 mm HP-5 MS column (0.25 μm film thickness) was used for separating the pesticides. The column was held at 40°C for 5 min, increased to 70°C at a rate of 40°C min^{-1}, and again ramped at 5°C min^{-1} to 325°C held for 5 min. Helium at 0.8 mL min^{-1} of constant flow was used as the carrier gas. The single ion-monitoring (SIM) detection mode was acquired in the electron impact (EI) mode. The interface temperature was maintained at 240°C and the detector tension was of 2.50 kV. For each pesticide, three ions (Table 2) were selected and integrated. Calibration curves for all the targets analytes were obtained by using the direct SPME procedure by extracting six aqueous standards with increased concentration over a range between 0.12 and 10.88 $\mu\mathrm{g\,L}^{-1}$ in order to evaluate the linearity of mass detector response.

RESULTS AND DISCUSSION

The pesticides studied present physical–chemical properties that cover a wide range of water solubility (10^{-8}–10^{-4} $\mathrm{mol\,L}^{-1}$), polarity, $\log K_{\mathrm{ow}}$ (octanol–water partition coefficient) values in the range 2–7, vapor pressure (10^{-8}–10^{-4} mmHg), and Henry's constant (10^{-11}–10^{-4} $\mathrm{atm\,m^3\,mol}^{-1}$). These pesticides can be classified as relatively both polar and non-polar compounds and would be expected that their partition could occur both in a polar fiber such as PA or in a non-polar fiber such as polydimethylsiloxane (PDMS).[18] However, phenol compounds have not been extracted by PDMS fiber and then a polar fiber was the choice.[19] Besides, octanol–water partition coefficient and acidic properties for these compounds suggest

Table 2. Linearity and DL for direct SPME method.

Pesticide	Ions (m/z)	Linear range ($\mu g\,L^{-1}$)	Slope	Intercept	Linearity	DL ($\mu g\,L^{-1}$)
Trifluralin	306^a; 307; 264	0.17–5.16	4.68×10^5	3.59×10^4	0.9979	0.006
Simazine	201^a; 203; 186	0.36–10.88	1.95×10^4	1.23×10^4	0.9932	0.10
Atrazine	200^a; 215; 217	0.34–10.32	7.12×10^4	2.59×10^4	0.9977	0.04
Pentachlorophenol	266^a; 264; 268	0.13–3.90	1.12×10^6	1.37×10^5	0.9929	0.004
Bifenthrin	181^a; 182; 165	0.12–3.56	4.93×10^5	4.49×10^4	0.9914	0.005
cis-Permethrin	183^a; 184; 163	0.13–4.02	4.05×10^5	3.28×10^4	0.9959	0.010
trans-Permethrin	183^a; 184; 163	0.13–4.04	3.55×10^5	3.75×10^4	0.9964	0.010

[a] Ions used for quantification.

that salt addition and pH adjustment can increase the extraction efficiency in a direct SPME procedure.

In the procedure, the extraction of pesticide was performed in a single extraction step with the fiber immersed directly in the water sample containing the analytes. The pesticides were partitioned from the sample to the polymeric film of PA on the fiber and then desorbed onto the injector of GC/MS.

Linearity, Detection Limits, and Recovery

The reconstructed SIM chromatogram for standard of pesticides obtained by the direct SPME method proposed is presented in Fig. 1. In Table 2 it can be observed that reference curves showed good linear behavior (r^2) and the detection limits (DL) obtained for the relationship signal-to-noise (S/N) of 3. The recovery studies were made in concentrations range from DL to 30 times DL in deionized water. The results obtained are presented in Table 3. The observed recovery ranged from 94% to 110% with precision ranging from 10% to 25% for all pesticides studied attesting the good performance of the proposed method.

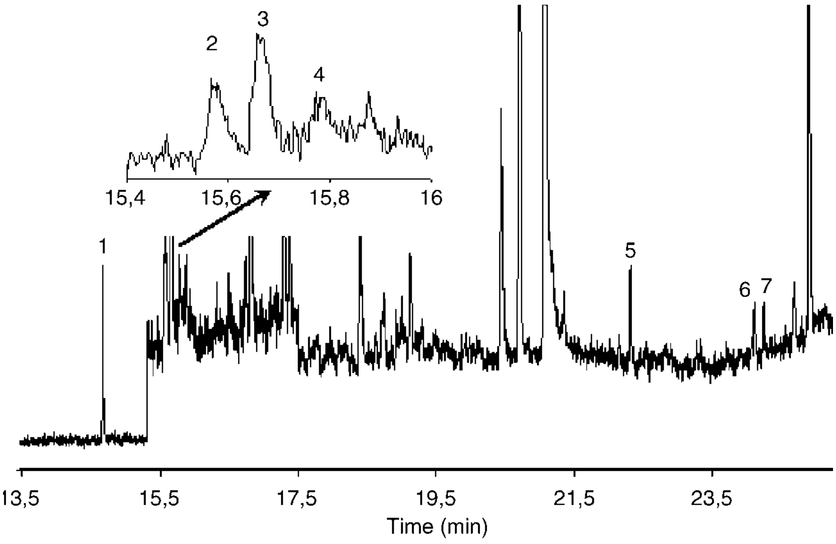

Figure 1. Reconstructed SIM chromatogram for pesticides standard obtained by SPME proposed method for level 1 recovery test (Table 3). 1, Trifluralin; 2, simazine; 3, atrazine; 4, pentachlorophenol; 5, bifenthrin; 6, *cis*-permethrin; 7, *trans*-permethrin.

Table 3. Recovery of pesticides by using the proposed direct SPME method.

	Level 1		Level 2		Level 3	
Pesticide	Concentration ($\mu g\,L^{-1}$)	% Rec[a]	Concentration ($\mu g\,L^{-1}$)	% Rec[a]	Concentration ($\mu g\,L^{-1}$)	% Rec[a]
Trifluralin	0.020	98 ± 13	0.060	97 ± 8	0.180	96 ± 9
Simazine	0.400	101 ± 12	1.200	100 ± 9	3.600	98 ± 8
Atrazine	0.080	107 ± 17	0.240	104 ± 13	0.720	97 ± 7
Pentachlorophenol	0.004	103 ± 10	0.012	97 ± 9	0.036	95 ± 15
Bifenthrin	0.010	100 ± 24	0.030	93 ± 16	0.090	106 ± 22
cis-Permethrin	0.010	94 ± 16	0.030	98 ± 6	0.090	95 ± 17
trans-Permethrin	0.010	100 ± 11	0.030	100 ± 9	0.090	108 ± 22

[a] Average ± ts at 95% confidence for three replicate determinations.

Determination of Pesticides in Real Water Sample

The proposed method was applied in a water sample collected in Cananéia. The chromatogram obtained is presented in Fig. 2(a). In spite of being an area with intense agricultural activity, the presence of the studied pesticides was not detected.

To verify the effectiveness of the proposed method, a study was accomplished where the concentration of 0.1 $\mu g\,L^{-1}$ was added for each pesticide in the water sample collected in Cananéia. This is the value recommended by the European Community as the maximum concentration allowed for drinking water. The chromatogram obtained is presented in Fig. 2(b). The results for recovery obtained for the average of three determinations made in different days were: trifluralin (106 ± 13)%; simazine (110 ± 10)%; atrazine (103 ± 20)%; pentachlorophenol (132 ± 18)%; bifenthrin (98 ± 8)%, and *cis*-permethrin (93 ± 15)%. The high recovery value observed from pentachlorophenol may be related to dissolved organic carbon (mainly humic acid) usually observed for surface water samples. However, further investigations are necessary to confirm this supposition.

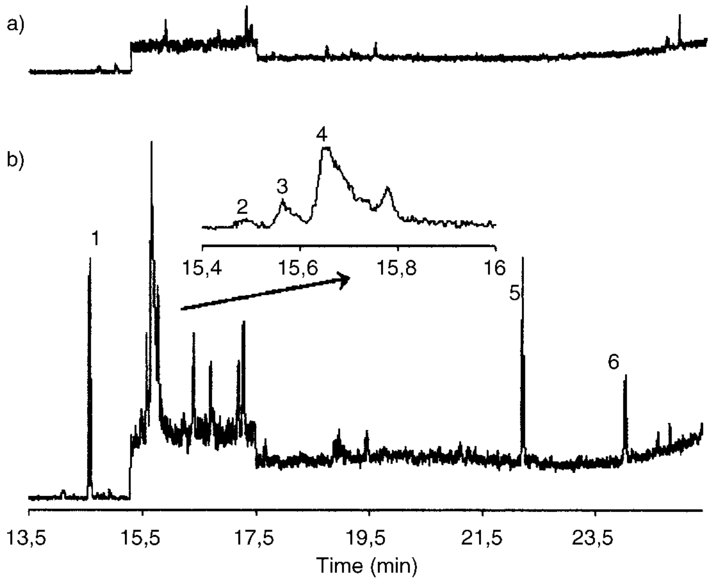

Figure 2. Reconstructed SIM chromatogram: (a) Cananéia water sample; (b) Cananéia spiked water sample at level 0.1 $\mu g\,L^{-1}$ for each pesticide. 1, Trifluralin; 2, simazine; 3, atrazine; 4, pentachlorophenol; 5, bifenthrin; 6, *cis*-permethrin.

CONCLUSIONS

A direct SPME followed by GC/MS in SIM acquisition mode has been proposed for fast determination of some pesticides in water samples under non-equilibrium conditions. The analytical performance of the results and simple sample preparations showed a potential application as a screening tool for chemical characterization, source discrimination, and monitoring plans in environmental samples saving time and costs.

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