Talanta 100 (2012) 246–253

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Hollow fibre-based liquid-phase microextraction technique combined with gas chromatography–mass spectrometry for the determination of pyrethroid insecticides in water samples

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ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form
12 April 2012
Accepted 19 April 2012
Available online 15 May 2012

Keywords:
Pyrethroids
GC/MS
HF-LPME
Water samples

ABSTRACT

A simple, easy-to-use, efficient and environmentally friendly method has been developed for the simultaneous analysis of nine pirethroid pesticides in water samples by the combination of hollow fibre-based liquid-phase microextraction (HF-LPME) and gas chromatography–mass spectrometry (GC/MS). For the developed method, nine pirethroid pesticides (esbiothrin, prallethrin, bifenthrin, tetramethrin, phenothrin, permethrin, cyfluthrin, cypermethrin and deltamethrin) were concentrated and well separated under optimal conditions. Several factors that influence the efficiency of HF-LPME were investigated and optimized by means of experimental design. The proposed method has good linearity in the concentration range of 10–400 $\mu g\ L^{-1}$ with correlation coefficients between 0.995 and 0.999. Overall enrichment factors for the optimized method ranged from 139 to 255 times except for cypermethrin and deltamethrin which ranged from 35 to 128. Detection and quantitation limits of the chromatographic method were in the range of 0.002–0.012 $\mu g\ L^{-1}$ and 0.003–0.026 $\mu g\ L^{-1}$ respectively, with RSD values between 4.2% and 18.4%. The recoveries varied in the range of 69.4%–122.7% except for cypermethrin and deltamethrin (17.5%–64.1%) with relative standard deviations between 1.0% and 24.0% for intra and inter-day experiments at different concentrations (0.1 $\mu g\ L^{-1}$, 0.5 $\mu g\ L^{-1}$, 1 $\mu g\ L^{-1}$). The HF-LPME method optimized was applied to the analysis of three spiked real water samples with good results.

1. Introduction

Pyrethroids are the synthetic analogues of pyrethrins which were developed as pesticides from the extracts of dried and powdered flower heads of *Chrysanthemum cinerariaefolium* [1]. As the fourth generation of synthetic organic insecticides after organonitrogen, organochlorine and organophosphorus, pyrethroids have been paid more and more attention and widely used due to their relatively low mammalian and avian toxicity [2,3]. However, they were highly stable to light and temperature and they are very lipophilic compounds. The presence of residues of pyrethroids in environment may possibly contribute to human exposure by ingestion, inhalation or skin absorption. Appreciable levels of pyrethroid residues can occur in food commodities from crops, food of animal origin (e.g. milk, eggs, and meat), soils, sediments, and surface, ground and drinking water. Contamination of fresh-water ecosystems appears either because of the direct discharge of industrial and agricultural effluents or as a result of effluents from sewage treatment works; residues can thus accumulate in the surrounding biosphere [4]. So, the frequent use of this kind of pesticides may inevitably bring us some negative effect such as potential nerve disorders and endocrine-disrupting diseases. Therefore, effective and convenient water sample pretreatment method for monitoring them in water samples is needed.

Pyrethroids were usually determined by gas chromatography (GC) [5–7] and high-performance liquid chromatography (HPLC) [8,9]. Sometimes immunoassay was also used [10,11]. Several pretreatment methods such as solid phase extraction (SPE) [12] and liquid–liquid extraction (LLE) [13] have been reported for the extraction of pyrethroid residues in different matrices. When preconcentration techniques were focused on miniaturization and efficiency, solid-phase microextraction (SPME) [14], stir bar sorptive extraction (SBSE) [15] and single-drop microextraction (SDME) [16] were developed for analysis of pyrethroid residues. But the methods mentioned above had some drawbacks.

In the last few years, the use of liquid membrane extractions has been suggested as an alternative for the analysis of a large group of especially hydrophilic compounds in different matrices

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http://dx.doi.org/10.1016/j.talanta.2012.04.039

[17–20]. Among the configurations (flat sheet, spiral wound or hollow fibre) found for these membranes, hollow fibres gather the best properties due to their stability, low price and user-friendly preparation. Hollow fibre can be used for the HF-LPME [21], which consists of a polymeric microporous fibre supporting a solvent with a high affinity for the target compounds. The solvent fills the pores of the fibre wall. This fibre is submerged in a stirred water sample (donor phase) and the analytes can be extracted into the organic phase (acceptor phase) like in a LLE. The benefit of membrane-based extraction, particularly HF-LPME, is that it allows the performance of a classical LLE using only a few microlitres of organic solvent, providing a high enrichment of the compounds in the acceptor phase. After the extraction, the acceptor phase can be transferred to a suitable form to inject it in an HPLC or a GC system [22].

To our knowledge, no previous work is available in the literature where the HF-LPME process has been used to extract pyrethroid compounds from water samples. Consequently, the aim of this work was to study the combination of HF-LPME with GC/MS for the determination of nine pyrethroids (esbiothrin, prallethrin, bifenthrin, tetramethrin, phenothrin, permethrin, cyfluthrin, cypermethrin and deltamethrin) in water samples. Several factors including, extraction solvent and time, the effect of adding sodium chloride (to evaluated salting out effect) and trioctyl phosphine oxide (TOPO, used as a modifier) were studied in order to achieve the highest extraction efficiency. After selection of the optimum sample pretreatment conditions, the performance of the HF-LPME–GC/MS method was evaluated for linearity, precision, and detection and quantitation limits. Finally, the method was applied to real water samples including rain water, spring water and groundwater.

2. Material and methods

2.1. Reagents and solutions

The pyrethroid standards (esbiothrin, prallethrin, bifenthrin, tetramethrin, phenothrin, permethrin, cyfluthrin, cypermethrin and deltamethrin) were supplied by DTS-OABE Company (Orozko, Spain). Structure and chemical properties of these compounds are given in Table 1. 1-octanol (for synthesis), n-undecane (for synthesis), isooctane (for gas chromatography, $\geq$99.8%) and sodium chloride (GR for analysis, $>$99.5%) were all from Merck (Darmstadt, Germany), while cyclohexane ($>$99%) and methanol (HPLC gradient grade, 99.8%) were obtained from Prolabo. Dihexyl ether (97%) and trioctyl phosphine oxide (99%) were purchased from Aldrich (Augsburg, Germany). Ultrapure reagent water purified by a Milli-Q gradient system (Millipore, Bedford, MA, USA) was used throughout this work. Q3/2 Accurel PP polypropylene hollow-fibre membranes (HF) (200 μm wall thickness, 600 μm inner diameter, 0.2 μm pore size) were obtained from Membrana (Wuppertal, Germany).

Standard stock solutions of pyrethroid insecticides were prepared in isooctane and methanol at a concentration of 5 mg L^{-1}. Working solutions were prepared by appropriate dilution in isooctane (for GC calibration) or a mixture of methanol:water (1:500, for sample spiking) and stored at 4 °C. Methanol standard solutions were prepared each week to avoid pyrethroid degradation [23].

2.2. Sample collection

In this experiment, three environmental water samples such as rain water, groundwater and spring water were collected for validating the proposed method. Rain water sample was collected (on 13th July 2011) in the grounds of the University of the Basque Country/EHU, Spain, spring water was collected (on 20th July 2011) at Eretza downstream of the city of Barakaldo, Spain, and groundwater was collected (15th July 2011) from the hydrogeological subunit of Eguino, from a downstream placed in the Aizkorri's mountain range, Spain. The last water sample, as opposed to the collected spring water, came from a karstic aquifer. All water samples were taken using glass bottles. pH and conductivity parameters of the samples were determined before any treatment was applied. Finally, the collected water samples were filtered through a 0.45 μm micropore membrane and stored at 4 °C.

2.3. Hollow fibre-based liquid-phase microextraction (HF-LPME)

The hollow fibre was closed with the aid of a spatula, and cut manually into pieces of 1 cm length with a porous volume of ~3.3 μL (porosity of ~66%) [25]. After the fibre was impregnated with the organic phase (organic phase fills the fibre pores) for around 30 s, it was dipped into the reagent water to eliminate the excess solvent and then placed into the aqueous sample (10 mL) for extraction as illustrated in Fig. 1. In the optimized method, the sample containing the fibre was stirred at 1500 rpm allowing the contact between the donor and the organic acceptor phase into the pores of the fibre while the fibre was kept floating in the solution. After the stirring, the fibre was transferred, using forceps, to 50 μL of suitable solvent (isooctane) in a chromatographic vial and placed in the ultrasound bath for 15 min to assist the transfer of the pyrethroid compounds from the fibre to the GC injection solvent. Finally, the fibre was carefully removed and the solution was analyzed by GC/MS [22].

2.4. GC/MS analysis

All the analyses were performed using a 6890 series gas chromatograph equipped with a split/splitless injector, autosampler and a 5973-N mass spectrometric detector (Agilent Technologies, Palo Alto, CA, USA). Analytes were separated using a BPX5 (SGE Analytical Science Pty Ltd, Australia), 30 m × 0.25 mm × 0.25 μm column. The temperature programme was 100 °C, hold 2 min, rate 45 °C min^{-1} to 220 °C, rate 25 °C min^{-1} to a final temperature of 320 °C, hold 2 min. Helium was used as a carrier gas at a flow rate of 1.5 ml min^{-1}. Injection volume was 1 μL and the injector temperature was set at 270 °C. The MS was operated in the electron impact ionization (EI) mode (70 eV). The transfer line, quadrupole and ion source temperatures were 330 °C, 150 °C and 230 °C, respectively. Samples were analyzed in selected ion monitoring (SIM) mode. Scan runs were made with a mass range from m/z 40 to 500.

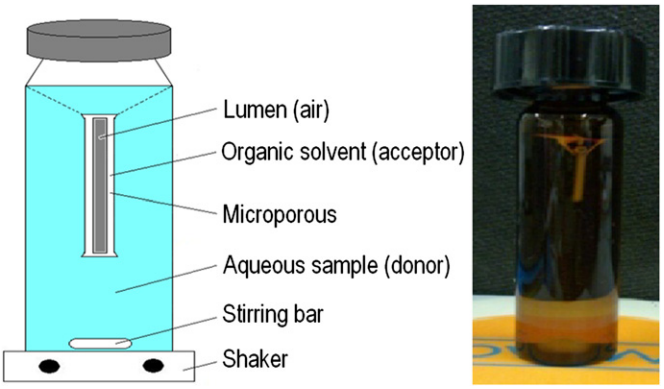


Fig. 1. Extraction set-up of HF-LPME with a 1 cm long fibre, immersed into a 10 mL water sample.

2.5. Definitions

The enrichment factor, E_e, is defined as the ratio between the concentration of analyte in the acceptor (C_A) after the extraction and that in the sample before extraction (C_D) as it is shown in Eq. (1). C_A was calculated by using the chromatographic peak area ratio and the calibration curve of the standard solutions by direct injection into GC/MS.

$$E_e = C_A/C_D \quad (1)$$

Another variable is the extraction efficiency E, which was selected as a response variable for the optimization of the extraction process. E indicates the percentage of the total analyte present initially in the sample that was extracted into the organic solvent. However, in membrane extraction, high enrichment of the analyte or good quantitative results can be obtained even at low extraction efficiency and it is merely dependent on the volume ratio of V_S to V_A, the extraction time and the partition coefficient of the analyte between the aqueous sample and the organic phase. The extraction efficiency (E) of each compound was calculated by the following equation:

$$E = (C_A V_A/C_D V_D) \quad (2)$$

Where C_A and C_D are the concentrations in the acceptor and donor phase and V_A and V_D are the respective volumes.

Spike recovery is tested by adding a known amount of analytes into a certain amount of samples followed by extraction and its analysis using the established method. It is expressed by the percentage of recovered amount of the spiked analyte (total amount detected minus original amount in the sample) over the amount spiked [26]. This parameter was used in spiked real environmental samples to assess the recovery of the analytical methodology.

3. Results and discussion

3.1. Method optimization

In HF-LPME, the amount of analyte extracted at a certain time depends on the mass transfer of the analyte from the aqueous sample to the organic solvent in the hollow fibre and the analyte's partition coefficient between the aqueous sample and the organic phase. There are several parameters, such as type of organic solvent, extraction time, addition of NaCl, addition of a modifier such as TOPO and stirring speed that could have an impact on the extraction process.

Thus, all of the above-mentioned factors affecting the extraction efficiency of the method were optimized. To evaluate the significance of these factors, a series of 10 mL aqueous samples spiked at a concentration of 1 μg L^{-1} of each pyrethroid compound was extracted in triplicate. The sample volume, fibre length and stirring speed were chosen based on best conditions for the applied methodology.

3.1.1. Selection of fibre length, sample volume and stirring speed

As with other microextraction techniques, the extraction in HF-LPME can be enhanced by stirring of the sample solution, thereby reducing the time required to attain thermodynamic equilibrium especially for the higher molecular mass analytes. In HF-LPME the organic solvent is sealed and protected by the hydrophobic hollow fibre membrane, so it is easier to handle and can tolerate higher stirring speed [26]. Therefore, we selected 1500 rpm as stirring speed for subsequent experiments because lower stirring rates do not create a vortex where the fibre can be suspended.

In case of the fibre length, membranes with a length of 1 cm were selected for further experiments. Obviously, longer membranes, accommodating a larger 1-octanol volume, are expected to improve the yield of the extraction, at the expense of also increasing the volume of the solvent used in the further desorption step. However, the length and, consequently, the volume capacity of the hollow fibres were adjusted to the injection solvent volume and to the size of the vials used in the present studies. Due to the low cost, a new fibre was used for each extraction.

The sample volume needed is just 10 mL, which allows the vortex formation where the fibre can be suspended avoiding the contact between the fibre and the stir bar, taking into account the bottles we used for the extraction process.

To sum up, the fibre length, sample volume and stirring speed were set in 1 cm, 10 mL and 1500 rpm respectively.

3.1.2. Effects of the acceptor phase and injection solvent

Different extraction solvents were studied in order to see if the extraction efficiency could be improved. 1-octanol, dihexyl ether, n-undecane and cyclohexane were the solvents studied as acceptor phases suspended in the membrane pores. The polarity of these solvents decrease in the order: 1-octanol, dihexyl ether, n-undecane and cyclohexane. The extraction conditions used were the following: 10 mL water sample spiked at 1 μg L^{-1} of each analyte and extracted for 5 h at a stirring speed of 1500 rpm. As it can be seen in Fig. 2, 1-octanol gave the best extraction efficiency except for cyfluthrin and deltamethrin. Additionally, since the viscosity of 1-octanol was higher, the fibre can be suspended better in the vortex during the stirring (see Fig. 1). Another candidate solvent, cyclohexane, showed the best stability during and after the extraction resulting in lower RSD values, but at the same time, it showed the lowest efficiencies, probably

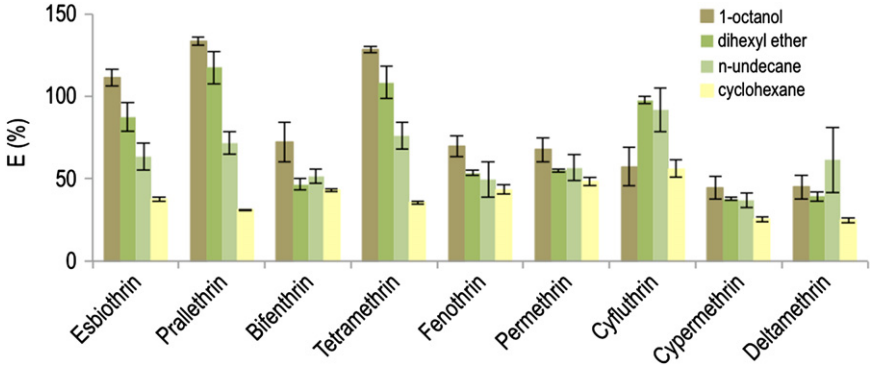


Fig. 2. The influence of the organic solvent in the extraction efficiency of pyrethroid insecticides at a concentration of 1 μg L^{-1} (n=3). Error bars correspond to the standard deviation. Extraction conditions; sample volume, 10 mL; spiked concentration of the analytes, 1 μg L^{-1}; extraction time, 5 h; stirring speed, 1500 rpm.

because of its low boiling point. Finally, with n-undecane and dihexyl ether solvents pyrethroids showed intermediate behaviour. Therefore, 1-octanol was chosen as the extraction solvent.

The injection solvent to which the compounds were transferred after the concentration in the membrane was also varied to evaluate the extraction efficiency of the different compounds. The studied solvents were acetonitrile and isooctane, obtaining more reproducible results by using isooctane.

3.1.3. Extraction time

To determine the influence of the extraction time, aqueous standard solutions spiked at a concentration of 1 μg L^{-1} of each pyrethroid were extracted for different extraction times ranging from 10 min to 24 h at a stirring rate of 1500 rpm using 1-octanol as an organic solvent. Fig. 3 shows the extraction time profile for all the analytes.

The extraction efficiency increased with the extraction time up to 6 h, where after no increase was observed indicating that the equilibrium was attained. During prolonged extraction time (10–24 h, data not shown) the equilibrium was maintained even to the studied 24 h, so, this behaviour showed that no solvent losses occurred. Therefore, an extraction time of 6 h was chosen to assure that equilibrium was reached.

3.1.4. Ionic strength

The addition of salt to the sample will lead to higher ionic strength in the sample. This effect, commonly called "salting out effect", generally results in liquid–liquid extractions with higher enrichment of uncharged species [25]. Thus, the effect of the salinity of the sample was studied by adding 0%, 1%, 5%, 10% and 15% (w/w) of NaCl to the aqueous solution spiked at analyte concentration of 1 μg L^{-1}. In principle the higher ionic strength in the sample, the lower solubility of these compounds would be, leading to a higher partitioning to the organic solvent in the fibre [27]. This process is attributed to the decrease of the affinity of organic compounds to water layer. However, at high ionic strength other processes can become relevant such us adsorption to glassware being very important at trace levels [28]. This could be the cause for the decrease in enrichment of studied compounds (having high log K_{OW} of the considered pyrethroids, 4.38–6.94, Table 1). A second possible reason could be the increment of the viscosity and density of the aqueous phase which could negatively affect the kinetics of the process and, consequently, the extraction efficiency [29]. The increase in the viscosity of the sample slows down the migration of the less polar compounds from the bulk of the sample to the organic solvent [30]. Also, for pyrethroid insecticides, in particular, for which log K_{OW} is high, the presence of ionic species in aqueous solution has a negative effect, blocking migration of the analytes towards the fibre and adversely affecting recovery yields. Fig. 4 depicts that the optimal extraction was achieved when no NaCl was added. These results showed that the addition of salt did not improve the extraction of these compounds, but at the same time, the effect of salt has not an important significance in the process, except for bifenthrin and phenothrin. For these analytes the addition of NaCl made the extraction process get worse. Therefore, this extraction method could be suitable for the analysis of several pyrethroid insecticides in sea water samples, due to a 3% of salt content can be normally found in this type of water but not for the extraction of bifenthrin and phenothrin [22].

3.1.5. TOPO content

The addition of TOPO to the organic phase is often used in the membrane extraction techniques to enhance the enrichment of compounds containing acidic or alcohol groups [29] as well as the most polar compounds [22]. The mechanism by which TOPO increases the mass transfer into the organic phase is via hydrogen bonding to the analytes. The effect of the addition of 0%, 5% and 10% (w/w) of TOPO to the 1-octanol was studied. The interaction between TOPO and pyrethroid compounds was not helping the extraction into the membrane. The obtained results showed that the TOPO chromatographic signal avoided the quantitation of cyfluthrin and cypermethrin in SIM chromatograms. The peak areas of the rest of the analytes were also increased due to the co-elution of the *m*/*z* ions coming from the TOPO addition. Therefore, in the optimal conditions, TOPO was not added.

3.2. Quality assurance

After evaluating the different parameters that might affect the extraction, the following optimized conditions were selected for all further experiments: 1 cm hollow fibre impregnated with 1-octanol solution and 10 mL aqueous sample (without salt and without TOPO addition) stirred at 1500 rpm for 6 h.

As it is shown in Fig. 5, the different properties of this group of compounds, as well as the wide range of log K_{OW} (Table 1), give differences in the extraction efficiency values. Fig. 5 shows that *E* values close to 100% can be observed in the case of esbiothrin, pralletrhrin, bifenthrin and tetramethrin, at all three levels of concentration. On the other hand, *E* ranges from 43% to 86% for permethrin, cyfluthrin and cypermethrin. As it can be seen in Fig. 5 phenothrin gives scattered results at different concentration levels. The reason for this effect is not clear but the analyte adsorption to container walls may explain it. The extent of analyte loss due to adsorption to container walls depends on a number of factors and one of them is the initial sample concentration. Sample concentration affects directly the loss percentage due to adsorption to container walls [31]. As it can seen in the case of phenothrin, the recovery increases (the loss percentage decreases) as its initial concentration increased. Hence, it is

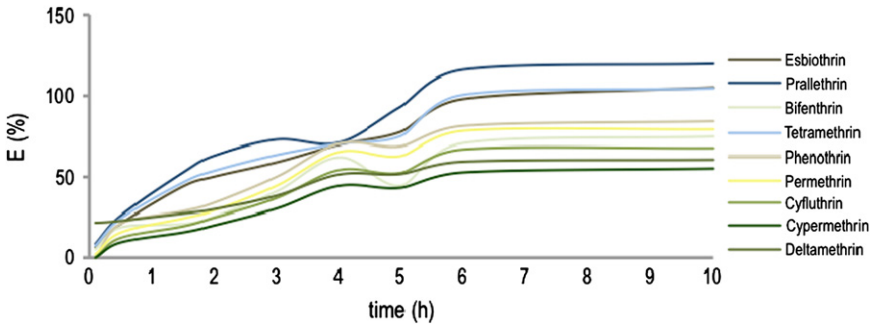
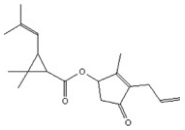
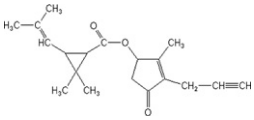
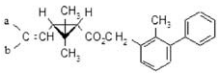
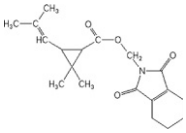
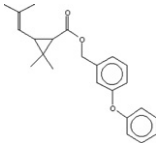
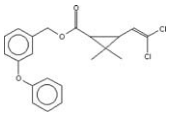
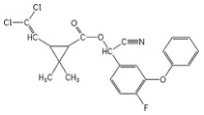
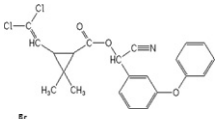
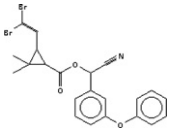


Fig. 3. Time profile for the HF-LPME of pyrethroid insecticides at a concentration of 1 μg L^{-1} (n=3). Extraction conditions; organic solvent, 1-octanol; sample volume, 10 mL; stirring speed, 1500 rpm.

Table 1
Structure, properties and GC/MS(SIM) conditions for analyses of pyrethroid compounds.

Analyte	Structure	Water solubility (mg/l) 25 °C [24]	Log K_{OW} (25 °C) [24]	Target and confirmation ions (m/z)
Esbiothrin		4.6	4.68	123, 81
Prallethrin		8	4.49	123, 81
Bifenthrin		$< 1 \times 10^{-3}$	> 6	181, 166
Tetramethrin		1.83	4.6	164, 123
Phenothrin		$< 9.7 \times 10^{-3}$	6.01 (20 °C)	123, 183
Permethrin		6×10^{-3}	6.1 (20 °C)	183, 163
Cyfluthrin		0.002	6.0	163, 206
Cypermethrin		0.01	6.94	163, 181
Deltamethrin		$< 0.2 \times 10^{-3}$	4.6	253, 181

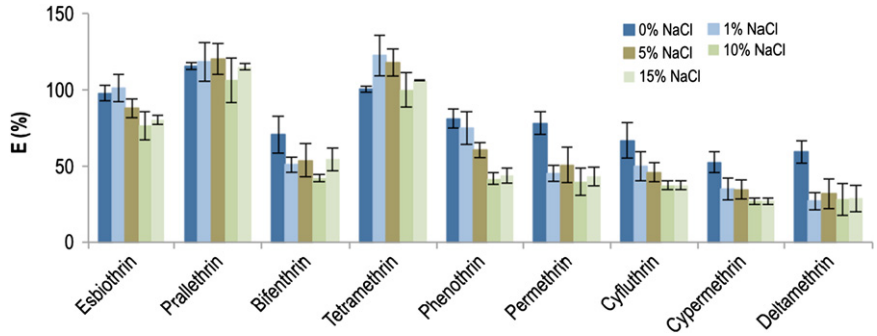


Fig. 4. The influence of NaCl addition on the extraction efficiency of the nine pyrethroid compounds at a concentration of 1 μg L^{-1} (n=10). Errors bars correspond to the standard deviation. Extraction conditions; organic solvent, 1-octanol; sample volume, 10 mL; spiked concentration of the analytes, 1 μg L^{-1}; extraction time, 6 h; stirring speed, 1500 rpm.

expected that adsorption effect will be more significant at low concentrations. In the same way, this theory could be used to explain the difference in the extraction of bifenthrin, which is better extracted at bigger concentration levels. Finally, deltamethrin showed an extraction efficiency of 18% and 20% in the highest levels (0.5 and 1 μg L^{-1}) but it was not detected for the lowest concentration level (0.1 μg L^{-1}), due to its detection limit.

It was expected that the less hydrophobic analytes (log-$K_{OW} < 5$, see Table 1) might diffuse from the aqueous sample to the organic solvent more slowly, achieving in this way lower

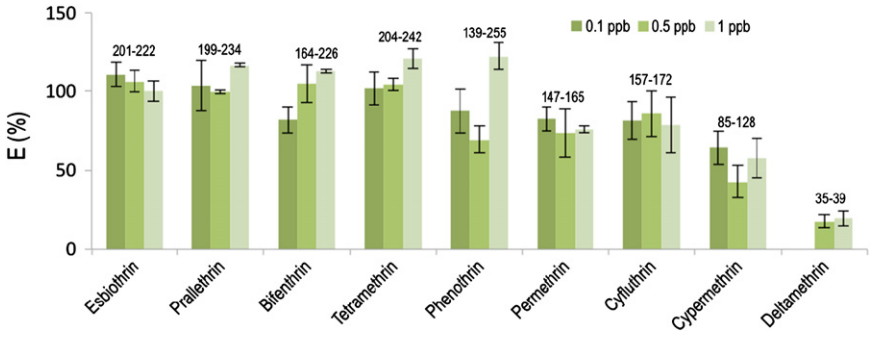


Fig. 5. E (depicted in the bars) and E_e (indicated by the numbers) values of pyrethroid compounds achieved by HF-LPME under the optimized extraction conditions at three concentration levels of each analyte. Extraction conditions; organic solvent, 1-octanol; sample volume, 10 mL; spiked concentration of the analytes, 0.1, 0.5 and 1 μg L^{-1}; extraction time, 6 h; stirring speed, 1500 rpm.

Table 2
Detected concentrations (μg L^{-1}) of pyrethroid compounds in different water types spiked at 1 μg L^{-1} level of each analyte by HF-LPME–GC/MS(SIM), under optimized conditions.

Pyrethroids	Quantified concentration (μg $L^{-1} \pm s$; $n=12$)			E_e[a]		
	Spring water	Rain water	Groundwater	Spring water	Rain water	Groundwater
Esbiothrin	0.85 ± 0.05	1.0 ± 0.1	0.90 ± 0.02	166	188	176
Prallethrin	0.95 ± 0.03	0.96 ± 0.03	0.96 ± 0.01	219	222	221
Bifenthrin	0.9 ± 0.1	1.0 ± 0.3	0.6 ± 0.2	129	141	88
Tetramethrin	0.9 ± 0.3	1.0 ± 0.1	0.74 ± 0.02	181	204	149
Phenothrin	1.0 ± 0.1	1.2 ± 0.2	1.0 ± 0.1	175	194	160
Permethrin	1.0 ± 0.1	1.2 ± 0.2	0.9 ± 0.1	159	181	139
Cyfluthrin	0.9 ± 0.1	1.1 ± 0.3	0.8 ± 0.1	118	153	105
Cypermethrin	0.9 ± 0.2	1.1 ± 0.3	0.8 ± 0.2	98	121	89
Deltamethrin	0.9 ± 0.1	1.0 ± 0.2	0.7 ± 0.2	106	115	84

[a] E_e is calculated by using the concentration obtained from the direct injection into the GC/MS after the extraction process (concentration obtained in the final volume of 50 μL isooctane) and that in the sample before extraction (10 mL of water).

extraction efficiencies. But otherwise, as we can see in the results described above, the highest extraction efficiencies were obtained for esbiothrin, prallethrin, bifenthrin and tetramethrin, which are within the less hydrophobic compounds. So, it might be because of another type of mechanism. Furthermore, deviations for some pyrethroid insecticides such as deltamethrin have been reported by several authors and attributed to the glass adsorption phenomena [4]; particularly synergism that could play an important role in pesticide extraction efficiency must be taken into consideration.

The enrichment factor values (indicated by number in Fig. 5) were about 35 times for deltamethrin and between 85 and 255 times for the rest of the compounds.

For quantitative purposes the linear dynamic range was also assessed. A linear behaviour in the range of 10–400 μg L^{-1} with r^2 values ranging between 0.995 and 0.999 was observed. Limits of detection (LOD) and quantitation (LOQ) were calculated using the mean area value of the extraction of a blank plus three and ten times its standards deviation of five blank replicates, respectively. LODs were in the range of 0.002–0.012 μg L^{-1} and LOQs were between 0.003 and 0.026 μg L^{-1}. This shows the capability of HF-LPME for trace organic compounds analysis in water samples. Thus, the sensitivity of the method was good since the detection limits were usually at low ng L^{-1} levels, enabling determination of these insecticides below the European regulatory limit of 0.1 μg L^{-1} in drinking waters [32].

The precision of the analysis was evaluated by repeating the analysis of reagent water samples spiked with concentration of 0.1, 0.5 and 1 μg L^{-1} of each pyrethroid. Six measurements were repeated over a 1 day period to find out the repeatability within a day and two times in 2 consecutive days for the reproducibility between days. The RSD for reagent water samples spiked at 0.1, 0.5, and 1 μg L^{-1} was 1.1%–14.8% for repeatability. On the other hand, the RSD% in terms of reproducibility for reagent water samples spiked at 1 μg L^{-1} was 7.3%–16.5%, whereas the range found at 0.5 and 1 μg L^{-1} levels was 1.0%–24.0%.

3.3. Analysis of real water matrices

Application of the method to monitor pyrethroid pesticides in real water matrices was evaluated by repeating the analysis of spiked real water samples such as spring water, rain water and groundwater, all of them spiked with 1 μg L^{-1} of each pyrethroid. Table 2 summarizes the concentration values (μg L^{-1}) obtained for the nine pyrethroid insecticides when analyzing spiked real water matrices. The spike recoveries in terms of concentrations ranged from 0.85 to 1.2 μg L^{-1} with RSD below 28% for spring water and rain water and between 0.6 and 1 μg L^{-1} with RSD values below 28.6% for groundwater which are reasonable values. We differentiate between spring water and groundwater taking into account that collected spring water could come mainly from rain and that groundwater was collected at a downstream coming from karstic aquifer where the water contains higher carbonate concentration. Real water matrices are, in their nature, more complex than ultrapure water; the effect of this on the extraction of the pyrethroid insecticides seems negligible except for bifenthrin and tetramethrin in the case of groundwater sample. It is widely known that these compounds are adsorbed to dissolved organic matter (DOM) [31]. Groundwater was possibly the sample with highest DOM concentration between the three samples selected and, this fact could have influenced in the spike recovery for these two compounds.

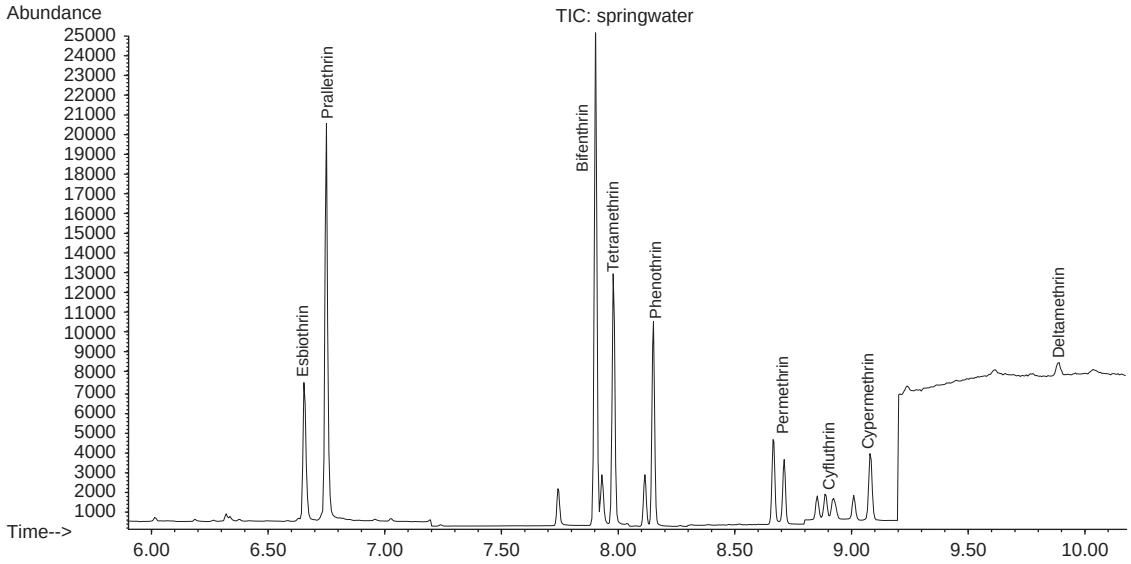


Fig. 6. Total ion chromatogram from GC/MS analysis of the extract from 10 mL of spring water spiked with 1 μg L^{-1} of each pyrethroid.

A total ion current chromatogram obtained after HF-LPME–GC/MS(SIM) analysis of spring water spiked at 1 μg L^{-1} level is presented in Fig. 6. It is apparent that very high selectivity was achieved under the optimized conditions, with low background and the absence of interferences for the nine pyrethroid insecticides in real water matrices at trace levels. The remarkable sensitivity and selectivity provided by HF-LPME–GC/MS(SIM) in the analysis of pyrethroid pesticides in different water matrices suggest the method could be established as a suitable procedure for screening trace levels.

4. Conclusions

The proposed extraction method for the determination of trace levels of pyrethroid compounds by HF-LPME was deeply studied. The main advantage of the developed method was that 9 pyrethroid pesticides can be simultaneously analyzed using a minimal amount of organic solvent (50 μL) by means of an environmentally friendly technique. The hollow fibre is also cheap and disposable and the sample volume is just 10 mL, which could reduce practical problems when high sample throughput was needed. So, in this method, 1 cm hollow fibre impregnated with ~3.3 μL 1-octanol and a low-volume (10 mL) water sample are required. From systematic assays it was established that neither sodium chloride nor trioctyl phosphine oxide addition nor an equilibration time of 6 h (1500 rpm) were the most appropriate conditions. Although the extraction time needed to perform the analysis is not very short (6 h), the methodology allows the simultaneous analysis of several samples (as many as stirrers available in the laboratory).

The proposed method gave reasonably high extraction efficiency values (69.4%–122.7%) except for cypermethrin (42.7%–57.7%) and deltamethrin (17.5%–19.6%) and showed good repeatability and reproducibility at three concentration levels except for bifenthrin, phenothrin and deltamethrin. Detection limits are very low as a result of the high concentration enrichment capacity of HF-LPME, thus, this technique is suitable for the determination of pyrethroid insecticides in water samples at ng L^{-1} levels with acceptable reproducibility.

When the optimized HF-LPME method was applied to the analysis of three spiked real water samples (rain water, spring water and groundwater) the extraction did not seem to be affected by different water matrices in the cases of rain and spring water. However, the extraction of groundwater occurs in less extent, perhaps due to its greater complexity. Therefore, a deeper study of real water properties such as the content of humic and fulvic acids, organic material and more factors that can compete with target compounds is recommended to draw further conclusions.

In short, the cost-effectiveness and reliability of the HF-LPME–GC/MS method should undoubtedly make it a valuable tool for monitoring of pyrethroid insecticides in real water matrices, covering the maximum limits admissible for pesticides in water samples set by the international regulatory organizations.

Acknowledgments

Authors thank the Bizkaia Council and the Basque Country Government for financial support (Project DIPE07/17, SAIOTEK S-PE09UN44 and IT47-10) and the SGIker technical support (UPV/EHU, MICINN, GV/EJ, ERDF and ESF). I, San Roman also thank to University of Basque Country for her pre-doctoral grant.

References

[1] S.S. Albaseer, R.N. Rao, Y.V. Swamy, K. Mukkanti, J. Chromatogr. A 1217 (2010) 5537–5554.
[2] C. Goncalves, M.F. Alpendurada, J. Chromatogr. A 968 (2002) 177–190.
[3] M. Yasin, P.J. Baugh, G.A. Bonwick, D.H. Davies, P. Hancock, M. Leinoudi, J. Chromatogr. A 754 (1996) 235–243.
[4] P. Serôdio, J.M.F. Nogueira, Anal. Bioanal. Chem. 382 (2005) 1141–1151.
[5] D.L. Wang, D.P. Weston, M.J. Lydy, Talanta 78 (2009) 1345–1351.
[6] M.L. Feo, E. Eljarrat, D. Barcelo, J. Chromatogr. A 1217 (15) (2010) 2248–2253.
[7] J.B. Cai, B.Z. Liu, X.L. Zhu, Q.D. Su, J. Chromatogr. A 964 (2002) 205–211.
[8] Q. Zhou, J. Xiao, G. Xie, W. Wang, Y. Ding, H. Bai, Microchim. Acta 164 (3–4) (2009) 419–424.
[9] F.A. Pavan, R.M. Dallago, R. Zanella, A.F. Martins, J. Agric Food Chem. 47 (1999) 174–176.
[10] K.C. Ahn, P. Lohstroh, S.J. Gee, N.A. Gee, B. Lasley, B.D. Hammock, Anal. Chem. 79 (2007) 8883–8890.
[11] A.L. Queffelec, P. Nodet, J.P. Haelters, D. Thouvenot, B. Corbel, J. Agric. Food Chem. 46 (1998) 1670–1676.
[12] M.B. Woudneh, J. Agric. Food Chem. 54 (2006) 6957–6962.
[13] J. Wu, J. Lu, C. Wilson, Y.J. Lin, H. Lu, J. Chromatogr. A 1217 (41) (2010) 6327–6333.
[14] W.P. Liu, J.J. Gan, J. Agric. Food Chem. 52 (2004) 736–741.
[15] E.V. Hoeck, F. David, P. Sandra, J. Chromatogr. A 1157 (2007) 1–9.
[16] A.S. Pinheiro, J.B. Andrade, Talanta 79 (2009) 1354–1359.
[17] A. Schafer, M.M. Hossain, Bioprocess Eng. 16 (1996) 25–33.

[18] P. Dzygiel, P. Wieczorek, L. Mathiasson, J.A. Jonsson, Anal. Lett. 31 (1998) 1261–1274.
[19] L. Zhao, H.K. Lee, Anal. Chem. 74 (2002) 2486–2492.
[20] M. Charalabaki, E. Psillakis, D. Mantzavinos, N. Kalogerakis, Chemosphere 60 (2005) 690–698.
[21] J.A. Jönsson, L. Mathiasson, J. Chromatogr. A 902 (2000) 205–225.
[22] L. Bartolome, J. Lezamiz, N. Etxebarria, O. Zuloaga, J.A. Jönsson, J. Sep. Sci. 30 (2007) 2144–2152.
[23] M.L. Alonso, G. Recio, R.M. Alonso, R.M. Jiménez, J.M. Laza, J.L. Vilas, R. Fañanás, Int. J. Environ. Anal. Chem., http://dx.doi.org/10.1080/03067319.2011.620705, in press.
[24] C.D.S. Tomblin (Ed.), The e-Pesticide Manual, Version 2.0, British crop protection council Surrey UK, 2000–2001.
[25] S. Zorita, T. Barri, L. Mathiasson, J. Chromatogr. A 1157 (2007) 30–37.
[26] P. Araujo, J. Chromatogr. B 877 (2009) 2224–2234.
[27] D.A. Lambropoulou, T.A. Albanis, J. Chromatogr. A 1072 (2005) 55–61.
[28] S. Zorita, P. Hallgren, L. Mathiasson, J. Chromatogr. A 1192 (2008) 1–8.
[29] M. Polo, G. Gómez-Noya, J.B. Quintana, M. Llompart, C. García-Jares, R. Cela, Anal. Chem. 76 (2004) 1054–1062.
[30] M. García-López, I. Rodríguez, R. Cela, Anal. Chim. Acta 625 (2008) 145–153.
[31] Saeed S. Albaseer, R.. Nageswara Rao, Y.V. Swamy, K. Mukkanti, Trends Anal. Chem. 11 (30) (2011) 1771–1780.
[32] European Union Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption. Official Journal L 330, 05/12/1998, pp. 0032–0054.