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A rapid and sensitive analytical method for the determination of 14 pyrethroids in water samples

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ABSTRACT

A simple, efficient and environmentally friendly analytical methodology is proposed for extracting and preconcentrating pyrethroids from water samples prior to gas chromatography-negative ion chemical ionization mass spectrometry (GC-NCI-MS) analysis. Fourteen pyrethroids were selected for this work: bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenvalerate, fenpropathrin, τ-fluvalinate, permethrin, phenothrin, resmethrin, tetramethrin and tralomethrin. The method is based on ultrasound-assisted emulsification-extraction (UAEE) of a water-immiscible solvent in an aqueous medium. Chloroform was used as extraction solvent in the UAEE technique. Target analytes were quantitatively extracted achieving an enrichment factor of 200 when 20 mL aliquot of pure water spiked with pyrethroid standards was extracted. The method was also evaluated with tap water and river water samples. Method detection limits (MDLs) ranged from 0.03 to 35.8 ng L^{-1} with RSDs values ≤3–25% ($n = 5$). The coefficients of estimation of the calibration curves obtained following the proposed methodology were ≥0.998. Recovery values were in the range of 45–106%, showing satisfactory robustness of the method for analyzing pyrethroids in water samples. The proposed methodology was applied for the analysis of river water samples. Cypermethrin was detected at concentration levels ranging from 4.94 to 30.5 ng L^{-1}.

1. Introduction

Pyrethroids are synthesized derivates of pyrethrins, which are natural insecticides that are produced by certain species of chrysanthemum (*Chrysanthemum cinerariaefolium*). In the last decades, they have increasingly replaced organochlorine pesticides due to their relatively lower mammalian toxicity, selective insecticide activity and lower environmental persistence. Thus, they are applied in urban area primarily for structural pest control, in agricultural areas on crops such as almonds, alfalfa, cotton, lettuce, pistachios, and peaches, and in the home in pet sprays and shampoos. Pyrethroids enter surface, ground and drinking water from rainfall or runoff from agricultural and urban applications.

Pyrethroid molecules typically contain 2–3 asymmetric carbon atoms (chiral centers), making them a family of pesticide with one of the highest chirality.

Toxic effects of pyrethroids on non-target organism have been reviewed and reported to be in the μg L^{-1} toxicity range [1]. In fish such as bluegill and lake trout, LC50 values were estimated less than 1 μg L^{-1} [2]. Even though effects to humans are still unclear, the US Environmental Protection Agency (EPA) has classified some of them (cypermethrin, permethrin and biphenthrin) as possible human carcinogens [3]. Pyrethroids are persistent compound with high hydrophobicity (log K_{ow} in the range 5.7–7.6) and very low water solubility (of a few μg L^{-1}) therefore they are rapidly and completely adsorbed to sediment particles [4]. Thus, low concentrations of pyrethroids are usually present in water making the development of analytical methods including extraction and pre-concentration necessary to reach the limits of detection required for their analysis. Generally, pyrethroids of greatest interest to water quality include bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, λ-cyhalothrin, and permethryn. The most common extraction techniques for water samples are generally based on liquid–liquid extraction [5,6], and solid-phase extraction (SPE) [7]; however, solid-phase microextraction (SPME) [8,9] and stir bar sorptive extraction (SBSE) [10,11] were recently applied for pyrethroid determinations in water. SPME and SBSE are simple, solvent-less techniques allowing the extraction and concentration in a single step [8–11]. Also these methods provide enhance sensitivity because the extracted fraction (on a fiber or on a stir bar) can be introduced quantitatively into a GC system by thermal desorption. However, SPME and SBSE analytical techniques are not very cheap although they are generally used for routine analysis.

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Dispersive liquid–liquid microextraction (DLLME) technique has also been successfully used to extract pyrethroids from tap water and river water samples [12]. The novel technique appears, simple, rapid and low consumption solvent. However, the limit of detection of the method are in the order of $\mu g\,L^{-1}$ [12], resulting higher when compared to those found by using other techniques as SPE, SPME or SBSE.

The aim of this work was to develop a simple, efficient and rapid method for the simultaneous extraction of 14 different synthetic pyrethroids in water samples at environmentally relevant concentrations, based on ultrasound-assisted emulsification-extraction (UAEE) without further cleanup step. This method has been previously developed by Fontana et al. [13] for PBDE determinations in water. However, to our knowledge, there are no works concerning the pyrethroid extraction by UAEE. Moreover, the optimization of GC-NCI-MS analysis has been carried out in order to increase the sensitivity of the method. Many pyrethroids possess one or more halogenated atoms which make them sensitive to GC-NCI-MS analysis.

Most of pyrethroid analysis have been carried out by gas chromatography with electron capture detection (GC-ECD) and a fewer number of works have reported GC-NCI-MS determination of pyrethroids [14–17] using methane as reagent gas. In this work, an accurate optimization of NCI-MS parameters, in terms of source temperature and system pressure have been carried out and described for the first time for 14 pyrethroids, choosing ammonia as reagent gas since it has been demonstrated that the use of ammonia in GC-NCI-MS provides lower limit of detection and quantification than methane for most organochlorine compounds [18].

Finally, the optimized procedure was applied for the determination of pyrethroids in water samples collected from Ebro River Delta (Spain).

2. Materials and methods

2.1. Standards and reagents

All certified pyrethroid standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). They consist of: (i) a standard mixture of seven pyrethroids containing: cyfluthrin, cypermethrin, deltamethrin, fenvalerate, permethrin, phenothrin and tetramethrin; (ii) single analytical standards of bifenthrin, λ-cyhalothrin, esfenvalerate, fenpropathrin, τ-fluvalinate, resmethrin and tralomethrin. d_6-trans-permethryn, used as surrogate standard, and d_6-trans-cypermethrin, used as syringe standard, were also purchased from Dr. Ehrenstorfer. Ethyl acetate and chloroform were obtained from Sigma Aldrich (Barcelona, Spain). The solvents used in this study were all pesticide grade. Pure water was obtained from Merck (Darmstadt, Germany).

Standard solutions were prepared in ethyl acetate in order to check the linearity of the method. These solutions were prepared at five different concentrations ranging between 0.005 and 91 $ng\,mL^{-1}$ with d_6-trans-permethryn and d_6-trans-cypermethrin always at 45 $ng\,mL^{-1}$.

2.2. Sample collection

Surface water samples were collected from Ebro River Delta (Tarragona, Spain) in six sampling campaigns during April and May 2008 at four different locations: Sites I (Illa de Mar) and II (Olles), the two main draining channels from the northern delta moiety to the sea (Fangar bay) and Sites III (Campredó) and IV (Ala) the two main draining channels from the southern delta moiety to the sea (Alfacs bay). Samples were collected in amber glass bottles and transported to the laboratory under cooled conditions (4 °C). Upon reception, samples were filtered through 0.45 μm Nylon filters (Whatman, Maindstone, UK) to eliminate particulate matter and other suspended solid matter and then stored at 4 °C in the dark until analysis.

2.3. Sample preparation

Before extraction, 20 mL of water sample were placed in a 40 mL glass-centrifuge tube and fortified with d_6-trans-permethrin (4.5 ng) as surrogate standard. The water sample was agitated and 1 mL of chloroform was added and mixed. The resulting mix was immersed into an ultrasonic bath (Raypa, UCI-200) for 5 min at 35 °C. During the sonication, the solution became turbid due to the dispersion of fine chloroform droplets into the aqueous bulk. The emulsification phenomenon favored the mass-transfer process of pyrethroids from the aqueous bulk to the organic phase. The emulsion was centrifuged at 3500 rpm for 5 min in order to disrupt the emulsions and separate both phases (the organic phase remained at the bottom of the conical tube). The organic phase was completely transferred to a vial and completely evaporated under nitrogen stream. The sample was then redissolved with d_6-trans-cypermethrin (4.5 ng), as syringe standard, and with ethyl acetate for GC-NCI-MS analysis. The final sample volume was 100 μL.

In order to estimate the analytical parameters of the UAEE method (recoveries, reproducibility, limits of detection and quantification), five different replicates were carried out with pure water sample spiked with the 14 pyrethroids included in the present study. Tests were carried out at two different levels of spike, the low level set at 125 $ng\,L^{-1}$ of each pyrethroid, and the high level set at 550 $ng\,L^{-1}$ of each pyrethroid. Since the sensitivity of the method was high dependent on the selected pyrethroid, the low and high levels were chosen in order to be able to quantify the less sensitive analyte.

2.4. GC-NCI-MS operating conditions

GC-NCI-MS analysis was performed on a Trace DSQ II (Austin Texas USA) gas chromatograph coupled to mass spectrometer. A DB-5MS capillary column (15 m × 0.25 mm i.d., 0.1 μm film thickness) containing 5% phenyl methyl siloxane was used with helium as carrier gas at constant flow of 1 mL/min. The temperature program was from 100 °C (held for 1 min) to 230 °C at 15 °C min^{-1}, then from 230 to 310 °C (held for 2 min) at 10 °C min^{-1}, using the splitless injection mode during 0.8 min. Inject volume was 3 μL. Transfer line temperature was 275 °C.

Initial experiments were carried out to optimize the NCI parameters such as source temperature and system pressure. All optimization experiments were carried out using a standard solution of pyrethroids, including the surrogate and the internal standard in the SIM mode. The optimization of the source temperature was undertaken modifying its value at 180, 200, 225, 250 and 275 °C. The optimization of the system pressure was carried out between 1.02×10^{-4} and 2.04×10^{-4} torr (1.02×10^{-4}, 1.36×10^{-4}, 1.7×10^{-4} and 2.04×10^{-4} torr) using ammonia (Quality electronic, AIR LIQUIDE) as reagent gas. Finally, the inlet temperature value has also been optimized undertaking its value at 250, 275 and 290 °C.

3. Results and discussion

3.1. Chromatographic analysis

Synthetic pyrethroids contain two or three chiral centers, making them a family of chiral pesticides with a large number of stereoisomers. Thus, multiple peaks were observed in the chromatogram for individual pyrethroids, corresponding to the separation of diastereoisomers (Fig. 1). Table 1 shows the retention

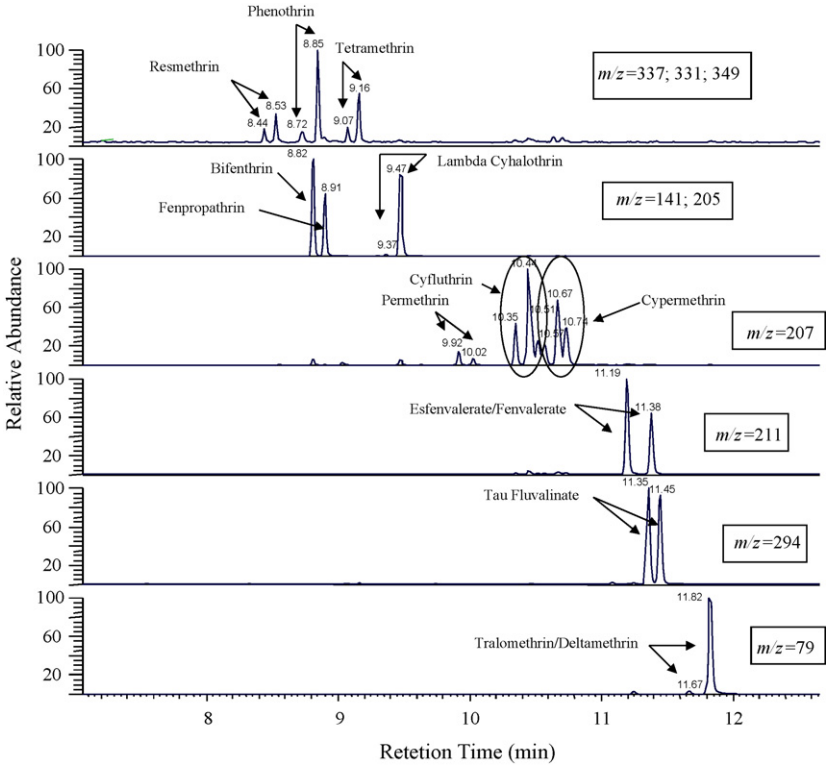

Fig. 1. GC-NCI-MS chromatograms of 14 studied pyrethroids selected in this study.

Table 1
Retention time, selected ions monitored, LOD and LOQ for the 14 studied pyrethroids.

Coumpound	Rt (min)	*m/z* ions		LOD (injected pg)	LOQ (injected pg)
		Quantification	Confirmation		
Resmethrin 1	8.44	337	167	1.22	4.06
Resmethrin 2	8.53	337	167	1.49	4.97
Phenothrin 1	8.72	331	167	0.30	0.99
Bifenthrin	8.82	205	241	0.02	0.05
Phenotrin 2	8.85	331	167	1.82	6.05
Fenpropathrin	8.91	141		0.07	0.22
Tetramenthrin 1	9.07	349	167	0.97	3.22
Tetramethrin 2	9.10	349	167	1.64	5.47
λ-Cyhalothrin	9.48	205	241	0.02	0.05
Permethrin *cis*	9.92	207	171	1.34	4.47
d_6-trans-Permethrin	10.00	213		1.88	6.25
Permethrin *trans*	10.02	207	171	1.55	5.18
Cyfluthrin 1	10.35	207	171	0.22	0.73
Cyfluthrin 2 + 3	10.44	207	171	0.08	0.27
Cyflutrin 4	10.51	207	171	0.06	0.19
Cypermethrin 1	10.57	207	171	0.10	0.32
d_6-trans-Cypermethrin 1	10.64	213		0.19	0.63
Cypermethrin 2 + 3	10.67	207	171	0.14	0.46
d_6-trans-Cypermethrin 2	10.71	213		0.19	0.63
Cypermethrin 4	10.74	207	171	0.16	0.54
Esfenvalerate/Fenvalerate 1	11.19	211	167	0.08	0.26
τ-Fluvalinate 1	11.35	294	258	0.02	0.05
Es/Fenvalerate 2	11.37	211	167	0.05	0.18
τ-Fluvalinate 2	11.45	294	258	0.02	0.06
Tralomethrin/Deltamethrin[a]	11.82	79	137	1.08	3.60
Esfenvalerate 1[b]				0.03	0.11
Esfenvalerate 2				0.02	0.66
Fenvalerate 1				0.23	0.75
Fenvalerate 2				0.02	0.05
Tralomethrin				0.45	1.50
Deltamethrin				1.81	6.02

[a] λ-cyhalothrin and deltamethrin shows an addition small peak at 9.36 and 11.67 min., respectively related to isomerization event.
[b] LOQ and LOD of esfenvalerate, fenvalerate, tralomethrin and deltamethrin separately, determined injecting their pure standard solutions.

time as well as the selected ions monitored (one for quantification and the second one for confirmation) for each pyrethroid.

Resmethrin, phenothrin and tetramethrin were resolved in two peaks related to *cis* and *trans* isomers. Infact, they are a mixture of four stereoisomers. One chromatographic peak was showed for bifenthrin, which has eight possible stereoisomers. However, the active ingredient contains at least 97% of *cis* isomer. One main peak was observed for fenpropathrin and for λ-cyhalothrin, that is a new insecticide with a unique chemical configuration consisting of dimethyl cyclopropane carboxylate moiety. A total separation of permethrin into *cis* and *trans* isomers can also be observed, while cyfluthrin and cypermethrin, which contain a third asymmetric centre, were resolved into three peaks. Also fenvalerate being a mixture of four diastereoisomers was resolved in two peaks. Esfenvalerate is one of the four isomers found in fenvalerate and in particular it is the biologically active component of fenvalerate. That because esfenvalerate and fenvalerate were reported together. Two peaks were also observed for τ-fluvalinate which is one form of fluvalinate and consists of four active diastereoisomers.

Under the GC conditions commonly used in pesticide residue analysis, tralomethrin breaks down to deltamethrin. It was found that this transformation occurs in the injector port of the GC system [19]. Although deltamethrin could have eight possible isomers, the 98% of *cis* isomers is normally present in the commercial product, while tralomethrin is a mixture of two active diastereoisomers.

Pyrethroid isomerization has been reported as the result of exposure to polar solvents [20–22], heat [23], and light [20,24]. Extensive isomerization has been observed during GC analysis for λ-cyhalothrin and deltamethrin [25]. For this reason, a smaller additional peak was observed for these two coumpounds (Fig. 1).

Regarding the surrogate standard (d_6-trans-permethrin) one peak was observed while the syringe standard showed two peaks of comparable intensity related to the two diastereoisomers of the d_6-trans-cypermethrin.

The optimization of inlet temperature value showed the best value at 275 °C for all studied pyrethroids including the surrogate (d_6-trans-permethrin) and the syringe (d_6-trans-cypermethrin) standard. The worst inlet temperature value was 250 °C as expected considering the high molecular weight of these compounds thus their high boiling point (ranged between 140 and >450 °C).

3.2. NCI-MS detection

Table 1 shows the selected ions monitored, one for quantification and the second one for confirmation. The NCI mass spectrum of pyrethroids was generally characterized by intensive peaks obtained by loss of the ester substituents that forms stabilized carboxylate ions [14,15].

Once defined the MS experiment by selecting ion masses for each of our analytes, different experiments were conducted to optimize the NCI parameters such as source temperature and system pressure. The variation in peak area of single pyrethroid isomers vs. source temperature and system pressure are given in Fig. 2.

In the beginning, the system pressure value was set at 1.7×10^{-4} torr for source temperature optimization. As can be seen, source temperature value of 250 °C was optimal for the great majority of studied pyrethroids with the exception of phenothrin, permethrin and esfenvalerate/fenvalerate for which 225 °C gave better results and fenpropathrin for which 275 °C was the best temperature value. Once the optimal source temperature value was known, the optimization of system pressure was carried out setting the source temperature at 250 °C. Pyrethroid peak areas were more or less comparable when working at a pressure of 1.36 and 2.04×10^{-4} torr, but lower than those obtained working at 1.7×10^{-4} torr. The worst results were observed at a pressure of 1.02×10^{-4} torr.

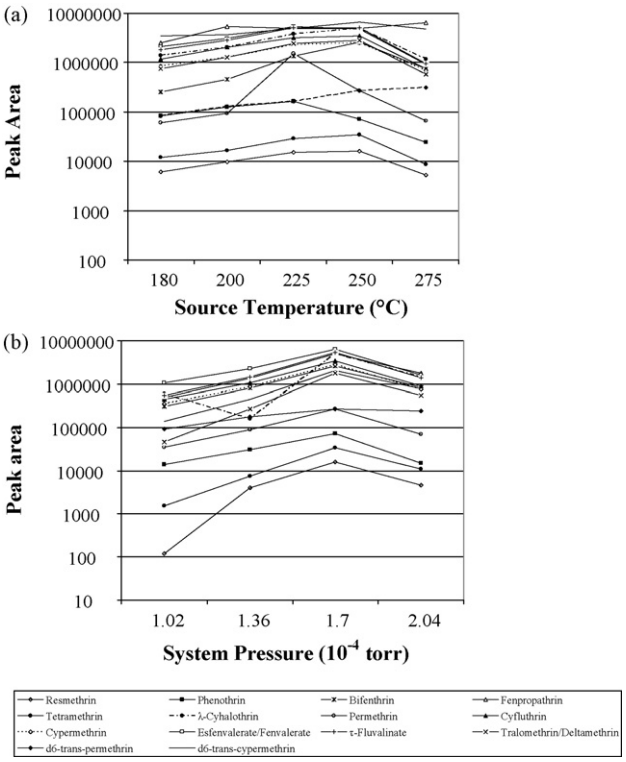

Fig. 2. Variation of peak area of pyrethroids vs. source temperature (a) at system pressure of 1.7×10^{-4} torr and vs. system pressure (b) using ammonia as moderating gas at source temperature of 250 °C.

3.3. Quantitative analysis

In order to evaluate the instrumental method developed, different quality parameters such as linearity, intra- and inter-assay variation, and sensitivity were studied. The results are presented in Tables 1 and 2.

As regards the linearity, calibration curves were determined for all 14 pyrethroids. Unfortunately the information on the diastereoisomer composition of pyrethroid standards is not available. Thus, the calibration curves were determined by the integration of all the peaks corresponding to the different diastereoisomers of a single pyrethroid. For example, the area of cypermethrin was related to the integration of all three peaks observed for cypermethrin (cypermethrin 1 + cypermethrin 2 + 3 + cypermethrin 4). The linear calibration range studied was from 0.005 to 91 ng mL^{-1}. Good correlations were obtained within the interval studied with correlations coefficient ranging between 0.998 and 0.999 (Table 2).

Table 2
Linearity, Intra- and Inter-assay variation obtained using the GC-NCI-MS approach.

Coumpound	R^2	Intra-assay variation ($n = 5$) (%RSD)	Inter-assay variation ($n = 5$) (%RSD)
Resmethrin	0.999	2	5
Phenothrin	0.998	3	20
Bifenthrin	0.998	4	6
Fenpropathrin	0.998	5	5
Tetramethrin	0.998	4	3
λ-Cyhalothrin	0.999	4	6
Permethrin	0.999	2	5
Cyfluthrin	0.998	3	3
Cypermethrin	0.998	3	6
Esfenvalerate/Fenvalerate	0.999	3	2
τ-Fluvalinate	0.999	3	4
Tralomethrin/Deltamethrin	0.999	3	10

Table 3
Pyrethroid recoveries at spiked levels of 125 ng L^{-1} (low spike) and 550 ng L^{-1} (high spike) of each pyrethroid, associated RDS values, MLODs and MLOQs obtained using the optimized UAEE plus GC-NCI-MS method in water sample.

Compound	%Recovery ($n = 5$) low spike	%Recovery ($n = 5$) high spike	%RSD ($n = 5$) low spike	% RSD ($n = 5$) high spike	MLOD[c] (ng L^{-1})	MLOQ[c] (ng L^{-1})
Resmethrin	68	47	5	23	13.3, 35.8	44.3; 119
Phenothrin	63	71	25	20	4.4, 26.9	14.7; 89.6
Bifenthrin	100	100	4	5	0.04	0.12
Fenpropathrin	100	100	9	5	0.2	0.67
Tetramethrin	88	100	20	13	19.0, 22.7	63.3; 75.6
λ-Cyhalothrin	100	100	8	5	0.03	0.11
Permethrin	95	98	4	3	14.4, 15.3	48.1; 50.9
Cyfluthrin	94	100	9	2	0.10, 0.27, 0.17	0.33; 0.88; 0.57
Cypermethrin	100	89	3	1	0.14, 0.27, 0.29	0.45; 0.88; 0.97
Esfenavalerate/Fenvalerate	100	105	11	3	0.14, 0.10	0.48; 0.32
τ-Fluvalinate	100	98	7	4	0.03, 0.03	0.11; 0.09
Tralomethrin/Deltamethrin	70	100	20	15	0.38	1.25
d_6-trans-Permethrin	76	80	13	10	–	–

[c] LODs and LOQs were estimated for each isomer of a specific pyrethroid and are reported in order of retention time of each isomer.

Limits of detection (LODs) and limits of quantification (LOQs) defined as the minimum amount of analyte which produces a peak with a signal-to-noise ratio equal to 3 and to 10, respectively, were determined for single pyrethroid isomers estimating the relative isomer abundance by the relative peak area observed for the different isomers of a selected pyrethroid (Table 1). LODs varied from 0.02 to 1.88 injected pg while LOQs ranged between 0.05 and 6.25 pg. The sensitivity decreased considerably for resmethrin, phenothrin and tetramethrin which are the three pyrethroids without halogen atoms in their molecular structure. Generally the LODs increased with increase in the degree of halogenation.

In order to evaluate the intra-assay variation of the instrumental method used, five consecutive injections were performed under optimum NCI conditions. The relative standard deviation (RSD) among the five concentration values estimated for each pyrethroid was calculated (Table 2). RSD values were lower than 5% for all studied pyrethroids indicating a very good intra-assay variation. Moreover, five injections were carried out on five different days to establish the inter-assay variation of the method (Table 2). The RSD values ranged from 2% to 20%. As expected the RSD values obtained for inter-assay variation were higher than those obtained for intra-assay variation. In particular, variation of ~2% was observed between RSD values of inter- and intra-assay variation for each pyrethroid, except for phenothrin and deltamethrin for which RSD inter-assay variation values are significantly higher (20% and 10% for phenothrin and deltamethrin, respectively) than those found for intra-assay variation (3% for both of them).

3.4. Ultrasound-assisted emulsification-extraction

Once the instrumental methodology was optimized and their analytical parameters defined, the sample preparation method based on an UAEE was tested. The UAEE technique has been recently reported by Fontana et al. [13] as extraction method for the PBDE determinations in water samples. This analytical protocol has served as basis for our development.

In our method, sample intake was increased up to 20 mL of water in order to increase the sensitivity. It was not possible to increase to higher values due to the capacity of our centrifuge tubes. The amount of organic solvent (chloroform) was set at 1 mL; lower amounts of solvent make the organic phase collection difficult.

Analytical parameters of the developed method are reported in Table 3. Recovery tests were carried out by spiking a pure water sample at spiked levels of 125 ng L^{-1} (low spike) and 550 ng L^{-1} (high spike). Five replicates were done in order to evaluate the reproducibility of the method. Percentage of recovery ranged from 63% to 100% and from 47% to 105% for low and high spike, respectively. RSD values ranged from 3 to 25% and from 1 to 23% for low and high spike, respectively. Also the percentage of recovery for the surrogate standard (d_6-trans-permethrin) showed satisfactory values (76% and 80% for low and high spike respectively), with RSD lower than 15%. This method has been successfully applied for the determination of pyrethroid pesticide residue in real water sample (tap water and river water) at spike level of 125 ng L^{-1} of each pyrethroid. Recoveries falling in the range from 45% to 106% for tap water sample and from 65% to 100% for river water sample, respectively (Table 4). The only exceptions were found for phenothrin (30% of recovery) in river water sample and resmethrin (20%) in tap water. Their low recoveries were probably due to their possible lower solubility in the solvent extraction (chloroform) since they don't have any halogen atom in their molecular structure.

As regards the sensitivity, method limit of detection (MLOD) and method limit of quantification (MLOQ) values ranged between 0.03 and 35.8 ng L^{-1}, and 0.09 and 119 ng L^{-1}, respectively. However, it should be pointed that MLODs were lower than 0.4 ng L^{-1} for bifenthrin, fenpropathrin, λ-cyhalothrin, cyfluthrin, cypermethrin, esfenvalerate, fenvalerate, τ-fluvalinate, tralomethrin and deltamethrin. Only for the rest (resmethrin, phenothrin, tetramethrin and permethrin) higher MLODs were obtained.

The analytical performance of UAEE plus GC-NCI-MS for pyrethroid determinations in water samples was compared with other analytical techniques previously reported in the literature. It can be observed that the analyte recoveries for UAEE plus GC–MS method are comparable with those obtained using the common techniques for pyrethroid determinations, whereas our MLODs were lower than those reported in the literature. For example, using liquid–liquid extraction plus GC-ECD, the recoveries of pyrethroids (bifenthrin, cyfluthrin, cypermethrin, esfenvaler-

Table 4
Recovery percentages for pyrethroids in tap water and river water at spiked level of 125 ng L^{-1} of each pyrethroid.

Compound	Tap water sample	River sample
Resmethrin	20	65
Phenothrin	56	30
Bifenthrin	105	100
Fenpropathrin	106	100
Tetramethrin	45	96
λ-Cyhalothrin	96	93
Permethrin	106	87
Cyfluthrin	103	100
Cypermethrin	94	90
Esfenvalerate/Fenvalerate	94	100
τ-Fluvalinate	93	100
Tralomethrin/Deltamethrin	105	95

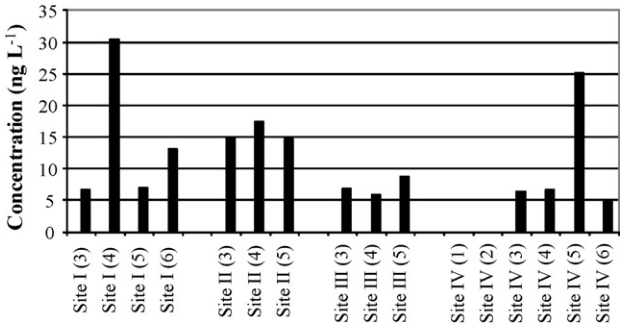

Fig. 3. Cypermethrin concentration levels found in river samples collected from four different sites of Ebro River Delta (Numbers 1–6 corresponded to different sampling campaigns done during April and May 2008: 14/4/08; 5/5/08; 13/5/08; 15/5/08; 19/5/08; 22/5/08).

ate/fenvalerate, λ-cyhalothrin, permethrin) ranged between 75% and 115% with detection limits of 1–3 ng L^{-1} [5]. For SPE method using C_{18} cartridge plus liquid chromatography-electrospray ionization mass spectrometry (LC-ESI-MS), pyrethroid recoveries (fenpropathrin, λ-cyhalothrin, deltamethrin, fenvalerate, permethrin, τ-fluvalinate, bifenthrin) were found between 71% and 115% with MLODs ranging 0.2–0.7 ng L^{-1} [7]. Using a SPME technique plus liquid chromatography with fluorescence detection, pyrethroid recoveries (cypermethrin, deltamethrin, cyfluthrin, tetramethrin, permethrin, λ-cyhalothrin) were between 81% and 134% with LODs of 0.05–2.18 ng L^{-1} [9]. And finally, applying the novel SBSE method plus GC–MS, pyrethroid recoveries (cyfluthrin, λ-cyhalothrin, cypermethrin, fenvalerate, τ-fluvalinate, permethrin) ranged from 94% to 105% with LODs of 5.4–40 ng L^{-1} [11].

3.5. Real water sample analysis

The developed method was applied for the determination of pyrethroids in 16 real water samples collected from Ebro River Delta (Terragona, Spain). The river samples showed low levels of pyrethroid contamination and in particular of cypermethrin, which was found in 14 out 16 analyzed samples. Concentration levels ranged from 4.93 to 30.5 ng L^{-1} (Fig. 3). As regards the isomeric pattern found in real samples, it is characterized by the presence of the three peaks corresponding to cypermethrin 1, cypermethrin 2 + 3 and cypermethrin 4. The contribution of each cypermethrin peaks corresponded to 18–28%, 43–55% and 17–30% of total cypermethrin, for cypermethrin 1, cypermethrin 2 + 3 and cypermethrin 4 respectively. These contributing values were very similar to those evaluated in the commercial mixture (17% for cypermethrin 1, 52% for cypermethrin 2 + 3 and 30% for cypermethrin 4). Thus, we can assume that the presence of cypermethrin in the samples is due to the application of the technical mixture in the studied area.

4. Conclusion

An analytical method based on the use of UAEE plus GC-NCI-MS technique was developed for the simultaneous analysis of 14 pyrethroids in water samples. This method showed high percentage of recoveries, good reproducibility and low detection limits, resulting adequate for the determination of low levels of pyrethroids in water samples. The extraction equilibrium is established within a few minutes. All these results disclosed that UAEE plus GC-NCI-MS is a sensitive, rapid, versatile and reproducible technique. Additionally, it is important to point out that this methodology is a low organic solvent consuming extraction technique, which turns it into a low cost and environmentally friendly technique.

The proposed method has been used successfully for real water samples confirming the reliability and efficiency of this method for trace analysis of pyrethroids in environmental water samples.

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