Journal of Chromatography A, 1217 (2010) 2248–2253

Contents lists available at ScienceDirect

Journal of Chromatography A

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

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

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ARTICLE INFO

*Article history:*
Received 6 May 2009
Received in revised form 14 January 2010
Accepted 10 February 2010
Available online 16 February 2010

*Keywords:*
Ultrasound-assisted emulsification-extraction
Pyrethroid analysis
Water analysis
Mass spectrometry

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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doi:10.1016/j.chroma.2010.02.018

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 $1.02 \times 10^{-4}$ and $2.04 \times 10^{-4}$ torr ($1.02 \times 10^{-4}$, $1.36 \times 10^{-4}$, $1.7 \times 10^{-4}$ and $2.04 \times 10^{-4}$ 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