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Microwave-assisted extraction of pyrethroid insecticides from semi permeable membrane devices (SPMDs) used to indoor air monitoring

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Abstract

A rapid and environmentally friendly methodology was developed for the extraction of pyrethroid insecticides from semi permeable membrane devices (SPMDs), in which they were preconcentrated in gas phase. The method was based on gas chromatography mass–mass spectrometry determination after a microwave-assisted extraction, in front of the widely employed dialysis method. SPMDs were extracted twice with 30 mL hexane:acetone, irradiated with 250 W power output, until 90 °C in 10 min, this temperature being held for another 10 min. Clean-up of the extracts was performed by acetonitrile–hexane partitioning and solid-phase extraction (SPE) with a combined cartridge of 2 g basic-alumina, deactivated with 5% water, and 500 mg C_{18}.

Pyrethroids investigated were Allethrin, Prallethrin, Tetramethrin, Bifenthrin, Phenothrin, λ-Cyhalothrin, Permethrin, Cyfluthrin, Cypermethrin, Flucythrinate, Esfenvalerate, Fluvalinate and Deltamethrin. The main pyrethroid synergist compound, Pyperonyl Butoxide, was also studied. Limit of detection values ranging from 0.3 to 0.9 ng/SPMD and repeatability data, as relative standard deviation, from 2.9 to 9.4%, were achieved. Pyrethroid recoveries, for spiked SPMDs, with 100 ng of each one of the pyrethroids evaluated, were from 61 ± 8 to 103 ± 7% for microwave-assisted extraction, versus 54 ± 4 to 104 ± 3% for dialysis reference method. Substantial reduction of solvent consumed (from 400 to 60 mL) and analysis time (from 48 to 1 h) was achieved by using the developed procedure.

High concentration levels of pyrethroid compounds, from 0.14 to 7.3 μg/SPMD, were found in indoor air after 2 h of a standard application.

Keywords: Semi permeable membrane device (SPMD); Pyrethroid; Residues; Microwave-assisted extraction; Indoor air; Mass–mass spectrometry

1. Introduction

Pyrethroids are extensively used against insect pests as human lice, mosquitoes, flies or cockroaches in household treatments [1]. Pyrethroids are not easily absorbed through the skin, but are absorbed through the gut and pulmonary membrane. The *World Health Organization* (WHO) considers pyrethroids as neuropoisons, paralyzing the nervous system in mammals and insects [2]. Furthermore, some pyrethroids are classified by the *U.S. Environmental Protection Agency* as class C (possible human carcinogens) [3].

The sources of indoor air pyrethroid contamination are carpets and wallpaper; electric vaporisers to prevent mosquitoes biting; anti flea pet treatments and principally the use of insecticide sprays [4]. Cypermethrin, Cyfluthrin, Deltamethrin and Cyhalothrin are widely used against malaria vectors; moreover Permethrin is employed for prevention and control of dengue [2]. Home insecticides employed in developed countries against insects, as flies, mosquitoes or cockroaches, are mainly composed of combinations of Permethrin, Tetramethrin, Phenothrin, Cypermethrin, Allethrin and Prallethrin as active principle, being also formulated with Piperonyl Butoxide, a synergist compound which increases the insecticide effectivity, and essential oils. Some physico-chemical properties of pyrethroids studied in this paper are shown in Table 1.

Active air samplers for pyrethroids are commonly based on solid-phase extraction made on pumping high volumes of air (5–1400 L) through Tenax or polyurethane foam filters [6–9]. The need of electricity to operate the aforementioned devices and their continuous maintenance are the main drawbacks of

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Table 1
Pyrethroids and Piperonyl Butoxide physico-chemical properties

Compound	Molecular formula	Molecular weight (g/mol)	Vapor pressure[a] (Pa)	Boiling point[a] (°C)	Partition coefficient[a] (log K_{ow})
Allethrin	$C_{19}H_{26}O_3$	302.4	2×10^{-2} (30 °C)	160	4.96
Prallethrin	$C_{19}H_{24}O_3$	300.4	1×10^{-5} (25 °C)	313	–[b]
Piperonyl Butoxide	$C_{19}H_{30}O_5$	338.4	1×10^{-5} (25 °C)	180	4.29
Tetramethrin	$C_{19}H_{25}NO_4$	331.4	9×10^{-4} (30 °C)	180–190	4.49
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	422.9	2×10^{-5} (25 °C)	100	8.00
Phenothrin	$C_{23}H_{26}O_3$	350.5	2×10^{-4} (20 °C)	290	7.54
λ-Cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	449.9	1×10^{-6} (20 °C)	187–190	5.26
Permethrin	$C_{21}H_{20}Cl_2O_3$	391.3	1×10^{-6} (20 °C)	200	6.10
Cyfluthrin	$C_{22}H_{18}C_{12}FNO_3$	434.3	1×10^{-6} (20 °C)	–[b]	5.94
Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	416.3	2×10^{-7} (20 °C)	220[c]	6.60
Flucythrinate	$C_{26}H_{23}F_2NO_4$	451.4	1×10^{-6} (25 °C)	108	2.08
Esfenvalerate	$C_{25}H_{22}ClNO_3$	419.9	2×10^{-7} (25 °C)	151–167	6.22
Fluvalinate	$C_{26}H_{22}ClF_3N_2O_3$	502.9	9×10^{-11} (25 °C)	164	3.85
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	505.2	1×10^{-8} (25 °C)	300	4.60

[a] All data were obtained from Extension Toxicology Network-Pesticide Information Profiles (EXTOXNET-PIP) [1] and International Programme on Chemical Safety (IPCS-Intox) [5].

[b] Data not found.

[c] Decomposition temperature.

these expensive high volume sampling equipments. The use of a very low volume active sampler to collect directly 100 mL air using a syringe has been also reported [10].

On the other hand, there is only a single precedent of the use of passive samplers for indoor determination of pyrethroids and it is based on the determination of the aforementioned pesticides in suspended dust [11].

Semi permeable membrane devices (SPMDs) are broadly employed as environmental passive water samplers being also used for air sampling with excellent results for pollutants like polychlorinated biphenyls [12] and polyaromatic hydrocarbons [13]. These devices can provide a high preconcentration of pollutants from ultratrace levels in air, evaluating long term low-dose contamination. The accumulation of pyrethroid insecticide residues (Fenvalerate, Deltamethrin and Allethrin) in SPMD has been previously reported in water contamination monitoring studies [14,15], but in our knowledge there is no precedents on their use for pyrethroids determinations in air.

On the other hand, dialysis is the common way of extraction of whatever pollutant from SPMDs, being employed as a default procedure [16]. The development of new extraction techniques, for a wide number of analytes and matrices, as microwave-assisted extraction (MAE) or pressurized solvent extraction (PSE), has been rising in the last decades, reducing the long extraction times (24–48 h), and the high solvent volumes (300–500 mL) and avoiding the evaporation of high solvent volumes required on using the traditional extraction procedures such as dialysis or Soxhlet.

MAE has been applied to a wide range of sample types for environmental analysis of pollutants, such as vegetables, soils, sediments and water with an assured efficiency [17–19]. The solvent choice is very important in microwave-assisted extraction, where a medium with a permanent dipole moment (dielectric constant) is required to catch the microwave radiation. Because of that solvents such as water ($\varepsilon' = 78.3$), acetonitrile ($\varepsilon' = 37.5$), acetone ($\varepsilon' = 20.7$) or solvent mixtures of polar and unpolar reagents should be necessary for the use of microwave radiation to extract pollutants in transparent solvents as hexane ($\varepsilon' = 1.9$) or toluene ($\varepsilon' = 2.3$), being only possible to do the direct MAE extraction with unpolar solvents in samples with a high dielectric loss [20].

Previous studies carried out in our laboratory demonstrate that MAE is a rapid and easy tool for the extraction of several pollutants from SPMDs, such as: organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons [21]; or polybrominated diethyl ethers and polychlorinated naphtalenes. Recently a rapid dialysis procedure has been also established for PAHs and PCBs extraction from SPMDs using PSE extraction [22]. Both methodologies MAE and PSE improve analytical methods performance and could be use as post treatment of samples preconcentrated on SPMDs.

Pyrethroid compounds present high stability under microwave treatments, being determined previously in soils after MAE [23] and in strawberries by using focussed MAE [24].

So, the purpose of this study was to develop a methodology for determination of pyrethroid residues, preconcentrated on SPMD by using MAE treatment of the membrane instead of dialysis.

2. Experimental

2.1. Apparatus

A Finnigan (Waltham, MS, USA) Trace gas chromatograph with a Teknokroma TRB-META.X5 (30 m × 0.32 mm i.d., 0.25 μm film thickness) column (Barcelona, Spain) and a Finnigan ion trap mass spectrometer detector Polaris Q was used for pyrethroid mass–mass determinations.

A Milestone Ethos SEL microwave laboratory systems (Sorisole, Italy) was employed for the SPMD microwave-assisted extraction. Closed Teflon reactors of 100 mL internal