Determination of pyrethroid insecticides in environmental samples

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Pyrethroids are synthesized derivates of pyrethrins, which are extremely toxic for aquatic life and possible human carcinogens. After the ban on some organophosphorus insecticides, applications of pyrethroid insecticides increased sharply.

In this article, we discuss different aspects of current analytical methodology, such as sample preparation, extraction, purification and final determination. Most pyrethroid analyses are performed by gas chromatography (GC) coupled to electron-capture detection or mass spectrometry (MS), although there are options based on tandem MS (MS^2) or comprehensive two-dimensional GC (GC × GC) coupled to time-of-flight MS (ToF-MS). We discuss the advantages and the disadvantages of the different instrumental techniques.

Keywords: Comprehensive two-dimensional gas chromatography; Electron-capture detection; Enantiomeric separation; Environmental analysis; Gas chromatography; Liquid chromatography; Mass spectrometry; Pyrethroid; Tandem mass spectrometry; Time-of-flight mass spectrometry

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1. Introduction

Pyrethroids are synthesized derivates of pyrethrins, which are natural insecticides that are produced by certain species of chrysanthemum (*Chrysanthemum cinerariaefolium*). Pyrethroids were developed in order to maintain the effective insecticidal activity of the pyrethrins while increasing stability to light and residence time in the environment [1]. However, they are more toxic to mammals than natural insecticides. In recent decades, they have increasingly replaced organochlorine pesticides due to their relatively lower mammalian toxicity, selective insecticide activity and lower environmental persistence than the organochlorines.

Pyrethroids typically contain 2–3 asymmetric carbon atoms (chiral centers), so they have high chirality. Each pyrethroid contains 2 or 4 enantiomer pairs, or 2 or 4 diastereoisomers. The chirality of pyrethroids may arise from the acid moiety, the alcohol moiety or both [2,3]. Pyrethroids are persistent compounds with high hydrophobicity (log K_{ow} 5.7–7.6, Table 1) [4–9] and very low water solubility (a few μg/L), so they are rapidly and completely adsorbed to solid particles [10]. Even though they are eventually degraded by microorganisms in soil and water, and can also be degraded by sunlight on the surface of water, soil or plants, some of the more recent pyrethroids can persist in the environment for a few months before they are degraded.

For the past three decades, organophosphorus pesticides have been the insecticides most commonly used by both professional pest-control bodies and homeowners. Nevertheless, the decision of the US Environmental Protection Agency (EPA) to phase out certain uses of the organophosphate insecticides – because of their potentially toxic effects on humans – has led to their gradual replacement by pyrethroid pesticides.

Pyrethroids are currently the most prevalent household insecticides for both indoor and outdoor applications. They are active ingredients of many insect-control products (e.g., spray, powder, mosquito coil, electro-evaporator paper, and treated wood) intended for indoor use. They are also used as pet shampoos and lice treatments.

After the ban on the use of some organophosphorus insecticides (e.g., chlorpyrifos) for non-agricultural applications, sales of insecticides containing pyrethroids for residential and non-residential applications (e.g., schools and parks) have increased sharply. Currently, pyrethroids

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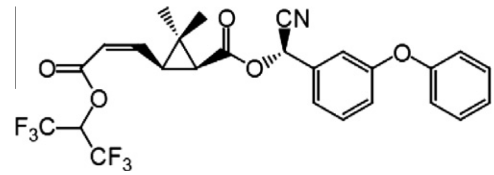
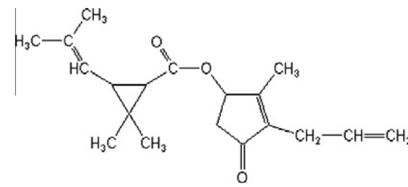
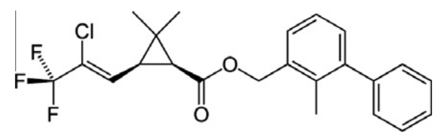
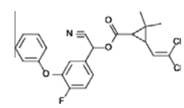
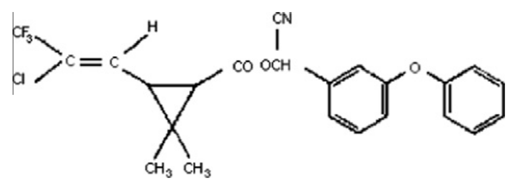
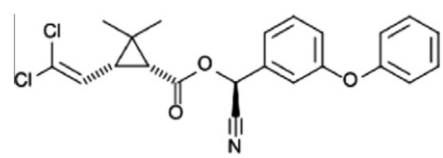
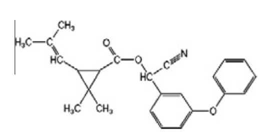
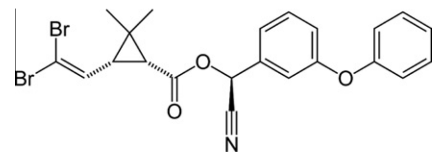
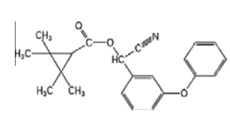
Table 1. List of pyrethroids usually determined in environmental samples

Pyrethroid (acronym)	Formula	MW	log K_{OW} [Ref.]	Molecular structure
Esters				
Acrinathrin (ACRI)	$C_{26}H_{21}F_6NO_5$	541.4	6.7 [8,9]	
Allethrin (ALLE) (Bioallethrin)	$C_{19}H_{26}O_3$	302.4	4.8 [4]	
Bifenthrin (BIFE)	$C_{23}H_{22}ClF_3O_2$	422.9	8.2 [9]	
Cyfluthrin (CYFL) (β-isomer)	$C_{22}H_{18}Cl_2FNO_3$	453.3	5.7 [8]	
Cyhalothrin (CYHA) (γ- and λ-isomers)	$C_{23}H_{19}ClF_3NO_3$	449.9	6.9 [4,8,9]	
Cypermethrin (CYPE) (α, β, θ and ζ isomers)	$C_{22}H_{19}Cl_2NO_3$	416.3	6.6 [4] 6.0 [8] 6.4 [9]	
Cyphenothrin (CYPH)	$C_{24}H_{25}NO_3$	375.5	6.3 [4]	
Deltamethrin (DELT)	$C_{22}H_{19}Br_2NO_3$	505.2	6.1 [4] 6.2 [8,9]	
Fenpropathrin (FENP)	$C_{22}H_{23}NO_3$	349.4	5.6 [9]	

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