



# Group-selective enrichment and determination of pyrethroid insecticides in aquaculture seawater via molecularly imprinted solid phase extraction coupled with gas chromatography–electron capture detection

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## ABSTRACT

Two types of molecularly imprinted polymers (MIPs) for the simultaneous determination of six pyrethroid insecticides have been developed using deltamethrin (D-MIPs) and cypermethrin (C-MIPs) as template molecules. A comparison of the performance of D-MIPs, C-MIPs, and the corresponding non-imprinted polymers (NIPs) were conducted. Stronger group-selective interactions between the C-MIPs and the six pyrethroid insecticides were achieved. The MISPE method based on the C-MIPs displayed higher extraction recoveries (86.4–96.0%) with RSD values ranging from 2.4 to 7.8% for the six pyrethroid insecticides in aquaculture seawater. After the C-MIP cartridge procedure, the limits of detection and quantification for fenvalerate, deltamethrin, cypermethrin, cyfluthrin, and bifenthrin were in the 16.6–37.0 and 55.3–109.1 ng L<sup>-1</sup> ranges, respectively, and 0.68 and 2.26 μg L<sup>-1</sup> for phenothrin, respectively. The proposed MISPE method coupled with gas chromatography–electron capture detection was successfully used for the determination of the six pyrethroid insecticides in aquaculture seawater.

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## 1. Introduction

Pyrethroid insecticides are extensively used for pest control in aquaculture areas because of their relatively low mammalian toxicity and environmental persistence. However, because of their widespread usage and high hydrophobicity, pyrethroid insecticides are usually adsorbed into the sediment, resulting in low residue concentration in water and accumulation in marine products. Some of the pyrethroid insecticides exhibit high toxicity to fish and invertebrates at trace concentrations in both seawater and sediment. This toxicity has been linked to disruptions in the endocrine system, which can adversely affect reproduction and sexual development, as well as the immune system [1–4]. Therefore, in monitoring pyrethroid insecticides in aquaculture seawater, sensitive analytical methods that have low solvent consumption and are sensitive to trace levels of pesticide residues in aquaculture seawater must be employed.

Pyrethroid insecticides are usually determined using gas chromatography coupled with electron-capture detection (GC-ECD), mass spectrometry (GC-MS), or liquid chromatography–electrospray ionization mass spectroscopy

(LC-MS) [5–7]. The MS instruments exhibit high selectivity and sensitivity; however, high costs were needed [8]. GC-ECD exhibits sufficient sensitivity and selectivity, as well as lower costs compared to MS, for many pyrethroid insecticides because of the one or more halogenated atoms present in their structures [9]. However, positive errors may occur because of the effect of complicated matrices. Therefore, cleanup steps are necessary to remove the coextracted matrix of interference and improve the selectivity of the GC-ECD analysis. Several pretreatment methods, such as solid phase extraction (SPE) [10], stir bar sorption extraction (SBSE) [11], liquid-phase microextraction (LPME) [12], solid-phase microextraction (SPME) [13], and liquid–liquid extraction (LLE) [14], have been widely used. However, SBSE, LPME, and SPME need long equilibrium times and strict experimental control and they have low sensitivity, thus limiting their application in large-scale analyses [11–13,15]. Liquid–liquid extraction is a conventional and effective isolation technique used for water samples, but emulsions limit its application [14]. Molecularly imprinted solid phase extraction (MISPE) based on selective molecularly imprinted polymers (MIPs) has been used for the isolation and clean-up of pyrethroid insecticides in different matrix samples [16,17]. However, most reported MIPs for pyrethroid insecticides were used for isolation and purification of single target analyte. Meanwhile, the concentrations of pyrethroid insecticides residues were usually low in aquaculture seawater samples.

Therefore, the objective of the present study is to develop a new MIPs with group-selectivity and good enrichment capability

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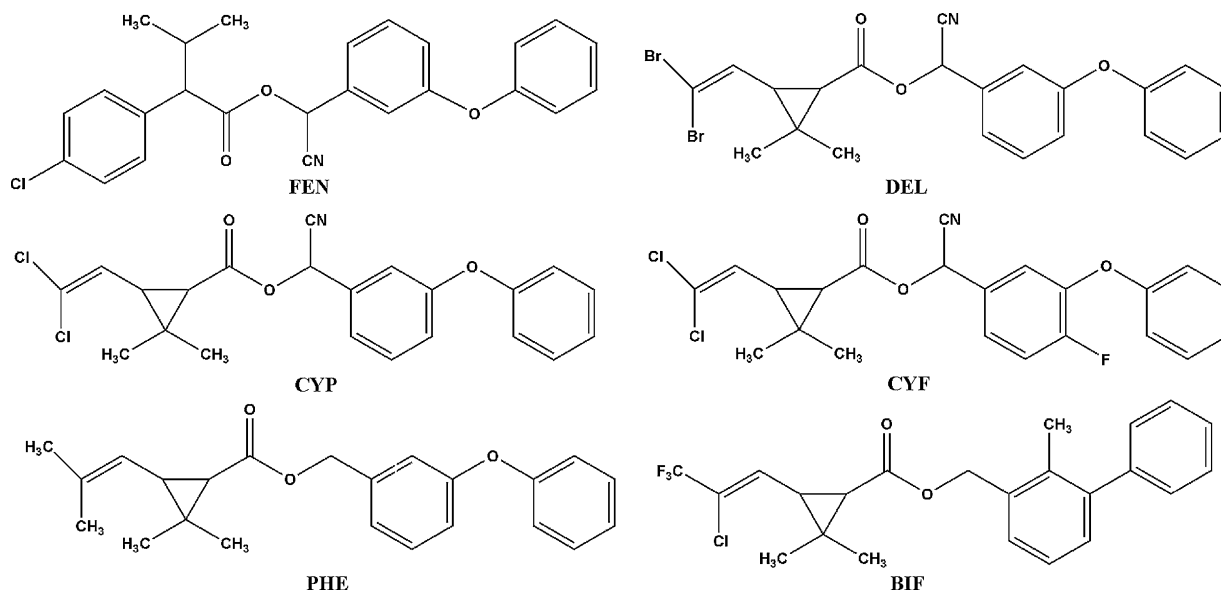


Fig. 1. Chemical structures of pyrethroid insecticides.

targeted to six pyrethroid insecticides and use it as a specific sorbent of SPE for directly enrichment and purification of pyrethroid insecticides from aquaculture seawater samples. The performance of multi-residue analytical method for the determination of six pyrethroid insecticides residues in aquaculture seawater via GC-ECD coupled with MISPE was evaluated.

## 2. Experimental

### 2.1. Chemicals

Fenvalerate (FEN), deltamethrin (DEL), cypermethrin (CYP), cyfluthrin (CYF), phenothrin (PHE), and bifenthrin (BIF) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methacrylic acid (MAA) was obtained from Sigma-Aldrich (Steinheim, Germany), and the cross-linker ethylene glycol dimethacrylate (EGDMA) was from Fluka (Steinheim, USA). The initiator, 2,2'-azobis(2-isobutyronitrile) (AIBN), was purchased from the China National Pharmaceutical Group Corporation (Shanghai, China), and HPLC grade acetonitrile and methanol were from Fisher Scientific Co. (USA). All other reagents were of analytical grade. The aquaculture seawater samples were collected in a clean plastic bucket and passed through 25 mm diameter Whatman GF/C filters.

### 2.2. Polymer synthesis

The MIPs were synthesized via bulk polymerization. The DEL or CYP template (1 mmol) was dissolved in acetonitrile/acetone (9:1, v/v, 10.0 mL). The functional monomer (MAA, 4 mmol), the cross-linker monomer (EGDMA, 20 mmol), and the initiator (AIBN, 90.0 mg) were then added. The mixture was sonicated for 10 min under a N<sub>2</sub> atmosphere and then placed in a water bath at 60 °C for 24 h. After polymerization, the polymers were crushed and passed through a 50 μm sieve. The fine particles were further removed via sedimentation in acetone. The template molecules were extracted with methanol/formic acid (9:1, v/v) via Soxhlet extraction until the template molecules were undetectable by GC-ECD, and thermal annealing of the polymers was conducted at 120 °C for 6 h. Non-imprinted polymers (NIPs) were similarly prepared except for the absence of a template.

### 2.3. Adsorption capacity

The adsorption capacity of the MIPs and NIPs were obtained via batch rebinding experiments. In the binding assay, polymer particles (15.0 mg) were added to a 1.5 mL acetonitrile/acetone (9:1, v/v) solution of pyrethroid insecticides in various concentrations (from 0.25 to 1000 mg L<sup>-1</sup>) and incubated for 24 h with stirring at 25 °C. The polymers were then removed via filtration, and the solutions were evaporated to dryness under a N<sub>2</sub> atmosphere and redissolved with 0.5 mL isooctane/acetone (9:1, v/v) followed by GC-ECD analysis. Three replicate binding assays were performed for each concentration. The amounts of rebound pyrethroid insecticides [B] were calculated by subtracting the amount of free pyrethroid insecticides [F] from the initial amount. Scatchard analysis was performed using the Scatchard equation [18].

### 2.4. BET analysis

The polymer pore parameters and surface areas were measured using a Micromeritics ASAP 2020 analyzer (Norcross, GA) and analyzed using the Brunauer–Emmett–Teller (BET) method. A 500.0 mg sample of the dried polymers was degassed at 150 °C for 24 h under a N<sub>2</sub> flow approximately 12 h prior to measurement. The N<sub>2</sub> adsorption/desorption isotherms were recorded at 77 K. The Barret–Joyner–Halenda (BJH) method was applied to acquire the pore size distribution.

### 2.5. MISPE

The MISPE column was prepared by packing 30.0 mg MIPs or NIPs into 3.0 mL SPE cartridges (Supelco, USA) with two frits at each end. First, the MISPE cartridges were sequentially preconditioned with 10.0 mL acetonitrile and 2.0 mL 20% acetonitrile in water prior to sample loading. Afterward, the cartridges were dried under a N<sub>2</sub> stream. Each cartridge was eluted with 3.0 mL acetonitrile/formic acid (9:1, v/v) at 0.5 mL min<sup>-1</sup>. Finally, the elution fractions were dried under a gentle N<sub>2</sub> stream, redissolved in 1.0 mL isooctane/acetone (9:1, v/v), and then filtered through a 0.22-μm nylon filter for subsequent GC-ECD analysis.

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