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# Trace analysis of synthetic pyrethroids: comments on the current state of the art in sampling and chromatographic methods

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## Abstract

*Synthetic pyrethroids were launched in 1970's, and since then are widely used for pest control due to the advantage of selective activity and relatively lower mammalian toxicity compared to other classes of pesticides. In the present manuscript, the latest developments in sampling methods and quantitative analysis of synthetic pyrethroids are reviewed. Analysis of pyrethroids chromatographic methods viz., GC, HPLC, SFC, GC-MS, GC-MS/MS, LC-MS, and LC-MS/MS was discussed.*

**Keywords:** Pesticides, pyrethroids, passive sampling, GC, HPLC, GC-MS, LC-MS.

## Introduction

Since the emergence of synthetic pyrethroids (SPs) for pest's control, they found wide application in agriculture for fighting or controlling mosquitoes, cockroaches and parasites. Though SPs (Figure-1) have high insecticidal activity, they pose detrimental effects on many non- targeted species such as aquatic organisms with $LC_{50}$ values as low as 1.0ppb[1]. SPs are usually not sprayed onto water but agricultural run-offs are the major rout of polluting water bodies such as lakes, ponds, rivers with pesticides[2].

The threshold concentration of permethrin in drinking water was set by WHO as low as 20µg $L^{-1}$. On the other hand, the maximum concentration of individual and total pesticides was set by the EU directive on drinking water quality (98/83/CE) as 0.10µg $L^{-1}$ and 0.50µg $L^{-1}$, respectively[3,4]. Although SPs are unlikely to contaminate groundwater via leaching mechanism due to strong adsorption on soil, sediment-dwelling aquatic organisms as well as organisms that live just above the sediment may be intoxicated by the bio available pyrethroids existing in the aqueous phase[5].

Variations in the reported SPs' toxicity could be attributed to the fact that SPs are applied as a complex mixture of stereoisomer's rather than one single pure compound[6]. In general, straightforward multi residue procedures for the determination of SPs have been reported[7–9]. Due to the fact that SPs are adsorb on soil particulates which renders them non-bioactive, it is noticeable that most published literature deal with methods of analysis of SPs in in water and agricultural commodities[10].

Only a few publications have discussed analytical aspects of SPs[11–14] and their subsequent determination. The present paper is a follow-up commentary review, which describes the current state of the art techniques of sampling, and chromatographic analysis of SPs with a special reference to the new advances introduced in the last 10 years.

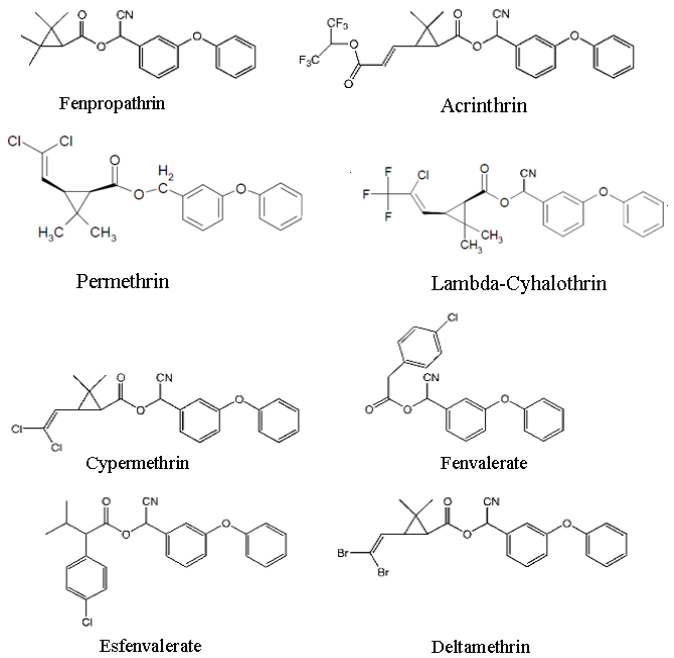


**Figure-1:** Chemical structures of the commonly used synthetic pyrethroids.

## Sampling procedures

Preparation of a lab sample that practically represents the bulk sample is always a challenge in the field of analytical chemistry. For environmental analysis, in particular, the process of preparing a representative sample starts with sampling. Errors committed during sampling cannot be corrected at a later stage. In addition, due to the fact that most environmental sampling is carried out far from the laboratory where final analysis is

performed, sample preservation could be considered as a part of sampling and is a possible source of sample contamination and/or analytes' loss. In conventional direct sampling, 1-3 L sample volume of surface waters is sampled, kept in sunlight-protected containers (e.g., amber glass jugs). To maintain pyrethroids integrity and prevent degradation, samples must be preserved on ice until analysis[15]. Other physicochemical parameters that are measured in situ include appearance and pH. However, preserving sample integrity during transportation and storage is always troublesome. For SPs, collecting the analyte(s) directly on a solid medium is recommended[14,16]. Samples of soil and sediment are first air-dried to remove any water content. The samples are then ground and sieved a 2-mm sieve.

However, due to several drawbacks associated with direct sampling, passive sampling has attracted considerable scientific attention due to the tangible advantages it offers over the conventional direct sampling.

**Passive Samplers:** Contrary to active sampling, analyte molecules in passive sampling have free flow from sampled medium to collection medium. Passive samplers eliminate almost most of the problems encountered when active sampling is applied. Typically, relatively high detection limits are obtained in classical monitoring strategies of pesticides due to the need of analysis of small volumes of water samples[17]. This disadvantage is eliminated when using passive samplers, which allow continuous monitoring of a contaminated site over a long period of time leading to very low detection limits. In contrast to air passive samplers which are seen as a mature technology[18], water and sediment passive samplers are still facing several obstacles to reach their optimum conditions. A wide range of designs of passive samplers and related devices has been proposed. Although passive sampling is not yet applied in regulatory compliance monitoring, these gadgets have been gaining acceptance by industry and regulators[18]. Passive samplers for water are based either on equilibrium or non-equilibrium mechanism. Solid-phase micro extraction, passive diffusion bag samplers (PDBS), and the diffusive multi-layer sampler (DMLS) are examples of equilibrium samplers[19]. In non-equilibrium sampling, however, eliminating the need for reaching equilibrium with the water body surrounding the sampling device is an advantage. Semi-permeable membrane devices (SPMDs) for hydrophobic organic pollutants[20] is an example of non-equilibrium samplers. Trimethylpentane solvent passive samplers (TRIMPS) is an equilibrium based passive sampler. TRIMPS is based on SPMD and constructed from low-density polyethylene membrane bags containing 2,2,4-trimethylpentane as a solvent. It has been applied for monitoring SPs in a water irrigation area for tracing the levels of applied pesticides[21]. The application of TRIMPS gave results that are comparable to those obtained using spot sampling. In addition, by using TRIMPS, neither clean up nor dialysis procedures of medium analysis is needed. However, accuracy of analysis using TRIMPS is questionable as release of solvent trapped within the membrane to the surrounding water was reported[22]. 882897.

A passive sampler composed of a semi-permeable membrane device (SPMD) was used to measure organic contaminants in water[23]. The adsorbing phase in the sampler was a thin film of neutral lipid. Triolein (MW≥600Da), is an example of lipids used in SPMD where it is enclosed in thin-walled lay flat tubing made of a non-porous polymer such as low-density polyethylene (LDPE). The potential of SPMD to monitor the concentration of SPs in surface waters was investigated[24]. Unfortunately, quantitative analysis was not possible because this sampler lacks a PRC representative of pyrethroid compounds. It was found that SPs accumulate irreversibly in the SPMD. However, the use of SPMDs has been discouraged over the last ten years in favour of using low-cost single-phase polymers such as LDPE and silicone rubber as a result of high flexibility offered by these samplers which allows fashioning to any size or thickness for varying field applications[25]. Ahrens et al.[26] tested the applicability of five passive samplers of different characteristics for monitoring the concentration of a broad range of pesticides in water (including a few SPs). The tested samplers were Chemcatcher®$C_{18}$, polar organic chemical integrative sampler (POCIS)-A, POCIS-B, Chemcatcher®SDB-RPS, and silicone rubber (SR). It was found that for hydrophobic compounds (such as SPs) SR sampler was more suitable. The study also found that the active sampler detected four pesticides (including alpha-cypermethrin) which were undetectable by the passive samplers, while there were 29 pesticides detected by the tested passive samplers but whereas the actives ampler failed to detect. It was concluded that physicochemical properties of pesticides affect their uptake by the passive samplers[26].

Comparing spot and passive sampling strategies for monitoring nine pesticides including two pyrethroids viz., permethrin and cypermethrin revealed that lower limits of detection for the two studied pyrethroids were obtained when passive sampling was applied[27]. The passive sampler used was POCIS fitted with polyether sulfone membrane (0.1µm pore size) and the receiving phase was Oasis HLB sorbent (0.2g). This situation, however, could be a result of rapid degradation of pyrethroids which prevent their accumulation in aquatic environment or as a result high tendency of pyrethroids to get adsorbed on to solid materials of. Recently, Xue et al[28] evaluated four materials (i.e., LDPE film (25µm thickness), polyurethane film(400µm thickness), polymethyl methacrylate film (40µm thickness), and polyoxymethylene film (100µm thickness) as adsorbing phases for passive sampling of SPs from surface water. The evaluation tests revealed that the PE film exhibited the highest accumulation rate. The PE sampler was able to detect pyrethroids ($C_{free}$) at a concentration of as low as 1.0ng/L through the use of performance reference compounds (PRC). However, equilibrium was not achieved even after 30 d contact between the sampler and the aquatic medium.

Passive samplers are generally used for sampling substances with high $K_{ow}$ values such as pyrethroids[21]. However, passive samplers applied for low $K_{ow}$ have been reported[26]. Nevertheless, the use of passive samplers for pesticides

monitoring requires optimization of several parameters such as medium temperature, analyte(s) concentration, effect of the boundary layer, sorbent saturation by moisture, etc. Another important aspect that needs to be assessed is to what extent the biological and particulate matter affects the passive sampler's permeability[29]. Furthermore, stability of synthetic pyrethroids on passive samplers requires rigorous evaluation. Other factors that affect the choice of the appropriate passives ampler include its practicability and cost-effectiveness. In addition, studies showed that reliability of results obtained by passive sampling devices is compound-specific[30–32] and selecting the appropriate passive sampling device represents a challenge. In general, for non-target screening studies, due to the fact that analysed compounds possess different physical and chemical properties, passive sampling device must be applicable for as many compounds as possible[26]. Booij et al[33] studied the sampler equilibrium under both laboratory and field conditions using a mechanistic model and found that passive sampling devices used for sampling hydrophobic organic contaminants (including pyrethroids) reach equilibrium in the field at a slower rate than in the laboratory. Consequently, it was estimated that the actual estimation of contaminant concentration maybe underestimated by a factor of 10 or more.

The fact that passive sampling is based on measuring freely dissolved contaminants in water make them more suitable for determining the bio available concentrations of contaminants rather than total concentration. While active sampling has the advantage of providing a better accuracy (when appropriate extraction method is used), screening of pesticides is better achieved using passive samplers especially when dissolved concentrations of such compounds are very low[26,27,34].

A relatively recent presentation of new discussions about the applicability of passive samplers for monitoring of environmental pollutants has come to the conclusion that the use passive samplers has been gaining more acceptance and with ongoing research and advances especially in the field of sampling calibration, they can be used for monitoring water quality within a regulatory framework[18].

## Analytical methods

**Gas chromatography:** Complexity of environmental samples necessitates high selectivity and robustness of the analytical methods used for pesticides quantitation. SPs in environmental samples and food commodities are favourably determined using chromatographic techniques[13]. It is obvious from Figure-2 that methods based on gas chromatography with various detection methods (GC-ECD, GC-NPD and GC-MS) count for more than 75% of all chromatographic methods reported for the quantitation of residues of SPs. Among traditional GC detectors, electron-capture detector (ECD) exhibited high sensitivity to halogen containing compounds like SPs[35,36].

Nevertheless, isomer conversion was reported during the determination of SPs by gas chromatography, and has been attributed to several factors such as polar solvents[37,38], heat[39], and light[40,41]. During isomeric analysis of cypermethrin, unexpected peaks were seen and were attributed to isomer conversion[42]. Mastovská and Lehotay[43] observed that when analysing deltamethrin in neat acetonitrile solution nearly 30% of it was converted to its isomer. However, no isomerization of deltamethrin was observed when analysed in samples' matrix reach of highly acidic components. These observations suggest that matrix components may have some influence on isomerization. It has been suggested that the addition of acid to the final sample preparation may block the epimerization reaction in the ground state of SPs in solution[40]. In addition, analyte degradation is also a problem if injection port temperature was not carefully controlled. For example, during GC analysis of tralomethrin, it was reported that it rapidly degraded to deltamethrin at injection port of GC and hence was detected as deltamethrin but not as its original structure (tralomethrin)[11,44–46]. Table-1 summarizes GC conditions for the determination of pyrethroids in water, soil and sediment.

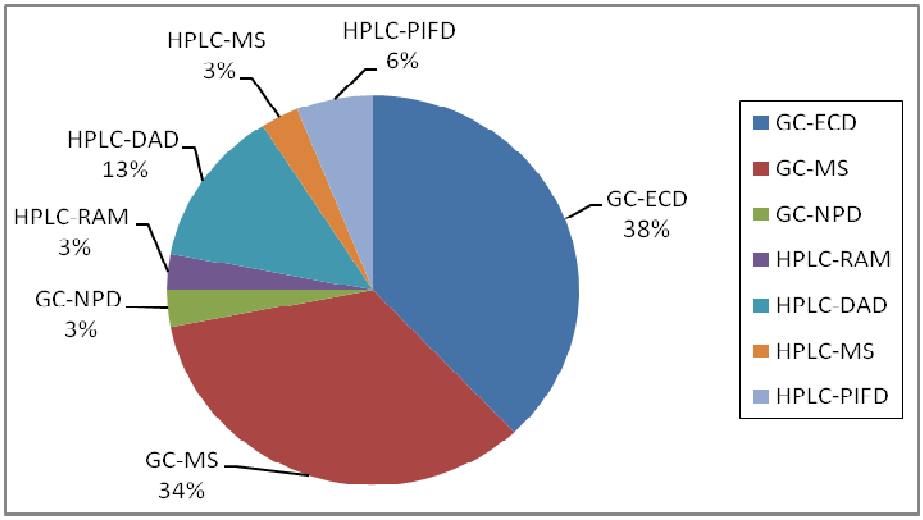


**Figure-2:** Various detection techniques used in chromatographic analysis of synthetic pyrethroids.

**Table-1:** GC conditions for the determination of pyrethroids.

| Detection | Column and operating conditions | Pyrethroids | Ref. |
|---|---|---|---|
| GC/ECD | (60m×0.25mm×0.25µm). The injector and detectors temp. 240°C and 310°C. The oven temp. 80°C, (1 min), then 15°C/min to 210°C (10 min), then 2°C/min to 290°C (14 min). Carrier gas (He, 1 mL $min^{-1}$) and makeup gas ($N_2$, 30 mL $min^{-1}$). | Esfenvalerate, Bifenthrin, Cyfluthrin, Fenvalerate, λ-Cyhalothrin, permethrin | 57 |
| GC/MS | (60m×0.25mm×0.1 µm). Oven temp: 50°C (0.5 min), then 20°C/min to150°C; then 4°C/min to 230°C (6 min), then 3°C/min to 300°C (1 min), the carrier gas (He). Injection and interface temp. 220°C, 290°C respectively. | Allethrin, Prallethrin, Cinerin-I,II, Jasmolin-I, Resmethrin, Bioresmethrin, Tetramethrin, Fenpropathrin, Phenothrin, Permethrin, L-Cyhalothrin, Cyfluthrin, Flucythrinate, Fenvalerate, Delta/tralomethrin, Pyrethrin-I, Pipronyl-Butaoxide, Cypermethrin | 3 |
| GC/ECD | (30m×0.32mm×0.25µm). Inlet temp. 250°C; detector temp., 300°C; oven temp. 150°C (1.0 min), then 15°C/min to 280°C (5.0 min); carrier gas (He, 2.1 mL $min^{-1}$) | Bifenthrin, Permethrin, Deltamethrin | 4 |
| GC/NICI-MS | (25m×0.25mm×0.25µm). Oven temp. 100°C (1 min), then 35°C/min to 240°C, then 8°C/min to 300°C, (2 min). MS conditions: ion source 250°C; e-volt. 70 eV; photomultiplier voltage 450V; filament and source currents 4.4 and 345 mA, respectively. | Fenvalerate, permethrin, Cypermethrin, Cyfluthrin, Deltamethrin | 47 |
| GC/ECD | (15m×0.53mm×1.5 µm). The injector and detector temp. 250 and 280°C. Oven temp.: 200°C to 250°C then 5°C /min (1 min). Carrier gas (He, 20 mL $min^{-1}$), makeup gas (He, 10 mL $min^{-1}$), the detector gas ($H_2$, 83 mL $min^{-1}$). | Esfenvalerate, Cis- Permethrin, Trans, Permethrin | 58 |
| GC/NICI-MS | (15m×0.32mm×0.25µm); oven temp. 100°C (1 min), then 20°C/min to 230°C, then 10°C/min to 310°C (2 min). The injector and transfer line temp. 270°C. | Fenvalerate, Permethrin, Cypermethrin, Cyfluthrin, Deltamethrin | 46 |
| GC/ECD | (22m×0.32mm×0.17µm). The oven temp. 108°C (5 min), then 20°C/min to 220°C, then 2°C/min to 260°C (10 min). The detector temp. 310°C, and argon-methane (95:5, v/v) was used as make-up gas (35mL $min^{-1}$) and helium as the carrier gas. | Fenpropathrin, Deltamethrin, Permethrin, Cypermethrin | 59 |
| GC/ECD | (30m×0.25mm×0.25µm). The oven temp. 50°C (2 min), then 30°C/min to 100°C, then 10°C/min to 250°C, then 3°C/min to 280°C (15 min). The injection temp. 260°C. The detector temp. 320°C. Carrier gas (He, 1.8 mL $min^{-1}$), makeup gas ($N_2$, 30 mL $min^{-1}$). | Bifenthrin, Cypermethrin, Permithrin, Cyfluthrin, Esfenvalerate, Deltamethrin, λ-Cyhalothrin | 60 |
| GC/ECD | (30m×0.32mm×0.25µm). The oven temp. 80°C (2 min), then 15°C/min to 190°C (2 min), then 10°C/min to 220°C (5 min) then 10°C/min to 260°C (7 min). Carrier gas (He). | λ- Cyhalothrin, α- Cypermethrin | 61 |
| GC/MS | (30m×0.25mm×0.25µm). The oven temp. 80°C (2 min), then 15°C/min to 190°C (4 min), then 10°C/min to 230°C (5 min) then 10°C/min to 290°C (6 min). Carrier gas (He, 1 mL/min). For MS, the trap and transfer line temp. 180 and 250°C respectively. Scan mode in the range *m/z* 55–430, with a background mass of 45. | λ- Cyhalothrin, α- Cypermethrin, Deltamethrin | 62 |
| GC/ECD | (30m×0.32mm×0.25µm). The oven temp. 60°C (2 min), then 30°C/min to 200°C, then 3°C/min to 230°C, then 4°C/min to 300°C. The carrier gas (He). Detector temp. 300°C. The injector temp. 260 and 290°C depending on the fibre used. | Transfluthrin, Allethrin, Tetramethrin, λ- Cyhalothrin, permethrin, Cyfluthrin, Cypermethrin, Fluvalinate, Fenvalerate, Deltamethrin | 63 |
| GC/EI-MS/MS<br><br>GC/NCI- | (30m×0.32mm×0.25µm). The oven temp. 60°C, (2 min), then 20°C/min up to 210°C, then 3°C/min up to 270°C (7 min). Carrier gas (He, 1 mL $min^{-1}$). The transfer line temp. was 300°C. An electron energy of 70eV was applied the damping gas was (Helium, 0.3 | Tetramethrin, Bifenthrin, Phenoptharin, λ-Cyhalothrin, permethrin, Cyfluthrin, Cypermethrin, Flucythrin, | 64 |

| | | | |
|---|---|---|---|
| MS/MS | mL/min). The source temp. used were 250°C for the EI and 150°C for the NCI mode. A maximum ion time of 25 mswas employed and methane was used as the reagent gas (1.5 mL $min^{-1}$) for NCI, (full scan mode m/z 50–650). | Esfenvalerate Fluvalinate, deltamethrin | |
| GC/MS | (30m×0.25mm×0.25µm). The oven temp. 70°C (2 min), then 25°C/min to 200°C, then 8°C/min to 280°C (10 min), carrier gas (He). The transfer line, ion source, and quadrupole analyzer temp. 280, 230, and 150°C, respectively. a solvent delay of 5 min was selected. | Phenoptharin, permethrin, Cypermethrin, Esfenvalerate, deltamethrin, Fenvalerate, acrinathrin | 55 |
| GC/ECD | (30m×0.25 mm×0.1 µm). Injection port temp. 250°C; detector temp. 280°C. Oventemp. 150°C (5 min), then 15°/min to 250°C (5 min); then 3°/min to 270°C, (5 min). Carrier gas ($H_2$, 1.8 mL $min^{-1}$); makeupgas ($N_2$, 20 mL $min^{-1}$). | Bifenthrin, permethrin, Cypermethrin, Deltamethrin | 65 |
| GC/MS | (30m×0.25mm×0.25µm). The oven temp. 70°C (2 min) to 150°C, then 25°C/min, then 3°C/min to 200°C, then 8°C/min to 280°C (10 min); carrier gas (He, 1.5 mL/min). MS conditions: The transfer line, ion source and quadrupole analyser temp. 280°C, 230°C and 150°C, respectively and a solvent delay of 4 min was used. EI mass spectra were recorded at 70 eV electron energy with an ionisation current of 34.6µA. ( SIM mode), two characteristic ions for each compound were selected, | Bifenthrin, λ-Cyhalothrin, permethrin, Cypermethrin, Esfenvalerate, Fenvalerate, Deltamethrin, Acrinathrin, Fenpropathrin, Trans-Resmethrin | 66 |
| GC/MS | (30m×0.25mm×0.25 µm). The oven temp. 70°C (2 min), then 25°C/min to 200°C, then 8°C/min to 280°C (10 min). Carrier gas (He). The transfer line, ion source, and quadrupole analyzer temp. 280, 230, and 150°C, respectively (full scan mode then 70 eV electron energy). | Fenpropathrin, Acrinathrin, Cis-permethrin, Trans-permethrin, Cypermethrin, Fenvalerate, Esfenvalerate, Deltamethrin | 55 |
| GC/MS | (30 m×0.25 mm×0.25 µm). The carrier gas (He). Interface temp. 280 °C, Septum purge 3 mL/min. Electron multiplier voltage between 1750 and 2100 V, (SIM mode), m/z range 45–515 a.m.u. selected ions. | Bifenthrin, permethrin, Cypermethrin, Fenvalerate, Deltamethrin | 67 |
| GC/MS | (30m×0.25×mm×0.25 µm). Injection; 280°C, oven temp. 70°C (2 min), then 25°C/min to 150°C, then 3 C/min to 200°C, then 8°C/min, 280°C (10 min); carrier gas (He, 1 mL $min^{-1}$). MS conditions: Electron impact ionization (70 eV), Ion source temp. 230°C, quadrupole temp.150°C. | λ-Cyhalothrin, Fluvalinate | 68 |
| GC/ECD GC/NPD | (30m×0.32mm×1.00 µm). The inlet temp. 220°C. The detector temp. 325 and 300°C, NPD and ECD, respectively. The carrier gas (He, 3 mL/min). For NPD used ($H_2$, 3.5 mL/min) and (air, 60 mL/min), make-up gas (He, 4.5 mL/min). The ECD used ($N_2$, 35.3 mL/min, make-up gas). Oven temp. 90 °C. (For NPD, 7 °C/min to 160°C, (10 min), then 30°C/min to 270°C, (10 min). (For ECD, 7°C/min to 160°C, (10 min), 20°C $min^{-1}$ to 220°C, (5 min) then 20°C/min to 270°C (5 min). | Esfenvalerate | 69 |
| GC/MS | (30m×0.25mm×0.25 µm). The oven temp. 60°C (2 min) then 20°C/min to 230°C, then 5°C/min to 270°C (5 min). Carrier gas (He, 1.2 mL $min^{-1}$). Trap and transfer-line temp. 250°C and 270°C. Positive electron-impact mode, electron energy 70 eV. | o-phenylphenol, Empenthrin, Tefluthrin, Transfluthrin, Allethrin, Piperonyl-butoxide, Biphenthrin, Phenoyhrin, λ-cyhalothrin, Cyphenothrin, Permethrin, Cyfluthrin, Cypermethrin, Deltamethrin | 70 |
| GC/ECD | (30m×0.25mm×0.25 µm); the oven temp: 100°C, to 250°C then 10°C/min, then 3°C/min to 280°C (15 min). Carrier gas (He, 3.8 mL $min^{-1}$) and makeup gas ($N_2$, 1.8 mL $min^{-1}$). | Esfenvalerate, Bifenthrin, Cis-permethrin, Trans-permethrin | 71 |
| GC/MS | (30m×0.25mm×0.25 µm). Injector temp. 250°C, the carrier gas (He, 0.8 mL/min). The oven temp. 82°C (1 min), then 10°C/min to 130°C, then 4°C/min to 160°C (10 min), 10°C/min to 280°C (15 min). The transfer line temp. 290°C | Cyhalothrin, Cypermethrin, Deltamethrin, permethrin | 72 |

**Gas chromatography-mass spectroscopy (GC-MS):** Francesc et al.[47] reported a GC-MS/MS method to analyze pyrethroids from soil. They reported method's limits detection to be as low as 0.08-0.54 µg $kg^{-1}$ when using electron impact ionization mode (EI) and 0.12 – 1.40 µg $kg^{-1}$ when using the negative chemical ionization mode (NCI) with average recovery values of 84–120%. However, for the water and soil applications, although, GC and especially GC-MS will preserve its popularity, the introduction of LC-MS has gained a significant importance especially for new problem areas, which include more polar transformation products.

**Supercritical-Fluid Chromatography (SFC):** Wenclawiak et al[48] conducted separation of synthetic pyrethroids and natural pyrethrins and by supercritical fluid chromatography (SFC); for efficient separation a negative temperature gradient and a positive pressure gradient were applied. Comparable density of both gradients was designed for obtaining efficient analytes'separation. A linear isothermal pressure gradient applied was from 11.1 up to 22.3 MPa at 0.2 MPa $min^{-1}$ increment. For optimal thermal conditions, a negative isobaric temperature gradient. Constant analytes' retention times were obtained throughout the experiment. A self-made Guthry-Restrictor was positioned 15 mm beneath the detector jet of the FID system. One of the most interesting features of SFC, which may offer it a bright future, is that several types of chromatographic columns can be employed (eg., micro-packed (packed capillary) and open tubular GC columnsand packed HPLC columns).

**High Performance Liquid Chromatography (HPLC):** High performance liquid chromatography – especially with UV detection-(HPLC-UV/DAD) is considered an analytical technique that can be reliably used for the analysis of several classes of pesticides. An HPLC coupled with radiometric (RAM) detector was reported for the quantitation of some synthetic pyrethroids in sediment and aqueous samples[44]. Monitoring nonradioactive reference standards in the samples was achieved by placing a UV-detector in-line prior to the RAM detector. Although pyrethroids don't have intrinsic fluorescence nature in organic solvents that are usually used for sample preparations (such as ACN or MeOH); they can be made strongly fluorescent sensitive via derivatization using sample irradiation with UV light (PIF)[49]. Off-line flow through extraction and on-column direct large volume injection RP-HPLC method was reported by Chalányová et al for the determination of three pyrethroids in soil samples with UV detection[50]. Although the column used was $C_{18,}$ this method enabled diastereoisomeric separation of cypermethrin (three peaks for four isomers) and permethrin (two peaks for two diastereoisomers). Table-2 summarizes the most elution solvents and types of stationary phases used for the determination of pyrethroids by HPLC.

**Table-2:** LC conditions for the determination of pyrethroids.

| LC mode and Detector | Column | Elution mode and solvent | Pyrethroids | Ref. |
|---|---|---|---|---|
| NP-HPLC/ RAM | Silica (250mm×4.6mm×5µm) | Gradient (hexane/ dioxane), (2mL $min^{-1}$) | Tralomethrin, Deltamethrin | 45 |
| HPLC/ESI-MS (SIM) | C18 (250mm×4.6mm×5µm) | Gradient (ACN: (ammonium formate, (1mL $min^{-1}$) | Fenpropathrin, Deltamethrin, λ-Cyhalothrin, Fenvalerate Permethrin-Fluvalinate, Bifenthrin | 73 |
| RP-HPLC/ DAD | C18 (150mm×4.6mm×5µm) | ACN: Water (85:15, v/v). (1.5 mL $min^{-1}$) | Cypermethrin, Fenvalerate permethrin | 64 |
| RP-HPLC/ DAD | C18 (250mm×4.6mm), and homemade C18 precolumn (10mm×3mm) | Gradient ACN: Water (1mL $min^{-1}$) | Fenpropathrin, Tetramethrin Allethrin, Deltamethrin, Fenvalerate, Permethrin, Bifenthrin | 74 |
| RP-HPLC/ PIF-FD | C18 (250mm×4.6mm×3.5µm) | Gradient ACN: Water (1mL $min^{-1}$) | Fenpropathrin, λ-Cyhalothrin Deltamethrin, r-Fluvalinate Fenvalerate, Permethrin, Bifenthrin | 75 |
| RP-HPLC/ PIFD | C18 (250mm×4.6mm×3.5µm) | Gradient ACN/Water, (1 mL $min^{-1}$) | Fenpropathrin, Deltamethrin λ-Cyhalothrin, Fenvalerate Permethrin-Fluvalinate, Bifenthrin | 50 |
| RP-HPLC/ UV | C18 (125mm×4mm), with a (4mm×4mm) precolumn. | MeOH/ Water (4:1, v/v). (1 mL $min^{-1}$) | Kadethrin, Cypermethrin Permethrin | 51 |
| RP-HPLC/ DAD | C18 (150mm×3.0mm×3µm) | Gradient ACN: Water. (0.5 mL $min^{-1}$) | Tetramethrin, Allethrin , Resmethrin, Pyrethrin, Phenothrin, Deltamethrin Fenvalerate, Permethrin τ-Fluvalinate, Bifenthrin | 76 |

**Liquid chromatography-mass spectrometry (LC-MS):** The emergence of LC–MS as a powerful and efficient technique for quantifying and identifying organic analytes has found its way for analysing pesticides' residue. The use of SIM mode or full mode depends on the target compounds. The higher sensitivity of SIM over full scan mode is useful when target compounds are known[52].

Another interesting feature of MS is the its ability to perform quantification as well as confirmation of compounds of compounds of the same class such as pyrethroids, which is otherwise difficult to achieve using other detectors. However, enhancement of the signals of all pesticides in the seawater was observed during the quantitation of synthetic pyrethroids using electrospray ionization (LC/ESI-MS) in positive mode. High salt content in sea water is thought to be responsible of this phenomenon due to its effect on the ionization source[52]. In ESI-MS, ionization of analyte that is otherwise a challenge is highly suppressed (ion suppression). Contaminants present in the environmental matrices are ionized with the compound of interest[53]; which is often observed as a loss in signal. Thus, any interfering compound will cause a variation in the ESI response to the targeted analyte. The presence of metaboilites, surfactants and humic substances has been reported to have detrimental effects on SPs recovery[54]. Although, complete elimination of matrix effect has been a challenge, the so-called matrix matched calibration, standard addition and isotope dilution have been applied in order for minimizing matrix effect. Extracting analytes using SPE for MS detection may suffer from ion suppression effects. However, rinsing cartridges of SPE with mill-Q water or water containing 5- 20% of an organic solvent can reduce the extent of ion suppression. The content of organic solvent should be optimized to prevent the possibility of the sample analytes' partial elution[55].

## Conclusion

The success of the final analytical step is dependent upon the prior steps from sampling to extraction. Failure at any stage may render the whole analytical process unreliable. Although hyphenated techniques such as LC-MS and GC-MS are becoming familiar for the analysis of pesticides, GC-ECD and HPLC-PDA are still in use and can provide reliable results especially for target analysis. Although, non-target analysis was not covered in this review, it should be emphasised that toxicity assessment requires that such data must be taken into account.

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