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Review

# Chromatographic methods for the determination of pyrethrin and pyrethroid pesticide residues in crops, foods and environmental samples

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**Abstract**

An overview is given of current progress in the analysis of pyrethrin and pyrethroid pesticide residues in crops, foods and environmental matrices. Extraction and clean-up are considered as the sample pretreatment prior to the determination. The conventional procedures (liquid–liquid partition and column chromatography) as well as the newly developed methods (solid-phase extraction, supercritical fluid extraction) are reviewed. GLC, HPLC and TLC chromatographic methods as the final determination of individual pyrethrin and pyrethroid residues and multi-residue, the enantiomer and diastereomer separation as well as the GC–MS confirmation are discussed and summarized in tabular form.

*Keywords:* Food analysis; Environmental analysis; Fruits; Vegetables; Reviews; Enantiomer separation; Extraction methods

## Contents



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## 1. Introduction

Pyrethrum, the powdered flower-heads of *Chrysanthemum cinerariaefolium*, and the pyrethrins extracted from these flowers have been used as insecticides for many hundreds of years. The term "pyrethrum" refers to the plant, the flower or the crude, concentrated or refined extracts, and the term "pyrethrin" is reserved for describing the active constituent(s) of pyrethrum. Pyrethrum has been used for over 50 years for the control of stored-product pests and as a grain protectant. They are powerful to kill a wide range of insect species and are harmless to mammals under normal circumstances. They are often properly formulated and combined with a suitable antioxidant, such as piperonyl butoxide, to develop the synergistic effect. However, the pyrethrins are too unstable under light, this property restricts their use against pests in agriculture. But the outstanding properties of the natural pyrethrins attracted the attention of organic chemists throughout the world. A succession of research works carried out in Japan, Switzerland, USA and the UK clarified the structure of the natural esters [1]. Research showed that the photolabile centres of the molecular framework of pyrethroids may be replaced with alternative units, producing compounds with more stability under light, but still retaining the powerful insecticidal activity and low mammalian toxicity. In 1953, the first synthetic pyrethroid —bioallethrin was developed. This compound showed higher activity against the housefly, however, it was still photolabile. Bioresmethrin (1969) was the first synthetic pyrethroid to approach the potency of pyrethrin against a wide range of insect species. However, it was no more stable under light than previous pyrethrin. Seven years later, the first photostable synthetic pyrethroid —fenvalerate (1976) was discovered by the substitution of sensitive furan ring and isobutenyl side chain. Then, the permethrin (1977), cypermethrin (1977), deltamethrin (1977) were commercialized successively. Due to the limitations on the high fish toxicity and low miticidal activity of these cyclopropane based pyrethroids, some new so-called second generation pyrethroids, such as cyfluthrin (1980), flumethrin (1982), fenpropathion (1983), fluvalinate (1983), cyhalothrin (1985), biphenthrin (1985), tefluthrin (1987), were discovered and developed successively [1]. It is now twenty years since the UV-stable pyrethroids were launched commercially. Due to their very low rates of use (10 g active ingredient/ha), excellent efficacy, low hazard to users and rather low environmental impact, the pyrethroids were used widely. They occupied 18.0–19.2% of the sales of insecticide in the world in 1990–1994 [2]. However, the rapidly growing trends stagnated in recent years due to the resistance of insect pests to pyrethroids. Today, these pyrethroids are used worldwide in the control of agricultural, forestry, household, industrial, stored product and veterinary pests in the Integrated Pest Management (IPM) programme of modern society.

As a major group of insecticide widely used in the world, the residue analysis of pyrethrins and pyrethroids in crops, foods and environmental matrices is of importance in agricultural and environmental sciences. Generally, the development of residue analysis for pesticides is frequently driven by toxicological purpose or by a need to identify a terminal residue. In the first case, the compound (s) is identified as being potentially hazardous to human health or to the environment. Fortunately, up to now only the parent pyrethrin and pyrethroid are the main component of any residue present at harvest following normal agricultural application, and no metabolite(s) was proved to be significantly toxic. In the second case, the determination of terminal residue is mainly aimed at inspecting and monitoring of food or environmental samples. In either event, the need arises to identify and measure small amounts of these compounds. The residue analysis of pyrethrins and pyrethroids has been reviewed by Miyamoto [3], Papadopoulou-Mourkidou [4,5] and Sharp [6]. This review paper will focus on the methodology of residue analysis of pyrethrins and pyrethroids in biological and environmental matrices including the sample pretreatment, chromatographical determination and confirmation.

## 2. Sample pretreatment: extraction and clean-up

The sample pretreatment includes the extraction and clean-up. The extractive and clean-up methods of pyrethoids in food and environmental samples have been summarized in the review paper of

Papadopoulou-Mourkidou [5] and also scattered in the analytical methods of individual pyrethroid [7] as well as vast amounts of references. Pyrethrin and pyrethroid pesticides are non-polar in nature and non-systemic in plants, thus the extractions of these pesticides are rather simple compared to the organophosphate and carbamate pesticides. The extractive solvent and the method used depend on the nature of sample.

Basically, the representative subsamples are homogenized once, or several times with a single non-polar solvent, such as hexane or benzene, or with a binary solvent mixture, such as hexane–acetone, hexane–isopropanol or light petroleum–diethyl-ether. The pyrethrin and pyrethroid, together with a wide variety of other lipophilic compounds are co-extracted during this process. The samples of cereals and grains are simply extracted by shaking in the presence of appropriate solvents. After filtering over anhydrous sodium sulphate, the filtrate consists of the analytes of interest and the co-extractives. It can be directly concentrated and passed over the column clean-up process if the co-extractives do not interfere. If there are too much co-extractives to interfere with the final determination, it can be cleaned-up through the liquid–liquid partition and/or column chromatography. The clean-up procedure is also influenced by the final determination. If the detection is selective enough, the clean-up procedures need not be so rigorous, otherwise more efficient clean-up procedures are needed.

Samples with low water content, such as tea, tobacco and straw, are usually homogenized with binary solvent mixture, such as acetone–hexane (1:1), hexane–isopropanol (3:1), or single polar solvent, such as methanol, acetone or acetonitrile. Presoaking a sample with distilled water for 5 min may improve the extraction rate.

Moist samples such as vegetables and fruits are usually homogenized with a binary solvent mixture such as acetone–hexane (1:1), acetone–hexane (1:4) or hexane–isopropanol (3:1) in the presence of granular anhydrous sodium sulphate. If samples are not extracted immediately, they are sometimes crushed, chopped and gently dried at 40–50°C prior to storage and analysis.

Soil samples after mixing and removing the stones and any vegetation, are extracted with acetone–hexane, methanol, acetone and acetonitrile by shaking or end-over-end tumbling for 2 h.

Animal tissue samples having a high lipid content of ca. 10% (w/w) or lower are homogenized with acetone–hexane or diethyl ether–light petroleum in the presence of anhydrous sodium sulphate.

Milk samples are macerated with acetone–hexane or hexane. Water samples are partitioned with hexane with addition of sodium chloride.

The clean-up procedure consists of liquid–liquid partition and column chromatography. Liquid–liquid partition is a well established technique used for the separation of pesticides from the coextractives. When the analysed sample is of a solid nature including the animal tissue and plant origin, the subsamples can be homogenized with a mixture of an nonpolar solvent and a water-immiscible solvent, such as hexane–acetone. After the suction-filter of the homogenate, the filtrate is partitioned with an apolar solvent in the presence of sodium chloride aqueous solution. The pyrethrins and pyrethroids are partitioned into the organic phase and the co-extractives remained in the aqueous phase. The solvent partition system used in the pyrethrins and pyrethroids residue analysis includes acetone–hexane [8,9], acetone–dichloromethane [10,11], acetone–light petroleum [12,13,69], acetonitrile–hexane [14], methanol–toluene [15,16], acetonitrile–light petroleum [17].

Recently published methods use solid-phase extraction (SPE) in place of liquid–liquid partition method. An investigation of the extraction of 29 pesticides residues including the pyrethroids in rice was carried out with bonded-silica absorbents. Satisfactory recovery was obtained with nonpolar or moderately polar pesticides whose water solubility is less than 25 000 mg/l. Among the various absorbents, the octyl ($C_8$), ethyl ($C_2$) and cyclohexyl (CH) sorbents were superior to others in strength and selective elution [18]. The extraction of 44 halogened pesticides in 4 crops (broccoli, carrot, celery and orange) by using the SPE method was investigated. Around 50 ml of acetonitrile added to crop samples, the extracting solvent is concentrated to 1–2 ml, add 7 ml water, then put on the $C_{18}$ column and eluted with hexane or 2.5% acetone in hexane. The recovery of permethrin, fenveralate was 92–125% in broccoli, orange and celery, however, the recovery rate in carrot was relatively low [19].

The pyrethrins and pipenoyl butoxide residues in human plasma were extracted with a $C_{18}$ sorbent. One ml of plasma and 3 ml of water were applied to the $C_{18}$ column and eluted with methanol–water (5:95), only a few mls of methanol is needed to elute the pyrethrins and pyrethroids quantitatively. The recovery of pyrethrin I, pyrethrin II and pipenoyl butoxide (60 ng) was 81.5, 72 and 70%, respectively [20]. An experiment on the column extraction of residues of various kinds of pesticides including the pyrethroids of cypermethrin, fenpropathrin, fenvalerate and permethrin from 8 kinds of vegetables and fruits was carried out recently [21]. A representative portion of plant samples was homogenized. Florisil was mixed with the sample to obtain free-flowing powdered sample before the extraction. The powdered sample was added onto the column and extracted with around 20 ml dichloromethane–acetone (9:1) or ether acetate. The filtrate was concentrated and dissolved in small amounts of hexane. The recovery of cyhalothrin, cypermethrin and deltamethrin (fortified in 0.05–1.0 ppm) ranged from 75 to 89%. The recovery of permethrin in orange (fortified at 0.2 mg/kg) was 91–103% [21]. DePaoli and Barbina used SPE with RPC-18 cartridges and GLC determination to analyse the flumethrin residue in honey samples [22]. The advantage of saving on solvents with the SPE method attracted attention.

The sample extraction with supercritical fluid extraction (SFE) is a relatively new technique in comparison with other techniques discussed. The advantages of SFE over conventional liquid extraction methods are that it saves time and solvents, gives more efficient extraction and is more selective in isolating the pesticide residues from biological and environmental matrices [23,24,26]. Besides, it can easily be coupled to other chromatographic techniques. It is based on the enhanced dissolving power of supercritical fluids above their critical points and their low viscosity relative to the liquid solvents. This rapid mass transfer during extraction improves the efficiency of the extraction process, it was proved especially useful in the extraction of those non-extractive pesticides which often referred to as "bound residue" [25]. At present, carbon dioxide ($CO_2$) is most often used as the extractive solvent in SPE because of its moderate critical temperature (31°C) and pressure (73 atm; 1 atm=101 325 Pa). It is non-flammable, non-toxic and relatively inexpensive. Methanol can be used as the modifier and is added to adjust the dissolving power of the fluid. The bound deltamethrin residue in soil extracted by the SFE method was compared to the radioassay method. The recovery of bound deltamethrin in wheat determined by GLC was 90.6%, similar to those obtained by radioassay method (95.2%) [25]. In an experiment on the determination of fluvalinate residue in honey, by using the SFE method [$CO_2$ as extractant and benzene–isopropanol (7:3) as organic modifier] and HPLC determination, the recovery at 0.5–10 mg/kg level was 53–94% [27].

Adsorption chromatography is often used as an additional clean-up for eliminating the interference of co-extractives. Commonly used sorbents include Florisil, silica gel and alumina. These adsorbents show a polar nature, thus retaining the lipid fraction on elution with organic solvents of low polarity. So, they are suitable for the clean-up of apolar analytes, such as pyrethrins and pyrethroids and organochlorine pesticides [83].

The application of synthetic magnesium silicate —Florisil can be traced back to nearly 40 years ago [28,29]. However, it is still recommended in the official AOAC methods nowadays [30]. For the purpose of standardizing the adsorptive ability of Florisil, it is recommended to activate at 130°C for at least 8 h, then deactivated to an appropriate degree by the addition of water. If too much water is added, the efficiency in fat retention will be insufficient. It is usually deactivated with 5% water. A Florisil column combined with liquid–liquid partition was used as the clean-up procedure in the determination of biphenthrin [31,32], cyhalothrin [33,181], cypermethrin [14,34,38–41,168], deltamethrin [36], fenpropathrin [42], fenvalerate [43,44], fluvalinate [45–48,163], permethrin [9,49], phenothrin [42] and multi-residue determination including pyrethroids, organophosphate and organochlorine pesticides [13,56,198].

Neutral alumina is also a popular sorbent for column clean-up next to Florisil. It is also necessary to standardize the activity of alumina by adding an appropriate amount (7–10%) of water after the activating process at 130°C for 3–6 h [57]. The adsorptive ability of alumina is more potent than that of Florisil. Thus the un-deactivated alumina may

induce the low recovery of pesticide. The neutral alumina showed a strong retaining activity for fats and lipids. It was reported that 1 g of neutral alumina (2.5 grade activity) can retain 40 mg fat [58]. A liquid–liquid partition combined with alumina column clean-up was used to determine the residue of permethrin in 7 crops [59] and Brinjal plant [52] as well as the residue of cypermethrin, deltamethrin, fenvarelate and permethrin in vegetables and fruits [54,60].

Silica gel is still another adsorbent used for additional clean-up of samples after liquid–liquid partition, although the efficiency of silica gel in retaining the fat and lipid in the samples is less than the above two adsorbents. It is usually combined with active charcoal. In a method for determining the pyrethroid residues in vegetables, grains and soil samples recommended by DFG (Deutsche Forschungsgemeinschaft), a column of silica gel–active charcoal was used in the determination of the apple, wheat, onion and rape samples containing pyrethroid residues of less than 0.1 mg/kg as a supplemental clean-up step [71]. It was also recommended for use in the determination of cypermethrin, deltamethrin and fenvarelate residues in chicken tissue [62], permethrin in water, sediment and fish samples [50], phenothrin residues in rice and straw [42], fenpropathrin residues in fruits, vegetables, mushroom and tea [42] and multi-residue determination in vegetables and fruits [8].

Gel permeation chromatography (GPC) using cross-linked dextran gels has become a valuable technique in pesticide residue analysis. This technique is widely used for the separation of proteins and the biomolecules in an aqueous or buffered solvent system. Separation is achieved on the basis of molecular size, partition and absorption. So, the different elution fractions may contain different classes of compounds. Its use as a clean-up procedure for pesticide residue was first reported by Ruzicka [64], who used Sephadex CH-20 to separate a number of organophosphate pesticides. He concluded that GPC was of limited value because certain amount of colored co-extractives coeluted with pesticides. The Bio-Beads SX-2 GPC and the Bio-Beads SX-3 with the ability of preventing a greater portion of high molecular mass materials were recommended as a clean-up technique in pesticide residue analysis [65,66]. Then, the application of GPC (SX-3 Bio-Beads) as a clean-up procedure in the determination of pyrethroid residues was adopted and applied [30,67,68]. Now, GPC was accepted by the Association of Official Analytical Chemists (AOAC) [30] and applied widely as the most applicable clean-up stage for multi-residue analysis procedure. An additional clean-up procedure of cereal sample extracts with organochlorine, organophosphate, pyrethroid pesticides and insect growth regulators by using the GPC (Bio-Beads SX-3) was reported [70]. A satisfactory recovery (94–99%) was obtained. However, an overlap occurred between the organophosphate, pyrethroid and insect growth regulators. Deutsche Forschungsgemeinschaft (DFG) recommended the GPC as a clean-up procedure in the Manual of Pesticide Residue Analysis [71]. Around 95–150 ml of cyclohexane–diethyl ether is needed to quantitatively elute the pyrethroids from the GPC column. In conclusion, the GPC offers a number of advantages over other clean-up procedures. It can be automated and has good clean-up efficiency and excellent recovery. It is regarded as suitable for the determination of residues with specific GLC detector. Now, the automatic clean-up system for the determination of pesticide multi-residue analysis in the world are mainly based on the GPC method [72].

The extraction and clean-up methods of pyrethrins and pyrethroids in crops, foods and environmental matrices are listed in Table 1.

## 3. Chromatographic methods

Almost all of the analytical methods for pyrethrins and pyrethroid residues are based on chromatographic techniques, mainly GC and some HPLC and TLC. The active ingredients of pyrethrum are composed of pyrethrin I, pyrethrin II, cinerin I, cinerin II, jasmolin I and jasmolin II. Pyrethrin I and II are highly insecticidal, and cinerin I, II, and jasmolin I, II are much less bioactive. In the determination of pyrethrin residue, it usually determines the total residues of the above 6 components. However, the pyrethrin I and II are concerned from the viewpoint of bioactivity. While in case of pyrethroids, it is usually the parent pyrethroid compounds that are determined. It was proved by toxicological experiments that the

Table 1
Extration and clean-up methods of pyrethrins and pyrethroids in crops, foods and environmental matrices

| Compound/substrate | Extraction solvent | Partition solvent | Column clean-up | References |
|---|---|---|---|---|
| Biphenthrin (pumpkin) | Acetone | Hexane | Florisil | [31] |
| Biphenthrin (peach, tomato) | Acetone | Hexane | Florisil | [90] |
| Cyhalothrin (apple) | Acetone | Hexane | Florisil | [33] |
| Cyhalothrin (bovine liver, muscle, kidney), | Acetone–hexane (1:4) (into DMF) | DMF back into hexane | Florisil | [180] |
| (milk) | Diethyl ether–hexane (into DMF) | DMF back into hexane | Florisil | [180] |
| Cyhalothrin, fenvalerate, flucythrinate (cotton leaf) | Isopropanol–hexane (1:3) or hexane | Hexane | Florisil | [181] |
| λ-Cyhalothrin (water) | Solid-phase extraction | – | – | [35] |
| Cypermethrin (egg, animal tissue) | Hexane–acetone (1:1) | Hexane | Florisil | [112] |
| Cypermethrin (insect) | Acetone, acetonitrile, hexane–acetone | Hexane | Florisil or alumina | [9,38] |
| Cypermethrin (cattle tissue) | | Hexane | Florisil | [182] |
| Cypermethrin (wheat, soil) | Acetonitrile–$H_2O$ (7:3) | Chloroform | – | [144] |
| Cypermethrin (water) | Solid-phase extraction | – | – | [35] |
| Cypermethrin (fruit, vegetable, tobacco, tea, straw, meat, egg) | Acetone–hexane (1:1) | – | Florisil | [34] |
| (milk) | Acetone–hexane (1:1) | Hexane | Florisil | [34] |
| (soil) | Shaking with hexane | – | Florisil | [34] |
| (water) | Shaking with hexane | – | – | [34] |
| Cypermethrin, permethrin (fruit, vegetable) | Light-petroleum–acetone | Dichloromethane | Florisil | [168] |
| Cypermethrin, alphamethrin (crops, fruits) | Acetonitrile–$H_2O$–hexane (1:1:4) | CN phase "Bond-Elut" cartridge | – | [73] |
| Cypermethrin, fenvalerate, deltamethrin (chicken) | Hexane (fat, skin) Acetonitrile (brain) Hexane–acetone (1:2) (blood) | Acetonitrile | Silica gel | [62] |
| Cypermethrin, fenvalerare, fenpropathrin, permethrin (crops) | Acetone | Hexane | Florisil, silica gel or alumina | [183] |
| Cypermethrin, fenvalerate (soil, vegetable) | Diethyl ether | Hexane | Florisil or Nuchar charcoal-$CF_1$ cellulose (2:5) | [14] |
| Cypermethrin, fenvalerate, permethrin (egg, celery, milk, beef) | Acetonitrile–$H_2O$ (7:13) | Hexane | Florisil | [14] |

Table 1 (*continued*)

| Compound/substrate | Extraction solvent | Partition solvent | Column clean-up | References |
|---|---|---|---|---|
| Cypermethrin, fenvalerate, permethrin (celery, lettuce) | Benzene–hexane (1:1) (Permethrin)<br>Diethyl ether–hexane (3:7) (cyp. and fen.) | Hexane | Florisil | [184] |
| Cypermethrin, Fenvalerate, fenpropathrin, permethrin (cotton, tomato, celery, onion) | Acetone | Hexane | Florisil or Alumina | [185] |
| Deltamethrin (orange) | Acetonitrile | Hexane or light petroleum | Florisil | [186] |
| Deltamethrin | | | | |
| (crops) | Hexane | – | Florisil | [75] |
| (soil) | Acetone | Hexane | Florisil | [75] |
| Deltamethrin (milk, animal tissue) | Water–acetone (3:10) | Residue dissolved in benzene–hexane (1:1) | Florisil | [188] |
| Deltamethrin | | | | |
| (crops) | Diethyl ether–light petroleum (1:1) | Residue dissolved in acetonitrile, evaporated dissolved into light petroleum–diethyl ether (1:1) | Florisil | [36] |
| (soil) | Acetone–hexane (1:1) | Hexane | Alumina | [36] |
| (milk) | Hexane | Residue dissolved in acetonitrile, evaporated, dissolved into benzene–hexane (1:1) | Florisil-25% cellulose–charcol | [36] |
| Deltamethrin (alfalfa) | Acetone–hexane (3:7) | Hexane | Alumina | [189] |
| Fenpropathrin (tea, vegetables, fruits) | Water–acetone (1:8) or methanol | Dichloromethane or hexane, acetonitrile | Silica or Florisil | [190] |
| Fenpropathrin, fluvalinate, flucythrinate, λ-cyhalothrin (vegetables) | Acetone | Hexane | – | [191] |
| Fenvalerate (tomato) | Hexane–isopropanol (3:1) | Hexane | Florisil, Sep-Pak cartridge | [43] |
| Fenvalerate (water) | $C_{18}$ cartridge extraction | – | Alumina | [95] |
| Fenvalerate | | | | |
| (crops) | Acetone | Petroleum ether | Florisil | [194] |
| (cotton seed) | Chloroform and propylene carbonate | Petroleum ether | Florisil | [194] |
| Fenvalerate (cabbage) | Acetone–hexane (1:1) | Hexane | Florisil | [192] |
| Fenvalerate | | | | |
| (oily plants, animal tissue) | Hexane–isopropanol (3:1) | Hexane | Florisil | [44] |
| (low oily plants) | Hexane | – | Florisil | [44] |
| (soil) | Acetone–hexane (1:1) | Hexane | Florisil | [44] |
| Fenvalerate, permethrin, deltamethrin (fruits, vegetables) | Acetone | Dichloromethane | Fluck charcoal–MgO–diatomaceous earth and alumina | [10] |

(*Continued on p. 374*)

Table 1 (*continued*)

| Compound/substrate | Extraction solvent | Partition solvent | Column clean-up | References |
|---|---|---|---|---|
| Flucythrinate (vegetables, fruits, hop) | Dichloromethane or light petroleum | Residue dissolved into hexane | Florisil | [193] |
| Flumethrin (honey) | $C_{18}$ column solid extraction | – | Silica cartridge | [22] |
| Fluvalinate (apple) | Methanol | Into isoctane ($BF_3$/methanol derivatation) | Florisil | [163] |
| Fluvalinate (fruits, vegetables) | Hexane–acetone (1:1) | Pentane | Florisil or GPC | [80] |
| (soil) | Hexane–acetone (1:1) | Hexane | Florisil or GPC | [80] |
| (cotton seed) | Hexane–ethanol (97:3) | Heptane | GPC | [80] |
| (water) | Pentane or pentane–diethyl ether (10:1) | Pentane | Florisil | [80] |
| Permethrin, deltamethrin (lettuce, alfalfa) | Light petroleum–acetone (1:1) | Light petroleum | – | [195] |
| Permethrin, cypermethrin, deltamethrin (crops, fish, egg) | Water–acetonitrile | – | $C_8$ reversed phase and Silica gel–alumina | [103] |
| Permethrin (plants) | Dichlomethane–$H_2O$ | – | Alumina | [59] |
| Permethrin (plants) | Acetone–hexane (1:1) | Hexane | Florisil or Alumina | [9] |
| Permethrin (water) | Diethyl ether–hexane (5:95) | Hexane | – | [165] |
| Permethrin (water) | Hexane | – | Florisil | [50] |
| (sediment) | Hexane–acetone (4:1) | Acetone removed by water | Florisil | [50] |
| (fish) | Hexane–acetone (3:2) | Acetone removed by water | Silica gel | [50] |
| Permethrin (potato) | Acetone–hexane (3:1) | Diethyl ether | Alumina–florisil (1:1) silica gel, Cellulose–Nuchar charcoal (5:2) | [196] |
| Permethrin (wheat, grain) | Acetone | Hexane | Florisil, Sep-Pak | [158] |
| Permethrin (fruits, vegetables, animal tissue) | Acetone–hexane (1:4) | Acetone removed by water | Florisil | [49] |
| (oily plants) | Acetone–hexane (1:1) (into DMF) | DMF back into hexane | Florisil | [49] |
| (milk egg) | Acetone–hexane(1:1) (into DMF) | DMF back into hexane | Florisil | [49] |
| (soil) | Acetone–hexane (1:4) | Hexane | Florisil | [49] |
| (water) | Hexane | – | Florisil | [49] |
| Permethrin (cotton) | Methanol–benzene | – | Florisil | [51] |
| Piperonyl butoxide (fruits, vegetables) | Acetone | Dichloromethane | Florisil or silica gel | [72] |
| Piperonyl butoxide) (egg, animal tissue) | Ethanol–diethyl ether–hexane | (Saponified with alcoholic KOH) | GPC | [197] |
| Pyrethrin (fruits, vegetables) | Acetone | Dichloromethane | Florisil or silica gel | [72] |
| Pyrethrin (milk, milk products) | Light petroleum | Acetonitrile | Florisil or silica gel | [197] |
| Pyrethrin (vegetable, fruits) | Acetone | Diethyl ether | Florisil or silica gel | [198] |
| (rice) | Acetonitrile | Diethyl ether | Florisil or silica gel | [198] |

metabolites of pyrethroids are relatively non-toxic or of low toxicity. They are largely converted by hydrolytic or oxidative reactions to polar metabolites which are then eliminated in the faeces and/or urine, unchanged or as conjugates, before the sensitive sites can be reached [80]. For this reason, the different methods developed for pyrethroid residues analysis has dealt primarily with the analysis of parent compound and considered to be satisfactory for monitoring exposure to pyrethroids.

### *3.1. Gas chromatographic methods*

GC is still the method of first choice for the analysis of pyrethrin and pyrethroid residues. Although there is a lack of pyrethroid specific detection systems, many pyrethroid pesticides (biphenthrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, fenvalerate, flucythrinate, fluvalinate, permethrin) possess one or several halogen atom (s) in the molecule of compound, which are sensitive to electron-capture detection (ECD). Some derivatization methods have been developed to create a sensitive group in the molecule of those pyrethroid pesticides which have not a halogen atom (allethrin, resmethrin, phenothrin, tetramethrin) [42,74] or to improve the sensitivity and the peak tailing situation in some halogenated pyrethroids [41,45,62,75–79]. Generally, a detection method should have one to two orders of magnitude of sensitivity higher than the established maximum residue limit (MRL) of compounds of interest. Due to the relatively low chronic toxicity, the MRL of most pyrethroids are generally established at several ppm level, around one order of magnitude higher than that of organophophate and carbamate pesticides. Nowadays, the minimum detection level in the determination of pyrethroid residues is around in 0.01–0.05 ppm level, two orders of magnitude higher.

With regard to detection in GC, ECD is most frequently selected in the pyrethroid residue analysis. It is most suitable for the determination of residue of those pyrethroids which possess the chloro group (biphenthrin, cyfluthrin, cypermethrin, fenvalerate, permethrin) or fluoro group (cyhalothrin, flucythrinate), bromo group (deltamethrin, tralomethrin) or chloro and fluoro groups (fluvalinate). These pyrethroids show a high response to ECD, the minimum detection limit is ranged in nanogram to picogram level.

Flame ionization detection (FID) can be used in the determination of non-halogen containing pyrethroids (allethrin, fenpropathrin, phenothrin, resmethrin, terallethrin, tetramethrin). However, the detection limit is only in microgram to several tens of nanogram level. This sensitivity is not enough in residue analysis. For the analysis of non-halogen containing pyrethroids by ECD, the formation of halogenated derivatives prior to the GC–ECD determination is needed to improve the sensitivity to ECD [42,62,74,81]. The detection limit can be improved to nanogram to picogram level.

A few papers reported the use of nitrogen–phosphorus detection (NPD) to determine the residue of fenvalerate in plants [82], in soil [91] as well as the cypermethrin and fevalerate residue in environmental samples [84].

A selective detection method —Hall electrolytic conductive detection (halogen mode) (HECD) was reported to determine the halogenated pyrethroid residues in vegetables [85]. Results showed that the response degree of pyrethroids to this detector was not related with the number of halogen molecule in the compound. Those pyrethroids, such as cyfluthrin (F,2 Cl), cypermethrin (2 Cl), fenvalerate (Cl), permethrin (2 Cl), showed higher response, but other pyrethroids which showed low response also have more halogen groups, such as cycloprothrin (2 Cl), cyhalothrin (Cl, 3 F), flucythrinate (2 F), fluvalinate (Cl, 3 F) tralomethrin (4 Br). The mechanism of response needs to be further clarified.

A new detection method for GC called microwave-induced plasma atomic emission detection (MIP-AED) was developed by Hewlett–Packard and was used in the pesticide residue analysis in fruits and vegetables [86]. The GC–AED is one type of spectrochemical method, however, the incorporation of a microwave-induced plasma (MID) generator and a photodiode array is a creative approach and has demonstrated its accuracy, reproducibility and simplicity. The response of the GC–MID-AED as a function of percent of Cl atoms in the compounds is clearly linear. The recovery of 0.27–0.55 ppm tested pyrethroids (*cis*-cypermethrin, *trans*-cypermethrin, *cis*-permethrin, *trans*-permethrin) fortified to 10 vegetables and fruits ranged from 80.8 to 120.4%,

averaged at 93.2% in permethrin and 100.7% in cypermethrin. It is also powerful for qualitative confirmation in pesticide residue analysis [86].

The selection of stationary phases is vital factor for the satisfactory analysis of pyrethroid residue. In general, the rule of "like dissolves like" is beneficial in the selection of stationary phases. Various column packing materials used for the GLC analysis of pyrethroid residues were reviewed by Papadopoulou-Mourkidou [5]. Most commonly used stationary phases in the analysis of non-polar pyrethroids are OV-1, OV-101, SE-30, SP 2100, DC 200 etc. Sometimes, for the purpose of separating the more polar metabolites from the non-polar parent compounds, the mixed stationary phases including non-polar and moderately stationary phase are selected, such as OV 210+OV 17, DEGS+SE 30, SP 2401+SP 2250 etc. The column materials as well as the GLC parameters for the analysis of pyrethroid residues are summarized in Table 2.

As a rule, the conventional packed column is mainly used in the determination of individual pyrethroid residues. For the purpose of improving the resolving ability, a GC system equipped with longer packing column or capillary column has been applied popularly. Due to several chiral centers in the molecule of pyrethroids, different amounts of stereoisomers exist. The determination of the ratio of different stereoisomers is important because the different biological activity is performed in various stereoisomer of same pyrethroid [1]. The separation of stereoisomers can be realized by the selection of appropriate stationary phases: biphenthrin [31,32], S-bioallethrin [87,88,115], cyhalothrin [35,89,90,181], cypermethrin [14,35,38–40,73,91], deltamethrin [37,41], fenpropathrin [92], fenvalerate [44,46,77,93,94,96], flumethrin [22], fluvalinate [80,98–100], permethrin [19,36,53,101–104,210] and pyrethrins [100,105–108,115,198]. However, the resolution of enantiomers of pyrethroids are generally not satisfactory by the GC method. It can be realized by HPLC, especially with the application of chiral column. This will be discussed in a separate section of this paper.

### 3.2. HPLC methods

Twenty-five years have elapsed since the first paper on the application of HPLC to pesticide residue analysis was published [109]. Since then, HPLC has had accelerated application in this field. In comparison with GC analysis, the relatively low sensitivity of the conventional HPLC detection systems makes the minimum detection limit in the pesticide residue analysis only at the nanogram level. However, the development in the HPLC in recent years including the introduction of high-performance columns and the improvement of new detectors and detection techniques have broadened the application of HPLC in the pesticide residue analysis. Besides, HPLC allows the quantisation of non-volatile and heat-labile compounds without need of derivatization and does not require a perfect clean-up procedure as in the case of GC–ECD systems. Another advantage of HPLC over GC is that HPLC not only has satisfactory resolution on the diastereomer of pyrethroids, but also on the enantiomers. The advance of HPLC in the residue analysis has been reviewed in some publications [110,111]. Some review papers on pyrethroids analysis including the HPLC application were published in recent years [3–5]. HPLC was applied to the determination of residues of cypermethrin in animal tissue and eggs [111,112], fenvalerate in vegetables and fruits [113], milk [114], fluvalinate in honey [27], pyrethrins and pipenoyl butoxide in human blood [116], tralomethrin and deltamethrin residue in environmental matrices [117] as well as the multi-residue determination in grain [126,127] as well as in fruits and vegetables [8].

The column of HPLC was long and narrow, such as 50 cm×2 mm I.D., in the early stages. As time passed, the dimensions of the HPLC column changed with the introduction of microparticulate packing materials together with special packing techniques. For an internal diameter (I.D.) of 4 mm, the column length shrunk to 20 cm or less. And the particle size of the packing materials was reduced to 5 μm or less, which resulted in higher back pressure and greater efficiency.

The reversed-phase column was used popularly in recent ten years due to the wider separation ability and lower solvent cost [118]. Nonpolar components, such as pyrethrins and pyrethroids, are strongly retained on the RP columns, while very polar samples are only slightly retained. In normal phase, bonded or other, the mobile phase is hydrophilic and the least polar sample components will elute first [118]. RP-HPLC was applied to determine the

Table 2
GLC analysis of pyrethrin and pyrethroid residues in crops, foods and environmental matrices

| Compounds/substrates | Detection | GLC conditions[a] | Retention time (min) | Reference |
|---|---|---|---|---|
| Allethrin (mosquito coil) | FID | P2, 2.1 m×3 mm I.D., 0.28% OV17+3% OV210 /Chromosorb W HP 80/100, *Tc*: 190°C, *Td*: 250°C | | [87] |
| Biphenthrin (pumpkin) | ECD | C, 30 m×0.25 mm I.D., DB 1, *Tc*: 60°C-(15 °C/min), *Ti*: 250°C, *Td*: 300°C; C, 25 m×0.32 mm I.D., OV1701, *Tc*: 6°C(1 min)–(40°C/min)–280°C | | [200] |
| Cyhalothrin(apple) | ECD | C, 15 m×0.37 mm I.D., DB 1 (1.5 μm), *Ti*: 190°C, *Tc*: 220°C, *Td*: 270°C | 10 | [61] |
| Cypermethrin, fenvalerate (soil, vegetables) | ECD | C, 25 m×0.3 mm I.D., Hp cross-linked methyl silicone (0.33 μm), *Ti*: 220°C, *Td*: 385°C, *Tc*: 90°C(1 min)–150°C–(20°C/min)–250°C(10 min) | Cyp.: 2.09, 2.11, 2.12, 2.13 Fenv.: 2.28, 2.33 | [14] |
| Cypermethrin, fenvalerate (celery, egg, milk, beef | ECD | C, 25 m×0.3 mm I.D., SE 54 (0.5 μm) or Cpsil 8, *Tc*: 40°C(2 min)–(20°C/min)–180°C–(1°C/min)–250°C | | [14] |
| Cypermethrin (insect) | ECD | P, 0.5 m×3 mm I.D., 5% Ov101/GCQ, *Ti*: 270°C, *Td*: 300°C, *Tc*: 240°C | | [9] |
| Cypermethrin, fenvalerate, permethrin (celery, lettuce) | ECD | P, 1.8 m×0.2 mm I.D., 1.5% OV101 or 2% OV 210/GCQ 100/120 mesh, *Tc*: 210°C (Per.), 220°C(Cyp.), 230°C(Fenv.) | | [184] |
| Cypermethrin cattle tissue) | ECD | P, 8 m×4 mm I.D., 15% $QF_1$+10% DC200/GCQ 80/100 mesh, *Tc*: 235°C | | [182] |
| Cypermethrin (soil, wheat) | ECD | P, 0.8 m×3 mm I.D., 2% OV101/GCQ 100/120 mesh, *Tc*: 210°C | 4.3 | [144] |
| Cypermethrin, permethrin (fruits, vegetables) | ECD | C, 30 m×0.25 mm I.D., DB 1 (1 μm), *Tc*: 50°C (1 min)–(15°C/min)–280°C | | [168] |
| Cypermethrin, permethrin, cyfluthrin, | ECD, | C, 30 m×0.25 mm I.D., DB 1 (0.25 μm), *Ti*: 250°C, *Td*: 270°C, *Tc*: 269°C(2°C/min)–(10°C/min)–180°C–(4°C/min)–240°C 25 min) | | [91] |
| Cypermethrin, fluvalinate, deltamethrin (soil, water, plant) | NPD | C, 15 m×0.53 mm I.D., SPB608 (0.5 μm), *Ti*: 220°C, *Td*: 220°C, *Tc*: 150°C(2 min)–(10°C/min)–220°C(10 min) | | |
| Cypermethrin (water) | ECD | C, 50 m×0.32 mm I.D., OV101, *Ti*: 70°C–250°C(150°C/min), *Tc*: 89°C–(10°C/min)–240°C(45 min)–(15°C/min)–260°C | | [35] |
| Cypermethrin (plant) | ECD | P, 1.4 m×3 mm I.D., 3% SP2100/GCQ 80/100 mesh, *Ti*: 240°C, *Td*: 275°C, *Tc*: 240°C | | [201] |
| Cypermethrin, alphamethrin (crops, fruits, soil) | ECD | P, 2.7 m×4 mm I.D., 2% OV225/GCQ 100/120 mesh, *Tc*: 245°C; C, 25 m×0.32 mm I.D., SE54 (0.5 μm), *Tc*: 40°C(2 min)–(20°C/min)–180°C–(1°C/min)–250°C | 16 | [73] |
| Cypermethrin (cattle) | ECD | C, 20 m×0.46 mm I.D., Hypersil (5 μm) | | [111] |
| Deltamethrin (milk, butter) | ECD | P, 0.4 m×4 mm I.D., 3% SE30/Chromosorb W AW DMCS 100/120 mesh, *Ti*: 250°C, *Td*: 300°C, *Tc*: 250°C; C, 25 m×0.3 mm I.D., SE30 (0.25 μm), *Ti*: 250, *Td*: 300°C, *Tc*: 90°C–(15°C/min)–280°C | | [37] |
| Deltamethrin (bean) | ECD | P, 2.5 m×0.25 mm I.D.. 3% SE30 / Chromosorb W HP, *Td*: 340°C, *Tc*: 200°C | | [202] |
| Deltamethrin (rape seed, pollen) | ECD | P, 0.1 m×2.3 mm I.D., 2.5% DEGS/Varaport 30 100/120 mesh, *Tc*: 185°C | | [203] |
| Deltamethrin (rice) | ECD | P, 1.5 m×6.3 mm I.D., 2% OV101/Chromosorb W DMCS 60/80 mesh, *Tc*: 270°C | | [63] |

(*Continued on p. 378*)

Table 2 (*continued*)

| Compounds/substrates | Detection | GLC conditions[a] | Retention | Reference |
|---|---|---|---|---|
| Deltamethrin (oily plants, soil) | ECD | P, 1 m×2 mm I.D. 5% OV101/Chromosorb W HP 100/120 mesh, *Ti*: 250°C, *Td*: 300°C, *Tc*: 245°C | 3.0 | [36] |
| Fenpropathrin (vegetables, bean) | ECD | P, 0.5 m×2 mm I.D., 5% PEG 20 m/GCQ 80/100 mesh, *Ti*: 140°C, *Tc*: 110°C | | [137] |
| Fenpropathrin (tomato, vegetaable) | ECD | C, 12 m×0.2 mm I.D., HP 1 (0.33 μm), *Ti*: 260°C, *Tc*: 60°C–(18°C/min)–250°C | | [167] |
| Fenpropathrin fruits, vegetables, tea) | ECD | P, 1.1 m×3 mm I.D., 5% SE 30/Chromosorb W AW-DMCS 60/80 mesh, *Ti*: 300°C, *Td*: 300°C, *Tc*: 230°C | 2,8 | [190] |
| Fenvalerate (plants, soil) | ECD | P, 1.22 m×2 mm I.D., 3% Dexsil 300/Supelcoport 100/120 mesh, *Ti*: 280°C, *Td*: 300°C, *Tc*: 280°C; C, 25 m×0.37 mm I.D., SE30, *Ti*: 280°C, *Td*: 320°C, *Tc*: 255°C | | [44] |
| Fenvalerate, permethrin, Cypermethrin, Deltamethrin (fruits, vegetables) | ECD | P, 0.5 m×1.75 mm I.D., 3% SE30/GCQ 100/120 mesh; P, 0.9 m×2 mm I.D., 1.5% SP2250 1.95% SP2201/Supelcoport 100/120 mesh | | [10] |
| Fenvarelate, cypermethrin, deltamethrin (water) | ECD | C, 30 m×0.53 mm I.D., SupelcoCPB20 (0.5 μm), *Tc*: 150°C(1 min)–(4°C/min)–220°C (25 min) | Cyp: 41.3, 41.8 Fenv:45.2, 46.3,47.9, 52.3 Delt.: 49.3 | [97] |
| Fenvalerate (cabbage) | ECD | P, 3% OV1+3% Apiezon L/GCQ 80/100 mesh, *Ti*: 230°C, *Td*: 235°C, *Tc*: 225°C | 4.1 | [192] |
| Fenvalerate (vegetables) | ECD | C, 15 m×0.53 mm I.D., RSC150 (1.2 μm). *Tc*: 225°C | | [204] |
| Fenvalerate, flucythrinate (water, sediment) | ECD | P, 1.82 m×2 mm I.D., 3% OV1/Supelcoport 80/100 mesh, *Tc*: 250°C | | [205] |
| Fenvalerate, permethrin (bean, soil) | ECD | P, 1 m×4 mm I.D., 1% SE30/GCQ 100/120 mesh, *Td*: 350°C, *Tc*: 210°C | | [206] |
| Fenvalerate (water, sediment) | ECD | C, 25 m×0.53 mm I.D., H5, *Ti*: 240°C, *Td*: 320°C, *Tc*: 90°C(1 min)–(7°C/min)–285°C (15 min) | | [94] |
| Fenvalerate (tomato) | ECD | P, 0.61 m×3.2 mm I.D., 5% OV101/GCQ 80/100 mesh, *Ti*: 225°C, *Td*: 290°C, *Tc*: 225°C; P, 0.5 m×4 mm I.D., 3% SP2100/Supelcoport 100/120 mesh, *Ti*: 250°C, *Td*: 350°C, *Tc*: 240°C | | [43] |
| Fenvalerate (fruits, vegetables) | NPD | C, 15 m×0.53 mm I.D., DB 17 (!μm), *Td*: 280°C; C, 30 m×0.53 mm. I.D., SPB 5 (2.5 μm), *Tc*: 140°C–170°C–(10°C/min)–260°C | | [207] |
| Fenvarelate (water) | ECD | C, 30 m×0.53 mm I.D., DB1707, *Ti*: 180°C, *Td*: 325°C, *Tc*: 120–(10°C/min)–240°C(50 min) | | [77] |
| Fluvalinate, fenvalerate, permethrin, cypermethrin, tralomethrin (vegetables, fruits) | ECD | C, 25 m×0.2 mm I.D., CBP-1 (0.25 μm), *Ti*: 270°C, *Td*: 270°C, *Tc*: 60°C–(32°C/min)–250°C | | [208] |
| Fluvalinate (fruits, vegetables, soil) | ECD | C, 10 m×0.25 mm I.D., DB-1 (0.1 μm), *Ti*: 240°C, *Td*: 270°C, *Tc*: 210°C | | [209] |

Table 2 (*continued*)

| Compounds/substrates | Detection | GLC conditions[a] | Retention | Reference |
|---|---|---|---|---|
| Permethrin (grain, water, sediment, fish) | ECD | P, 1.2 m×3 mm I.D. 6% $QF_1$+3% DC200/ Chromosorb W HP 80/100 mesh, *Ti*: 260°C, *Td*: 310°C, *Tc*: 210°C | | [211] |
| Permethrin (air, water) | ECD | C, 30 m×0.53 mm I.D. DB-5 (0.25 μm) or 15 m×0.53 mm I.D., OV 17 (1.5 μm), *Ti*: 235°C, *Td*: 350°C, *Tc*: 60°C(2 min)–(25°C/min)–40°C–(4°C/min)–270°C | | [165] |
| Permethrin (water, sediment, fish) | ECD | P, 1×4 mm I.D., 3% OV1 or 5% OV1/GCQ 100/120 mesh | | [50] |
| Permethrin, deltaamethrin (alfalfa, lettuce) | ECD | P, 1 m×3 mm I.D., 3% OV210/GCQ, *Ti*: 220°C, *Td*: 250°C, *Tc*: 200°C | *cis*-Perm.: 4.9 *trans*-Perm. 5.9 Delt.: 4.8 | [195] |
| Permethrin, cypermethrin, deltamethrin (fish, egg) | ECD | C, 50 m×0.32 mm I.D., OV1/SE30 (0.25 μm), *Ti*: 265°C, *Td*: 300°C, *Tc*: 89°C(1 min)–(10°C/min)–245°C(22 min)–(10°C/min)–265°C | | [103] |
| Permethrin (plant) | ECD | P, 1.22 m×4.8 mm I.D., 3% $QF_1$ /GCQ 100/120 mesh, *Ti*: 250°C, *Td*: 300°C, *Tc*: 210°C | | [59] |
| Permethrin (animal tissue) | ECD | C, 12 m×0.2 mm I.D., OV101, *Ti*: 250°C, *Td*: 300°C, *Tc*: 220°C | *cis*-Perm.: 8.8, *trans*-Perm.9.2 | [226] |
| Permethrin (soil, water, animal tissue, milk) | ECD | P, 1.2 m×4 mm I.D., 5% OV210 or 2% SP2370/GCQ 100/120 mesh, *Ti*: 230°C, *Td*: 300°C, *Tc*: 220°C(SP2370), 230°C (OV210) | *cis*-Perm.: 4.4, *trans*-Perm. 5.2 | [49] |
| Permethrin (cotton leaf) | ECD | P,1.8 m×2 mm I.D., 5% SP2100 or SP2401/Supelcoport, *Td*: 350°C, *Tc*: 210°C | | [51] |
| Piperonyl butoxide | ECD | (Brominated to yield 4,5,7-tribromo-0-propyl-1,3-benzodioxol). P, 2 m×2 mm I.D., 2% OV210+1% ov17/GCQ 100/120 mesh, *Ti*: 250°C, *Td*: 300°C, *Tc*: 220°C | 4,5,7-tribromo-6-propyl-1,3-benzodiioxal 8.12 | [72] |
| Pyrethrin (fruits, vegetables) | ECD | C, 15 m×0.32 mm I.D., OV1 (0.1–0.15 μm)-*Ti*: 60°C, *Td*: 290°C, *Tc*: 60°C–(60°C/min)–180°C–(3°C/min)–240°C(20 min) | Cine5.41 Jasm.1: 6.13 Pyr.I: 6.26 Cin.II: 10.4 Jasm.II: 11.3 Pyr.II: 11.52 | [72] |
| Pyrethrin (potato) | ECD | C, 25 m×0.2 mm I.D., Shimadzu HiCap CBP-1, *Ti*: 270°C, *Tc*: 60°C(2 min)–(32°C/min)–250°C | | [105] |
| Pyrethrin (fruits, vegetables, rice) | ECD | C, DB-210, *Ti*: 240°C, *Td*: 280°C, *Tc*: 60°C(2 min)–(8°C/min)–280°C | Cine. I: 25.19 Jasm.I: 26.53 Pyr.I: 26.82 Cin.II: 30.08 Jasm.II: | [54] |

(*Continued on p. 380*)

Table 2 (*continued*)

| Compounds/substrates | Detection | GLC conditions[a] | Retention | Reference |
|---|---|---|---|---|
| | | | 31.05<br>Pyr.II:<br>33.81 | |
| Pyrethrin<br>(water) | ECD | C, 25 m×0.2 mm I.D., CBP-1 (0.25 μm), *T*i: 270°C *T*d: 270°C, *T*c: 50°C (2 min)–(4°C/min)–260°C(10 min) | | [208] |
| Pyrethrin<br>(aerosol, shampoo) | ECD | C, 15 m×0.32 mm I.D., Durabond DB-1 (0.25 μm), *T*i: 270°C, *T*d: 320°C, *T*c: 190°C | Cin.I: 2.20<br>Jasm.I: 2.4<br>Pyr.I: 3.10<br>Cin.II: 7.10<br>Jasm.II:<br>9.05<br>Pyr.II: 10.2<br>PB.: 4.20 | [212] |

[a] P: Packing column; C: Fused-silica capillary column; *T*c: Column temperature; *T*d: Detector temperature; *T*i: Inlet temperature.

residues of pyrethrins and pipenoyl butoxide in pharmaceutical preparation [119], milk [120], water [121], human blood [122] and grain [123] samples, fluvalinate and permethrin residues in tobacco [124], permethrin in air [125] and multi-residue determination in grains [126].

Ultraviolet (UV) detection is the most popular detection method in the analysis of pesticide residues. It is usually operated in the range of 200–350 nm. The fluorescence detection showed a higher sensitivity than absorption detection. More convenient fluorimetric detectors are equipped with monochromators to select various emission and excitation wavelengths [118]. A fluorimetric HPLC detection on Hitachi Gel 3010 column (290 nm excitation and 340 nm emission wavelength) was reported in the determination of pipenoyl butoxide in grains, rice and beans [123].

Mass spectrometric (MS) detection is of importance in pesticide residue analysis due to its high sensitivity. It can be used for absolute identification of an unknown compound, not by its retention time, but on the basis of molecular mass, empirical formula and fragmentation pattern [118].

The application of radioactivity detection depends on a suitable radioactive isotope labelling. It possesses a great potential in HPLC analysis of pesticide residue and in particular in the studies of pesticide metabolism. A research on the residue analysis of deltamethrin, tralomethrin and related metabolites in water, sediments and fish tissues at ppb and ppt level by HPLC–radioactivity detection was reported [117].

The HPLC parameters in the determination of pyrethrin and pyrethroid residues in various matrices are summarized in Table 3.

### 3.3. TLC methods

For the determination of residues of pyrethrins and pyrethroids in various biological and environmental matrices, TLC is less widely used compared to GC and HPLC in recent years. This is mainly attributed to the low detection limit of TLC methods. The development of modern, instrumentalized HPTLC makes the TLC application more promising [128]. The technique for the automated multiple development (AMD) of TLC has been developed for the pesticide residue analysis. It makes the HPTLC silica gel plates developed automatically in many (for example 20–30) individual steps, thereby permitting the mobile phase to advance somewhat further in each succeeding cycle. Solvent mixtures of different composition can be used for each cycle, so that a reproducible gradient elution is obtained. The final determination is usually based on measuring the UV absorbance in a TLC scanner, using up to six different wavelengths. Applying the AMD technique results in much better separation than would be obtained with conventional TLC. Therefore, several pesticides can be simultaneously determined in the same extract. A high throughput can also be achieved because up to 18 spots can be applied onto a single TLC plate [148]. So, TLC has retained its status as a valid and simple method for the quali-

Table 3
HPLC analysis of pyrethrin and pyrethroid residues in crops foods and environmental matrices

| Compounds/substrate | Detector | HPLC conditions | Retention times (min) | References |
|---|---|---|---|---|
| Bioresmethrin (wheat) | UV (225 nm) | 100×4.6 mm I.D., 10 μm Spherisorb S, propanol–hexane (3:997) at 1 ml/min | | [222] |
| Cypermethrin (egg, animal tissue | UV (212 nm) | 200×4.6 mm I.D., 5 μm Hypersil. Hexane–30% water-saturated dichloromethane (85:15) at 15 ml/min | | [112] |
| Cypermethrin (cattle) | UV (212 (nm) | 200×10 mm, I.D., 10 μm LiChrosorb Si60, Hexane–30% water-saturated dichloromethane (8:2) at 5 ml/min | | [111] |
| Cypermethrin (soil) | UV (212 nm) | 200×4.5 mm I.D., 5 μm Partisil-5, light petroleum (+0.1% acetic acid): dioxane or ethanol (99:1) or (95:5) at 1.6 ml/min | | [213] |
| Cypermethrin (Cotton leaves, lettuce) | UV | 200×4.5 mm I.D., 5 μm Hypersil ODS, Acetonitrile–$H_2O$ (25:75) | | [214] |
| Deltamethrin (formulation) | UV (230 nm) | 150×4.7 mm, I.D., 5 μm LiChrosorb RP-8 hexane–dipropyl ether (93:7) at 1.17 ml/mim or 100×4.7 mm I.D., 10 μm LiChrosorb Si-60, acetonitrile–1% $H_2SO_4$(70:30) at 1.33 ml/min | | [215] |
| Fenvalerate (crops) | UV | 300×3.9 mm I.D., 10 μm μPorasil, 2.5% ethyl acetate in hexane | | [216] |
| Fluvalinate (honey) | UV | 150×4.6 mm I.D., Novapak$C_{18}$-RP-HPLC, acetonitrile–water (8:2) at 1.5 ml/min | | [217] |
| Permethrin, fenvarelate, deltamethrin, phenothrin, (wheat) | UV (235 nm) | 300×3.9 mm I.D., μBondapak $C_{18}$, methanol–water (4:1) at 2.5 ml/min | 5–15 | [218] |
| Permethrin, fenvarelate, deltamethrin, Bioresmethrin, piperonyl butoxide (grain) | UV (206 nm) | 250×4.6 mm I.D., 5 μm Spherisorb ODS, methanol–water (4:1) and 2,2,4-trimethylpentane–propan-2-ol (9:1) at 1 ml/min | | [127] |
| Permethrin (cotton) | UV (254 280 nm) | 150×4.6 mm I.D., Whatman Partisil ODS, methanol–water (65:35) at 1 ml/min | 20 | [219] |
| Permethrin (lettuce) | UV (254 nm), Infrared | 250×4.6 mm, I.D., 5 μm Partisil, 1-tetradecane–dichloromethane–cyclohexane (3:7:0.27) at 0.9 ml/min | 10 | [220] |
| Permethrin, phenothrin, deltamethrin, bioresmethrin, fenvalerate, | UV (225 nm) | 150×3.9 mm I.D., NovaPak $C_{18}$, 75% aqueous acetonitrile at 1 ml/min | PB: 5.5<br>Delt.: 11.5<br>Bior.: 11.5 | [126] |

(Continued on p. 382)

Table 3 (*continued*)

| Compounds/substrate | Detector | HPLC conditions | Retention times (min) | References |
|---|---|---|---|---|
| piperonyl butoxide (grain) | | | Fenv.: 12.2<br>*trans*-Per. 13.5<br>*cis*-Phen.: 14.0<br>*trans*-Phen.: 15.6<br>*cis*-Per.: 16.2 | [220] |
| Piperonyl butoxide (human blood) | LC-235 Diode array (210–260 nm) | 250×4 mm, I.D., 7 μm LiChrosorb RP-18, | | [221] |
| Piperonyl butoxide (grains) | Fluoro-metry | Hitachi: Gel 3010, 500×2.1 mm I.D., ethanol at 1.0 ml/min | 5 | [123] |
| Pyrethrin (standard) | UV | 150×8 mm I.D., Nucleosil-5 $NO_2$, 4% tetrahydrofuran in hexane at 2.0 ml/min, or 200×8 mm I.D., Nucleosil-5 CN, 1% tetra-hydrofuran in hexane at 2.0 ml/min | Jasm. I: 12.80<br>Cin.I: 14.30<br>Pyr.I: 18.50 | [138] |
| Tralomethrin, delta-methrin (fish) | UV (220 nm) | 250×4.6 mm I.D., 5 μm Phenomevex, Zorbak silica, hexane–dioxane gradient:) 0 min: 100% A (96:4), 10 min:100%A, 15 min:100% B (50:50), 20 min:100% B, 22 min: 100% A | Delt: 10<br>S-Tral.: 12.5<br>R-Tral.: 15.5<br>$Br_2CA$: 19.5 | [117] |

tative and quantitative analysis of pyrethroid residues and their metabolites. A general review of pesticide residue analysis by TLC has been published [129]. A certain amount of papers on the metabolic studies of synthetic pyrethroids by using the autoradiographic thin-layer chromatography on silica gel 60 F 254 plates under UV light were reported: cypermethrin in soil [130] and in animal [111,131], deltamethrin in animal [133,146], fenpropathrin in water [134,135], soil and plant [135,136], fenvalerate in plant [137], permethrin in insect [139–141], plant [142,143], permethrin and cypermethrin in soil and plant [144].

Chromogenic reagents for the detection of pyrethroids have also been reported, including phosphomolybdic acid (20%, w/v, in ethanol) for the detection of cypermethrin, delatamethrin and permethrin [145], palladium chloride (0.5%, w/v, in 12 $mol/dm^3$ HCl) for the detection of deltamethrin [146], sodium hydroxide (20% in dist. $H_2O$) —copper (II) acetate (1% in dist. $H_2O$) —phosphomolybdic acid (1% in dist. $H_2O$) —*o*-tolidine (0.1% in 10% HAc) for the detection of pyrethroid pesticides with a nitrile group (cypermethrin, delatamethrin, fenvarelate) [147] as well as $Br_2$ treatment, 0.1% *o*-tolidine and UV irradiation (5 min) or under sunlight for 2 min [149], silver nitrate impregnated alumina G plate and irradiation with UV radiation for the detection of halogenated pyrethroids as well as anisaldehyde and sulfuric acid or $SbCl_3$ or $SbCl_5$ for the detection of pyrethrins [150].

The $R_F$ value and separation of various pyrethrins and pyrethroids and their metabolites in different solvent systems are summarized in Table 4.

## 4. Multi-residue determination

A multi-residue determination is required for the survey and the monitoring of pesticide residue in various samples. Chapman and Harris [185] firstly reported a multi-residue method for the determination of cypermethrin, fenpropathrin, fenvalerate and permethrin in asparagus, carrot, onion, radish and tomato with GLC–ECD. The multi-residue determination method for pyrethroids in various vegetables and fruits were also reported by using

Table 4
TLC analysis of pyrethroids and metabolites

| Compound[a] | Plate[b] | Developing solvent system[c] and $R_F$ value | | | | | References |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 22 | 23 | |
| Allethrin | A | 0.18 | – | – | – | – | [147,149] |
| α-Cypermethrin | | 0.35 | 0.11 | – | – | – | |
| Cypermethrin | | 0.54, 0.49<br>0.45 | 0.13, 0.10 | 0.38 | – | – | |
| Deltamethrin | | 0.44 | 0.12 | 0.31 | – | – | |
| Fenvalerate | | 0.42, 0.40 | 0.08 | 0.42 | 0.78 | 0.72 | |
| 4′-Hydroxyfenvalerate | | – | – | – | 0.62 | 0.41 | |
| Permethrin | | 0.68, 0.59 | 0.30, 0.22 | – | – | – | |
| 3-PBAc | | – | – | – | 0.49 | 0.38 | |
| | | 4 | 5 | 7 | 8 | 9 | |
| *cis*-Permethrin | A(4,5,8,9,)<br>B(7) | 0.84 | 0.93 | 0.60 | 0.80 | 0.66 | [142,143]<br>[199] |
| *trans*-Permethrin | | 0.84 | 0.92 | 0.68 | 0.66 | 0.92 | |
| 4′-Hydroxy-*cis*-permethrin | | 0.55 | – | – | – | – | |
| 4′-Hydroxy-*trans*-permethrin | | 0.58 | – | – | – | – | |
| 3-PBAc | | 0.32 | 0.64 | 0.06 | – | – | |
| 3−PBAl | | 0.45 | – | 0.27 | – | 0.73 | |
| | | 6 | 10 | | | | |
| Cypermethrin | A | 0.85 | – | | | | [111,142] |
| 3-PBAc | | 0.80 | – | | | | |
| Permethrin | | – | >0.7 | | | | |
| Hydroxypermethrin | | – | 0.1–0.7 | | | | |
| | | 11 | 12 | 13 | 14 | 15 | |
| *cis*-Permethrin | A | 0.87 | 0.86 | 0.88 | 0.75 | 0.79 | [150] |
| *trans*-Permethrin | | 0.82 | 0.79 | 0.85 | 0.67 | 0.69 | |
| *cis*-Cypermethrin | | 0.57 | 0.64 | 0.83 | 0.48 | 0.46 | |
| *trans*-Cypermethrin | | 0.49 | 0.56 | 0.80 | 0.42 | 0.37 | |
| Deltamethrin | | 0.53 | 0.60 | 0.82 | 0.45 | 0.44 | |
| Fenvalerate | | 0.45 | 0.52 | 0.80 | 0.39 | 0.36 | |
| | | 16 | 17 | 18 | 19 | 20 | |
| Deltamethrin | A | 0.57 | 0.66 | 0.92 | 0.63 | 0.89 | [133,146] |
| 2′-Hydroxydeltamethrin | | 0.37 | 0.48, 0.57 | 0.78, 0.93 | 0.41 | 0.65, 0.66 | |
| 4′-Hydroxydeltamethrin | | 0.24 | 0.41 | 0.72 | 0.33 | 0.51, 0.54 | |
| 5′-Hydroxydeltamethrin | | – | 0.47 | 0.76 | 0.38 | 0.72, 0.74 | |
| t-Hydroxydeltamethrin | | – | 0.39 | 0.61 | 0.24 | 0.60 | |
| 4′-Hydroxy, t-hydroxy-deltamethrin | | – | 0.10 | 0.21 | 0.07 | 0.36, 0.41 | |
| *cis*-Cypermethrin | | 0.68 | – | – | – | – | |
| 2′-Hydroxy-*cis*-cypermethrin | | 0.49 | – | – | – | – | |
| 4′-Hydroxy-*cis*-cypermethrin | | 0.32 | – | – | – | – | |
| Fenvalerate | | 0.56 | – | – | – | – | |
| 2′-Hydroxyenvalerate | | 0.38 | – | – | – | – | |
| 4′-Hydroxyfenvalerate | | 0.25 | – | – | – | – | |

Table 4 (*continued*)

| Compound[a] | Plate[b] | Developing solvent system[c] and $R_f$ value | | | | | References |
|---|---|---|---|---|---|---|---|
| Biphenthrin | | 0.71 | – | – | – | – | |
| 4′-Hydroxybiphemthrin | | 0.38 | – | – | – | – | |
| 5′-Hydroxybiphenthrin | | 0.34 | – | – | – | – | |
| PBAl | | – | 0.28 | 0.56 | 0.25 | 0.50 | |
| PBAld | | – | 0.61 | 0.85 | 0.57 | 0.75 | |
| PBAc | | – | 0.16, 0.58 | 0.63, 0.86 | 0.30, 0.59 | 0.35 | |
| 4′-Hydroxy-PBAl | | – | 0.10 | 0.25 | 0.05 | – | |
| 5′-Hydroxy-PBAl | | – | 0.10 | 0.22 | – | – | |
| 4′-Hydroxy-PBAc | | – | 0.06, 0.26 | 0.28, 0.49 | 0.08 | – | |
| 5′-Hydroxy-PBAc | | – | – | 0.30 | 0.07 | – | |
| | | 21 | | | | | |
| Deltamethrin | A | 0.86 | | | | | [132] |
| $Br_2CA$ | | 0.53 | | | | | |
| 3′-PBAld | | 0.80 | | | | | |
| 3-PBAc | | 0.37 | | | | | |
| 3-PBAl | | 0.46 | | | | | |
| 4′-Hydroxy-3-PBAc | | 0.08 | | | | | |
| 4′-Hydroxy-3-PBAl | | 0.05 | | | | | |

[a] A. Silica gel G; B. Silver nitrate impregnated alumina G.

[b] 1. Light petroleum (b.p. 60–80°C)–diethyl ether (9:1); 2. cyclohexane–toluene (7:3); 3. cyclohexane–toluene (6:4); 4. toluene–diethyl ether–acetic acid (7.5:2.5:0.1); 5. chloroform–acetic acid (9.5:0.5); 6. ethyl acetate–acetic acid–$H_2O$ (7.0:0.4:0.4); 7. benzene–ethyl acetate (6:1); 8. hexane–diethyl ether (10:1); 9. cyclohexane (saturated with formic acid)–diethyl ether (3:2); 10. benzene–ethyl acetate–methanol (1.5:0.5:0.1); 11. hexane–chloroform–acetic acid (9.5:0.5); 12. hexane–benzene (4.5:5.5); 13. benzene; 14. hexane–chloroform–benzene (4.5:0.5:5.0); 15. hexane–chloroform (7:3); 16. hexane–ethyl acetate (4:10); 17. benzene–ethyl acetate (6:1); 18. benzene (saturated with formic acid)–diethyl ether (10:3) (two times development); 19. carbon tetrachloride–diethyl ether (3:1); 20. acetic acid–hexane (1:1) (three times development); 21. chloroform–acetic acid (9.9:0.1); 22. hexane–acetone–acetic acid (2.5:2.5:0.1); 23. toluene–diethyl ether–acetic acid (7.5:2.5:0.1).

GLC–ECD with packed column [10,63]. Capillary column GLC system were adopted popularly since the end of the 1980s [13,14,16,54,56,97,127, 152,153]. Due to the longer column length and thinner stationary phase layer, a large amounts of pesticides including pyrethrins and pyrethroids could be separated and determined in a single injection, even the various isomers of pyrethroids can be separated successfully [5]. The application of the GLC–ECD with 15 m×0.32 mm, 0.10–0.15 μm OV-1 fused-silica capillary column to separate and determine 9 pyrethroids (biphenthrin, cyfluthrin, cyhalothrin, cypermethrin I, II, III, IV, delatamethrin, fenpropathrin, fenvalerate I, II, flucythrinate, I, II, *cis*-permethrin, *trans*-permethrin) was recommended as an official method in Germany [71]. The limit of detection was 0.005 mg/kg and the limit of determination was 0.03 mg/kg. Nakamura et al reported a multi-residue method for determining 48 pesticides (including 6 components of pyrethrins and 6 pyrethroids) in vegetables and fruits with capillary column GLC–ECD. The recovery was ranged from 63.1% to 107.5% [198]. A multi-residue method including 143 pesticides (included 2 pyrethrins) was reported [92]. T. Itoyama et al developed a multi-residue method for determining 92 pesticides (included 11 pyrethroids) in brown rice. By using the GC–ECD methods, the detection limit of pyrethroids was 0.01 mg/kg and recovery ranged from 92.8% to 116% [187]. The application of HPLC to multi-residue determination of pyrethroids was limited. However, there were few reports on the multi-residue determination methods by using HPLC [63,126,127]. Most of the multi-residue methods using HPLC were concerned with residue determination of pyrethroids in grains [63,126,127,154,198]. A method for the determination of 5 pyrethroids and synergist pipenoyl butoxide in paddy rice was recommended in Australia [126]. The detection limit is much lower than that with GLC–ECD. The GLC and

HPLC parameters in the multi-residue analysis of pyrethrins and pyrethroids in various matrices are listed in Table 5.

## 5. Enantiomer and diastereomer separation

Pyrethroids are synthesized, marketed and used either as a single, most active isomer or as isomeric mixtures containing two to eight different stereoisomers, depending on the number of chiral centers in the molecule. It is regarded in stereochemistry that any molecule containing an asymmetric carbon atom to which are attached four different chemical groups may exist in two forms that are mirror images (enantiomers). If there are $n$ asymmetric carbon atoms, the total number of arrangements is $2^n$. If some of the asymmetric centres are of the same configuration in the two isomers and others are different, the compounds are diastereomers. The molecules of pyrethroids often consist several asymmetric centers, thus different enantiomers and diastereomers may exist in various pyrethroids. Table 6 lists the isomer numbers of various pyrethroids. It was proved that the individual enantiomers have widely different biological activity. So, it is essential to determine the ratio of individual enantiomer not only in the analysis of formulation, but also in the analysis of residues of pyrethroids. For these reasons, chiral analysis is likely to acquire increasing importance.

Currently pyrethroids are generally analysed by GLC or HPLC. By using the packing GLC column chromatography or the capillary column chromatography, the diastereomers (*cis*, *trans*) of pyrethroids can be separated satisfactory by the selection of column stationary phases, however, the separation of enantiomers (*R*, *S*) of pyrethroids is not always successful. An attempt to separate individual enantiomers of fenvalerate by GLC following derivatization with (1*R*,2*S*,5*R*)-(−)-menthol was reported, but epimerization may occur during this procedure [151]. An investigation by using GLC–ECD with an apolar DB-5 (50% phenyl methyl polysiloxane) capillary column (25 m length×0.25 mm I.D., 0.1 μm film) at a temperature of 230°C to separate the eight enantiomer peaks of cypermethrin was carried out [155]. Four pairs with the elution order of *cis*, *trans*, *cis*, *trans* were obtained. Separation onto three well resolved cypermethrin peaks is achieved on the SB-10 biphenyl 30 column (30% biphenyl methyl polysiloxane) at 240°C. By using the more polar DB 1701 column (14% cyanopropyl phenyl methyl polysiloxane), on-column isomerization of the α-cyano moiety was observed at 230°C and higher temperature [155]. Similar effects were also observed on this stationary phase from cyfluthrin, cypermethrin and deltamrthrin, which all possess the α-cyano group in the molecule. Permethrin which lacks the α-cyano group, could be separated into *cis* and *trans* isomers. It revealed that the isomerization occurring is not a *cis–trans* isomerization, which indicates that the point of isomerization in the molecule is the chiral α-C atom bearing the cyano group. Five partially resolved allethrin peaks are observed with the chiral Lipodex C column indicating chiral separation of *cis*-enantiomers, but it showed no enantioselectivity for the *trans*-allethrin isomers. The GLC separation of pyrethroid isomers on apolar stationary phases governed firstly by diffusion as in the vapour pressure of the compounds and secondly by the solubility and the interactions of the analytes with the stationary phases. The *cis*-isomer of pyrethroid always elute before the *trans*-isomer on columns with nonpolar or moderate polar stationary phases, whereas on the polar 100% cyanopropyl phase, the elution order of the allethrin isomers is reversed, indicating better solubility of the *cis*-isomer caused by the enhanced dipole interaction [155]. The application of HPLC with chiral stationary phases in the separation of pyrethroid enantiomers gave promising results. Four isomers of phenothrin were resolved on a chiral polymer column [156]. The application of chiral column in the separation of enantiomers of pyrethroids with or without the α-cyano-3-phenoxybenzyl alcohol was achieved by some authors [157–159]. Cayley and Simpson [160] made a more systemic Pirkle-type stationary phases. Unfortunately, the separation of many enantiomers were incomplete. A modified Pirkle-type column with (*R*)-N-3,5-dinitrobenzoyl-1-naphthylglycine ionically bonded to 3-aminopropylsilanized silican (Oi phase III) was successfully used to separate the various enantiomers of pyrethroids and obtained better results than earlier chiral stationary phases [161]. Especially in the separation on the

Table 5
GLC and HPLC multi-residue analysis methods of pyrethrins and pyrethroids in crops, foods and environmental matrices

| Compounds/substrates | Detector | GLC or HPLC conditions | Retention time (min) | References |
|---|---|---|---|---|
| Allethrin, biphenthrin, fenpropathrin, cyhalothrin, cyfluthrin, deltamethrin, fenvalerate, flucythrinate, fluvalinate, permethrin (fruits, vegetables) | GLC–ECD | 1. GLC, C, 5 m×0.53 mm I.D., HP (2.65 μm), *Tc*: 230°C (2 min)–(20°C/min)–260°C(5 min); 2. GLC, C, 25 m×0.32 mm I.D., Ultra-2(0.17 μm) cross-linked 5% phenyl methylsilicone, *Ti*: 150°C(1 min)–(4°C/min)–270°C (5 min), *Tc*: 50°C 2.5 min)–(22°C/min)–210°C(12 min)–(50°C/min)–250°C(8 min) | All.: 3.04<br>Biph.+Fenpro.: 7.76<br>Cyh.; 9.83<br>Per.: 11.97<br>Cyfl.: 13.7<br>Flucy.: 14.85<br>Fenv.: 16.68<br>Fluv.: 18.24<br>Delt.: 19.65 | [55] |
| Bioresmethrin, cismethrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, permethrin, phenothrin resmethrin (fruits, vegetables) | GLC–ECD | 1. GLC, P, 1 m×4 mm I.D. 3% OV17/GCQ, *Ti*: 250°C, *Td*: 255°C, *Tc* 235°C<br>2. GLC, C, 25 m×0.23 mm I.D., OV101 (0.12 μm), *Ti*: 220°C, *Td*: 275°C, *Tc*: 50°C(2 min)–(25°C/min)–210°C | Cis.: 20.2; Bior.: 20.4;<br>Phen.: 25.3, 26.0;<br>*cis*-Perm.: 34.4;<br>*trans*-Perm.: 37.4;<br>Cyp.: 45.5, 46.8, 48.3, 49.5<br>Fenv.: 60.3, 65.3<br>Delt.: 72.5, 79.7 | [63] |
| 20 Pesticides including 9 pyrethroids (bioresmethrin, cismethrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, permethrin, phenothrin, tetramethrin (grain) | GLC–ECD | C, 25 m×0.23 mm I.D. OV101 (0.12 μm), *Ti*: 215°C, *Td*: 275°C, *Tc*: 60°C(2 min)–(30°C/min)–215°C(55 min)<br>: | | [127] |
| 13 Pesticides including 5 pyrethroids (biphenthrin, cyhalothrin, cypermethrin, fenvalerate, deltamethrin) (vegetables) | GLC–ECD | C, 12 m×0.53 mm I.D., Megabone HP-5, *Ti*: 270°C, *Td*: 280°C, *Tc*: 160°C(40 min)–(2°C/min)–265°C | Biph.: 28.8<br>Cyh.: 33.7,41.3<br>Fenv.: 44.2<br>Delt.: 47.6 | [56] |
| 48 pesticides including 3 pyrethrins (cinerin I, II, jasmolinl, II, pyrethrin I, II) and 5 pyrethroids (cyhalothrin, cypermethrin, deltamethrin, flucyrinate, permethrin) (fruits, vegetables) | GLC–ECD | 1. C, 30 m×0.25 mm, I.D. DB-5, *Ti*: 240°C, *Td*: 280°C, *Tc*: 60°C(2 min)–(8°C/min)–280°C<br>2. C, 30 m×0.25 mm I.D., DB-210, *Ti*: 200°C, *Td*: 280°C, *Tc*: 60°C(2 min)–(8°C/min)–280°C | Cin.I: 25.19<br>Jasm.I: 26.53<br>Pyr.I: 26.82<br>Cin. II: 30.08<br>Jasm. II: 31.05<br>Pyr. II: 33.81<br>Per.: 32.74, 32.87<br>Flucy.: 35.06, 38.51<br>Cyh.: 31.07,31.09<br>Cyp.: 34.57,34.77<br>35.03,37.45,37.59 | [198] |
| 25 Pesticides including 5 pyrethroids (bioresmethrin, deltamethrin, fenvalerate, phenothrin, permethrin, piperonyl butoxide (fruits, vegetables) | HPLC–UV | 15 m×0.53 mm, I.D., Novapak $C_{18}$, 75% aqueous acetonitrile at 1 ml/min | PB.: 5.5<br>Delt.: 11.5<br>Bior.: 11.5<br>Fenv.: 12.2<br>*trans*-Perm.: 13.5<br>*cis*-Phen. 14.4<br>*trans*-Phen.: 15.6<br>*cis*-Perm.: 16.2 | [85] |

Table 5 (*continued*)

| Compounds/substrates | Detector | GLC or HPLC conditions | Retention time (min) | References |
|---|---|---|---|---|
| 30 Pesticides including 3 pyrethroids (cypermethrin, deltamethrin, fenvalerate) (water) | GLC–ECD | 1. C, 2.25 m×0.2 mm, I.D., HP Ultra (0.33 μm), *Tc*: 90 (1 min)–(30°C/min)–180°C–(4°C/min)–270°C(15 min)<br>2. C, 30 m×0.53 mm, I.D. Supelco SPB 20 (0.23 μm), *Tc*: 150°C(1 min)–(2°C/min)–270°C(25 min) | Cyp.: 30.52<br>Fenv.: 34.26<br>Delt.: 39.16<br>Cyp.: 60.5<br>Fenv.: 65.43<br>Delt.: 71.34 | [97] |
| 25 pesticides including 6 pyrethroids (cyhalothrin, cyfluthrin, cypermethrin, fenvalerate, flucyrinate, tralomethrin) (fruits, vegetables, tea, soybean, potato) | GLC–ECD | C, 15 m×0.53 mm I.D., DB-1, *Ti*: 320°C, *Td*: 300°C, *Tc*: 100°C(0.5 min)–(10°C)min)–280°C | | [11] |
| Allethrin, bioallethrin, cinerin, I, II, cyfluthrin, cypermethrin, jasmolin I, II, permethrin, pyrethrin I, I (crops) | GLC–ECD | 1. C, 10 m×0.25 mm, I.D., DB-5 (0.1 μm), *Tc*: 70°C–(40°C/min)–185°C–(3°C/min)–220°C<br>2. C, 25 m×0.25 mm, I.D., DB-1701 (0.15 μ), *Tc*: 70°C(1 min)–(30°C/min)–180°C–(1°C/min)–220°C | | [88] |
| Pyrethrins, piperonyl butoxide (fruits, vegetables) | GLC–ECD | 1. C, 15 m×0.32 mm I.D., OV1 (0.1–0.15 μm), *Ti*: 60°C, *Td*: 290°C, *Tc*: 60°C–(60 °C/min)–180°C–(3°C/min)–240°C(20 min) (for pyrethrins)<br>2. P, 2 m×2 mm I.D., 2%OV210/GCQ00/120 mesh, *Ti*: 250°C, *Td*: 300°C, *Tc*: 220°C (for PB) | CinI.: 1.5.6, 2.1.4<br>Jas.I: 1.6.2, 2.2.05<br>Pyr.I: 1.6.5, 2.2.05<br>Cin.II: 1.10.06, 2.4.5<br>Jas.II: 1.11.5, 2.6.5<br>Pyr.II: 1.11.9, 2.6.5<br>PB: 8.20 | [225] |
| Pyrethroids (fruits, vegetables, soil, water) | GLC–ECD | 1. C, 15 m×0.32 mm I.D., OV1(0.1-0.15 μm), *Ti*: 270°C, *Td*: 290°C, *Tc*: 70°C–(60°C/min)–180°C–(3°C/min)–245°C(20 min)<br>2. P, 1.2 m×2 mm I.D., 10% SE30/Chromosorb W HP 80/100 me, *Ti*: 270°C, *Td*: 300°C, *Tc*: 200°C–(3°C/min)–279°C(5 min) | Biph.:1.8.6<br>Fenpro.: 1.8.6, 2.9.2<br>Cyh.: 1.10.6<br>*cis*-Per.: 1.11.9, 2.13.7<br>*trans*-Per.: 1.12.2, 2.13.7<br>Cyf.: 1.13.5<br>Cyp: 1.13.8, 141, 14.2, 14.5 2. 16.3<br>Flucy: 1.14.0, 15.0 2. 30.0<br>Fenv.: 1.16.0, 16.6 2.18.2, 18.8<br>Delt.: 1.17.9, 2. 20.3 | [201] |
| 13 Pyrethroids and metabolite 3-PBAc (tea) | GLC–ECD | C, 25 m×0.25 mm, I.D., CBP-1 (0.25 μm), *Ti*: 230°C, *Tc*: 250°C (Pyr.); 160°C (PBAc) | 3-PBAc-HFIP: 7.9<br>Fenpro.: 15.6 | [95] |
| 19 Pesticides including fenvalerate (fruits, vegetables) | HPLC | 220×4.6 mm, I.D., Spheri-5 RP $C_{18}$-HPLC (5 μm), mobile solvent from acetone–water (1:1) to acetonitrile–water (8:2) | | [221] |

Table 6
Separation of pyrethroid enantiomers by chiral HPLC

| Pyrethroids | Theoretical no. of isomers | No. of peaks observed* | Chiral column | Mobile phase | References |
|---|---|---|---|---|---|
| Allethrin | 8 | 8[1] | Phase II[a], | A | [161] |
| Allethrin | 8 | 5[3] | Chiral β-cyclodextrin RP-HPLC column (Cyclobond) | B | [225] |
| Bioallethrin | 2 | 2[1] | Phase Ia[b] | C | [160] |
| Bioallethrin | 2 | 2[1] | Phase II | A | [161] |
| Cyfluthrin | 8 | 8[2] | Phase Ia | E | [162] |
| λ-Cyhalothrin | 2 | 2[2] | Phase Ia | C | [160] |
| Cypermethrin | 8 | 8[1] | Phase IIc[c] +IId[d] (Sumichiral OA-4700) | D | [161] |
| Cypermethrin | 8 | 7[1] | Phase Ia | C | [160] |
| Fenpropathrin | 2 | 2[2] | Phase Ia | C | [160] |
| Fenvalerate | 4 | 4[2] | Phase Ia | C | [157] |
| | 4 | 4[2] | Phase Ib[e](Bakerbond Covalently bonded Chiral column) | C | [114] |
| | 4 | 4[1] | Phase Ia | C | [160] |
| | 4 | 4[1] | Phase III[f] | A | [161] |
| | 4 | 4[2] | Phase Ic[g](Sumichiral OA-2000) | A | [161] |
| | 4 | 4[2] | Phase Ia | A | [159] |
| Fluvalinate | 2 | 2[1] | Phase Ia | A | [160] |
| Permethrin | 4 | 4[2] | Phase Ia | C | [157] |
| | 4 | 4[2] | Phase Ia | F | [160] |
| | 4 | 4[1] | Phase III | G | [161] |
| Phenothrin | 4 | 4[2] | Phase Ia | F | [160] |
| | 4 | 4[2] | Phase Ia | C | [156] |
| | 4 | 4[1] | Phase III | G | [161] |
| Resmethrin | 4 | 4[2] | Phase Ia | E | [160] |
| | 4 | 4[1] | Phase III | G | [161] |
| Terqllethrin | 2 | 2[1] | Phase Ia | A | [161] |
| Tetramethrin | 4 | 4[1] | Phase III | A | [161] |

* [1]=isomers well resolved; [2]=isomers particially resolved; [3]=4 *cis*-isomers are co-eluted in one earlier peak; [4]=*trans*-isomers are separated satisfactorily.

Chiral column: [a] Phase II: Chiral materials of IIa and IIb are derived from (*S*)-or (*R*)-1-(α-naphthyl)ethylamine with (*S*)-valine chemically bonded to 3-aminopropylsilanized glycine silica gel [161].

[b] Phase Ia consists of the (*R*)-N-(2,5,-dinitrobenzoyl) phenylglycine chiral liquid phase ionically bonded to 3-aminopropylsilanized silica gel [157].

[c] Phase IIc: Chiral material of Phase IIc is derived from (*S*)-1-(α-naphthylethylamine with (*S*)-*tert*-leucine chemically bonded to 3-aminopro-pylsilanized silica gel [161].

[d] Chiral material of Chase IId is derived from (*R*)-1-(α-naphthyl)ethylamine with (*S*)-*tert*-leucine chemically bonded to 3-amino-propylsilanized silica gel [161].

[e] Phase Ib consists of (*R*)-N-(2,5-dinitrobenzoyl)phenyl chiral liquid phase ionically bonded to 3-aminopropylsilanized silica gel [114].

[f] Phase III: The chiral material is derived from the polymerization of triphenylme-thylmethacrylate [(+)−poly(triphenylmethyl methacrylate) [226].

[g] Phase Ic is a modified Pirkle type 1-A chiral material containing (*R*)-N-(3,5-dinitrobenozyl)-1-naphthylglycine ionically bonded to 3-aminopropylsilanized silica gel [161].

Mobile phase: A=hexane–1,2-dichloroethane–ethanol (500:30:0.15); B=acetonitrile–$H_2O$ (22:78); C=0.1% propan-2-ol in hexane; D=hexane–1,2-dichloroethane–ethanol (500:10:0.05); E=0.05% propan-2-ol in hexane; F=0.025% propan-2-ol in hexane; G=hexane–1,2-dichloroethane (500:1).

eight isomers of cypermethrin and allethrin which contains one chiral center in the alcohol moiety, and two chiral centers in the acid moiety, the Pirkle-type column is difficult to separate these eight isomers. The adjacent peaks of two diastereomeric isomers [(α*R*) (1*S*) *trans* and (α*S*) (1*R*) *trans*] unfortunately overlap. Even by using the Oi Phase II (Phase IIc), the two diastereomeric isomers [(α*S*) (1*S*) *trans* and (α*R*) (1*S*) *trans*] are combined in one peak. However, the combination of OiPhase II and Sumichiral OA 2700 [urea derivative derived from (*R*)-1-(α-naphthyl)ethylamine with (*S*)-*tert.*-*l*eucine chemically bonded to 3-aminopropylsilanized silica] (Phase IId) give satisfactory resolution for pyrethroids with a variety of acid and alcohol moieties containing one to three chiral centres (Fig. 1). The separation of enantiomers of 5 synthetic pyrethroids was achieved with HPLC by using a Pirkle column [162]. Complete separation of enantiomer peaks was obtained in almost all cases. Unfortunately, some peaks overlapped. In the separation of enantiomers of cypermethrin and allethrin by using the chiral β-cyclodextrin RP-HPLC column, the eight enantiomers of both pyrethroids were separated into five to six partially resolved peaks [155]. It separated the *trans*-isomer better than the *cis*-isomer. The chiral columns in the separation of enantiomers of various pyrethroids are listed in Table 6.

It can be concluded from the above that chiral HPLC has been shown to be a useful technique for the analysis of a wide range of pyrethroids with a range of acid and alcohol moieties. It is a rapid non-destructive technique in which there is a little chance of epimerization during the course of analysis and is suitable for the analysis of technical formulations and terminal residue in biological and environmental matrices. However, it should be mentioned that the commercial ionic column lost the selectivity rapidly when exposed to formulation and required extensive cleaning using hexane–tetrahydrofuran (1:1) and rejuvenation using "chiral column regenerating solution" after two weeks of daytime use [162].

## 6. GC–MS confirmation

The identification and confirmation of analytical results is an essential process in eliminating the confusion of similar compounds. GC–MS is an excellent tool for the identification and confirmation of results in pesticide residue analysis [223]. The most significant advantage of mass spectrometry is its high sensitivity. A full mass spectrum of a pesticide can be obtained with only a few nanograms of compound. It can provide valuable structural information from very small amounts of sample. When the sample is injected into the GC column, the eluents come out from the column and elute into the detector for quantitative determination and elute into

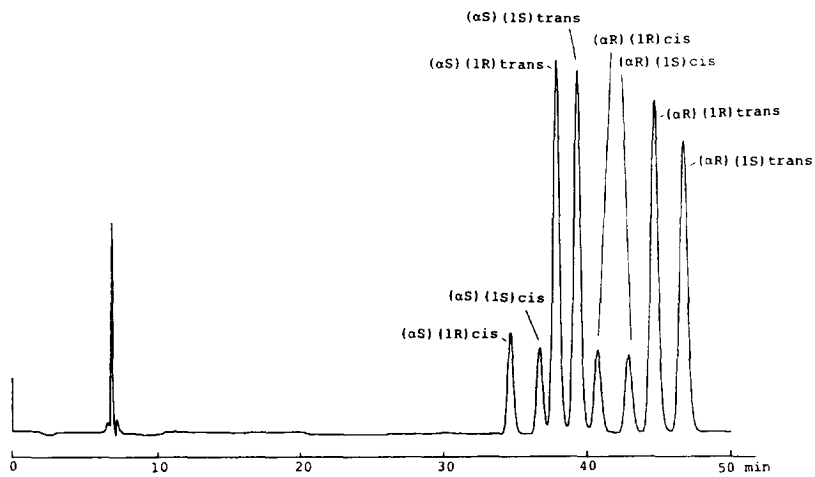


Fig. 1. Separation of isomers of allethrin with a chiral column on HPLC [161].

the MS simultaneously for confirmation results. The vast majority of studies on pesticide residue confirmation using MS reported to date, have relied on electron impact (EI) ionization at 70 eV electron beam energy. The data is helpful for identifying the pesticide according to the major fragments *m/z*. It has attained even greater importance due to advances in chromatography. The GLC and HPLC combined with MS are applied more and more popularly in published papers in recent years for the purpose of carrying out the determination and confirmation simultaneously. For example the GC–MS has been used for the determination and confirmation of bioallethrin [175], biphenthrin [31], fenpropathrin [136], fenvarelate [82,164,166], fluvalinate [80], permethrin [165], pyrethrins [105,170–172], resmethrin [173,174], as well as the multi-residue of pyrethrins and pyrethroids [61,152,167,169,176,177]. The MS analysis of pesticides and their degradation products has been reviewed in several papers [178,179]. A GC–MS method was recently developed for determining 8 organonitrogen pesticides and 8 pyrethroids in fruits and vegetables [61]. The detection limit was 5 ng/kg. Table 7 lists the most abundant fragments and their relative intensity for 21 pyrethrins and synthetic pyrethroids.

## 7. Conclusions

Recently published methods for the determination of pyrethrin and pyrethroid residues in crops, foods and environmental matrices are reviewed. The sample pretreatment, including the extraction and clean-up are discussed. Some new extraction methods, such as SPE and SFE, are becoming increasingly important. GLC–ECD is the first choice in the determination of pyrethroid residue due to the fact that most of the pyrethroids are halogen-containing. For the non-halogen containing pyrethroids, the formation of halogenated derivatives prior to the GLC–ECD determination is recommended. NPD, FID were also applied. HECD and MIP-AED are new attempts in the determination of pyrethroid

Table 7
The main fragments and their relative intensities for pyrethrin and pyrethroids

| Pesticides | Main fragments *m/z* (intensities) | | | | | | References |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | |
| Allethrin | 123(100) | 79(40) | 43(31) | 81(31) | 91(29) | 136(27) | [226] |
| Biphenthrin | 181(100) | 166 | 422 | 197 | | | [31] |
| Bioallethrin | 135(100) | 303(70) | 151(44) | 183(31) | 165(30) | 123(25) | [88] |
| Bioremethrin | 171 | | | | | | [88] |
| Cinerin I | 123(100) | 43(35) | 93(33) | 121(27) | 81(27) | 150(27) | [226] |
| Cinerin II | 107(100) | 93(57) | 121(53) | 91(50) | 149(35) | 105(33) | [226] |
| Cyfluthrin | 163(100) | 206(64) | 226(53) | 77(40) | 91(36) | 127(30) | [223] |
| Cyhalothrin | 197(100) | 181(96) | 200(78) | 141(32) | 77(21) | 161(15) | [223] |
| Cypermethrin | 163(100) | 181(79) | 165(68) | 91(41) | 77(33) | 51(29) | [226] |
| Deltamethrin | 253(100) | 181(82) | 209(62) | 77(31) | 93(28) | 198(27) | [37,223] |
| Fenpropathrin | 181(100) | 125(100) | 265(50) | | | | [224] |
| Fenvalerate | 167(100) | 123(78) | 181(43) | 152(41) | 225(36) | 77(23) | [223] |
| Flucyrinate | 189(100) | 157(52) | 181(33) | 187(18) | 225(16) | | [45] |
| Fluvalinate | 251(100) | 181(90) | 206(76) | 483(20) | 77(16) | 234(18) | [226] |
| Jasmolin I | 123(100) | 43(52) | 55(34) | 93(25) | 91(24) | 81(23) | [226] |
| Jasmolin II | 107(100) | 91(69) | 135(69) | 93(67) | 55(66) | 121(58) | [226] |
| Permethrin | 183(100) | 163(100) | 165(25) | 44(15) | 184(15) | 91(13) | [226] |
| Piperonyl butoxide | 177 | | | | | | [88] |
| Pyrethrin I | 123(100) | 43(62) | 91(58) | 81(47) | 105(450) | 55(43) | [226] |
| Pyrethrin II | 91(100) | 133(70) | 161(55) | 117(48) | 107(47) | | [226] |
| Resmethrin | 123(100) | 171(67) | 128(52) | 143(49) | 81(38) | 91(28) | [226] |
| Tetramethrin | 154(100) | 123(41) | 207(13) | 81(11) | 107(9) | | [223] |
| Tralomethrin | 181(100) | 253(90) | 77(410 | 200(38) | 93(30) | 152(21) | [223] |

residues and gave promising results. HPLC has had accelerated application in the pyrethrin and pyrethroid residue analysis, especially in the detection of natural pyrethrins and the separation of enantiomers of pyrethroids. TLC is promising due to the development of modern instrumentalized HPTLC. The multi-residue determination and the GC–MS confirmation of pyrethrins and pyrethroids are also reviewed.

## 8. Abbreviations

| | |
|---|---|
| ALL | Allethrin |
| AMD | Automated multiple development |
| BIOR | Bioresmethrin |
| BIP | Biphenthrin |
| CA | Chrysanthemic acid |
| CIN | Cinerin |
| CYF | Cyfluthrin |
| CFH | Cyhalothrin |
| CYP | Cypermethrin |
| DELT | Deltamethrin |
| ECD | Electron-capture detection |
| FENV | Fenvalerate |
| FENPRO | Fenpropathrin |
| FID | Flame ionization detection |
| FLUCY | Flucyrinate |
| FLUV | Fluvalinate |
| GC | Gas chromatography |
| GPC | Gel permeation chromatography |
| HECD | Hall electrolytic conductive detector |
| HFIP | Hexafluoroisopropyl alcohol |
| HPLC | High-performance liquid chromatography |
| HPTLC | High-performance thin-layer chromatography |
| JASM | Jasmolin |
| MIP-AED | Microwave-induced plasma-atomic emission detection |
| MS | Mass spectrometry |
| MRL | Maximum residue limit |
| NPD | Nitrogen–phosphorus selective detection |
| PBAc | Phenoxybenzyl acid |
| PBAl | Phenoxybenzyl alcohol |
| PBAld | Phenoxybenzyl aldehyde |
| PERM | Permethrin |
| PYR | Pyrethrin |
| RESM | Resmethrin |
| RP-HPLC | Reversed-phase high-performance liquid chromatography |
| SFE | Supercritical fluid extraction |
| SPE | Solid-phase extraction |
| TLC | Thin-layer chromatography |
| TRAL | Tralomethrin |
| UV | Ultraviolet |

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