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Selective enrichment of 17 pyrethroids from lyophilised agricultural samples

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Abstract

The screening of agricultural samples to determine 17 synthetic pyrethroids was investigated. Samples were lyophilised without losses of the insecticides, and then extracted with *n*-hexane. A simple, continuous preconcentration–elution system was developed, which included a silica sorbent column (packed with 50 mg) and used an air stream to carry the eluent (ethyl acetate) which minimised the eluate volume thus increasing the preconcentration factor; so no evaporation step was required. Pyrethroids were determined by gas chromatography–electron capture detection (GC–ECD) by using a 5% phenylmethylpolysiloxane-coated fused-silica capillary column; gas chromatography–mass spectrometry was used to identify the pyrethroids detected by GC–ECD monitoring. Limits of detection varied between 0.1 and 0.8 ng/ml (except for piperonyl butoxide, 25 ng/ml) with linear ranges from 1 to 200 ng/ml; the precision of the method was high (3–6%). Recoveries of 17 insecticides from 14 different agricultural samples fortified at levels of 20–100 ng/g ranged from 66 to 102% (bifenthrin and deltamethrin were those providing the lowest values, 66–87%). Pyrethroids were detected in eight samples (from the 100 unfortified agricultural samples tested) at concentrations lower than the established maximum residue limits (MRLs).

Keywords: Food analysis; Fruit; Vegetables; Pyrethroids; Pesticides

1. Introduction

Pyrethroids are a relatively newly developed group of insecticides widely used in the control of agricultural, forestry and stored products' pests [1]. Considering that they are harmless for mammals under normal circumstances and toxic metabolites are absent, their maximum residue limits (MRLs) are, in general, higher than those of organophosphorous, organochlorine or carbamate pesticides [2]. Notwithstanding their relatively low toxicity, the residue analysis of pyrethroids in crops, foods and environmental matrices is of importance in agricultural and environmental sciences. Almost all the analytical methods for the determination of pyrethroid residues in agricultural commodities are based on the use of chromatographic techniques [3–23], mainly gas chromatography (GC).

Despite the chromatographic technique used, extensive sample pretreatment is required, including preconcentration and clean-up steps. In a general procedure, representative subsamples from fresh vegetables/fruits are homogenised and extracted once or several times using either a single solvent

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[5–9,13,14] or a binary solvent mixture [10]. When a water miscible solvent is used, subsequent liquid–liquid partition with an immiscible solvent such as *n*-hexane [5,13,14] or toluene [7,8] is included. The clean-up of the final organic extract is then carried out by solid-phase extraction [5–10,21] or gel permeation chromatography [6,15]. Supercritical fluid extraction [18,19] as well as matrix solid-phase dispersion [11,20] have also been proposed for this determination. All these methods have been applied to the determination of residues of pyrethroids in fresh agricultural samples. However, lyophilisation can be used for sample pretreatment, particularly for sample preservation. In the case of agricultural and food analysis, the use of freeze-drying led to the solution of a variety of problems encountered in the storage of these type of samples [24].

The aim of this work was to develop a simple and fast method, which allows the screening of agricultural samples for the determination of synthetic pyrethroids. The organic extractant was added to the lyophilised samples and the analytes retained on a silica column inserted into a flow configuration more simple than that described elsewhere for organochlorine pesticides [25] with the view of carrying out the analyte preconcentration and matrix clean-up in a single step. The high sensitivity and selectivity of the proposed method allows the determination of 16 synthetic pyrethroids and piperonyl butoxide (a synergist found in combination with pyrethroids) in lyophilised fruit and vegetable samples at concentrations lower than their MRLs.

2. Experimental

2.1. Chemicals and standards

All reagents were of analytical grade or better. Bifenthrin, lambda-cyhalothrin, deltamethrin, fenpropathrin, fenvalerate (*cis* and *trans* isomers), permethrin (*cis* and *trans* isomers), cyfluthrin isomers, β-cyfluthrin, cypermethrin isomers, α-cypermethrin, synergist piperonyl butoxide and endosulfan sulphate (internal standard, I.S.) were obtained from Riedel-de-Haën (Seelze, Germany). Cyfluthrin and cypermethrin have four isomers: 1(*RS*)*cis*,α(*RS*) which is isomer I; 1(*RS*)*trans*,α(*RS*), isomer III; 1(*RS*)*cis*,α(*SR*), isomer II; and 1(*RS*)*trans*,α(*SR*), isomer IV; α-cypermethrin is the isomer III of cypermethrin and β-cyfluthrin is the mixture of isomers II and IV of cyfluthrin at ratio 1:2. The silica sorbent was obtained from Varian (Zug, Switzerland). Solvents (ethyl acetate, *n*-hexane, isopropanol, acetonitrile) were purchased from Merck (Darmstadt, Germany).

Stock standard solutions of each pyrethroid and piperonyl butoxide (synergist for pyrethrins) were prepared in *n*-hexane at concentrations of 5 mg/ml and stored in glass stoppered bottles in the dark at 4°C.

2.2. Instruments and apparatus

Experiments were carried out by using a Hewlett-Packard 5890 A gas chromatograph equipped with a ^{63}Ni electron-capture detection (ECD) system. Chromatographic separation was achieved by using a fused-silica capillary column (30 m×0.25 mm I.D.) coated with 5% phenylmethylpolysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). Peak areas were measured with a Hewlett-Packard 3392 A integrator. The injector and detector temperatures were maintained at 225 and 325°C throughout. The column temperature was raised from 170°C (hold 2 min) to 255°C (hold 15 min) at 10°C/min and then to 285°C (hold 6 min) at 8°C/min. Nitrogen (6.0, Air Liquide, Seville, Spain) at a flow-rate of 1 ml/min was used as carrier gas. Confirmatory analyses were carried out on a Fisons 8000 GC instrument interfaced to a Fisons MD800 mass spectrometer and controlled by a computer running MASSLAB software (Thermo, Madrid, Spain); the chromatographic column and temperature program were both similar to those used with ECD, using ultrapure helium (6.0 Air Liquide), as carrier gas (1 ml/min). The injection port and transfer line temperatures were maintained at 225 and 300°C, respectively. The ion source temperature was 200°C for the 70-eV electron impact mode, with scanning from m/z 70 to 500. In all analyses, 1 μl of the organic extract was injected in the split mode (1:25 ratio).

The flow system consisted of a Gilson Minipuls-2 peristaltic pump fitted with Solvaflex pumping tubes, two Rheodyne 5041 injection valves, PTFE tubing (0.5 mm I.D.) and commercially available connec-

tors. A laboratory-made glass column (2 cm×4 mm I.D.) packed with ~50 mg of silica was also employed; small cotton beads were used on the ends to prevent material losses. The sorbent column was sequentially conditioned with 0.5 ml of acetonitrile and 1 ml of *n*-hexane before retention. A glass column (3 cm×5 mm I.D., packed with cotton wool) was also constructed for filtration purposes. A Hetossic laboratory freeze-dryer, type CD-53-1 (Birkerod, Denmark) was also employed.

2.3. Sample preparation

Vegetables and fruits were purchased at local markets in Córdoba. Because legally established limits of pyrethroid residues have been set for raw materials, samples were analysed unwashed, in a raw state [26]. Sampling was done according to the legally established protocol [27]. Thus, a raw global sample consisting of ~5 kg was reduced by quartering to ~500 g and then pulped in a high-speed blender and fractions of ~50 g lyophilised by freeze-drying at 6 Pa for 8 h. Lyophilised samples were conserved in glass containers, at −20°C in the dark, until analysis, the concentration of pyrethroids remaining constant for at least 3 months. An accurately weighed amount of 0.1–1 g of lyophilised sample was placed into a 100-ml amber glass bottle with 15 ml of *n*-hexane and 0.1 ml of 0.75 μg/ml endosulfan sulphate (I.S.). Once stoppered, the mixture was shaken (10 min) and 5 ml of the *n*-hexane phase was continuously aspirated and filtered into the manifold shown in Fig. 1.

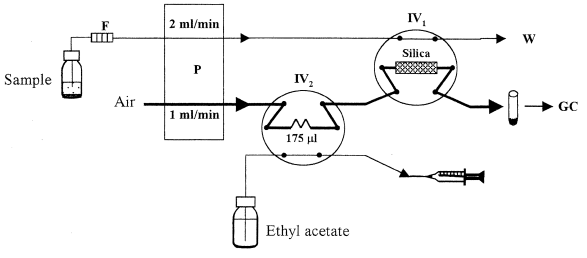

Fig. 1. Scheme of the solid-phase extraction unit designed for the screening and determination of pyrethroids and piperonyl butoxide in lyophilised agricultural samples. F, filter; GC, gas chromatograph with ECD or MS detector; IV, injection valve; P, peristaltic pump; W, waste.

2.4. Screening procedure

The continuous preconcentration and elution system designed is shown in Fig. 1. In the preconcentration step, a volume of 5 ml of standard solution or treated sample containing 1–200 ng/ml of each pyrethroid in *n*-hexane, was continuously introduced into the system at 2 ml/min. A cotton column was used to filter fine particles in order to avoid clogging the sorbent column. The analytes were retained on the silica column (50 mg), located in the loop of injection valve (IV_1), the sample matrix being sent to waste. Simultaneously, the loop of the second valve (IV_2) was filled with the eluent (ethyl acetate). Prior to the elution, by switching IV_1, residual organic solution inside the column and the connectors were flushed by passing an air stream through the carrier line of IV_2 at 1 ml/min for 4 min. In the elution step, IV_2 was switched and 175 μl of the eluent were injected into an air stream and passed through the sorbent column to elute the pyrethroids (position in bold lines). The extract was collected in a glass vial and 1-μl aliquot injected into the gas chromatograph. After each determination, the sorbent column was cleaned with 0.5 ml of isopropanol to remove residual compounds from the matrix and then conditioned with 0.5 ml of acetonitrile and 1 ml of *n*-hexane.

3. Results and discussion

3.1. Lyophilisation of the samples

Fresh vegetables and fruits contain abundant amount of water — normally more than 80% — which favours biodegradation and hydrolysis reactions. Lyophilisation of fresh samples provides at least three advantages, namely to facilitate both the storage and conservation of the samples, and to simplify the extraction procedure. In this way, preliminary experiments were focused on the lyophilisation of the samples; spinach and apple were selected as vegetable and fruit sample tests, respectively.

For this purpose, chopped fresh test samples (~100 g) were spiked with the 17 analytes studied at a concentration of 50 ng/g; the resulting mixture was

split in two fractions. One half was manually extracted first with acetone and then with *n*-hexane, according to the standard method [14] and the other half was lyophilised, directly extracted with *n*-hexane, and the standard method followed. Results of these experiments (repeated four times) provided the following conclusions: (i) studied pyrethroids and the synergist were not evaporated during the lyophilisation process; (ii) although the percentages of recovery were similar (~80%) in the two parallel sets, the precision was higher in lyophilised samples than in fresh ones; and (iii) the direct extraction of the lyophilised samples with *n*-hexane provided cleaner extracts than those of fresh ones.

3.2. Solid phase extraction unit

The optimisation of the solid-phase extraction (SPE) system was done by using a standard solution containing 100 ng/ml of each pyrethroid and 1 μg/ml of piperonyl butoxide (according to its lower sensitivity by ECD) in *n*-hexane. Several sorbents (LiChrolut-EN, RP-C_{18}, Florisil, alumina, Bond Elut-CN, Bond Elut-2OH and silica) were assayed using 5 ml of standard solution. The whole eluate was collected in glass vials, evaporated to dryness under N_2 and the residue redissolved in 200 μl of ethyl acetate. Complete retention was only achieved with silica (>95%); the other sorbents provided lower efficiency (viz. 10–40%). Different organic solvents (ethyl acetate, acetonitrile, isopropanol and acetone) were assayed as eluent. Ethyl acetate was the best eluent (~100% elution). A column packed with 50 mg of silica and an eluent volume of 175 μl were selected as optimum. The influence of the sample and eluent flow-rates were examined over the range 0.2–4.0 ml/min. Complete retention and elution were achieved at flow-rates lower than 2.4 and 1.2 ml/min, respectively. A sample and eluent flow-rates of 2.0 and 1.0 ml/min were finally chosen.

In order to attain the highest enrichment factor, the breakthrough volume was evaluated by passing different volumes of standard solutions, containing 100 ng of each pyrethroid and 1 μg of piperonyl butoxide, in *n*-hexane. Sample volumes up to 25 ml can be used with negligible changes in the chromatographic signal. However, a sample volume of 5 ml is enough to reach concentrations lower than the MRLs established for these pesticides, thanks to the high sensitivity of the method. Finally, endosulfan sulphate was selected as internal standard among others compounds as it was quantitatively retained on the silica column and eluted with ethyl acetate; it was added directly to the standards or samples, at concentration of 5 ng/ml.

To ensure the applicability of the optimised SPE unit to real samples, 0.5 g of lyophilised test samples (spinach and apple) were extracted with 10 ml of *n*-hexane for 10 min. The yellowish extracts were spiked with 100 ng of each pyrethroid (1 μg of piperonyl butoxide) and a volume of 5 ml was aspirated into the SPE system. The peaks corresponding to target compounds were correctly identified in both chromatograms against those corresponding to sample matrices, without overlapping. Therefore, the proposed system can be applied to the determination of these pesticides in agricultural samples.

3.3. Linearity and precision

Calibration graphs were obtained by using aliquots of 5 ml of *n*-hexane containing each pesticide at known concentrations (1–200 ng/ml for pyrethroids and 50–1500 ng/ml for piperonyl butoxide). In the case of mixture of isomers, the global analytical signal was obtained by summing the peak areas of all isomers. Figures of merit are listed in Table 1. The precision of the method as relative standard deviation (RSD, $n=20$) was acceptable for all pesticides.

3.4. Screening and determination of pyrethroids in agricultural samples

Prior to the screening of agricultural samples, the *n*-hexane volume and the extraction time were optimised. For this purpose, several amount of 1 g of lyophilised test samples (fortified with variable amounts of pesticides depending on the extractant volume) were extracted with 15, 25 and 50 ml of *n*-hexane and the mixture was mechanically shaken for different times (5–20 min). In all cases, 5 ml of the extract was introduced into the SPE system. The influence of the volume of extractant was negligible and the optimum extraction time was 10 min.

A total of 100 agricultural samples of 14 different

Table 1
Analytical figures of merit of the proposed method

Compound	Sensitivity[a] (10^{-2})	Linear range (ng/ml)	Limit of detection (ng/ml)	RSD (%)	m/z[b]
Piperonyl butoxide	0.5	50–1500	25	4.4	149, **176**, *338*
Bifenthrin	16.5	1–200	0.1	5.3	152, 165, **18**
Fenpropathrin	17.9	1–200	0.1	5.0	**97**, 181, *349*
λ-Cyhalothrin	22.9	1–200	0.1	3.3	141, **181**, 209
Permethrin	5.6	2–200	0.8	6.2	163, **183**, *390*
Cyfluthrin	28.8	1–200	0.4	4.7	**77**, 163, 227
β-Cyfluthrin	19.2	1–200	0.2	4.9	**77**, 163, 227
Cypermethrin	14.0	1–200	0.4	3.8	77, 181, **209**
α-Cypermethrin	21.2	1–200	0.1	3.1	77, 181, **209**
Fenvalerate	18.0	1–200	0.2	5.7	**169**, 181, *419*
Deltamethrin	14.3	1–200	0.2	6.3	**181**, 209, 253

[a] Relative area (analyte/internal standard peak area ratio) ng/ml; sample volume, 5 ml.
[b] m/z values in italics are M^+ ions; those in bold face correspond to the base peak.

types (namely: spinach, chard, tomato, green pepper, potato, cauliflower, mushroom, strawberry, apple, pear, orange, kiwi, peach and plum) purchased at various local markets were analysed following the proposed method. Initially, 0.1 g of lyophilised sample was weighed and analysed, and when negative results were obtained, the sample amount was increased to 1 g: in all instances, quantitation was done by ECD. Positive findings were confirmed by MS, using 2 g of lyophilised sample with 30 ml of extractant and aspirating 25 ml of extract into the SPE unit. As can be seen in Table 2, only eight samples were found to contain pyrethroids at detectable levels and in all cases the concentrations found were lower than the established MRLs. By way of example, Fig. 2 shows the chromatograms for strawberry, spinach and apple samples. In all cases, the identification of pyrethroids was done by comparing the mass spectrum for the corresponding peak with that in the pesticide library. Spectral comparisons resulted in coincidence above 85%.

Finally, in order to assess the potential of the proposed method, 14 uncontaminated agricultural samples, including those listed above, were spiked at three different levels. Fortification process was carried out as follows: 2 ml of acetone containing 1–5 μg of each pyrethroid (10–50 μg of piperonyl butoxide) was added to 50 g of the blended commodity, slightly shaken and left to stand for ~20 min for acetone evaporation. Samples were then frozen prior to lyophilisation. Each sample was spiked three times and analysed in duplicate ($n=6$). Tables 3 and 4 list the average recovery values obtained for each analyte spiked to the seven vegetable and seven fruit

Table 2
Summary of the pyrethroids found in agricultural samples (±SD, $n=6$)

Sample	Water (% w/w)	Pyrethroid found	Concentration (ng/g)[a]	MRL[ab] (μg/g)
Spinach	90	Cypermethrin	420±20	0.50
Chard	92	Cypermethrin	90±5	0.50
Strawberry	91	λ-Cyhalothrin	24±2	0.02
Pear	82	λ-Cyhalothrin	55±3	0.10
Apple	83	Permethrin	170±12	1.00
Green pepper	91	Bifenthrin	96±7	0.20
Tomato	93	Fenvalerate	650±40	1.00
Orange	81	Bifenthrin	85±5	0.10

[a] Amount per g of fresh sample.
[b] Established by the European Union.

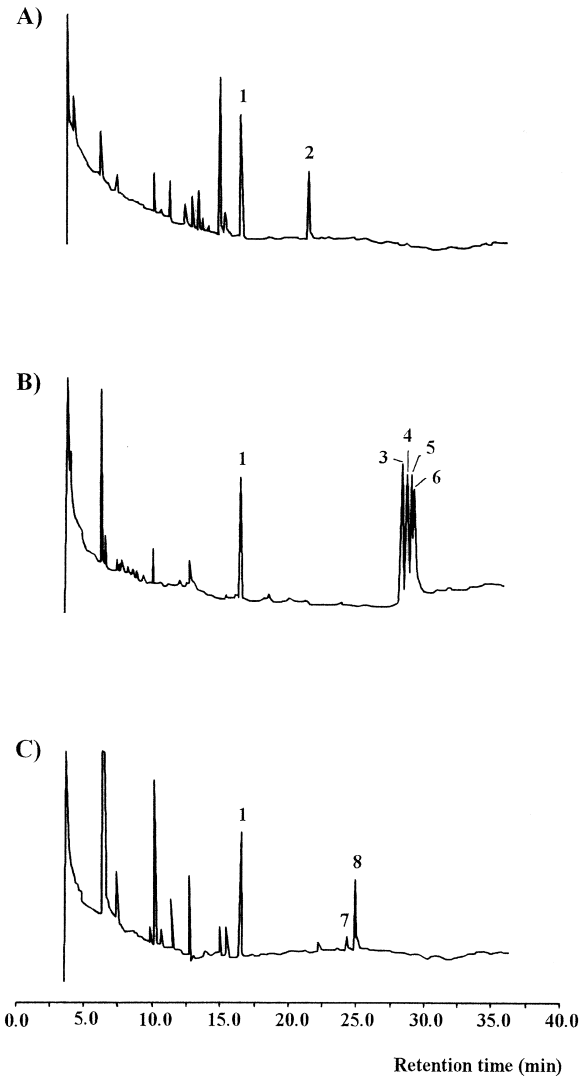

Fig. 2. GC–ECD chromatograms for (A) 5 g of strawberry, (B) 2.5 g of spinach and (C) 2.5 g of apple. Peaks: 1, internal standard; 2, λ-cyhalothrin; 3, cypermethrin I; 4, cypermethrin III; 5, cypermethrin II; 6, cypermethrin IV; 7, permethrin *cis*; 8, permethrin *trans*.

samples studied at the three spiked concentrations (average results of seven samples and each sample analysed six times, $n=42$). From the results obtained, several conclusions can be made, namely: (i) average recoveries increased as the amount spiked increased; (ii) average recovery values were slightly higher for vegetables than for fruits (especially for

Table 3
Average recovery (±SD) of spiked pyrethroids from the seven vegetable samples tested[a]

Compound	20 ng/g[b]	40 ng/g[b]	100 ng/g[b]
Piperonyl butoxide[c]	87±2	91±2	96±4
Bifenthrin	67±3	69±4	73±5
Fenpropathrin	86±3	94±3	98±4
λ-Cyhalothrin	87±6	95±4	102±5
Permethrin	83±2	87±3	93±6
Cyfluthrin	91±7	93±5	96±2
β-Cyfluthrin	87±1	92±3	96±4
Cypermethrin	91±6	96±6	99±7
α-Cypermethrin	87±4	90±4	97±3
Fenvalerate	86±4	90±4	94±2
Deltamethrin	75±2	77±5	84±4

[a] For details, see text.
[b] Concentration spiked.
[c] Spiked level was ten times higher than for pyrethroids.

permethrin and β-cyfluthrin); (iii) bifenthrin and deltamethrin provided the lowest recoveries in all the samples studied (~66–87%), probably as consequence of their higher degradation during sample treatment by interaction with food fluids. Among the samples studied, spinach for vegetables and strawberry for fruits provided recovery values that fitted the average values given in Tables 3 and 4, respectively, and can therefore be used as model samples. Fig. 3 shows the chromatograms for an unfortified and a fortified tomato sample. The efficiency of the clean-up step is also shown in the upper part of this

Table 4
Average recovery (±SD) of spiked pyrethroids from the seven fruit samples tested[a]

Compound	20 ng/g[b]	40 ng/g[b]	100 ng/g[b]
Piperonyl butoxide[c]	85±6	93±4	96±2
Bifenthrin	66±2	72±6	74±5
Fenpropathrin	85±2	95±4	99±4
λ-Cyhalothrin	91±4	97±6	101±4
Permethrin	86±2	92±5	100±5
Cyfluthrin	88±4	95±4	99±4
β-Cyfluthrin	91±6	95±4	99±4
Cypermethrin	90±7	94±3	98±4
α-Cypermethrin	87±4	91±2	97±2
Fenvalerate	84±6	91±4	96±3
Deltamethrin	76±5	82±6	87±5

[a] For details, see text.
[b] Concentration spiked.
[c] Spiked level was ten times higher than those pyrethroids.

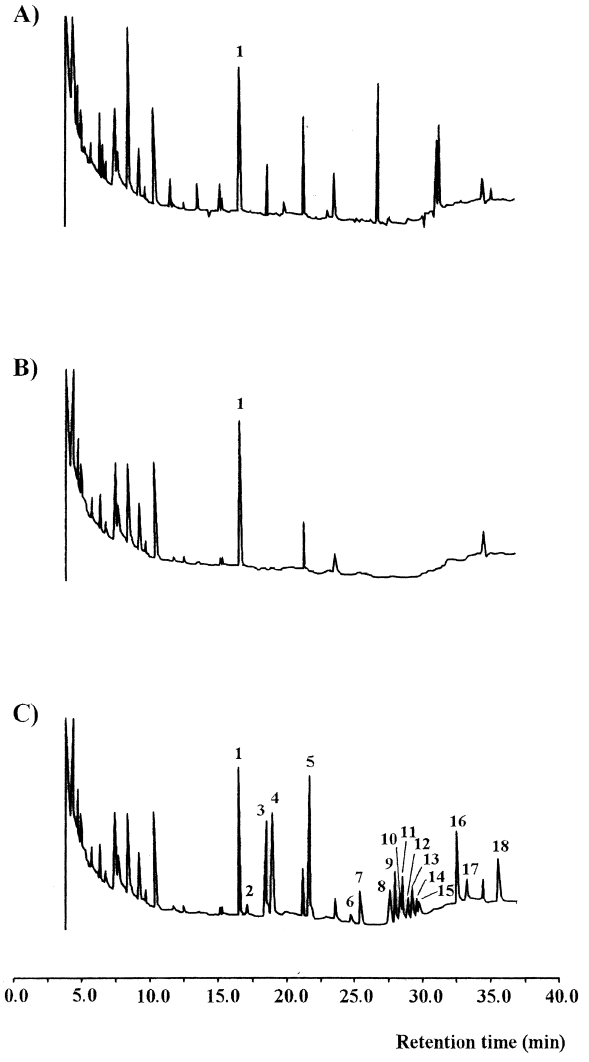

Fig. 3. GC–ECD chromatograms for a sample of tomato (4 g) unfortified without (A) and with (B) clean-up step and fortified (C) with 40 ng/g of each pyrethroid and 400 ng/g of piperonyl butoxide. Peaks: 1, internal standard; 2, piperonyl butoxide; 3, bifenthrin; 4, fenpropathrin; 5, λ-cyhalothrin; 6, permethrin *cis*; 7, permethrin *trans*; 8, cyfluthrin I; 9, cyfluthrin III; 10, cyfluthrin II; 11, cyfluthrin IV; 12, cypermethrin I; 13, cypermethrin III; 14, cypermethrin II; 15, cypermethrin IV; 16, fenvalerate *cis*; 17, fenvalerate *trans*; 18, deltamethrin.

figure. Few peaks from the matrix appear in the chromatograms, the majority of them located at the beginning of the chromatogram, before the internal standard, so, they do not interfere with analyte determination.

4. Conclusions

The proposed method is simple and sensitive enough for application to agricultural samples containing the analytes at concentrations lower than the MRLs. Its most salient advantage over conventional methods is that it requires a single manual extraction with an organic solvent; the following steps corresponding to preconcentration, clean-up and elution are carried out in an automatic way, using an extraordinary simple flow injection configuration. The simplicity of the method developed can be ascribed to sample lyophilisation which minimised the presence of natural pigments as well as other concomitants in the final extract. Although the lyophilisation of the agricultural samples is the most time-consuming step, it allows simultaneous processing of a large number of samples.

Acknowledgements

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