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Clean-up of aqueous acetone vegetable extracts by solid-matrix partition for pyrethroid residue determination by gas chromatography–electron-capture detection

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Abstract

Disposable, ready-to-use cartridges filled with macroporous diatomaceous material are used to carry out a partition clean-up that, in a single step, is capable of transferring pesticide residues from aqueous acetone extracts into light petroleum–dichloromethane (75:25, v/v). This procedure takes the place of some functions (such as separatory-funnel partition, drying over anhydrous sodium sulphate and partial adsorption clean-up) usually performed by separate steps in classical schemes. Fourteen pyrethroid pesticides, including tefluthrin, tetramethrin, cyphenothrin, cyfluthrin, flucythrinate, τ-fluvalinate, deltamethrin, bioallethrin, fenpropathrin, λ-cyhalothrin, permethrin, α-cypermethrin, esfenvalerate and tralomethrin were determined using the described procedure with satisfactory recoveries for most of them, at spiking levels ranging from 0.08 to 0.82 mg/kg for the different compounds. Crops subjected to the described procedure included strawberry, apple, and orange gave extracts containing a mass of co-extractives that was between 5 and 30 mg. Compared with classical schemes, the described procedure is simple, less labour intensive, allows parallel handling of several extracts and does not require the preparation and maintenance of equipment. Troublesome emulsions such as those frequently observed in separation funnel partitioning do not occur.

Keywords: Vegetables; Fruits; Food analysis; Extraction methods; Pyrethroids; Pesticides

1. Introduction

Synthethic pyrethroids are increasingly used as insecticides on many crops, due to some interesting properties, such as effectiveness at low doses, low environmental persistence, easy biodegradation and low mammalian toxicity.

As pyrethroids are relatively non-polar compounds, general multiresidue methodology for non-fatty foods is applicable [1–3] for the determination of their residues in vegetables. Polar, water-miscible solvents, such as acetone, acetonitrile or methanol, are the most frequently used solvents for the extraction of pesticide residues from vegetable samples in multiresidue procedures (see Ref. [4] and references cited therein).

With these solvents, pesticide residues are usually separated from the crude aqueous solvent extract by dilution with a salt solution and multiple separatory-funnel partitions into dichloromethane to remove unwanted hydrophilic co-extractives. Under these conditions, a wide range of both polar and non-polar pesticides, including pyrethroids (PYR) can be recovered [1–3].

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The dichloromethane extract is subjected to clean-up based on one or a combination of basic clean-up steps, such as size-exclusion chromatography (SEC) and/or adsorption clean-up on Florisil, silica gel, deactivated alumina, charcoal in a mixture with magnesia and diatomaceous earth, or Florisil (see Ref. [5] and references therein). Also, some papers specifically devoted to the determination of PYR pesticides [5–7] follow the same scheme.

Most of these procedures share the same drawbacks, including (i) large volume of solvents for extraction, partition and clean-up, (ii) time-consuming operations, especially separatory-funnel partition, (iii) the occurrence of troublesome emulsions in the step partition with certain vegetables, the washing and preparation of glassware, the preparation and maintenance of costly apparatus (in the case of SEC) and (iv) most importantly, the number of separate handling operations, which strongly affect the throughput of the residue laboratory.

Some of us published papers [4,8] in which the advantages of the use of solid-phase partition cartridges in the framework of multiresidue methodology based on acetone extraction was demonstrated as a substitute for separatory-funnel partition and low-activity adsorption clean-up.

As pyrethroids are an important class of pesticides to be analyzed, we deemed it useful to study the applicability of our procedure to cover pyrethroids, so that it can be enlarged to become the core of a multiresidue, multiclass methodology.

2. Experimental

2.1. Reagents

Analytical-reagent-grade light petroleum (b.p. 40–60°C), dichloromethane and acetone were redistilled from an all-glass apparatus.

Ready-to-use Extrelut-20 cartridges (code no. 11737) were obtained from Merck (Darmstadt, Germany) and used with a 30×0.70 mm Luer-lock needle as the flow restrictor.

Pesticide reference standards from the collection in this laboratory were kindly supplied by the main manufacturer of pesticides and were >99% pure.

2.2. Apparatus

The GC analyses of pyrethroids were carried out on a Hewlett-Packard Model 5890 gas chromatograph with electron-capture detection (ECD). A wide-bore, fused-silica column (HP 50+; cross-linked 50% phenyl–50% methylsilicone; 15 m×0.53 mm, 1 μm film thickness) was used. The gas flow-rates were carrier gas (helium) 10 ml/min, split vent, 9 ml/min and septum purge vent, 1 ml/min, with the column head pressure set at 10.5 kPa and the auxiliary gas to the detector was nitrogen at 60 ml/min. The column oven temperature programme was: 50°C (2 min), 10°C/min to 180°C, then 5°C/min to 270°C and finally at 270°C (20 min), with an overall run time of 53 min. The split–splitless injector, equipped with a bottom-tapered glass liner, was operated in splitless mode with a purge-off time of 60 s; its temperature was set at 240°C. The detector temperature was set at 300°C.

A source of pure nitrogen, capable of delivering gas at a flow-rate of 2 l/min, measured with a rotameter, was used.

Hobart Food Cutter was used to prepare samples for the extraction.

The homogenizer, an Ultra Turrax T 25, IKA, Janke and Kunkel, with an S25 dispersing tool, was obtained through Tecnochimica Moderna (Rome, Italy).

Rotary evaporator (t=40°C, reduced pressure).

2.3. Preparation of analytical sample

Samples of fruits and vegetables were cut in quarters or in coarse pieces and fed to the Hobart Food Cutter. The machines were operated for 2 min and, at the end of operation, the contents of the homogenizing vessel were thoroughly hand mixed using a fork before taking the aliquots for the analytical procedure.

2.4. Analytical procedure

Prepare aqueous acetone extracts of fruits and vegetables by homogenizing 50 g of the prepared analytical sample together with 100 ml (i.e., a solvent to crop ratio of 2:1, ml:g) of acetone in suitable tubes with the Ultra Turrax T 25 apparatus

at ca. 9500 rpm for 3 min. Add 5 g of Celite and mix.

Filter (using a water-jet vacuum pump) through a Schleicher and Schuell, 589 black ribbon paper disk, held on a glass, slotted-sieve Buchner funnel (70 mm I.D.) and collect the eluate in a 250-ml graduated cylinder.

Wash the cake on the filter and the homogenizing tubes with acetone and use the washings to bring the total volume to 200 ml.

Take an aliquot containing 20 ml of the extract (equivalent to 5.0 g of crop) and transfer it to the top of an Extrelut-20 cartridge. Allow the liquid to drain and wait 10 min to obtain an even distribution on the filling material. Pass nitrogen at a flow-rate of 2 l/min through the column, from bottom to top, for 30 min.

Disconnect the Extrelut-20 column from the gas line, attach a 30×0.70 mm I.D. Luer-lock needle (supplied with the cartridge) to the column outlet as a flow restrictor and elute the column with four 20 ml portions of light petroleum–dichloromethane, (75:25, v/v).

Collect the eluates and concentrate them to a small volume using the rotary evaporator, then to dryness by manually rotating the collecting flask.

For some samples, use adsorption chromatography on Florisil as a further clean-up step.

Prepare a 2.50-g activated Florisil column in a glass column (300×10 mm I.D. with a PTFE stopcock) that is half filled with light petroleum and with a cotton plug at the bottom. Let the Florisil settle and top it with a 1–1.5 cm layer of anhydrous sodium sulphate. Drain and discard the light petroleum until the level reaches that of the sodium sulphate layer. Transfer the sample extract (dissolved in 1 ml of hexane) and use further 3×1 ml portions to wash the flask. Elute the column with a single 80 ml fraction of *n*-hexane–benzene–ethyl acetate (171:19:10, v/v/v) at a flow-rate of 2–3 ml/min. Collect the eluate and concentrate it to a small volume using the rotary evaporator, then to dryness by manually rotating the flask.

Quantitation was carried out by the internal standard technique with a single level calibration. For quantitation of pyrethroids in the differently spiked samples, the final sample extract is redissolved in a suitable volume of internal standard (PCB 153: 2,2′,4,4′,5,5′-hexachlorobiphenyl) so that the concentration of each pyrethroid at any spiking level is comparable to that of pyrethroids in standard mixtures A and B. Under these conditions, problems arising from possible lack of linearity of the electron capture detector are circumvented.

3. Results and discussion

As discussed in the Section 1, liquid–liquid partition is used in multiresidue methods based on hydrophilic solvent extraction to remove water and water-soluble co-extractives and to bring the residues into a low-boiling, medium polarity solvent that is amenable to subsequent clean-up steps. However liquid–liquid partition is a time-consuming operation and we reported on the advantages of carrying out the same operation on solid-phase, ready to use, disposable cartridges filled with a macroporous diatomaceous earth, which is used to hold one of the liquid phases (the crude aqueous acetone extract) while the other (the partition solvent) is simply poured in portions onto the cartridge and allowed to drain. This type of cartridge is commercially available from different manufacturers. We used Extrelut-20 cartridges that can hold ca. 20 ml of crude aqueous acetone extract, leaving ca. 1 cm of the bed at the bottom unwetted. On the basis of our previous experience with Extrelut-20 [4,8], under the conditions adopted, no pretreatment of Extrelut-20 cartridges is necessary to ensure good lot-by-lot repeatability.

Before running the eluting mixture through the column, acetone is partially removed with an upward stream of nitrogen. This reduces the acetone in the partition solvent, thus preventing the carryover of water and, by reducing the eluting strength of the draining mixture, allows a partial clean-up by adsorption.

With different combinations of flow/time and eluting mixture strength parameters, the recovery of compounds of different polarity can be modulated. For instance 2 l/min×30 min and light petroleum was suitable for eluting non-polar organophosphate pesticides, while 2 l/min×30 min and a light petroleum–dichloromethane (75:25, v/v) mixture were used to elute dimethoate [8]. A range of more

polar compounds, such as fungicides [4], can also be eluted with dichloromethane alone (1 l/min×20 min) by leaving more acetone on the cartridge and, as a consequence, in the eluate.

One is interested in keeping the "strength" of the system, i.e. the amount of acetone and the polarity of the eluting solvent as low as possible, to obtain a cleaner extract. As pyrethroid pesticides are relatively non-polar compounds, like the majority of OP pesticides, in preliminary experiments (see Table 1) we tried conditions similar to those used for OP pesticides, that is, nitrogen (2 l/min×30 min) and 4×20 ml portions of either light petroleum or light petroleum–dichloromethane (75:25, v/v). The results in Table 1 were obtained by loading aqueous acetone solutions containing 0.4–0.8 μg of PYR pesticides (a "virtual" 0.1 mg/kg spiking level for a 5-g sample). It appears that the light petroleum–dichloromethane (75:25, v/v) mixture can recover a little bit more of difficult compounds, such as fluvalinate and esfenvalerate. Therefore, that mixture was used in subsequent tests.

Fourteen PYR pesticides were taken into consideration. As not all of them could be separated in a single run under the GC conditions adopted, we prepared two standard mixtures (A and B), each composed of those pesticides that could be separated in a single run.

Indeed, two pairs out of the fourteen pyrethroid pesticides considered, namely tetramethrin and cyhalothrin, cypermethrin and flucythrinate, were not separated under the GC conditions adopted, while tralomethrin and deltamethrin appear at the same retention time, because tralomethrin is converted into deltamethrin at the high temperature present in the injector port, as we proved by GC–MS examination. As is normal practice in multiresidue methodology, further separation and/or identification techniques should be used to assign the identity of tentatively identified contaminants in extracts from real samples with incurred residues. In Table 2, we have reported the concentration of solutions for standard mixture A and standard mixture B, used for GC–ECD quantitation and for spiking vegetable samples, along with the corresponding spiking levels obtained by adding 0.4, 0.8 and 2.0 ml of the spiking solution to 50 g vegetable samples.

Recovery experiments from vegetables have been carried out with orange at spiking level 1, and with strawberries at spiking levels 2 and 3 (see Table 3),

Table 1
Average recovery (%) of fourteen pyrethroid pesticides from aqueous acetone solutions loaded onto Extrelut-20 cartridges, eluted with two different eluting solvents

Pesticide	Added (μg)	Mean (n=6) recovery (%), S.D., CV%					
		Light petroleum			Light petroleum–dichloromethane (75:25, v/v)		
Mix A							
Tefluthrin	0.49	108	2.4	2.2	110	2.5	2.3
Tetramethrin	0.82	97	1.8	1.8	102	0.9	0.9
Cyphenothrin	0.51	105	1.1	1.1	108	4.5	4.2
Cyfluthrin	0.49	98	3.8	3.9	103	3.3	3.2
Flucythrinate	0.40	97	2.5	2.6	105	2.7	2.6
Fluvalinate	0.41	60	5.0	8.3	79	2.0	2.5
Deltamethrin	0.40	79	2.6	3.3	86	3.1	3.7
Mix B							
Bioallethrin	0.42	100	2.4	2.4	106	0.9	0.8
Fenpropathrin	0.40	103	1.0	1.0	98	1.6	1.6
λ-Cyhalothrin	0.42	64	5.7	8.9	79	3.2	4.0
Permethrin	0.40	105	2.3	2.2	106	4.2	4.0
Cypermethrin	0.41	98	2.1	2.2	108	1.1	1.0
Esfenvalerate	0.40	58	1.1	1.9	68	5.4	7.9
Tralomethrin	0.42	81	2.5	3.1	86	4.1	4.8

Nitrogen, 2 l/min×30 min; 4×20 ml.

Table 2
Composition of standard mixtures A and B, consisting of fourteen pyrethroid pesticides, used for either GC–ECD determination or for spiking vegetable samples and the corresponding spiking levels obtained by adding 0.4, 0.8 and 2.0 ml of spiking solution to 50 g samples of vegetables

Pesticide	Concentration (μg/ml)		Spiking level (mg/kg) by adding ml		
	GC–ECD	Spiking	No. 1 0.4	No. 2 0.8	No. 3 2.0
Mix A					
Tefluthrin	0.25	12.26	0.10	0.20	0.49
PCB 153 (IS)	0.10	–	–	–	–
Tetramethrin	0.41	20.56	0.16	0.33	0.82
Cyphenothrin	0.25	12.65	0.10	0.20	0.51
Cyfluthrin	0.25	12.26	0.10	0.20	0.49
Flucythrinate	0.20	10.07	0.07	0.16	0.40
Fluvalinate	0.20	10.14	0.08	0.16	0.41
Deltamethrin	0.20	10.10	0.08	0.16	0.40
Mix B					
Bioallethrin	0.21	10.60	0.08	0.17	0.42
PCB 153 (I.S.)	0.10	–	–	–	–
Fenpropathrin	0.20	10.10	0.08	0.16	0.40
λ-Cyhalothrin	0.21	10.56	0.08	0.17	0.42
Permethrin	0.20	10.10	0.08	0.16	0.40
Cypermethrin	0.20	10.13	0.08	0.16	0.41
Esfenvalerate	0.20	10.10	0.08	0.16	0.40
Tralomethrin	0.21	10.47	0.08	0.17	0.42

Table 3
Average recovery (%) of fourteen pyrethroid pesticides from oranges and strawberries with the entire described procedure (i.e., acetone extraction, Extrelut-20 partition clean-up, Florisil adsorption clean-up)

Pesticide	Orange			Strawberry					
	Spiking level 1 mg/kg	Recovery (%) ($n=3$)		Spiking level 2 mg/kg	Recovery (%) ($n=3$)		Spiking level 3 mg/kg	Recovery (%) ($n=3$)	
		Mean	S.D.		Mean	S.D.		Mean	S.D.
Mix A									
Tefluthrin	0.10	105	1.3	0.20	106	1.6	0.49	106	2.1
Tetramethrin	0.16	61	10.9	0.33	80	1.3	0.82	72	0.5
Cyphenothrin	0.10	107	13.2	0.20	108	0.5	0.51	108	0.5
Cyfluthrin	0.10	90	5.3	0.20	112	3.5	0.49	122	2.3
Flucythrinate	0.08	90	4.2	0.16	115	2.9	0.40	118	2.9
Fluvalinate	0.08	92	4.9	0.16	109	5.3	0.41	117	4.5
Deltamethrin	0.08	72	3.8	0.16	106	3.2	0.40	116	1.7
Mix B									
Bioallethrin	0.08	92	8.4	0.17	103	0.4	0.42	107	0.5
Fenpropathrin	0.08	123	13.2	0.16	104	0.7	0.40	115	12.0
λ-Cyhalothrin	0.08	93	7.7	0.17	102	2.4	0.42	110	2.2
Permethrin	0.08	92	1.0	0.16	97	4.0	0.40	107	2.4
Cypermethrin	0.08	95	7.4	0.16	106	1.2	0.41	116	3.7
Esfenvalerate	0.08	89	7.0	0.16	103	2.7	0.40	113	4.2
Tralomethrin	0.08	66	5.5	0.17	94	2.6	0.42	113	8.1

both with the entire described procedure (acetone extraction, Extrelut-20 partition clean-up, Florisil adsorption clean-up), and with apples at the three spiking levels (see Table 4). In the latter case, no adsorption clean-up was performed, as the apple extract is sufficiently clean to be analyzed, even at the lowest spiking level. The spiking levels ranged from ca. 0.08 to 0.82 mg/kg for the different compounds. Generally, the recovery values were satisfactory with the exception of some sporadic values, for instance, 66% tralomethrin from orange at spiking level 1; 35% tralomethrin from apples at spiking level 3 and 53% deltamethrin from apples at spiking level 3. No satisfactory explanation can be proposed for these instances, nor for instances where unexpectedly high values were obtained, such as for fenpropathrin from apples at spiking level 2, and others.

The major part of water-soluble, polar coextractives from the vegetable extracts is retained on the Extrelut-20 cartridges. Indeed, some crops, such as apples spiked at level 2, processed by acetone extraction and Extrelut-20 partitioning give sufficiently clean extracts without Florisil adsorption clean-up. Typical GC–ECD chromatograms of standard solutions and of apples spiked at level 2 are displayed in Figs. 1 and 2 for Mix A and Mix B, respectively.

For other crops tested, such as orange, a further clean-up using Florisil adsorption chromatography gives sufficiently clean extracts at the lowest level tested (typical chromatograms of standard solutions and of oranges spiked at level 1 with Mix A and Mix B are displayed in Figs. 3 and 4, respectively).

The main feature of the described procedure is that the column appears to perform several functions in a single step, viz., the removal of water and hydrophilic coextractives, the transfer of pesticide residues into a low-boiling solvent and a low-activity adsorption clean-up.

In classical schemes, the same functions are carried out through separate, time-consuming and labour- and glassware-intensive operations. Unlike the classical separatory-funnel partitioning, with the described procedure, the extraction is rapid, emulsions do not occur and addition of salt solution and drying of the extraction solvent with anhydrous sodium sulphate are not necessary.

In comparison with the described procedure, the procedure reported by Hopper [9] for partitioning of

Table 4
Average recovery (%) of fourteen pyrethroid pesticides from apples with the acetone extraction, followed by an Extrelut-20 partition clean-up

Pesticide	Spiking level 1 mg/kg	Recovery (%) (n=3)		Spiking level 2 mg/kg	Recovery (%) (n=3)		Spiking level 3 (mg/kg)	Recovery (%) (n=3)	
		Mean	S.D.		Mean	S.D.		Mean	S.D.
Mix A									
Tefluthrin	0.10	114	3.8	0.20	116	1.1	0.49	103	2.7
Tetramethrin	0.16	129	1.4	0.33	116	1.2	0.82	101	1.4
Cyphenothrin	0.10	104	1.3	0.20	109	1.3	0.51	100	0.7
Cyfluthrin	0.10	107	8.1	0.20	126	1.9	0.49	106	1.6
Flucythrinate	0.08	111	4.8	0.16	124	0.4	0.40	106	2.1
Fluvalinate	0.08	107	4.1	0.16	125	3.6	0.41	100	2.5
Deltamethrin	0.08	103	4.4	0.16	122	6.1	0.40	53	4.4
Mix B									
Bioallethrin	0.08	112	8.7	0.17	134	5.5	0.42	105	1.4
Fenpropathrin	0.08	96	0.8	0.16	152	55.2	0.40	97	2.1
λ-Cyhalothrin	0.08	101	17.7	0.17	114	4.7	0.42	108	4.5
Permethrin	0.08	113	6.0	0.16	88	5.5	0.40	97	2.4
Cypermethrin	0.08	101	3.6	0.16	122	6.1	0.41	105	6.7
Esfenvalerate	0.08	100	0.1	0.16	113	4.9	0.40	102	5.9
Tralomethrin	0.08	94	2.6	0.17	95	6.5	0.42	35	20.5

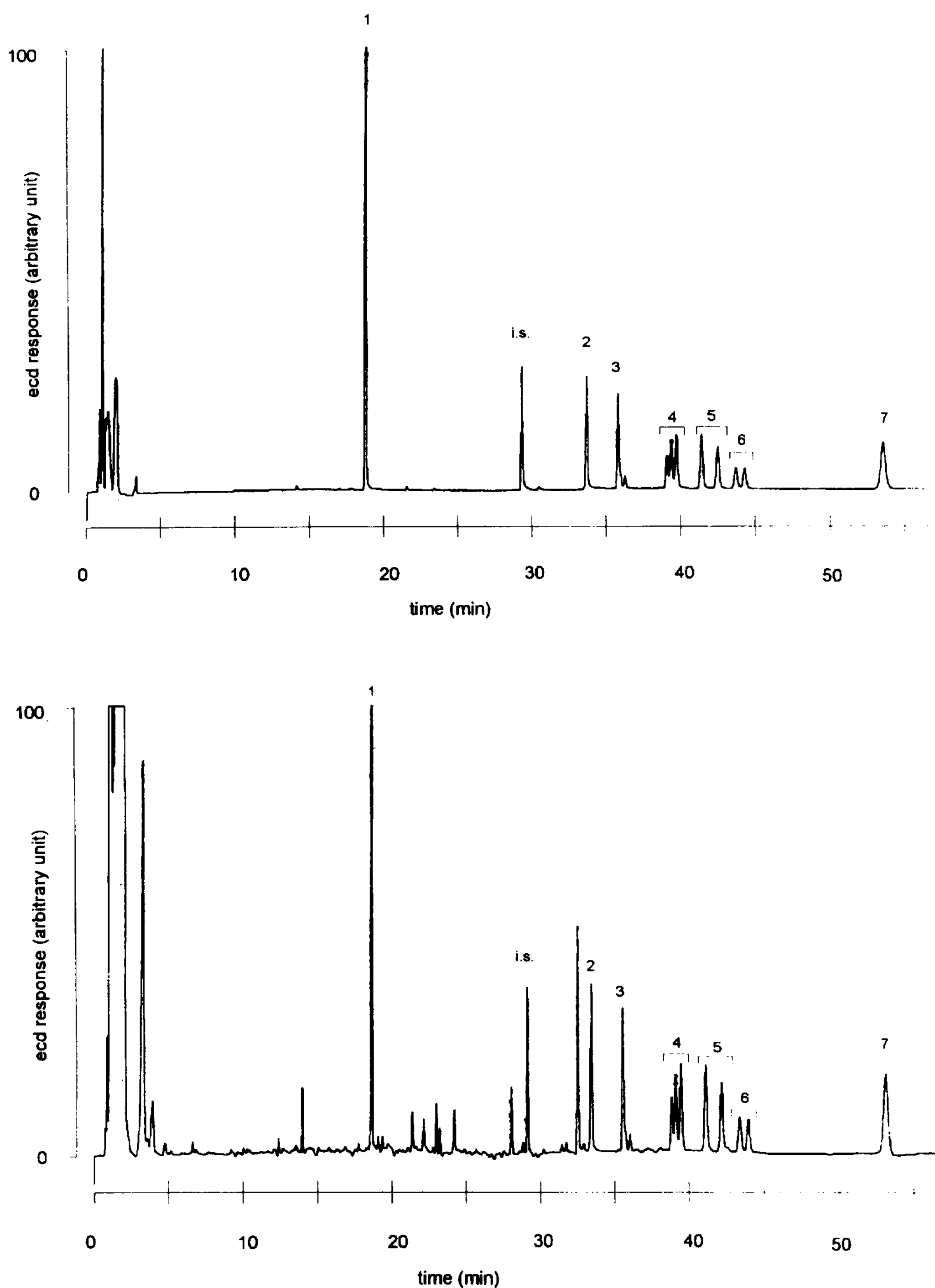

Fig. 1. GC–ECD chromatogram of Mix-A standard solution (top); GC–ECD chromatogram of apples spiked with Mix-A standard solution at level 2 analyzed by acetone extraction and Extrelut-20 partition (without Florisil adsorption cleanup) (bottom). 1=Tefluthrin t_R=18.43; IS PCB 153 t_R=28.96; 2=tetramethrin t_R=33.32; 3=cyphenothrin t_R=35.44; 4=cyfluthrin t_R=38.36,39.00,39.39; 5=flucythrinate t_R= 41.05,42.08; 6=fluvalinate t_R=43.29,43.88; 7=deltamethrin t_R=53.22

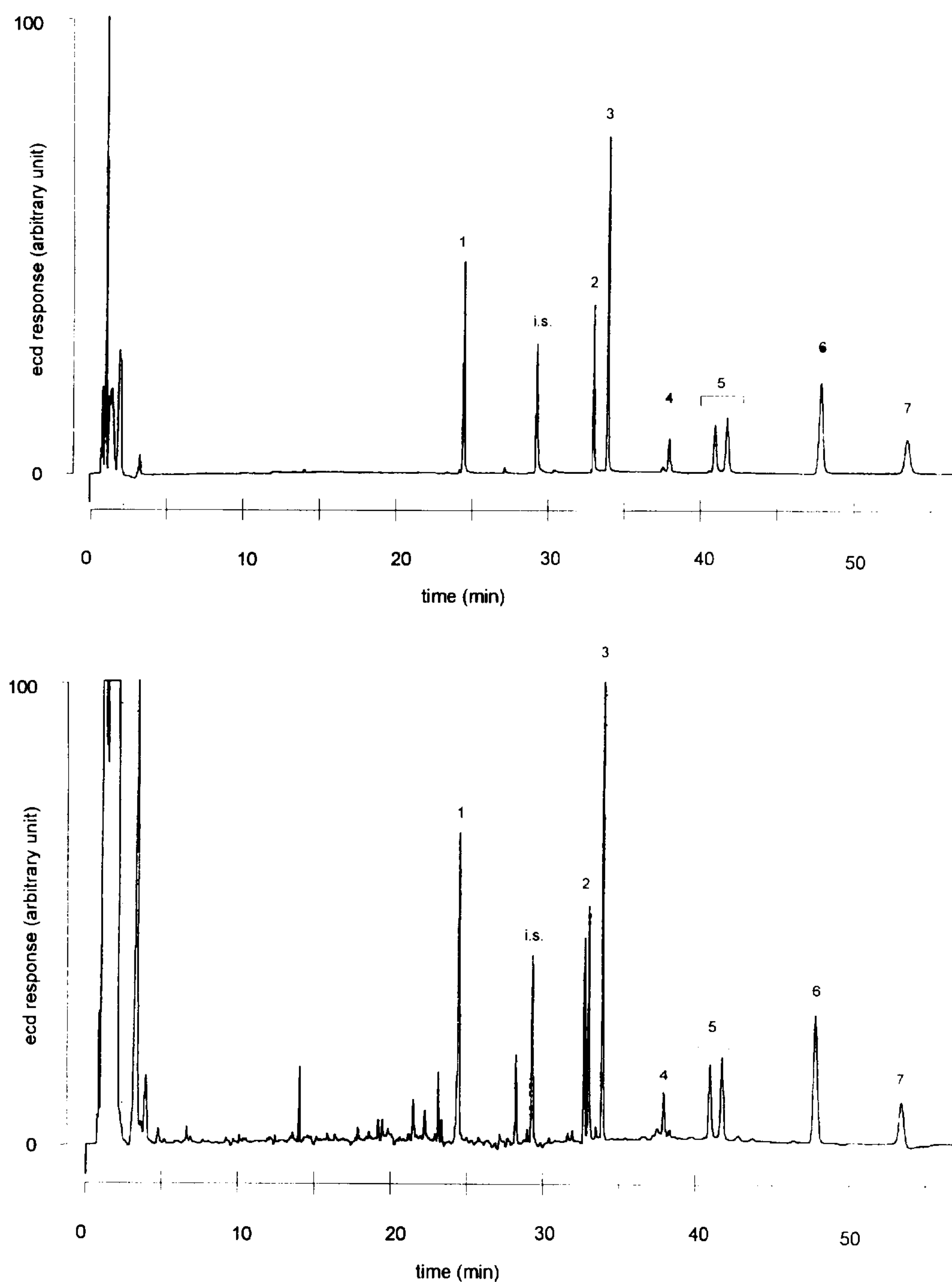

Fig. 2. GC–ECD chromatogram of Mix-B standard solution (top); GC–ECD chromatogram of apples spiked with Mix-B standard solution at level 2 analyzed by acetone extraction and Extrelut-20 partition (without Florisil adsorption cleanup) (bottom). 1=Bioallethrin t_R=24.15; IS PCB 153 t_R=28.96; 2=fenpropathrin; t_R=32.68 3=λ-cyhalothrin t_R=33.60; 4=permethrin t_R=37.64; 5=cypermethrin t_R=40.66,41.44; 6=esfenvalerate t_R=47.50; 7=tralomethrin t_R=53.19.

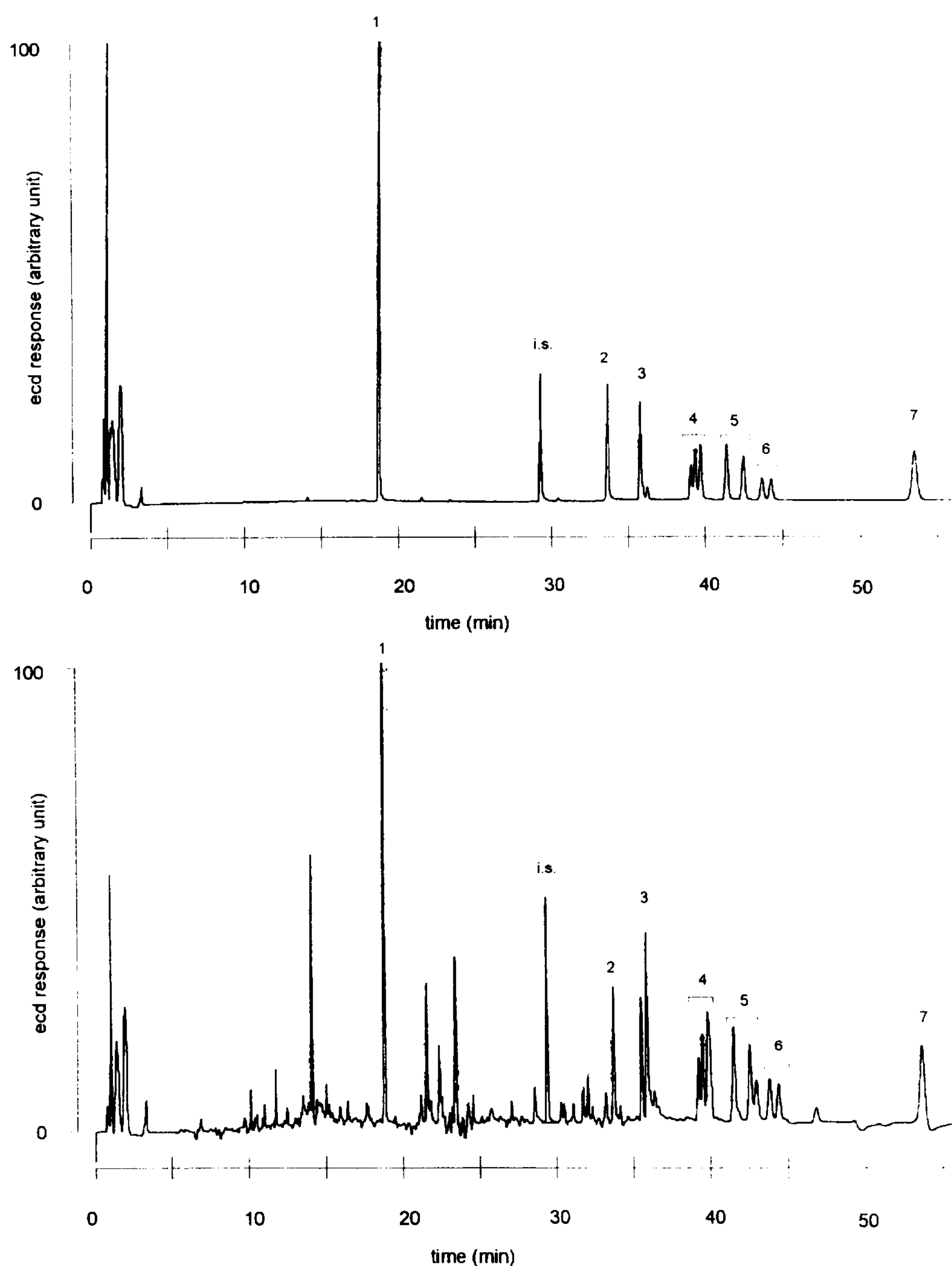

Fig. 3. GC–ECD chromatogram of Mix-A standard solution (top); GC–ECD chromatogram of oranges spiked with Mix-A standard solution at level 1 analyzed by acetone extraction, Extrelut-20 partition and Florisil adsorption cleanup (bottom). 1=Tefluthrin t_R=18.43; IS PCB 153 t_R=28.96; 2=tetramethrin t_R=33.32; 3=cyphenothrin t_R=35.44; 4=cyfluthrin t_R=38.36,39.00,39.39; 5=flucythrinate t_R=41.05,42.08; 6=fluvalinate t_R=43.29,43.88; 7=deltamethrin t_R=53.22.

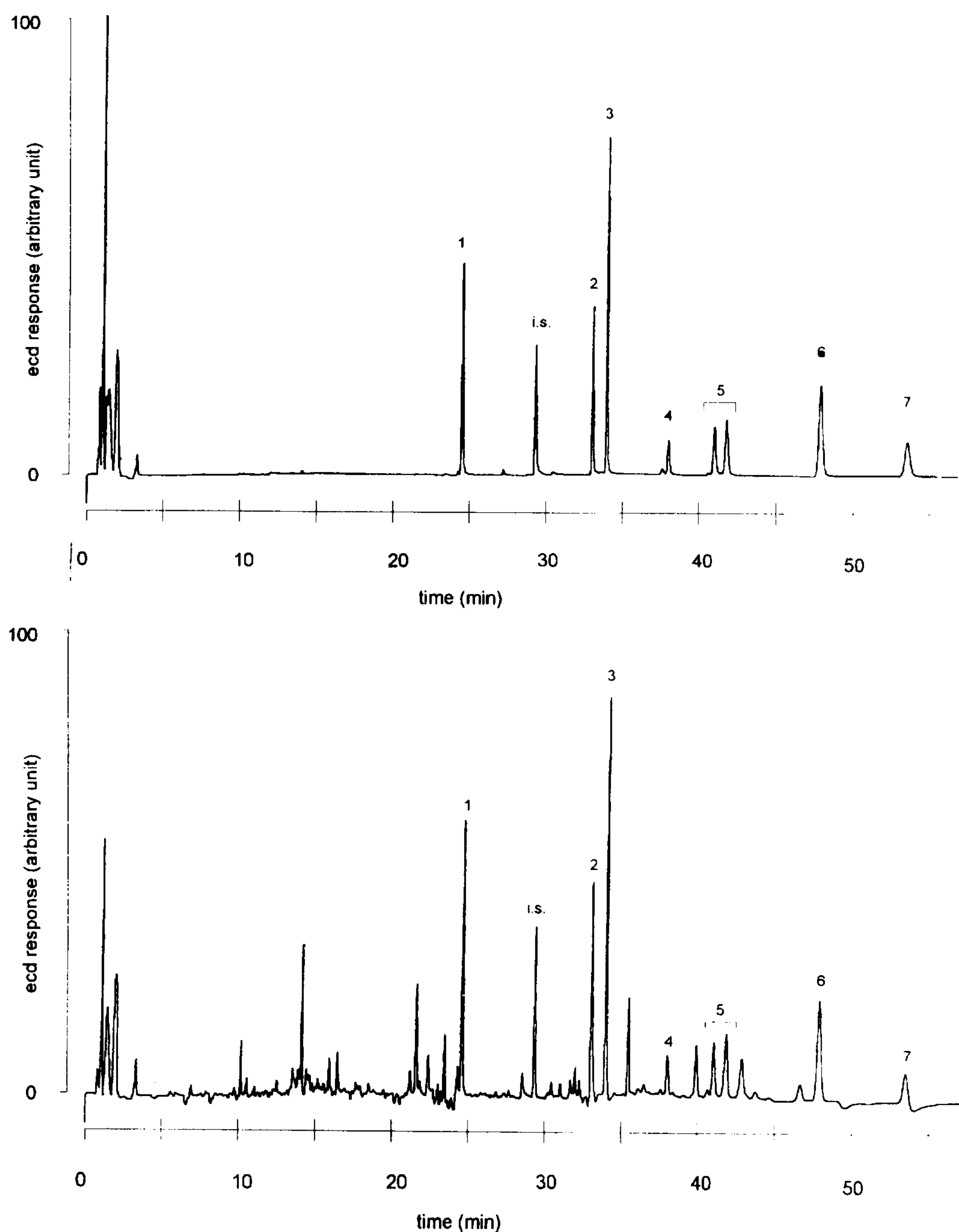

Fig. 4. GC–ECD chromatogram of Mix-B standard solution (top); GC–ECD chromatogram of oranges spiked with Mix-B standard solution at level 1 analyzed by acetone extraction, Extrelut-20 partition and Florisil adsorption cleanup (bottom). 1=Bioallethrin t_R=24.15; IS PCB 153 t_R=28.96; 2=fenpropathrin; t_R=32.68 3=λ-cyhalothrin t_R=33.60; 4=permethrin t_R=37.64; 5=cypermethrin t_R=40.66,41.44; 6= esfenvalerate t_R=47.50; 7=tralomethrin t_R=53.19.

organophosphorous pesticide residues on a "hydromatrix" partition column requires very large volumes of solvents and reagents to condition the column prior to use and appears to be a lengthy procedure. Compared with instrumental clean-up techniques (e.g. SEC and sweep co-distillation), the described procedure is very simple, rapid and inexpensive and does not require the preparation and maintenance of costly apparatus or skilled operators.

Although methods have been reported for both multiresidue methods [10,11] and methods specifically proposed for pyrethroids [12], in which matrix solid-phase dispersion (MSPD) extraction is used for simultaneous extraction and clean-up, at present we do not rely on this approach because it appears that efficient extraction depends on a critical ratio between crops (water) and adsorption material, especially with Florisil-based methods, and, furthermore, they have been set up to work with reduced test portions (10 g) without any indication on how to reliably obtain such small test portions from large laboratory samples.

In conclusion, unlike the classical procedures, separation of pyrethroid residues from hydrophilic co-extractives is carried out in a single step on ready-to-use, disposable cartridges filled with a macroporous diatomaceous earth. The essential features of this procedure include the single step, straightforward operation, low-cost disposable items, reduced time and the possibility of parallel handling of several samples.

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