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Determination of cypermethrin, fenvalerate and *cis*- and *trans*-permethrin in soil and groundwater by high-performance liquid chromatography using partial least-squares regression[1]

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Abstract

The partial least-squares (PLS-2) method was applied to the simultaneous determination of the pyrethroids cypermethrin, fenvalerate and *cis*–*trans*-permethrin by HPLC. The PLS-2 method was also applied to the resolution of the ternary mixtures of cypermethrin, fenvalerate and *trans*-permethrin, *cis*-permethrin being determined from a calibration graph. The results obtained were compared and the best solution was applied to determine the four pyrethroids in soil and groundwater samples

Keywords: Water analysis; Environmental analysis; Soil; Partial least-squares regression; Pyrethroids; Pesticides; Cypermethrin; Fenvalerate; Permethrin

1. Introduction

Natural pyrethrins, active constituents of pyrethrum flower extract, have been used to control indoor pest insects since the discovery of their insecticidal activity in the last century [1]. By modifying the structures of natural pyrethrins, many synthetic pyrethroids have been produced with improved physical and chemical properties and greater biological activity. The pyrethroids constitute another group of insecticides in addition to organochlorine, organophosphorus, carbamates and other types. These pyrethroids are now being used worldwide as insecticides in agriculture, forestry, public health and household applications because of their selective insecticidal activity, rapid biotransformation and excretion by the mammalian catabolic system [2–5] and their non-persistence in the environment. Despite the fact that the most recent pyrethroids are also the most stable, they are still photo- and biodegraded considerably faster than the persistent chlorinated insecticides [4,6–8]. However, high toxicity to fish and honey bees is observed for most pyrethroids [5].

Pyrethroids are synthetized, tested, marketed

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and used either as a single, more active isomer or as isomeric mixtures containing two or more different stereoisomers, depending on the number of chiral centers in the molecules and the synthesis route [9]. The commercial products generally consist of a mixture of both optical (1*R*–1*S* or *d*–*l*) and geometric (*cis*–*trans*) isomers. This implies the need for valid analytical methods for enantiomer determination. However, in gas chromatography (GC) and high-performance liquid chromatography (HPLC), it is very difficult to establish simultaneous separation conditions. HPLC, using chiral columns, is currently the foremost technique for this purpose, although chiral detection, derivatization with chiral reagents and gas–liquid chromatography all have a role to play [10–14].

As their range of applications has increased, the need to separate various pyrethroids has arisen, especially for multi-residue analyses. Appreciable levels of pyrethroid residues may occur in food commodities from crops, in foods of animal origin (milk, eggs, meat), in soils, sediments and in surface waters. Methods for the analysis of pyrethroid residues in various matrices usually involve extraction with polar solvents or solid-phase extraction, clean-up by adsorption or gel permeation chromatography and determination by GC with electron-capture [15–22], flame ionization [23,24] or mass spectrometric [25] detection, or HPLC with UV [16], infrared [26] or radiometric [27] detection. These two approaches have been the most often used in the determination of pyrethroid residues in recent years [28]. On the other hand, some applications of supercritical fluid chromatography [29–31], polarographic [32], voltammetric [33], spectrophotometric [34], spectrofluorimetric [35], capillary isotachophoretic [36,37] and immunoassay [38] methods have also been applied to their determination. However, most of these techniques involve time-consuming separation steps.

In previous work [39] we studied several data preprocessing algorithms to determine cypermethrin, fenvalerate and *cis*–*trans*-permethrin by multivariate calibration methods. Mean-centering and the selection of the region of the chromatogram to realize calibration were found to be advantageous. In this paper, we propose the resolution of quaternary mixtures of cypermethrin, fenvalerate and *cis*–*trans*-permethrin by HPLC, without prior separation, using a C_{18} column. Mixture analysis was carried out by application of the multivariate PLS-2 method to the chromatograms obtained at 210 nm. The procedure was applied to the determination of cypermethrin, fenvalerate and *cis*–*trans*-permethrin in groundwater and soil.

2. Experimental

2.1. Apparatus

A Soxhlet battery furnished with 250-ml flasks and their corresponding heating mantles was purchased from Selecta (Spain). A Model 461 rotary vacuum evaporator (Büchi, Flavil, Switzerland) thermostated by water circulation with an A-35 vacuum pump (Eyela, Tokyo, Japan) was used.

2.2. Chemicals and materials

Pesticide standards (Pestanal quality) of cypermethrin and fenvalerate (99%) were obtained from Riedel-de Haën (Seelze, Germany) and that of permethrin (24.6% *cis* and 73.4% *trans*) was supplied by Dr. Ehrenstorfer (Augsburg, Germany). Standard solutions of these compounds were prepared by dissolving the appropriate amounts in acetonitrile (ACN). Gradient-grade ACN and *n*-hexane (Riedel-de Haën) and purified HPLC-grade water provided by a Milli-Q water filtration/purification system from Millipore (Bedford, MA, USA) were used. Anhydrous sodium sulphate was obtained from Panreac (Barcelona, Spain). Sep-Pak C_{18} and C_8 cartridges were supplied by Cromblab (CA, USA).

2.3. HPLC system

A Waters (Milford, MA, USA) Model 990 liquid chromatographic system, equipped with a Model 600E constant-flow pump, a Rheodyne

six-port injection valve with a 20-μl sample loop and a Model 990 UV–visible photodiode-array detector, was used. The detector was also interfaced with an Olvetti PCS-386 personal computer and a Waters plotter. The absorbance (A), wavelength (λ) and time (t) were digitized using Waters Model 991 software, which allows representation and storage of absorption spectra obtained at preset times. An IBM 486-DX microcomputer, provided with a Grams/386 software package and PLSplus V2.1 G [40], was used for treatment of data.

The chromatographic separation was performed on a Hypersil C_{18} column (15 × 0.46 mm I.D.; 5 μm particle size). The mobile phase was ACN–water (85:15, v/v). The solvents were filtered daily through a 0.45-μm cellulose acetate (water) or polytetrafluoethylene (ACN) membrane filter before use and degassed with helium during and before use. Samples of 20 μl were injected at a solvent flow-rate of 1.5 ml min^{-1}. Photometric detection was performed at 210 nm.

2.4. Procedure for analysis of mixtures of cypermethrin, fenvalerate and cis–trans-permethrin

A calibration matrix for cypermethrin, fenvalerate and *cis–trans*-permethrin was performed using a fifteen-sample set in the range 0–10 μg ml^{-1} by the PLS-2 method. Volumes of 20 μl were injected into the chromatographic system and separation was performed on a C_{18} column with ACN–water (85:15, v/v) as the mobile phase at a flow-rate of 1.5 ml min^{-1}. A mean-centering pretreatment of data was applied. The optimized calibration matrix, in the chromatographic region between 150 and 210 s, was used to determine cypermethrin, fenvalerate and *cis–trans*-permethrin in groundwater and in soil samples by the PLS-2 method.

2.5. Procedure for the determination of cypermethrin, fenvalerate and cis–trans-permethrin in groundwater

Double extraction with n-hexane was used. Water samples (500 ml) were shaken with 50 ml of n-hexane for 2 min each. The combined organic phases were dried by passing them through anhydrous Na_2SO_4 and evaporated using a rotary vacuum evaporator. The samples thus concentrated were eluted with 1 ml of ACN and cypermethrin, fenvalerate and *cis–trans*-permethrin were determined as described above.

2.6. Procedure for the determination of cypermethrin, fenvalerate and cis–trans-permethrin in soil

A 10-g amount of ground soil was weighed, spiked with cypermethrin, fenvalerate and *cis–trans*-permethrin and passed through a 55-mesh sieve. The soil sample was placed in an extraction thimble and extracted with n-hexane for 8 h in a Soxhlet extractor at a flow ratio of 10 cycles h^{-1}. The resulting extract was evaporated to dryness using a rotary vacuum evaporator. The residue was dissolved in 10 ml of ACN and the solution was passed through a Sep-Pak C_{18} cartridge preconditioned with 5 ml of ACN. Subsequently, the cartridge was washed with 2 ml of ACN and combined with the previous eluate. The combined eluates were evaporated to 1 ml under a gentle stream of nitrogen and the pesticides were determined as described above.

3. Results and discussion

Fig. 1 shows substantial overlapping of the peaks corresponding to cypermethrin, fenvalerate and *trans*-permethrin whereas *cis*-permethrin is partially resolved ($R = 0.8$) using ACN–water (85:15, v/v) at a flow-rate of 1 ml min^{-1}. The HPLC separation of these analytes was discussed in the accompanying paper [40] and multivariate calibration methods were used to resolve the mixture of the pyrethroids. Several pretreatments of calibration matrix data (mean-centering, selection of chromatogram region, smoothing, baseline correction, averaging and differentiation) were studied, and it was found to be advantageous to apply the first two in order to optimize the calibration matrix. The results obtained for PLS-1, PLS-2 and PCR were similar.

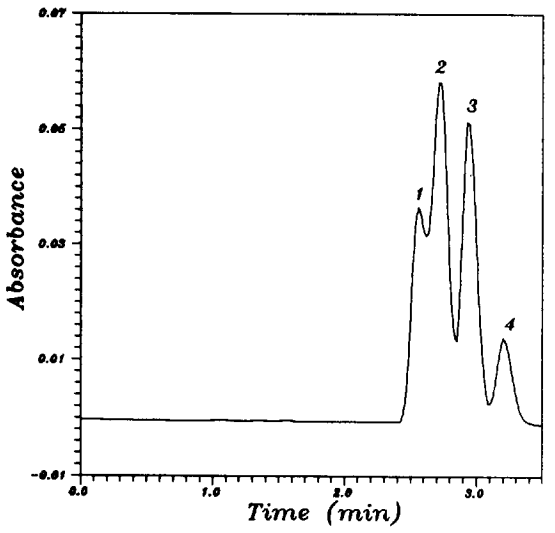

Fig. 1. Chromatogram of the elution profile at 210 nm of (1) cypermethrin (6 μg ml^{-1}), (2) fenvalerate (6 μg ml^{-1}), (3) *trans*-permethrin (4.5 μg ml^{-1}) and (4) *cis*-permethrin (1.5 μg ml^{-1}). Flow-rate, 1.5 ml min^{-1}.

Under the optimum conditions already established, for the preprocessing of the data and using a fifteen-sample training set, we applied the PLS-2 method for the resolution of mixtures containing between 0 and 10 μg ml^{-1} each of cypermethrin, fenvalerate and *cis–trans*-permethrin. In addition, the PLS-2 method was also used for the resolution of a ternary mixture of cypermethrin, fenvalerate and *trans*-permethrin, *cis*-permethrin being determined from a calibration graph. The calibration graph for *cis*-permethrin was established by injecting, in duplicate, aliquots of prepared standards. Table 1 list the straight-line equations obtained, for the concentration interval 0.5–10 μg ml^{-1}, using peak area and peak height as analytical signals.

3.1. Determination of cypermethrin, fenvalerate and cis–trans-permethrin in synthetic mixtures

The proposed PLS-2 method, applied to either the four-component training set or the three-component training set, and the calibration graph used for the determination of *cis*-permethrin allow the resolution of synthetic mixtures. In Table 2 the compositions of the mixtures studied and the results obtained by both strategies are summarized. It can be observed that the results obtained by both approaches are good, but in general those obtained using the four-component training set showed higher recoveries for *cis*-permethrin.

3.2. Optimization of the isolation of cypermethrin, fenvalerate and cis–trans-permethrin in groundwater

The isolation of the pyrethroids from groundwater was tested by solid-phase extraction (SPE) with C_{18} and C_8 cartridges and liquid–liquid extraction (LLE) with *n*-hexane. First, we tried the SPE of these compounds. Samples of 500 ml of groundwater, spiked with 16 μg l^{-1} of cypermethrin, fenvalerate and total permethrin, were passed through Sep-Pak C_{18} and C_8 disposable cartridges at flow-rates of 3–5 ml min^{-1}. The cartridges were previously preconditioned with 5

Table 1
Calibration data for *cis*-permethrin

Signal	Equation[a]	r^2	Standard deviation		Standard error of estimate ($\times 10^4$)
			Slope ($\times 10^5$)	Intercept ($\times 10^4$)	
Peak height	$H = 6.6777 \cdot 10^{-3}\ C - 2.5122 \cdot 10^{-3}$	0.9972	14.40	6.80	14.8
Peak area	$A = 7.6659 \cdot 10^{-4}\ C - 1.2773 \cdot 10^{-4}$	0.9952	16.24	7.70	16.7

[a] C = Concentration of *cis*-permethrin (μg ml^{-1}). The results were obtained from eight experimental points.

Table 2
Recoveries of cypermethrin (Cyp), fenvalerate (Fen) and *cis–trans*-permethrin (Per) in the synthetic mixtures

Added (mg kg^{-1})				Recovery (%)[a]							
Cyp	Fen	*t*-Per	*c*-Per	Cypermethrin		Fenvalerate		*trans*-Permethrin		*cis*-Permethrin	
				1	2	1	2	1	2	1	3
8.0	4.0	3.0	1.0	100.5	121.0	104.2	83.9	99.3	72.5	99.0	111.0
3.0	4.0	3.5	1.2	108.0	116.0	108.0	80.2	97.1	70.0	98.3	109.5
2.0	10.0	3.0	1.0	102.5	104.5	100.0	97.0	98.3	97.3	98.0	96.0
4.0	2.0	7.5	2.5	100.2	102.2	95.7	95.5	99.8	98.8	99.4	94.4
2.0	3.0	4.5	1.5	109.9	114.5	108.0	99.7	106.2	104.4	106.7	93.5
4.0	4.5	1.5	0.5	98.3	97.2	106.0	84.8	106.0	102.7	106.0	110.0
4.0	6.0	6.0	2.0	99.7	93.7	97.0	102.2	98.7	99.3	99.0	94.3
4.0	8.0	4.5	1.5	99.5	98.2	101.9	102.1	100.9	100.4	100.7	101.4
6.0	4.0	6.0	2.0	100.3	101.8	96.0	98.5	107.0	99.8	101.0	96.2
6.0	8.0	3.0	1.0	100.7	102.8	100.4	98.4	99.7	100.0	100.0	105.0
8.0	4.0	4.5	1.5	98.9	100.2	97.8	96.8	100.0	99.6	100.0	98.0
8.0	6.0	3.0	1.0	101.5	101.0	102.5	101.3	96.7	98.0	96.0	94.1

[a] Results obtained by (1) PLS-2 method with the calibration matrix considering four components, (2) PLS-2 method with the calibration matrix considering three components and (3) calibration graph.

ml of ACN followed by 5 ml of ultra-pure water. After the preconcentration step, the cartridges were dried on a vacuum source by passing air through them for 10 min. The samples thus concentrated were eluted with 5 ml of ACN and the pesticides were determined, independently, with an appropriate calibration graph for each one. The results obtained are presented in Table 3. It can be seen that SPE was not adequate. Subsequently, LLE was used. Here, 500-ml groundwater samples, spiked with 16 $\mu g\ l^{-1}$ of cypermethrin, fenvalerate and total permethrin, were shaken with 50 ml of *n*-hexane, as described under Experimental. It was found that all the compounds were removed effectively from their aqueous solutions using LLE.

3.3. Optimization of the isolation of cypermethrin, fenvalerate and cis–trans-permethrin in soil

The isolation of cypermethrin, fenvalerate and *cis–trans*-permethrin from soil was investigated using ultrasonic, electromechanical and Soxhlet extraction methods with *n*-hexane as extractant. Amounts of 10 g of ground, air-dried soil were spiked with 5 mg kg^{-1} of each analyte. Ultrasonic and electromechanical agitation were

Table 3
Recoveries in the preconcentration of 16 $\mu g\ l^{-1}$ of cypermethrin, fenvalerate and *cis–trans*-permethrin from groundwater

Extraction	Adsorbent	Extractant	Recovery (%)[a]			
			Cypermethrin	Fenvalerate	*cis*-Permethrin	*trans*-Permethrin
SPE	C_{18}	–	26.3 (9.6)	29.4 (8.3)	31.6 (8.8)	33.7 (9.1)
	C_8	–	40.0 (8.8)	37.8 (9.5)	36.3 (8.2)	35.9 (8.0)
LLE	–	*n*-Hexane	98.4 (3.8)	95.2 (4.1)	99.6 (4.0)	100.7 (3.6)

[a] The results are averages of three determinations, with R.S.D.s in parentheses.

tested with three 50-ml portions of *n*-hexane and Soxhlet extraction for various times. The extracts were evaporated to dryness and the residues were dissolved in 10 ml of ACN and passed through a Sep-Pak C_{18} cartridge in order to eliminate interferences from the mixture, as other workers have proposed [41]. It was found that the Soxhlet extraction for 8 h was the most adequate way to recover all the analytes (Table 4).

3.4. Applications

3.4.1. Determination of cypermethrin, fenvalerate and cis–trans-permethrin in groundwater

PLS-2 was applied to the determination of cypermetrin, fenvalerate and *cis–trans*-permethrin in groundwater, as described under Experimental, by using the four-component training set. Preconcentration of the pesticides using LLE was carried out prior to their determination. Samples were spiked with cypermethrin at levels between 4 and 20 $\mu g\ ml^{-1}$, with fenvalerate between 6 and 16 $\mu g\ ml^{-1}$, with *trans*-permethrin between 3 and 12 $\mu g\ ml^{-1}$ and with *cis*-permethrin between 1.5 and 4 $\mu g\ ml^{-1}$, and the recoveries were calculated (Table 5). Satisfactory results were found in all instances, with recoveries ranging from 70.2 to 126.0%.

3.4.2. Determination of cypermethrin, fenvalerate and cis–trans-permethrin in soil

The proposed method was applied to the determination of the pesticides in soil. A sample soil (AL-08) was collected from the top 15 cm in a greenhouse in Almería (Spain) after 6 months without agricultural activity. Its characteristics and composition have been described elsewhere [42]. Samples were spiked with cypermethrin at levels between 2 and 4 mg kg^{-1}, with fenvalerate between 1.2 and 3.6 mg lg^{-1}, with *trans*-permethrin between 2.1 and 4.9 mg kg^{-1} and with *cis*-permethrin between 0.7 and 1.6 mg kg^{-1}. Table 6 shows the results obtained by the PLS-2 method, with recoveries ranging from 80.0 to 115.4%. The results confirm the suitability of *n*-hexane to remove the se pesticides from the soil matrix.

4. Conclusions

The partial least-squares (PLS-2) method was successfully applied to the simultaneous determination of cypermethrin, fenvalerate and *cis–trans*-permethrin, without a prior separation step, by HPLC. Better results were obtained by applying the PLS-2 method to a four-component training set. *n*-Hexane has shown to be a good solvent for LLE of the analytes from ground-

Table 4
Recoveries in the isolation of 32 mg kg^{-1} of cypermethrin, fenvalerate and *cis–trans*-permethrin in soil by several extraction methods

Method	Time (h)	Recovery (%)[a]			
		Cypermethrin	Fenvalerate	*cis*-Permethrin	*trans*-Permethrin
Electromechanical extraction	2.0	17.4 (8.3)	14.7 (9.1)	23.2 (9.9)	28.5 (7.5)
	4.0	25.0 (7.0)	18.6 (8.7)	23.9 (9.5)	34.2 (8.1)
Ultrasonic extraction	0.5	25.3 (7.6)	36.8 (7.0)	23.5 (7.9)	16.3 (8.1)
	2.0	12.8 (8.8)	11.9 (9.3)	38.1 (8.8)	18.1 (9.3)
Soxhlet extraction	4.0	85.5 (5.4)	71.4 (5.9)	62.5 (6.3)	61.2 (6.0)
	8.0	92.5 (4.5)	97.1 (4.1)	93.8 (4.9)	102.0 (4.7)

[a] The results are averages of three determinations, with R.S.D.s in parentheses.

Table 5
Recoveries of cypermethrin (Cyp), fenvalerate (Fen), and *cis–trans*-permethrin (Per) in groundwater by the PLS-2 method

Added ($\mu g\ l^{-1}$)				Recovery (%)[a]			
Cyp	Fen	*t*-Per	*c*-Per	Cyp	Fen	*t*-Per	*c*-Per
16.0	12.0	6.0	2.0	97.7 (3.6)	99.2 (3.8)	112.3 (4.1)	113.0 (4.0)
20.0	12.0	6.0	2.0	112.8 (3.1)	101.2 (3.8)	82.7 (4.2)	83.0 (4.2)
10.0	10.0	7.5	2.5	90.4 (4.0)	101.4 (4.1)	85.0 (4.0)	84.9 (4.0)
14.0	6.0	6.0	2.0	93.8 (3.6)	85.7 (4.4)	94.7 (4.1)	95.0 (4.1)
8.0	6.0	6.0	2.0	110.2 (4.2)	100.1 (4.4)	115.2 (4.2)	116.0 (4.1)
4.0	8.0	13.0	4.0	103.0 (4.5)	70.2 (4.2)	103.7 (3.5)	104.7 (3.5)
12.0	6.0	3.0	2.0	105.3 (4.1)	78.3 (4.4)	125.0 (4.7)	126.0 (4.7)
6.0	16.0	4.5	1.5	89.7 (4.3)	93.6 (3.6)	85.8 (4.6)	122.0 (4.6)

[a] The results are averages of three determinations, with R.S.D.s in parentheses.

Table 6
Recoveries of cypermethrin (Cyp), fenvalerate (Fen), and *cis–trans*-permethrin (Per) in soil by the PLS-2 method

Added ($\mu g\ l^{-1}$)				Recovery (%)[a]			
Cyp	Fen	*t*-Per	*c*-Per	Cyp	Fen	*t*-Per	*c*-Per
4.0	3.5	4.9	1.6	85.0 (3.6)	88.6 (3.5)	95.9 (3.4)	93.7 (3.9)
3.3	3.6	2.3	0.7	90.9 (3.8)	86.1 (3.6)	95.7 (3.9)	114.3 (4.3)
3.0	2.5	3.0	1.0	83.3 (4.3)	84.0 (3.9)	83.3 (3.7)	80.0 (4.0)
4.0	3.5	4.9	1.6	85.0 (3.7)	88.6 (3.7)	93.9 (3.5)	93.7 (4.0)
2.0	3.0	2.2	0.8	90.0 (4.4)	80.0 (3.9)	95.5 (4.0)	87.5 (4.6)
3.3	2.4	3.4	1.1	81.8 (4.1)	95.8 (4.2)	85.3 (3.8)	90.9 (4.1)
3.3	1.3	2.5	0.8	100.3 (4.1)	115.4 (4.6)	108.0 (3.9)	112.5 (4.6)
2.0	1.2	2.1	0.7	95.0 (4.3)	108.3 (4.7)	95.2 (4.1)	100.0 (4.6)

[a] The results are averages of three determinations, with R.S.D.s in parentheses.

water and for Soxhlet extraction from soil samples. The method was applied to the determination of cypermethrin, fenvalerate and *cis–trans*-permethrin in groundwater and soil samples with good results.

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