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Multiresidue analysis of insecticides in soil by gas chromatography with electron–capture detection and confirmation by gas chromatography–mass spectrometry☆

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Abstract

A rapid multiresidue method has been developed for the analysis of nine insecticides (organochlorines, pyrethroids and organophosphorus) in soil. The method is based on the sonication extraction of residues from a certain amount of soil placed in a small column, using ethyl acetate. The effect of the residence time of insecticides in soil, the material of the columns used (glass or plastic columns) and the soil moisture content on the recovery of these compounds was also studied. Residues were determined by gas chromatography with electron-capture detection. The average recovery through the method obtained for these compounds varied from 90 to 108% with a relative standard deviation between 1 and 11%. The results of this study pointed out that the recoveries of insecticide residues obtained with plastic or glass columns at different soil moisture content were similar and that the residence of these compounds in soil during several days did not affect their recovery from soil. Confirmation of residue identity was performed by gas chromatography coupled with mass spectrometry.

Keywords: Soil; Environmental analysis; Pesticides

1. Introduction

Horticultural crops may be affected by different pests causing serious damages to plants and consequently important yield reductions. Therefore, insecticides and acaricides are widely used to control pests in these crops. In the application of pesticides one part of the amount used reaches the target while other part is deposited on the soil where it is subjected to different processes that will determine the fate of these agrochemicals. The large number of insecticide residues found in different environmental compartments requires the development of analytical methodologies that allow the simultaneous determination of different pesticides with effective and fast extraction procedures, using minimum clean-up steps.

Analysis of insecticide residues is commonly carried out by gas chromatography (GC) with nitro-

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gen–phosphorus detection (NPD) [1], electron-capture detection (ECD) [2] or coupled with mass spectrometry (MS) [3,4]. In these methods pesticides are mainly extracted from soil matrixes using conventional techniques such as shaking or Soxhlet extraction. Supercritical fluid extraction (SFE) [5–7] and microwave-assisted extraction (MAE) [8,9] are other techniques employed in the last years with successful results. The use of SFE in sample analysis seems to be a good alternative, although optimisation of the operating conditions is still considered a critical step in the development of a SFE extraction method for the routine analysis of real samples [10]. On the other side, the use of microwave-assisted extraction requires special microwave systems. Ultrasonic solvent extraction has also been applied, with good results, to the extraction of soil samples and represents several advantages. Sonication provides a more efficient contact between the solid and the extracting solvent, usually resulting in a greater recovery of the analyte [11]. Extraction by sonication of soil samples placed in small columns has recently been reported as a rapid and sensitive procedure for the simultaneous determination of herbicides in soil [12,13].

The aim of this work was to develop a rapid analytical multiresidue method for the determination in soil of insecticides, based on the sonication extraction of residues from a certain amount of soil placed in small columns and using ethyl acetate as extracting solvent. The effect of the residence time of insecticides in soil was also studied in order to evaluate if the adsorption on the soil colloids has some influence on the pesticide recovery. In addition, the influence of the material of the columns used (glass or plastic columns) was studied because adsorption of some pesticides to different kinds of plastic has been reported [14] and this fact would affect the pesticide recovery. Finally, the effect of soil moisture content on the recovery of these compounds was also examined. The insecticides included in this work (Table 1), belonged to three pesticide groups (organochlorine, pyrethroids and organophosphorus) and were the following: lindane, heptachlor, endosulfan-I, endosulfan-II, endosulfan-sulfate, tetradifon, chlorpyrifos, λ-cyhalothrin and acrinathrin.

2. Experimental

2.1. Materials

2.1.1. Chemicals and solvents

Insecticide standards were obtained from commercial sources: lindane, heptachlor, endosulfan-I, endosulfan-II, endosulfan-sulfate, tetradifon and chlorpyrifos from Reidel-de Häen (Germany), λ-cyhalothrin from Zeltia Agraria (Spain) and acrinathrin from Roussel Uclaf (USA). Ethyl acetate was for pesticide residue analysis (Scharlau, Spain). Anhydrous sodium sulfate was purchased from Merck (Germany).

2.1.2. Standards

Three stock solutions of the studied compounds were prepared containing 5, 2.5 and 0.5 μg/ml of each insecticide and were used to fortify soil samples.

2.1.3. Extraction columns

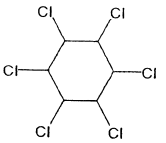
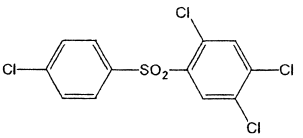
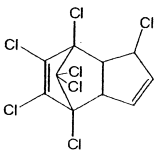
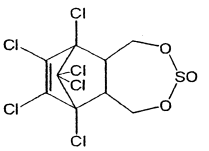
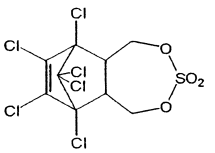
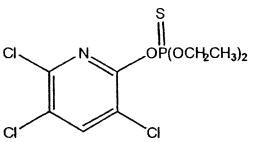
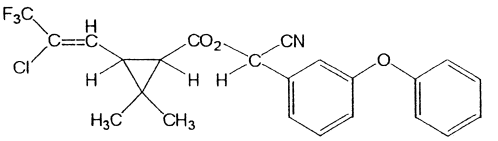
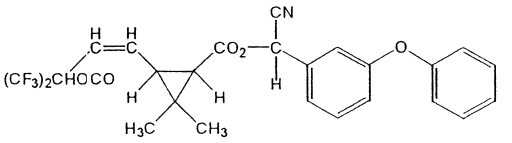
Polypropylene columns (20 ml) purchased from Becton-Dickinson (Spain) and glass columns (20 ml) from Afora (Spain), with Whatman No.1 filter paper circles of 2 cm diameter at the end, were used in the extraction step.

2.2. Apparatus

2.2.1. GC–ECD

A Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron-capture detector and automatic injector was used for the analysis of insecticides. A non-polar fused-silica capillary column, HP-1 (30 m×0.25 mm I.D. and 0.25 μm film thickness), was employed, with helium as carrier gas at 1 ml/min. The column temperature was maintained at 150°C for 1 min, then programmed at 25°C/min to 230°C, held 0.5 min and programmed at 12°C/min to 280°C, held 8 min. An alternative longer program of oven temperature was also used: the column temperature was maintained at 80°C for 1 min, then programmed at 8°C/min to 220°C, held 10 min and programmed at 10°C/min to 270°C, held 15 min. Injector port was maintained at 270°C and the

Table 1
Insecticides analysed in this study

Compounds	Formula	Structure
Lindane	$C_6H_6Cl_6$	
Tetradifon	$C_{12}H_6Cl_4O_2S$	
Heptachlor	$C_{10}H_5Cl_7$	
Endosulfan	$C_9H_6Cl_6O_3S$	
Endosulfan-sulfate	$C_9H_6Cl_6O_4S$	
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	
Cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	
Acrinathrin	$C_{26}H_{21}F_6NO_5$	

detector temperature was 300°C. A 2-μl volume was injected in the splitless mode.

2.2.2. GC–ion-trap detection (ITD)

A Perkin-Elmer 8500 gas chromatograph equipped with a Finnigan ion-trap detector, operating in the electron impact mode, was used. A fused-silica capillary column, BP-1 crosslinked dimethyl siloxane from SGE Australia (15 m×0.22 mm I.D. and 0.25 μm), was employed with helium as a carrier gas at 10 p.s.i. which gave a flow-rate of 0.9 ml/min (1 p.s.i.=6894.76 Pa). Temperature settings were injector 270°C, and detector 250°C. The oven temperature was maintained at 110°C for 1 min and then programmed at 30°C/min to 220°C, held for 0.5 min and programmed at 15°C/min to 270°C, held 5 min.

Mass spectrometric acquisition parameters: the transfer line temperature was 250°C; mass range, 40–350 u; scan-rate, 0.5 s/scan, 3-μscan; radio frequency and voltage, 1.1 MHz and 0–7.5 kV; automatic gain control, from 78 to 25 μs; solvent delay, 3 min.

2.2.3. Extraction equipment

An ultrasonic water bath (Raypa, Spain) was used in the extraction procedure. The generator of this apparatus has an output of 150 W and a frequency of 33 kHz.

A 12-port vacuum manifold (Visiprep, Supelco, Spain) was employed for the filtration of the extracting solvent.

2.3. Soil samples

The main physical–chemical properties (organic matter, pH, texture and field capacity) of soils are given in Table 2. Soil samples were collected from the plough layer (0–10 cm) of two experimental plots located in the region of Madrid (Spain). These samples were sieved (2 mm) and stored at room temperature until fortified.

2.4. Procedure

Two filter paper circles were placed at the end of the plastic column and 2 g of sodium sulfate anhydrous were added, then 5 g of the sieved soil were placed in the columns. Soil samples were fortified with 0.5 ml of a mixture of the different insecticides to reach final concentrations of 0.1, 0.5 and 1 μg/g and the moisture content was adjusted by adding water to the soils in the columns. Some samples were extracted after 20 min, to allow solvent evaporation, and the remained samples were stored in the capped columns at 4°C until analysed at different times (1, 15 and 30 days).

To investigate the influence of column material on the recoveries, 5 g of the studied soils were placed in glass and plastic columns, as indicated above, and were fortified to give a final concentration of 0.5 μg/g. After adjusting the moisture content, the capped columns were stored at 4°C until extraction at different times (15 and 30 days).

Soil samples were extracted with 4 ml of ethyl acetate for 15 min in an ultrasonic water bath at room temperature. The water level in the bath was adjusted to equal the extraction solvent level inside the columns, which were supported upright in a tube rack and closed with screw-type valves. After extraction, the columns were placed on the multiport vacuum manifold where the solvent was filtered and collected in graduate tubes. Soil samples were extracted again with another 4 ml of ethyl acetate (15 min). The extracting solvent was filtered and soil samples washed with 1 ml of additional solvent. The total extract collected was adjusted to 10 ml in the tubes and stored at 4°C until analysed by GC.

Table 2
Characteristics of the selected soils

Soil	pH	% Organic matter	% Sand	% Silt	% Clay	Field capacity (% at −33 kPa)
A	7.69	0.97	44.34	37.44	18.22	14.76
B	6.70	1.75	64.81	23.65	11.54	13.30

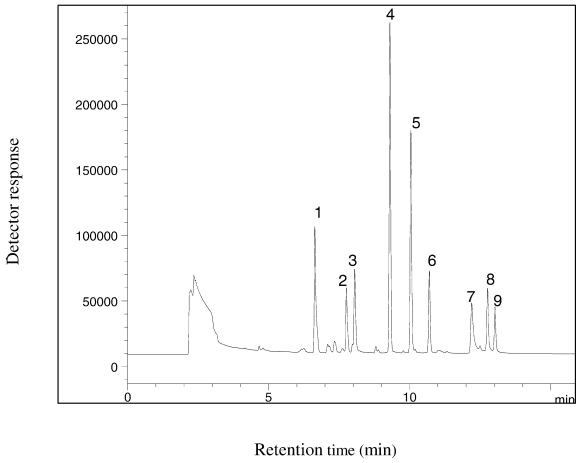


Fig. 1. Chromatogram of a mixture of the studied insecticides at a concentration of 0.1 μg/ml using the short temperature program, where: (1) lindane, (2) heptachlor, (3) chlorpyrifos, (4) endosulfan-I, (5) endosulfan-II, (6) endosulfan-sulfate, (7) tetradifon, (8) cyhalothrin and (9) acrinathrin.

3. Results and discussion

3.1. Recovery

A good separation of the studied compounds was accomplished in 15 min using the short program of oven temperature (Fig. 1). Soil samples were fortified to reach final concentrations of 0.1, 0.5 and 1 μg/g with the nine insecticides studied and the soil moisture content was adjusted at 5% (w/w) corresponding to 34 and 38% of the field capacity for soils A and B, respectively. Table 3 shows the recovery of these compounds through the method, following the procedure described above and using the short temperature program. The recoveries obtained varied from 90.4 to 108.5% with a relative standard deviation between 0.9 and 11.3%.

3.1.1. Soil moisture content

To test the influence of the soil moisture content on the recovery, samples of soil A and B were fortified at 0.1, 0.5 and 1 μg/g, the soil moisture content was adjusted by adding water at 10%, corresponding to 75 and 68% of field capacity for soils A and B, respectively, and the results were compared with those obtained at 5% of soil moisture content. Table 4 shows the results obtained at both moisture contents. Good recoveries were always obtained, with values in the range of 86–111%. In general, similar recoveries were obtained for soil A and B at the different moisture contents studied. These values were statistically compared by using the two-tailed paired *t*-test. The following equations were used:

$$\mu = t\,Sd/\sqrt{n} \quad Sd = \sqrt{\frac{\sum(d-\bar{d})^2}{n-1}}$$

where n is the number of samples ($n=12$) and $\bar{d}$ is an estimate of the difference between the recoveries obtained through the method at the two moisture contents. The calculated values of μ ($\alpha=0.05$) for each compound in soils A and B, were found to be

Table 3
Recovery of insecticides in fortified soil samples with 5% of moisture content

Compounds	% Recovery (mean±SD)[a]					
	0.1 μg/g		0.5 μg/g		1 μg/g	
	Soil A	Soil B	Soil A	Soil B	Soil A	Soil B
Lindane	101.6±7.7	105.0±8.6	96.2±2.4	97.2±7.7	93.9±3.5	93.1±5.6
Heptachlor	99.3±8.2	108.5±7.6	93.6±3.2	97.5±9.3	94.2±4.0	90.4±5.0
Chlorpyrifos	108.3±5.4	95.8±7.3	97.5±2.5	97.3±5.4	96.7±1.9	96.4±4.1
Endosulfan-I	99.7±1.6	102.2±5.7	97.9±2.0	98.7±5.9	96.6±2.0	95.5±3.7
Endosulfan-II	100.2±0.9	100.6±5.4	97.2±1.9	98.0±6.9	96.1±2.0	95.6±3.0
Endosulfan-sulfate	100.9±6.4	96.8±10.2	95.1±1.2	97.4±6.7	97.2±2.1	96.0±7.5
Tetradifon	98.2±4.0	100.5±11.3	95.2±2.7	96.4±6.9	98.3±2.3	104.0±3.7
Cyhalothrin	99.7±1.5	94.7±7.5	94.6±3.9	96.8±7.2	98.1±1.7	101.1±7.3
Acrinathrin	99.7±1.9	98.9±9.4	97.5±4.5	96.2±7.0	98.7±1.9	102.0±7.9

[a] Results are the mean of four replicates±standard deviation.

Table 4
Recoveries of the studied insecticides in soils A and B at different soil moisture contents (5 and 10%) and at the three concentration levels tested (0.1, 0.5 and 1 μg/g)

Compound	% Recovery (mean±SD)[a]											
	Soil A						Soil B					
	0.1 μg/g		0.5 μg/g		1 μg/g		0.1 μg/g		0.5 μg/g		1 μg/g	
	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
Lindane	101.6±7.7	105.7±4.1	96.2±2.4	95.5±2.1	93.9±3.5	97.2±2.9	105.0±8.6	95.5±2.8	97.2±7.7	97.5±2.0	93.1±5.6	92.5±9.4
Heptachlor	99.3±8.2	109.5±1.9	93.6±3.2	94.2±3.2	94.2±4.0	98.6±6.6	108.5±7.6	94.2±6.2	97.5±9.3	95.5±3.9	90.4±5.0	90.0±11.7
Chlorpyrifos	108.3±5.4	111.0±1,3	97.5±2.5	97.0±2.2	96.7±1.9	96.9±1.4	95.8±7.3	90.9±6.7	97.3±5.4	97.8±2.0	96.4±4.1	88.4±8.5
Endosulfan-I	99.7±1.6	99.1±3.1	97.9±2.0	95.3±3.3	96.6±2.0	95.3±1.8	102.2±5.7	93.3±6.8	98.7±5.9	98.4±1.7	95.5±3.7	94.2±5.3
Endosulfan-II	100.2±0.9	96.9±2.1	97.2±1.9	94.8±3.3	96.1±2.0	94.9±2.3	100.6±5.4	92.6±4.1	98.0±6.9	97.3±1.8	95.6±3.0	92.6±5.3
Endosulfan-sulfate	100.9±6.4	99.1±4.5	95.1±1.2	96.4±3.6	97.2±2.1	93.1±3.1	96.8±10.2	91.9±9.8	97.4±6.7	97.8±2.3	96.0±7.5	85.8±10.8
Tetradifon	98.2±4.0	97.0±3.1	95.2±2.7	96.8±4.4	98.3±2.3	94.9±3.3	100.5±11.3	94.4±6.9	96.4±6.9	97.8±1.3	104.0±3.7	90.7±9.7
Cyhalothrin	99.7±1.5	93.9±1.0	94.6±3.9	95.9±4.2	98.1±1.7	93.2±3.2	94.7±7.5	86.6±2.7	96.8±7.2	97.9±1.0	101.1±7.2	90.6±11.6
Acrinathrin	99.7±1.9	96.2±1.6	97.5±4.5	95.5±4.1	98.7±1.9	93.8±4.3	98.9±9.4	92.2±4.2	96.2±7.0	95.6±3.7	102.0±7.9	90.4±12.1

[a] Results are the mean of four replicates at each moisture content±standard deviation.

Table 5
Influence of the residence time on the recovery of insecticides from soil

Compound	% Recovery (mean±SD)[a]							
	Soil A				Soil B			
	25 min	1 day	15 days	30 days	25 min	1 day	15 days	30 days
Lindane	95.8±2.1	99.6±3.5	95.3±4.4	92.2±4.6	97.3±5.2	96.5±6.5	100.7±1.6	95.1±9.4
Tetradifon	96.0±3.5	98.7±2.1	100.4±5.1	94.9±4.4	97.1±4.6	99.1±6.6	99.6±1.3	101.4±7.9
Heptachlor	93.9±3.0	100.3±4.0	93.2±5.5	93.4±4.3	96.8±6.7	99.2±9.7	103.2±2.7	97.0±9.7
Endosulfan-I	96.6±2.9	97.6±2.0	92.9±5.3	92.4±5.0	98.5±4.0	95.1±4.4	90.8±2.8	90.3±7.0
Endosulfan-II	96.0±2.8	98.5±2.3	97.9±4.0	93.2±4.3	97.6±4.7	96.4±4.3	100.2±2.0	93.6±6.8
Endosulfan-sulfate	95.7±2.6	100.1±4.0	94.5±6.4	95.0±4.0	97.6±4.7	96.6±5.5	100.0±1.3	96.7±6.9
Chlorpyrifos	97.2±2.2	98.8±1.7	97.8±5.6	95.2±2.8	97.5±3.8	96.2±4.4	100.8±1.9	102.1±7.1
Cyhalothrin	95.2±3.8	99.6±3.3	102.1±6.0	96.4±10.3	97.3±4.8	98.0±6.8	104.5±2.1	106.7±11.5
Acrinathrin	96.5±4.2	101.0±3.8	98.6±6.9	95.9±9.2	95.9±5.2	95.9±7.2	103.4±1.4	105.3±9.6

[a] Results are the mean of eight replicates obtained from a fortified soil at 0.5 μg/g using polypropylene columns.

Table 6
Recovery of insecticides in plastic and glass columns

Compound	% Recovery (mean±SD)[a]							
	Soil A				Soil B			
	15 days		30 days		15 days		30 days	
	Plastic	Glass	Plastic	Glass	Plastic	Glass	Plastic	Glass
Lindane	95.3±4.4	98.5±3.8	92.2±4.6	96.2±3.8	100.7±1.6	101.0±3.9	95.2±9.4	95.7±5.8
Tetradifon	100.4±5.1	99.9±5.8	94.9±4.4	98.6±8.4	99.6±1.3	102.4±3.8	101.4±7.9	97.8±7.2
Heptachlor	93.2±5.5	93.1±4.5	93.4±4.3	95.0±5.1	103.2±2.7	103.4±4.6	97.0±9.7	96.4±3.9
Endosul-I	92.9±5.3	90.3±6.3	92.4±5.0	94.5±3.0	90.8±2.8	93.2±2.7	90.3±7.0	94.0±6.6
Endosul-II	97.9±4.0	98.9±2.6	93.2±4.3	96.8±7.1	100.2±2.0	101.6±3.2	93.6±6.8	92.8±5.5
Endosulf-sulfate	94.5±6.4	96.6±7.0	95.0±4.0	98.4±2.7	100.0±1.3	102.4±3.4	96.7±6.9	94.5±3.5
Chlorpyrifos	97.8±5.6	97.5±3.4	95.2±2.8	99.2±5.5	100.8±1.9	103.1±3.6	102.1±7.1	97.9±5.8
Cyhalothrin	102.1±6.0	100.5±5.7	96.4±10.3	100.8±8.3	104.5±2.1	105.3±4.7	106.7±11.5	97.6±7.3
Acrinathrin	98.6±6.9	100.0±7.0	95.9±9.2	98.1±8.3	103.4±1.4	103.3±4.4	105.3±9.6	97.2±4.3

[a] Results are the mean of eight replicates±standard deviation.

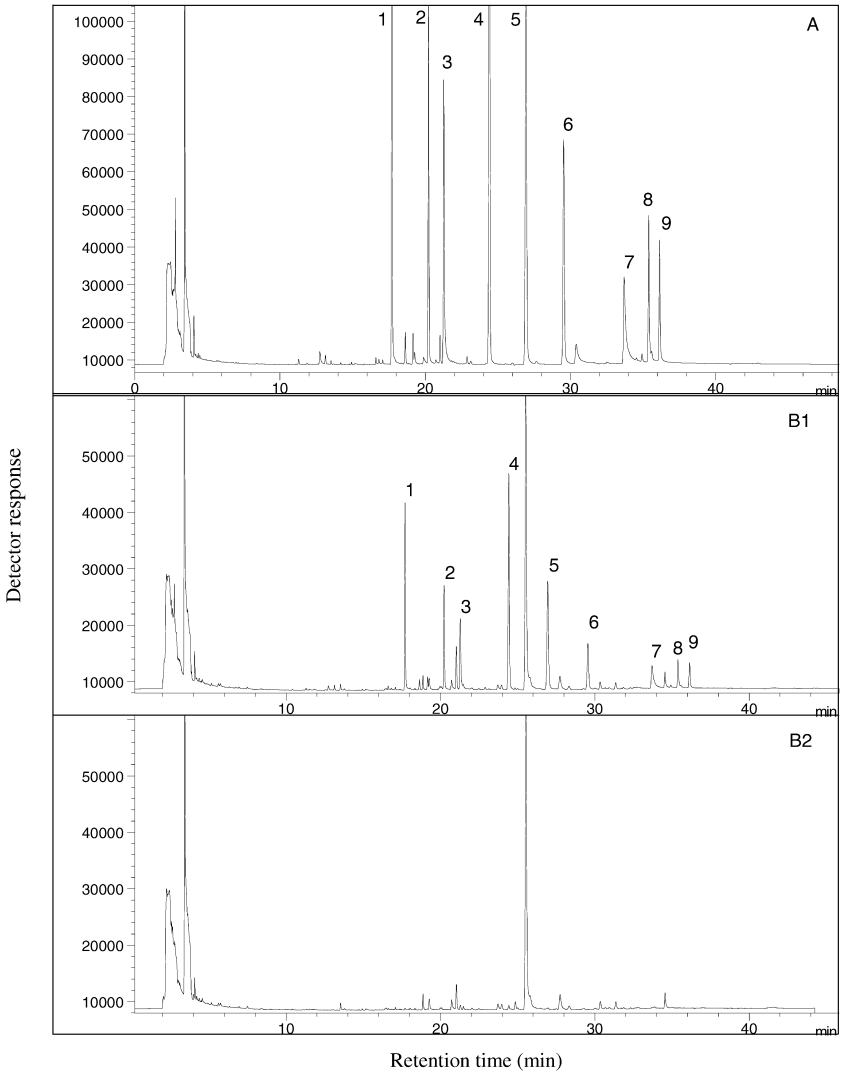


Fig. 2. Chromatogram of an insecticide mixture at 0.1 μg/ml (A), of a fortified soil sample at 0.02 μg/g (B1) and of an unfortified soil sample (B2). All the chromatograms were obtained using the long temperature program.

higher than the corresponding value of $\bar{d}$ ($\mu > |\bar{d}|$) indicating that the recoveries in the two cases are not significantly different [15].

3.1.2. Residence time

To study the influence of the residence time of these compounds in the two soils studied on the insecticides recovery, analyses were carried out at 25 min, and 1, 15 and 30 days after fortification of samples at 0.5 μg/g. The results are shown in Table 5. It can be observed that the recoveries are very similar and always higher than 90% at the different times studied. Relative standard deviations were in all cases lower than 12%.

3.1.3. Column material

Two materials were tested, glass and plastic (polypropylene), and analyses were performed at 15 and 30 days after soil fortification at 0.5 μg/g. Results are shown in Table 6. The recoveries ob-

Table 7
Residue levels found in real soil samples obtained from tomato fields (mg/g)[a]

Field	Endosulfan-II	Endosulfan-sulfate	Tetradifon
1	nd	0.024±0.002	nd
3	nd	0.022±0.006	nd
4	nd	0.020±0.002	nd
6	0.035±0.030	0.162±0.135	nd
7	nd	0.074±0.112	nd
9	nd	0.022±0.006	0.017±0.013
10	nd	0.022±0.009	nd

[a] Values are the mean of four replicates±standard deviation. nd, below the detection limit (0.01 μg/g).

tained with both types of columns varied in the range of 90.3–106.7%, with relative standard deviations between 1.3 and 11.5%. Results were compared using the two-tailed paired *t*-test and following the same procedure described above. In this case $n=8$. The two periods of time were examined individually. In both periods, the calculated values of μ for each compound in soil A and B were higher than $|\bar{d}|$, indicating that no significant differences were observed on the recoveries after, 15 or 30 days, using glass or plastic columns.

3.2. Detection limit and linearity

A limit of detection somewhat lower than 0.1 μg/g can be obtained using the short temperature program proposed. Nevertheless, a longer temperature program can be employed if a better detection limit is needed. Fig. 2A shows the chromatogram of a standard insecticide mixture at 0.1 μg/ml analysed in these conditions. Moreover, a chromatogram of a soil sample fortified at 0.02 μg/g (B1) and an unfortified soil sample (B2) are also depicted. In these conditions, the detection limit of the proposed method is, at least, 0.01 μg/g for the studied compounds, considering a signal-to-noise ratio equal or higher than 3. The detector response was linear in the assayed range. The linearity of the method was tested by analysing solutions over the range of 0.05–0.5 μg/ml of the studied insecticides.

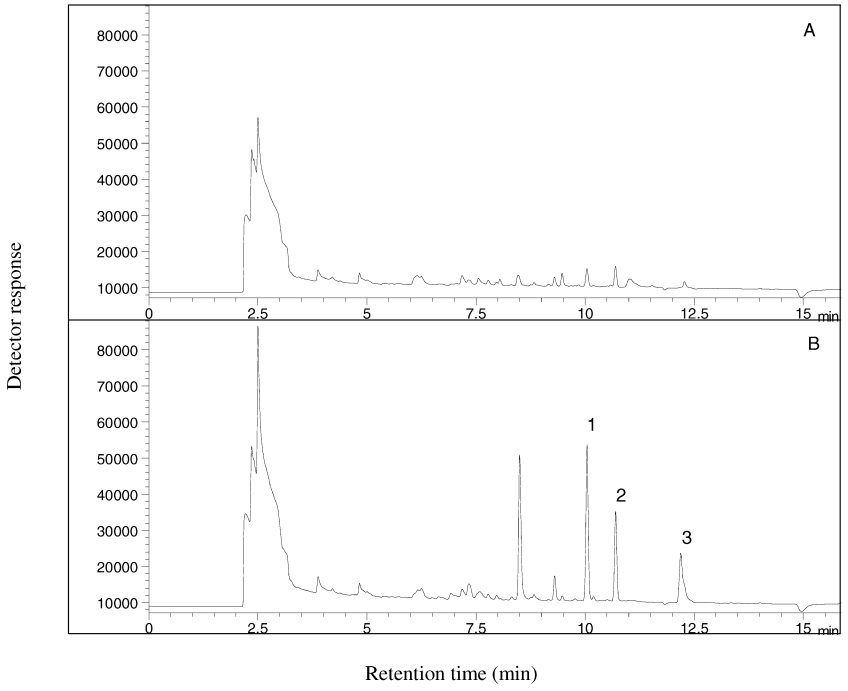


Fig. 3. Chromatograms of soil samples obtained from two commercial fields after harvest. (A) No peaks of the studied compounds were detected; (B) three compounds were detected: (1) endosulfan-II (0.063 μg/g), (2) endosulfan-sulfate (0.030 μg/g) and (3) tetradifon (0.027 μg/g).

Table 8
Retention times and main ions and their relative abundance in the mass spectra of the insecticides studied

Compounds	$t_{r\ (min)}$	m/z (%)
Lindane	4.05	109 (100), 181[a] (85), 217 (33)
Heptachlor	4.43	100 (100), 272[a] (98), 337 (10)
Chlorpyrifos	5.00	97 (100), 197[a] (80), 258 (30), 352[b] (8)
Endosulfan-I	5.42	160 (100), 195[a] (80), 237 (59), 267 (58)
Endosulfan-II	6.14	195[a] (100), 162 (99), 243 (57), 267 (50)
Endosulf-sulfate	6.40	274[a] (100), 239 (69), 387 (30)
Tetradifon	7.40	111 (100), 159[a] (77), 229 (25), 356[b] (15)
Cyhalothrin	8.09	181[a] (100), 197(41), 225 (14)
Acrinathrin	8.24	93 (100), 181[a] (78), 357 (41)

[b] Ion selected for quantitation.
[b] Molecular ion.

3.3. Real samples

The proposed method was applied to the analysis of real soil samples collected from 10 commercial orchards located in the West of Spain. Results are presented in Table 7. It can be observed that some of the insecticides studied in this work (endosulfan-II, endosulfan-sulfate and tetradifon) were detected at levels in the range of 0.02–0.16 μg/g. Fig. 3 shows representative chromatograms of soil samples obtained from two commercial fields.

3.4. GC–MS confirmation

The confirmation of residue identity of the studied insecticides was performed by GC–MS. The retention times of the compounds and the selected ions for quantitation are summarised in Table 8. The selected ions are in agreement with those reported by other authors for the mass spectra of these compounds [3,16,17]. The quantitation of the insecticides was performed by selecting the base peak of their mass spectra, after the acquisition of the total ion chromatogram of the sample. The absence of coextracted interferences at the insecticide retention times was confirmed by blank extracts analysis. All the insecticides studied can be identified by their mass spectra, in the NBS library, at levels near 1 ng per compound.

4. Conclusions

The results of this study point out that the proposed method of extraction by sonication of soil samples placed in small columns using ethyl acetate as extracting solvent provides a rapid and sensitive procedure for the simultaneous determination of the selected insecticides. The method is simple and with a low solvent consumption, reducing the risk for human health and the environment, and it represents an improvement in comparison with other traditional multiresidue methods.

Pesticides recovery through the method were not affected by the soil moisture content or the residence time of these compounds in soil. In addition, significantly differences were not found between the recoveries obtained using polypropylene columns and glass columns.

Satisfactory results were obtained in the routine analysis of real samples, confirming the reliability and efficacy of this method for the analysis of insecticide residues in soil.

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