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Multiresidue Analysis of Pesticides in Soil by Gas Chromatography with Nitrogen−Phosphorus Detection and Gas Chromatography Mass Spectrometry

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A rapid multiresidue method for the simultaneous determination of 25 fungicides and insecticides in soil was developed. Soil samples are extracted by sonication with a water−acetonitrile mixture, and the pesticides are partitioned into dichloromethane. Final determination was made by gas chromatography (GC) with nitrogen−phosphorus detection (NPD). Confirmation analysis of pesticides was carried out by GC−MS in the selected ion monitoring (SIM) mode. The identification of compounds was based on retention time and on comparison of the primary and secondary ions. The average recovery by the GC−NPD method obtained for these compounds varied from 68.5% to 112.1% with a relative standard deviation between 1.8% and 6.2%. The GC−NPD method presents good linearity over the range assayed 50−2000 μg/L, and the detection limit for the pesticides studied varied from 0.1 to 10.4 μg/kg. The proposed method was used to determine pesticide levels in soil samples from experimental greenhouse pepper cultivation.

KEYWORDS: Multiresidue; soil; pesticides; gas chromatography; environmental analysis

INTRODUCTION

In the application of pesticides in agricultural crops, a fraction of the amount used reaches the soil, even when the pesticide is applied to plant foliage. Methods for the determination of different pesticides in soil are very important from an agricultural and environmental point of view.

The growing of peppers in greenhouses is one of the main cultivation activities in the Region of Murcia (Spain). It is for that reason that it is important to know the present state of contamination by pesticides in the soils of these greenhouses. In addition, the contamination of the soil by pesticides is one of the most significant problems faced by farmers when moving to organic farming.

A large variety of methods have been used in the determination of different pesticides in soil. A wide variety of techniques have been used to extract pesticides from soil, including agitation (*1*), sonication (*2*−*4*), and Soxhlet (*5*) extraction. A number of disadvantages were observed with these extraction methods; they are laborious, time-consuming, and large quantities of solvent waste are generated as a result of the determination of trace amounts of contaminants in soil. Supercritical fluid extraction (SFE) (*6*, *7*), solid-phase extraction (SPE) (*8*), and microwave-assisted extraction (MAE) (*9*) have also been used as rapid techniques, using low solvent volumes for the extraction of pesticide in soil. MAE and sonication employing techniques are the most used extraction methods for pesticides in soil (*10*).

Pesticide residues have been generally analyzed by gas chromatography with different detectors, such a nitrogen−phosphorus (NPD) (*8*, *9*, *11*), or electron-capture detectors (ECD) (*4*, *6*, *7*, *12*).

Numerous method use gas chromatography coupled mass spectrometry (GC−MSD) (*3*, *11*−*14*), due to the possibility of confirming pesticide identity in soil. In the case of thermally instable pesticides, high-performance liquid chromatography (HPLC) (*15*, *16*) has been also employed.

The aim of this work was to develop a simple method for the determination of 25 pesticides in soil, commonly used in the growing of peppers in greenhouses in Murcia (Spain) (*17*), using sonication. Some of the pesticides studied are considered to be new generation, as is the case with pyridaben and tebuconazole because their decomposition is quicker and has a less damaging effect on the environment. The determination of these new generation pesticides is usually carried out by means of gas chromatography or HPLC (*18*, *19*). The method presents advantages as compared to other conventional methods given the use of a low volume of organic solvent in the sample extraction and the fact that a cleanup is not required. Final determination was by gas chromatography (GC) with nitrogen−phosphorus detection (NPD) with confirmation by gas chromatography (GC) with mass-selective detection (MSD).

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Table 1. Retention Time (RT, min), Molecular Mass (MW), Target (T), Qualifier Ions (Q_1, Q_2, and Q_3) (*m*/*z*), and Abundance Ratios (%) of Qualifier Ion/Target Ion (Q_1/T and Q_2/T)[a] of the Studied Fungicides and Insecticides

pesticide	RT	MW	T	Q_1	Q_2	Q_3	Q_1/T	Q_2/T
			Standard Solution 1					
1 chlorothalonil	14.78	265.9	266	264	268	270	75.2	50.3
2 pirimicarb	15.69	238.3	166	72	238	167	50.4	25.3
3 chlorpyrifos methyl	16.59	322.6	286	288	125	290	68.6	48.5
4 malathion	18.80	330.4	173	127	125	93	85.3	83.5
5 chlorpyrifos ethyl	19.23	350.6	197	199	314	97	93.2	70.1
6 procymidone	21.96	284.1	96	283	285	67	70.2	47.3
7 hexaconazole	23.52	314.2	83	214	216	82	61.9	40.9
8 buprofezin	24.58	305.5	105	106	104	172	48.2	46.7
9 tebuconazole	27.43	307.8	125	250	70	83	99.6	46.0
10 phosalone	29.68	367.8	182	121	184	367	37.5	30.8
11 λ-cyhalothrin	30.37	449.9	181	197	208	209	83.6	53.6
12 pyridaben	31.52	364.9	147	117	148	132	13.2	12.7
13 cypermethrin I	32.69	416.3	181	163	165	77	87.2	75.3
14 cypermethrin II	32.84	416.3	181	163	165	209	95.0	80.3
15 cypermethrin III	32.97	416.3	163	181	165	209	81.2	65.9
16 cypermethrin IV	33.02	416.3	163	181	165	209	81.4	64.2
17 deltamethrin	36.00	502.2	181	253	251	255	66.5	41.9
			Standard Solution 2					
18 diazinon	14.47	304.3	179	137	152	199	96.8	67.8
19 pirimiphos-methyl	18.31	305.3	290	276	305	233	80.1	36.9
20 triadimefon	19.39	293.8	57	208	85	210	76.5	28.9
21 pyrifenox I	21.21	295.2	171	173	262	100	67.1	20.9
22 pyrifenox II	22.62	295.2	171	173	262	92	66.0	23.8
23 triadimenol I	21.67	295.8	112	168	128	70	85.2	58.6
24 triadimenol II	22.05	295.8	112	168	128	70	84.3	60.8
25 oxyfluorfen	24.73	361.7	252	302	331	361	43.2	41.5
26 cyproconazole	25.04	291.8	222	224	138	125	36.2	24.3
27 pyriproxyfen	29.93	321.4	136	96	78	137	10.7	10.2
28 acrinathrin	30.71	541.4	181	208	93	289	63.3	52.6
29 cyfluthrin I	32.22	434.3	163	206	165	227	69.3	65.9
30 cyfluthrin II	32.36	434.3	163	206	165	227	71.0	66.2
31 cyfluthrin III	32.48	434.3	163	206	165	227	67.2	66.8
32 cyfluthrin IV	32.54	434.3	163	206	227	199	65.7	52.4
33 fluvalinate-tau I	34.72	502.9	250	252	209	181	33.6	29.3
34 fluvalinate-tau II	34.85	502.9	250	252	209	181	35.0	28.6

[a] Q/T (%) ratios are the results of abundance values of the qualifier ion (Q_1, Q_2) divided by the abundance of the target ion (T) × 100.

MATERIALS AND METHODS

Materials and Standards. Pesticide standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany) with purity ranging from 93% to 100%. The solvents acetone, acetonitrile, dichloromethane, ethyl acetate, and cyclohexane, residue analysis grade, were purchased from Scharlau (Barcelona, Spain).

Stocks solutions (1000 μg/mL) of each pesticide standard were prepared by dissolving 0.025 g of the pesticide in 25 mL of ethyl acetate/cyclohexane (1/1, v/v).

A pesticide intermediate standard solution (10 μg/mL) was prepared by transferring 1 mL from each pesticide solution to a 100 mL volumetric flask and diluting to volume with ethyl acetate/cyclohexane (1/1, v/v) to obtain a concentration of 10 μg/mL. Several standard solutions, with concentrations of 0.05−2 μg/mL, were injected to obtain the linearity of detector response and the detection limits of the pesticides studied.

Apparatus. An Agilent (Waldbronn, Germany) model HP 6890 gas chromatograph equipped with a nitrogen−phosphorus detector and automatic split-splitless injector model Agilent 7683 was used for the analysis of pesticides. An HP-5MSI fused silica capillary column (30 m × 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Agilent Technologies, was employed, with nitrogen as makeup gas at 25 mL/min. Helium was used as the carrier (constant pressure eluting, bromophos 20.08 min). Hydrogen and air were used as detector gases at 3 and 60 mL/min. The injector and detector were operated at 250 and 325 °C, respectively. The column temperature was maintained at 70 °C for 2 min and then programmed at 25 °C/min to 150 °C, increased to 200 °C at a rate of 3 °C/min, followed by a final ramp to 280 °C at a rate of 8 °C/min, and held for 10 min. The total analysis time was 41.87 min. One microliter of samples was injected in splitless mode.

An Agilent model HP 6890 gas chromatograph equipped with a model 5973N mass spectrometer was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from *m*/*z* 50 to 500 at 3.21 s per scan. The ion source temperature was 230 °C, and the quadrupole temperature was 150 °C. The electron multiplier voltage (EM voltage) was maintained at 1300 V, and a solvent delay of 4.5 min was employed. Gas chromatography was performed under the same conditions used in GC−NPD.

Analysis was performed with selected ion monitoring (SIM) mode using primary and secondary ions. The target and qualifier abundances were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from *m*/*z* 50 to 500. Table 1 lists the pesticides along with their retention times, molecular mass, the target and qualifier ions, and their qualifier to target abundance ratios. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. Retention times had to be within ±0.1 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for positive confirmation. The concentration of each compound was determined by comparing the peak areas in the sample to those found for mixtures of pesticide standards of known concentration.

For the extraction of samples, a sonic dismembrator 200 W generator equipped with standard titanium probe (Dr. Hielscher GmbH. Stahnsdorf, Germany) was used.

An Eppendorf model 5810R centrifuge (Hamburg, Germany) and a Büchi model R-205 rotavapor (Flawil, Switzerland) were used in the centrifugation and evaporation to dryness of samples, respectively.

Sample Preparation. *Soil Samples*. The soil samples were taken in Campo de Cartagena, Murcia (southeastern Spain). Soil samples were

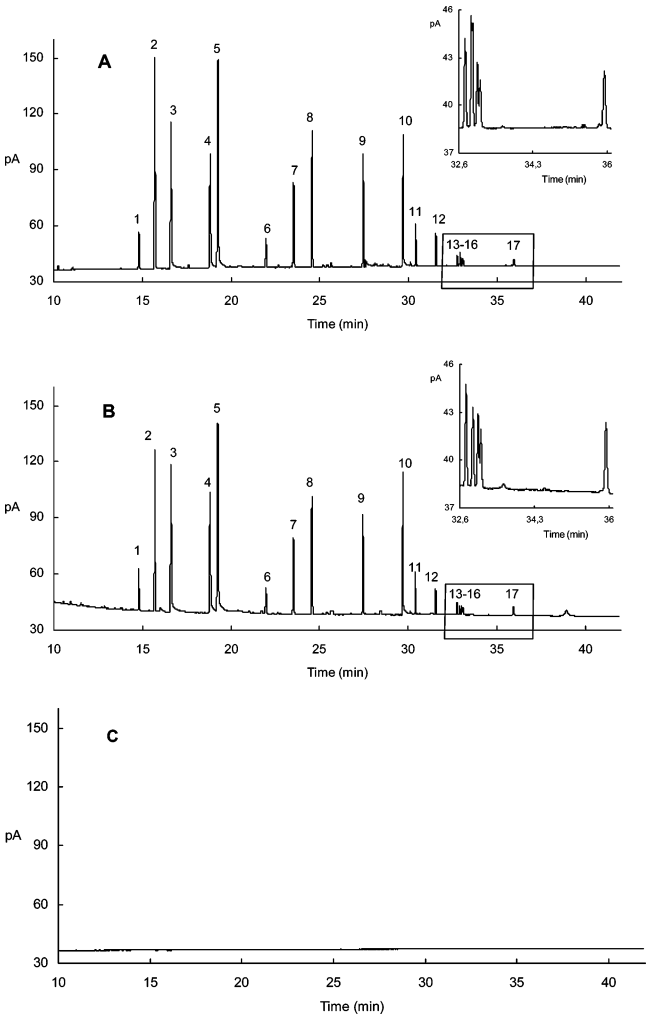

Figure 1. Chromatograms (NPD) obtained for (**A**) standard solution 1 (1 mg/kg), (**B**) spiked soil sample (1 mg/kg), and (**C**) a control soil sample. For peak numbers, see Table 1.

passed through a 2 mm sieve, homogenized, and then extracted with their naturally occurring water content (10% moisture). The characteristics of the soils were as follows: soil A, pH 7.80; organic matter content 2.54%, sand 15%, silt 30%, and clay 55%; soil B, pH 7.70; organic matter content 1.15%, sand 25%, silt 35%, and clay 40%; soil C, pH 7.91; organic matter content 3.49%, sand 21%, silt 33%, and clay 46%.

Real samples were taken in five experimental greenhouses of peppers from the Region of Murcia. Samples were colleted from the plough layer (0−20 cm). Soil samples were sieved (2 mm), homogenized, and stored at −18 °C until analysis.

Procedure. Soil (5 g) was weighed in a 100 mL beaker. Samples were extracted, according to the procedure described by Navarro et al. (*2*) with some modification, with 30 mL of acetonitrile/water (2/1) by sonication (15 min at 0.5 cycles and 60% amplitude). After sonication, 20 mL of dichloromethane was added and then centrifuged for 10 min at 1900*g*. Extract was filtered quantitatively through a glass funnel containing a filter paper 1PS, 150 mm diameter (Watman Int. Ltd., Maidstone, UK). The organic phase was concentrated to dryness using rotary vacuum evaporation. The residue was redissolved in 5 mL of ethyl acetate/cyclohexane (1/1, v/v), and an aliquot was analyzed using GC−NPD under conditions described above.

RESULTS AND DISCUSSION

Gas Chromatographic Determination. The compounds were distributed among two solutions (Table 1), which may help when showing the compounds in the chromatograms.

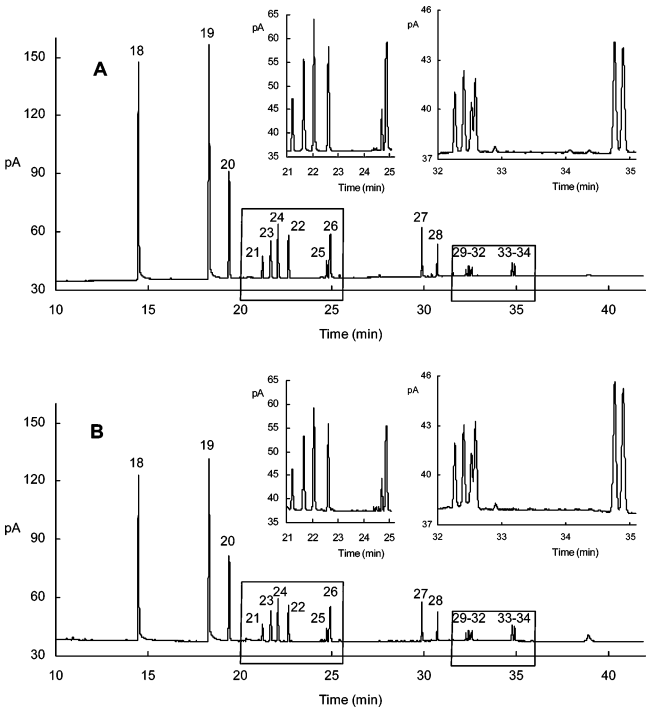

Figure 2. Chromatograms (NPD) obtained for (**A**) standard solution 2 (1 mg/kg) and (**B**) spiked soil sample (1 mg/kg). For peak numbers, see Table 1.

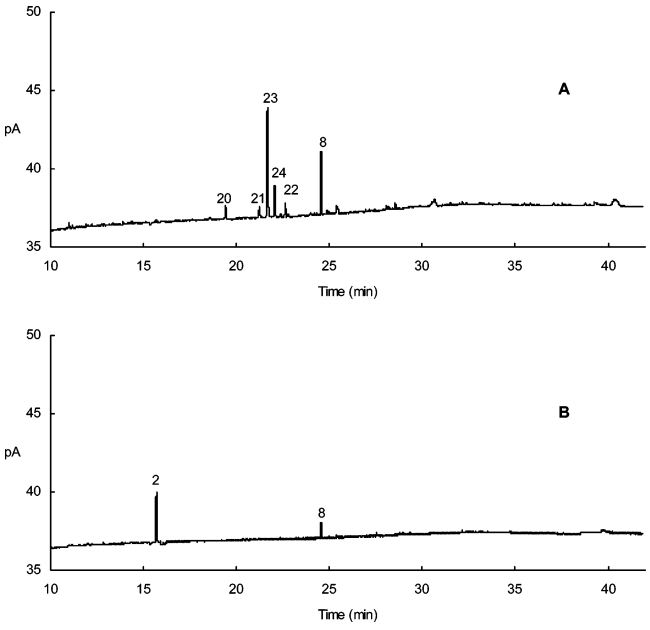

Figure 3. Chromatograms (NPD) for two soil samples (soil A and B) collected from experimental greenhouses of peppers from the Region of Murcia.

Figure 1 shows chromatograms of a standard solution 1 and a soil sample spiked (soil A) with the compounds of the standard solution 1 (Figure 2, same for standard solution 2). Three solvents (acetonitrile, acetone, and ethyl acetate) were tested as extractants, and the best results were obtained with acetonitrile for all compounds. All pesticides were satisfactorily separated with high sensitivity and selectivity. The developed method provides clean blank extracts without interferences during GC, and, therefore, cleanup of soil samples was not required.

Method Validation. *Linearity and Detection Limit.* Several standards solutions, with concentrations of 0.05−2 μg/mL, were

Table 2. Limits of Detection (LOD, μg/kg), Limits of Quantification (LOQ, μg/kg), and Repeataability (RSD, %) of the Studied Pesticides by GC–NPD and GC–MSD

	GC–NPD				GC–MSD			
			RSD[a]				RSD[a]	
pesticide	LOD	LOQ	peak area	RT	LOD	LOQ	peak area	RT
			Standard Solution 1					
1 chlorothalonil	6.2	20.5	2.2	0.01	9.3	30.9	2.1	0.01
2 pirimicarb	0.2	0.6	2.5	0.01	2.4	7.9	2.6	0.01
3 chlorpyrifos methyl	0.5	1.5	3.0	0.01	0.5	1.7	3.3	0.02
4 malathion	0.2	0.7	3.1	0.02	2.6	8.6	4.1	0.02
5 chlorpyrifos ethyl	0.1	0.4	2.3	0.02	0.2	0.6	5.3	0.01
6 procymidone	5.1	17.0	4.1	0.01	5.6	18.6	6.1	0.03
7 hexaconazole	0.6	20.1	3.3	0.01	1.3	4.4	5.2	0.02
8 buprofezin	0.4	1.3	2.0	0.01	0.7	2.3	4.1	0.01
9 tebuconazole	0.3	1.0	1.8	0.02	3.5	11.6	3.8	0.01
10 phosalone	0.4	1.4	1.6	0.01	0.4	1.3	3.3	0.01
11 λ-cyhalothrin	6.9	22.9	2.2	0.01	9.0	29.8	3.0	0.02
12 pyridaben	7.3	24.4	2.3	0.02	10.3	34.3	6.3	0.01
13 cypermethrin I			3.1	0.01			5.6	0.01
14 cypermethrin II			3.4	0.01			5.3	0.01
15 cypermethrin III			3.1	0.01			5.0	0.01
16 cypermethrin IV			2.0	0.01			6.0	0.01
Σcypermethrin	4.2	13.9			9.8	32.5		
17 deltamethrin	10.4	34.5	2.5	0.01	15.6	51.9	3.9	0.02
			Standard Solution 2					
18 diazinon	1.5	5.0	1.6	0.02	3.4	11.3	2.6	0.02
19 pirimiphos-methyl	0.1	0.3	1.8	0.02	0.2	0.7	3.2	0.01
20 triadimefon	0.7	2.4	2.5	0.02	1.9	6.2	4.7	0.01
21 pyrifenox I			2.8	0.01			3.9	0.01
22 pyrifenox II			2.5	0.01			4.5	0.01
Σpyrifenox	0.9	2.9			2.2	7.2		
23 triadimenol I			2.1	0.01			2.8	0.02
24 triadimenol II			2.0	0.01			2.6	0.01
Σtriadimenol	1.0	3.4			1.8	6.6		
25 oxyfluorfen	4.1	13.5	2.7	0.01	9.1	30.3	3.9	0.01
26 cyproconazole	1.0	3.3	2.3	0.02	4.6	15.4	4.4	0.01
27 pyriproxyfen	1.2	4.1	3.2	0.01	5.2	17.4	5.1	0.02
28 acrinathrin	3.3	11.0	1.7	0.01	7.8	26.1	5.7	0.01
29 cyfluthrin I			1.9	0.01			4.9	0.01
30 cyfluthrin II			3.3	0.01			5.3	0.01
31 cyfluthrin III			1.9	0.01			6.0	0.01
32 cyfluthrin IV			2.3	0.01			5.8	0.01
Σcyfluthrin	5.2	17.3			9.7	32.3		
33 fluvalinate-tau I			2.0	0.01			5.6	0.02
34 fluvalinate-tau II			2.8	0.02			5.8	0.02
Σfluvalinate-tau	3.2	10.7			6.0	19.9		

[a] Repeatability of the chromatographic method. Relative standard deviation of peak areas and retention times ($n = 10$).

injected in GC−NPD and GC−MSD to obtain the linearity of detector response and the detection limits of the 25 compounds studied. The NPD and MSD response for all pesticides was linear in the concentration assayed with determination coefficients >0.999 for all pesticides. Table 2 summarizes the limits of detection (LOD; obtained at a signal-to-signal ratio 3) and the limits of quantification (LOQ, obtained at a signal-to-signal ratio 10) obtained for the individual pesticides in soil by GC−NPD and GC−MSD. In the case of the GC−NPD, the LOD and LOQ were in most cases a little lower than that obtained by GC−MSD (in the SIM mode). The range of LOD achieved is in the lower end of that obtained by other authors (*7*, *14*).

Repeatability. The repeatability of our chromatographic method was determined by performing the analysis of a sample spiked at 0.2 μg/g of pesticide. The sample was injected 10 times with an automatic injector, and the relative standard deviation (RSD) values obtained for peak areas by GC−NPD and GC−MSD ranged from 1.6 to 4.1 and 2.1 to 6.3, respectively. The relative standard deviation (RSD) values obtained for retention times by GC−NPD and GC−MSD ranged from 0.01 to 0.02 and 0.01 to 0.03, respectively (Table 2).

Recovery. Soil samples were fortified with 0.5 and 1.5 μg/g of pesticide. After evaporation of the spiking solvent, the samples were allowed to equilibrate for 2 h before extraction and analyzed following the procedures described above. Three soils with different physicochemical properties are studied to validate the method. The recoveries obtained for all pesticides ranged from 68.5% to 112.1% for soil A, 72.3% to 108.9% for soil B, and 70.1% to 111.9% for soil C (Table 3). The relative standard deviation (RSD) was <6.2% in the most unfavorable case. Similar recoveries have been obtained for soils with different physicochemical properties.

Real Samples. Soil from experimental greenhouses of peppers from the Region of Murcia was sampled and analyzed following the extraction methods described above. Pesticide levels encountered in the collected samples are shown in Table 4. The chromatograms obtained for two representative soil samples are

Table 3. Recovery of Pesticides from Spiked Soil Samples[a]

pesticide	fortification level, μg/g	mean recovery ± RSD,[b] %[a] soil A	soil B	soil C
		Standard Solution 1		
chlorothalonil	0.5	78.5 ± 4.0	76.5 ± 3.2	74.5 ± 3.9
	1.5	85.1 ± 3.2	88.6 ± 3.6	81.6 ± 3.5
pirimicarb	0.5	68.5 ± 3.3	72.3 ± 2.9	70.1 ± 4.7
	1.5	72.3 ± 2.6	77.0 ± 3.9	73.6 ± 4.5
chlorpyrifos methyl	0.5	93.9 ± 2.9	92.1 ± 3.8	85.3 ± 4.2
	1.5	94.7 ± 2.1	99.1 ± 3.1	93.1 ± 3.7
malathion	0.5	91.0 ± 2.5	95.4 ± 2.9	90.4 ± 4.2
	1.5	96.2 ± 2.0	98.4 ± 2.2	95.0 ± 3.2
chlorpyrifos ethyl	0.5	85.4 ± 5.8	80.1 ± 6.1	82.5 ± 4.8
	1.5	92.7 ± 3.2	86.3 ± 4.1	89.8 ± 4.6
procymidone	0.5	75.8 ± 3.7	85.6 ± 3.1	74.6 ± 3.8
	1.5	85.0 ± 3.1	89.1 ± 2.0	83.1 ± 2.7
hexaconazole	0.5	81.9 ± 4.0	84.8 ± 2.6	80.5 ± 4.1
	1.5	89.9 ± 3.7	93.7 ± 2.3	92.7 ± 2.6
buprofezin	0.5	83.8 ± 4.2	81.5 ± 4.8	85.5 ± 3.3
	1.5	89.9 ± 2.9	99.9 ± 2.2	90.3 ± 2.7
tebuconazole	0.5	78.6 ± 3.6	77.5 ± 4.1	75.2 ± 3.1
	1.5	86.3 ± 3.3	89.7 ± 3.0	80.7 ± 2.4
phosalone	0.5	92.1 ± 2.8	90.4 ± 3.9	96.1 ± 4.9
	1.5	99.5 ± 2.6	96.5 ± 2.9	100.3 ± 3.9
λ-Cyhalothrin	0.5	102.1 ± 6.2	99.0 ± 4.7	104.2 ± 5.3
	1.5	96.8 ± 3.7	100.8 ± 4.3	102.1 ± 4.7
pyridaben	0.5	81.8 ± 3.3	88.8 ± 3.0	85.6 ± 4.8
	1.5	92.1 ± 3.0	96.8 ± 2.9	99.2 ± 3.5
cypermethrin	0.5	93.6 ± 3.6	103.8 ± 4.6	90.7 ± 4.9
	1.5	95.2 ± 2.6	100.6 ± 3.9	92.6 ± 3.2
deltamethrin	0.5	110.8 ± 5.0	108.9 ± 4.5	111.9 ± 4.8
	1.5	105.4 ± 4.3	104.1 ± 3.3	108.1 ± 3.7
		Standard Solution 2		
diazinon	0.5	84.2 ± 3.9	89.0 ± 3.8	80.3 ± 4.8
	1.5	91.9 ± 2.9	98.9 ± 3.0	89.4 ± 2.7
pirimiphos-methyl	0.5	81.6 ± 3.4	80.4 ± 2.9	86.7 ± 4.9
	1.5	84.9 ± 2.5	86.0 ± 2.6	90.1 ± 3.6
triadimefon	0.5	78.0 ± 2.4	82.1 ± 3.3	75.6 ± 5.3
	1.5	84.8 ± 1.8	85.3 ± 2.5	80.9 ± 4.0
pyrifenox	0.5	83.2 ± 4.9	80.7 ± 4.8	86.4 ± 4.2
	1.5	89.7 ± 4.1	89.0 ± 4.0	93.1 ± 3.3
triadimenol	0.5	82.8 ± 3.2	79.8 ± 3.5	86.8 ± 3.8
	1.5	84.1 ± 3.0	90.5 ± 2.3	88.7 ± 2.9
oxyfluorfen	0.5	78.5 ± 2.9	81.4 ± 4.1	74.8 ± 4.8
	1.5	86.6 ± 2.3	89.9 ± 3.4	84.6 ± 4.4
cyproconazole	0.5	80.3 ± 3.8	85.6 ± 4.2	85.2 ± 3.2
	1.5	83.3 ± 3.5	89.1 ± 3.2	91.4 ± 2.8
pyriproxyfen	0.5	79.8 ± 4.8	78.7 ± 4.0	82.3 ± 4.5
	1.5	87.6 ± 3.5	85.6 ± 3.1	89.6 ± 4.0
acrinathrin	0.5	87.1 ± 5.1	93.9 ± 3.9	90.4 ± 4.3
	1.5	92.8 ± 4.0	96.5 ± 3.3	98.7 ± 3.0
cyfluthrin	0.5	102.5 ± 3.6	97.5 ± 2.3	107.0 ± 2.9
	1.5	100.3 ± 2.8	104.1 ± 2.4	103.8 ± 2.1
fluvalinate-tau	0.5	112.1 ± 5.2	108.3 ± 3.3	108.1 ± 5.3
	1.5	106.4 ± 4.4	107.5 ± 2.7	103.9 ± 4.2

[a] $n = 5$. [b] RSD = relative standard deviation.

Table 4. Pesticide Residues Found in Real Soil Samples

soil	pirimicarb[a] (μg/g)	pyrifenox[a] (μg/g)	triadimenol[a] (μg/g) Σtriadimenol+triadimefon	buprofezin[a] (μg/g)
A		0.08 ± 0.005	0.42 ± 0.03	0.03 ± 0.003
B	0.02 ± 0.003			0.01 ± 0.002
C			0.09 ± 0.004	
D			0.16 ± 0.01	0.01 ± 0.001
E		0.10 ± 0.008	0.24 ± 0.02	

[a] Mean of four determinations ± RSD.

depicted in Figure 3. Analysis of real samples showed the validity of method used, which allowed the determination and identification of pesticides present in the samples.

The results of this study show that the proposed method is rapid, simple, and sensitive, requiring small volumes of solvents. The proposed method offers a good recovery and a low detection. The method presents advantages as compared to other conventional methods given the use of low volume of organic solvent in the sample extraction, and, therefore, cleanup of soil samples was not required. Another advantage of the method is the application to the analysis of pesticides in soil samples collected in greenhouses of peppers from the Region of Murcia.

LITERATURE CITED

(1) Huang, L. Q.; Pignatello, J. J. Improved extraction of atrazine and metolachlor in field soil samples. *J.-Assoc. Off. Anal. Chem.* **1990**, *73*, 443−446.

(2) Navarro, S.; Oliva, J.; Barba, A.; Garcia, C. Determination of simazine, terbuthylazine and their chlorotriazine metabolites in soil, using sonication microextraction and gas chromatography. *J. AOAC Int.* **2000**, *83*, 1239−1243.

(3) Ma, L. L.; Muir, D.; Wang, X. T.; Xu, X. B. Simultaneous analysis organic pollutants in soils by gas chromatography and by gas chromatography−mass spectrometry. *Int. J. Environ. Anal. Chem.* **2005**, *85*, 89−98.

(4) You, J.; Weston, D. P.; Lydy, M. J. A sonication extraction method for the analysis of pyrethroids, organophosphate, and organochlorine pesticides from sediment by gas chromatography with electron-capture detection. *Arch. Environ. Contam. Toxicol.* **2004**, *47*, 141−147.

(5) Lartiges, S.; Garrigues, P. Gas chromatographic analysis of organophosphorus and organonitrogen pesticides with different detectors. *Analusis* **1995**, *23*, 418−421.

(6) Synder, J. L.; Grob, R. L.; McNally, M. E.; Oostdyk, T. S. Supercritical fluid extraction of selected pesticides from fortified soils and determination by gas chromatography with electron capture detection. *J. Environ. Sci. Health* **1994**, *A29*, 1801−1816.

(7) Rissato, S. R.; Galhiane, M. S.; Apon, B. M.; Arruda, M. S. P. Multiresidue Analysis of pesticides in soil by supercritical fluid extraction/gas chromatography with electron-capture detection and confirmation by gas chromatography−mass spectrometry. *J. Agric. Food Chem.* **2005**, *53*, 62−69.

(8) Redondo, M. J.; Ruiz, M. J.; Boluda, R.; Font, G. Optimization of a solid-phase extraction technique for the extraction of pesticides from soil samples. *J. Chromatogr., A* **1996**, *719*, 69−76.

(9) Lopez-Avila, V.; Benedicto, J.; Bauer, K. M. Stability of organophosphorus pesticides when extracted from solid matrixes with microwave energy. *J. AOAC Int.* **1998**, *81*, 1224−1232.

(10) Andreu, V.; Pico, Y. Determination of pesticides and their degradation products in soil: critical review and comparison of methods. *Trends Anal. Chem.* **2004**, *23*, 772−789.

(11) Pérez, R. A.; Sánchez-Brunete, C.; Miguel, E.; Tadeo, J. L. Analytical methods for the determination in soil of herbicides used in forestry by GC−NPD and GC−MS. *J. Agric. Food Chem.* **1998**, *46*, 1864−1869.

(12) Castro, J.; Sánchez-Brunete, C.; Tadeo, J. L. Multiresidue analysis of insecticides in soil by gas chromatography with electron-capture detection and confirmation by gas chromatography−mass spectrometry. *J. Chromatogr., A* **2001**, *918*, 371−380.

(13) Mogadati, P.; Louis, J. B.; Rosen, J. D. Multiresidue determination of pesticides in high-organic-content soils by solid-phase extraction and gas chromatography/mass spectrometry. *J. AOAC Int.* **1999**, *82*, 705−715.

(14) Papadopoulou-Mourkidou, E.; Patsias, J.; Kotopoulou, A. Determination of pesticides in soil by gas chromatography. *J. AOAC Int.* **1997**, *80*, 447−454.

(15) Slobodnik, J.; Hogenboom, A. C.; Louter, A. J. H.; Brinkman, U. A. Th. Integrated system for on-line gas and liquid chromatography with a single spectrometric detector for the automated analysis of environmental samples. *J. Chromatogr., A* **1996**, *730*, 353−371.

(16) Pacáková, V.; Štulík, K.; Jiskra, J. High-performance separations in the determination of triazine herbicides and their residues. *J. Chromatogr., A* **1996**, *754*, 17−31.

(17) Vademécum de productos fitosanitarios y nutricionales, 2004. Carlos De Liñán. 20×bb Ed.

(18) Belmonte Vega, A.; Garrido Frenich, A.; Martínez Vidal, J. L. Monitoring of pesticides in agricultural water and soil samples from Andalusia by liquid chromatography coupled to mass spectrometry. *Anal. Chim. Acta* **2005**, *538*, 117−127.

(19) Rial-Otero, R.; Gonzalez-Rodriguez, R. M.; Cancho-Grande, B.; Simal-Gandara, J. Parameters affecting extraction of selected fungicides from vineyard soils. *J. Agric. Food Chem*. **2004**, *52*, 7227−7234.

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