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Multiresidue Determination of Pesticides in Soil by Gas Chromatography−Mass Spectrometry Detection

CONSUELO SÁNCHEZ-BRUNETE, BEATRIZ ALBERO, AND JOSÉ L. TADEO*

Departamento de Medio Ambiente, INIA, Ctra. de la Coruña Km. 7, 28040 Madrid, Spain

An analytical multiresidue method for the simultaneous determination of various classes of pesticides in soil was developed. Pesticides were extracted from soil with ethyl acetate. Soil samples were placed in small columns, and the extraction was carried out assisted by sonication. Pesticides were determined by gas chromatography with electron impact mass spectrometric detection in the selected ion monitoring mode. Spiked blank samples were used as standards to counteract the matrix effect observed in the chromatographic determination. Pesticides were confirmed by their retention times, their qualifier and target ions, and their qualifier/target abundance ratios. Recovery studies were performed at 0.2, 0.1, and 0.05 μg/g fortification levels of each pesticide, and the recoveries obtained ranged from 87.0 to 106.2% with a relative standard deviation between 2.4 and 10.6%. Good resolution of the pesticide mixture was achieved in ~41 min. The detection limits of the method ranged from 0.02 to 1.6 μg/kg for the different pesticides studied. The developed method is linear over the range assayed, 25−1000 μg/L, with determination coefficients >0.999. The proposed method was used to determine pesticide levels in real soil samples, taken from different agricultural areas of Spain, where several herbicides and insecticides were found.

KEYWORDS: Multiresidue; soil; pesticides; GC-MS; SAESC

INTRODUCTION

The high crop yields obtained in agriculture at present rely on the wide use of pesticides. As a consequence, these chemicals are frequently found in soil and other environmental matrices where the risk they may pose has to be controlled. Multiresidue methods, allowing the analysis of different pesticide classes, have been generally developed for the determination of these compounds in several matrices.

The classical extraction technique used in the determination of pesticide residues in soil samples has been the solid−liquid partitioning with organic solvents, followed sometimes by subsequent cleanup procedures before the gas chromatographic determination (*1*, *2*). The drawbacks of the traditional extraction methods, such as the use of large amounts of solvents and glassware and the high time consumption, can be reduced by using other extraction techniques developed recently. Supercritical fluid extraction (SFE) (*3*), solid-phase extraction (SPE) with the stationary phase packed in a cartridge or in disks (*4*, *5*), and microwave-assisted extraction (MAE) (*6*, *7*) are different techniques that have been used with that aim. In addition, a method for the preparation of soil samples based on the sonication of soil samples placed in small columns (SAESC) has recently been developed in our laboratory for the rapid and sensitive analysis of herbicides, insecticides, or fungicides (*8*−*11*).

Several chromatographic methods have been published for the determination of different individual classes of pesticides in soils. Pesticide residues have been generally analyzed by gas chromatography with different detectors, such as nitrogen−phosphorus (NPD) (*2*−*8*) or electron-capture detectors (ECD) (*12*) for organonitrogen and organophosphate or organohalogen pesticides, respectively. High-performance liquid chromatography (HPLC) (*13*) has been also employed, particularly when pesticides are thermally instable.

Gas chromatography coupled with mass spectrometry (GC-MS) is more often used at present for pesticide analysis in soil (*5*, *14*) due to the possibility of confirming pesticide identity.

The main objective of this work was to develop a rapid and simple multiresidue method for the analysis of 50 pesticides in soil samples, based on SAESC using a low volume of organic solvent and their determination by GC-MS. The developed method was applied to the determination of pesticides levels in soils collected from several agricultural areas of Spain.

MATERIALS AND METHODS

Materials and Standards. Pesticide standards were obtained from Reidel-de Haën (Seelze, Germany), and all compounds were of 99% purity. Ethyl acetate, residue analysis grade, was purchased from Scharlau (Barcelona, Spain), and anhydrous sodium sulfate, reagent grade, was obtained from Merck (Darmstadt, Germany).

Stock solutions (500 μg/mL) of each pesticide standard were prepared by dissolving 0.050 g of the pesticide in 100 mL of ethyl acetate and stored at 4 °C.

A pesticide intermediate standard solution (5 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 to obtain a

* Author to whom correspondence should be addressed (telephone 34 91-347-6821; fax 34 91-357-2293; e-mail tadeo@inia.es).

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concentration of 5 μg/mL. A set of calibration standard solutions of 5.0, 1.0, and 0.5 μg/mL was prepared by dilution. The solutions containing 5.0, 1.0, and 0.5 μg/mL of each pesticide were used to fortify soil samples. The internal standards were prepared by dissolving lindane and hexazinone in ethyl acetate to make a 500 μg/mL solution.

Apparatus. *Extraction Equipment.* Polypropylene columns (20 mL) of 10 cm × 20 mm i.d., Becton-Dickinson, Spain, with Whatman no. 1 filter paper circles of 2 cm diameter (Whatman, Maidstone, U.K.) were used. One-way stopcocks were employed to close the columns.

An ultrasonic water bath (Raypa, Barcelona, Spain) was used in the extraction step. The generator of this ultrasonic bath has an output of 150 W and a frequency of 35 kHz. A vacuum manifold (Supelco Visiprep, Madrid, Spain) was employed to remove the extraction solvent.

GC-MS Analysis. GC-MS analysis was performed with an Agilent 6890 (Waldbronn, Germany) gas chromatograph equipped with an automatic split−splitless injector model HP 7683 and a mass spectrometric detector (MSD) model HP 5973. A fused silica capillary column (ZB-5MS), 5% phenyl polysiloxane as nonpolar stationary phase (30 m × 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Phenomenex (Torrance, CA), was employed. Operating conditions were as follows: injector port temperature, 280 °C; helium as carrier gas at a flow rate of 1.0 mL/min; pulsed splitless mode (pulsed pressure 45 psi = 310 kPa for 1.5 min). 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 and the equilibration time 2 min. A 2 μL volume was injected splitless, with the split valve closed for 1 min.

The mass spectrometric detector (MSD) was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from *m*/*z* 60 to 500 at 3.62 s per scan. The ion source temperature was 230 °C and the quadrupole temperature 150 °C. The electron multiplier voltage (EM voltage) was maintained 1000 V above autotune, and a solvent delay of 5 min was employed.

Analysis was performed with selected ion monitoring (SIM) using one target and one or two qualifier 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* 60 to 500 Quantification was based on the peak area ratio of the target ion divided by the peak area of the internal standard in samples versus those found in the calibration standard. Standards were prepared in blank matrix extracts, to counteract the matrix effect. Blank matrix extracts were made following the procedure for sample preparation described below, using a blank soil sample without pesticide fortification. **Table 1** lists the pesticides along with their retention times, the target and qualifier ions, and their qualifier to target abundance ratios. The SIM program used to determine and confirm pesticides in soil is indicated in **Table 2**. 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 ±0.3 min of the expected time, and qualifier-to-target ratios had to be within a 20% range for positive confirmation.

Sample Preparation. *Soil Samples.* Soil used in the recovery assay was collected from the plow layer (0−10 cm) of an experimental plot located in the region of Madrid (Spain). Soil samples were sieved (2 mm) and stored at room temperature until fortified. The characteristics of the selected soil were as follows: pH, 7.69; organic matter content, 0.97%; sand, 44.34%; silt, 37.44%; and clay, 18.22%.

Real samples were collected from several Spanish regions: 16 samples from tomato fields in Badajoz, 8 samples from forested fields in Badajoz, and 18 samples from corn fields in Badajoz and Albacete. Samples were collected from the plow layer (0−10 cm), sieved (2 mm), and stored at −18 °C until analysis.

Procedure. Two filter paper circles were placed at the end of a plastic column, and anhydrous sodium sulfate (2 g) was added; sieved soil (5 g) was then placed in the column. In the recovery assays, soil samples were previously fortified with 0.5 mL of a mixture of the different pesticides to reach final concentrations of 0.05, 0.1, and 0.2 μg/g, allowing 20 min for solvent evaporation.

Table 1. Retention Times (t_R, min), Molecular Weights (MW), Target (T) and Qualifier Ions (Q_1 and Q_2) (*m*/*z*), and Abundance Ratios (%) of Qualifier Ion/Target Ion (Q_1/T and Q_2/T)[a]

	pesticide	t_R	MW	T	Q_1	Q_2	Q_1/T	Q_2/T
1	EPTC	7.93	189.3	128	189		24.2	
2	molinate	10.81	187.3	126	187		21.5	
3	propachlor	12.30	211.7	120	176		38.2	
4	ethalfluralin	13.33	333.3	276	316	264	76.2	21.0
5	trifluralin	13.73	335.5	306	264		74.8	
6	simazine	15.19	201.7	201	186	200	56.8	15.3
7	atrazine	15.46	215.7	200	215	201	57.4	9.9
8	lindane	15.87	290.8	181	219		132	
9	terbuthylazine	16.18	229.7	214	229		28.2	
10	diazinon	16.87	304.3	179	137	304	111	48.3
11	chlorothalonil	17.35	265.9	266	264		100	
12	triallate	17.46	304.7	86	268	269	54.9	53.4
13	metribuzin	18.84	214.3	198	199		30.0	
14	parathion-methyl	19.22	263.2	263	109	125	105.5	79.4
15	tolclofos-methyl	19.46	301.1	265	267		100	
16	alachlor	19.66	269.8	160	188		88.4	
17	prometryn	19.96	241.4	241	184		73.1	
18	terbutryn	20.63	241. 4	226	241		48.7	
19	fenitrothion	20.76	277.2	277	125		151.5	
20	pirimiphos-methyl	20.95	333.4	290	276	305	85.9	81.0
21	dichlofluanid	21.12	333.2	123	224	167	47.0	32.3
22	aldrin	21.34	364.9	263	293		38.1	
23	malathion	21.45	330.4	173	127		104.3	
24	metolachlor	21.64	283.8	162	238		57.0	
25	fenthion	21.83	278.3	278	279		100.1	
26	chlorpyrifos	21.95	350.6	314	197		201.5	
27	triadimefon	22.12	293.8	208	181		19.0	
28	butralin	22.85	295.3	266	267		100	
29	pendimethalin	23.54	281.3	252	281		13.0	
30	phenthoate	24.11	320.4	274	246		28.9	
31	procymidone	24.31	284.1	283	96		118.8	
32	methidathion	24.60	302.3	145	85		83.8	
33	endosulfan I	24.94	406.9	241	195	339	35.5	27.3
34	profenophos	25.85	373. 6	208	339		75.6	
35	oxadiazon	26.21	345.2	175	258	334	51.9	23.4
36	cyproconazole	26.71	291.8	222	139		51.3	
37	endosulfan II	27.00	406.9	195	237	339	83.7	36.4
38	ethion	27.59	384.5	231	153		67.5	
39	ofurace	28.11	281.7	132	160		79.4	
40	benalaxyl	28.26	325.4	148	206		25.9	
41	endosulfan sulfate	28.37	423.0	272	229	387	63.6	52.9
42	hexazinone	28.83	252.3	171	128		13.9	
43	nuarimol	28.92	314.7	235	203	314	78.1	53.5
44	bromopropylate	29.95	428.1	341	183		42.4	
45	tetradifon	30.66	356.1	159	111	356	52.2	60.7
46	cyhalothrin	31.47	449.9	181	197		81.2	
47	fenarimol	31.61	331.2	139	219	330	76.2	31.9
48	pyrazophos	31.78	373.4	221	373		16.4	
49	coumaphos	32.81	362.8	362	226		62.0	
50	cypermethrin	34.25	416.3	181	163		122.1	
51	fluvalinate tau-I	36.27	502.9	250	252		38.0	
52	fluvalinate tau-II	36.42	502.9	250	252		37.9	

[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.

Soil samples were extracted with 4 mL of ethyl acetate for 15 min in an ultrasonic water bath at room temperature. Ethyl acetate was selected as extraction solvent due to the good results obtained in previous works (*9*−*11*, *15*). 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 one-way stopcocks. After extraction, the columns were placed on the multiport vacuum manifold, where the solvent was filtered and collected in graduated tubes. Soil samples were extracted again with another 4 mL of ethyl acetate (15 min). The extracting solvent was filtered, and soil samples were washed with 1 mL of additional solvent. The total extracts collected in 10 mL graduated tubes were concentrated with a gentle stream of air to an appropriate volume (10 mL for the highest and intermediate levels and 5 mL for the lowest level and real samples) and stored at 4 °C until analyzed by GC-MS. A 0.5 mL of the internal standard solution of 1 μg/mL (lindane and hexazinone) was added before GC analysis.

Chromatographic standards were prepared using blank sample extracts. These blank extracts were fortified with 0.5 mL of the pesticide standard solution of 1 μg/mL and with 0.5 mL of the internal standard solution (lindane and hexazinone) of 1 μg/mL.

Table 2. SIM Program Used To Analyze and Confirm Pesticides in Soil

group	time (min)	pesticide	*m/z*	dwell time (ms)	scan rate (cycles/s)
1	5.00	EPTC, molinate	128,189,126,187	100	2.15
2	11.70	propachlor	120, 176	100	4.26
3	12.70	ethalfluralin, trifluralin	276, 316, 264, 306	100	2.15
4	14.40	simazine, atrazine	201, 186, 200, 215	100	2.15
5	15.70	lindane (IS)[a], terbuthylazine	183, 219, 214, 229	100	2.15
6	16.60	diazinon	179, 137, 304	100	2.86
7	17.15	chlorothalonil, triallate	266, 264, 86, 268, 269	100	1.72
8	17.90	metribuzin	198, 199	100	4.26
9	19.00	parathion-methyl, tolclofos-methyl	263, 109, 265, 267	100	2.15
10	19.59	alachlor, prometryn	160, 188, 241,184	100	2.15
11	20.40	terbutryn, fenitrothion, pirimiphos-methyl, dichlofluanid	226, 241, 277, 125, 290, 276, 123, 224	50	1.90
12	21.26	aldrin, malathion	263, 293, 127, 173	100	2.15
13	21.59	metolachlor, fenthion, chlorpyrifos, triadimefon	162, 238, 278, 279, 197, 314, 208, 181	50	1.90
14	22.50	butralin, pendimethalin	266, 267, 252, 281	100	2.15
15	23.85	phenthoate, procymidone	274, 246, 96, 283, 285	100	1.72
16	24.45	methidathion, endosulfan I	145, 195, 241, 339	100	2.15
17	25.40	profenophos, oxadiazon	208, 339, 175, 258, 334	100	1.72
18	26.40	cyproconazole, endosulfan II	222, 139, 195, 237, 339	100	1.72
19	27.30	ethion	231	100	8.33
20	27.90	ofurace, benalaxyl, endosulfan sulfate	132, 160, 148, 206, 229, 272, 387	50	2.17
21	28.60	hexazinone (IS),[a] nuarimol	171, 128, 203, 235, 314	100	1.72
22	29.50	bromopropylate, tetradifon	341,183, 111, 159, 356	100	1.72
23	31.10	cyhalothrin, fenarimol, pyrazophos	181, 197, 139, 219, 330, 221, 373	50	2.17
24	32.50	coumaphos, cypermethrin	362, 226, 163, 181	100	2.15
25	36.00	fluvalinate tau-I, fluvalinate tau- II	250, 252	100	4.26

[a] IS, internal standard.

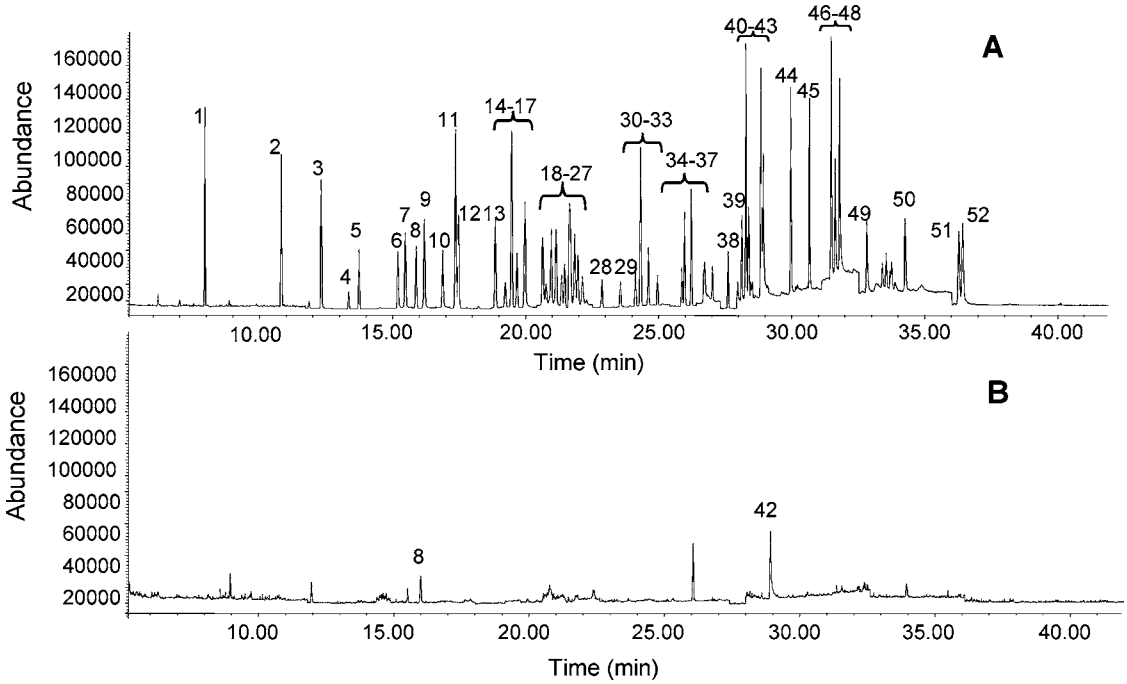

Figure 1. GC-MS-SIM chromatograms of (**A**) a standard mixture solution at 0.025 μg/mL except for metribuzin, cyhalothrin, and fluvalinate (0.050 μg/mL) and (**B**) a blank soil sample. See **Table 1** for peak identification. Peaks 8 and 42 are internal standards.

RESULTS AND DISCUSSION

Gas Chromatographic Determination. Pesticide residue levels were determined by GC-MS-SIM. **Figure 1** shows representative GC-MS-SIM chromatograms of a blank sample and a standard pesticide mixture at 0.025 μg/mL. All pesticides were satisfactorily separated with adequate sensitivity, although metribuzin, cyhalothrin, and fluvalinate were present in the mixture at double concentrations to obtain a better response.

When standards were prepared by spiking blank soil samples with known amounts of pesticides, higher peak areas were obtained for the same pesticide concentration. This can be explained by a matrix effect that improves transfer of analytes from the injection port to the column and enhances the chromatographic response of some pesticides, particularly organophosphorus compounds. This effect has also been observed by other authors in the analysis of pesticides in different matrices (*1*, *16*, *17*). Therefore, the quantification of pesticide residues was carried out using fortified blank samples. The absence of coextracted interferences was confirmed by blank extract analysis. The developed method provides clean blank extracts without interferences during GC and, therefore, cleanup of soil samples was not required.

Method Validation. *Linearity*. The linearity of all pesticides was determined using blank soil samples fortified at levels of 25, 50, 100, 250, 500, and 1000 μg/L, containing 50 μg/L of the internal standards, lindane and hexazinone. In the cases of

Table 3. Limits of Detection (LOD, μg/kg), Limits of Quantification (LOQ, μg/kg), Calibration Data, and Repeatability (RSD, %) of the Studied Pesticides

			calibration data		RSD[a]	
pesticide	LOD	LOQ	equation	determination coefficient	peak area	t_R
EPTC	0.03	0.1	$y = 2.52x + 1.03$	0.996	2.8	0.01
molinate	0.05	0.2	$y = 2.47x + 7.40 \times 10^{-1}$	0.999	2.3	0.04
propachlor	0.1	0.3	$y = 2.18x + 6.51 \times 10^{-1}$	1.000	2.2	0.01
ethalfluralin	1.6	5.3	$y = 3.71 \times 10^{-1}x + 2.08 \times 10^{-2}$	1.000	2.7	0.04
trifluralin	0.8	2.6	$y = 1.53x - 9.84 \times 10^{-2}$	1.000	2.6	0.01
simazine	0.8	2.6	$y = 9.49 \times 10^{-1}x + 2.44 \times 10^{-1}$	1.000	2.5	0.03
atrazine	0.7	2.3	$y = 1.53x + 9.77 \times 10^{-2}$	1.000	4.1	0.02
terbuthylazine	0.6	2.0	$y = 2.06x + 5.80 \times 10^{-1}$	1.000	2.5	0.02
diazinon	0.8	2.6	$y = 8.99 \times 10^{-1}x + 2.43 \times 10^{-1}$	1.000	3.3	0.02
chlorothalonil	0.03	0.1	$y = 2.13x + 4.82 \times 10^{-1}$	1.000	4.7	0.01
triallate	0.6	2.0	$y = 1.81x + 4.63 \times 10^{-1}$	1.000	2.5	0.02
metribuzin	1.6	5.3	$y = 4.29x - 1.98 \times 10^{-1}$	1.000	4.5	0.02
parathion-methyl	1.5	5.0	$y = 6.36 \times 10^{-1}x - 7.78 \times 10^{-2}$	0.999	5.6	0.03
tolclofos-methyl	0.03	0.1	$y = 4.10x - 8.32 \times 10^{-1}$	1.000	2.6	0.02
alachlor	0.8	2.6	$y = 1.11x + 1.90 \times 10^{-1}$	1.000	3.7	0.02
prometryn	0.2	0.7	$y = 2.56x + 2.24 \times 10^{-1}$	1.000	3.5	0.01
terbutryn	0.7	2.3	$y = 1.75x - 2.86 \times 10^{-1}$	1.000	5.1	0.02
fenitrothion	1.5	5.0	$y = 6.05 \times 10^{-1}x - 1.35\ 10^{-1}$	0.999	5.9	0.01
pirimiphos- methyl	0.8	2.6	$y = 1.18x + 2.84 \times 10^{-1}$	1.000	3.6	0.01
dichlofluanid	1.5	5.0	$y = 1.65x + 4.32 \times 10^{-1}$	0.999	9.5	0.02
aldrin	1.4	4.6	$y = 6.04 \times 10^{-1}x + 2.33 \times 10^{-1}$	0.999	2.1	0.01
malathion	1.2	4.0	$y = 1.22x + 2.82 \times 10^{-1}$	1.000	6.7	0.02
metolachlor	0.2	0.7	$y = 3.41x + 5.90 \times 10^{-1}$	1.000	4.2	0.01
fenthion	0.8	2.6	$y = 2.61x - 2.08$	0.995	7.8	0.01
chlorpyrifos	0.9	3.0	$y = 0.69x + 1.35 \times 10^{-1}$	1.000	3.9	0.01
triadimefon	1.4	4.6	$y = 1.07x + 2.13 \times 10^{-1}$	1.000	4.0	0.01
butralin	1.5	5.0	$y = 2.04x - 6.96 \times 10^{-1}$	0.999	5.7	0.02
pendimethalin	1.4	4.6	$y = 1.67x - 4.38 \times 10^{-1}$	0.999	6.1	0.01
phenthoate	1.3	4.3	$y = 1.39x + 2.38 \times 10^{-2}$	1.000	8.3	0.02
procymidone	0.05	0.2	$y = 1.18x + 4.02 \times 10^{-1}$	0.999	5.2	0.01
methidathion	1.0	3.3	$y = 2.47x + 4.39 \times 10^{-1}$	1.000	7.9	0.01
endosulfan I	1.3	4.3	$y = 2.30 \times 10^{-1}x + 1.06 \times 10^{-1}$	0.999	3.7	0.02
profenophos	1.2	4.0	$y = 5.45 \times 10^{-1}x + 1.26 \times 10^{-1}$	1.000	5.6	0.01
oxadiazon	0.2	0.7	$y = 1.32x + 4.84 \times 10^{-1}$	0.999	4.6	0.01
cyproconazole	1.2	4.0	$y = 2.16x + 2.56 \times 10^{-1}$	1.000	7.7	0.02
endosulfan II	1.2	4.0	$y = 2.44 \times 10^{-1}x + 1.30 \times 10^{-1}$	0.999	6.0	0.01
ethion	1	3.3	$y = 2.29x + 2.61 \times 10^{-1}$	1.000	8.2	0.01
ofurace	0.2	0.7	$y = 6.94 \times 10^{-1}x + 3.60 \times 10^{-1}$	0.998	9.3	0.01
benalaxyl	0.02	0.07	$y = 3.58x + 1.09$	1.000	5.5	0.01
endosulfan sulfate	0.2	0.66	$y = 5.86 \times 10^{-1}x + 2.55 \times 10^{-1}$	0.999	4.8	0.02
nuarimol	0.1	0.3	$y = 2.15 \times 10^{-1}x + 4.65 \times 10^{-2}$	1.000	3.8	0.01
bromopropylate	0.02	0.07	$y = 3.85 \times 10^{-1}x + 5.59 \times 10^{-2}$	1.000	3.2	0.01
tetradifon	0.02	0.07	$y = 1.87 \times 10^{-1}x + 8.47 \times 10^{-2}$	0.998	9.7	0.01
cyhalothrin	0.7	2.3	$y = 2.74 \times 10^{-1}x + 4.35 \times 10^{-1}$	0.995	2.6	0.01
fenarimol	0.1	0.3	$y = 1.77 \times 10^{-1}x + 7.68 \times 10^{-2}$	0.998	6.3	0.01
pyrazophos	0.02	0.07	$y = 8.86 \times 10^{-1}x + 2.15 \times 10^{-1}$	0.999	4.3	0.01
coumaphos	0.2	0.7	$y = 1.68 \times 10^{-1}x + 4.05 \times 10^{-2}$	1.000	5.5	0.01
cypermethrin	0.2	0.7	$y = 1.59 \times 10^{-1}x + 4.91 \times 10^{-2}$	1.000	6.6	0.01
fluvalinate tau-I	0.4	1.3	$y = 5.18 \times 10^{-1}x + 5.38 \times 10^{-2}$	1.000	8.5	0.01
fluvalinate tau-II	0.4	1.3	$y = 5.18 \times 10^{-1}x + 5.38 \times 10^{-2}$	1.000	8.5	0.04

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

metribuzin, cyhalothrin, and fluvalinate, double concentrations were used. The MS response for all pesticides was linear in the concentration range assayed with determination coefficients >0.999 for all pesticides. **Table 3** summarizes calibration data of the studied pesticides.

Repeatability. The repeatability of our chromatographic method was determined by performing the analysis of a sample spiked at 50 μg/L (100 μg/L for metribuzin, cyhalothrin, and fluvalinate). The sample was injected 10 times with an automatic injector, and the relative standard deviation (RSD) values obtained for the retention times ranged from 0.01 to 0.04%, whereas for peak areas the values ranged from 2.2 to 9.7% (**Table 3**). The repeatability of the whole analytical method was also determined by replicate analysis of a fortified sample during different days. The repeatability of the method, expressed as RSD, was <11% for all compounds.

Stability. Stock standard solutions and working solutions were found to be stable when stored at 4 °C, for at least 3 months and 1 week, respectively. Moreover, the stability of a fortified blank sample kept in the autosampler for 24 h was assayed, and differences from a freshly prepared sample were <4%.

Specificity. The specificity of the proposed method was assessed by analyzing blank soil samples. The absence of background peaks, above a signal-to-noise ratio of 3, at the retention times of target pesticides, showed that no interferences occurred.

Recovery. **Table 4** shows the pesticide recovery results. The soil was fortified at 0.2, 0.1, and 0.05 μg/g before extraction by adding 1 mL volume of the appropriate working standard solution and internal standards at a concentration of 0.05 μg/mL. Metribuzin, cyhalothrin, and fluvalinate were added at double concentrations to obtain 0.4, 0.2, and 0.1 μg/g because of their lower sensitivity in GC-MS. The extracts were analyzed by GC-MS-SIM. The fortified samples were allowed to stand for 20 min, to let the fortification solvent (ethyl acetate) evaporate before extraction. Four sample replicates, spiked at each fortification level, were extracted. Recoveries of some pesticides, such as organophosphorus compounds, were >115% when calibration without spiked blanks was used (data not shown); therefore, the quantification of pesticide residues was carried out with fortified blank samples.

Table 4. Recoveries[a] of the Studied Pesticides

compound	fortification level 0.2 μg/g	0.1 μg/g	0.05 μg/g	compound	fortification level 0.2 μg/g	0.1 μg/g	0.05 μg/g
EPTC	100.1 ± 3.8	96.3 ± 3.5	90.6 ± 2.7	triadimefon	99.9 ± 8.1	99.5 ± 8.2	97.0 ± 8.5
molinate	103.1 ± 2.9	95.1 ± 4.3	90.4 ± 2.9	butralin	103.3 ± 4.4	96.5 ± 5.6	92.6 ± 6.8
propachlor	101.7 ± 3.8	95.6 ± 3.1	92.2 ± 4.1	pendimethalin	104.4 ± 5.5	101.1 ± 7.3	87.9 ± 10.2
ethalfluralin	98.8 ± 10.4	94.8 ± 4.3	87.5 ± 7.3	phenthoate	106.2 ± 9.5	96.3 ± 7.3	96.7 ± 8.1
trifluralin	104.1 ± 4.5	96.3 ± 4.7	88.5 ± 7.0	procymidone	99.1 ± 5.0	98.9 ± 4.9	96.6 ± 5.9
simazine	100.2 ± 5.0	96.4 ± 5.1	94.0 ± 5.5	methidathion	104.9 ± 8.6	99.0 ± 10.0	97.8 ± 6.3
atrazine	102.7 ± 3.3	96.6 ± 4.0	96.1 ± 5.1	endosulfan I	94.4 ± 3.6	98.3 ± 3.4	100.6 ± 5.2
terbuthylazine	100.8 ± 3.1	97.0 ± 3.8	94.5 ± 4.8	profenophos	98.0 ± 6.8	103.5 ± 7.6	103.9 ± 5.8
diazinon	101.4 ± 9.1	98.6 ± 5.5	94.9 ± 4.9	oxadiazon	94.5 ± 4.7	96.9 ± 4.2	98.0 ± 8.3
chlorothalonil	100.4 ± 3.3	95.8 ± 4.4	94.2 ± 5.5	cyproconazole	96.5 ± 8.9	96.8 ± 7.9	89.2 ± 4.5
triallate	98.4 ± 2.7	98.0 ± 4.0	93.8 ± 3.5	endosulfan II	101.3 ± 6.0	95.8 ± 6.7	104.0 ± 8.3
metribuzin	104.7 ± 6.8	97.1 ± 7.3	96.2 ± 7.0	ethion	104.0 ± 10.6	102.2 ± 8.9	103.6 ± 6.5
parathion-methyl	103.0 ± 5.3	97.1 ± 9.5	94.1 ± 7.3	ofurace	98.2 ± 8.1	96.1 ± 8.6	101.2 ± 10.5
tolclofos-methyl	101.5 ± 3.3	98.1 ± 4.0	94.8 ± 4.1	benalaxyl	100.0 ± 6.8	98.9 ± 5.3	99.6 ± 4.6
alachlor	101.1 ± 3.4	97.8 ± 5.4	94.6 ± 5.1	endosulfan sulfate	99.0 ± 6.6	98.4 ± 6.3	100.8 ± 8.7
prometryn	100.6 ± 4.9	94.1 ± 5.9	92.5 ± 6.1	nuarimol	99.0 ± 3.4	102.2 ± 5.2	105.1 ± 5.6
terbutryn	100.1 ± 6.0	95.0 ± 5.6	93.9 ± 6.0	bromopropylate	96.6 ± 2.8	102.7 ± 4.6	99.7 ± 6.0
fenitrothion	100.3 ± 9.8	98.5 ± 6.6	97.4 ± 7.7	tetradifon	93.1 ± 5.1	99.2 ± 3.4	90.6 ± 7.1
pirimiphos-methyl	100.1 ± 6.0	96.1 ± 5.8	96.5 ± 6.1	cyhalothrin	96.6 ± 3.7	99.5 ± 4.0	96.7 ± 6.1
dichlofluanid	96.5 ± 5.1	100.1 ± 7.2	98.6 ± 6.3	fenarimol	89.0 ± 7.1	98.8 ± 6.6	100.0 ± 7.4
aldrin	96.4 ± 2.7	97.1 ± 4.4	93.9 ± 3.7	pyrazophos	99.3 ± 4.9	101.4 ± 2.7	97.8 ± 5.3
malathion	103.9 ± 6.1	95.7 ± 9.5	99.6 ± 7.4	coumaphos	96.6 ± 4.6	101.2 ± 4.8	96.2 ± 5.1
metolachlor	97.7 ± 3.9	96.0 ± 4.6	95.6 ± 5.9	cypermethrin	87.0 ± 3.7	102.6 ± 4.4	98.8 ± 7.3
fenthion	98.0 ± 5.9	94.4 ± 2.4	91.3 ± 2.9	fluvalinate tau-I	91.9 ± 9.2	101.2 ± 5.5	104.0 ± 6.8
chlorpyrifos	98.3 ± 4.6	94.2 ± 5.7	98.4 ± 5.2	fluvalinate tau-II	91.9 ± 9.2	100.9 ± 8.5	96.2 ± 7.6

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

Table 5. Pesticide Residues Found in Real Soil Samples

	pesticide	forested fields[a] range of residues (μg/kg)	forested fields[a] positive samples (%)	tomato fields[b] range of residues (μg/kg)	tomato fields[b] positive samples (%)	corn fields[c] range of residues (μg/kg)	corn fields[c] positive samples (%)
4	ethalfluralin			17–228	43.8		
6	simazine	225–2531	100				
7	atrazine	6–23	50				
16	alachlor					3–117	100
19	fenitrothion					7–14	27.8
24	metolachlor					17–22	16.7
29	pendimethalin			5–38	43.8	5–20	16.7
37	endosulfan II			16–76	50		
41	endosulfan sulfate			9–99	100		

[a] Eight forested fields were sampled 1 month after reforestation. [b] Sixteen tomato fields were sampled after harvest. [c] Eighteen corn fields were sampled after harvest.

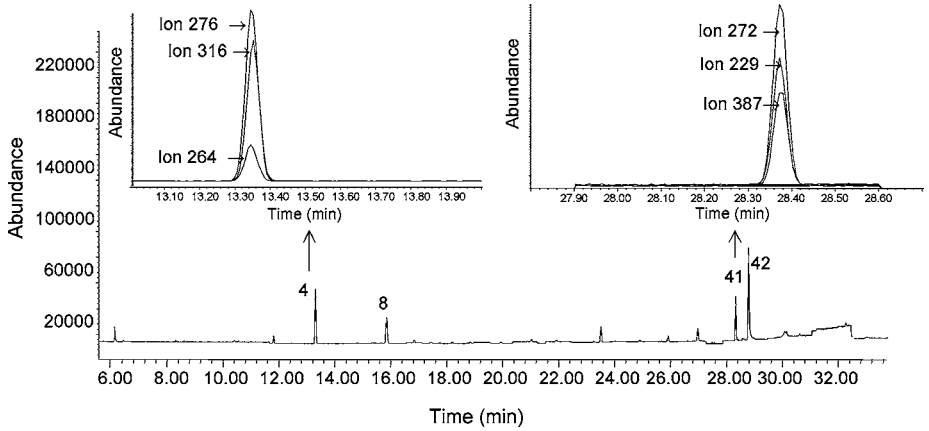

Figure 2. GC-MS-SIM chromatogram of a soil sample collected from a tomato field. Peak 4 is ethalfluralin (227 μg/kg), and peak 41 is endosulfan sulfate (70 μg/kg). Peaks 8 and 42 are internal standards.

The recoveris obtained for all pesticides ranged from 87.0 to 106.2%. The precision of the method, obtained as the RSD of analyte recoveries, is good, <11%. These values were obtained with freshly fortified soil samples, but, as this method is based on that of previously published papers where good recoveries were obtained for aged residues of pesticides from different groups (*10*, *11*), the proposed method can be used for the analysis of freshly added as well as weathered pesticide residues in soil. The obtained values are similar to the recoveries reported by other authors using SPE (*1*, *5*) or supercritical fluid extraction (*18*) for the analysis of pesticides in soil.

Detection and Quantification Limits. The limits of detection (LOD) of the proposed method were determined by considering a value 3 times the background noise obtained for blank samples, whereas the limits of quantification (LOQ) were determining considering a value 10 times the background noise. **Table 3**

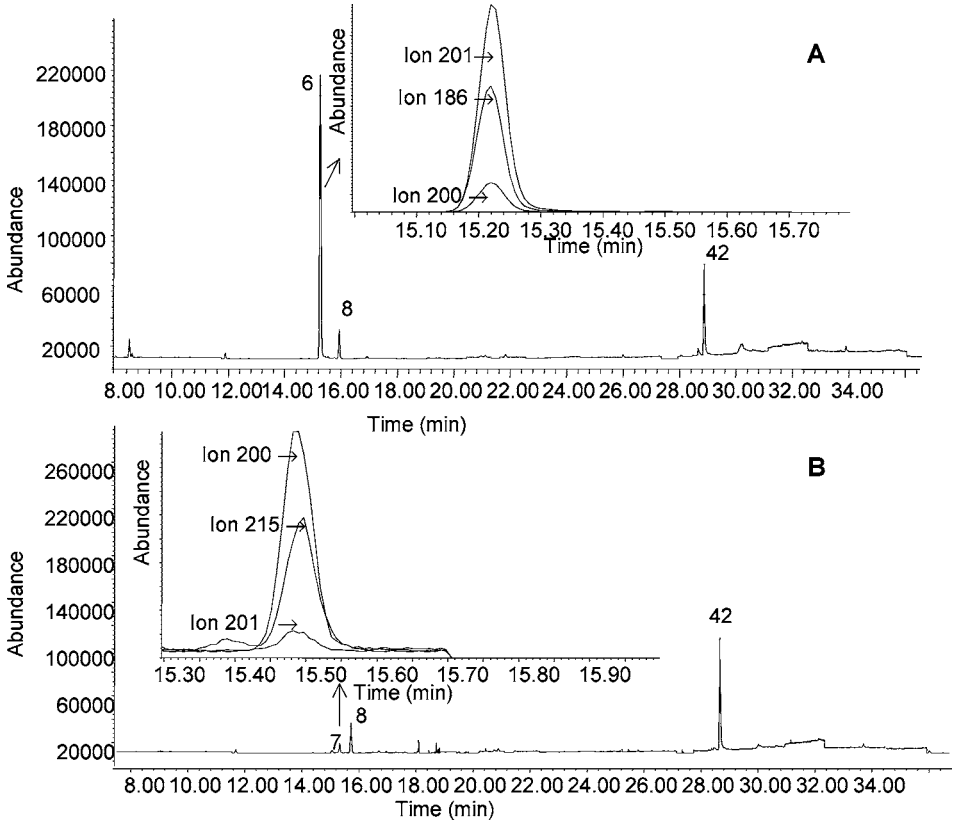

Figure 3. GC-MS-SIM chromatograms of (**A**) a soil sample collected from a forested field [peak 6 is simazine (446 μg/kg)] and (**B**) a soil sample collected from a corn field. Peak 7 is atrazine (11 μg/kg). Peaks 8 and 42 are internal standards.

summarizes the LODs and LOQs obtained for the individual pesticides in soil. The range of LOD achieved is in the lower end of that obtained by other authors (*1*, *18*).

Real Samples. The developed method was applied to the determination of pesticides in soil samples collected in Spain from several commercial orchards after harvest and from forested marginal fields 1 month after reforestation. Sixteen samples from tomato fields, 8 samples from forested fields, and 18 samples from corn fields were analyzed. In samples taken from tomato fields, pendimethalin, endosulfan II, endosulfan sulfate, and ethalfluralin were found. In soil samples taken from forested fields, simazine and atrazine were the herbicides found, and in samples taken from corn fields, the herbicides atrazine, alachlor, and metolachlor, together with the insecticide fenitrothion, were found. Pesticide levels encountered in the collected samples are shown in **Table 5**. **Figures 2** and **3** depict representative chromatograms obtained in the analysis of soil samples, together with the confirmation of the identity of the pesticides found.

Conclusion. A rapid and sensitive method, based on the sonication-assisted extraction of samples placed in small columns, has been developed for the simultaneous determination of 50 pesticides in soil by GC-MS-SIM. With the proposed analytical method, the extraction of samples is performed with a low volume of ethyl acetate, and a subsequent cleanup is not required. The good reproducibility and the low detection and quantification limits achieved with this method allow its application to monitoring of pesticide residues in soil. This method was applied to the analysis of pesticides in soil samples collected in various agricultural areas of Spain, where several herbicides and insecticides were found.

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