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Capillary Gas Chromatography with Atomic Emission Detection for Pesticide Analysis in Soil Samples

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A method for the simultaneous determination of 10 pesticides (organochlorines, organophosphorus compounds, and pyrethrins) in soils using capillary gas chromatography with atomic emission detection (GC-AED) is reported. Soil samples are first "cleaned-up" with 25 mL of an ascorbic acid solution (pH 2.15). The aqueous phase is extracted with ethyl acetate, and the solid residue is then extracted twice with 10 mL of ethyl acetate. The three resultant organic extracts are combined, concentrated to dryness, and reconstituted in 1 mL of acetone. The pesticides are selectively detected by monitoring chlorine and bromine in the first run and sulfur emission line wavelength in the second run. Each chromatographic run takes 19 min. Detection limits are between 25 and 75 pg, depending on the compound, which corresponds to 1.7 and 5.0 ng/g in the soil samples, respectively. Recoveries of the pesticides from spiked preparations result in an overall mean recovery of 95.3% ($n = 120$) at fortification levels ranging from 10 to 60 ng/g, depending on the compound. The method is reliable and can be useful for routine monitoring in soils.

KEYWORDS: Gas chromatography-atomic emission detection; pesticide analysis; organochlorine compounds; organophosphorus compounds; pyrethrins; soils

INTRODUCTION

Pesticides have potentially adverse effects on vegetable or animal resources and human health (*1*). Because of their widespread use, they are detected in many types of environmental matrixes. The most are applied directly to soil or sprayed over crops fields, and hence are released directly to the environment. Soil analyses, therefore, are of great interest, because they are the basis for important decisions as regards crop management and environmental monitoring. The US Environmental Protection Agency (EPA) has identified twelve priority persistent bioaccumulative and toxic (PBT) compounds of special interest (*2*), a list which includes three of the pesticides analyzed in this paper (DDT and its break-down products, DDE and DDD).

Pesticides almost always contain heteroatoms, often several in a single molecule. Gas chromatography (GC) using atomic emission detection (AED) is a highly selective analytical technique of great importance in the determination of pesticides in environmental samples (*3*−*11*), owing to its ability to detect specific elements. Although gas chromatography has been used widely for the determination of pesticides in soil and sediment samples, we have found few references to the use of GC combined with AED in the same samples (*3*, *5*, *9*, *10*).

The atomic emission detector is much more versatile and selective than the most commonly used element-selective detectors, such as the nitrogen−phosphorus detector (NPD), flame photometric detector (FPD), electron-capture detector (ECD) or electrolytic conductivity detector (ELCD), because it can detect all elements separately, except helium (*8*). The GC-AED system then, is a powerful multielement analyzer, with the flexibility to be both general and selective. The eluent from the chromatograph enters a microwave-induced helium plasma, where the high-temperature fragments and excites the atoms to higher electronic states. A photodiode array spectrometer is used to simultaneously measure the intensity of the light emitted by the excited atoms as they undergo transitions to lower energy levels. Compared to gas chromatography-mass spectrometry (GC-MS), the instrumentation used in GC-AED is easier to operate and maintain, and its chromatograms can be interpreted by a semi-skilled analyst.

Extraction techniques for pesticide analysis in soil samples must be adapted to each particular pesticide or pesticide family. The separation of pesticides from solid samples usually involves solvent extraction from the sample matrix followed by preconcentration, normally by evaporation. Methods for residue analysis usually include a cleanup step to remove interfering co-extractives, because solvents are nonselective and therefore tend to extract endogenous material from the soil, which may produce spurious peaks on the chromatogram. Such cleanup steps may vary and include gel permeation chromatography (*12*), solid-phase extraction (SPE) (*5*, *6*, *8*), and headspace solid-phase microextraction (HS-SPME) (*13*−*14*). Recently, supercritical fluid extraction (SFE) has gained ground in this area (*1*), although this technique presents several disadvantages, such as high equipment costs, a marked influence of the soil moisture

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content on recoveries, and typically, low recoveries for polar substances. In the present study, a gas chromatography-atomic emission detection procedure (GC-AED) for the simultaneous analysis of 10 pesticides, including organochlorine, organophosphorus, and pyrethrins, in soil samples is described. The method is rapid and involves a simple sample treatment step.

EXPERIMENTAL PROCEDURES

Instrumentation. An Agilent 6890 gas chromatograph (Waldbronn, Germany) directly coupled by a transfer line to a G2350A microwave-induced plasma atomic emission detector (Agilent) were used. Updated G2070AA ChemStation application with the G2360AA GC-AED software was used to control and automate many features of the GC and AED systems. Pulsed splitless (40 psi) injection of 3-μL volumes was performed with a 7683 automatic injector (Agilent) at an injection temperature of 300 °C; the transfer line temperature was 325 °C. No glass wool-packed liner was used, because its use is known to lead to the thermodegradation and/or absorption of some pesticides (*15*). The chromatograph was fitted with a 30 m × 0.32 mm i.d., 0.25-μm HP-5, 5% dimethyl polysiloxane capillary column from Agilent. The oven temperature was programed as follows: 50 °C for 1 min, rising to 185 °C at 50 °C/min and holding for 2 min, rising to 205 °C at 3 °C/min, to 250 °C at 50 °C/min and holding for 2.2 min, and finally to 310 °C at 30 °C/min and holding for 1.5 min. Helium was used as the carrier gas at 3.2 mL/min, in the constant-flow mode. Helium was also used as the makeup gas in the AED at 40 mL/min. The solvent venting was switched on immediately after injection and switched off 4.5 min after injection. The spectrometer was purged with nitrogen at a flow rate of 2.5 L/min. Oxygen and hydrogen were used as reagent gases, each at 20 psi. Filter and backamount adjustment were set according to Agilent default specifications.

An IKAKS 130 basic shaker (IKA, Staufen, Germany) was used for automatic shaking, and a Hermle Z 252μ centrifuge (HERMLE Labortechnik, Wehingen, Germany) for phase separation. A Büchi vacuum V-500 rotatory evaporator R-200 coupled with a Büchi heating bath B-490 (BÜCHI Labortechnik AG, Flawil, Switzerland) was used to concentrate the sample extracts.

Reagents. Pesticide standards with a purity higher than 94% were obtained from Ehrenstorfer (Augsburg, Germany). Stock standard solutions of 1000 μg/mL were prepared by exact weighing and dissolving in acetone and stored in the dark at 4 °C. Working standard solutions were prepared freshly by dilution in the same solvent. Analytical-reagent grade acetone and ethyl acetate were supplied by Lab-Scan (Dublin, Ireland). Dichloromethane and hexane were purchased from Romil (Cambridge, UK). Helium, nitrogen, oxygen and hydrogen (99.999% purity) were purchased from Air Liquid (Madrid, Spain).

Samples. Six sampling points were selected from the agricultural area of Murcia for taking surface soil samples. Samples of soil (100 g) were collected in plastic (polypropylene) bottles from each sampling site. In the laboratory, the samples were dried in the air at room temperature, crushed by a mortar and stored at 4 °C to prevent any changes induced by microbial action. Samples were extracted within 48 h of arrival in the laboratory.

Procedures. A 5-g portion of soil was treated with 25 mL of ascorbic acid at pH 2.15. The mixture was automatically shaken for 5 min, after which the liquid phase was separated from the solid residue by centrifugation at 4000 rpm for 4 min and decanted into a reservoir to be extracted with 10 mL of ethyl acetate by automatically shaking for 5 min at 480 rpm. The organic phase was separated from the aqueous phase by centrifugation at 4000 rpm for 4 min and stored. The soil residue was then extracted twice with 10 mL of ethyl acetate while, being manually shaken for 5 min. The three organic phases were combined and concentrated by removing the solvent on a rotatory evaporator at 40 °C and 240 mbar for 15 min, aproximately. Finally, the dry extract was collected with 1 mL of acetone and injected into the gas chromatograph instrument.

Recovery Assays. Fortified samples were prepared by adding 500 μL of acetone containing a known amount of each pesticide to 5 g of soil. The solvent was evaporated at room temperature for 4 h, and the sample was then homogenized in a mechanical shaker for 5 min, and subsequently stored at room temperature in the darkness for 30 min, prior to extraction according to the above procedure. Three replicates were analyzed at each fortification level. Samples were fortified at levels ranging from 10 to 60 ng/g, depending on the pesticide.

Table 1. Pesticides Chromatographed

pesticide	purity	molecular formula	retention time (min)
chlorpropham	99.5	$C_{10}H_{12}ClNO_2$	5.6
lindane	98.5	$C_6H_6Cl_6$	6.5
diazinon	94.0	$C_{12}H_{21}N_2O_3PS$	6.7
chlorpyriphos	99.5	$C_9H_{11}Cl_3NO_3PS$	9.0
α-endosulfan	97.0	$C_9H_6Cl_6O_3S$	11.0
p,p′-DDE	98.7	$C_{14}H_8Cl_4$	12.0
p,p′-DDD	97.5	$C_{14}H_{10}Cl_4$	13.2
p,p′-DDT	98.5	$C_{14}H_9Cl_5$	13.8
permethrin	98.8	$C_{21}H_{20}Cl_2O_3$	16.7
deltamethrin	98.5	$C_{22}H_{19}Br_2NO_3$	18.2

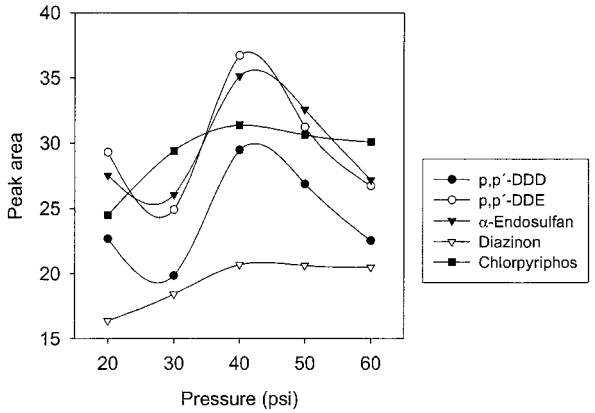

Figure 1. Influence of pulse pressure on the peak area for α-endosulfan, p,p′-DDD and p,p′-DDE, ascertained by monitoring the Cl 479 nm emission line, and for chlorpyriphos and diazinon, by monitoring the S 181 nm emission line (200 ng/mL).

RESULTS AND DISCUSSION

Chromatographic Parameters. The optimized program temperature elutes the 10 pesticides between 5.5 and 19 min, as shown by their respective retention times (**Table 1**). The chromatogram started at 50 °C, before increasing to 185 °C, which was maintained for 2 min to elute chlorpropham; the oven temperature was then slowly increased to 205 °C, thus permitting lindane, diazinon, chlorpyriphos, α-endosulfan and p,p′-DDE to elute. The following pesticide to be eluted was p,p′-DDD, as the temperature was increased to 250 °C, and at this temperature, the signal of p,p′-DDT was obtained. In the final ramp to 310 °C, permethrin was eluted, and when this temperature was maintained, deltamethrin was eluted. Separation was carried out using a constant helium flow rate of 3.2 mL/min, which reduced the analysis necessary with no overlapping peaks. The effect of the injection temperature for these pesticides was investigated in previous studies (*11*), and as a result, 300 °C was selected. To avoid the necessity of frequent maintenance, a 3-μL volume was injected in splitless mode. To improve the efficiency of sample transfer, the carrier gas inlet pressure was increased just before the beginning of a run and returned to the normal value after a specified amount of time (*16*). **Figure 1** shows the signals obtained for some of the studied pesticides when the pressure applied was varied between 20 and 60 psi. A pressure of 40 psi was adopted, because this provided the maximum signal for all pesticides.

Optimization of the AED Parameters. When extracted from soil samples, pesticides are often isolated together with numerous other synthetic and natural organic compounds. Using GC-AED, it is possible to monitor every element in a pesticide,

Table 2. Calibration Data for the Target Pesticides

pesticide	monitored emission line (nm)	slope (ml/ng)[a]	ordinate[a]	corr coef	linearity range (ng/mL)
chlorpropham	Cl 479	0.0249 ± 0.0003	3.6066 ± 0.0940	0.9998	60–1000
lindane	Cl 479	0.2984 ± 0.0074	–1.8604 ± 0.5800	0.9990	15–750
diazinon	S 181	0.1843 ± 0.0005	0.3274 ± 0.656	0.9999	35–1000
chlorpyriphos	Cl 479	0.0664 ± 0.0018	–0.3187 ± 0.1715	0.9996	50–1000
α-endosulfan	Cl 479	0.1961 ± 0.0068	–1.1782 ± 0.6981	0.9990	20–1000
p,p′-DDE	Cl 479	0.1125 ± 0.0048	–0.7099 ± 0.4133	0.9991	30–1000
p,p′-DDD	Cl 479	0.1870 ± 0.0061	–1.7870 ± 0.5113	0.9995	25–1000
p,p′-DDT	Cl 479	0.0491 ± 0.0015	–1.3331 ± 0.1376	0.9995	50–1000
permethrin	Cl 479	0.0409 ± 0.0007	1.3600 ± 0.1807	0.9998	50–1000
deltamethrin	Br 478	0.0194 ± 0.0001	0.0464 ± 0.0134	0.9999	70–1000

[a] Mean ± standard deviation ($n = 3$).

providing multiple channels of corroborative data. Nevertheless, for technical reasons, not all the elements can be detected simultaneously in one GC run. The system scanned the seven elements contained as heteroatoms in the pesticides under study, requiring three separate injections, each with a 19 min run time. Nitrogen (174 nm), carbon (179 nm), carbon (193 nm), and sulfur (181 nm) can be observed simultaneously, because their emission line wavelengths are close and these elements require oxygen and hydrogen as scavenger gases. A second injection is required to monitor bromine (478 nm), chlorine (479 nm), hydrogen (486 nm) and carbon (496 nm), which only require oxygen as the reagent gas. Finally, while phosphorus (178 and 186 nm) could be observed with the first group; it needs a separate injection, because it requires hydrogen as the only scavenger gas. As phosphorus emission lines were not used, owing to the low sensitivity, only two sequential runs were necessary for quantification purposes.

To determine the optimum helium makeup gas flow rate that allows maximum sensitivity in the detection of the pesticides, a standard solution of 1 μg/mL was injected, using different makeup gas flow rates ranging from 40 to 100 mL/min. As expected, a reduction in the makeup gas flow was accompanied by an increase in peak area. Several flow-rates were assayed, and 40 mL/min was adopted as the optimum value for C, N, S, H, Br, and Cl.

Calibration Graphs and Repeatability. Linear calibration curves were obtained for all the pesticides in different concentration ranges, depending on the compound. **Table 2** shows the characteristics of the calibration graphs used to quantify every pesticide, with the wavelength emission line indicated for each compound being the most sensitive in every case. The correlation coefficients derived from the linear regressions are better than 0.999 for all the studied pesticides. It is worth noting that, although lindane and diazinon are eluted with very close retention times, their detection and quantification pose no problems, because they are monitored at different emission lines, which is one of the great advantages of the AED system. The repeatability was calculated using the relative standard deviation for 10 successive injections of a mixture of the pesticides and was in the range of 4.0−5.8% (RSD), depending on the compound. Detailed results are presented in **Table 3**. Detection limits were calculated using a signal-to-noise ratio of 3 for all the investigated compounds. Values are also given in **Table 3** for the standards and for soil samples when using the optimized extraction procedure.

Optimization of the Extraction Procedure. Preliminary experiments carried out by extracting the pesticides directly from the soil using dichloromethane, ethyl acetate, or hexane did not isolate the pesticides, because numerous compounds were co-extracted. Furthermore, interpretation of the chromatograms was impossible, especially when monitoring the sulfur (181 nm) emission line, due to interference from other sulfur-containing compounds in the soils. The low solubility of the studied pesticides in water led us to include a cleanup step with water, to eliminate interferences, discarding the aqueous phase and then using an organic solvent to extract the pesticides from the solid residue. The beneficial effect of adding acid to the extraction medium on pesticide recoveries from soil samples has been documented (*9*). For this reason, an ascorbic acid solution was used, which improved the results. To select the most suitable organic solvent, 1 g of spiked soil previously cleaned-up with 5 mL of ascorbic acid was extracted, using dichloromethane, hexane, or ethyl acetate. **Figure 2** shows the extraction percentages obtained in each case. Ethyl acetate was selected

Table 3. Accuracy and Detection Limits for the Pesticides

pesticide	RSD (%)[a]	detection limit (pg)[b]	detection limit (ng/g)[c]
chlorpropham	4.5 (150)	70	4.7
lindane	5.2 (75)	25	1.7
diazinon	5.7 (100)	35	2.3
chlorpyriphos	5.5 (100)	60	4.0
α-endosulfan	5.5 (100)	35	2.3
p,p′-DDE	5.0 (100)	45	3.0
p,p′-DDD	5.1 (100)	35	2.3
p,p′-DDT	5.8 (100)	55	3.7
permethrin	5.6 (100)	65	4.3
deltamethrin	4.0 (150)	75	5.0

[a] Values in brackets are the pesticide concentrations in ng/mL. [b] Corresponding to S/N = 3 from blanks. [c] Calculated for 5 g of soil, according to the optimized extraction procedure.

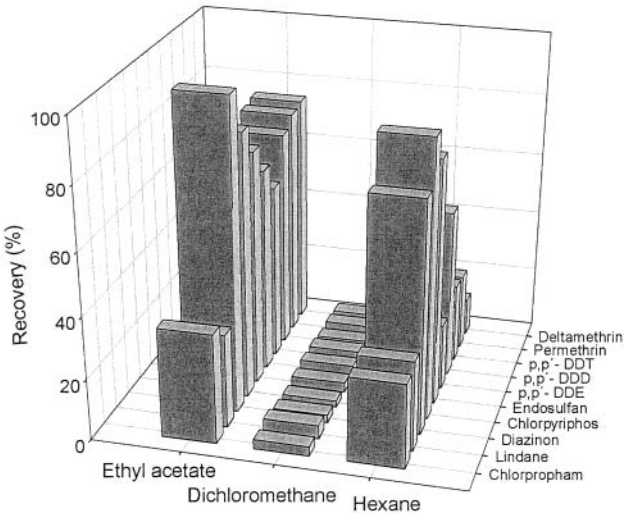

Figure 2. Extraction percentages obtained for each pesticide at 100 ng/g fortification level in a soil sample, using ethyl acetate, hexane, and dichloromethane as the organic solvents.

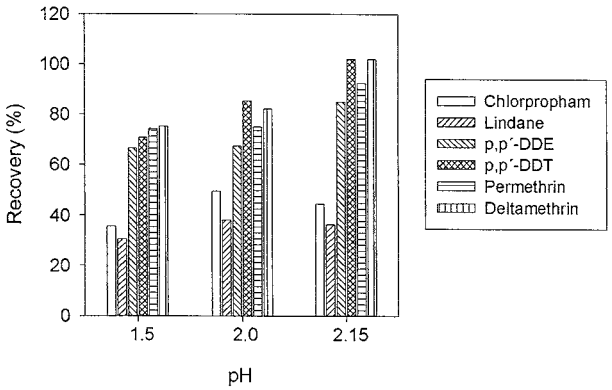

Figure 3. Variation of the extraction percentage of some pesticides with the pH of the ascorbic acid solution for solid samples only. Fortification levels: chlorpropham (35 ng/g); lindane (10 ng/g); p,p′-DDE (15 ng/g); p,p′-DDT (15 ng/g); permethrin (40 ng/g); and deltamethrin (30 ng/g).

because it provided the best recoveries. All of these experiments involved a double extraction in 5 mL of the organic solvent and shaking manually for 5 min. Attempts were made to avoid the second extraction stage by increasing the volume of ethyl acetate, but it proved necessary for all the pesticides except chlorpropham, for which the second extraction did not provide signal. This need for double extraction was corroborated by injecting into the chromatograph the second extract, previously dried and reconstituted in 1 mL of acetone.

Different solutions of ascorbic acid from pH 1 to 2.5 were assayed to select the pH value that eliminated most impurities; values above 2.5 did not alleviate impurity problems. **Figure 3** shows the results obtained when 1 g of soil was automatically shaken for 5 min with 5-mL ascorbic acid solutions at different pHs. A value of 2.15 was selected, because this led to recoveries above 80% for all the compounds, except chlorpropham and lindane, which provided recoveries close to 40%.

Table 4. Mean Recovery Efficiencies and RSD Obtained in Fortified Soil Samples, Using the Proposed Method

		recovery (%), RSD (%) in parentheses[a]					
pesticide	spike level, ng/g	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6
chlorpropham	35	114.6 (11.5)	108.5 (10.8)	91.6 (11.2)	105.3 (8.8)	102.1 (9.2)	105.9 (14.3)
	60	104.9 (6.4)	113.2 (5.5)	105.6 (8.9)	100.7 (8.8)	111.4 (14.3)	99.2 (5.5)
lindane	10	96.6 (8.3)	97.5 (10.2)	100.8 (5.6)	95.7 (10.3)	100.2 (3.9)	98.4 (3.2)
	16	97.5 (7.7)	108.3 (3.7)	101.7 (6.9)	100.6 (7.9)	99.0 (15.0)	100.6 (8.2)
diazinon	12	85.4 (10.2)	83.0 (8.2)	87.5 (10.4)	98.6 (7.9)	87.9 (8.4)	95.9 (10.2)
	20	93.9 (7.4)	92.0 (9.9)	100.1 (6.7)	85.0 (11.3)	82.7 (12.5)	89.1 (12.4)
chlorpyriphos	20	88.1 (3.2)	90.0 (7.6)	86.8 (6.5)	87.0 (7.3)	102.5 (10.8)	88.9 (6.0)
	30	92.6 (5.6)	92.4 (13.4)	92.4 (13.4)	96.2 (14.3)	105.1 (2.2)	86.4 (5.4)
α-endosulfan	12	86.1 (8.7)	89.5 (12.2)	78.9 (4.5)	99.7 (5.7)	105.6 (4.1)	90.6 (8.7)
	20	89.6 (8.4)	87.4 (11.8)	94.2 (2.9)	91.5 (10.1)	93.7 (13.3)	96.2 (4.0)
p,p′-DDE	15	102.9 (6.5)	80.7 (9.6)	82.6 (16.7)	96.8 (6.3)	91.4 (10.2)	99.4 (5.5)
	25	98.9 (4.9)	89.2 (15.4)	88.4 (15.2)	101.8 (6.3)	103.4 (6.6)	108.0 (4.9)
p,p′-DDD	15	104.3 (6.3)	88.1 (14.4)	90.2 (17.9)	97.4 (8.2)	107.4 (5.9)	101.2 (7.1)
	25	99.1 (6.0)	91.6 (12.8)	88.0 (11.5)	86.9 (9.0)	100.3 (12.0)	114.8 (9.3)
p,p′-DDT	15	100.1 (7.8)	88.7 (2.8)	95.9 (8.8)	100.1 (8.0)	98.7 (8.3)	101.4 (7.8)
	25	93.8 (7.1)	99.7 (4.8)	99.7 (9.0)	98.7 (9.1)	101.2 (9.9)	98.9 (6.9)
permethrin	40	101.5 (8.2)	84.2 (9.7)	91.2 (10.9)	83.7 (9.7)	102.8 (12.0)	82.8 (4.5)
	60	89.7 (9.5)	94.7 (4.5)	87.3 (5.0)	83.5 (7.0)	89.2 (9.1)	83.8 (5.2)
deltamethrin	30	93.7 (6.3)	98.9 (10.7)	99.0 (4.7)	97.6 (7.9)	104.3 (11.6)	79.0 (13.9)
	45	96.0 (2.6)	94.8 (12.8)	89.3 (2.6)	96.0 (5.4)	95.5 (8.8)	77.7 (6.5)

[a] $n = 3$.

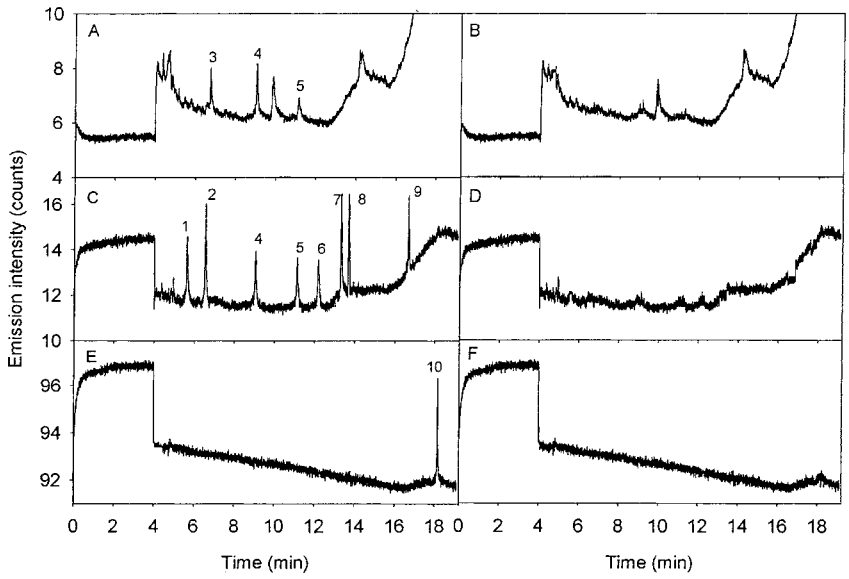

Figure 4. GC-AED chromatograms obtained from soil 4, previously fortified with a standard mixture of pesticides (A, C, E) and a negative control of soil 4 (B, D, F). (A, B) S 181 nm, (C, D) Cl 479 nm, and (E, F) Br 478 nm. (1) chlorpropham (55 ng/g); (2) lindane (15 ng/g); (3) diazinon (19 ng/g); (4) chlorpyriphos (30 ng/g); (5) α-endosulfan (15 ng/g); (6) p,p′-DDE (20 ng/g); (7) p,p′-DDD (20 ng/g); (8) p,p′-DDT (20 ng/g); (9) permethrin (45 ng/g) and (10) deltamethrin (60 ng/g).

Automatic and manual shaking were compared for their effect on pesticide extraction from the solid residue, with similar results being obtained when the soil was shaken manually with 10 mL of ethyl acetate for 5 min or automatically for 20 min. Therefore, manual shaking was adopted, because of the reduction in time. Under the selected conditions (i.e., 5 g of soil automatically stirred with 25 mL of an ascorbic acid solution (pH 2.15) as the cleanup step and the solid residue extracted twice with 10 mL of ethyl acetate by shaking manually for 5 min), the extraction percentages were nearly 100% for all the pesticides, except chlorpropham and lindane, which showed recoveries lower than 50%. Several alternatives were assayed to solve this problem. These included inverting the order of the procedure, i.e., first extracting the pesticides in ethyl acetate and then cleaning-up this organic extract with the ascorbic acid solution. However, this did not provide clean chromatograms. Neither did neutralization of the soil with sodium bicarbonate prior to the cleanup step with the ascorbic acid improve the recoveries for the two mentioned pesticides, because dirty extracts were obtained. The reason for obtaining such low recovering values for chlorpropham and lindane was found to be that the unrecovered fraction of the two pesticides did not remain in the solid residue but was extracted into the ascorbic acid solution. This was experimentally verified by extracting with ethyl acetate the aqueous phase obtained in the cleanup stage and then combining this organic phase with those obtained from the solid residue. In this way, recoveries near 100% were obtained for both pesticides.

To check the performance of the procedure, soil samples of 1−10 g were submitted to the optimized extraction procedure. Because impurities could not be totally eliminated from the 10 g sample, a sample mass of 5 g was selected and cleaned with 25 mL of ascorbic acid (pH 2.15).

Analysis of Soil Samples and Recovery Study. Six soil samples of 5 g were used to test the optimized extraction method. The slopes of the calibration graphs with the standards directly prepared in acetone and the standard addition calibration graphs obtained from the soil samples were similar, confirming the absence of any matrix effect. Sample analyses were run in triplicate. Two of the analyzed samples provided signals for lindane, which were in a range of 0.07−0.11 mg/kg, and one of these soils also contained chlorpropham at 0.225 mg/kg concentration. The recoveries of pesticides from spiked soils varied from 77.7 to 114.6%, with an average recovery ± SD ($n = 120$) of 95.3 ± 7.9%, as can be seen in **Table 4**. **Figure 4** shows the chromatograms obtained for a spiked and a negative control soil using different emission lines.

CONCLUSION

The use of the selective AED device in GC allows a group of 10 important pesticides to be quantified in soils. The multiresidue procedure developed is relatively simple. The analytical characteristics and recovery data prove its reliability, which makes it suitable for the monitoring of pesticide pollution in soils.

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