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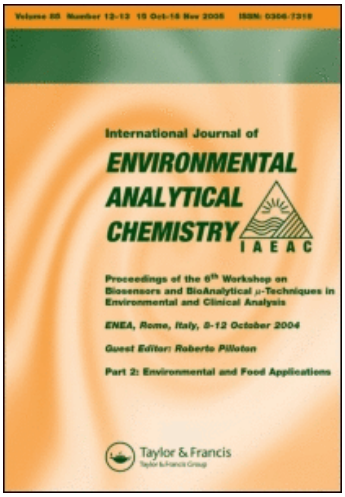

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ANALYSIS OF PESTICIDES IN WATER SAMPLES USING GC-ECD AND GC-MS/MS TECHNIQUES

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A pesticide multiresidue method for determining dichlorvos, naled, lindane, diazinon, chlorpyrifos-methyl, dichlofluanid, chlorpyrifos, folpet, α- and β-endosulfan, endosulfan-sulphate, fenpropathrin and acrinathrin in water samples at the levels required by the EEC Drinking Waters Directive has been developed. The pesticides were selected among the most used during the last 20 years in Almería (Spain), where there is a high agricultural activity. Solid Phase Extraction (SPE) was selected as extraction method after being compared with Liquid-Liquid Extraction (LLE). Moreover, different gas chromatographic detectors (Electron Capture Detector, ECD; Mass Spectrometer, MS; Tandem Mass Spectrometer, MS/MS) were compared. The best results of repeatability and sensitivity were obtained for ECD and MS/MS.

Keywords: Pesticides; water; SPE; GC-ECD; GC-MS; GC-MS/MS

INTRODUCTION

Monitoring pesticides in water samples has been an issue of great relevance in the last decades. The EEC Drinking Waters Directive[1] establishes a concentration threshold of 0.1 $\mu g\ l^{-1}$ for each individual pesticide or 0.5 $\mu g\ l^{-1}$ for the total amount of them, including their main metabolites. This requires the development of analytical methodologies sensitive and selective enough to fulfil these requirements.

Chromatographic methods are widely used for analytical separation, identification and quantification of as many pesticides as possible in one run. In practice, Gas Chromatography (GC) using long capillary columns and with selective and sensitive detectors, such as Electronic Capture Detector (ECD)[2–6], has been one

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of the most often employed analytical techniques for the determination of pesticides. Relative retention times are the criteria applied for identification of chromatographic peaks, but an additional confirmatory technique is also necessary. To this end, the coupling of GC with Mass Spectrometry (MS) has been extensively used, as it increases the selectivity and certainty of identification, avoiding false positives in pesticide multiresidue determinations in water[7–10]. The sensitive and selectivity can even be improved by using Tandem Mass Spectrometry (MS/MS). Most matrix interferences are avoided and the target compounds are identified by their secondary spectra. Other alternatives for the confirmation of residues are the use of different GC detectors[11], as well as the use of two GC columns with different polarity[12,13]. The last option is very useful in laboratories that do not have GC-MS instrumentation available and it is still recommended in some official analytical methods.

However, in order to reach the levels of sensitivity for the determination of the amounts of pesticides allowed in drinking water, an extraction and enrichment steps are always necessary prior to their instrumental analysis. Several methods[14,15] have been developed to accomplish this task, including: Liquid Liquid Extraction (LLE)[16,17], Solid Phase Extraction (SPE)[6,18–21], Extraction Disk[9,22,23], Supercritical Fluid Extraction[24,25], Solid Phase Microextraction[26,27], Micro Liquid Liquid Extraction[28–30] or Extraction using Hollow Fibber Membranes[31,32]. At present, the two most common preconcentration methods of pesticides from environmental samples are LLE and SPE.

LLE is a simple, effective and fully developed technique, however, it is time-consuming, expensive and sometimes harmful by the large volumes of solvents to be handled. Because of these drawbacks, SPE, using disposable cartridges with an appropriate sorbent, has been used as an alternative[33,34]. Chemically bonded silica-based sorbents are generally used in SPE columns. However, when a SPE method is applied, the breakthrough volume of each analyte should be taken into account. Sample volumes should be considered carefully during the preconcentration in trying to increase the limits of detection, and preventing the loss of the early eluting compounds[35,36].

In the present study, the following aspects were taken into account: (a) The list of pesticides more extensively used in agricultural treatments during the last 20 years in the region (Almeria, SE Spain), with potential occurrence in water samples. In these respect, key properties such as water solubility, hydrolysis, mobility (expressed by Koc) or leachability (expressed by the Groundwater Ubiquity Score, GUS)[37] were considered. (b) The assessment and optimization of a GC-ECD multiresidue method for analytical separation and quantification of pesticides. (c) The alternative characterization of all the compounds by GC-MS with EI and the MS/MS option, for the confirmation of the residues or even as a

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quantification method. (d) The optimization of the isolation and preconcentration of the pesticides from water samples via LLE and SPE techniques.

The advantages and limitations of using, on one hand, LLE or SPE methods and, on the other, GC-ECD or GC-MS techniques for quantitative and qualitative determinations of dichlorvos, naled, lindane, diazinon, chlorpyrifos-methyl (chlorpyrifos-m), dichlofluanid, chlorpyrifos, folpet, α-endosulfan, β-endosulfan, (endosulfan-sulphate endosulfan-s), fenpropathrin and acrinathrin in water samples are discussed.

EXPERIMENTAL

Chemicals and reagents

Pesticide standards were obtained from Riedel-de-Haën (Seelze-Hannover, Germany) always with a purity higher than 99 %. The internal standard (ISTD), pentachloronitrobenzene (99 % of purity) was supplied by Aldrich (St. Louis, MO, USA). Stock standard solutions, 200 μg ml^{-1}, were prepared in n-hexane and stored in a freezer (–30°C). Working standard solutions were prepared by appropriate dilutions and stored in a refrigerator (4°C). Pesticide quality solvents: n-hexane, dichloromethane, acetonitrile, methanol and acetone were supplied by Panreac (Barcelona, Spain). Organic free water was prepared by distillation and then by Milli-Q SP treatment (Millipore Corporation, USA). Anhydrous Na_2SO_4, purchased from Panreac for pesticide residue analysis, was purified by heating at 300°C overnight and later Soxhlet extracted for twelve hours with dichloromethane. NaCl analytical reagent grade and glass wool were supplied by Panreac. Sep-Pak cartridges for solid phase extraction packed with 500 mg of C_{18} were purchased from Waters (Milford, MA, USA).

Apparatus

A gas chromatograph Hewlett-Packard (Palo Alto, CA, USA) model 5890 equipped with a ^{63}Ni ECD, a split/splitless injector operated in the splitless mode, a fused-silica capillary HP-1 column (60 m × 0.25 mm id. × 0.25 μm film thickness) (Hewlett-Packard) and an autosampler HP 7673. A HP 3365 Chemstation software was used for instrument control and data treatment. Nitrogen was the carrier and make up gas (purity 99.999%).

A Saturn 2000 ion trap mass spectrometer from Varian Instruments (Sunnyvale, CA, USA) was used. The gas chromatograph was fitted with an autosam-

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pler 8200, a split/splitless programmed temperature injector SPI/1078 operated in the splitless mode and a DB5-MS column (30 m × 0.25 mm id. × 0.25 μm film thickness) (J&W Scientific, Folsom, CA, USA). The ion trap mass spectrometer was operated in the electron ionization (EI) mode and the MS/MS option was used. The computer, which controlled the system, had an EI-MS/MS library specially created for the target analytes in our experimental conditions. In addition, other EI-MS libraries were available. The carrier gas used was helium (purity 99.999%).

Chromatographic conditions

GC-ECD

An 1 μl aliquot of the extract was injected by the autosampler in the injector with the split closed for 2 min. The temperature for injector and detector were 250 and 300°C, respectively. The temperature column was programmed from 130°C (hold 1 min at 130°C) to 150°C at 14°C min^{-1}, then from 150°C to 200°C at 1°C min^{-1} and finally from 200°C to 260°C at 14°C min^{-1} (hold 20 min at 260°C). The carrier gas was set at 0.85 ml min^{-1} and the make up at a flow rate of 60 ml min^{-1} at 150°C oven temperature.

GC-MS

5 μl were injected by the autosampler at a flow rate of 1 μl s^{-1}. For that, the solenoid valve was opened for eliminating the solvent during 0.3 min while the temperature was held lightly below the boiling point of the solvent, later it was closed during 2.6 min for concentrating the analytes in the column head and finally was opened again for purging the injection inlet. The carrier gas was set at a flow rate of 1 ml min^{-1} at 150°C oven temperature. The injector temperature was programmed from 60°C (hold 0.3 min at 60°C) to 280°C at 100°C min^{-1} (hold 30 min at 280°C). The column was programmed from 60°C (hold 2.9 min at 60°C) to 150°C at 40°C min^{-1} and finally from 150°C to 275°C at 5°C min^{-1} (hold 10 min at 275°C). The mass spectrometer was calibrated weekly. The temperature for the manifold, transfer-line and trap were 45, 260 and 200°C, respectively. The instrument was operated under Automatic Gain Control (AGC) with 24300 counts of AGC-target (25 ms of maximum ionization time). The scan range was set to 85–450 u at 0.6 scan s^{-1}.

GC-MS/MS

The sample was injected in the gas chromatograph under the same conditions used in GC-MS. The MS/MS parameters are shown in Table I.

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TABLE I MS/MS parameters

Pesticide	*Activation Time (min)*	*n/z Range*	*Parent Ion (m/z)*	*Excitation Amplitude (V)*	*Excitation Storage level (m/z)*
dichlorvos	5.0–9.0	85–195	185	75	81
naled	9.0–12.3	135–195	185	40.5	50
ISTD	2.3–13.2	225–275	265	44	60
lindane	13.2–13.5	100–195	183	69	80
diazinon	13.5–14.3	150–315	304	59	110
chlorpyrifos-m	14.3–15.7	125–295	286	66	80
dichlofluanid	15.7–16.8	110–235	224	65	98
chlorpyrifos	16.8–18.0	250–325	314	39	80
folpet	18.0–19.5	120–270	260	51	90
α-endosulfan	19.5–21.0	90–250	241	83	80
β-endosulfan	21.0–22.6	90–250	241	83	80
endosulfan-s	22.6–25.0	120–280	272	95	119
fenpropathrin*	25.0–27.0	115–275	265	0.24	100
acrinathrin	27.0–29.0	140–190	181	86	79

*. resonant wave form.

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Extraction procedures

Liquid-Liquid Extraction (LLE)

A 500 ml water sample containing 10% NaCl was extracted in a separatory funnel twice with dichlorometane (2 × 50 ml) and once with n-hexane (25 ml), shaking for two minutes and allowing the phases to separate for 10 min. The combined organic extracts were dried over sodium sulphate. These extracts were evaporated just to the point of dryness in a rotary evaporator. An aliquot of the ISTD solution (50 µl, 1 µg ml^{-1}) was added and the volume made up to 1 ml with acetone:n-hexane (1:9) v/v.

Solid Phase Extraction (SPE)

The C_{18} extraction cartridges were conditioned by successive elution of 10 ml of a mixture acetonitrile:dichloromethane (1:1) v/v, 5 ml of methanol and 3 ml of Milli-Q water. All the solvents were passed by gravity throughout the cartridges. Then, an aliquot of 500 ml water sample was aspirated through the cartridge

under vacuum. The sample flow rate was controlled at ca. 8–10 ml min^{-1}. The cartridge was not allowed to dry completely during the extraction process. Before eluting the pesticides, the cartridge was dried by passing air for 15 min and N_2 for other 15 min. Pesticides were eluted by gravity with 5 ml of dichloromethane:acetonitrile (1:1) v/v followed by 2 ml of n-hexane. The extract was dried over anhydrous Na_2SO_4 supported in a column that was later washed with 1 ml of dichloromethane. The final extract was evaporated to dryness under a stream of nitrogen. An aliquot of the ISTD solution (50 µl, µg ml^{-1}) was added and the volume made up to 1 ml with acetone:n-hexane (1:9) v/v.

RESULTS AND DISCUSSION

GC-ECD analysis

The GC-ECD conditions were optimized to separate the pesticides monitored. Different temperature programs were tested for the resolution of standard mixtures. A chromatogram of a standard solution using the final program described in the Experimental Section is shown in Figure 1a. Pesticides were separated properly and thus accurately calibrated. These conditions are also suitable for the separation among the analytes and other pesticides used in this area, such as vinclozolin, procymidone, malathion or buprofezin.

Retention time windows (RTW) defined as retention times averages ± 3 standard deviation (SD) of retention times are shown in Table II.

To determine the linearity of the chromatographic method, standard solutions of the pesticides with concentrations ranging from 0.5 to 1000 µg l^{-1} were injected and quantified using internal standard calibration. Calibration curves and the different associated parameters were studied using both areas and heights relative to the internal standard showing no significant differences in all cases except for folpet that showed better regression coefficient using relative areas. The linear correlations were fairly good ($r^2 = 0.990 - 0.999$).

Detection (LOD) and quantification (LOQ) limits were calculated on the values of the blank at the RT of the analytes (8 injections). Besides LOQ were calculated as the lowest concentration where the RSD (%) is estimated to be less than 10 %[38]. They are shown in Table II. The LOQ values were higher when the criterion used to calculate was the lowest concentration of pesticide for which RSD is lower than a pre-established value (10%). We consider that this last approach estimates more realistic values. RSD (%) was measured in both ranges

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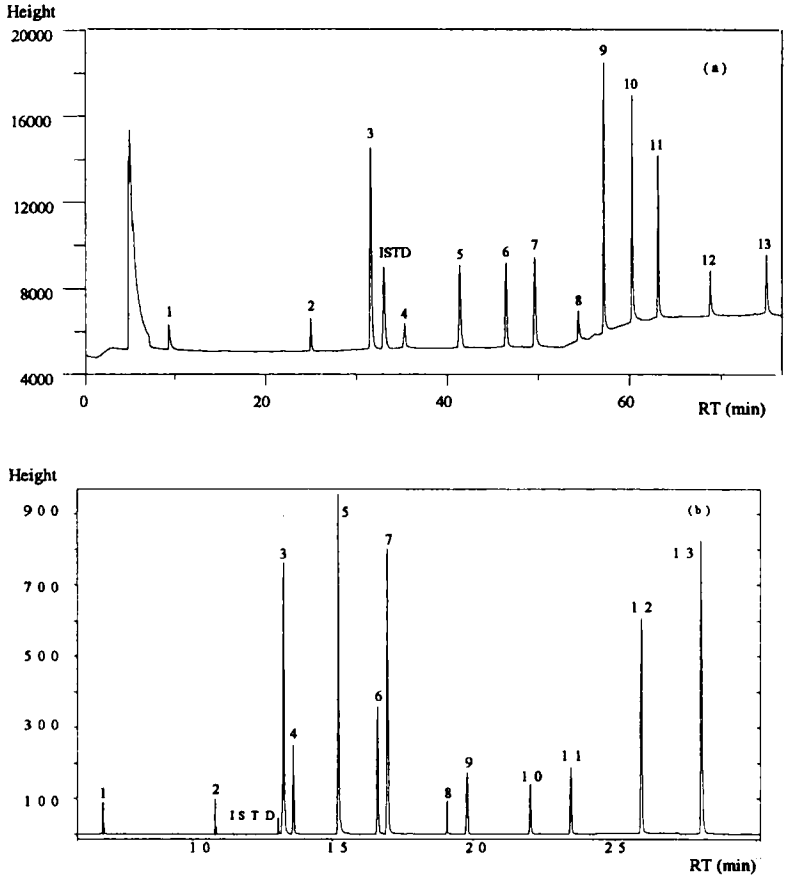

FIGURE 1 Gas chromatograms with ECD (a) and MS/MS (b) of a standard solution of the pesticides in n-hexane at 200 μg l^{-1}.1, dichlorvos; 2, naled; 3, lindane; 4, diazinon; 5, chlorpyrifos-m; 6, dichlofluanid; 7, chlorpyrifos; 8, folpet; 9, α-endosulfan; 10, β-endosulfan; 11, endosulfan-s; 12, fenpropathrin; 13, acrinathrin

of concentrations, at 50 and 400 μg l^{-1}, respectively, finding values lower than 9 % in all cases.

GC-MS and GC-MS/MS analyses

The gas chromatographic conditions were optimized to separate the pesticides studied with the column available. All of them were properly separated in less than 29 min as it is shown in Figure b. The RTW for the compounds are shown in Table III.

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TABLE II Retention Time Windows (RTW) and calibration data (n=8) of GC-ECD method

Pesticide	*RTW (min)*	*Linear Ranges ($\mu g\ l^{-1}$)*	r^2	*RSD (%)*	*LOD[a] ($\mu g l^{-1}$)*	*LOQ[a] ($\mu g l^{-1}$)*	*LOQ[b] ($\mu g l^{-1}$)*
dichlorvos	9.30–9.32	1–100/100–1000	0.999/0.995	4.0/3.5	0.2	0.7	1.0
naled	24.99–25.03	15–100/100–1000	0.996/0.999	6.2/5.7	0.3	0.9	15.0
lindane	31.47–31.53	0.5–50/50–1000	0.992/0.993	2.2/2.2	0.1	0.2	0.5
ISTD	32.94–32.98	–	–	–	–	–	–
diazinon	35.25–35.31	2–50/50–400	0.995/0.999	2.9/2.7	0.2	0.8	2.0
chlopyrifos-m	41.35–41.41	0.5–50/50–1000	0.995/0.993	2.7/2.4	0.1	0.3	0.5
dichlofluanid	46.48–46.54	1–100/100–1000	0.993/0.990	2.5/2.3	0.1	0.4	1.0
chlopyrifos	49.56–49.60	0.5–50/50–1000	0.991/0.990	2.0/2.1	0.1	0.4	0.5
folpet*	54.36–54.42	15–100/100–1000	0.996/0.999	8.5/8.0	0.5	1.8	15.0
α-endosulfan	57.15–57.17	0.5–100/100–1000	0.994/0.997	1.2/1.4	0.1	0.3	0.5
β-endosulfan	60.24–60.28	0.5–100/100–800	0.992/0.993	1.2/1.9	0.1	0.4	0.5
endosulfan-s	63.10–63.12	1.5–50/50–1000	0.993/0.993	3.0/2.7	0.4	1.4	1.5
fenpropathrin	68.73–68.75	1.5–100/100–1000	0.998/0.993	2.2/2.3	0.3	1.0	1.5
acrinathrin	74.96–74.98	2–100/100–1000	0.997/0.990	2.3/2.2	0.6	2.1	2.0

*. calibration using relative areas; [a], based on the values of the blank at the RT of the analytes; [b], based on the lowest concentration where the RSD (%) is estimated to be less than 10 %.

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TABLE III Retention Time Windows (RTW) and calibration data (n-8) of GC-MS and (GC-MS/MS) methods

Pesticide	*RTW (min)*	*ion*	*Linear Range (μg l^{-1})*	r^2	*RSD (%)*	*LOD (μg l^{-1})*	*LOQ (μg l^{-1})*
dichlorvos*	6.85–6.88	185(95)	20–400(20–800)	0.990(0.973)	4.1(9.7)	6.0(5.0)	20.0(20.0)
naled	11.43–11.53	85(153)	100–400(40–800)	0.987(0.999)	19.7(18.2)	40.0(10.0)	100.0(40.0)
ISTD	13.12–13. 19	265(237)	–	–	–	–	–
lindane	13.28–13.34	183(148)	1–800(0.5–800)	0.999(0.992)	7.0(3.1)	0.3(0.1)	1.0(0.5)
diazinon	13.68–13.70	304(179)	1–400(0.5–200)	0.999(0.996)	6.2(5.7)	0.4(0.1)	1.0(0.5)
chlorpyrifos-m	15.27–15.33	286(208)	1–800(0.5–200)	0.999(0.996)	8.2(7.5)	0.3(0.1)	1.0(0.5)
dichlofluanid	16.63–16.69	224(123)	1–800(1–800)	0.999(0.997)	6.5(5.0)	0.3(0.3)	1.0(1.0)
chlorpyrifos	16.99–17.01	314(258)	1–800(0.5–200)	0.999(0.990)	4.5(4.0)	0.3(0.1)	1.0(0.5)
folpet	19.11–19.19	260(232)	80–800(40–400)	0.990(0.995)	13.7(14.3)	20(10.0)	80.0(40.0)
α-endosulfan	19.83–19.89	241(170)	2–800(0.5–800)	0.999(0.992)	5.6(4.9)	0.5(0.1)	2.0(0.5)
β-endosulfan	22.07–22.11	241(170)	10–800(0.5–400)	0.999(0.996)	6.1(6.0)	2.0(0.1)	10.0(0.5)
endosulfan-s	23.52–23.58	272(237)	5–800(0.5–800)	0.999(0.998)	5.8(5.2)	1.0(0.1)	5.0(0.5)
fenpropathrin	26.01–26.08	265(210)	5–800(0.5–800)	0.998(0.995)	8.1(8.4)	1.0(0.1)	5.0(0.5)
acrinathrin	28.13–28.16	181(152)	10–400(1–800)	0.993(0.995)	9.7(9.5)	4.0(0.2)	10.0(1.0)

*. Height relative to that of the ISTD.

In order to increase the sensitivity, volumes of 5 µl were injected, provided that the samples do not present important matrix effect such as water. Hence, the flow rate of injection was set at 1 µl s^{-1} to obtain good peak symmetry. Other values generated peak tailing. Different time programs were studied for the solenoid valve opening. The time for eliminating the solvent and then for concentrating the analytes in the column head were set at 0.3 and 2.6 min, respectively, because of the higher signal obtained for most of them in these conditions. The injector temperature was programmed from 60 to 280°C to avoid breakdown of the most thermolabile compounds.

For the mass spectrometer detector, AGC was switched on in order to optimize the sensitivity by filling completely the trap with target ions. In full scan mode, the mass range (85–450 u) and background mass (85 u) were selected to optimize the sensitivity, ejecting as much as possible the matrix and solvent ions. All the compounds were characterized by their full scan mass spectra in these experimental conditions.

In the MS/MS mode, a parent ion was chosen for each analyte by taking into consideration its *m/z* and its relative abundance (both as high as possible), so as to improve sensitivity. An isolation window of 2 u was used when the compounds exhibited ion clusters in their MS spectra and wider windows would therefore catch additional neighbouring ions and worse repeatability. The AGC target was set at 2000 counts because higher values caused electrostatic interactions between ions in the ion trap chamber. A non-resonant wave form (second ionization) was selected for all the compounds except for fenpropathrin which needed more cleavage energy to obtain a good quality secondary spectrum. The objective was to generate spectra with the parent ion as their molecular peaks (between 10 and 20 % of relative abundance). The excitation amplitude was studied for this propose. The EI-MS/MS spectra of the pesticides in our experimental conditions were stored in an own-made EI-MS/MS library. The main ions are shown in Table IV. The base peak was selected for quantification in all cases.

The target analytes were searched at RTW and were identified by comparing their spectra with those in EI-MS and EI-MS/MS libraries. A positive analyte identification required a minimum spectral fit of >700 and a signal-to-noise ratio (S/N) of >3 (for quantification ions). For quantification, S/N must be higher than 10.

The use of the full scan mode allows to compare the spectrum obtained with own-made and commercial EI-MS libraries but the spectral fit and sensitivity are not as good as they should be when dirty samples are analyzed with coelution problems between matrix and target peaks at trace levels. With MS/MS, if a coeluted interference has the same identification ion as the analyte, such interference can be avoided using special experimental conditions for the second ionization and quantifying with a specific ion from the analyte.

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TABLE IV *M/z* and (relative abundance) in MS/MS spectra

Pesticide	*m/z*
dichlorvos	185(34) 131(100) 109(88) 95(95)
naled	185(10) 169(52) 154(100) 142(22) 107(11)
ISTD	265(13) 237(100)
lindane	183(28) 148(100) 109(38)
diazinon	305(40) 195(14) 179(100) 162(54)
chlorpyrifos-m	286(16) 241(31) 208(100) 180(36) 144(35) 136(42)
dichlofluanid	224(15) 189(8) 123(100)
chlorpyrifos	314(30) 286(51) 258(100)
folpet	260(14) 232(100) 200(9) 130(31)
α-endosulfan	241(9) 206(47) 170(100) 136(38) 99(15)
β-endosulfan	241(11) 206(41) 170(100) 136(33) 99(12)
endosulfan-s	272(15) 237(100)
fenpropathrin	264(7) 237(15) 210(100) 172(27) 125(24)
acrinathrin	181(13) 152(100)

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The instrument calibration was performed using standard solutions of the pesticides with concentrations ranging from 0.5 to 800 μg l^{-1}. The ISTD was used at 50 μg l^{-1}. Both areas and heights relative to the ISTD were considered for the calibration graphs. Good linearity was found in all cases as can be seen in Table III. The method repeatability was studied injecting eight samples with 100 μg l^{-1} of each pesticide. LOD and LOQ were studied as in the GC-ECD analysis Section 5.

All the compounds exhibited good linearity in the studied range using the three detectors ($r^2 > 0.99$), except for naled in GC-MS and dichlorvos in GC-MS/MS. When GC-ECD was used, two different linear ranges were considered. Comparing the results obtained for repeatability, lower RSD (%) values were obtained using GC-ECD (1.2–8.5 %). In general, GC-MS/MS presents better values than GC-MS. Naled and folpet show worse repeatability results (> 13 %) using mass spectrometric techniques. LOD and LOQ in ECD and MS/MS are similar except for dichlorvos, naled and folpet which are higher quantifying with the ion trap. Higher data were obtained in the MS mode.

Optimization of the LLE procedure

Water samples (500 ml Milli-Q) containing 10% NaCl and spiked at the level of 50 ng l^{-1} for each pesticide were extracted using three sequential portions of 50, 50 and 25 ml of dichloromethane (Method 1) or using two sequential portions of

50 ml each, one of dichloromethane and other additional portion of 25 ml of n-hexane (Method 2). The extracts obtained were quantified by GC-ECD. All the pesticides were well recovered (between 70 and 130 %) using both methods, except naled and folpet with recoveries higher than 175 % in both cases. These results did not improve enough when the Milli-Q water samples were spiked at 400 ng l^{-1} of each pesticide.

The high recovery values can be explained taking into account the poor chromatographic response of these analytes, with height low peaks, because of which slight baseline variations or background interferences have a great influence in the quantification.

LOD and LOQ for the compounds studied, except for diazinon, were low enough to allow the determination of pesticide residues in supply water samples as established by the European Community legislation.

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Optimization of the SPE procedure

Three aliquots of 500 ml of Milli-Q water spiked with 400 ng $l^{-1}$of each pesticide were used to optimize the SPE procedure. C_{18} was selected due to its capacity to extract pesticides belonging to different chemical classes with a wide range of polarities.

Three eluent mixtures (1:1) v/v were tested: dichloromethane:acetonitrile; dichloromethane:acetone and acetone:hexane. Dichlorometane:acetonitrile was selected because it provided good recoveries at the studied concentration level (71–103 %) for most of the pesticides, except for fenpropathrin and acrinathrin, and in addition, originated the cleanest extract. Mixtures of acetone were a bad choice due to the appearence of interfering peaks. Repeatability was always lower than 36 % expressed as RSD (%). LOD and LOQ were calculated on the bases of the extraction of Milli-Q water blanks (10 extractions) at a signal-to-noise ratio of 3 and 10, respectively. They were low enough to determine pesticide residues at the required levels by the European Community legislation. The results are shown in Table V.

Aliquots of 500 ml of Milli-Q water were spiked at the concentration range of 50–1600 ng l^{-1} and analyzed using the SPE procedure to find the concentration of saturation. This was higher than 1600 ng l^{-1} for naled, lindane, diazinon, dichlofluanid and folpet pesticides. The recoveries of fenpropathrin and acrinathrin increased from 63 to 101 % and from 52 to 92 %, respectively, when the concentration decreased from 400 to 100 ng l^{-1} and, therefore, samples with concentrations of fenpropathrin and acrinathrin higher than 100 ng l^{-1} should be diluted prior to the extraction.

TABLE V Recovery percentages and (RSD %) in the SPE approach with GC-ECD quantification

Pesticide	*R (%)**	*LOD (ng l^{-1})*	*LOQ (ng l^{-1})*
dichlorvos	78(7.1)	2.2	7.4
naled	103(14.3)	9.3	31.0
lindane	102(2.6)	0.7	2.4
diazinon	81(4.7)	7.2	23.9
chlorpyrifos-m	93(4.3)	5.6	18.7
dichlofluanid	96(9.5)	1.6	5.4
chlorpyrifos	81(10.7)	1.6	5.5
folpet	97(6.3)	28.9	96.2
α-endosulfan	71(29.0)	0.4	1.3
β-endosulfan	83(20.0)	1.6	5.5
endosulfan-s	96(16.5)	4.9	16.5
fenpropathrin*	101(25.9)	1.9	6.2
acrinathrin*	92(35.5)	1.6	5.4

. (n=3); spiking level: 400 ng l^{-1} (100 ng l^{-1})

Volumes of water of 100, 200, 300, 400, 500 and 600 ml spiked with 200 μg l^{-1} of each pesticide were also used to obtain the breakthrough volume[36]. Good recoveries were obtained using sample volumes ≤ 500ml. A breakthrough took place for all pesticides when 600 ml were extracted, therefore, a volume of 500 ml was chosen.

Comparing the results obtained for LLE and SPE methods by GC-ECD analysis, the SPE technique was selected because it was efficient, less harmful to the analyst, more sensitive, and much faster than the LLE method.

Finally, the efficiency of the proposed SPE method was also assessed by quantifying the results with GC-MS (full scan) and GC-MS/MS. Recoveries and repeatability studies, at a 400 ng l^{-1} (100 ng l^{-1} for fenpropathrin and acrinathrin) concentration level, in Milli-Q water, are shown in Table VI.

LOD and LOQ were suitable to allow the determination of pesticide residues in water at 100 ng l^{-1}, except for naled and folpet in the MS mode. In general, good recoveries were obtained for all the pesticides, with RSD values between 6.3 and 21.2 % for MS and 5.8–35.4 % for MS/MS mode.

Comparing the results obtained with the different detectors, ECD and MS/MS have proved their capability for the determination of pesticides in water samples at the required levels. α- and β-endosulfan present less repeatability using ECD ≥20 %) than MS/MS (≤9.9 %). Most of the pesticides have good recoveries and

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RSD independently of the detector used. The best LOD and LOQ values were obtained with ECD and MS/MS detection.

TABLE VI Recovery percentages and (RSD %) in the SPE approach with GC-MS and GC-MS/MS quantifications

Pesticide	*GC-MS*			*GC-MS/MS*		
	*R (%)**	*LOD (ng l^{-1})*	*LOQ (ng l^{-1})*	*R (%)**	*LOD (ng l^{-1})*	*LOQ (ng l^{-1})*
dichlorvos†	64(7.3)	12.5	41.7	83(9.0)	12.3	40.9
naled	153(21.2)	81.5	271.7	106(23.8)	28.4	95.1
lindane	95(8.3)	3.9	13.0	84(3.8)	3.1	0.2
diazinon	98(7.5)	27.8	92.5	80(6.3)	1.1	3.5
chlorpyrifos-m	83(9.2)	2.4	8.1	86(8.3)	0.8	2.5
dichlofluanid†	95(7.6)	28.7	95.6	77(6.2)	2.2	7.5
chlorpyrifos	85(9.9)	4.1	13.5	75(6.0)	0.4	1.3
folpet	116(14.5)	48.4	160.8	94(15.3)	22.5	80.4
α-endosulfan	97(10.6)	17.9	59.6	77(9.9)	2.0	6.8
β-endosulfan	103(6.7)	29.5	98.3	88(6.3)	1.3	4.2
endosulfan-s	102(6.3)	13.0	43.3	91(5.8)	4.8	16.1
fenpropathrin†	122(6.8)	3.8	12.5	95(20.7)	1.4	4.8
acrinathrin†	104(6.3)	8.1	27.0	84(35.4)	0.8	2.8

*. (n=3); spiking level: 400 ng l^{-1} (100 ng l^{-1})
†. Height relative to that of the ISTD;

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CONCLUSIONS

A pesticide multiresidue method using SPE with detection and quantification by GC-ECD and GC-MS/MS has been proposed after comparing the results obtained with LLE and GC-MS. The sensitivity was enough for the quantification of the pesticides at the level of 100 ng l^{-1}. The repeatability expressed as RSD (%) was 2.6–35.5 % for ECD and 3.8–35.4 for MS/MS, and the recoveries of the pesticides were 71–103 % for ECD and 75–103 % for MS/MS. When complex water samples are analyzed, better results are obtained using GC-MS/MS.

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References

1. *EEC. Drinking Water Directive*, Official Journal N 229/11 Directive 80/778/EEC, (1988).
2. C. de la Colina, A. Pena, M.D. Mingorance and F. Sánchez Rasero, *J. Chromatogr. A*, **733**, 275–281 (1966).
3. K.K. Chee, M.K. Wong and H.K. Lee, *J. Chromatogr. A*, **736**, 211–218 (1996).
4. W.C. Quayle, I. Jepson and I. A. Fowlis, *J. Chromatogr. A*, **773**, 271–276 (1997).
5. M. Veningerová, V. Prachar, J. Kovacicová and J. Vhnák, *J. Chromatogr. A*, **774**, 333–347 (1997).
6. J.J. Jimenez, J.L. Bernal, M. del Nozal and J.M. Rivera, *J. Chromatogr. A*, **778**, 289–300 (1997).
7. A.R. Fernández Alba, A. Valverde, A. Agüera and M. Contreras, *J. Chromatogr. A*, **686**, 263–274 (1994).
8. M. Psathaki, E. Manoussaridou and E.G. Stephanou, *J. Chromatogr. A*, **667**, 241–248 (1994).
9. J.S. Salau, R. Alonso, G. Batlló and D. Barceló, *Anal. Chim. Acta*, **293**. 109–117 (1994).
10. E. Viana, J.C. Moltó, J. Mañés and G. Font, *J. Chromatogr. A*, **678**, 109–117 (1994).
11. H. Steinwantdter, *Fresenius J. Anal. Chem.*, **336**, 8–11 (1990).
12. F. Hernández, I. Morell, J. Beltrán and F.J. López, *Chromatographia*, **37**, 303–312 (1993).
13. Chemistry Research Division, U.S. Environmental Protection Agency, *Methods for the determination of organic compounds in drinking water* (U.S. Department of Commerce, N.T.I.S., Springfield, VA, 1991), pp. 192–198.
14. M. Bizink, A. Przjazny, J. Czerwinski and M. Wiergowski, *J. Chromatogr. A*, **754**, 103–123 (1996).
15. A. Balinova, *J. Chromatogr. A*, **754**, 125–135 (1996).
16. T. Pihlström, A. Hellström and V. Axelsson, *Anal. Chim. Acta.*, **356**, 155–163 (1997).
17. J. Gandras, G. Bormann and R.-D. Wilken, *Fresenius J. Anal. Chem.*, **353**, 70–74 (1995).
18. E. Viana, M.J. Redondo, G. Font and J.C. Moltó, *J. Chromatogr. A*, **733**, 267–274 (1996).
19. C. Aguilar, F. Borrull and R.M. Marcé, *J. Chromatogr. A*, **771**, 221–231 (1997).
20. J. Schulein, D. Martens, P. Spitzauer and A. Kettrup, *Fresenius J. Anal. Chem.*, **352**, 565–571 (1995).
21. H.F. Schoder, *Fresenius J. Anal. Chem.*, **353**, 93–97 (1995).
22. J. Hodgeson, J. Collins and W. Bashe, *J. Chromatogr. A.*, **665**, 395–401 (1994).
23. I. Tolosa, J. W. Readman and L.D. Mee, *J. Chromatogr. A*, **725**, 93-106 (1996).
24. T. Greibrokk, *J. Chromatogr. A*, **703**, 523–536 (1995).
25. J.S. Ho, P.H. Tang and W.L. Budde, *J. Chromatogr. Sci*, **33**, 1–8 (1995).
26. J. Dugay, C. Miege and M.C. Hennion, *J. Chromatogr. A*, **795**, 27–42 (1998).
27. J. Beltrán, F.J. López, O. Cepria and F. Hernández, *J. Chromatogr. A*, **808**, 257–263 (1998).
28. J.L. Vílchez, P. Espinosa, F.J. Arrebola and A. González-Casado, *Anal. Sci.*, **13**, 817–819 (1997).
29. A. Fernández-Gutiérrez, J.L. Martínez Vidal, F.J. Arrebola, A. González-Casado, J.L. Vilchez, *Fresenius. J. Anal. Chem.*, **360**, 568–572 (1998).
30. R. Heyer, A. Zap and H.J. Stand, *Fresenius J. Anal. Chem.*, **351**, 752–757 (1995).
31. M. Bizink and A. Przjazny, *J. Chromatogr. A*, **773**, 417–448 (1996).
32. J.D. Petty, J.N. Huckins, D.B. Martin and T.G. Adornato, *Chemosphere*, **30**, 1891–894 (1981).
33. N.C. Fladung, *J. Chromatogr.*, **692**, 21–26 (1995).
34. D. Eastwood, M.E. Dominguez, R.L. Lidberg and E.J. Poziomek, *Analusis*, **22**, 305–309 (1994).
35. S. Sennert, D. Volmer, K. Levsen and G. Wunsch, *Fresenius J. Anal. Chem.*, **351**, 642–649 (1995).
36. M.-C. Hennion and P. Scribe. *Environmental Analytical Techniques, Applications and Quality Assurance* (Elsevier Science Publishers, 1993) pp-23–77.
37. D.I. Gustafson, *Environ. Toxicol. Chem.*, **8**, 339–357 (1989).
38. H. Kaiser, *Two papers on he imit of detection of a complete analytical procedure*, Hafner. New York. 1969, pp-72.

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