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Pesticide trace analysis using solid-phase extraction and gas chromatography with electron-capture and tandem mass spectrometric detection in water samples

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Abstract

Gas chromatography (GC) with electron-capture detection (ECD), mass spectrometry (MS) and tandem mass spectrometry (MS–MS) were employed for the identification of 12 pesticides in water samples. For this purpose, a solid-phase extraction procedure with C_{18} cartridges was used, optimising the breakthrough volume and the saturation concentration. In GC–MS–MS, the lowest detectable concentrations for the pesticides were between 2 and 26 ng l^{-1}, recoveries ranged from 70 to 133% in water samples spiked at 100 ng l^{-1} and the relative standard deviations were in the range 5.3 to 17.4%. The proposed analytical methodology was applied to analyse pesticides in wetland samples from Almería (Spain).

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

The development and use of pesticides have played an important role in the increase of agricultural productivity. The majority of such substances are applied directly to soil or sprayed over crop fields and hence released directly to the environment. For that, pesticides can enter as contaminants into natural waters either directly in applications or indirectly from drainage of agricultural lands. The amount and kind of pesticides in water of a given area depends largely on the intensity of production and kind of crops. However, the transport of pesticides out of their area of application results in the presence and accumulation of these compounds in many parts of the hydrosphere. For example, atmospheric precipitation is an important route of transport of pesticides, resulting in contamination of environmental waters far away from agricultural areas. Substantial amounts of pesticides have been found in ice and water of polar regions [1,2], lakes [3], seawater [4], rainwater [3,5–7] or potable water [8,9].

Gas chromatography (GC) using the highly sensitive electron-capture detection (ECD) is an analytical technique of great importance in the determination of pesticides residues in environmental waters [7,10–12]. This is due not only to the sensitivity and specificity of ECD, but also to the power of GC for separating compounds of similar molecular structure. Consequently, multiresidue analysis is the common-

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est way of determining pesticides. Once the chromatographic separation is reached, information regarding the complexity (number of components), quantity (peak height or area) and identity (retention time) of the components in a mixture is provided. The certainty of identification based solely on retention time value is very poor, even for not very complex samples, a supplementary confirmation of the residues is necessary. Only when the identity is firmly established the quantitative information from the chromatogram can be correctly interpreted without producing false-positive results.

Spectroscopic techniques, conversely to chromatographic techniques, present a rich source of qualitative information from which component identity may be inferred with a reasonable degree of certainty. Thus, spectroscopic and chromatographic techniques provide complementary information about the concentration of the components and their identity in a sample.

Nowadays, GC interfaced to mass spectrometry (GC–MS) is the preferred analytical technique for the confirmation of residues [13]. Generally, three modes of GC–MS operation are available: electron impact (EI), positive and negative chemical ionisation (PCI, NCI). GC–MS in the EI mode is commonly used in determination of pesticides in water, and positive and negative chemical ionisation modes are alternative methods, which depending on the compounds, offer better selectivity and or sensitivity than EI. For increasing the sensitivity, selected ion monitoring (SIM) is commonly used in the determination of pesticides in waters. This mode allows the analysis of trace amounts of pesticides but reduces the qualitative information.

The use of tandem mass spectrometry (MS–MS) improves the selectivity of the technique with a drastic reduction of the background and without losing identification capability. It enables analysis of pesticides at trace levels in the presence of many interfering compounds [14,15]. In spite of high sensitivity and selectivity of the technique a reduced number of papers have applied this technique [16,17]. Evidently, the sensitivity is still not high enough to directly determine the trace amounts of pesticides in water samples at the level required by the EU Drinking Waters Directive [18] of 0.1 $\mu g\ l^{-1}$ for each pesticide and 0.5 $\mu g\ l^{-1}$ for the total amount of them. Therefore, a concentration procedure for the analytes must be applied.

In a previous paper [16] a 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 EU after solid-phase extraction (SPE) was described. In this paper the determination of another 12 pesticides by GC–ECD and GC–MS techniques using off-line SPE with C_{18} is presented. In addition to EI full mass spectra, MS–MS spectra (secondary mass spectra) were also obtained to confirm the presence of the pesticides in real water samples. The monitored pesticides have been used in agricultural treatment in Almería (Spain) and are chosen on the basis of potential occurrence in environmental water samples from this area.

2. Experimental

2.1. Chemicals and reagents

Standards of the pesticides were obtained from Riedel-de Haën (Seelze–Hannover, Germany) always with purity higher than 99%. The internal standard (I.S.), pentachloronitrobenzene (99% purity) was supplied by Aldrich (St. Louis, MO, USA). Stock standard solutions, 200 $\mu g\ ml^{-1}$, were prepared by exact weighing and dissolving them in a mixture of acetone–*n*-hexane (1:9, v/v) (except for captan and chlorothalonil which were dissolved in acetone) and stored in a freezer (−30°C). Working standard solutions were prepared by appropriate dilutions in *n*-hexane 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, USA). Anhydrous Na_2SO_4 purchased from Panreac for pesticide residue analysis was purified by heating at 300°C overnight and later was Soxhlet extracted for 12 h with dichloromethane. Glass wool was supplied by Panreac. Sep-Pak cartridges for SPE packed with

500 mg of C_{18} were purchased from Waters (Milford, MA, USA).

2.2. GC–ECD analysis

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 gas chromatograph equipped with a ^{63}Ni ECD system, a split/splitless injector operated in the splitless mode, a fused-silica capillary HP-1 chromatographic column (60 m×0.25 mm I.D.); film thickness 0.25 μm and an HP 7673 autosampler were employed. HP 3365 Chemstation software was used for instrument control and data treatment. Operating conditions were as follows: initial column temperature 130°C (1 min), increased at 14°C min^{-1} to 150°C, then increased at 1°C min^{-1} to 200°C and finally increased at 14°C min^{-1} to 260°C, held for 20 min: injector temperature 250°C; detector temperature 300°C. This last temperature was not optimised because it was high enough to ensure the volatilization of the pesticides. Carrier gas N_2 at a flow-rate 0.85 ml min^{-1}; make-up gas N_2 at a flow-rate 60 ml min^{-1}; purge off time 2 min; injection volume 1 μl.

2.3. GC–MS analysis

A Saturn 2000 ion trap mass spectrometer from Varian Instruments (Sunnyvale, CA, USA) equipped with an autosampler 8200, a split/splitless programmed temperature injector SPI/1078 operated in the splitless mode and a DB5-MS (30 m×0.25 mm I.D.), film thickness 0.25 μm chromatographic column was employed. The ion trap mass spectrometer was operated in the 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 under our experimental conditions. In addition, other EI-MS libraries were available.

GC conditions were as follows: initial column temperature 60°C (2.9 min), increased at 40°C min^{-1} to 150°C and finally increased at 5°C min^{-1} to 275°C (held for 10 min); initial injector temperature 60°C (0.3 min) and increased at 100°C min^{-1} to 280°C (held 30 min); carrier gas He (99.999%) at a flow-rate of 1 ml min^{-1} at 150°C oven temperature; manifold, transfer-line and trap temperatures were 45, 260 and 200°C, respectively; flow-rate 1 μl s^{-1}; injection volume 5 μl.

GC–MS conditions were: solvent delay 4.5 min; 70 eV of electron impact energy; scan rate 0.6 scans s^{-1}; scanned-mass range 85–450 m/z. The automatic gain control (AGC) was switched on with a target fixed at 20 000 counts. The mass spectrometer was calibrated weekly.

For GC–MS–MS, the sample was injected under the gas chromatographic conditions described for GC–MS. The MS–MS parameters are shown in Table 1.

Table 1
MS–MS parameters

Pesticide	Activation time (min)	m/z range	Parent ion (m/z)	Excitation amplitude (V)	Excitation storage level (m/z)
Etoprophos	5.0–12.0	85–175	158	39	69
Dichloran	12.0–12.9	160–215	206	67	90
I.S.	12.9–13.5	225–275	265	44	60
Chlorothalonil	13.5–14.5	160–275	266	1[a]	100
Vinclozolin	14.5–16.0	100–225	212	98	93
Parathion-m	14.5–16.0	100–275	263	52	100
Fenitrothion	16.0–16.6	115–270	260	100	100
Malathion	16.6–18.0	90–185	173	70	89
Captan	18.0–20.0	70–125	114	31	35
Procymidone	18.0–20.0	70–135	283	80	111
Dieldrin	20.0–20.9	160–290	279	2[a]	123
Buprofezin	20.9–26.0	155–260	249	52	90
Pyrazophos	26.0–29.0	170–275	265	60	100

[a] Resonant wave form.

2.4. Analysis of water samples

The analytical procedure can be summarised as follows:

C_{18} cartridge
↓
Preconditioning
10 ml acetonitrile–dichloromethane (1:1)
5 ml Methanol
3 ml Milli-Q water
↓
Extraction 500 ml water sample
↓
Dry: 15 min air + 15 min N_2
↓
Elution
5 ml acetonitrile–dichloromethane
2 ml *n*-hexane
↓
Na_2SO_4 drying. Wash with 1 ml dichloromethane
↓
Evaporation
Redissolve in 1 ml acetone–*n*-hexane (1:9, v/v)
Add I.S.
↓
GC–ECD; GC–MS and GC–MS–MS

In order to study the concentration of saturation [20], 500-ml aliquots of Milli-Q water were spiked with a mixture of pesticide standards in the concentration range 50–1600 ng l^{-1} and the SPE procedure was applied using 500 mg C_{18} cartridges. Concentration of saturation was not reached for most pesticides when 1600 ng l^{-1} were passed with exception of dieldrin (200 ng l^{-1}) and buprofezin (400 ng l^{-1}). So, samples with concentrations of dieldrin and buprofezin larger than the ones previously mentioned should be diluted prior to the extraction.

3. Results and discussion

3.1. ECD analysis

Fig. 1 shows the GC–ECD chromatogram of a mixture of the 12 target pesticides, the I.S. and other pesticides currently used in the area. A satisfactory baseline separation among analytes was reached, which is suitable for obtaining accurate calibrations. This situation was also adequate for the resolution among the analytes and potential interferent compounds, from other pesticides used in this area or background interferences co-extracted from complex matrix.

Retention time windows (RTWs), defined as retention time (t_R) averages ±3 standard deviation of retention time are summarised in Table 2. The linearity for the different pesticides by measuring height or area ratio relative to the internal standard was studied. The determination coefficients calculated for the linear regression equations, in two concentration ranges, were all above 0.990 (Table 2). The precision of quantitative measurement of pesticides was studied in both ranges, at 50 and 400 μg l^{-1}, respectively, values ranged from 0.9–5.7%.

Detection (LODs) and quantitation (LOQs) limits were calculated on the values of the blank at the retention times of the analytes (eight injections). LOQs were calculated as the lowest concentration whose relative standard deviation (RSD) is estimated to be less than 10% [19]. In general, similar LOQ values were obtained with both methods (Table 2).

3.2. GC–MS and GC–MS–MS analysis

Fig. 2 shows the GC–MS–MS chromatogram of a mixture of the pesticide standards. All 12 pesticides were resolved and eluted in a reasonable time (<29 min), under the conditions described in the experimental section. RTWs of target analytes are given in Table 3. Less time is required for resolving the pesticides using MS than for the GC–ECD due to the capability of monitoring selective ions for the target analytes.

The injection volume was set at 5 μl, after study (from 1 to 5 μl), in order to increase sensitivity but, at the same time, taking into account that this volume did not show significant interferences. The injection of larger volumes (50–100 μl) would involve the application of a previous clean-up step. In addition, the flow-rate of injection was optimised at 1 μl s^{-1} due to the adequate symmetry of the peaks obtained. Other values generated peak tailing.

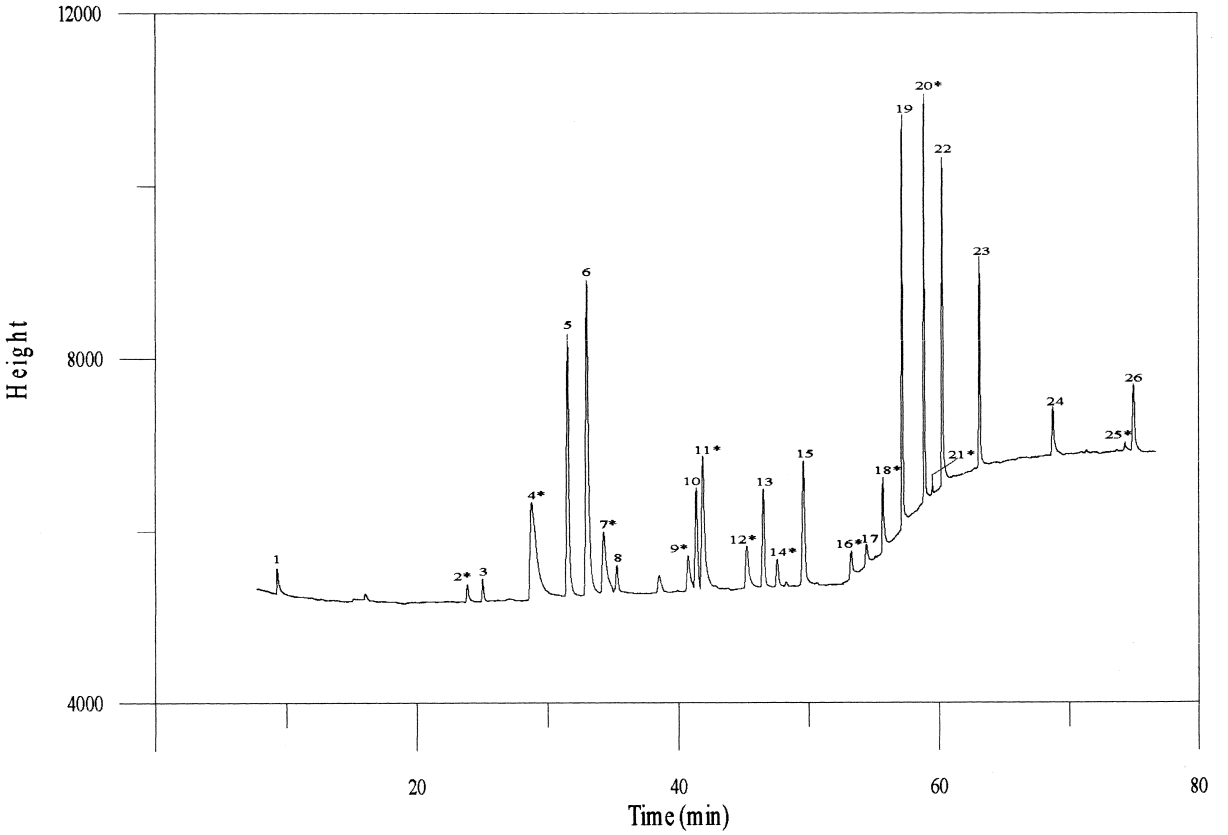

Fig. 1. GC–ECD chromatogram of a standard solution of the pesticides in *n*-hexane at 40 μg l^{-1}: 1, dichlorvos; 2*, etoprophos; 3, naled; 4*, dichloran; 5, lindane; 6, I.S.; 7*, chlorothalonil; 8, diazinon; 9*, parathion-m; 10, chlorpyrifos-m; 11*, vinclozolin; 12*, fenitrothion; 13, dichlofluanid; 14*, malathion; 15, chlorpyrifos; 16*, captan; 17, folpet; 18*, procymidone; 19, α-endosulfan; 20*, dieldrin; 21*, buprofezin; 22, β-endosulfan; 23, endosulfan sulphate; 24, fenpropathrin; 25*, pyrazophos and 26, acrinathrin. (* Target pesticides in this study).

The injector temperature was programmed from 60 to 280°C to avoid breakdown of the most thermolabile compounds.

For the MS, AGC was switched on in order to optimise sensitivity by completely filling the trap with target ions. In full scan mode, the mass range (85–450 u) and background mass (85 u) were selected to optimise sensitivity ejecting as much as possible the matrix and solvent ions. All the compounds were characterised by their full scan mass spectra under 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 had ion clusters in their MS spectra and wider windows would therefore catch additional neighbouring ions and lower precision. 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, the collision induced dissociation (CID), was selected for all the compounds except for chlorothalonil and dieldrin which needed more cleavage energy to obtain a good quality secondary spectra. The object 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 proposes. The EI-MS–MS spectra of the pesticides under our experimental conditions were stored in an laboratory-made EI-MS–MS library. The main ions are shown in Table

Table 2
Retention time windows (RTWs) and calibration data ($n=8$) of GC–ECD method[a]

Pesticide	RTW (min)	Linear ranges ($\mu g\ l^{-1}$)	r^2	RSD (%)	LOD[b] ($\mu g\ l^{-1}$)	LOQ[b] ($\mu g\ l^{-1}$)	LOQ[c] ($\mu g\ l^{-1}$)
Ethoprophos	23.80–23.86	1–100/100–1000	0.998/0.990	3.1/2.8	0.1	0.5	1.0
Dichloran	28.69–28.78	0.5–100/100–1000	0.997/0.996	3.6/3.4	0.1	0.4	0.5
I.S.	32.94–32.98	–	–	–	–	–	–
Chlorothalonil	34.21–34.25	0.5–100/100–1000	0.999/0.997	3.8/3.5	0.1	0.4	0.5
Parathion-m	40.73–40.77	0.5–100/100–1000	0.999/0.994	5.7/4.9	0.2	0.8	0.5
Vinclozolin	41.85–41.89	0.5–50/50–1000	0.993/0.997	1.8/1.6	0.1	0.5	0.5
Fenitrothion	45.21–45.27	1–100/100–1000	0.999/0.990	2.2/1.8	0.2	0.8	1.0
Malathion	47.56–47.60	0.5–100/100–1000	0.999/0.990	2.3/2.1	0.1	0.4	0.5
Captan	53.23–53.25	1–100/100–1000	0.996/0.999	2.3/2.0	0.1	0.5	1.0
Procymidone	55.65–55.67	0.5–100/100–1000	0.992/0.992	1.5/0.9	0.1	0.4	0.5
Dieldrin	58.85–58.87	0.5–100/100–1000	0.994/0.997	1.2/1.1	0.1	0.4	0.5
Buprofezin	59.47–59.49	10–100/100–1000	0.996/0.990	5.4/4.9	3.0	10.0	10.0
Pyrazophos	74.30–74.32	10–100/100–1000	0.992/0.998	3.5/3.1	2.0	10.0	10.0

[a] Calibration obtained using relative heights to that of the I.S.
[b] Based on the values of the blank at the t_R of the analytes.
[c] Based on the lowest concentration where the RSD is estimated to be less than 10%.

4. The base peak was selected for quantification in all cases.

The target analytes were searched into RTWs and were identified by comparing with the EI-MS and EI-MS–MS libraries. A positive analyte identification required a minimum spectral fit of >700 and a

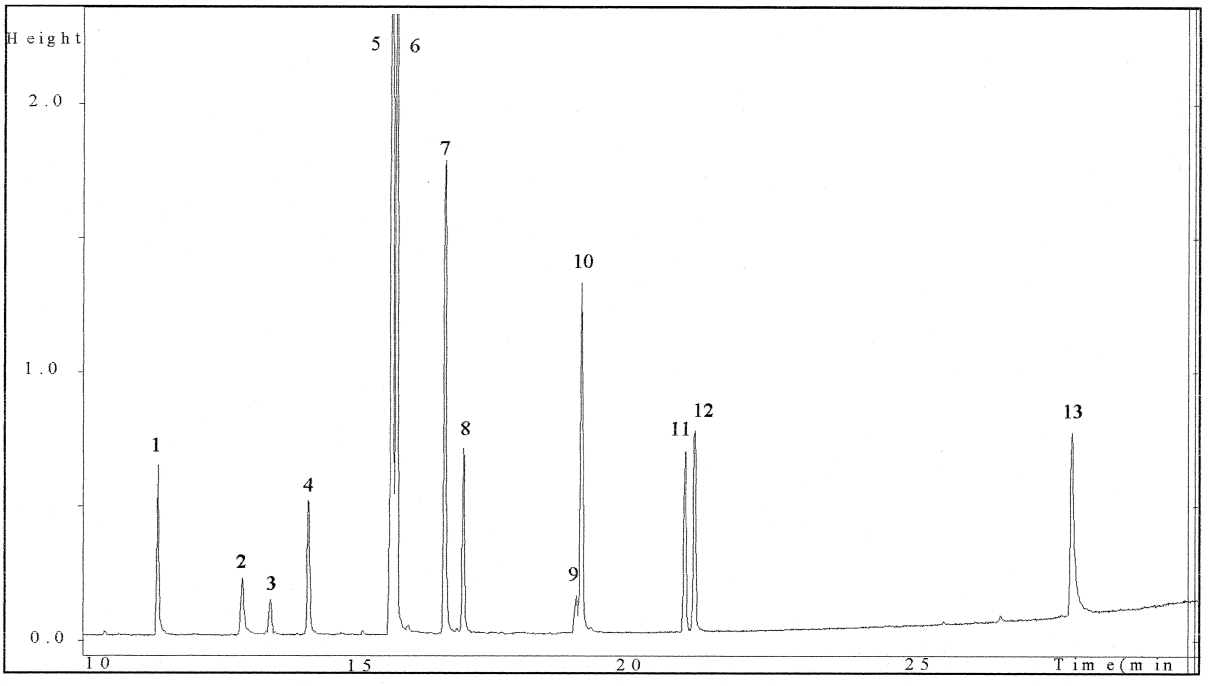

Fig. 2. GC–MS chromatogram of a standard solution of the pesticides in *n*-hexane at 200 $\mu g\ l^{-1}$: 1, etoprophos; 2, dichloran; 3, I.S.; 4, chlorothalonil; 5, vinclozolin; 6, parathion-m; 7, fenitrothion; 8, malathion; 9, captan; 10, procymidone; 11, dieldrin; 12, buprofezin and 13, pyrazophos.

Table 3
Retention time windows (RTWs) and calibration data ($n=8$) of GC–MS and (GC–MS–MS) methods[a]

Pesticide	RTW (min)	Ion	Linear range ($\mu g\ l^{-1}$)	r^2	RSD (%)	LOD ($\mu g\ l^{-1}$)	LOQ ($\mu g\ l^{-1}$)
Etoprophos	11.14–11.20	158 (94)	10–400 (1–400)	0.992 (0.996)	5.4 (16.2)	1.0 (0.3)	4.0 (1.0)
Dichloran	12.74–12.78	206 (176)	20–400 (5–400)	0.997 (0.997)	3.9 (7.3)	6.0 (1.0)	20.0 (5.0)
I.S.	13.12–13.19	265 (237)	–	–	–	–	–
Chlorothalonil	13.96–14.15	266 (231)	10–800 (0.6–400)	0.997 (0.998)	4.5 (5.7)	3.0 (0.2)	10.0 (0.6)
Vinclozolin	15.43–15.47	212 (115)	1–800 (0.5–200)	0.998 (0.992)	0.8 (2.3)	0.3 (0.1)	1.0 (0.5)
Parathion-m	15.53–15.59	263 (136)	20–400 (10–400)	0.984 (0.999)	3.2 (5.1)	1.5 (3.0)	5.0 (10.0)
Fenitrothion	16.41–16.49	260 (138)	5–800 (5–800)	0.991 (0.997)	2.7 (7.3)	1.0 (1.5)	5.0 (5.0)
Malathion	16.76–16.83	173 (99)	10–400 (1–200)	0.996 (0.996)	5.6 (8.7)	2.0 (0.4)	6.0 (1.0)
Captan	18.86–18.92	114 (79)	80–800 (40–800)	0.981 (0.995)	11.2 (13.3)	25.0 (15.0)	80.0 (40.0)
Procymidone	18.94–19.00	283 (255)	10–800 (0.5–200)	0.998 (0.993)	2.2 (5.5)	1.0 (0.1)	4.0 (0.5)
Dieldrin	20.85–20.89	277 (206)	5–400 (0.5–400)	0.996 (0.993)	4.3 (8.3)	1.0 (0.1)	5.0 (0.5)
Buprofezin	21.03–21.09	175 (193)	10–800 (0.5–200)	0.997 (0.999)	5.7 (11.6)	1.0 (0.1)	4.0 (0.5)
Pyrazophos	28.07–28.17	221 (210)	20–200 (2–800)	0.995 (0.998)	12.3 (15.2)	5.0 (0.6)	20.0 (2.0)

[a] Calibration data in GC–MS obtained using relative heights to that of the I.S. except for dichloran and pyrazophos; using relative areas in GC–MS–MS.

signal-to-noise ratio (S/N) of >3 (for quantification ion). For quantification, S/N must be higher than 10.

The use of the full scan mode allows one to compare the spectrum obtained with laboratory-made and commercial EI-MS libraries, but the spectral fit and sensitivity are not as good as they should be when complex samples are analysed 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 CID and quantifying with a specific ion from the analyte.

The instrument calibration for GC–MS and GC–MS–MS was performed by injecting standard solutions of each pesticide at levels ranging from 0.5 to 800 $\mu g\ l^{-1}$. The results are shown in Table 3. Good linearity of the response was found for all pesticides at concentrations belonging to the cited interval, with determination coefficients higher than 0.991, except in GC–MS for parathion-m (0.984) and captan (0.981). The method precision varied from 0.8 to 12.3% in GC–MS and 2.3 to 16.2% in GC–MS–MS. LOD ($S/N=3$) and LOQ ($S/N=10$) values for the different pesticides were calculated. Captan shows poor LOD and LOQ values in both MS and MS–

Table 4
m/z and (relative abundance) in MS–MS spectra

Pesticide	m/z
Etoprophos	158 (15), 139 (54), 130 (72), 114 (75), 94 (100)
Dichloran	206 (11), 176 (100)
I.S.	265 (13), 237 (100)
Chlorothalonil	265 (10), 231 (100), 213 (11), 205 (48), 170 (13)
Parathion-m	263 (16), 246 (73), 233 (21), 153 (60), 136 (100), 123 (13), 109 (7)
Vinclozolin	212 (29), 177 (20), 161 (18), 149 (20), 140 (14), 115 (100), 109 (52)
Fenitrothion	261 (22), 196 (18), 170 (36), 154 (33), 138 (100), 122 (41)
Malathion	173 (11), 143 (12), 125 (38), 117 (27), 109 (8), 99 (100)
Captan	114 (10), 79 (100)
Procymidone	282 (48), 255 (100), 240 (22), 220 (10)
Dieldrin	253 (16), 243 (100), 219 (23), 206 (99), 179 (19)
Buprofezin	248 (14), 193 (100), 164 (7)
Pyrazophos	265 (8), 210 (100)

MS, probably due to its poor chromatographic response and relatively high background presented for their ions.

In summary, good linearity is obtained with the three chromatographic methods in the studied concentration ranges. The determination coefficients were all above 0.991, except in GC–MS for parathion-m and captan. GC–MS presents better precision than GC–MS–MS, although the best repeatability values were obtained using the GC–ECD method. LODs and LOQs in ECD and MS–MS were similar except for buprofezin and pyrazophos, which were lower using the GC–MS–MS method, and for dichloran, parathion-m, fenitrothion, malathion and captan which were higher using the GC–MS–MS method. However, worse or equal (fenitrothion) LODs and LOQs were always obtained in the GC–MS mode than in the GC–MS–MS.

3.3. SPE procedure

Three 500-ml aliquots of Milli-Q water spiked with 100 ng l^{-1} of each target pesticide were used to study the extraction efficiency of the analytes. Good recoveries (76–122%) were obtained for all pesticides, except for captan (142%). This high value is due to the poor chromatographic signal peak of the pesticide employing GC–ECD (Table 5). The RSDs of the recovery values were $<9.4\%$. LODs and LOQs 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 allow the analysis of pesticides in water samples at the levels required by the EU Drinking Waters Directive [18].

On the other hand, volumes of water samples of 100, 200, 300, 400, 500 and 600 ml spiked with a mixture of pesticide standards were also used to determine the breakthrough volume [20]. Good recoveries were obtained using volumes ≤ 500 ml of sample. A breakthrough took place for all pesticides when 600 ml of water was passed. A volume of 500 ml was chosen as optimum volume of sample to use.

Finally, recoveries and repeatability studies of the proposed SPE method were also assessed using GC–MS and GC–MS–MS methods (Table 6). In general, good recoveries (79–126% for GC–MS and 70–133% for GC–MS–MS) were obtained for all pesticides, except for captan in GC–MS because the LOQ was higher than the concentration level studied. Values higher than 100% in the GC–MS mode can be explained by matrix interferences. However, in the GC–MS–MS mode interferences are minimised and only captan showed a very high recovery. This is due to its poor chromatographic response with a low quantitation ion, because of which slight baseline variations or backgrounds interferences have a great influence in the quantification. Better LOQ and LOD values were obtained using GC–MS–MS rather than GC–MS for all pesticides. LOD values were suitable

Table 5
Recoveries and RSDs in the SPE approach with GC–ECD quantification

Pesticide	% Recovery (RSD, %)[a]	LOD (ng l^{-1})	LOQ (ng l^{-1})
Ethoprophos	76 (7.9)	4	14
Dichloran	110 (8.8)	5	17
Chlorothalonil	109 (5.2)	6	20
Parathion-m	107 (9.4)	27	90
Vinclozolin	97 (3.7)	1	3
Fenitrothion	101 (2.5)	1	4
Malathion	122 (4.8)	18	60
Captan	142 (2.8)	3	10
Procymidone	118 (8.4)	5	16
Dieldrin	84 (4.3)	1	3
Buprofezin	79 (8.4)	24	80
Pyrazophos	106 (4.1)	21	71

[a] $n=3$; spiking level 100 ng l^{-1}.

Table 6
Recoveries and RSDs in the SPE approach with GC–MS and GC–MS–MS quantifications

Pesticide	GC–MS			GC–MS–MS		
	% Recovery (RSD, %)[a]	LOD (ng l^{-1})	LOQ (ng l^{-1})	% Recovery (RSD, %)[a]	LOD (ng l^{-1})	LOQ (ng l^{-1})
Ethoprophos	113 (6.7)	7	25	88 (17.4)	2	8
Dichloran	126 (4.4)	14	46	111 (10.6)	4	14
Chlorothalonil	114 (7.0)	7	24	92 (6.4)	3	10
Vinclozolin	83 (2.5)	6	20	99 (5.3)	4	12
Parathion-m	125 (4.0)	12	38	114 (9.8)	9	30
Fenitrothion	119 (3.5)	4	13	98 (10.9)	3	11
Malathion	125 (11.6)	27	89	84 (14.8)	5	15
Captan	<LOQ	80	267	133 (14.5)	26	86
Procymidone	86 (3.5)	10	32	87 (9.2)	6	21
Dieldrin	79 (5.1)	10	33	70 (10.8)	2	5
Buprofezin	110 (8.2)	12	40	101 (12.9)	3	9
Pyrazophos	94 (17.3)	13	44	82 (16.6)	6	20

[a] $n=3$; spiking level 100 ng l^{-1}.

to allow the determination of the pesticide residues in water at the required levels by the European legislation, except for captan in the GC–MS mode.

Comparing the results obtained with the three detection methods, ECD and MS–MS have proved their capability for the determination of pesticide residue in water samples at the required levels.

3.4. Application to environmental water samples

The proposed analytical procedure was used for the analysis of seven wetland water samples collected from the Campo de Dalías (Almería). Analyses of laboratory reagents blank, laboratory spiked blank and laboratory spiked matrix samples were performed together with the set of samples. Laboratory reagents blank rejected any contamination of interference due to reagents during processing samples. Analysis of samples was carried out if recoveries were between 60 and 130% in both laboratory spiked blank and laboratory spiked matrix samples.

Chlorothalonil was detected in one water sample at a concentration of 18 ng l^{-1} by MS–MS. It was confirmed by its MS–MS spectrum. However, its analysis was not possible using GC–ECD, because the chromatographic peak became confused with the background signals. The GC–ECD and GC–MS–MS chromatograms are shown in Fig. 3.

It has been demonstrated that when GC–ECD is used to analyse wetland water samples, interfering peaks make the quantification of pesticide traces difficult. Nevertheless, MS–MS solves this problem selecting the quantification ion for each compound. Therefore, the use of GC–MS–MS is recommended when complex water samples must be analysed.

4. Conclusions

A multiresidue method using SPE has been proposed for the determination of pesticides in wetland water samples. Target analytes were detected and quantified by GC–ECD and GC–MS–MS techniques, although for confirmatory purposes the latter technique was chosen. The recoveries of the pesticides varied from 76 to 142% for ECD and 70 to 133% for MS–MS; while the precision expressed as RSDs were 2.5–9.4% for ECD and 5.3–17.4% for MS–MS. The limit of detection was better than 30 ng l^{-1}. This method is simple and sufficiently sensitive and selective.

When complex water samples are analysed, better results are obtained using GC–MS–MS. This operation mode is more selective than both the GC–MS

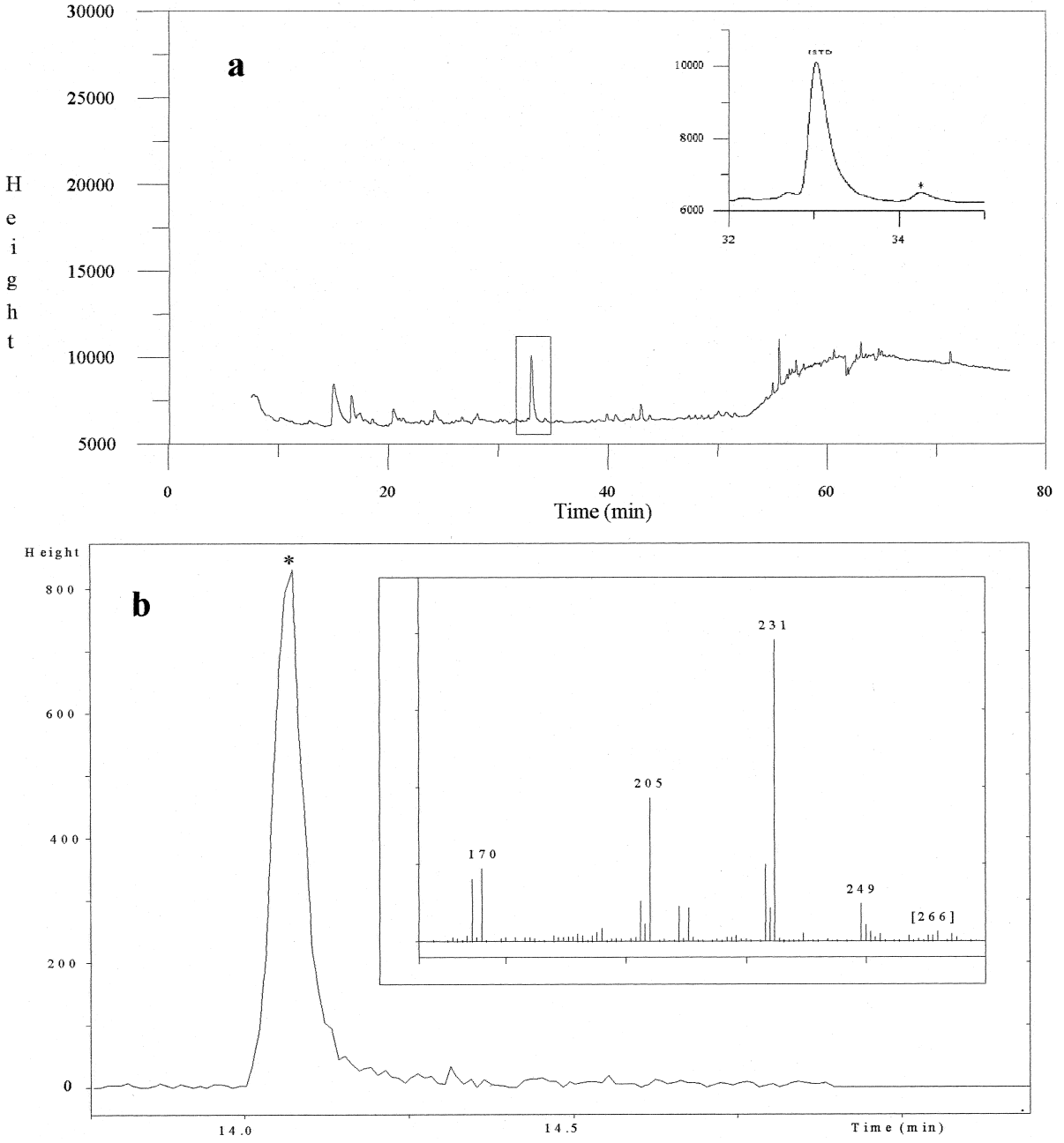

Fig. 3. Gas chromatogram of chlorothalonil (*) in a wetland water sample using (a) ECD and (b) MS–MS monitoring the quantification ion (m/z 231) and showing the spectrum obtained.

(full scan) and GC–ECD, avoiding coelution problems between matrix and target peaks. A study of seven wetland water samples from Almería (Spain) has been carried out finding chlorothalonil in one sample. The concentration level detected is lower than the level permitted by EU regulation (0.1 μg l^{-1}).

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