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Determination of pesticides in environmental waters by solid-phase extraction and gas chromatography with electron-capture and mass spectrometry detection

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Abstract

A group of pesticides with different chemical structures was determined by solid-phase extraction on LiChrolut EN cartridges and gas chromatography with electron-capture detection or mass spectrometry. The parameters affecting the solid-phase extraction process were optimized and the responses obtained by both GC detection systems were compared. The use of an electron-capture detector enabled the organochlorine pesticides studied to be determined at ng l^{-1} levels whereas mass spectrometry under selective ion monitoring acquisition enabled levels of low $\mu g\, l^{-1}$ to be reached. The R.S.D. ($n=6$) of the method in tap water was lower than 8.1% for electron-capture and mass spectrometric detection. The methods developed were used to determine the pesticides studied in tap and river water and some pesticides could be found in Ebro river and Ebro delta water.

Keywords: Environmental analysis; Water analysis; Pesticides; Triazines; Organochlorine compounds

1. Introduction

Pesticides are a group of persistent pollutants with highly toxic properties which are currently used for crop protection and this causes residues to rise in different environmental matrices [1]. According to European Community (EC) directives, a pesticide residue must not be present at a concentration greater than 0.1 $\mu g\, l^{-1}$ in drinking water and the requirements for surface water are 1–3 $\mu g\, l^{-1}$ [2]. Due to the complexity of the samples in which these pesticides must be determined chromatographic methods play an important role in this field; in particular gas chromatography (GC) and high-performance liquid chromatography (HPLC) are used.

The use of HPLC is important because it is suitable for determining thermally labile and polar pesticides [3–6] which require prior derivatization if they are to be determined by GC. However, GC is a very efficient technique with high resolution and the very sensitive and specific detectors are available [7–11]; therefore, GC is the most common technique for determining environmental pesticide residues.

Of all the GC detection methods, the electron-capture detection (ECD) is highly sensitive to compounds with electronegative atoms in their molecules and is one of the most frequently used detection methods in environmental routine analysis [8,12,13].

Mass spectrometry (MS) has been used to analyse

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trace pollutants in environmental samples because of its identification capabilities in complex mixtures [8,10,13,14]. MS can be operated in the full scan or in the selective ion monitoring (SIM) mode. The full scan acquisition mode is widely used because it reveals structural information about the different compounds through the spectra but it is of limited sensitivity and so, for target compounds analysis, SIM acquisition is mostly used.

The main instrumental limitation of GC has been the low sample volume to be injected, especially in capillary columns, which limits the sensitivity of the technique. This limitation may be solved by different methods, one of them being the application of an extraction process; the most commonly used is solid-phase extraction (SPE) [8–10,12,15]. Another solution is the injection of large sample volumes by different systems recently developed [16–18] and another new technique is solid-phase microextraction (SPME) [19–21] developed by Pawliszyn.

SPE is a simple technique, in the off-line mode; it can be carried out with membrane extraction disks [8,22–26] or using cartridges packed with different sorbents – graphitized carbon black [27], C_{18} or C_8 [9,10,24,28–32] and styrene–divinylbenzene copolymer [3,33] being the most used. New sorbents have recently appeared based on highly crosslinked copolymers [34,35] which are claimed to have a high capacity for different kinds of environmental pollutants; one of these sorbents is an ethylvinylbenzene–divinylbenzene copolymer sold as LiChrolut EN.

The aim of this paper is to test a highly crosslinked copolymer for SPE in order to establish a method for determining several pesticides. This method consists of a preconcentration step using SPE with a high capacity sorbent (LiChrolut EN) followed by GC with ECD and MS. The response obtained under the different detection systems used, ECD and MS under full scan and SIM acquisition modes, is compared. The performance of the method was tested with tap water and different surface water samples.

2. Experimental

2.1. Chemicals

Pesticide standards were obtained from Riedel-de Häen (Seelze, Germany) except bentazone which was from Dr. Ehrenstorfer (Augsburg, Germany). Stock solutions (2000 mg l^{-1}) were prepared by weighing and dissolving each pesticide in ethyl acetate and storing at 4°C. Working standard solutions were prepared by diluting the stock solutions with ethyl acetate and they were stored in the same way.

The internal standards were 1-chlorooctadecane from Aldrich (Steinheim, Germany) and bromophos-ethyl from Riedel-de Häen for the GC–MS and GC–ECD analyses, respectively.

Ethyl acetate and hexane were of PAR quality (for residue analysis) (Panreac, Barcelona, Spain). Ultrapure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Helium (99.995% quality) and nitrogen (99.995% quality) were supplied by Carburos Metálicos (Tarragona, Spain).

SPE cartridges with 200 mg of porous ethylvinylbenzene–divinylbenzene copolymer (LiChrolut EN) were used (Merck, Darmstadt, Germany).

2.2. Instrumentation

A Hewlett–Packard (Palo Alto, CA, USA) 5890 gas chromatograph equipped with an electron-capture detector (^{63}Ni) and an HP5972 mass spectrometer was used. The GC system was equipped with two split/splitless injectors. The two capillary columns were HP-1 (crosslinked methylsilicone, 0.25-μm film thickness) 30 m×0.25 mm I.D. fused silica.

2.2.1. MS

The column was inserted directly into the ion source of the mass spectrometer. The data were acquired with the HP Chemstation equipped with the mass spectral libraries Hppest and Wiley 138 which were used to compare the experimental spectra obtained.

The chromatographic conditions were the following: the initial temperature was 60°C, which was increased to 150°C at 25°C min^{-1} and then to 205°C at 2°C min^{-1}. The total run time was 31.10 min. The injector and detector temperatures were set at 250°C and 280°C, respectively. A 1-μl aliquot of the sample was injected in the splitless mode. Helium

was the carrier gas used at a flow-rate of 2.00 ml min^{-1}.

The electron impact (EI) ionization conditions were: ion energy 70 eV and mass range 50–425 in the full scan mode. The MS was tuned to *m/z* 69, 219 and 502 for EI corresponding to perfluorobutylamine (PFTBA).

2.2.2. ECD

For ^{63}Ni electron capture detector the chromatographic conditions were as follows: the initial temperature was 60°C which was increased to 165°C at 35°C min^{-1} and then to 200°C at 2°C min^{-1}. This temperature was held for 3 min; finally it was increased to 205°C at 2°C min^{-1} and held for 6 min. The total run time was 32 min. The injector and detector temperatures were set at 250°C and the injection volume was 1 μl in the splitless mode. Helium was the carrier gas at a flow-rate of 1.5 ml min^{-1}.

2.3. Extraction process

Off-line trace enrichment was carried out using the Bond Elut-Vac Elut System (Varian, Harbor City, CA, USA). The cartridge was activated by passing 5 ml of hexane, 5 ml of ethyl acetate and 5 ml of Milli-Q water in sequence through it with a low vacuum.

Once activated, 500 ml of the spiked sample water, with the prior addition of 15 g l^{-1} of NaCl, was passed through the cartridge at a flow-rate of approximately 20 ml min^{-1} using a vacuum system. Then the cartridge was dried under vacuum and the elution was carried out by sequentially adding 5 ml of hexane and 10 ml of ethyl acetate under vacuum. The eluate was collected in a tube and the internal standard was added in a concentration of 15 mg l^{-1} for 1-chlorooctadecane (MS) and 50 mg l^{-1} for bromophos-ethyl (ECD).

The eluate was then evaporated with a rotary evaporator (Büchi, Switzerland) to 1 ml and a 1-μl aliquot was injected into the capillary column.

River water samples were filtered through a 0.45-μm membrane filter (MSI, Westboro, MA, USA) before being preconcentrated.

3. Results and discussion

3.1. Chromatographic separation

The pesticides studied in this paper include several types of compounds: organophosphorous insecticides

Table 1
Selected ions, linearity range and correlation coefficients for MS-SIM acquisition and linearity range and correlation coefficients for ECD

Compound	Selected ions[a] (relative abundance)		SIM		ECD	
			Linearity range (mg l^{-1})	r^2	Linearity range (mg l^{-1})	r^2
Molinate	*126* (100)	55 (95)	0.01–10	0.9995	n.d.[b]	n.d.
α-HCH	*181* (100)	219 (93)	0.025–10	0.9994	0.00025–10	0.9993
Simazine	*201* (100)	186 (67)	0.5–10	0.9993	n.d.	n.d.
Atrazine	*200* (100)	215 (59)	0.025–10	0.9996	n.d.	n.d.
Lindane	*181* (100)	219 (88)	0.025–10	0.9991	0.00025–10	0.9993
δ-HCH	*181* (100)	219 (99)	0.025–10	0.9986	0.00025–10	0.9995
Heptachlor	*100* (100)	272 (87)	0.05–10	0.9974	0.00025–10	0.9998
Ametryn	*227* (100)	212 (58)	0.25–10	0.9995	n.d.	n.d.
Prometryn	*241* (100)	184 (79)	0.05–10	0.9995	n.d.	n.d.
Terbutryn	*226* (100)	185 (74)	0.05–10	0.9984	n.d.	n.d.
Aldrin	*66* (100)	263 (51)	0.025–10	0.9992	0.00025–10	0.9989
Malathion	*173* (100)	125 (90)	0.05–10	0.9988	n.d.	n.d.
Bentazone	*119* (100)	198 (79)	2.50–10	0.9979	n.d.	n.d.
Heptachlor-endo	*81* (100)	183 (86)	0.05–10	0.9991	0.001–10	0.9998
α-Endosulfan	*195* (100)	237 (97)	0.10–10	0.9990	0.00050–10	0.9998
Dieldrin	*79* (100)	263 (20)	0.05–10	0.9994	0.001–10	0.9999
β-Ensosulfan	*195* (100)	241 (79)	0.10–10	0.9990	0.00025–10	0.9998

[a] The ions used in the quantification for scan acquisition mode are shown in italics.
[b] n.d.=not determined.

(malathion), organochlorine insecticides [hexachlorocyclohexane (α-HCH), δ-HCH, α-endosulfan, β-endosulfan, aldrin, dieldrin, heptachlor, heptachlorendo and lindane], triazines (ametryn, atrazine, simazine, prometryn and terbutryn), molinate and bentazone.

The separation of the 17 pesticides studied was optimized initially by GC–MS. Different internal standards were tested and 1-chlorooctadecane was chosen [24] because its retention time was between those of the pesticides and its detector response was good.

The response under full scan acquisition mode but quantifying only the base peak of each pesticide, shown in Table 1, was studied in the range between 0.25 and 50 mg l^{-1} and good linearity was obtained for most compounds with correlation coefficients (r^2) between 0.9973 and 0.9998.

In order to decrease the limit of detection, SIM acquisition was tested by selecting two ions of each pesticide from the spectrum of each compound under EI ionization. The acquisition process was time-scheduled and the corresponding ions of each pesticide are shown in Table 1. The linearity was checked in the interval 0.010–10 mg l^{-1} and the correlation coefficients were between 0.9974 and 0.9996. These results are shown in Table 1. The detection limits were between 0.005 and 1 mg l^{-1}.

As far as ECD is concerned, 17 pesticides were initially tested but the response was very different among the pesticides; the organochlorine pesticides gave a higher response than the others, as expected, so for this detector only the response of this kind of pesticide was studied. As in the MS system, different internal standards were tested and finally bromophos-ethyl was chosen [9], because of its retention time and detector response. Although it is an organophosphorous pesticide, it is not used on the crops in the area under study.

The linearity of the response for mixtures of the nine organochlorine pesticides and the internal standard was studied between 0.25 μg l^{-1} and 10 mg l^{-1}, depending on the pesticide under study. The responses of most of them were linear in the range studied with r^2 values between 0.9989 to 0.9999. The values obtained are shown in Table 1. The limit of detection ($S/N=3$) was between 0.1 and 0.5 μg l^{-1}. From the results shown in Table 1 it can be observed that GC–MS-SIM gives satisfactory results for the determination of all the pesticides studied but GC–ECD shows a greater sensitivity for organochlorine compounds.

Even for ECD which is very sensitive to organochlorine pesticide, it is necessary to carry out a concentration step prior to chromatographic determination in order to reach the levels of pesticides required by EC regulations. In this paper LiChrolut EN cartridges were tested because of their great capacity for different compounds as demonstrated previously by other authors [35].

3.2. Solid-phase extraction

The first parameter studied was the extraction solvent, using hexane and ethyl acetate. When the elution was carried out with hexane the results for the recoveries of each pesticide showed that it is appropriate for most apolar compounds being studied, that is to say the organochlorine ones. A 5-ml volume of solvent gave good recoveries for those pesticides and a greater solvent volume did not improve them.

In order to obtain good recoveries for all the 17 pesticides studied, elution was carried out with ethyl acetate and all the pesticides were recovered but organochlorine pesticides gave better recoveries with hexane. So, in order to recover all the pesticides under study, the elution was carried out with 5 ml of hexane followed by 10 ml of ethyl acetate and this was the solvent used in further experiments because it gave good recoveries for all the pesticides studied, although for heptachlor, heptachlorendo, aldrin and bentazone the recoveries were low with all the solvents.

The effect of two different pH values was also tested, the sample pH of about 6 was adjusted to a value of 2 by adding hydrochloric acid before the preconcentration step. It was shown that pH values of around 6 gave the best results. There was, in particular, a considerable decrease in the recoveries of organochlorine pesticides at pH 2 and so in further studies the pH value of the sample was not adjusted. It should be added that no increase in the recovery of bentazone at an acidic pH was obtained as was expected from results in the literature [4].

Another parameter tested was the addition of NaCl

[3,24] at four different concentrations, 5, 10, 15 and 20 g l^{-1}. The results showed an improvement in the recoveries of some pesticides such as aldrin and heptachlor when 15 g l^{-1} of NaCl was added and so this concentration was chosen for further studies.

To obtain enrichment factors that were high enough to enable pesticides to be monitored in water samples at low μg l^{-1} or ng l^{-1} ranges, large volumes of water have to be extracted. So, the next step was to study the recoveries of each compound at sample volumes of 100, 250, 500 and 1000 ml of Milli-Q water spiked with different amounts of pesticide so that the pesticide/sample volume ratio was always the same. In Table 2 the recoveries for each pesticide obtained with GC–MS-SIM are shown. For a volume of 1000 ml there was a considerable decrease in the recoveries of pesticides such as bentazone and some organochlorine compounds and so, a volume of 500 ml was chosen for further studies. Higher recoveries were obtained in general for the pesticides studied in a paper by using LiChrolut [35] but the results for the compounds studied in both papers are quite similar. They also match the results of other authors who use sorbents such as C_{18} [32] or PLPR-S [3] in the SPE process, which means that for some compounds no significant increase in recovery was obtained when the new sorbent was used.

Table 2
Recoveries of SPE of pesticides in Milli-Q water at different sample volumes

Compound	Recovery (%)			
	Sample volume (ml)			
	100	250	500	1000
Molinate	107	111	106	109
α-HCH	96	90	83	77
Simazine	93	97	90	70
Atrazine	106	95	89	79
Lindane	94	87	81	77
δ-HCH	112	106	84	61
Heptachlor	71	68	52	17
Ametryn	103	93	85	76
Prometryn	98	86	79	74
Terbutryn	77	76	69	56
Aldrin	66	55	40	12
Malathion	54	56	54	35
Bentazone	44	42	39	8
Heptachlor-endo	68	49	48	16
α-Endosulfan	85	72	69	23
Dieldrin	69	67	61	19
β-Endosulfan	73	60	52	8

The values are means of three determinations.

3.3. Analysis of real samples

The performance of the total system for real samples was tested with tap and Ebro river water samples. Table 3 shows the results of recoveries and relative standard deviations for tap and river water when 500 ml of sample spiked at a concentration of 5 μg l^{-1} and with an addition of 15 g l^{-1} of NaCl was preconcentrated through the cartridge, for GC–MS-SIM. From these results it can be seen that the recoveries obtained for tap water are similar to those for Milli-Q water; for river water, the recoveries are similar too but for bentazone and aldrin there was a decrease in the recovery.

The linearity for real samples was checked for MS and ECD. First, a 500-ml blank of tap water, preconcentrated using the LiChrolut EN cartridge, was analysed in order to see whether different peaks appeared in the chromatograms at the same retention times as the pesticides being studied. No compounds were detected so this sample was used as a blank. In the analysis of 500 ml of tap water spiked with different levels of pesticides, for MS under scan acquisition, linearity was tested between 1 and 100 μg l^{-1} and correlation values from 0.9972 to 0.9997 and detection limits from 0.2–5 μg l^{-1} were obtained. The corresponding results when the SIM mode was applied for tap water are shown in Table 4. Despite the low recoveries obtained for some of the pesticides under study, good linearity was obtained. Fig. 1 shows the chromatograms obtained when 500 ml of unspiked tap water and 500 ml spiked at 0.1 μg l^{-1} were analysed with MS-SIM.

Table 4 also shows the results obtained when tap water was analysed with ECD. This detection method enables low levels such as 0.5 ng l^{-1} to be determined whereas for MS-SIM levels of 0.05 μg l^{-1} can be reached. However these levels are sufficient for determining the pesticides at the levels required by EC in tap water and in river water. Fig. 2 shows the chromatogram obtained for the analysis of 500 ml of unspiked tap water sample and tap water spiked at 0.1 μg l^{-1} with ECD.

Table 3
Recoveries for GC–MS-SIM of pesticides in tap and river water for 500 ml of sample spiked at a concentration of 5 $\mu g\,l^{-1}$

Compound	Tap water		River water	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Molinate	102	5	94	9
α-HCH	79	7	74	8
Simazine	84	8	82	10
Atrazine	85	6	80	7
Lindane	77	8	74	12
δ-HCH	89	9	82	7
Heptachlor	55	3	57	7
Ametryn	88	5	91	9
Prometryn	80	8	85	6
Terbutryn	70	6	72	7
Aldrin	37	9	30	8
Malathion	59	4	63	8
Bentazone	33	8	22	10
Heptachlor-endo	53	7	52	7
α-Endosulfan	74	5	78	3
Dieldrin	66	5	69	6
β-Endosulfan	57	9	54	9

The values are means of three determinations.

The repeatability of the method in real samples was checked with tap water spiked at 5 $\mu g\,l^{-1}$ and R.S.D. values ($n=6$) were lower than 8.1 and 7.6% for all compounds for MS and ECD, respectively.

Ebro river water samples were taken to study recoveries in surface waters. Fig. 3 shows the chromatogram obtained for the analysis of Ebro river water spiked at a concentration of 0.1 $\mu g\,l^{-1}$ in the

Table 4
Linearity range and correlation coefficients for tap water by MS-SIM and ECD

Compound	SIM-MS			ECD		
	Linearity range ($\mu g\,l^{-1}$)	LOD ($\mu g\,l^{-1}$)	r^2	Linearity range ($\mu g\,l^{-1}$)	LOD ($ng\,l^{-1}$)	r^2
Molinate	0.05–20	0.02	0.9992	n.d.[a]	n.d.	n.d.
α-HCH	0.05–20	0.02	0.9993	0.0005–20	0.2	0.9993
Simazine	0.50–20	0.1	0.9995	n.d.	n.d.	n.d.
Atrazine	0.05–20	0.02	0.9994	n.d.	n.d.	n.d.
Lindane	0.05–20	0.02	0.9991	0.0005–20	0.2	0.9971
δ-HCH	0.05–20	0.02	0.9999	0.0005–20	0.2	0.9996
Heptachlor	0.10–20	0.05	0.9981	0.0005–20	0.2	0.9978
Ametryn	0.50–20	0.1	0.9982	n.d.	n.d.	n.d.
Prometryn	0.10–20	0.05	0.9993	n.d.	n.d.	n.d.
Terbutryn	0.10–20	0.05	0.9981	n.d.	n.d.	n.d.
Aldrin	0.05–20	0.02	0.9983	0.0005–20	0.2	0.9975
Malathion	0.10–20	0.05	0.9979	n.d.	n.d.	n.d.
Bentazone	10.0–20	5.00	0.9998	n.d.	n.d.	n.d.
Heptachlor-endo	0.10–20	0.05	0.9974	0.002–20	1	0.9995
α-Endosulfan	0.10–20	0.05	0.9993	0.001–20	0.5	0.9981
Dieldrin	0.10–20	0.05	0.9985	0.002–20	1	0.9996
β-Endosulfan	0.25–20	0.1	0.9993	0.001–20	0.5	0.9995

[a] n.d.=not determined;
LOD=limit of detection.

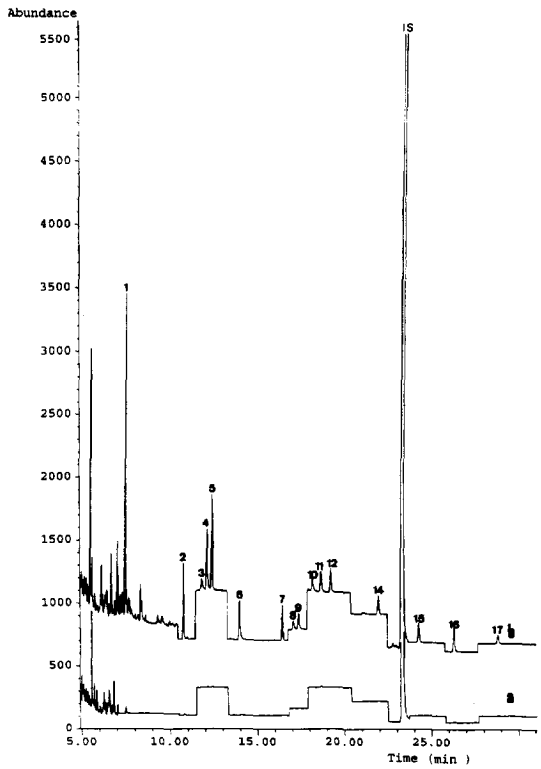

Fig. 1. Chromatogram obtained with MS-SIM after extracting a sample of (a) 500 ml of tap water and (b) 500 ml of tap water spiked with pesticides at 0.1 $\mu g\,l^{-1}$ and 15 $mg\,l^{-1}$ of internal standard (1-chlorooctadecane). Peaks: 1=molinate; 2=α-HCH; 3=simazine; 4=atrazine; 5=lindane; 6=δ-HCH; 7=heptachlor; 8=ametryn; 9=prometryn; 10=terbutryn; 11=aldrin; 12=malathion; 13=bentazone; 14=heptachlor-endo; 15=α-endosulfan; 16=dieldrin; 17=β-endosulfan.

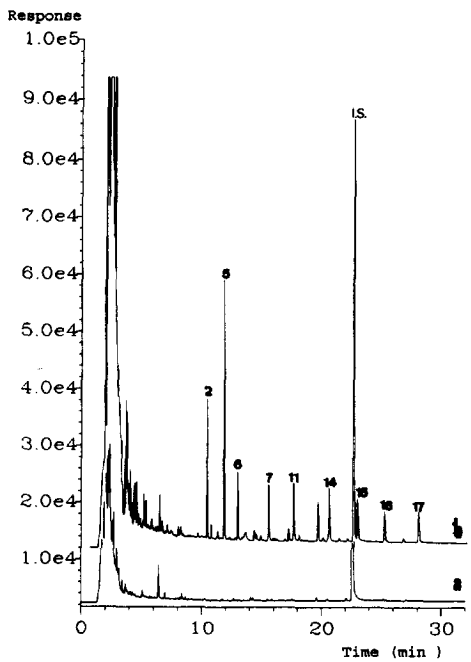

Fig. 2. Chromatogram obtained with ECD after extracting a sample of (a) 500 ml of tap water and (b) 500 ml of tap water spiked with pesticides at 0.1 $\mu g\,l^{-1}$ and 50 $mg\,l^{-1}$ of internal standard (bromophos-ethyl). For compound numbers, see Fig. 1.

MS-SIM acquisition mode. In the figure for the blank, that is, 500 ml of unspiked river Ebro water, some peaks that could be assigned to pesticides can be observed; they are molinate, lindane, terbutryn, aldrin and malathion. Fig. 4 shows the chromatogram for ECD; as can be observed, there are two peaks in the chromatogram for the blank that appear at the same retention time as two of the pesticides being studied, lindane and aldrin. These samples were first analyzed by GC–MS under full scan conditions; in the corresponding chromatogram obtained for an unspiked Ebro river sample, a peak at the same retention time as molinate was observed and its presence was confirmed by comparing the experimental spectrum with the spectrum of the standard. However, it could not be quantified because molinate was found in a concentration between the detection limit and the quantification limit of the method. Quantification was possible, though, when SIM detection was used and the concentration found for molinate was 0.07 $\mu g\,l^{-1}$ for SIM (this compound was not detected by ECD). For the other compounds that appear at the same retention time as some of the pesticides under study, no peaks appear in the chromatogram obtained under scan acquisition mode, so confirmation was not possible. The results obtained are shown in Table 5.

Different water samples from the Ebro delta area, the largest stretch of wetland in Catalonia, were analysed. In this zone, agriculture is the main basis of the economy, rice being the predominant crop. The samples were collected during pesticide spraying. Fig. 5 shows the total ion chromatogram obtained for 500 ml of sample after preconcentration. Some peaks were assigned to lindane, heptachlor, aldrin and malathion through the comparison between the experimental spectra and those of the

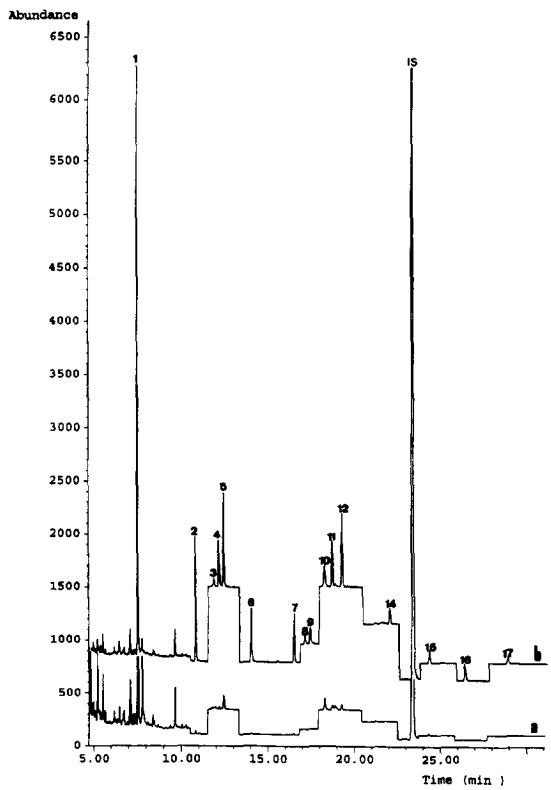

Fig. 3. Chromatogram obtained with MS-SIM after extracting a sample of (a) 500 ml of Ebro river water and (b) 500 ml of Ebro river water spiked with pesticides at 0.1 $\mu g\,l^{-1}$ and 15 $mg\,l^{-1}$ of internal standard (1-chlorooctadecane). For compound numbers, see Fig. 1.

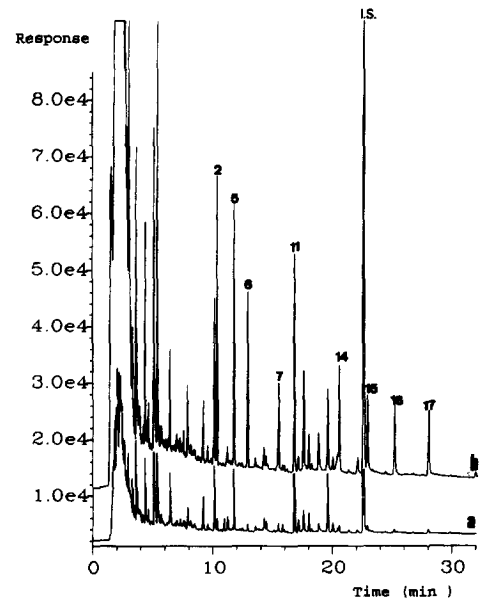

Fig. 4. Chromatogram obtained with ECD after extracting a sample of (a) 500 ml of Ebro river water and (b) 500 ml of Ebro river water spiked with pesticides at 0.1 $\mu g\,l^{-1}$ and 50 $mg\,l^{-1}$ of internal standard (bromophos-ethyl). For compound numbers, see Fig. 1.

standard; Fig. 6 shows the spectra corresponding to the peak of lindane in this sample and the spectrum obtained in the chromatogram of a standard solution of 50 $mg\,l^{-1}$. There was good concordance between both spectra even at this low concentration. Some of the other peaks in the chromatogram were assigned to different phthalates as had already been found in previous samples [24]. In Table 5 the corresponding concentration values obtained can be observed.

The samples collected in the Ebro delta were analyzed by the GC–MS-SIM system and also by ECD. Fig. 7 shows the corresponding chromatogram by MS under SIM acquisition and Fig. 8 the chromatogram obtained when the same sample was analyzed by ECD. The concentrations and relative standard deviations obtained by ECD and MS-SIM detection systems are shown in Table 5.

4. Conclusions

The solid-phase process using LiChrolut EN cartridges enables a sample volume of 500 ml to be preconcentrated with good recoveries for most compounds studied. The solvent for the extraction process is a mixture of 5 ml of hexane followed by 10 ml of ethyl acetate. It is not necessary to adjust the pH value of the sample before the preconcentration and the addition of 15 $g\,l^{-1}$ of NaCl is necessary in order to improve the recovery for some of the compounds under study.

The combination of SPE with GC–ECD and GC–MS enables the pesticides to be detected in water samples according to the requirements imposed by the EC although the developed methods are not suitable for bentazone. Detection limits of the pes-

Table 5
Concentration ($\mu g\,l^{-1}$) and R.S.D. ($n=3$) of pesticides found in Ebro delta water by MS-SIM and ECD

Compound	Scan		SIM		ECD	
	Concentration ($\mu g\,l^{-1}$)	R.S.D. (%)	Concentration ($\mu g\,l^{-1}$)	R.S.D. (%)	Concentration ($\mu g\,l^{-1}$)	R.S.D. (%)
Ebro river sample						
Molinate	n.q.[a]	n.q.[a]	0.07	5	n.d.[b]	n.d.[b]
Lindane	n.q.[a]	n.q.[a]	0.06	10	0.06	8
Aldrin	n.q.[a]	n.q.[a]	0.05	7	0.05	12
Ebro delta sample						
Lindane	1.9	7	2.1	9	2.1	8
Heptachlor	1.6	10	1.7	13	1.7	11
Aldrin	1.4	9	1.5	11	1.5	9
Malathion	4.4	12	4.3	10	n.d.[b]	n.d.[b]

[a] n.q=not quantified because is lower than the quantification limit.
[b] n.d.=not determined.

ticides in tap water were between 0.02 and 0.1 $\mu g\,l^{-1}$ when GC–MS-SIM acquisition mode was used and between 0.2 and 1 $ng\,l^{-1}$ for ECD.

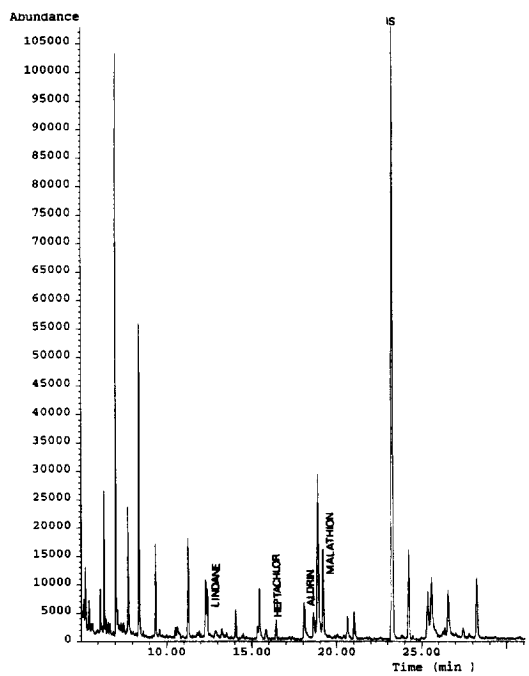

Fig. 5. Total ion chromatogram obtained for an Ebro delta sample of 500 ml by MS under scan acquisition mode.

Although for GC–MS under scan acquisition the detection limits are greater, more information is given through the spectrum obtained and this allows the identification of different substances. The method was applied to the analysis of drinking water and surface water. In Ebro river water and water from the Ebro delta some pesticides could be determined by

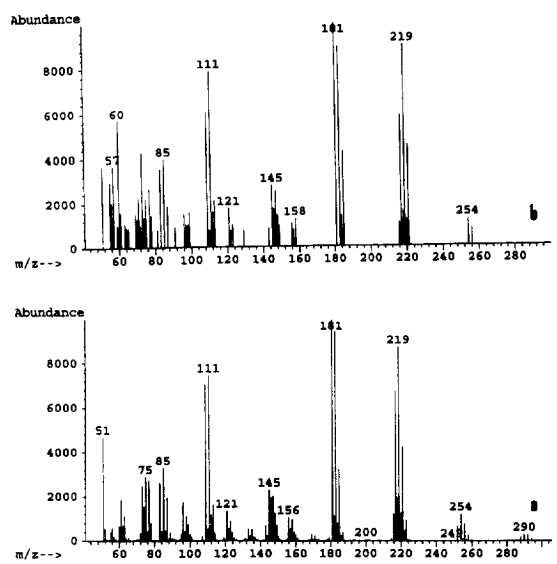

Fig. 6. (a) Spectrum of the peak lindane corresponding to the chromatogram shown in Fig. 5. (b) Spectrum of a standard of 50 $mg\,l^{-1}$ of lindane.

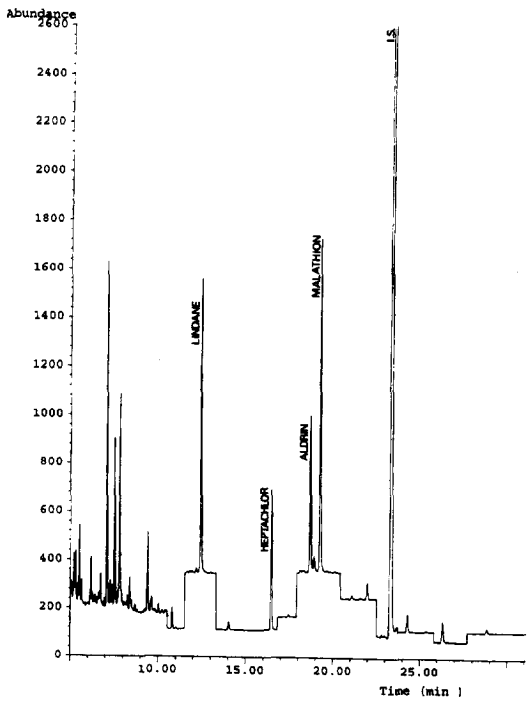

Fig. 7. Chromatogram obtained for an Ebro delta sample of 500 ml by MS under SIM acquisition. The sample is the same as in Fig. 5.

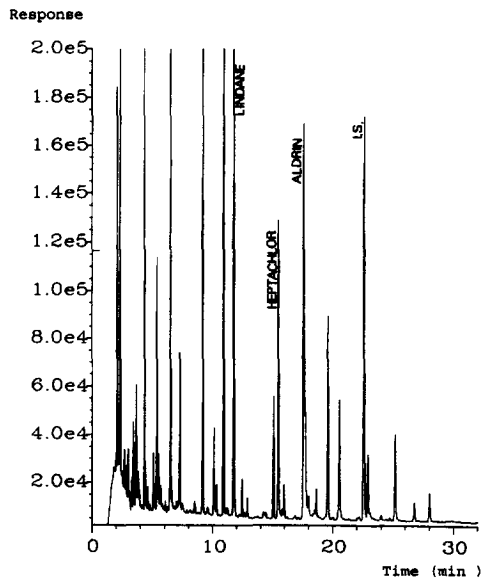

Fig. 8. Chromatogram obtained for a delta Ebro sample of 500 ml by ECD. The sample is the same as in Fig. 5.

GC–MS-SIM and GC–ECD, some of them being confirmed by GC–MS under full scan acquisition.

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