

Determination of various pesticides using membrane extraction discs and gas chromatography–mass spectrometry[☆]

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Abstract

A method for the determination of a group of pesticides in water by gas chromatography–mass spectrometry with electron impact ionization was developed. The preconcentration of 500 ml of water with C₁₈ and styrene–divinylbenzene (SDB) allowed the determination of pesticides at low- $\mu\text{g/l}$ levels. The use of SDB membrane extraction discs gave a large increase in the recovery of aldrin compared with the value obtained with C₁₈ discs. With SDB discs the recoveries were >85% for most compounds. The limits of detection were between 0.06 and 0.2 $\mu\text{g/l}$ in the full-scan mode. The mass spectra under positive and negative chemical ionization conditions with methane were also obtained and higher sensitivity with negative chemical ionization was obtained for most compounds.

1. Introduction

The identification and determination of pesticides in different water matrices is an analytical problem of increasing importance. Different techniques have been applied to the determination of pesticides, mainly employing GC [1–6] and HPLC [6–8] with a variety of detectors. In practice, capillary GC with electron-capture and nitrogen–phosphorus detection is the preferred separation technique for the determination of most pesticides, but HPLC is widely used for most polar compounds.

The advantage of the high sensitivity of these detectors contrasts with the lack of identification power of these techniques. The combination of

GC with mass spectrometry (GC–MS) is the most specific method for the analysis of complex matrices and it has been widely applied to the determination of pesticides [6,9–14]. In addition to the electron impact (EI) mode, which is the most routine confirmatory method, the use of GC–MS with positive-ion (PCI) and/or negative-ion chemical ionization (NCI) increases the already high identification power of mass spectrometry [5,11,15], in addition to an increase in sensitivity in some instances [10,13].

On the other hand, GC–MS shows low sensitivity even with selected-ion monitoring (SIM) and, in addition to the low levels of these compounds allowed in drinking water, the use of a preconcentration system is always required.

Various preconcentration methods based on different physico-chemical principles are commonly used, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE). Al-

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though most official methods for the determination of pesticides in water still use LLE, SPE is becoming more popular because it has some advantages over LLE [16,17]. SPE has already been used in some standard methods of the US Environmental Protection Agency (EPA) [18]. The most often used SPE approach utilizes short columns or cartridges containing sorbent particles [2,14], but the use of membrane extraction discs, originally described by Hagen *et al.* [19], is increasing because of the advantages of a higher sampling flow-rate and the elimination of some impurities such as plasticizers and oligomers extracted from the polymeric column and frit components [20,21]. PTFE filter discs containing octadecyl or octyl groups chemically bonded to silica are the most commonly used discs [19,22], but higher breakthrough volumes for some more polar compounds when styrene–divinylbenzene copolymer is used were demonstrated with cartridges [17,23].

In addition to the off-line methods of SPE, on-line systems have also been developed for LC [24,25] and also for GC [26–28]. In on-line LC–GC, precolumns containing the sorbent [27] are the most often used, but membrane extraction discs have also been applied [29]. Owing to the simplicity of the instrument required when off-line methods are used, these are actually preferred.

In this paper, the determination of a group of organochlorine, organophosphorus and chlorotriazine pesticides by GC–MS and off-line SPE with C_{18} and styrene–divinylbenzene discs is presented. In addition to EI mass spectra, CI mass spectra were also obtained to confirm the presence of these pesticides in real water samples.

2. Experimental

2.1. Chemicals

Standards of pesticides were obtained from Riedel-de-Häen (Seelze-Hannover, Germany). Stock standard solutions of each pesticide of

2000 $\mu\text{g/ml}$ were prepared by weighing and dissolving them in ethyl acetate and stored at 4°C in amber screw-capped vials with solid PTFE-lined cap. Working standard solutions were prepared by dilution and mixing of these solutions with ethyl acetate and stored in the same way as the stock standard solutions. The internal standard 1-chlorooctadecane was supplied by Aldrich (Steinheim, Germany).

Ethyl acetate was of Pesticide quality (Riedel-de-Häen) and methanol of HPLC quality (Scharlau, Germany). Water was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA).

Helium carrier gas and the reagent gas methane (both of 99.99% quality) were supplied by Carburos Metalicos (Tarragona, Spain).

2.2. Gas chromatography–mass spectrometry

A Hewlett-Packard (Palo Alto, CA, USA) model 5989 A MS Engine equipped with a dual EI–CI source in conjunction with an HP 5890 (Series GCII) and an HP-UX 59944C data system was used. The analytical column was an HP-1 (cross-linked methyl silicone gum, 0.33 μm film thickness) 12 m \times 0.2 mm I.D. fused-silica capillary column, which was inserted directly into the ion source.

The initial column temperature was 75°C, maintained for 1 min and then programmed at 20°C/min to 200°C, then at 2.5°C/min to 210°C and at 3°C/min to 225°C, and maintained at 225°C for 3 min. The total run time between injections was 19.25 min. The injector temperature was set at 250°C. A 1- μl volume of sample was injected in the splitless mode. The temperature of the transfer line was 250°C and the ion source and quadrupole temperatures were 200 and 100°C, respectively.

Helium was used as the carrier gas and methane as the reagent gas in the PCI and NCI modes at 1.8 and 1.7 Torr, respectively (1 Torr = 133.322 Pa). EI mass spectra were obtained at 70 eV. The mass range that was scanned was m/z 60–500.

The MS Engine was tuned to m/z 69, 219 and

502 for EI, m/z 219, 414 and 652 for PCI and m/z 264, 414 and 633 for NCI, corresponding to perfluorobutylamine (PFTBA).

The area of the base peak ion for each compound was used in the quantification procedure using the base peak of the internal standard, 1-chlorooctadecane.

2.3. Sample preparation

A standard Millipore 47-mm filtration apparatus was used. The membrane extraction discs were Empore discs manufactured by 3M (St. Paul, MN, USA), obtained from J.T. Baker (Deventer, Netherlands). The discs were 47 mm in diameter and 0.5 mm thick and each disc contained about 500 mg of C_{18} -bonded silica or styrene–divinylbenzene copolymer (SDB).

Prior to the extraction procedure, the discs were conditioned with about 20 ml of ethyl acetate as this was the final eluting solvent. After ethyl acetate had been left undisturbed on the disc for 1 min, vacuum was applied to draw ethyl acetate through the disc. A 20-ml volume of methanol was added and eluted under vacuum, 20 ml of Milli-Q-purified water were added and vacuum was applied, avoiding allowing the disc to dry completely.

The sample with 1% of NaCl added was passed through the disc under an adjusted vacuum at a speed about 10 ml/min. The disc was not allowed to dry completely during the extraction. After the sample had been processed, air was drawn through the disc for about 5 min to remove residual water.

After this operation, the pesticides trapped in the disc were collected using 2×15 ml of ethyl acetate. Ethyl acetate was left undisturbed on the disc for 1 min, then vacuum was applied to draw the ethyl acetate through. The ethyl acetate was transferred to a concentration tube marked at 100 μ l and, after the addition of the internal standard, the ethyl acetate solution was evaporated under vacuum to 100 μ l. A 1- μ l volume was injected into the GC–MS system.

River water samples were filtered through a 0.45- μ m PTFE filter prior to extraction.

3. Results and discussion

Fig. 1 shows the chromatogram of 22 pesticides and the internal standard 1-chlorooctadecane obtained under full-scan conditions and EI ionization. In Table 1 the retention time, the main ions and the relative abundance of each compound are included. Although 4,4'-DDE and dieldrin eluted almost at the same time, they could be quantified using selected ions, m/z 246 for 4,4'-DDE and m/z 79 for dieldrin.

The full-scan mode was used for the acquisition of the chromatogram as this allows the identification of the compounds, although better sensitivity under selected-ion monitoring (SIM) conditions was obtained.

The linearity of the response was checked at levels ranging from 2 to 100 μ g/ml and good linearity was obtained with correlations coefficients (r^2) from 0.990 to 0.9998 for all the compounds studied. The repeatability of the response for four injections was between 4.2 and 7.2% and the limit of detection (signal-to-noise ratio = 3) was between 0.3 and 0.8 μ g/ml.

For the chromatograms obtained with positive and negative chemical ionization, the main ions of each compound are given in Table 2. For triazines, under PCI conditions the base peaks corresponded to $[M - Cl]^+$ and two other important peaks corresponded to $[M + H]^+$ and $[M + C_2H_5]^+$. Some papers [11,13] have reported $[M + H]^+$ as a base peak whereas other workers [5] obtained $[M - Cl]^+$ as the base peak. In the NCI mode, the two triazines showed $[M - H]^-$ as the base peak according to some workers [11], instead of the low relative abundance (13%) obtained by others [13]. The sensitivity was better in the EI mode, which is in agreement with other workers [5,11,13].

In the PCI mode, all organophosphorus compounds exhibited a peak corresponding to $[M + 1]^+$ as one of the most abundant and in the NCI mode the major peaks corresponded to $[M]^-$ or $[M - 1]^-$. The sensitivity in the PCI mode was similar to that obtained under EI conditions but NCI increased the sensitivity.

The molecular peak, $[M + 1]^+$ or $[M - 1]^-$, of the organochlorine pesticides could be obtained

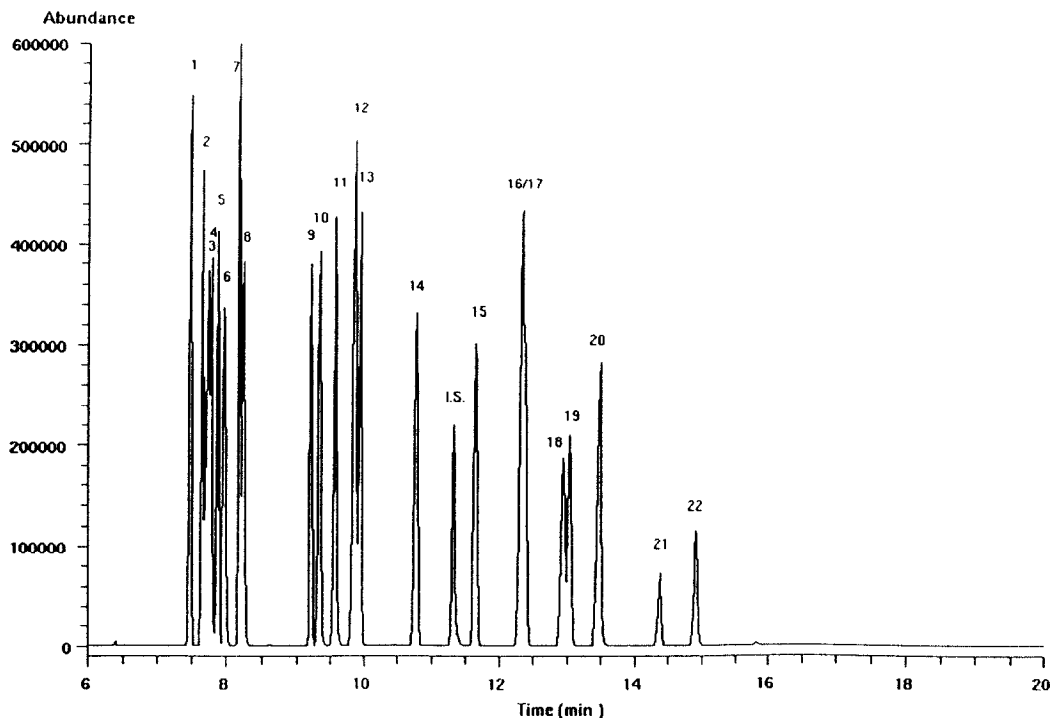


Fig. 1. Total ion chromatogram of the 22 pesticides and the internal standard. An amount of 100 ng of each pesticide was injected. Peaks: 1 = α -HCH; 2 = β -HCH; 3 = simazine; 4 = atrazine; 5 = lindane; 6 = δ -HCH; 7 = diazinon; 8 = disulfoton; 9 = heptachlor; 10 = fenitrothion; 11 = malathion; 12 = parathion; 13 = aldrin; 14 = epoxyheptachlor; 15 = α -endosulfan; 16 = 4,4'-DDE; 17 = dieldrin; 18 = endrin; 19 = β -endosulfan; 20 = 4,4'-DDD; 21 = endosulfan sulphate; 22 = 4,4'-DDT; I.S. = internal standard, 1-chlorooctadecane. For GC conditions, see text.

for most compounds under PCI or NCI conditions, but much higher sensitivity was obtained in the latter mode. The increase in sensitivity was in some instances three orders of magnitude, *e.g.*, the limit of detection of both endosulfan and endosulfan sulphate was about 1 pg.

From these results, it can be deduced that NCI allowed the confirmation of most of the compounds studied and higher m/z values were obtained compared with EI which implied an increase in selectivity. For some compounds an increase in sensitivity was also observed.

Owing to the low sensitivity of GC-MS, an extraction process is necessary in order to determine the pesticides at low ng/ml levels, taking into account that the standard level of tolerance in the European Community of these pollutants in drinking water is 0.1 ng/ml.

The extraction process was carried out using membrane extraction discs, and two different

sorbents, the commonly C_{18} and the newer SDB, were compared. The blank of these membrane extraction discs was initially checked and some peaks of low abundance were found, but only one eluted at the same time as one of the pesticides and was found with both types of discs, and was a phthalate co-eluting with malathion. However, this was not a drawback as the pesticide could be determined by its major ion, which was not present in the mass spectrum of the phthalate.

When an SPE method is developed, two important features are the capacity of the cartridges, column or disc and the maximum volume of the sample that can be preconcentrated without elution of the compound, known as the breakthrough volume. Before the study of these two steps, the addition of NaCl, recommended by some workers [30,31], was initially tested, and an improvement in the recovery of some com-

Table 1
Retention times (t_R) recorded under the experimental conditions, major ions and relative abundances in EI mass spectra of the pesticides studied

Pesticide	t_R (min)	Class ^a	Main ions, m/z (relative abundance, %)		
α -HCH	7.483	OC	219 (100)	181 (95)	183 (92)
β -HCH	7.654	OC	219 (100)	181 (98)	183 (92)
Simazine	7.739	TR	201 (100)	173 (70)	68 (65)
Atrazine	7.783	TR	200 (100)	215 (55)	173 (40)
Lindane	7.876	OC	181 (100)	183 (97)	219 (85)
δ -HCH	7.972	OC	183 (100)	109 (90)	219 (90)
Diazinon	8.188	OP	179 (100)	137 (70)	304 (60)
Disulfoton	8.245	OP	88 (100)	97 (35)	61 (20)
Heptachlor	9.220	OC	100 (100)	272 (55)	274 (42)
Fenitrothion	9.353	OP	125 (100)	109 (98)	277 (50)
Malathion	9.579	OP	127 (100)	173 (90)	125 (65)
Parathion	9.876	OP	109 (100)	97 (95)	137 (55)
Aldrin	9.954	OC	66 (100)	101 (42)	263 (40)
Epoxyheptachlor	10.786	OC	183 (100)	81 (85)	135 (80)
α -Endosulfan	11.659	OC	195 (100)	159 (80)	197 (75)
4,4'-DDE	12.350	OC	246 (100)	318 (80)	248 (60)
Dieldrin	12.350	OC	79 (100)	108 (25)	263 (12)
Endrin	12.943	OC	81 (100)	65 (75)	263 (40)
β -Endosulfan	13.045	OC	63 (100)	195 (90)	160 (80)
4,4'-DDD	13.489	OC	235 (100)	165 (60)	199 (20)
Endosulfan sulphate	14.374	OC	272 (100)	229 (80)	273 (75)
4,4'-DDT	14.912	OC	235 (100)	165 (60)	199 (20)

^a OC = Organochlorines, OP = organophosphorus, TR = triazines.

Table 2
Molecular masses (M_r), major ions and relative abundances obtained under PCI and NCI conditions

Pesticide	M_r	Ions, m/z (relative abundance, %)					
		PCI		NCI			
α -HCH	288	219 (100)	217 (80)	221 (50)	71 (100)	255 (50)	
β -HCH	288	219 (100)	166 (75)	221 (50)	71 (100)	325 (60)	255 (50)
Simazine	201	166 (100)	202 (87)	230 (25)	200 (100)	165 (20)	
Atrazine	215	180 (100)	216 (80)	244 (20)	214 (100)	179 (30)	
Lindane	288	219 (100)	217 (80)	221 (50)	71 (100)	255 (50)	
δ -HCH	288	219 (100)	217 (80)	221 (50)	71 (100)	255 (50)	
Diazinon	304	305 (100)	333 (21)	346 (5)	169 (100)	303 (10)	
Heptachlor	370	337 (100)	339 (90)	335 (70)	300 (100)	266 (98)	
Fenitrothion	277	248 (100)	278 (80)		277 (100)	168 (86)	
Malathion	330	285 (100)	331 (50)	359 (27)	157 (100)	330 (20)	
Parathion	291	292 (100)	262 (99)	332 (10)	291 (100)	154 (50)	
Aldrin	362	329 (100)	263 (70)	293 (62)	–	–	
Epoxyheptachlor	386	81 (100)	325 (37)		280 (100)	237 (98)	388 (67)
α -Endosulfan	404	71 (100)	277 (80)	407 (85)	406 (100)	404 (90)	242 (50)
4,4'-DDE	316	319 (100)	317 (75)	283 (65)	316 (100)	236 (40)	
Dieldrin	380	279 (100)	345 (99)		237 (100)	380 (20)	
Endrin	380	281 (100)	279 (93)	345 (92)	308 (100)	380 (50)	378 (47)
β -Endosulfan	404	277 (100)	325 (50)	405 (48)	406 (100)	404 (62)	370 (30)
4,4'-DDD	318	209 (100)	283 (44)	319 (24)	272 (100)	308 (50)	380 (40)
Endosulfan sulphate	423	325 (100)	423 (75)		386 (100)	97 (55)	422 (10)
4,4'-DDT	352	243 (100)	319 (40)	353 (15)	71 (100)	281 (40)	

pounds was observed. Different amounts of NaCl were added and when more than 4 g were added, some NaCl appeared in the concentrated sample, which implied a decrease in repeatability.

In order to determine the capacity of the discs, different concentrations between 1 and 10 ng/ml of the pesticides were studied by preconcentrating a volume of 200 ml of Milli-Q-purified water. No significant differences in the recoveries were obtained, so it could be deduced that the capacity of the discs was high enough at the concentration levels studied, as had already been demonstrated by other workers [3,19].

The recoveries of each compound with different volumes of samples were also studied and recoveries of each compound were determined for a concentration of 5 ng/ml. In Table 3 the

Table 3
Mean recoveries and relative standard deviations ($n = 3$) of pesticides in reagent water using a C_{18} membrane extraction disc

Pesticide	Volume (ml)			
	500		1000	
	Recovery (%)	R.D.S. (%)	Recovery (%)	R.D.S. (%)
α -HCH	98	5.3	78	7.8
β -HCH	97	4.5	100	5.7
Simazine	80	4.3	65	6.4
Atrazine	95	3.4	92	2.8
Lindane	90	6.5	80	4.5
δ -HCH	94	6.2	95	5.3
Diazinon	84	5.6	76	5.8
Heptachlor	94	6.2	59	8.2
Fenitrothion	102	4.5	81	6.5
Malathion	89	6.3	96	5.7
Parathion	85	5.8	78	5.3
Aldrin	52	8.9	40	9.3
Epoxyheptachlor	75	7.5	70	7.2
α -Endosulfan	85	5.3	72	6.4
4,4'-DDE	80	8.3	60	7.8
Dieldrin	85	4.3	80	5.6
Endrin	89	5.8	80	8.3
β -Endosulfan	70	6.8	60	9.8
4,4'-DDD	60	9.7	51	9.2
Endosulfan sulphate	72	8.5	60	9.3
4,4'-DDT	70	5.9	62	8.0

Spiking level: 5 ng/ml.

recoveries and relative standard deviations obtained for the C_{18} disc are shown; recoveries $>85\%$ were obtained for most compounds when 500 ml of the sample were preconcentrated. Higher volumes were also tested but good recoveries were obtained only for some compounds. The organophosphorus compound disulfoton was not recovered and further attempts to increase the recovery were not successful. A low recovery of aldrin was also observed even at 500 ml, as reported previously [3,19].

The results of recovery as a function of sample volume for the SDB disc are given in Table 4. The recovery of disulfoton was not improved but a substantial increase in the recovery of aldrin was observed compared with the results obtained with the C_{18} disc. Triazines showed high recoveries even at a volume of 1000 ml. It has

Table 4
Mean recoveries and relative standard deviations ($n = 3$) of pesticides in reagent water using an SDB membrane extraction discs

Pesticide	Volume (ml)			
	500		1000	
	Recovery (%)	R.D.S. (%)	Recovery (%)	R.D.S. (%)
α -HCH	96	4.3	90	5.3
β -HCH	110	5.8	92	6.8
Simazine	105	6.2	87	9.8
Atrazine	91	5.6	101	6.3
Lindane	85	4.5	87	5.8
δ -HCH	105	6.3	95	7.3
Diazinon	86	6.2	54	8.9
Heptachlor	97	5.9	49	9.2
Fenitrothion	84	7.3	18	12.3
Malathion	85	6.8	20	13.3
Parathion	87	6.3	47	10.2
Aldrin	95	5.4	99	7.2
Epoxyheptachlor	79	5.3	66	6.3
α -Endosulfan	82	6.3	58	9.2
4,4'-DDE	66	8.3	43	7.5
Dieldrin	92	4.5	97	6.8
Endrin	85	6.3	88	4.2
β -Endosulfan	108	3.2	78	7.3
4,4'-DDD	75	5.0	63	10.2
Endosulfan sulphate	89	6.0	58	6.2
4,4'-DDT	72	6.8	62	12.3

Spiking level: 5 ng/ml.

already been reported [23] that the breakthrough volume for triazines is much higher with SDB than C_{18} . A considerable decrease in the recovery of organophosphorus compounds was observed when 1000 ml of sample were pre-concentrated.

From these results it can be deduced that for the determination of the pesticides a volume of 500 ml gave a good recovery of most compounds. When some specific pesticides must be determined, *e.g.*, triazines, volumes of 1000 ml or even higher can be pre-concentrated. When only confirmation of the peaks is required, volumes of 1 l or higher can be pre-concentrated.

The application of the method to real samples was tested with different samples of Ebre river water. Special attention was given to samples from the location where water is used as a water supply for many cities and after treatment used as tap water. This location is before the Ebre

delta, which is an important agricultural zone and where the presence of some pesticides has been found [6].

The chromatogram obtained for 500 ml of Ebre river water pre-concentrated using a C_{18} membrane extraction disc is depicted in Fig. 2. No pesticides studied were found in the sample and some of the peaks could be assigned to different phthalates.

The same sample was pre-concentrated using an SDB disc and the chromatogram obtained is shown in Fig. 3. Although some of the peaks are the same as those obtained when the C_{18} disc was used, different selectivities of the discs was observed and no pesticides could be found.

In order to study the recovery of the method for real samples, the same sample was spiked with different amounts of a standard solution and the recoveries and repeatability ($n = 3$) obtained for a concentration of 5 ng/ml are given

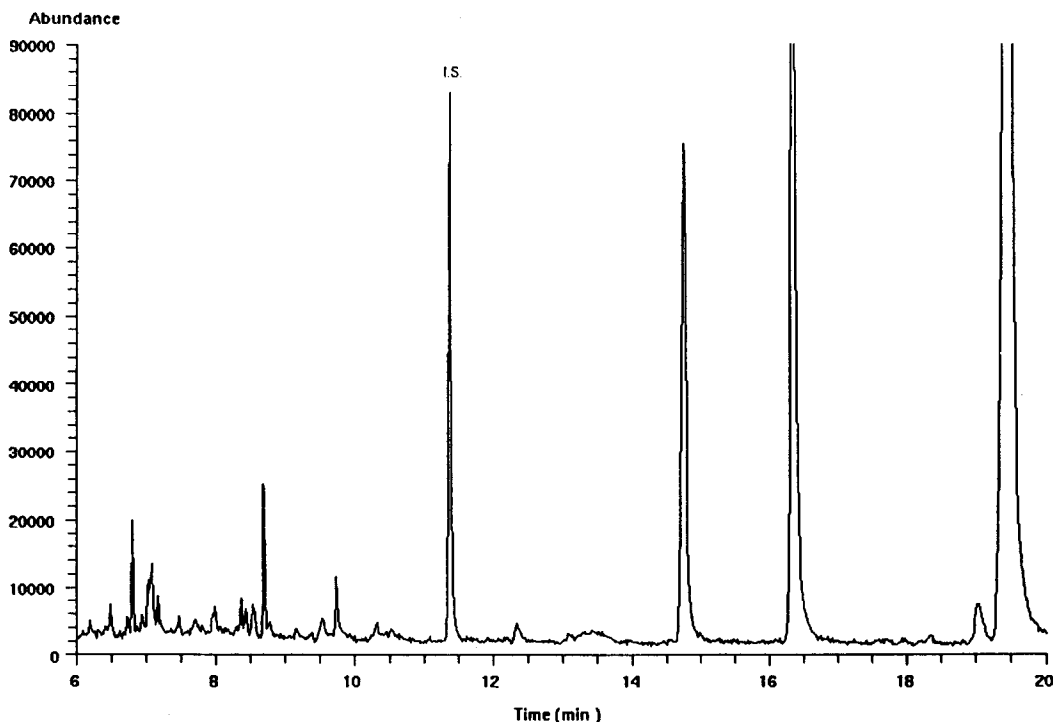


Fig. 2. Total ion chromatogram of a sample of 500 ml of Ebre river water after extraction with a C_{18} disc. For conditions, see text.

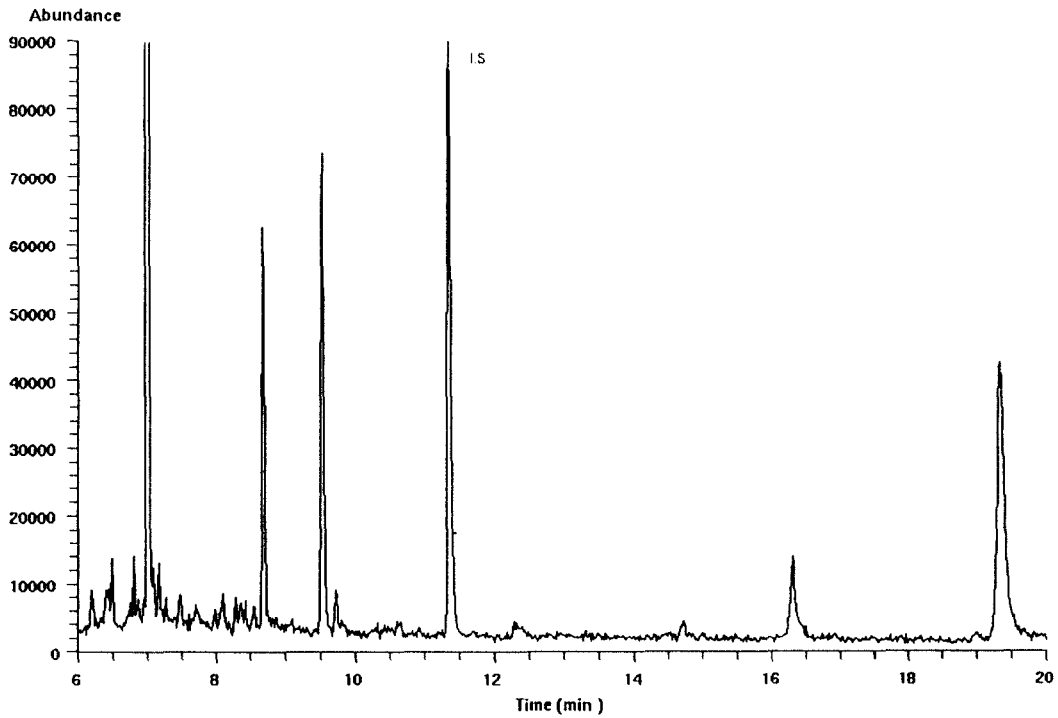


Fig. 3. Total ion chromatogram of a sample of 500 ml of Ebre river water extraction with an SDB disc. For conditions, see text.

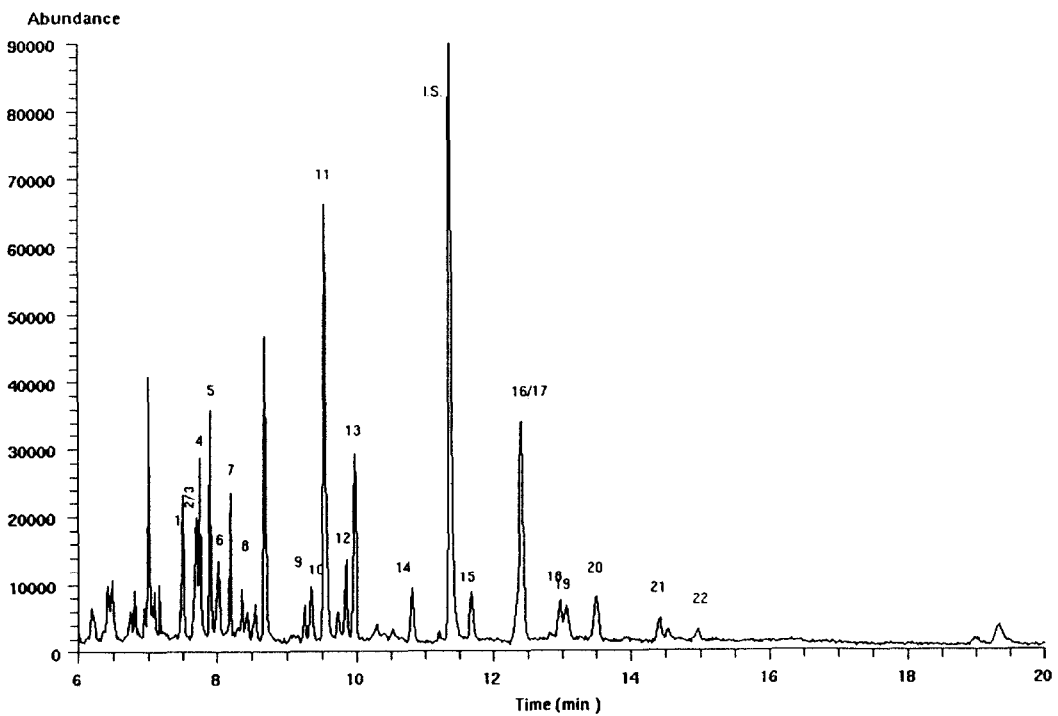


Fig. 4. Total ion chromatogram of a sample of 500 ml of Ebre river water spiked with each pesticide at a concentration of 0.8 ng/ml. For conditions, see text. Peak numbers as in Fig. 1.

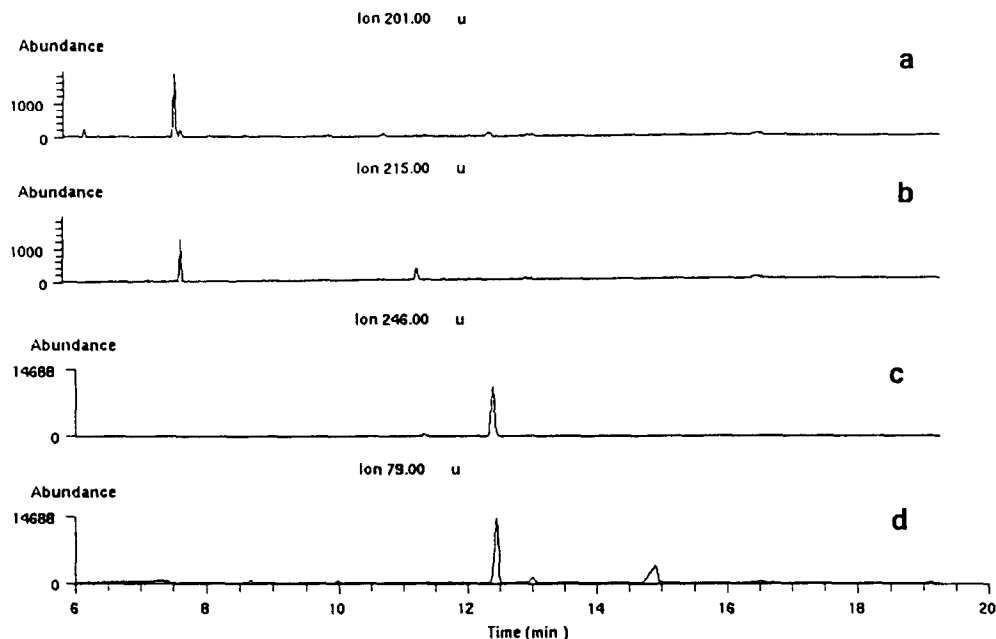


Fig. 5. Ion chromatogram obtained using EI ionization of different pesticides after pre-concentration in an SDB membrane extraction disc of 500 ml of river water spiked at 0.2 ng/ml. Pesticide: (a) simazine; (b) atrazine; (c) 4,4'-DDE; (d) dieldrin.

Table 5

Mean recoveries and relative standard deviations ($n = 3$) of pesticides at 5 ng/ml in 500 ml of Ebre river water using C_{18} and SDB membrane extraction discs

Pesticide	C_{18}		SDB	
	Recovery (%)	R.D.S. (%)	Recovery (%)	R.D.S. (%)
α -HCH	94	5.3	93	5.8
β -HCH	98	4.6	97	6.2
Simazine	82	6.5	98	5.8
Atrazine	89	3.6	96	4.7
Lindane	96	5.6	87	4.3
δ -HCH	90	4.8	93	6.4
Diazinon	86	5.2	85	6.7
Heptachlor	89	4.9	95	5.2
Fenitrothion	98	6.3	86	4.3
Malathion	92	5.8	88	7.2
Parathion	91	6.3	85	5.0
Aldrin	54	8.4	93	4.3
Epoxyheptachlor	80	5.3	82	4.6
α -Endosulfan	86	6.5	78	9.2
4,4'-DDE	72	7.3	73	7.5
Dieldrin	91	5.4	93	4.8
Endrin	86	6.3	92	7.2
β -Endosulfan	73	7.3	96	5.3
4,4'-DDD	78	8.0	73	7.8
Endosulfan sulphate	79	6.2	92	6.2
4,4'-DDT	66	7.8	73	6.8

in Table 5. It can be seen that the results are very similar to those obtained with Milli-Q-purified water.

The total ion chromatogram of the same Ebre river sample spiked with each pesticide at a concentration of about 0.8 ng/ml is shown in Fig. 4.

The limit of detection of the method in the full-scan mode with quantification from the ion chromatogram for real samples, determined for a signal-to-noise ratio of 3, was between 0.06 and 0.2 ng/ml when a volume of 500 ml was pre-concentrated. In Fig. 5, the ion chromatogram of different compounds in a river water spiked at 0.2 ng/ml is depicted.

4. Conclusions

The use of membrane extraction discs and GC-MS with EI ionization allowed the determination of a group of pesticides at levels of 0.06–0.2 $\mu\text{g/l}$ in the full-scan mode. SDB extraction discs gave better recoveries than C_{18} extraction discs for some compounds. A volume of sample of 500 ml gave good recoveries for most pesticides with the SDB disc. Mass spectra were

obtained with PCI and NCI with methane and higher sensitivity was achieved in general for organophosphorus and organochlorine compounds in the NCI mode and limits of detection as low as 1 pg were reached for some compounds.

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