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Determination of organophosphorus insecticides in natural waters using SPE-disks and SPME followed by GC/FTD and GC/MS

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Abstract Two methods for the analysis of ten organophosphorus insecticides in natural waters using solid phase extraction disks containing C_{18} and SDB and solid phase microextraction fibers containing polyacrylate (PA) are developed. Bromophos ethyl, bromophos methyl, dichlofenthion, ethion, fenamiphos, fenitrothion, fenthion, malathion, parathion ethyl and parathion methyl were determined by GC/MS and GC/FTD. The SPE-disks require only 1000 mL of sample and provide a method limit of detection in the range of 0.01-0.07 μg/L and recovery rates from 60.7 to 104.1%. The solid phase microextraction (SPME) technique requires 2-5 mL of water sample and provides a method limit of detection in the range of 0.01 to 0.05 μg/L for all detectors and the recoveries compared to distilled water ranged from 86.2 to 119.7%. The proposed methods were applied to the trace level screening determination of insecticides in river water samples originating from different Greek regions.

Introduction

The determination of pesticide residues in water samples is necessary for solving various environmental and biological problems [1]. EU regulations for drinking water quality set a limit in concentration of 0.5 μg/L for the sum of all pesticides and 0.1 μg/L for each compound, so that detection limits below 0.1 μg/L are required for monitoring potable water. The trace determination of pesticides requires both high performances from analytical instruments and efficient sample preparation [2]. The determination of low concentrations of organophosphorus insecticides in water by chromatographic techniques requires a previous concentration of the sample, e.g. by liquid-liquid partition requiring large amounts of toxic and expensive solvents.

Solid-phase extraction (SPE) disks and solid phase microextration (SPME) fibers have been used due to simplicity and robustness [3-5] in relation to liquid-liquid extraction [6].

Solid-phase microextraction (SPME) allows the simultaneous extraction and preconcentration of analytes from a sample matrix [7-8]. The analytes are extracted by absorption over the fiber which is directly exposed to the samples or to the headspace. Finally, the fiber is introduced into the gas chromatograph injector where the analytes are thermally desorbed. Different stationary phases, such as polydimethylsiloxane and polyacrylate, provided that a variety of different groups of analytes can selectively be extracted. The SPME method has been applied to the trace determination of organic micropollutants, including volatile organic compounds (VOCs) [9-11], phenol and its derivatives [12, 13], polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [14,15]. More recently, the method was applied to fatty acids [16] and other environmental pollutants, such as pesticides of chemical groups of triazines, triazoles, thiocarbamates, amides, chlorocetamides, organochlorines [8] and organophosphorus pesticides [17].

The process involved in SPME is based on a partition process that cannot be related to chromatographic data, thus explaining the difficulty involved in predicting the extraction properties of the fibers according to the analyte's properties [8].

Two efficient multi-residue methods for the pre-concentration and chromatographic analysis of 10 selected organophosphorus insecticides that belong to those mainly used in the Mediterranean [18] region and are included to the list of EU [19] were developed for the monitoring of the selected pesticides in various natural waters. The methods include SPE-disks, SPME and GC with flame thermionic (FTD) and MS detector for the determination of the ten organophosphorus insecticides bromophos ethyl, bromophos methyl, dichlofenthion, ethion, fenamiphos, fenitrothion, fenthion, malathion, parathion ethyl and parathion methyl in different waters (distilled, underground and surface waters). The methods were tested with spiked natural water samples (underground, river, lake and marine water). Both methods were applied for the monitoring of surface water in Greece.

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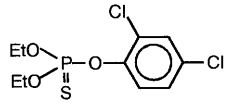
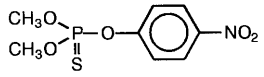
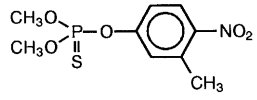
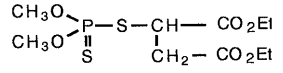
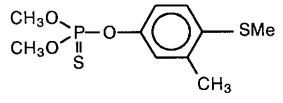
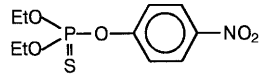
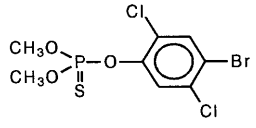
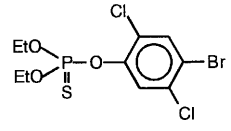
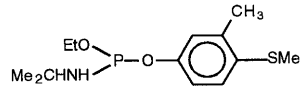
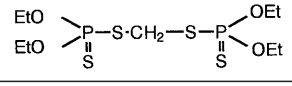
Experimental

Chemicals. HPLC-grade water, methanol, dichloromethane and ethyl acetate from Pestiscan (Labscan Ltd, Dublin, Ireland) were passed through a 0.45 μm filter before use. Sodium sulfate and sulfuric acids were from Merck (Merck Darmstadt, Germany). Bromophos ethyl, bromophos methyl, dichlofenthion, ethion, fenamiphos, fenitrothion, fenthion, malathion, parathion ethyl, parathion methyl and diazinon were purchased from Riedel-de-Haën (Seelze, Germany). The properties of selected organophosphorus insecticides are shown in Table 1.

Phosphate buffer employed for pH adjustment of the samples was prepared from 100 ml solution of 0.1 M dipotassium hydrogen phosphate (Merck) adding the appropriate amounts of 0.1 KOH and/or 0.1 NH_4Cl solutions (Merck).

Table 1 Chemical structure, molecular weight, solubility in water and soil sorption coefficient Koc (mL/g) of selected insecticides

Insecticides	Chemical structure	Cas No/	Molecular weight	Water solubility (mg/L)	$LogK_{ow}$[a]	Soil sorption (Koc)[b]
Dichlofenthion		[97-17-6]	315.2	245	5.14	294[c]
Parathion methyl		[298-00-0]	263.2	50	2.94	5100
Fenittrothion		[122-14-5]	277.2	30	3.40	11500
Malathion		[121-75-5]	330.4	145	2.84	1800
Fenthion		[55-38-9]	278.3	55	4.09	8900
Parathion ethyl		[56-38-2]	291.3	24	3.76	10950
Bromophos methyl		[2104-96-3]	366.1	40	4.88	905[c]
Bromophos ethyl		[4824-78-6]	394.0	2	5.68	5794[c]
Fenamiphos		[22224-92-6]	303.4	700	3.23	170
Ethion		[56-12-2]	384.5	1	5.07	4350

[a] Log K_{ow}, octanol water partition coefficients [20]

[b] Koc, sorption coefficient normalized to organic carbon content [21–23]

[c] Estimation by using the equation log Koc = –0.62 log S + 3.95 (r^2 = 0.86, n = 107) (where S is the solubility in mg/L), suggested for non-polar compounds [24]

SPE disks and SPME fibers. The Empore extraction disks were manufactured by 3 M and distributed by Varian (Harbor City, CA). The disks used were 47 mm in diameter and 0.5 mm thick. Each disk contained about 500 mg of C18 and SDB bonded silica (92 + 2%) and 10 + 2% PTFE. Empore filter Aid 400 glass beads (St. Paul, USA) were used as filtration aid when extracting samples with particulate content using extraction disks.

SPME holder and fiber assemblies for manual sampling were obtained from Supelco (Bellefonte, PA, USA) and used without modification. Polyacrylate 85 μm (PA) was used as the stationary phase in SPME for the extraction of insecticides. Before measurements the fiber was conditioned in the injector for 3 h at 220 °C, with the split vent open, to fully remove any contaminant which might have caused very high baseline noise and large ghost peaks. Then the fiber was repeatedly injected into the GC until interfering peaks disappeared. During this desorption process the GC column oven temperature was maintained at 220 °C.

Water samples. Water samples were collected, from river Arachthos, lake Pamvotis and Ionian sea in September 1999. Ground water was obtained from the main area of Ioannina (Greece). Distilled water was also used. The water samples were analyzed prior to spiking, to ensure that they were free of interfering compounds. Their characteristics are shown in Table 2. River water samples from Kalamas, Arachthos and Louros were collected in September 1999. The samples were stored in darkness at 4 °C and were analyzed within 48 h after collection.

SPE-disk analytical procedure. Empore extraction disks were conditioned with 10 mL acetone for 2 h. Natural water samples (n = 3) of 1 L each were spiked with a mixture of the 10 selected pesticides to the final concentations of 0.1, 0.2, 0.5, 1, 2, 5, and 10 μg/L. Methanol modifier (5 mL) was added to 1 L water samples to allow a better extraction [25]. The optimum values of pH for organophosphorus insecticides extraction with SPE was reported in the range of 6.5-7.5 [26]. The pH of the water samples (Table 1) were between 6.1 and 7.8, therefore, the pH of the samples was not adjusted. C_{18} and SDB disks already placed in a six station extraction manifold and covered with a thin layer (1 cm) of Empore filter aid 400 were washed with 10 mL of dichloromethane:ethyl acetate (1 : 1, v/v) with the vacuum on and with 10 mL of methanol for 3 min with the vacuum off. The disks were not allowed to become dry, as recommended [27, 28]. The water samples were allowed to percolate through the disks with a flow rate of 50 mL/min under vacuum. After sample extraction, the pesticides trapped in the disks were collected by using 2 × 10 mL of the solvent mixture dichloromethane:ethyl acetate (1:1, v/v) as eluting solvent. The fractions were evaporated to 4 mL on a rotary evaporator (35 °C). After careful evaporation of solvent to 0.5 mL in a gentle stream of nitrogen, extract residues were dissolved in 2 mL isooctane and evaporated to a final volume of 1 or 0.1 mL for GC injections.

Table 2 Characteristics of selected natural waters

Origin of water sample	pH	Conductivity μmhos/cm	Total suspended matter (mg/L)[a]	TOC[b] (mg/L)
Distilled water	6.15	2	–	b.d.l.[c]
Underground water	7.43	554	15	0.05
Arachthos river	7.65	286	127	3.10
Pamvotis lake	7.86	283	126	1.95
Ionian sea	7.45	14.400	240	1.32

[a] Total suspended matter was measured by filtration through a 0.45 μm PTFE filter (millipore), [b] TOC = total organic carbon, [c] b.d.l. = below detection limit (0.01 mg/L)

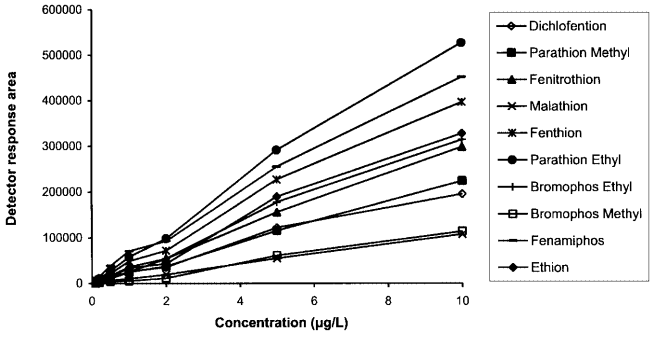


Fig. 1 SPME absorption-concentration profiles for the tested insecticides in water after 45 min extraction time, by using PA 85 μm fiber (desorption time 5 min at 240 °C)

SPME analytical procedure. 3 mL volume of standard solution or sample was placed in 4 mL vials, sealed with hole-caps and PTFE-line septa. The samples were stirred before and during extraction. The fiber was then exposed to the aqueous phase for an appropriate time period of 45 min, with stirring at room temperature (25 ± 2 °C). After extraction, the fiber was directly exposed to the hot injector of the GC systems for analysis. Thermal desorption of insecticides was carried out for 5 min. After this period no significant blank values were observed. The overall methanolic concentration during these experiments was always less than 0.5% (v/v).

An extraction time of 45 min was used for all experiments. The above described extraction conditions were employed in producing the absorption-concentration curves in Fig. 1 for each pesticide that exhibited absortion by SPME PA 85 μm fiber.

Quantification of samples was made using calibration curve of aqueous standards (between 0.1-10 μg/L using HPLC-grade water) extracted in the same way as the samples and using peak area measurements.

Gas chromatographic conditions. GC-FTD. Single pesticide standards and the extracts from the Empore disk preconcentration step were injected in a Shimadzu 14A capillary gas chromatograph equippped with flame thermionic detector (FTD) at 250 °C. The DB-1 column, 30 m × 0.32 mm i.d., contained dimethylpolysiloxane (J & W Scientific, Folsom, CA). The column was programmed from 100 °C (2 min) to 210 °C (30 min) at 5 °C/min and to 270 °C (4 min) at 20 °C/min. The injection temperature was 22 °C. The injection volume was 1.5 μL in the splitless mode with the valve opened for 60 s.

Helium was used as the carrier and nitrogen as make-up gas. The detector gases were hydrogen and air, and their flow rates were regulated according to results given by the simplex optimization of the analytical variables, in this instance air and hydrogen flow-rates in the detector. The ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire.

GC-MSD. A GC-MSD, QP 5000 Shimadzu equipped with capillary column DB-225, 15 m × 0.25 mm × 0.5 μm, containing 50% cyanopropylphenyl-methylpolysiloxane (J & W Scientific, Folsom, CA) was used at the following chromatographic conditions: Injector temperature 220 °C, column program of temperatures 55–200 °C (5 °C/min), 200–210 °C (1 °C/min), 210 °C (12 min), 210–270 °C (20 °C/min), 270 °C (5 min). Helium was used as the carrier gas at 96.5 KPa. The ion source and transfer line were kept at 200 °C and 240 °C, respectively. The spectra were obtained at 70 eV. The splitless mode was used for injection of 1 μL volume, with the valve opened for 30 s.

Characteristic ions of the selected insecticides were chosen for screening analysis in selected ion monitoring (SIM) mode (Table 3).

The ion traces were divided into three groups that were recorded sequentially during the injection, on the basis of the re-

Table 3 Retention times (t_R) and characteristic ions (% abundance) of all target insecticides analyzed with GC-EI-MS

Compounds	(t_R) (min)	GC-EI-MS m/z	ions	Relative itensity (%)
1. Dichlofenthion	30.58	279	$[M\text{-}Cl]^+$	72
		97	$[(OH)_2PS]^+$	100
2. Parathion methyl	31.26	263	$[M]^+$	95
		109	$[(CH_3O)_2PO]^+$	100
3. Fenitrothion	32.57	277	$[M]^+$	38
		125	$[(CH_3O)_2PS]^+$	100
4. Malathion	33.16	173	$[C_2H_5OOC\text{-}CH_2\text{-}CHCOOC_2H_5]^+$	87
		127	$[173–C_2H_5O]^+$	100
5. Fenthion	33.76	278	$[M]^+$	100
		125	$[(CH_3O)_2PS]^+$	76
6. Parathion ethyl	33.97	291	$[M]^+$	49
		109	$[(C_2H_5O)PSH]^+$	100
7. Bromophos methyl	34.80	329	$[M\text{-}Cl]^+$	74
		125	$[(CH_3O)_2PS]^+$	68
8. Bromophos ethyl	37.79	357	$[M\text{-}Cl]^+$	60
		97	$[(OH)_2PS]^+$	100
9. Fenamiphos	39.71	303	$[M]^+$	100
		154	$[CH_3S\text{-}C_6H_3\text{-}CH_3OH]^+$	42
10. Ethion	45.56	97	$[(HO)_2PS]^+$	100
		231	$[M–(C_2H_5O)_2PS]^+$	67
11. Diazinon	28.76	304	$[M]^+$	26
		137	$[OH\text{-}C_4H_4\text{-}CH_2\text{-}C\text{-}CH\text{-}CH_3]^+$	100

Table 4 Analyzed insecticides, retention times (t_R) in system GC-FTD, limits of detection, linearity data and RRF values in the GC-FTD, GC-MS systems by using SPE-disks C18

Peak No./ compounds	t_R (min)	RRF[a] (Diazinon)	Linearity	GC-FTD LOD[b] (µg/L)	GC-FTD R.S.D.[d]	GC-MS LOD[b] (µg/L)	GC-MS R.S.D.[d]
1. Dichlofenthion	27.50	1.06	0.990	0.05	10	0.06	11
2. Parathion methyl	28.12	1.46	0.995	0.05	8	0.06	9
3. Fenitrothion	30.07	1.25	0.985	0.05	8	0.07	10
4. Malathion	30.77	1.26	0.997	0.02	8	0.03	10
5. Fenthion	31.65	1.29	0.995	0.02	7	0.04	12
6. Parathion ethyl	31.93	0.60	0.991	0.05	9	0.05	9
7. Bromophos methyl	33.63	1.44	0.993	0.05	9	0.05	10
8. Bromophos ethyl	38.50	1.06	0.993	0.05	9	0.05	11
9. Fenamiphos	40.90	1.10	0.988	0.01	6	0.02	13
10. Ethion	52.23	0.52	0.982	0.02	11	0.03	15
11. Diazinon (I.S.)[c]	25.23	1.00	0.998	0.01	3	0.01	8

[a] RRF = relative response factor, [b] LOD = limit of detection, [c] I.S. = internal standard, [d] R.S.D. = relative standard deviation

tention times of the single substances. In this way, different compounds which give common fragment ions belong to a different retention time group and could be easily identified.

Results and discussion

Calibration curves and LODs

SPE method. The quantitative determination was performed with FTD by internal calibration using authentic standards. GC-FTD has frequently been the instrumental technique of choice for determination of organophosphorus insecticides for reasons of selectivity and sensitivity [29]. Sample analyses were run in triplicate. Each standard solution contained 1 µg/L diazinon as internal standard (I.S.).

Table 4 gives the retention times and relative response factors (RRF) for the internal standard diazinon as well as for 10 selected insecticides in GC-FTD with DB-1 column.

Limits of detections (LODs) were calculated by comparing the signal to noise ratio (S/N) at the lowest concentration to a $S/N \geq 3$.

SPME method. Series of seven levels were obtained by spiking HPLC-grade water with all the insecticides in a concentration range of 0.1 to 10 µg/L. The response of FTD system was calibrated for each analyte by direct injection in the splitless mode of standard insecticide mixtures. Each solution was run in triplicate. In all cases, there was linear regression ($p < 0.05$) for the analyte concentration range tested (Fig. 1). The regression line parameters

Table 5 Analyzed insecticides, limits of detection and linearity data in the GC-FTD, GC-MS by using SPME PA 85 μm fiber

Peak No./ compounds	Lin-earity	GC-FTD		GC-MS	
		LOD[a] (μg/L)	R.S.D[b]	LOD[a] (μg/L)	R.S.D[b]
1. Dichlofenthion	0.991	0.02	9	0.03	13
2. Parathion methyl	0.997	0.01	6	0.02	7
3. Fenitrothion	0.998	0.01	4	0.02	10
4. Malathion	0.999	0.01	6	0.04	8
5. Fenthion	0.995	0.01	3	0.03	11
6. Parathion ethyl	0.996	0.01	8	0.01	9
7. Bromophos methyl	0.994	0.01	9	0.02	12
8. Bromophos ethyl	0.988	0.01	9	0.03	13
9. Fenamiphos	0.995	0.01	6	0.05	11
10. Ethion	0.984	0.02	10	0.04	14

[a] LOD = limit of detection
[b] R.S.D. = relative standard deviation

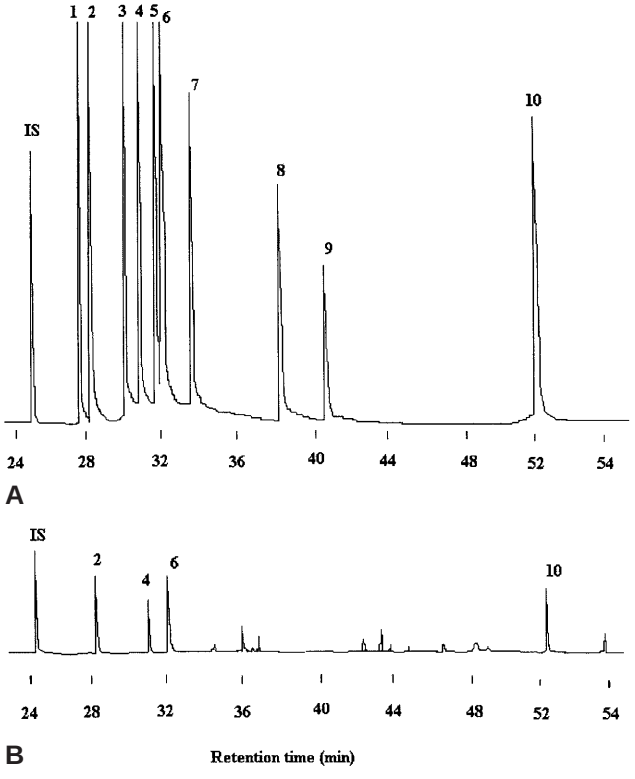


Fig. 2 GC-FTD chomatograms obtained by C18 disks, ca. 2 μg/L of 10 selected insecticides in spiked river water (*A*) and water sample of Kalamas river under the same experimental conditions (*B*). DB-1 column, 30 m long containing dimethylpolysiloxane was programmed from 100 °C (2 min) to 210 °C (30 min) at 5 °C/min and to 270 °C (4 min) at 20 °C/min. For peak numbers see Table 3

are shown in Table 5. Figures 2 and 3 show typical gas chromatograms obtained after extraction of the tested insecticides with C_{18} disks and PA fiber at 2 μg/L level water samples of river Arachthos. Due to the selectivity of the detector, no interference was noticed in the GC-FTD retention time data of these compounds.

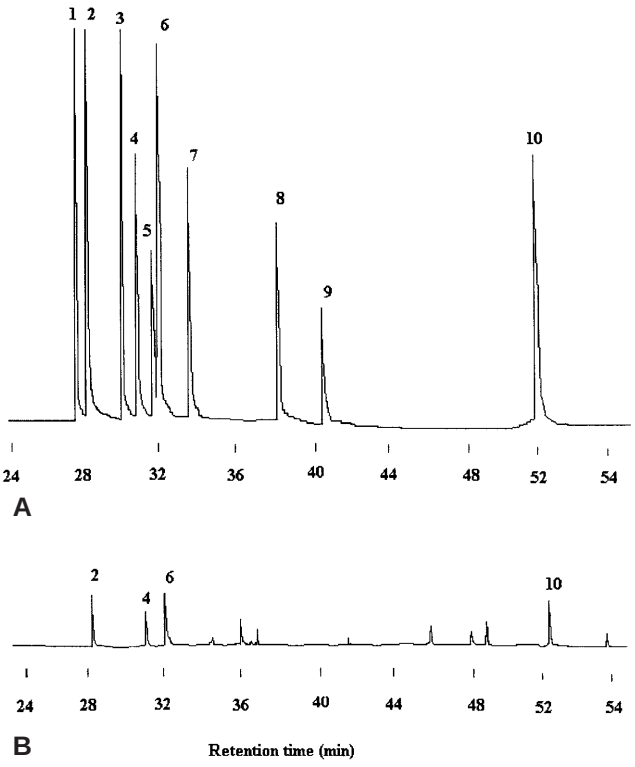


Fig. 3 GC-FTD chomatogram obtained by PA 85 μm fiber, ca. 2 μg/L of 10 selected insecticides in spiked river water (*A*), and water sample of Kalamas river under the same experimental conditions (*B*). DB-1 column, 30 m long containing dimethylpolysiloxane was programmed from 100 °C (2 min) to 210 °C (30 min) at 5 °C/min and to 270 °C (4 min) at 20 °C/min. For peak numbers see Table 3

The data of Tables 4 and 5 show that both techniques (SPE, SPME) allow the detection of the insecticides in water at concentrations lower than 70 ng/L, but SPME shows lower LODs and better linearity for almost all the analytes. The precision obtained, expressed as R.S.D, was lower than 10% in SPME method with the exception of ethion. The chromatographic separation and the precision of the method could be improved by automating the whole process due to the fact that the extraction efficiency is based on equilibrium, directly affected by the time [17].

Parameters influencing the SPME process. The different parameters that can affect the SPME (the appropriate time period for the extraction, pH, stirring rate, solvent content and the time for the desorption of the analytes) were optimized.

An extraction time of 45 min was selected although at this time equilibrium concentrations were not yet achieved for most pesticides. For routine analysis it is not necessary to reach a complete equilibrium as long as the exposure time of the fiber is kept exactly constant [17].

The effect of the pH was analyzed using different samples in the range from 2 to 10 by adding phosphate buffer, respectively. Varying the pH from 2 to 10 no significant effect was observed on the extraction of the analytes by

Table 6 Mean recovery of 10 selected organophosphorus insecticides in natural water samples by using C18 and SDB Empore extraction disks[a]

Peak No./compounds	Mean Recoveries (%)				
	Distilled water	Underground water	Arachthos river	Pamvotis Lake (Ioannina)	Ionian Sea
Disk C_{18}					
1. Dichlofenthion	97.8	81.9	81.6	76.1	80.6
2. Parathion methyl	104.1	94.5	81.9	76.2	87.2
3. Fenitrothion	101.2	82.4	84.4	74.8	81.6
4. Malathion	97.8	90.8	86.7	75.2	89.2
5. Fenthion	92.0	74.5	73.6	65.4	77.1
6. Parathion ethyl	93.3	78.5	86.0	73.2	78.9
7. Bromophos methyl	101.4	77.7	84.4	73.5	79.0
8. Bromophos ethyl	95.3	70.7	80.7	74.8	78.2
9. Fenamiphos	101.3	86.5	82.9	75.9	84.5
10. Ethion	98.5	90.1	83.2	76.9	87.3
Disk SDB					
1. Dichlofenthion	95.6	74.8	69.2	77.8	76.4
2. Parathion methyl	95.2	83.5	71.8	89.7	80.5
3. Fenitrothion	89.9	81.5	69.7	85.5	82.1
4. Malathion	83.1	79.8	68.5	80.9	82.5
5. Fenthion	94.7	60.7	60.7	74.7	78.6
6. Parathion ethyl	92.2	71.8	65.8	77.9	70.9
7. Bromophos methyl	84.8	76.1	69.7	71.8	75.8
8. Bromophos methyl	89.3	71.3	68.7	70.6	72.4
9. Fenamiphos	82.7	64.7	68.5	77.8	73.1
10. Ethion	91.3	79.8	64.9	75.2	76.8

[a] spiking levels of 0.1, 0.2, 0.5, 1, 2, 5, 10 μg/L, N = 3

the fiber, therefore further analyses were carried out without adjusting the pH. Furthermore, the pH of the natural water samples was in the neutral region (around 7) and the analytes have an acceptable response at this value. The optimum stirring rate was determined by analyzing samples containing 10 μg/L of target insecticides at different stirring rates. The obtained results show that with no agitation a very poor extraction level was achieved and that the extraction efficiency increased as the stirring rate increased. However, the amount of extracted analytes decreases for agitation over 1250 rpm because at the maximum speed the stirring bar begins to vibrate and agitation of the sample became worse. Thus, the selected optimum stirring rate was found to be 960 rpm.

In order to study the carry over effect of the fiber a blank desorption experiment was run. After extraction of ten studied insecticides, no carry over from previous run was observed, indicating that these compounds are readily desorbed from the fiber during the 5 min injector desorption for GC-FTD analysis.

Recoveries

The results of mean recoveries in the SPE method of the selected organophosphorus insecticides in natural water samples by using extraction disks are given in Table 6. Recoveries were calculated by using the internal standard method; recoveries obtained for distilled water samples with both disks (C_{18} and SDB) were higher than 80% for all the compounds, thus indicating that the use of the disks does not pose any problem to the analysis of such a type of water.

The recoveries obtained are within the EPA recommendations (from 65 to 115%) for these levels of detection in water samples.

The recoveries of all insecticides were higher in distilled water compared to underground and surface waters (river, lake and marine water). The main differences among the studied surface waters are the high conductivity and the total suspended matter in Ionian sea as well as the higher concentration of the total organic carbon in Arachthos river water.

The studied organophosphorus compounds were recovered with C_{18} disks from underground water samples in relatively high levels (70.7-94.5%), also from river (73.6-86.7) and marine waters (77.1-89.2%) compared to lake water (65.4-76.9%). The recoveries with SDB disks varied from 60.7 to 83.5% in underground water, from 60.7 to 71.8% in river water, from 70.9 to 82.5% in marine water and from 70.6 to 89.7 in lake water. Similar recoveries and detection limits in the range of 0.1-1 μg/L for pesticides were reported elsewhere [30, 31].

The SPME technique shows higher recoveries in comparison to SPE disks for all the analytes in almost all the types of waters. The mean recoveries compared to distilled water obtained for the 10 selected insecticides spiked in four different types of water are shown in Table 7.

Table 7 Mean recovery of 10 selected organophosphorus insecticides in natural water samples by using solid phase microextraction fiber PA 85 μm[a]

Peak No./compounds	Mean Recoveries (%)			
	Underground water	Arachtos river	Pamvotis Lake	Ionian Sea (Ioannina)
1. Dichlofenthion	114.2	97.5	104.2	108.2
2. Parathion methyl	115.4	94.0	93.7	106.0
3. Fenitrothion	119.7	90.5	89.8	110.2
4. Malathion	117.9	98.5	93.3	116.7
5. Fenthion	104.1	86.2	103.5	113.3
6. Parathion ethyl	103.4	92.6	103.4	101.3
7. Bromophos methyl	100.3	93.8	107.3	116.7
8. Bromophos ethyl	119.9	89.4	106.7	106.9
9. Fenamiphos	88.9	91.3	100.8	115.6
10. Ethion	102.2	102.1	101.0	105.9

[a] spiking levels of 0.1, 0.2, 0.5, 1, 2, 5, 10 μg/L, N = 3

Table 8 Concentrations (μg/L) of insecticides detected in water samples from Greek rivers using SPE (C18 disks) and SPME (PA 85 μm)

Compounds (peak number)	Kalamas river		Louros river		Arachthos river	
	SPE	SPME	SPE	SPME	SPE	SPME
1. Parathion methyl (2)	0.122	0.140	0.095	0.109	0.072	0.083
2. Malathion (4)	0.091	0.103	0.037	0.042	bdl[a]	0.020
3. Parathion ethyl (6)	0.112	0.120	0.062	0.068	0.023	0.025
4. Ethion (10)	0.107	0.131	0.031	0.038	0.028	0.034

[a] bdl: below detection limit

The recovery of all insecticides was over 86.2% and reached 119.7%, in river water from 86.2% to 102.1%, in lake water from 89.8% to 107.3 and in marine water from 101.3 to 116.7%.

The linearity was checked also in natural water samples and the obtained equations show correlation coefficients from 0.983 to 0.999 for both proposed methods.

Environmental levels

Natural water samples, collected from rivers Arachthos, Kalamas and Louros near Ioannina (Greece), were analyzed by both proposed methods using SPE-C18 disks and SPME, PA fiber (Table 8).

The corresponding GC-FTD chromatogram obtained by SPE and SPME for river water samples are shown in Fig. 2 and Fig. 3.

The obtained chromatograms show also the presence of several non-identified compounds in the sample. However, these peaks do not interfere with the retention times of the target analytes. The identity of these insecticides was confirmed in the SPE-C18 extract by GC-MS according to the procedure described previously.

The concentrations of insecticides detected are similar to those reported for surface waters in the Mediterranean region [3]. Some differences could be explained by considering that SPME technique shows higher recoveries in comparison with SPE for most of the analytes in all the types of water.

The effect of organic and particulate matter on the SPME fiber is unknown, but it appears to reduce the fiber's life and the adsorption capacity after several extractions possibly by covering the fiber surface irreversibly resulting in a carry over effect or alteration of the fiber surface. As a final result the fiber sorptive capacity and efficiency is reduced. Each fiber can be re-used many times with natural waters, e.g. 15-20 times depending on the water content of organic and particulate matter. Fibers have been used more than 100 times with distilled water and 27 times in run-off water as reported elsewhere [32-34].

Conclusions

The combined use of GC-FTD and GC-MS with the use of Empore extraction disks of C18 and SDB bonded silica provides a rapid, efficient and reproducible method for the simultaneous determination of various insecticides in waters. The use of C18 and SDB Empore disks was found to be an effective procedure for trace pre-concentration of these insecticides for natural waters. Limit of detection was at least 10 times below the drinking water permissible level (0.1 μg/L) for individual pesticides.

SPME with PA coating is a precise, reproducible technique for both qualitative and quantitative determination of priority of insecticide residues in natural water (surface and underground) samples. The fiber can be used repeatedly (in contrast to the solid phase extraction (SPE) where the disks are used only once). The small sample volume necessary (2-5 mL) may be attractive for many applications where the sample volume is limited. Combined to gas chromatography with mass spectrometry and flame thermionic detectors very low detection limits can be reached. Thus, the maximum level set by the European

Union for pesticides and drinking water can be verified without difficulty.

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