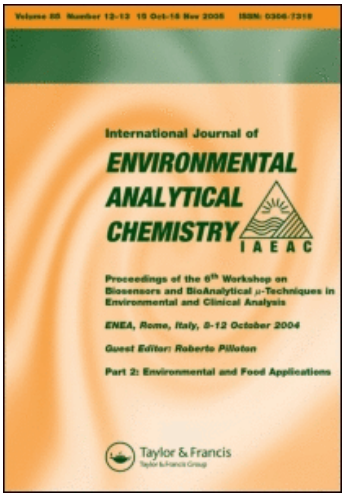

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Determination of Herbicides in Natural Waters Using Solid Phase Microextraction (SPME) and Gas Chromatography Coupled with Flame Thermionic and Mass Spectrometric Detection

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DETERMINATION OF HERBICIDES IN NATURAL WATERS USING SOLID PHASE MICROEXTRACTION (SPME) AND GAS CHROMATOGRAPHY COUPLED WITH FLAME THERMIONIC AND MASS SPECTROMETRIC DETECTION

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This study develops a method for solid phase microextraction (SPME) of ten widespread herbicides from water. The selected herbicides belong to different chemical groups are EPTC, molinate, propachlor, trifluralin, atrazine, propazine, terbuthylazine, prometryne, alachlor. Their determination was carried out by gas chromatography with flame thermionic and mass spectrometric detection. To perform the SPME, two types of fibre have been assayed: Carbowax-divinylbenzene (CW-DVB) of 65 μm thickness and polydimethylsiloxane-divinylbenzene (PDMS-DVB) of 65 μm thickness. The main factors affecting the SPME process such as pH, ionic strength, methanol content, memory effect, stirring rate and adsorption-time profile were studied. The method was applied to spiked natural waters such as ground water, sea water, lake water and river water in a concentration range of 0.1 to 10 μg/L. Limits of detection with each of the detectors were determined to be 1 – 20 ng/L in PDMS-DVB and 2–20 ng/L CW-DVB fibres. The recoveries of herbicides compared to distilled water were in relatively high levels 78.3–127.3 % and the average r^2 values of the calibration curves were above 0.99 for all the analytes. The SPME conditions were finally optimized in order to obtain maximum sensitivity and samples were applied for the trace-level determination in river water samples originating from Ioannina region (Greece).

Keywords: Water analysis; herbicides; SPME fibres; gas chromatography

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INTRODUCTION

Pesticide contamination of surface and ground waters from agricultural uses has been well documented around the world. Herbicides are widely used as pre- and post- emergent weed control agents for a wide variety of crops. The potential for the contamination of water and sediment is high owing to the physico-chemical properties of herbicides such as water solubility, adsorptivity (K_{oc}), and hydrolysis half-lives. Consequently they are found in various natural waters and soils in most countries[1–5].

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 quantification limits below the 0.1 μg/L are required for monitoring drinking water. In order to achieve the mentioned above requirements for the analysis of organic micropollutants in water by chromatographic techniques, a previous concentration of the sample is needed. Current methods of analysis for aqueous or solid samples involve liquid-liquid extraction (LLE), supercritical fluid extraction (SFE), solid-phase extraction (SPE)[6–11]. Liquid-liquid extraction though efficient but has some disadvantages such as the large amount consumption of solvents, the formation of emulsions and extensive time-consuming cleanup procedures. Although, SPE methods eliminated the above disadvantages of LLE, the presence of particulate matter in the samples can cause plugging of the cartridges or the disks, and the sample large volume requirement still pause certain problems to SPE applications.

Recently a commercially available technique, solid-phase microextraction (SPME), allows simultaneous extraction and preconcentration of analytes from a sample matrix[12]. In addition it is significantly more rapid and simpler than LLE and SPE, and the requirement of solvents has been eliminated[12–14]. In addition, SPME requires a small volume of sample[15]. Investigation of different stationary phases, concentrating on polydimethylsiloxane and polyacrylate, provided evidence that a variety of different groups of analytes can selectively be extracted[14,16,17]. The SPME method has been applied to the trace determination of organic micropollutants, including volatile organic compounds (VOCs)[18,19], phenol and its derivatives[20,21], polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)[22,23]. More recently, the method was applied to fatty acids[24] and other environmental pollutants, such as pesticides of chemical groups of triazines, organophosphates, thiocarbamates, amides, chloracetamides and organochlorines[15,25,26].

From studies published to date, it appeared that selection of a fibre based only to the physicochemical parameters of the compounds was difficult[15]. In classical solid phase extraction with a conventional stationary phase, it is easy to pre-

dict the compounds that would be extracted with good recoveries from the chromatographic data or from a good knowledge of the analyte retention time using extraction phase of interest as an analytical stationary phase. The process involved in SPME is different and 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 fibres according to the analyte properties.[15]

The aims of this work were to develop an efficient multi-residue method for the pre-concentration and chromatographic analysis of 10 selected herbicides that belong to those most used in the Mediteranean region[2] and are included to the list of EU[3] for control of their residues in water; to apply the analytical method developed for the monitoring of the selected pesticides in various environmental waters. The method include solid-phase microextraction (SPME) and gas chromatography with FTD and EI-MS for the determination of ten herbicides EPTC, Molinate, Propachlor, Trifluralin, Simazine, Atrazine, Propazine, Terbuthylazine, Prometryn, Alachlor from different waters (HPLC-grade water, underground and surface waters). The protocols was tested for the selected herbicides by means of a recovery study from spiked natural water samples (underground, river, lake and marine water). Finally the method was applied for the monitoring of surface water sources in Greece.

EXPERIMENTAL

Chemicals

The tested herbicides EPTC, Molinate, Propachlor, Trifluralin, Simazine, Atrazine, Propazine, Terbuthylazine, Prometryn and Alachlor were purchased from Promochem (Wesel, Germany). Their properties are presented in table I. Stock standard solutions were prepared to the required concentration in volumetric flasks using methanol (Pestiscan, Labscan Ltd, Dublin, Ireland). HPLC-grade water (Pestiscan, Labscan Ltd, Dublin, Ireland) was used throughout the analysis. Sodium chloride, potassium dihydrogen phosphate, hydrochloric acid and potassium hydroxidewere purchased from Merck (Darmstadt, Germany).

SPME fibers

SPME holder and fiber assemblies for manual sampling were obtained from Supelco (Bellefonte, PA, USA) and used without modification. Carbowax-divi-

nylbenzene 65 μm (CW-DVB) and polydimethylsiloxane – divinylbenzeze 65 μm (PDMS-DVB) were used as the stationary phase in SPME for the extraction of herbicides. Before measurements the fibres were conditioned in the injector for 3 hours at 220 °C, with the split vent open, to fully remove any contaminant which might have cause very high baseline noise and large ghost peaks. Then the fibre was repeatedly injected into the GC until interfering peaks disappeared. During this desorption process the GC column oven temperature was maintained at 240 °C.

TABLE I Molecular weight, solubility in water, octanol-water partition coefficient and soil sorption coefficient Koc (ml/g) of selected herbicides

Pesticides	*Molecular weight*	*Water Solubility (mg/L)*	*Log K_{ow}*[a]	*Soil sorption (Koc)*[b]
EPTC	189.32	375	3.20	200
Molinate	187.32	880	3.21	415
Propachlor	211.69	700	2.41	80
Trifluralin	335.28	20	3.97	8000
Simazine	201.66	3.5	2.20	130
Atrazine	215.69	70	2.21	160
Propazine	229.70	8.6	2.91	160
Terbuthylazine	229.72	8.5	3.06	170
Prometryne	241.37	33	3.34	610
Alachlor	269.77	242	2.63	120

a. Log K_{ow}, water octanol partition coefficients from Noble 1993 [30]
b. Koc, sorption coefficient normalized to organic carbon content from Jury et al. (1987) [31], Wauchop et al. 1(992) [32].

Water samples description

Water samples were collected, in September, of 1998 from Arachthos river, Pamvotis lake and Ionian sea. Ground water was obtained from the main area of Ioannina (Greece). All water samples were used without previous treatment and filtration. Distilled water was also used. The water samples were analyzed prior to have being spiked, to ensure that they were free of interfering compounds. Their characteristics are shown in table II.

SPME analytical procedure

Three (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 appro-

priate time period of 30 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 herbicides 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).

TABLE II Characteristics of selected environmental 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	115	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. TSM (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).

Aqueous herbicide-containing solutions were extracted under varying NaCl concentrations, pHs, stirring rates and methanol concentrations to establish optimum extraction parameters. To determine the effect of the sodium chloride concentration on the extraction, herbicides solutions of 10 μg/L containing 0, 5, 10, 25, 50 and 75 % (w/v) and saturated sodium chloride were prepared. Before introducing the needle of the SPME device to the injection port, the fibre was rinsed with a few milliliters of distilled water in order to remove small amounts of adhering sodium chloride. Analysis of the rinsing solutions indicated that no loss of analytes, due to rinsing of the fibre, was demonstrable. The above step is important for the protection of the fibre and the GC injection port. The optimum stirring rate was also determined by analyzing samples containing 10 μg/L of target herbicides at different stirring rates.

The effect of pH was investigated for the values 2, 4, 6, 8 and 10 by using appropriate concentrations of phosphate buffer. The phosphate buffer employed for pH adjustement of the samples was prepared from an 100 ml solution of 0.1 M dipotassium hydrogen phosphate adding the appropriate amounts of 0.1 N KOH and/or 0.1 N HCl solutions. The effect of methanol content on extraction was studied on aqueous solutions containing 0.5 %, 1 %, 5 %, 10 %, 15 % and 20 % methanol (v/v). An extraction time of 30 min was used for all experiments except for the adsorption -time profiles, noted below. Extractions at ambient tem-

perature of 10 μg/L of 10 μg/L of aqueous herbicide solutions saturated with sodium chloride at pH 7.0 were performed for a period time of 0–120 min.

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

Chromatographic analysis was performed using a Shimadzu 14A capillary gas chromatograph equippped with flame thermionic detector (FTD) at 250°C. Analytes were separated with a DB-1 column (J & W Scientific, Folsom, CA), 30m × 0.32mm i.d., contained dimethylpolysiloxane with a phase thickness of 0.25 μm. The temperature program used for the analysis was: from 55°C (2 min) to 210 °C (15 min) at 5 °C/min and to 270 °C at 10 °C/min. The injection temperature was 240°C. The splitless mode was used for injection with the valve opened for 60 sec. The linear purge was closed during desorption of analytes from the SPME fibre in the split/ splitless injector (5 min delay time).

Helium was used as the carrier and make-up gas at 83kPa. The detector gases were hydrogen and air, and their flow rates were 50ml/min and 500 ml/min, respectively. 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-1, 30 × 0.25 mm × 0.25 μm, contained 5% phenyl-methylpolysiloxane (J& W Scientific, Felsom, CA) was used at the following chromatographic conditions: Injector temperature 220°C, oven temperature programme 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C at 10°C/min. Helium was used as the carrier gas at 14 psi. The ion source and transfer were kept at 200 °C and 240 °C respectively. The spectra were obtained at 70 eV. The splitless mode was used for injection with the valve opened for 30 s.

Typical fragment ions of the selected pesticides were chosen for screening analysis in selected ion monitoring (SIM) mode (table III). The ion traces were divided into five groups that were recorded sequentially during the injection, on the basis of the retention times of the single substances. In this way different compounds which is possible to give common fragment ions belongs to different retention time groups, could be easily identified.

TABLE III Typical fragment ions and relative abundance (%) of the selected herbicides

Compounds	*(m/z) Main ions, (relative abundance, %)*
1. EPTC	189 (19) $[M]^+$, 128 (76) $[M\text{-}SCH_2CH_3]$, 43 (100) $[C_3H_7]$
2. Molinate	187 (25) $[M]^+$, 126 (100) $[M\text{-}S\ C_2H_5]$
3. Propachlor	211 (8) $[M]^+$, 176 (30) [M-Cl], 120(100) $[C_6H_5NCO]$
4. Trifluralin	335 (10) $[M]^+$, 306 (100) $[M\text{-}C_2H_5]^+$
5. Simazine	201 (78) $[M]^+$, 186 (62) $[M\text{-}CH_3]$, 173 (42) $[M\text{-}C_2H_5]$
6. Atrazine	215 (57) $[M]^+$, 200 (100) $[M\text{-}CH_3]$, 173 (32) $[M\text{-}C_3H_6]$
7. Propazine	229 (53) $[M]^+$, 214 (84) $[M\text{-}CH_3]$, 187 (30) $[M\text{-}C_3H_6]$
8. Terbuthylazine	229 (33) $[M]^+$, 214 (100) $[M\text{-}CH_3]$, 173 (48) $[M\text{-}C_3H_6\text{-}CH_3]$
9. Prometryne	241 (100) $[M]^+$, 226 (62) $[M\text{-}CH_3]$, 184 (72) $[M\text{-}C_3H_6\text{-}CH_3]$
10. Alachlor	269 (6) $[M]^+$, 188 (30) $[M\text{-}COCH_2Cl]$, 160 (38) $[M\text{-}CH_2OCH_3]$

RESULTS AND DISCUSSION

Parameters influencing the SPME process

SPME is an equilibrium process that involves the partitioning of analytes from a liquid sample into the polymeric phase according to their partition coefficients, K[12]. The mass extracted and the linear range depend on the partition coefficient and the volume of the stationary phase. The optimization of parameters that influence the partition coefficient and the choice of an appropriate stationary phase are thus extremely important. Stirring rate, pH, ionic strength, solvent content and the appropriate time period for the extraction are the main parameters that should be into account.

Addition of a salt (sodium chloride) often improves the recovery when conventional extraction methods are used. The influence of the salt concentration on the flame thermionic detector response, for the 10 studied herbicides at concentration level of 10 μg/L is shown in figure 1. These data show that the sodium chloride addition in pesticide solutions increases their extractability. This observation is in accordance with previous reported results for different group of pesticides.[25,31] Aqueous solubility of many organic compounds decreases in the presence of excess of salt. In addition, high salt content results in high ionic strength of the solution, which may cause a significant decrease of the activity coefficients of some analytes. For the hydrophobic compounds such as triflura-

lin, EPTC and terbuthylazine an optimum extraction is reached at about 25% saturated sodium chloride solution, such a maximum is not observed for compounds as atrazine, simazine, alachlor with less hydrophobic character. Thus the effect of salt addition is more pronounced for those compounds with a low hydrophobicity. The addition of salt to the water samples will further improve the detection limit of pesticides. The optimum selected extraction level for all the studied herbicides was observed at NaCl concentration of 25 % (w/v).

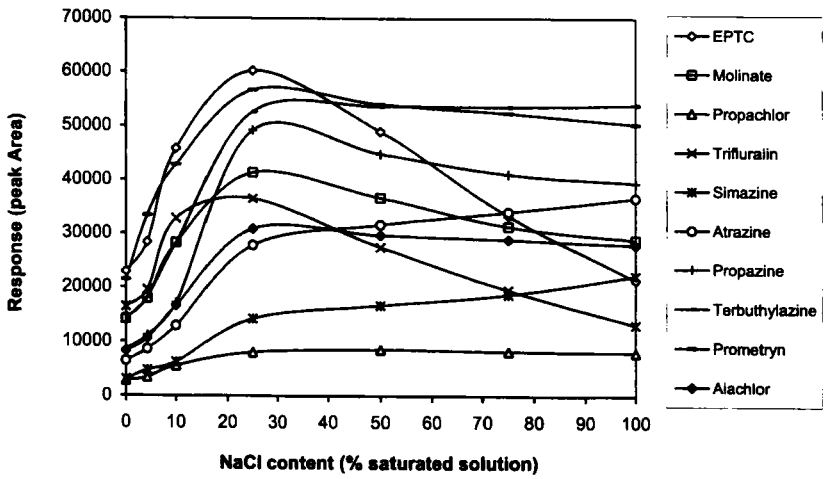

FIGURE 1 Influence of sodium chloride on detector response area, by using a Carbowax-divinylbenzene 65 μm fiber for ten herbicides at concentration level of 10 μg/L (desorption time 5 min at 240 °C)

The recoveries of the studied pesticides decrease with small amount addition of methanol (greater than 2 % (v/v)). Methanol addition decreases the absorptivity of SPME fibre by covering the main part of its available surface. Although methanol cannot be considered as a representative compound for all organics the results demonstrate that the effect of polar organics is less pronounced than expected. Similar conclusions depending on the properties of various pesticides were also reported by other workers[25–28].

In SPME techniques, a significant amount of the analytes often remain absorbed on the fibre after the desorption step in the GC injector. This problem becomes more serious when low volatility compounds are analyzed[29]. In order to study this effect a blank desorption experiment was run after extraction of ten studied herbicides at a 10 μg/L concentration. For the tested herbicides, no carry-over from previous run was observed, indicating that these compounds are read-

ily desorbed from the fiber during the 5 min injector desorption for GC-FTD analysis.

The rate at which the extraction process reaches at equilibrium is primarily dependent upon the rate of mass transfer in the aqueous phase[30] and is improved by stirring. The optimum stirring rate was determined by analyzing samples containing 10 μg/L of target herbicides at different stirring rates. From the obtained results it could be stated that with no agitation a very poor extraction level was achieved and that the extraction efficiency increased as the stirring rate increased. More rapid stirring or sonication of the solution reported to enhance or to not alter significantly SPME binding in other studies[20,25]. 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 800 rpm.

The investigation of pH effect on herbicides extraction by SPME fibres was undertaken with the aim of finding a pH at which the extraction of the herbicides was enhanced in general or was not significantly decrease for some chemical classes of the tested compounds. Varying the pH from 4 to 8 no significant effect was observed on the extraction of any analytes, with an optimum value around pH 4. On the contrary, at pH 2 and 10 the extraction levels for all herbicides were decreased (Figure 2). The above observation could be referred to the low ionic character of the mixture compounds. At pH 2, close to pKa the values of s-triazines their extraction level decrease due to the presence of ionic forms of the s-triazines molecules. The effect of pH upon pesticide extractability with SPME was optimum for most pesticides around pH 7, whereas at pH 2 extraction of some pesticides were significally impaired as reported elsewhere[25]. As a result of the above observations all subsequent SPME extractions were performed at pH 4.

Two factors are to be taken into account when the proper fibre is to be selected: the equilibration time and the amount extracted. The selection of the fibre is generally guided by the polarity of the analytes. Two fibres, 65 μm PDMS-DVB and 65 μm CW-DVB were compared by determining the recovery of the selected herbicides as compared to distilled water. The PDMS-DVB is a non polar and CW-DVB is a weakly polar fibre. PDMS fibres were preferred for the extraction of non-polar pesticides with very low solubility in water, such as organochlorine pesticides and some of the non-polar orgaphosphorus insecticides, whereas the more polar polyacrylate (PA) was shown to be more appropriate for the more polar nitrogen-containing herbicides and for phenols[15,20,26,30,31]. Mixed phase coatings such as PDMS-DVB and CW-DVB, have complementary properties to PDMS and PA. In the mixed phase, the DVB porous microspheres are immobilized onto the fibre by using either carbowax or PDMS as a glue to hold them

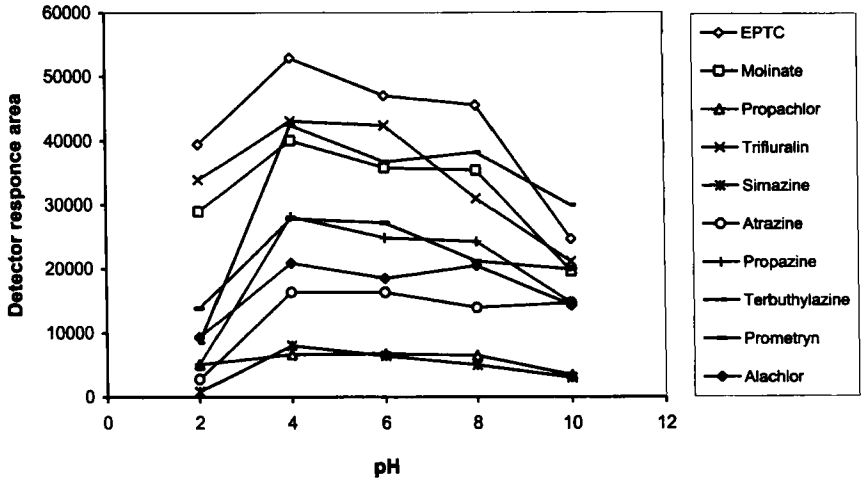

FIGURE 2 Influence of pH values on detector response area, by using a Carbowax-divinylbenzene 65 μm fiber for ten herbicides, at concentration level of 10 μg/L (desorption time 5 min at 240 °C)

together. In addition the pores of the template DVB are uniform resulting in less absorption discrimination as a function of analytes molecular weights. The results (figure 3a,b) show that the two coatings, PDMS-DVB and CW-DVB, extract the moderately polar compounds of the analyzed herbicides (log Kow values in the range 2.20–3.97) with the highest affinity. Since they have the same film thickness, the comparison is more accurate. No relationship had been found between the water solubility of the analyte and the extraction yields when compounds with different functionalities were considered. As an example, we consider the herbicides with the lowest water solubility simazine, propazine and terbuthylazine 3.5, 8.6, and 8.5 mg/L, respectively. The non-polar PDMS-DVB coating was expected to have greater affinity to the less soluble compounds, but this was not followed (tables V, VI). In the case of compounds with similar solubility and different Kow values such as trifluralin and prometryne, the non polar fibre was expected to have lower affinity to the less hydrophobic compound due to likely predominant hydrophobic interactions. However, this tendency was not evident (tables VI, VII). Hence, the observed affinities of the studied compounds can not be adequately explained based on solubility or hydrophobicity data.

Under the above studied optimum conditions, absorption-time profiles were generated for each herbicide and were presented in figure 4. Each data point is the average of three independent measurements. A unique absorption-time curve was produced reflecting the affinity of the pesticide for the SPME fiber coating and the response of the FTD to that herbicide. As it can be seen in the graph, the

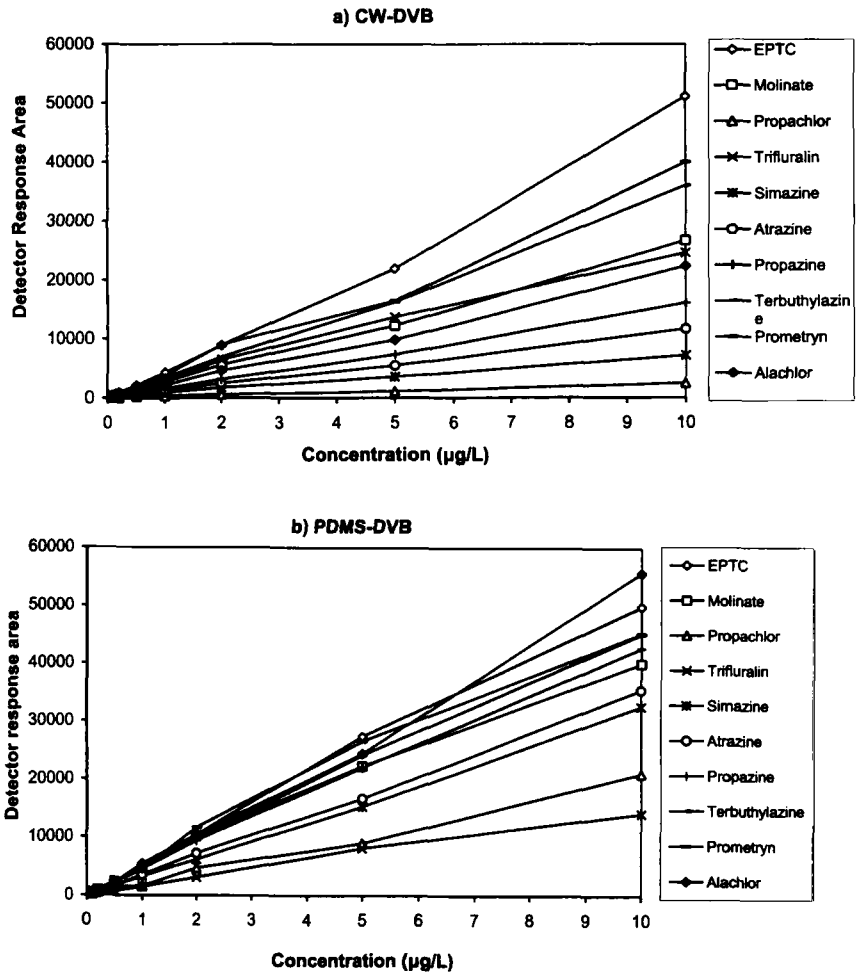

FIGURE 3 SPME absorption-concentration profiles for the tested herbicides after 30 min extraction time a) CW-DVB fibre b) PDMS-DVB fibre

desorption rate is high and the detector response is proportional to the adsorption, for the first 50 min, reaching a plateau after that time which corresponds to the equilibration time. The equilibration time is defined as the time after which the amount of extracted analyte remains constant and corresponds within experimental error to the amount extracted at an infinite extraction time. Although the advantages of using the equilibration time as the absorption period are interesting (higher extractions and smaller deviations), practical limitations in order to speed

up analysis must also be taken into consideration. It is not a requirement for analysis that equilibrium be reached to utilize SPME as long as the extractions are carefully timed and the mixing conditions and extractions volumes remain constant[20,22]. The use of the equilibrium time in the absorption step is not necessary if LOD and RSD values obtained are acceptable[29]. Since the above LOD and RSD limitations were full filled for the studied pesticides under the optimal extraction conditions previously discussed an adsorption time of 30 min has been selected for the extraction.

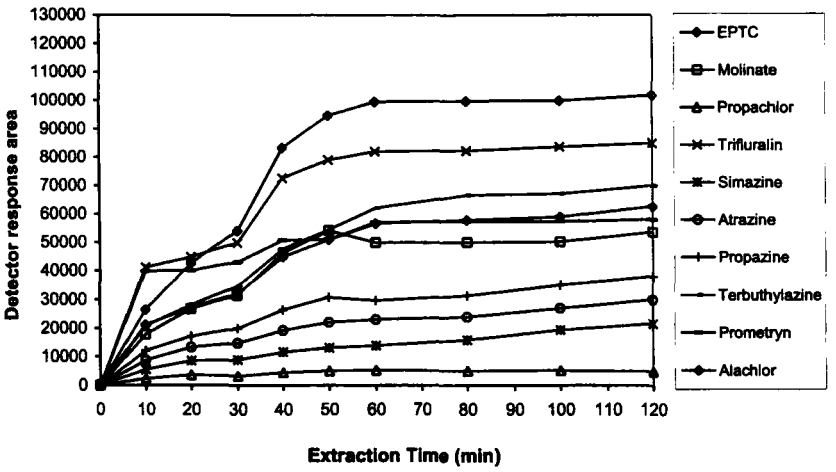

FIGURE 4 Influence of adsorption-time on detector response area, by using a Carbowax-divinylbenzene 65 μm fiber for ten herbicides at concentration level of 10 μg/L (desorption time 5 min at 240 °C)

Calibration Curve and Recoveries

Series of five levels were obtained by spiking HPLC-grade water with all the herbicides in a concentration range of 0.1 to 10 μg /L. Each solution was run in triplicate. In all cases, there was linear regression ($p < 0.05$) for the analyte concentration range tested. Figures 5 and 6 show typical gas chromatograms obtained after extraction of the tested herbicides with PDMS and CW fibres at 2 μg/L level water samples of Arachthos river. Due to the selectivity of the detector, no interferences were noticed in the GC-FTD retention time data of these compounds.

LODs were calculated by comparing the signal-to-noise ratio (S/N) of the lowest concentration to a S/N=3. The data of table IV show that the method allows detection of the herbicides in water at concentrations below 30 ng/L. The preci-

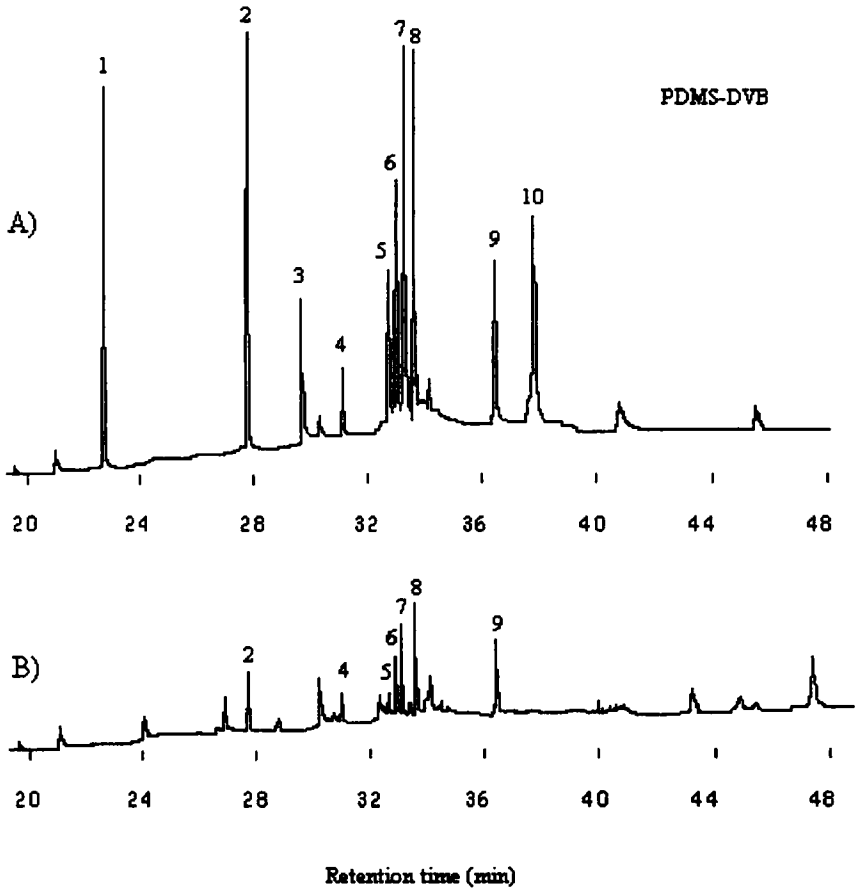

FIGURE 5 GC-FTD chomatogramobtained by PDMS-DVB fibre (A) ca 2 μg/L of 10 selected herbicides in spiked river water, and (B) Water sample of Kalamas river. DB-1 column, 30 m long containing dimethylpolysiloxane was programmed from 55°C (2 min) to 210°C (15 min) at 5°C/min and to 270°C (0 min) at 10°C/min. For peak numbers see table IV

sion obtained and expressed as R.S.D., was lower than 10 % for the FTD detector, excepting trifluralin, propazine and prometryne. More elevated values (≤ 16 %) were monitored for the MS detector. 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.

The mean recoveries obtained with the two fibres for the 10 selected herbicides spiked in four different types of water (see table II) are shown in tables V, VI. Significant differences on the obtained recoveries with both fibres, were reported for analytes such as molinate, propachlor, simazine, trifluralin and prometryne, at

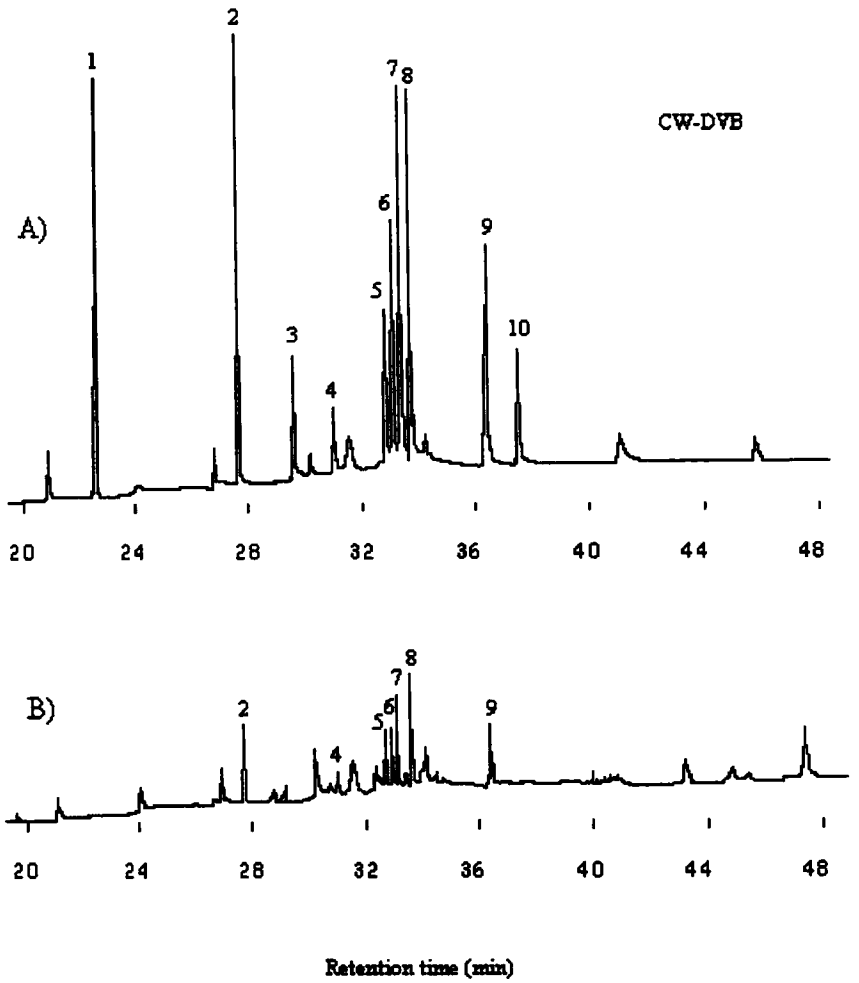

FIGURE 6 GC-FTD chomatogram obtained by CW-DVB fibre (A) ca 2 μg/L of 10 selected herbicides in spiked river water, and (B) Water sample of Kalamas river. DB-1 column, 30 m long containing dimethylpolysiloxane was programmed from 55°C (2 min) to 210°C (15 min) at 5°C/min and to 270°C (0 min) at 10°C/min. For peak numbers see table IV

least for two different types of water. It should be noted that the recoveries obtained for underground and river water samples were higher than the lake and marine water for the most of studied pesticides. The main difference between the studied surface water are the high salinity and conductivity in Ionian sea water and the higher concentration of the total organic carbon in Pamvotis lake water samples. The recovery of all pesticides was over 78.31 % and reached 127.3 %.

TABLE IV Analysed pesticides, retention times and limits of detections in the GC-FTD, GC-MS systems with capillary column DB-1, 30 m long (i.d.=0.32mm), with PDMS-DVB 65 μm and CW-DVB 65 μm fibres at the optimum value of parameters

Peak No./ Compounds	t_R (min)	PDMS-DVB 65 μm					CW-DVB 65 μm		
		Linearity	GC-FTD		GC-MS		Linearity	GC-FTD	
			LOD[a] (ng/L)	R.S.D.	LOD[a] (ng/L)	R.S.D.		LOD[a] (ng/L)	R.S.D.
1. EPTC	22.62	0.997	20	9	10	11	0.995	20	10
2. Molinate	27.71	0.995	10	8	5	11	0.997	15	10
3. Propachlor	29.65	0.992	0.5	9	10	5	0.993	5	7
4. Trifluralin	31.07	0.994	1	13	5	16	0.993	2	14
5. Simazine	32.65	0.998	5	9	10	14	0.998	4	12
6. Atrazine	32.88	0.999	3	7	5	9	0.998	3	8
7. Propazine	33.06	0.999	2	10	4	12	0.998	2	11
8. Terbuthylazine	33.58	0.998	1	8	5	8	0.997	2	9
9. Prometryne	36.40	0.991	3	12	10	14	0.990	5	13
10. Alachlor	37.78	0.996	10	8	10	10	0.996	10	9

a. LOD = Limit of detection.

TABLE V Mean recovery of 10 selected herbicides in environmental water samples by using solid phase microextraction fiber CW-DVB 65 μm.[a,b]

Peak No./Compounds	Mean Recoveries %			
	Underground water	Arachtos River	Pamvotis Lake	Ionian Sea
1. EPTC	109.9	126.8	109.6	95.0
2. Molinate	103.9	124.3	111.5	95.4
3. Propachlor	78.3	90.3	88.7	108.2
4. Triflurallin	127.3	81.3	94.0	104.7
5. Simazine	103.8	111.5	94.2	130.5
6. Atrazine	108.1	119.0	104.7	94.3
7. Propazine	96.6	111.2	105.7	109.0
8. Terbuthylazine	100.8	102.9	90.7	110.0
9. Prometryne	86.8	87.3	86.8	112.2
10. Alachlor	97.7	118.3	104.6	102.8

[a]Mean value for spiking levels of 0.1, 0.2, 0.5, 1, 2, 5, 10 μg/L, N=3.
[b]Mean of three replicate experiments in each spiking level, average R.S.D. values of 5–15 %.

TABLE VI Mean recovery of 10 selected herbicides in environmental water samples by using solid phase microextraction fiber PDMS-DVB 65 μm[a]

Peak No./Compounds	*Mean Recoveries %*			
	Underground Water	*Arachtos River*	*Pamvotis Lake*	*Ionian Sea*
1. EPTC	114.2	114.7	112.0	122.6
2. Molinate	99.5	106.7	74.4	118.9
3. Propachlor	115.4	84.2	72.4	92.8
4. Triflurallin	94.5	108.5	91.2	96.6
5. Simazine	84.7	83.3	72.6	103.1
6. Atrazine	133.0	120.9	118.0	117.4
7. Propazine	130.6	113.0	117.7	117.3
8. Terbuthylazine	113.3	104.8	100.4	105.2
9. Prometryne	105.8	113.1	107.0	103.2
10. Alachlor	105.7	119.2	90.5	117.6

[a]Mean value for spiking levels of 0.1, 0.2, 0.5, 1, 2, 5, 10 μg/L, N=3.
[b]Mean of three replicate experiments in each spiking level, average R.S.D. values of 5–15 %.

Both mixed phase coatings are suitable to extract the selected herbicides from water samples with no significant differences on LODs and linearity although PDMS-DVB fibre shows lower LODs for propachlor and molinate. The linearity was checked also with real samples of natural waters and the obtained equations shown correlation coefficients between 0.986 and 0.999.

Environmental levels

Natural water samples, collected from Kalamas river near Ioannina (Greece), are analyzed by the proposed method and by a standard SPE-C18 method[8]. The GC-FTD chromatograms obtained by SPME-PDMS-DVB as shown in figure 10 reveal the presence of seven herbicides in the following concentrations (μg/L): 0.132, for molinate, 0.353 for trifluralin, and 0.157, 0.311, 0.27, 0.131, 0.268, for simazine, atrazine, propazine, terbuthylazine, prometryne respectively. These results were in accordance with those obtained by SPE-C_{18} as follows: 0.125, 0.348, 0.145, 0.308, 0.26, 0.125, 0.253 respectively. The concentrations of pesticides detected are similar to those reported for surface waters in the Mediteranean region.[2–4]. The reported differences could be explained by considering that SPME technique shows higher recoveries in comparison to SPE for most of the analytes in all the types of water[8]. The obtained chromatogram shows the presence of several non-identified compounds in the sample, as well. However

such eluted compounds do not interfere the determination after analytes of interest. The identity of these herbicides was confirmed in the SPE-C18 extract by GC-MS according to the procedure described previously.

The effect of organic and particulate matter of water samples on the SPME fibre is unknown, but they appear to reduce the fiber life and the GC response after several extractions, possibly by covering fibre surface irreversibly resulting in a carry over effect or surface alteration. The fibre sorptive capacity and efficiency is reduced as a final result. Each fibre can be re-used many times with natural waters, e.g. 15–20 times depending on the water content of organic and particulate matter. Fibres were used more than 30 times for distilled and drinking water. Without salt addition in the water samples the fibre life is increased and could be used for about 100 times in distilled water. Fibres have been used more than 100 times with distilled water and 27 times in run-off water as reported elsewhere.[15,32,33]

CONCLUSIONS

In conclusion, SPME with PDMS-DVB and CW-DVB coatings is a precise, reproducible technique for both qualitative and quantitative determination of priority herbicide residues in environmental water (surface and underground) samples. Solubilities and/or hydrophobicities are not sufficient to explain the observed affinities and to be used as criteria for the fibre selection. Optimization of the parameters affecting the method sensitivity should be carefully developed in order to enable substantial increase in the amount extracted of most analytes and to improve the limit of detection.

Moreover, the fiber can be used repeatedly (without any matrix effects) (in contrast to the solid phase extraction (SPE) where the disks are used only once). Finally, the small sample volume necessary (2–5 ml) may be attractive for many applications where the sample volume is limited. If combined to gas chromatography with mass spectrometry and flame thermionic detector very low limits of detection (0.5–20 ng/L) can be achieved, as the total amount of extracted analytes is used for the determination. Thus the maximum level set by the European Union for pesticides and drinking water can be verified without difficulty.

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