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Journal of Chromatography A, 893 (2000) 347–358

JOURNAL OF CHROMATOGRAPHY A

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Solid-phase microextraction for the determination of systemic and non-volatile pesticides in river water using gas chromatography with nitrogen–phosphorous and electron-capture detection

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Received 4 February 2000; received in revised form 27 June 2000; accepted 4 July 2000

Abstract

A solid-phase microextraction (SPME) method combined with gas chromatography with nitrogen–phosphorous and electron capture detection for the analysis of the pesticides terbumeton, metribuzine, isomethiozine, pyridafenthion and triadimenol in river water has been developed. For this purpose, polyacrylate and polydimethylsiloxane coated fibres have been utilised and the factors affecting throughput, precision and accuracy of the SPME method have been investigated and optimised. These factors include: matrix influence, adsorption time, pH, salt effect, desorption time, temperature and also the lapse of time between sampling and injection. The performed analytical procedure showed detectability ranging from 2.0 ng l^{-1} to 3.0 μg l^{-1} and precision from 1.9 to 27.7% (as relative standard deviation) depending on the pesticide, the fibre and the detector used. The results demonstrate the suitability of the SPME method to analyse these non-volatile pesticides in river water.

Keywords: Water analysis; Environmental analysis; Solid-phase microextraction; Pesticides

1. Introduction

Large amounts of pesticides are used in agriculture in spite of their potential environmental adverse effects. This type of variable and diffuse pollution can create an important problem: pesticide removal from soil by water, which may cause general damage to the ecosystem [1]. This leaching phenomenon results in contamination of groundwater, a fact that becomes especially important when these water sources are employed for human consumption. Moreover, the use of systemic pesticides, which are incorporated into the soil and later adsorbed by the roots, increases the leaching problem.

Systemic triazine-based herbicides such as metribuzine, terbumeton or isomethiozine are widely used in Mediterranean countries [2]. They are especially utilised in extensive farms such as vineyards and in potato growing, which are, respectively the chief crops of Rioja and Llanada Alavesa (regions in the North of Spain). Also acaricides like pyridafenthion and systemic fungicides like triadimenol have

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00746-9

been introduced in the last few years in order to control pests on vines. Hence, the determination of these pesticides in river water is frequently required to ensure compliance with European regulated tolerances.

Studies involving the determination of pesticides in environmental matrices often deal with samples with low analyte concentrations containing a high number of interferent compounds. Thus, simple and highly sensitive analytical techniques are required to detect and quantify pollutants in water at trace levels. The first step in the analytical procedure includes extraction of the contaminants from the water matrix using either liquid–liquid or solid-phase extraction or purge-and-trap techniques.

Solid-phase microextraction (SPME) technology eliminates the use of organic solvents and has the advantage of simplicity. In this solvent-free extraction technique, developed by Pawliszyn and coworkers [3,4], the analytes are adsorbed directly from an aqueous [5] or gaseous phase [6] onto a fused-silica fibre coated with a liquid-polymeric phase. Once equilibrium between the aqueous phase and the coated fibre is reached, the latter can be directly injected into a gas (GC) or liquid chromatography (LC) port [7]. At equilibrium a linear relationship exists between the number of moles of the analyte adsorbed by the fibre and its concentration in the aqueous phase [8]. This property allows one to carry out accurate quantitative determinations of target analytes by means of appropriate calibrations. The sensitivity of the SPME method (amount of the analyte extracted by the solid phase) depends on the type of fibre and is directly proportional to partition coefficient (K) of the analyte.

SPME has been used for many applications, such as determinations of drugs in biological fluids [9], organic contaminants in soils [10], hydrocarbons in surface water and wastewater [11], caffeine in beverages [12] and volatile organic compounds in water [13]. Pesticides have also been determined by SPME in different matrices like wine [14,15], fruits [16,17], soils [18–20], honey [21] and aqueous samples [22–29].

Recently, the headspace SPME technique has also been developed to determine volatile pesticide concentrations in human body fluids at $\mu g\ l^{-1}$ levels [30,31]. In this technique the fibre is exposed to the headspace of the vial to allow the adsorption of the pesticides before entering the injector of the capillary GC system.

In this paper, we show that non-volatile pesticides can also be successfully extracted and detected from river water by SPME coupled with GC. To develop the method we have employed 100 μm polydimethylsiloxane (PDMS) and 85 μm polyacrylate (PA) coated fibres. The universality of their adsorption characteristics for most of the organic compounds makes them be good candidates for general SPME work. We have investigated the matrix influence, the effect of pH and addition of salt, as well as the effect of other important experimental parameters like adsorption–desorption time.

Finally, we have checked the applicability of the proposed method to the analytical determination of these pesticides in river water samples and determined the detection limits and the reproducibility. The samples were obtained from the riverbasin of the Ebro River, that waters the Rioja and Llanada Alavesa regions (Basque Country, Spain).

2. Experimental

2.1. Chemicals

Terbumeton (TER), metribuzine (MTB), isomethiozine (ISO), pyridafenthion (PYR) and triadimenol (TR) standards were supplied by Dr. Ehrenstorfer (Augsburg, Germany). These standards were used to prepare a 10 ml stock solution containing 100 $\mu g\ ml^{-1}$ of each analyte in acetonitrile, that was preserved at 4°C in a refrigerator. The stock mixed standard was diluted to the required concentration with water, obtained from Milli-Ro and Milli-Q water purification systems (Millipore, Milford, MA, USA).

The buffers were prepared by mixing citric acid, disodium hydrogenphosphate, sodium dihydrogenphosphate and/or sodium hydroxide, depending on the required value of pH, all of them analytical-grade chemicals (Merck, Darmstadt, Germany). In order to employ a small volume of buffer to get the desired pH, its concentration was 1.0 $mol\ l^{-1}$ in all cases.

2.2. Instrumentation

SPME was performed with commercially available 100 μm PDMS and 85 μm PA coated fibres and housed in the appropriate manual holder (Supelco, Bellefonte, PA, USA). For magnetic stirring, 12-ml Environmental Protection Agency (EPA) screw-cap vials supplied with a PTFE-lined septum (Kimble Glass, Vineland, NJ, USA) and a 0.2-in. stir bar were used (1 in.=2.54 cm). The magnetic stirrer was a Metrohm (Herisau, Switzerland) 728 Model.

Confirmation analyses were performed with a Hewlett-Packard system (Waldbronn, Germany) comprising a 5890 gas chromatograph provided with a splitless injector for capillary columns and a 5972 mass spectrometer with quadrupole mass filter and electron impact ionisation (EI) at 70 eV as ionization source.

Analyses by GC were performed with a Hewlett-Packard Model 6890 equipped with nitrogen–phosphorous (NPD) and electron-capture detection (ECD) systems. Two columns Hewlett-Packard HP-5, 30 m×0.32 mm I.D., 0.25 μm film thickness were used.

The gas chromatograph was operated in the splitless mode and the injector port temperature set at 270°C for the PDMS fibre and at 290°C for the PA fibre. Liners of 0.75 mm I.D. were used to minimise the sample loss and the broadening of peaks. The oven was initially set at 100°C, programmed up to 180°C at a rate of 30°C min^{-1}, subsequently from 180°C to 260°C at a rate of 50°C min^{-1} and finally held at 260°C for 8 min. Consequently, the total analysis time of a single run was 12.3 min. The carrier gas was helium, maintained at a flow-rate of 1.6 ml min^{-1}. The ECD temperature was 325°C, the anode flow at 6.0 ml min^{-1} and the make-up flow at 60 ml min^{-1}, both of them with nitrogen. NPD temperature was 325°C with hydrogen flow at 3.0 ml min^{-1}, air flow at 60 ml min^{-1} and make-up flow with nitrogen at 8.0 ml min^{-1}.

2.3. Procedures

2.3.1. Fibre – conditioning

The non-bonded 100 μm PDMS coated fibres were conditioned in the injection port of the GC for 1 h at 250°C and the partially crosslinked 85 μm PA polar coated fibres for 2 h at 300°C.

2.3.2. Extraction procedure

The required volume of acetonitrile was added to a volume of standard or sample to get a solution with the desired proportion of the organic solvent.

A 10.0-ml aliquot of this aqueous–organic solution was introduced to a vial, buffered by the addition of 500 μl of buffer solution and sealed with a PTFE-lined septum and a hole-cap.

Next, the fibre was immersed in this liquid phase for an appropriated period of time with magnetic stirring at room temperature. Then, the fibre is inserted into the hot injector port of the GC system for subsequent analysis.

The river water samples were filtered before extraction using Millipore PTFE-membrane filters with 0.45 μm pore size.

3. Results and discussion

3.1. Study of experimental variables

Firstly, chromatograms of the direct standard injections were registered to obtain initial information about chromatographic separation. Confirmation of each one of the chromatographic peaks was obtained by mass spectrometry (MS). Triadimenol (1*RS*,2*RS*;1*RS*,2*SR*) - 1 - (4 - chlorophenoxy) - 3,3 - dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, showed two peaks, TR1 and TR2 corresponding to diastereoisomers B (1*RS*,2*RS*) and A (1*RS*,2*SR*), respectively, both with similar EI-MS spectra. The ratio $(\text{peak area})_{TR1}/(\text{peak area})_{TR2}$ was 0.43±0.02 at concentration levels of 2.0, 10.0 and 100.0 μg l^{-1}, with relative standard deviations (RSDs) of 0.48% (n=15, five measures for each level of concentration). This relation is in agreement with the ratio 3:7 that has been reported for the distribution of both diastereoisomers of triadimenol [32] and so, both of them can be used to quantify this compound. Finally, the TR2 peak was chosen to quantify TR because this peak showed the best linearity and lower detection limit. On the other hand, the study of the chromatograms obtained by direct injection of standards stated that TER has no response in ECD. For

this reason, the preliminary studies related to the effectiveness of the extraction process were carried out using NPD.

The first step in developing a method for SPME is fixing the *fibre depth in the injector*. For this, the fibre retracted inside the adjustable needle of the SPME device was placed into the injection port. Then, this needle was set at 3.4 cm, since this was the length of the syringe needle specifically recommended for 0.75 mm Supelco liners and Hewlett-Packard split–splitless injectors. As we could check in several experiments, when the needle was in this position the length of the exposed fibre allowed one to get good sensitivity and reproducible results. Larger fibre depths in the injector provoked stress fibre and carryover effects, whereas other shorter ones caused loss of response.

The efficiency of analyte extraction by a SPME method can vary widely [33] due to matrix influence, adsorption time, desorption time and desorption temperature. In order to check the matrix influence an organic solvent was added to introduce partitioning selectivity, as is commonly done in LC. In spite of Arthur et al. [34] who showed that organic solvent concentrations higher than 10% do not affect K of non-polar analytes, the addition of acetonitrile in the

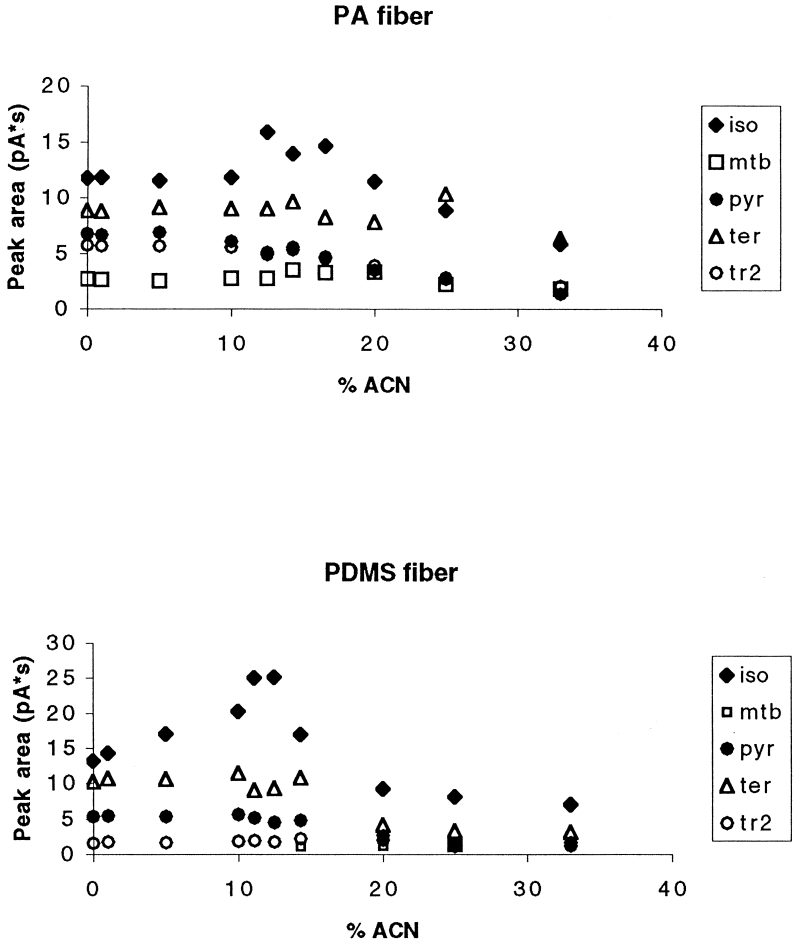

Fig. 1. The effect of acetonitrile percentage on the extraction efficiency. Each point is the average of three data points. The fibres were exposed for 2 min to a solution containing 1 μg ml^{-1} of each pesticide. The measurements was made using NPD under conditions described in the text.

range of 1–30% was tested in this work. In contrast with some authors that recommend maintaining the organic solvent below 1%, the results represented in Fig. 1 show that the higher extraction efficiency of ISO was obtained when acetonitrile concentrations are close to 10%, while the other studied analytes exhibited a similar response in the range of 1–15% of acetonitrile. Therefore, the best response for most of the analytes was achieved when the microextraction was carried out in a liquid phase with 14.3% of acetonitrile (acetonitrile–water, 1:6) for the PA fibre and in a liquid phase with 11.1% of acetonitrile (acetonitrile–water, 1:8) for the PDMS fibre.

Next, experiments focused on determining the adsorption time of SPME process were carried out. For this, triplicate solutions containing all the analytes were extracted with both fibres for periods of time ranging from 2 to 120 min. As the time for the analytes to be adsorbed from the liquid phase onto the stationary phase is primarily dependent on the rate of mass transfer [8], the extraction process can be improved by stirring or sonication. For such a reason, a magnetic stirrer was used to realize all the extraction experiments, setting the stirring rate at 40% of the maximum value. Fig. 2 shows the adsorption time profiles obtained for the analytes. As can be observed, the PDMS fibre allowed all analytes (except TER) to attain equilibrium in 15 min, whereas using the PA fibre 40 min was required. In order to not excessively increase the total analysis time [34,35], the adsorption time was set at 15 min. Although the analytes need more than 15 min to reach the equilibrium in the PA fibre, the obtained response for all of them exhibited a good repro-

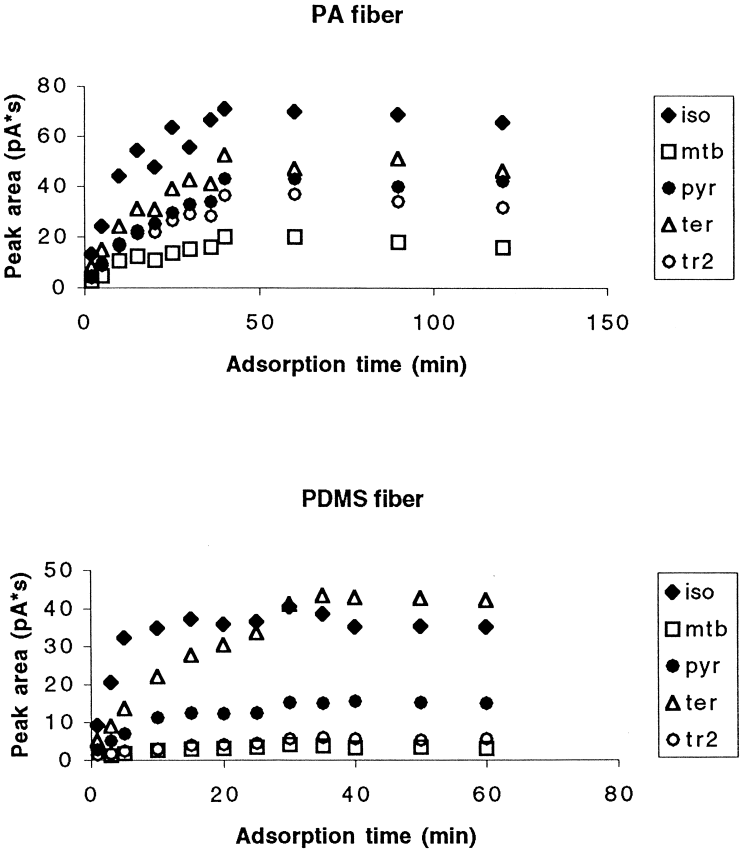

Fig. 2. The effect of equilibrium time on the chromatographic response of selected pesticides. Each point is the average of three data points. The fibres were exposed to solutions: A: water–acetonitrile (6:1) containing 1 μg ml^{-1} of each pesticide for the PA fibre; B: water–acetonitrile (8:1) containing 1 μg ml^{-1} of each pesticide for the PDMS fibre.

ducibility and it was considered suitable to achieve the limit of detection (LOD) required by the legislation on residue limits of these pesticides [36].

After the analytes have been trapped on the fibre, the *desorption temperature* was studied in the range 220–300°C for the PA fibre and 230–270°C for the PDMS fibre, working with triplicate solutions of 1 μg ml^{-1} of each pesticide (the maximum temperature in each fibre is limited by the manufacturer). In the case of the PA fibre, the peak areas of all analytes increased as the desorption temperature increased, and these areas gradually decreased when the temperature exceeded 290°C. For the PDMS fibre, the peak areas of most analytes (except for PYR and TER) were not affected practically by the temperature (Fig. 3). According to these results, desorption temperature was set at 290°C for the PA fibre and at 270°C for the PDMS fibre.

The influence of *desorption time* on the efficiency of the extraction was studied by placing the fibre with the adsorbed analytes in the injector for progressively longer periods of time. Desorption times from 0.5 to 8 min were tested setting the injector temperature to 290°C for the PA fibre and to 270°C for the PDMS fibre. It could be observed that the analytes were fully desorbed after 1 min into the injector and so this time was chosen to desorb the analytes from both fibres. It is proper to point out that in these experimental conditions carryover did not occur for any pesticide.

The *lapse of time that passes between sampling and injection* in fieldwork is one of the parameters

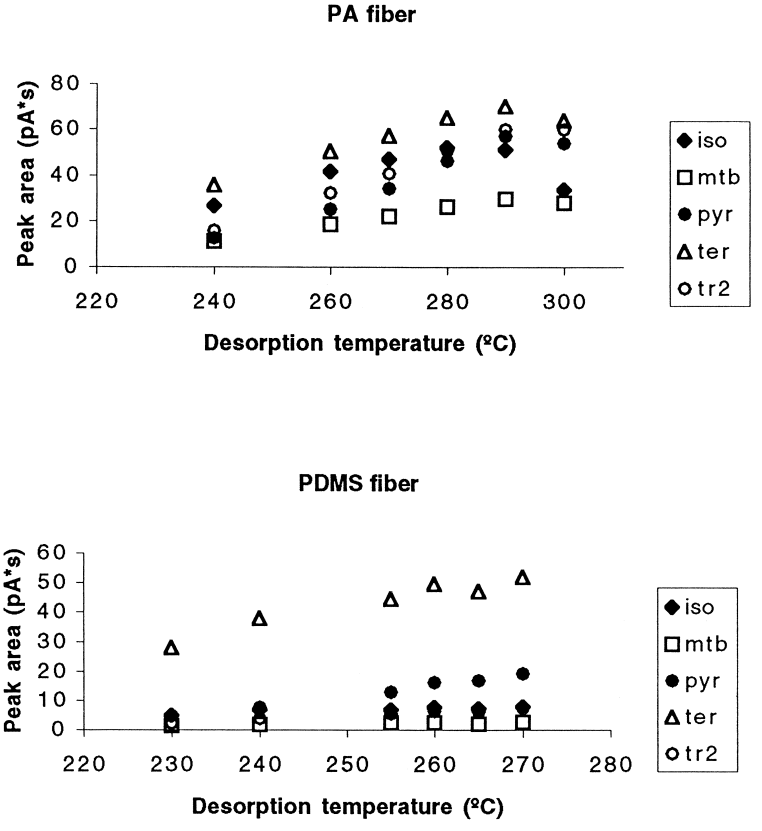

Fig. 3. The effect of desorption temperature on the peak areas of selected pesticides. Each point is the average of three data points. The fibres were exposed for 15 min to their respective solutions containing 1 μg ml^{-1} of each pesticide. The absorbed analytes were desorbed thermally for 1 min.

that has been found to affect the precision of SPME methods [37]. Because of this fact, the influence of this parameter was studied by varying the interval from 0.5 to 15 min. No significant change was observed in the extraction efficiency of both fibres, except for ISO using the PA fibre (Fig. 4). In this case, the signal decreased appreciably for intervals higher than 1 min, as the carryover effect increased considerably. Therefore, both fibres have to be inserted into the injection port of a gas chromatograph immediately after the extraction to avoid losses of the analytes.

Next, the *effect of ionic strength and pH* was investigated as a means to enhance the extraction of the analytes. Ionic strength was tested by addition of NaCl (up to 1.0 mol l^{-1}) to triplicate solutions. The responses obtained were similar to the ones obtained without the addition of NaCl. Thus, in this case salt addition did not produce any change in the efficiency of the extraction.

Subsequently, the influence of the pH on the extraction efficiency was studied. For this purpose, 10 ml solutions containing 1 μg ml^{-1} of each pesticide were buffered over the pH range 3.2–8.0 by addition of the appropriate buffer (the pK_a values of these pesticides are in the range 3.0–7.0 [32]). As Fig. 5 shows, no significant effect on the extraction of PYR, MTB and TR was observed. However, ISO (pK_a=5.03) was not extracted until pH 5.5 and the response of this pesticide and TER (pK_a=3.6)

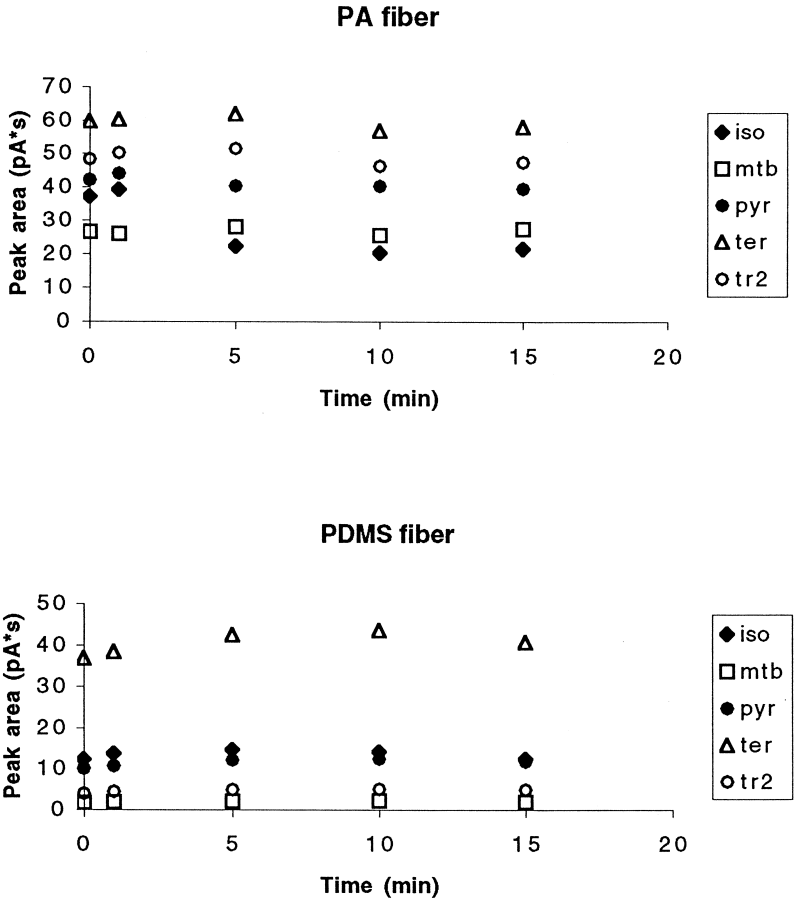

Fig. 4. The effect of time lapse between sampling and injection on the chromatographic response of selected pesticides. Each point is the average of three data points. The fibres were exposed for 15 min to their respective solutions containing 1 μg ml^{-1} of each pesticide. PA fibre during 1 min into injector port at 290°C, PDMS fibre during 1 min into injector port at 270°C.

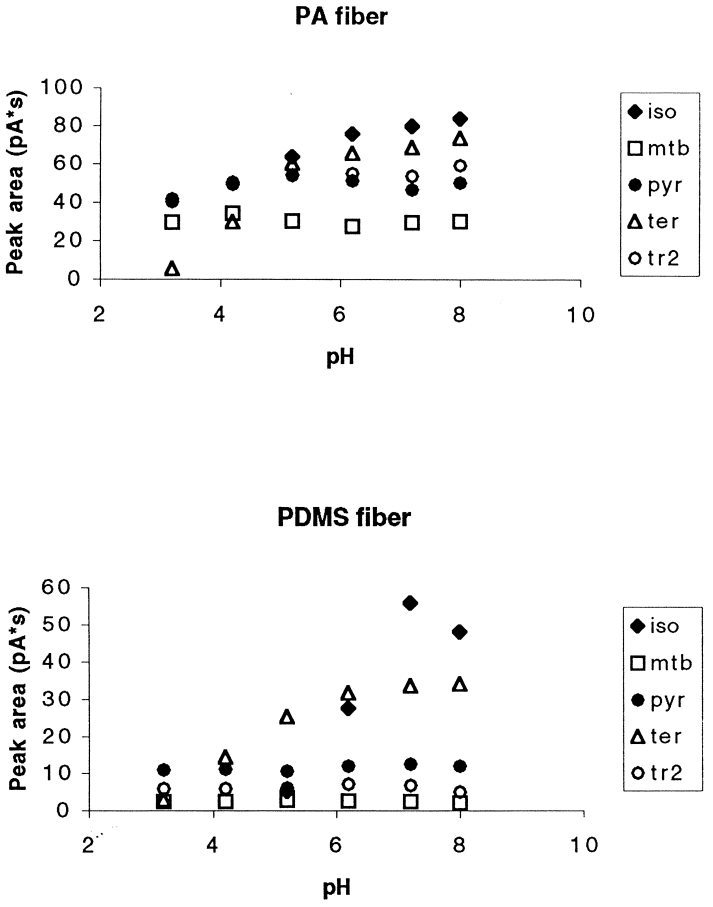

Fig. 5. The effect of pH on extraction efficiency of selected pesticides. The fibres were exposed for 15 min to their respective solutions containing 1 μg ml^{-1} of each pesticide.

increased as the pH values went up. Consequently, the pH for the simultaneous extraction of the studied pesticides was set at 7.2 in order to improve their LOD.

The pH range was obtained with several composition buffers: citric acid with disodium hydrogenphosphate, or sodium dihydrogenphosphate with disodium hydrogenphosphate, or sodium dihydro-

Table 1
Selected analytical conditions of the SPME method for the simultaneous determination of the five pesticides

Parameter	PA fibre	PDMS fibre
Relation acetonitrile–water	1:6	1:8
Adsorption time (min)	15	15
Desorption time (min)	1	1
Time between adsorption–desorption (min)	0	0
Desorption temperature (°C)	290	270
pH	7.2	7.2
Buffers	Citrate–phosphate	Citrate–phosphate

genphosphate with sodium hydroxide. The best results were obtained with citric acid mixed with disodium hydrogenphosphate for both fibres.

Finally, the experimental conditions of the SPME method of these pesticides were selected, according to all the results obtained in the study of the parameters that influence the efficiency of their extraction (Table 1).

With the aim of testing the precision of this SPME method, the RSDs were determined by performing 10 consecutive extractions at two different levels of concentration under the selected conditions. The

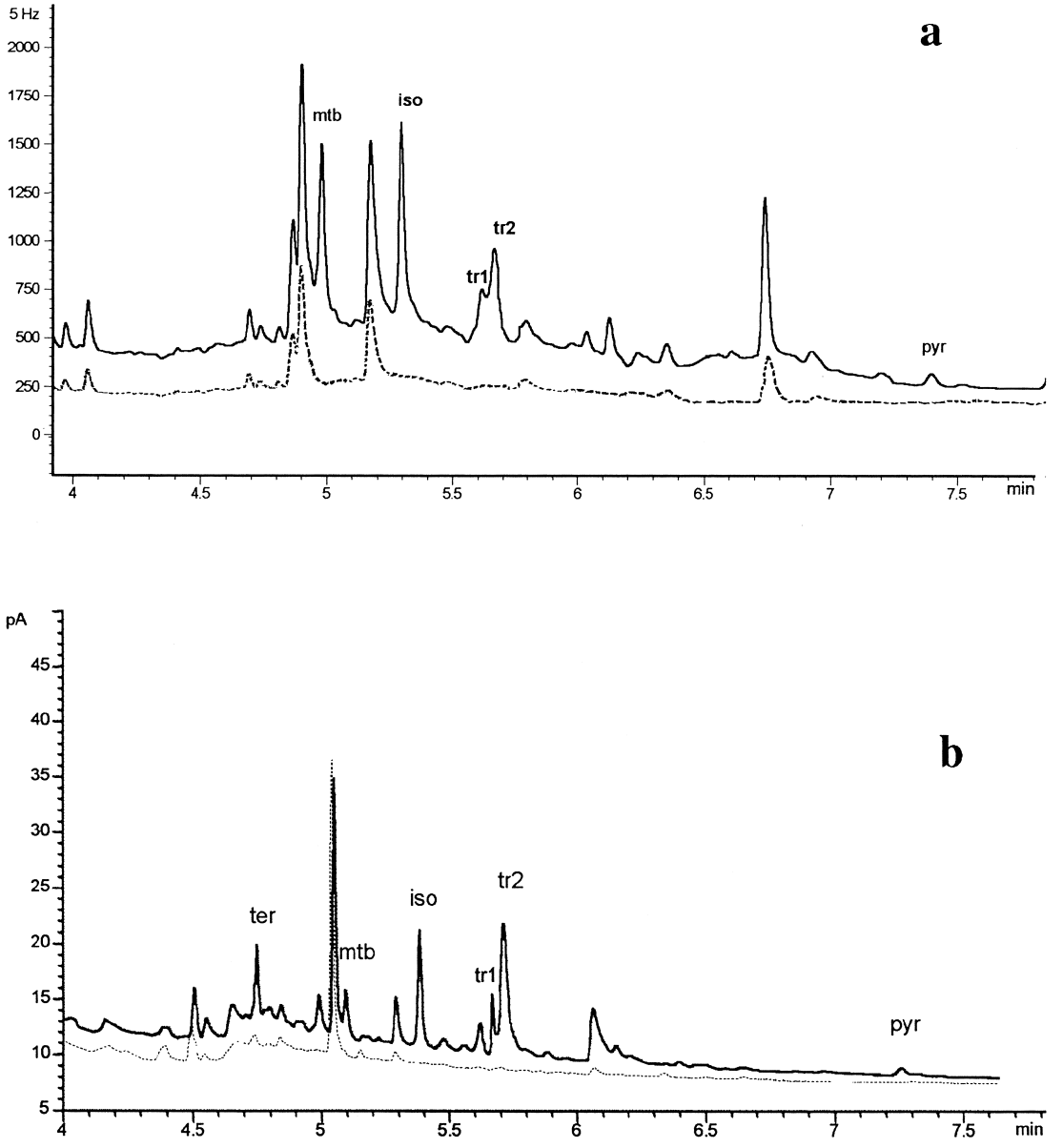

Fig. 6. Typical SPME–GC chromatograms of Ebro river water samples using the PA fibre. Experimental conditions in the text. (a) GC–ECD chromatograms. River sample spiked with 5.0 μg l^{-1} of ISO, MTB and 50 μg l^{-1} of TR and PYR. (b) GC–NPD chromatograms. River sample spiked with 5.0 μg l^{-1} of ISO, MTB, TER, TR and PYR. Dotted line: River water sample.

Table 2
Linearity, detection limits and precision data of studied pesticides obtained from extractions under selected conditions using PA and PDMS fibres and NPD and ECD

Compound	GC–NPD								GC–ECD							
	Slope±SD (pA s/ppb)	Intercept±SD (pA s)	Correlation coefficient	LOD ($\mu g\ l^{-1}$)	RSD (%, $n=10$)				Slope±SD (Hz s/ppb)	Intercept±SD (pA s)	Correlation coefficient	LOD ($\mu g\ l^{-1}$)	RSD (%, $n=10$)			
					5 $\mu g\ l^{-1}$	20 $\mu g\ l^{-1}$	50 $\mu g\ l^{-1}$	200 $\mu g\ l^{-1}$					1 $\mu g\ l^{-1}$	2 $\mu g\ l^{-1}$	10 $\mu g\ l^{-1}$	20 $\mu g\ l^{-1}$
PA fibre																
ISO	1.90±0.06	−67.8±15.1	0.9988	0.43	11.94		7.51		696.66±24.72	225.07±680	0.9987	0.007	5.91		6.22	
MTB	0.68±0.02	−21.5±4.9	0.9990	1.20	6.90		13.57		413.57±3.17	−143.34±87.17	0.9999	0.012	3.05		4.16	
PYR	0.84±0.05	−25.8±13.3	0.9953	0.96	15.95		4.47		12.33±0.98	−36.13±27.08	0.9936	0.398	27.50		13.30	
TER	0.80±0.01	−6.2±4.5	0.9993	1.02	11.73		7.73		–	–	–	–	–		–	
TR	0.66±0.04	−12.0±11.0	0.9947	1.24	4.67		10.44		10.25±0.53	−42.14±14.81	0.9972	0.479	24.90		6.97	
PDMS fibre																
ISO	4157.47±115.4	947.28±63.24	0.9991	0.13		8.12		1.72	1393.52±44.97	−3090.0±1034.3	0.9989	0.002		7.63		7.52
MTB	182.52±7.20	26.79±3.94	0.9984	2.97		11.81		2.73	59.53±2.27	184.45±52.33	0.9985	0.055		12.37		3.38
PYR	1209±66.91	216.32±36.65	0.9969	0.45		28.50		4.53	13.75±0.90	23.75±20.74	0.9957	0.237		4.76		9.33
TER	1863.99±55.78	128.91±30.55	0.9991	0.29		2.39		1.99	–	–	–	–		–		–
TR	178.08±2.00	11.99±1.09	0.9998	3.04		15.13		1.86	1.01±0.27	15.96±3.60	0.9255	0.097		28.80		12.80

results shown in Table 2 can be deemed excellent beside the values usually obtained with SPME methods and manual injection.

Likewise, the linearity of the chromatographic responses of all these pesticides was studied in the concentration range 1–800 μg l^{-1} for NPD and 1–50 μg l^{-1} for ECD. The correlation coefficients were greater than 0.994 in all cases.

The calculations of the detection limits were based on a $2N/m$ ratio, where N is the noise and m is the slope of the respective calibration equation. The noise was estimated using the very-short-term noise ASTM (ASTM E 685-93: American Society for Testing and Materials, West Conshohocken, PA, USA (2000)) with 2 min of selected time and a 0.1-min time range for each cycle. Table 2 shows the LODs obtained for each pesticide using the PA and PDMS fibres with both detectors. Due to the high sensitivity of this technique, a blank run before each sample was required when analysing trace levels of these pesticides to avoid unnoticed contaminations.

Thus, it can be concluded that the detection limits reached by the PA fibre are as a rule lower than those obtained by the PDMS fibre, with either of the two detectors. Also it can be noticed that the PA fibre may be used with greater guarantee of reproducibility at low levels of concentration with NPD.

Table 3
Recoveries relative to spiked river water with 5.0 μg l^{-1} of TER, PYR and TR, and 2.0 μg l^{-1} of ISO and MTB[a]

Pesticide	Sample	Mean (μg l^{-1})
ISO	Ebro River	2.00±0.12
	San Gines River	1.91±0.16
	Puente de Vitoria creek	2.12±0.19
MTB	Ebro River	1.94±0.11
	San Gines River	1.96±0.07
	Puente de Vitoria creek	2.09±0.14
TER	Ebro River	5.01±0.48
	San Gines River	4.90±0.52
	Puente de Vitoria creek	5.10±0.60
PYR	Ebro River	5.03±0.49
	San Gines River	4.70±0.68
	Puente de Vitoria creek	5.14±0.57
TR	Ebro River	5.04±0.16
	San Gines River	4.95±0.24
	Puente de Vitoria creek	5.13±0.25

[a] Organic matter analysis as COD: PYR, TER and TR were analysed with NPD. ISO and MTB were analysed with ECD. The PA fibre was used in all cases.

3.2. Analysis of river water samples

The effectiveness of the proposed method to determine these pesticides from river water was tested by performing replicate analyses of samples from three different zones of the riverbasin of the Ebro River: the San Gines River, the Puente de Vitoria creek and the Ebro River (up river from Laguardia, Basque Country, Spain). These sampling zones were chosen because of the different organic matter content of the water, which causes most of the matrix interferences. The organic matter present in river water samples was expressed as chemical oxygen demand (COD) and quantified using the potassium dichromate method (Table 3). Fig. 6 shows the chromatogram of a fortified river water sample obtained by the SPME–GC method using the PA fibre, overlaid with the chromatogram of an unspiked sample. No significant interferences with the studied pesticides were observed, since the unspiked samples did not show any peak in the retention time of these compounds.

The slopes of the calibration curves of the pesticides based on deionized water and river water were compared using both fibres. These slopes were independent of the matrix of the sample, since the difference between the respective slopes is less than 2.2%. This fact proves that the method based on a calibration curve can be used to analyse these pesticides in river waters.

Because the target analytes were not found in these river water samples, triplicate aliquots of each sample were artificially spiked with 2.0 μg l^{-1} of ISO and MTB and 5.0 μg l^{-1} of TER, PYR and TR and subsequently analysed using the proposed SPME method with the PA fibre. The results obtained are summarised in Table 3. The average concentrations obtained in the analysis of these spiked samples correspond to mean recoveries ranged from 94±14 to 106±9% for a significance level of 0.05. These results show that the proposed methodology is suitable for the determination of these pesticides from river water.

Acknowledgements

This work was supported by a pre-doctoral grant from the University of Basque Country and by the PI96/18 research project of the Education, University and Research Department of the Basque Government.

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