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Matrix effects on solid-phase microextraction of organophosphorus pesticides from water

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Abstract

This study develops a method for solid-phase microextraction (SPME) of eight organophosphorus pesticides, diazinon, fenthion, fenitrothion (sumithion), methyl-parathion, parathion, methyl-trithion, ethion and triazophos, from water. Determination is carried out by gas chromatography with nitrogen–phosphorus detection. To perform the SPME, poly(dimethylsiloxane) and polyacrylate fibers were initially compared on the basis of their absorption capacities for the selected pesticides, and polyacrylate was selected to accomplish the rest of assays. The main factors affecting the SPME process such as memory effect, stirring rate, extraction temperature and absorption–time profile were studied. The proposed method requires 2 ml of sample and reaches limits of detection ranging between 6 ng/l for fenthion and 136 ng/l for methyl-parathion, with relative standard deviations at the 500 ng/l level between 2% for diazinon and 13% for ethion. The method was applied to spiked tapwater, seawater, wastewater with high dissolved organic matter content (DOC=212 mg/l) and water containing 15 mg/l of sodium lauryl sulfate (SDS), which were previously analyzed to control interferences. Recoveries for diazinon, fenthion and methyl-trithion were better from seawater than from Milli-Q water. Recoveries for fenthion and ethion increased with the presence of SDS and those for methyl-parathion and triazophos decreased from the wastewater because of the presence of the organic matter. Finally, a wastewater from a pesticide producer industry was analyzed showing the presence of diazinon and ethion at concentrations of 0.97 μg/l and 0.67 μg/l, respectively. Results were in concordance with those obtained using a standard liquid–liquid extraction method.

Keywords: Water analysis; Environmental analysis; Matrix effects; Extraction methods; Sample preparation; Pesticides

1. Introduction

In order to reduce the environmental impact of pesticides, several priority lists of compounds, called "red" or "black lists" have been published as compounds to be monitored on the basis of their toxicity, persistence and input. In Europe a priority list of 132 compounds which considers pesticides used in quantities of over 50 000 kg per year and their capacity for probable or transient leaching, was published [1]. In the UK, a red list of substances which includes several pesticides, most of them common to the European Union (EU) list, was established [2]. In the last proposal presented by the European Commission [3] on 28 April for the modification of 80/778/CEE Directive concerning quality for water consumption [4] the maximum concentration permitted for individual pesticide

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nevertheless remains at 0.1 μg/l. These severe levels require the development of methods with very low limits of detection (LODs) approximately one order of magnitude lower than the US Environmental Protection Agency (EPA) methods. In relation to this a recent EU report [5] stated that analytical methods need a detection limit of 0.02 μg/l or less and an accuracy of around 20%.

In order to achieve the above mentioned requirements for the analysis of organic micropollutants in water by chromatographic techniques, a previous concentration of the sample is needed. Actual methods for the determination of non-volatile pesticides involve the concentration of large volumes of sample by liquid–liquid extraction or solid-phase extraction. The first one has the drawback of requiring the use of large amounts of toxic and expensive solvents, the formation of difficult to separate emulsions and extensive cleanup procedures that are time-consuming also increasing the probability of contamination of the extract. Solid-phase extraction became a good alternative to liquid–liquid extraction because it reduces the use of solvents and at the same time allows the automation of the process. However there are many steps to be carried out and much handling of the sample still remains the main problem.

Solid-phase microextraction (SPME) is a solventless technique for the concentration of organic micropollutants that allows the extraction of small volumes of sample; it can be easily automated. The analytes are extracted by absorption over the fiber which is directly exposed to the sample or to the headspace. Finally the fiber is introduced into the gas chromatograph injector where the analytes are thermally desorbed. Nowadays two types of polymers are commercially available: poly(dimethylsiloxane) and polyacrylate [6]. The first applications of this technique were in the extraction of volatile and non-polar compounds in water such as substituted benzenes [7–9] and volatiles included in EPA method 624 using poly(dimethylsiloxane) [10]. Next studies with poly(dimethylsiloxane) were carried out with non-volatile non-polar compounds such as polyaromatic hydrocarbons [11], selected polychlorinated biphenyls and also chlorinated pesticides [12,13]. Recently two SPME methods for polar compounds using polyacrylate have been developed for the analysis of phenols [14,15] and different groups of pesticides [16].

This study describes an application of the polyacrylate fiber for the analysis of eight organophosphorus pesticides, some of which, (fenthion, fenitrothion, methyl-parathion and triazophos) are included in the EU Priority List. The main purpose of this study is to know the ability of the proposed SPME method when different aqueous matrices must be analyzed.

2. Experimental

2.1. Materials

Film [100 μm thickness poly(dimethylsiloxane)] and 85 μm polyacrylate fibers (Supelco, Bellefonte, PA, USA) were used with a fiber holder (Supelco) for manual use. To perform SPME, autosampler vials (Varian, CA, USA) were filled with 2 ml of sample. To agitate the samples a 7 mm×2 mm magnetic stirbar (Bel-Art Products, Pequannock, NJ, USA) was placed in the sample vial and a magnetic stirrer (SBS Instruments, Barcelona, Spain) was used. All new fibers for SPME were previously conditioned in the gas chromatography (GC) injector itself for 2 h at 260°C. Once conditioned, the colour of the polyacrylate polymer changes from white to yellow.

2.2. Standards

Methyl-trithion (98.7% purity), methyl-parathion (99.0%), parathion (97.9%), ethion (99.0%), and diazinon (98.9%) at concentrations of 10 mg/l in toluene were purchased from Nanogens (Watsonville, CA, USA). Fenitrothion (sumithion) (95.0%), fenthion (99.0%) and triazophos (99.0%) were purchased from Dr. Ehrenstorfer Lab., Promochem (Augsburg, Germany).

A working solution in methanol (Suprasolv quality, Merck, Darmstadt, Germany) was prepared containing 1 mg/l of each of the eight organophosphorus compounds. Fresh samples of the assayed matrices were made by spiking appropriate amounts of the working solution at the different spiked levels. The content of methanol in the spiked aqueous samples was always less than 0.2%. Ultrapure water from a Milli-Q purification system (Millipore, Milford, MA, USA) was used to prepare all the

spiked samples when no specific comments are given.

2.3. Apparatus

The analysis was carried out in a Varian 3600 GC system equipped with a DB 1701 column (30 m× 0.25 mm, 0.25 μm of 14% cyanopropylphenyl–86% methylpolysiloxane) (J & W Scientific, Folsom, CA, USA). Helium was used as carrier gas at 2 ml/min, and a nitrogen–phosphorus detector working at 3.2 A intensity and maximum range (range 12) with air at 175 ml/min, nitrogen 28 ml/min (make up gas) and hydrogen 4 ml/min. The injector and detector temperatures were set at 260°C and 300°C isothermal, respectively. The column was kept at 70°C for 2 min, ramped at 30°C/min to 200°C and held for 1 min. The temperature was then increased at 2.4°C/min to 220°C and held for 1 min and finally increased at 3°C/min to 260°C and held for 1 min. Injections were carried out in the split injection mode (split ratio 1:1).

To control temperature during the assays, the complete set, the agitator, the fiber and the sample was introduced into a FKG 370 Eurocold refrigerator (Copenhagen, Denmark) during the extraction process for the 4°C extractions and into a T6200 Heraeus oven (W.C Heraeus, Germany) for all the extractions carried out over room temperature conditions. Samples were previously conditioned in order to reach the desired temperature.

2.4. Samples description

To compare poly(dimethylsiloxane) and polyacrylate fibers and to evaluate factors affecting the SPME process with polyacrylate fiber, spiked Milli-Q water was used.

The tapwater sample was obtained from the main of the Alicante (Spain) city, with 0.86 mg/l total dissolved salts. The seawater was sampled from the Albufereta beach in Alicante at 300 m from the land, containing 36 g/l total dissolved salts.

The wastewater 1 was taken from a tinned artichoke factory waste overflow, and it was selected because of its high natural organic matter content. The analysis of the dissolved organic carbon (DOC= 212 mg/l) was carried out by filtering the sample through a 0.45 μg/l glass wool filter and then analyzed by infrared combustion in a DOC analyzer (Shimadzu, Kyoto, Japan).

An artificial water sample was prepared to contain 15 mg/l of sodium lauryl (dodecyl) sulfate (SDS; 99% purity, Merck) in Milli-Q water. SDS is the tensioactive most used for domestic and industrial purposes. The level was chosen to simulate a very polluted water in order to discover its possible influence on SPME when using the polyacrylate fiber. The tap, sea, wastewater 1 and the water containing SDS were analyzed prior to being spiked, to ensure that they were free of interfering compounds.

The wastewater 2 was obtained from a waste of a pesticide producer industry prior to any waste treatment, containing a DOC level of 95 mg/l with high pesticide and pesticide-subproducts content. This industry is situated in an area of intense agricultural production at the Segura river valley (Murcia, Spain).

2.5. Procedure

A 2-ml volume of sample was placed in an autosampler vial together with a magnetic stirrbar and sealed. The fiber was introduced carefully directly into the aqueous phase and stirred at 85% (1343 rpm) of maximum speed, at 60°C for 45 min. Then the fiber was retrieved and introduced for a period of 2 min into the GC injector for the GC analysis. Special comments are given when different conditions were used.

2.6. Statistics

Least-squares regression analysis was used to describe the relationship between signal "y" and concentration "x" for calibration curves and between obtained results "y" and added amounts "x" for the matrix effect experiment. The following statistics from the regression analysis were computed: slope (b), intercept (a), standard deviation (s_a,s_b,$s_{y/x}$) and determination coefficient R^2. For studies of matrix effect, the slope of the regression lines multiplied by 100 was considered as % relative recovery mean of each pesticide after running all steps of the method, and the $s_b \times 100/b$ was considered as the relative standard deviation. Proportional

errors were validated by testing wether $b=1$ using a t-test. The probability level used was 95%.

3. Results and discussion

3.1. Fiber type comparison

Two commercially available fibers poly(dimethylsiloxane) and polyacrylate were compared. The first one has liquid properties whilst the second one is a solid. These differences basically affect the absorption equilibrium times for the analytes; thus, a faster diffusion and consequently, lower equilibrium times must be expected when using the liquid poly(dimethylsiloxane) than when using the solid polyacrylate.

On the other hand, poly(dimethylsiloxane) is non-polar whereas polyacrylate is more polar; because of this, the affinity for the selected pesticides, which have intermediate polarities, should be stronger using the polyacrylate fiber.

Bearing in mind these two aspects, comparison of the two fibers was made by extracting samples of 2 ng/ml of each pesticide during 45 min. This time was chosen because it allows the extraction of a new sample during the chromatographic analysis of the precedent sample. This time is not enough to reach the absorption equilibrium using the polyacrylate fiber, but it is in the same order as times reported in the literature to reach the absorption equilibrium of similar analytes when using a poly(dimethylsiloxane) fiber [16].

As shown in the bar graphs from Fig. 1, the extracted amount of target analytes was greater with polyacrylate than with poly(dimethylsiloxane), even when absorption equilibrium times were not reached for the first fiber as discussed below.

Because of the better extractive behaviour of the polyacrylate fiber for methyl-parathion, fenitrothion, fenthion, parathion and triazophos, this fiber was chosen to perform the rest of the experiments.

3.2. Carryover

In SPME a percentage of the analytes remain absorbed by the fiber after desorption in the GC injector. This problem becomes significant when low

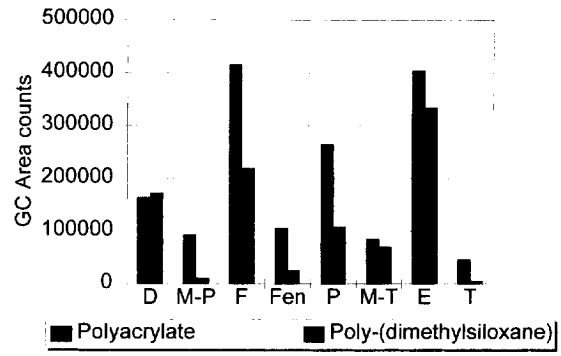

Fig. 1. Comparison in the extraction of 2 μg/l of the studied pesticides using 100 μm thickness film poly(dimethylsiloxane) fiber and 85 μm polyacrylate. D=diazinon; M-P=methyl-parathion; F=fenthion; Fen=fenitrothion; P=parathion; M-T=methyl-trithion; E=ethion; T=triazophos.

volatility compounds are analyzed. To study this effect a blank was run after an extraction of 2 ng/ml of the organophosphorus pesticides. Carryovers obtained were lower than 0.1% with the exceptions of diazinon (3.0%) and ethion (1.3%). Although in such conditions these carryovers allow the analysis of samples after calibration with very small errors, this problem could however be reduced by enlarging the desorption time or by running a blank after the calibration or contaminated samples. Some carryover problems difficult to eliminate even after the running of several blanks have been attributed to chemisorption processes [15].

3.3. Stirring rate

Dynamics in the extraction process has been studied in depth by Louch et al. [17] obtaining mathematical models of the process. One of the conclusions obtained is that in a real situation the extraction is controlled by the efficiency of the mixing technique. The optimum stirring rate was determined by analyzing vials containing 500 ng/l of target compounds mixed at different stirring rates. Triplicate injections were made. Fig. 2 shows the GC areas obtained at different agitation speeds expressed as rpm. The curves obtained show clearly that with no agitation a very poor extraction is achieved and this extraction increases with increased stirring. However, above 85% of the maximum speed (1343 rpm) the amount of analyte extracted decreases. This

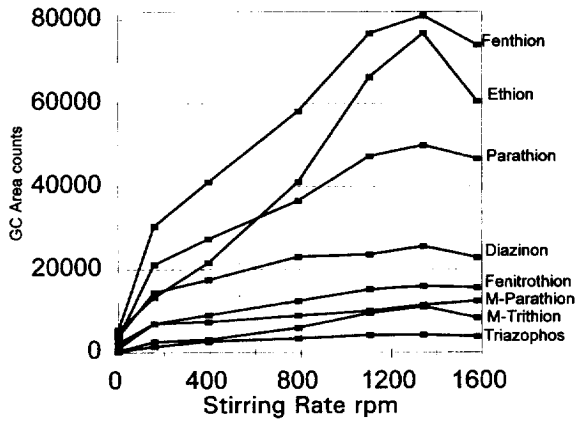

Fig. 2. Stirring rate effect (expressed as % of maximum speed 1580 rpm) in the extraction of 500 ng/l of the target pesticides from Milli-Q water with polyacrylate fiber, M=methyl.

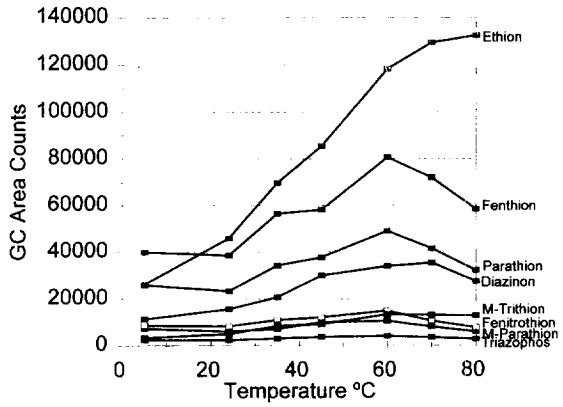

Fig. 3. Temperature effect in the extraction of 500 ng/l of the organophosphorus pesticides from Milli-Q water with polyacrylate fiber.

is because at the maximum speed the stirbar begins to vibrate and agitation of the sample is worse. The rest of the experiments were carried out at this optimum stirring rate (1343 rpm).

For practical purposes magnetic agitation was used in this study although other agitation systems, such as intrusive mixing and sonication [18], have been shown to be useful too. The first one allows efficient agitation with stirring rates over 20 000 rpm, but friction fenomena cause an important increase of temperature.

3.4. Temperature

The effect of temperature was studied by sampling 500 ng/l of the studied pesticides under different temperature conditions. Fig. 3 shows the GC areas obtained for the eight organophosphorus pesticides at the different temperatures. Triplicate analyses were made at each extraction temperature. Curves obtained show a clear increase in the amount of analyte absorbed when temperature increases. However, at temperatures of over 60°C there is a decrease in the amount extracted for all the analytes with the exception of ethion. There are two parameters directly affected by temperature that explain the results obtained. The diffusion of the analytes in the aqueous phase increases as temperature rises. Thus, the extraction, limited basically by mass transfer, is more efficient at higher temperatures. However the absorption is an exothermic process and increasing temperature has a negative effect in such processes. As a consequence of these two opposite parameters, extractions were higher at a temperature of 60°C except for ethion; in this case, extraction was higher at 80°C (maximum studied temperature). The rest of the experiments were carried out at 60°C. It has been reported that better conditions can be obtained by heating the sample and internally cooling the fiber [19] to improve the analyte diffusion and to favour the exothermic process; however, such a system is difficult to realize and real benefits are poor.

3.5. Absorption–time profile

The absorption–time profile was studied by monitoring the GC area counts as a function of exposure time. Fig. 4 represents the performance of the fiber for parathion, methyl-parathion, diazinon, methyl-trithion and ethion (the rest of the analytes were not represented in order to permit a better visualisation of the resulting curves) showing that an equilibrium time is reached in about 120 min for methyl-parathion, 150 min for parathion, 180 min for diazinon and 250 min for methyl-trithion. In the case of ethion equilibrium was not attained even after 480 min. Diffusion of the analytes is the limiting step in the absorption process, so high-molecular-mass compounds are expected to have longer equilibration

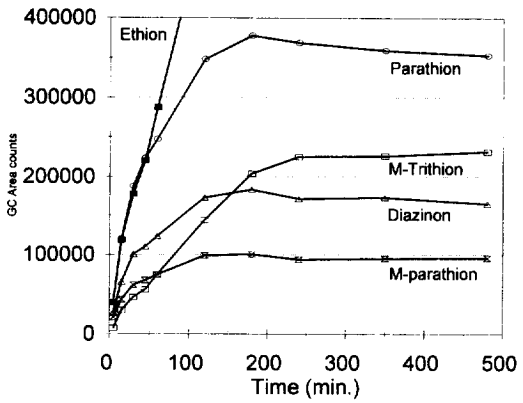

Fig. 4. Absorption–time profile for some of the studied pesticides.(The resulting curve for ethion is out of the selected scale).

times than low-molecular-mass analytes because of their smaller diffusion coefficients.

As expected, high equilibration times were obtained with the polyacrylate fiber when high-molecular-mass compounds are analyzed due to their low mass transport into the viscous polymer. 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. The use of the equilibrium time in the absorption phase can be unnecessary if LOD and R.S.D. values obtained are acceptable. This was the criterium in the selection of 45 min as the absorption time for the rest of the experiments. The amount of analyte extracted after 45 min expressed as a fraction of the maximum mass extracted at the equilibrium time was higher than 60% with the exception of methyl-trithion (25%) and ethion (less than 18%). Moreover extractions were repetitive (see R.S.D., Table 2).

3.6. Calibration curve

Series of five levels were obtained by spiking Milli-Q water with all the pesticides between a concentration range of 50 to 2000 ng/l. Each solution was run in triplicate. In all cases, there was significant linear regression ($p<0.05$) for the analyte concentration range tested. The regression line parameters are shown in Table 1. Fig. 5 shows the gas chromatogram obtained after extraction of the tested pesticides at the 0.5 μg/l level from Milli-Q water. Peaks shown in Fig. 5 have a good resolution with quite small widths at middle height (e.g. 0.09 min for parathion). Some tailing peaks are nevertheless observed. Tailing peaks could be attributed to the desorption from the fiber in the injection when volatile compounds are analyzed obliging the use of cryofocusing systems. In this case they could be attributed to the age of the column.

3.7. LODs and precision

LODs were calculated by comparing the signal-to-noise ratio (S/N) of the lowest detectable concentration to a $S/N=3$. A S/N of 10 was applied for the calculation of the quantification limits (LOQs). As shown in Table 2, the method allows both detection and quantification of organophosphorus pesticides in water at concentrations lower than 100 ng/l with the exception of methyl-parathion in accordance with EC

Table 1
Estimate parameters of the regression lines ($y=a+bx$) for the calibration curves

Compound	Slope		Intercept			
	b	s_b	a	s_a	$s_{y/x}$	R^2
Diazinon	52210	883	1542	901	1963	0.9991
Methyl-parathion	33650	467	−91	477	1039	0.9880
Fenthion	143856	3791	11258	3870	8429	0.9957
Fenitrothion	45236	718	−260	733	1597	0.9994
Parathion	105077	1825	4440	1863	4057	0.9990
Methyl-trithion	28300	1618	702	1652	3598	0.9981
Ethion	94799	6863	35702	7825	13588	0.9720
Triazophos	12926	347	−385	293	618	0.9986

$n=3$.

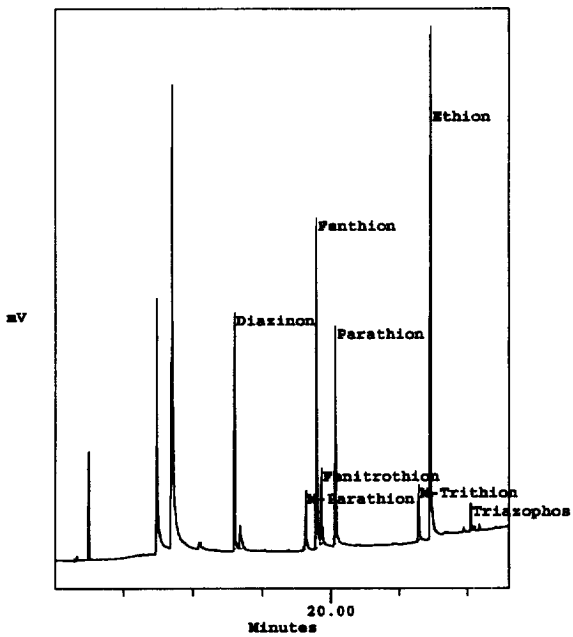

Fig. 5. Gas chromatogram obtained after an extraction of the tested pesticides with polyacrylate fiber at the 500 ng/l level from Milli-Q water.

legislations. The differences between the LODs of analytes like methyl-trithion and fenitrothion with small signals and low LODs with respect of diazinon and parathion is explained by the fact that a noisier baseline was observed in the elution times of analytes such as diazinon, parathion and methyl-parathion resulting in smaller *S/N* ratios (LODs) in comparison with other compounds with small signals but with less noisy baselines. Precision obtained, expressed as R.S.D., was lower than 10% with the exception of ethion (13%). Precision of the method could be improved by automating the whole process due to the fact that the extraction is based on an equilibrium directly affected by time.

Table 2
Limits of detection (LODs), limits of quantification and precision (R.S.D.) of the method

	LOD (ng/l)	LOQ (ng/l)	R.S.D. (%)[a]
Diazinon	33	111	2
Methyl-parathion	136	455	6
Fenthion	6	18	7
Fenitrothion	8	26	2
Parathion	31	102	3
Methyl-trithion	8	28	9
Ethion	30	100	13
Triazophos	56	184	9

[a] At the 500 ng/l level (n=7).

3.8. Matrix effects

The effects caused by the matrix in the extraction with SPME are not well known. In the present study, experiments were performed to investigate the influence of some matrices on the SPME. The selected matrices, tap, sea, wastewater 1 and Milli-Q water with 15 mg/l of SDS added were spiked at three concentration levels 0.1, 0.5 and 2 μg/l and then analyzed.

Data from Table 3 show, in general, a good agreement between the results obtained from Milli-Q water and those obtained from the selected matrices, therefore some results must be noted. Seawater relative recoveries for diazinon (122%), fenthion (104%) and methyl-trithion (117%) were significatively increased and such a tendency was also observed overall (106%). This is explained by the presence of salts that enhance the absorption of the analytes by the fiber. These results are in accordance with those encountered by other authors [16,20] when extracting BTEX (benzene, toluene, ethylbenzene, xylene) mediant poly(dimethylsiloxane) and pesticides with polyacrylate fiber.

The presence of 15 mg/l of SDS in the water had a negligible effect on relative recoveries for most pesticides. Only in the case of fenthion (110%) and ethion (120%) were recoveries significatively higher than 100%.

Natural organic matter content from wastewater 1 caused losses in the relative recoveries for methyl-parathion (77%) and triazophos (86%). The natural organic matter hinders the interaction between some analytes and the extracting fiber. This effect has already been observed when extracting BTEX with poly(dimethylsiloxane) [21].

3.9. Application to real samples

The wastewater 2 was analyzed by the proposed method and by a standard liquid–liquid extraction method (EPA Method 507). By SPME, 0.97 μg/l of

Table 3
Statistical data from the regression lines obtained for the matrix effect experiments

	b	s_b	Relative recovery mean (%)	R.S.D.$_b$ (%)
Tapwater				
Diazinon	0.983	0.036	99	4
Methyl-parathion	0.999	0.006	100	1
Fenthion	0.976	0.039	98	4
Fenitrothion	0.978	0.046	98	5
Parathion	1.022	0.081	102	8
Methyl-trithion	0.978	0.038	98	4
Ethion	1.083	0.022	108	2
Triazophos	1.001	0.063	100	6
Total	1.002	0.019	100	2
Seawater				
Diazinon	1.218	0.043	122	5
Methyl-parathion	0.980	0.039	98	4
Fenthion	1.041	0.007	104	1
Fenitrothion	1.057	0.036	106	3
Parathion	1.073	0.034	107	3
Methyl-trithion	1.174	0.037	117	5
Ethion	0.977	0.019	98	2
Triazophos	0.969	0.094	97	10
Total	1.061	0.026	106	2
Wastewater 1 (DOC 212 mg/l)				
Diazinon	0.992	0.028	99	3
Methyl-arathion	0.770	0.112	77	14
Fenthion	1.062	0.044	106	4
Fenitrothion	0.941	0.035	94	4
Parathion	1.008	0.023	101	2
Methyl-trithion	1.058	0.057	106	5
Ethion	1.026	0.082	103	8
Triazophos	0.858	0.042	86	5
Total	0.964	0.026	96	3
Tensioactive added water (15 mg/l SDS)				
Diazinon	0.987	0.050	99	5
Methyl-parathion	0.925	0.037	92	4
Fenthion	1.102	0.019	110	2
Fenitrothion	0.974	0.043	97	4
Parathion	1.051	0.021	105	2
Methyl-trithion	1.045	0.132	104	13
Ethion	1.203	0.078	120	6
Triazophos	0.925	0.064	92	7
Total	1.026	0.025	103	2

$n=3$.

diazinon and 0.67 μg/l of ethion were quantified. These results were in accordance with those obtained using the liquid–liquid extraction, that is, 1.06 μg/l and 0.58 μg/l for diazinon and ethion respectively. The chromatogram obtained after SPME (Fig. 6) shows the presence of several non-identified compounds in the sample. However such eluted compounds do not interfere with the determination of the analytes of interest. The identity of these pesticides was confirmed in the liquid–liquid extract by GC–

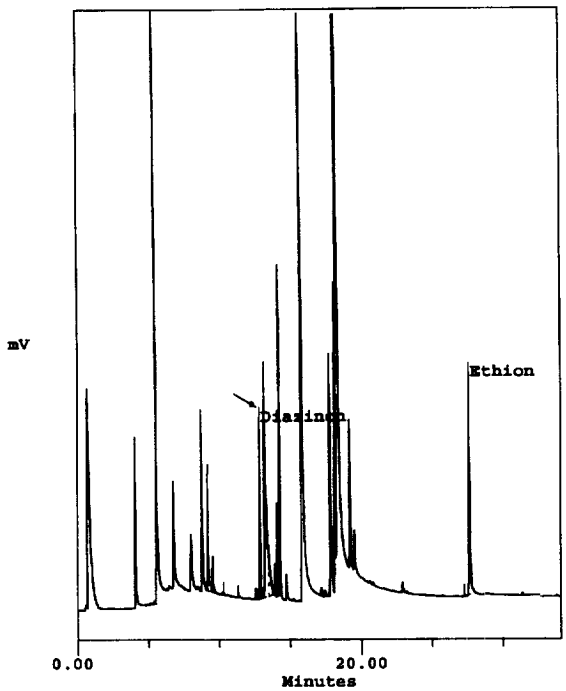

Fig. 6. Gas chromatogram obtained after SPME of wastewater (wastewater 2) from a pesticide producer industry, showing the presence of diazinon and ethion at concentrations of 0.97 μg/l and 0.67 μg/l, respectively.

MS (electron impact, EI+) scanning masses from 110 to 400. The use of this technique also allowed the identification of terbutylazine in the sample but the other peaks were not identified.

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