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Solid-phase microextraction and gas chromatography with mass spectrometric detection for the determination of pesticides in aqueous samples

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Abstract

Solid-phase microextraction (SPME) is a fast, alternative method for extracting organochlorine, triazine and thiocarbamate pesticides. An 85-μm polyacrylate fiber was used to extract the analytes directly from aqueous samples and then thermal desorption was carried out in the hot injector of a gas chromatograph–mass spectrometer. To enhance the sensitivity of SPME, the temperature and the length of the extraction and desorption steps and the pH and salt concentration of the sample were optimized. The linearity of most of pesticides for real samples was found to be between 0.07 and 30 μg l^{-1} when GC–MS under full-scan acquisition was used and between 0.005 and 10 μg l^{-1} when selected-ion monitoring (SIM) acquisition was used. Limits of detection at the sub μg l^{-1} level were achieved with GC and MS under the full-scan acquisition mode and at the ng l^{-1} level for MS under SIM acquisition. The repeatability of the method for tap water spiked at a level of 0.5 μg l^{-1} ($n=5$) was below 25% (R.S.D.). © 1998 Elsevier Science B.V.

Keywords: Extraction methods; Water analysis; Environmental analysis; Pesticides

1. Introduction

The determination of pesticides in environmental matrices is receiving increasing attention nowadays because of their toxicity. In order to reach the low levels allowed in drinking water by European Union (EU) regulations [1] an extraction and enrichment step is necessary prior to their instrumental determination.

The preconcentration step can be carried out by means of liquid–liquid extraction (LLE) [2,3] or solid-phase extraction (SPE) [4–9]. LLE is a very useful technique which is used in several US Environmental Protection Agency (EPA) methods [10] but some of its disadvantages are that it requires large amounts of solvents which are often toxic and flammable, it is tedious and time consuming. SPE is less time-consuming than LLE; however, SPE has the disadvantage that it still requires toxic organic solvents for the elution step. Recently, a new extraction technique, solid-phase microextraction (SPME) has been introduced by Pawliszyn and coworkers [11–17]. It has some advantages over the more conventional extraction techniques, LLE or SPE, as it is a solvent-free sample preparation technique so it minimizes the cost of high-purity solvents, it is easy to use and fast, and very small sample volumes are sufficient for the analysis.

The SPME process has two steps: the partitioning of the analytes between the sample matrix and a stationary phase which is coated on a fused-silica fiber, and the desorption of the trapped analytes into the analytical instrument. In the first step, the coated fiber is exposed to the aqueous sample or the

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headspace above it [14,18] for a certain period of time which depends on the analyte and the matrix, and which allows the analytes to be absorped according to their affinity towards the fiber coating. After the extraction step, the fiber is removed from the sample and transferred into the injection port of a gas chromatograph for the thermal desorption of the analytes followed by their separation and quantitation. The SPME process has also been successfully automated with minor modifications [19,20].

SPME has been successfully used to analyze a wide range of pollutants, such as BTEX (benzene, toluene, ethylbenzene and xylene) [12,14,21,22], phenols [23,24], polycyclic aromatic hydrocarbons (PAHs) [14,25] or pesticides [18,20,26–32]. These applications used different fiber coatings, but the most common was the polydimethylsiloxane (PDMS) which is relatively non-polar so it is useful for non-polar compounds and it is available in thicknesses ranging from 15 to 150 μm. For more polar analytes, such as phenols [24], and several pesticides, such as triazines [27,28] a polyacrylate coating has been used since it is a more hydrophilic fiber.

The main objective of this work is to develop a method to determine pesticides in aqueous samples based on SPME with a polar polyacrylate-coated fiber and gas chromatography–mass spectrometry (GC–MS) analysis.

2. Experimental

2.1. Materials

The pesticides included in this study can be divided into various subgroups according to their chemical structure: triazines (ametryn, atrazine, prometryn and terbutryn), thiocarbamates (molinate) and organochlorine pesticides [α-HCH, δ-HCH, lindane (γ-HCH), aldrin, dieldrin, α-endosulfan, β-endosulfan, heptachlor and heptachlor epoxide]. All pesticide standards used in this study were of 98–99% purity and purchased from Riedel-de Häen (Seelze, Germany) and they were used to prepare stock standards of 2000 mg l^{-1} in ethyl acetate, which was of PAR quality (for residue analysis) (Panreac, Barcelona, Spain). These standards were stored at 4°C and they were used to prepare dilute standard solutions and to spike water samples to the required concentrations.

Water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Helium carrier gas (99.995% quality) was supplied by Carburos Metálicos (Tarragona, Spain).

The SPME device was purchased from Supelco (Bellefonte, PA, USA). The fiber selected for this study was coated with 85-μm of polyacrylate. A magnetic stirring and heater unit from Selecta (Abrera, Spain) for stirring the water samples during the SPME process was used.

2.2. Instrumentation

GC analyses were performed using a Hewlett-Packard (Palo Alto, CA, USA) 5890 gas chromatograph equipped with an HP5972 mass spectrometer. A split/splitless injector in the splitless mode was used and it was held isothermally at 250°C. A merlin microseal high-pressure septum from Hewlett-Packard and an insert liner of 0.75 mm I.D. were used. Analytes were separated using a Hewlett-Packard HP-1 fused-silica capillary column (cross-linked methylsilicone film) of 30 m×0.25 mm with a phase thickness of 0.25 μm, which was inserted directly into the ion source of the mass spectrometer. The temperature programme used for the analysis was as follows: the initial temperature was 60°C, which was increased to 150°C at 25°C/min, and then to 205°C at 2°C/min; the temperature of 205°C was maintained for 5 min. The detector was set at 280°C. Helium was the carrier gas maintained at a flow-rate of 2 ml min^{-1}.

The electron impact ionization conditions were: ion energy 70 eV and the mass range scanned was 50–425 under full-scan acquisition mode. Selected-ion monitoring (SIM) acquisition was carried out by monitoring the base peak of each pesticide. The MS was tuned to m/z 69, 219 and 502 for EI corresponding to perfluorobutylamine (PFTBA).

The data were acquired with the HP Chemstation equipped with the mass spectral libraries Hppest and Wiley 138 which were used to compare the experimental spectra obtained.

2.3. SPME procedure

The polyacrylate fiber was conditioned before initial application in the hot port of the gas chromatograph by heating it at 300°C for 3 h according to instructions provided by the supplier; this treatment removed the impurities present in the coating and introduced during the manufacture of the fiber.

For the SPME process, 4 ml vials were filled with 3.5 ml of aqueous samples containing the mixture of pesticides and with the addition of 5 g l^{-1} of NaCl. First the fiber was exposed to the stirred sample for an optimized absorption time of 45 min at 55°C and then it was removed from the sample and introduced into the GC injector where the thermal desorption of the analytes at 250°C for 2 min was carried out; for real samples the desorption was carried out for 5 min. Fibers were reused but after several extractions its performance may be affected by particulate matter, specially when real samples are analyzed. In the present work the fiber was used for all the optimization process and also to analyze about 30 real samples.

Prior to analysis, tap and river water samples were filtered through a 0.45 μm membrane filter (MSI, Westboro, MA, USA).

3. Results and discussion

3.1. Chromatographic separation

The chromatographic conditions used for the separation of the pesticides was optimized in a previous paper [9]. To determine the linearity of the chromatographic method, 1 μl of the standard solutions of the pesticides was injected. Using the full-scan acquisition mode and quantifying only the base peak of each pesticide, the presence of outliers was checked by a statistical criterion [33] and good linearity was observed in the range from 0.25 to 50 mg l^{-1} for most of the pesticides with correlation coefficients, r^2, between 0.991 to 0.999. The detection limits of the chromatographic method were calculated by another statistical criterion with k value equal to 6 [33] and the obtained values were between 0.02 mg l^{-1} for dieldrin and 0.4 mg l^{-1} for β-endosulfan. In order to increase the sensitivity, the SIM acquisition mode was also tested, the acquisition process was time-scheduled and the conditions were the same as in a previous study [9]. The linearity was checked in the interval from 0.010 to 20 mg l^{-1} and correlation coefficients, r^2, were between 0.995 to 1.000 and the detection limits, calculated as mentioned above, were between 0.9 μg l^{-1} for dieldrin and 6 μg l^{-1} for ametryn.

3.2. Optimization of SPME

The different parameters that can affect the SPME process (the exposure time of the fiber in the aqueous sample, the temperature of the extraction process, the effect of pH and the ionic strength of the sample and the time and temperature for the desorption of the analytes) were optimized under SIM acquisition mode. In this work sampling from headspace was no tested due to the different polarity of the compounds studied although previous studies [14,18] have shown the ability of this technique to concentrate some compounds.

The first step to be optimized was the time required for the analytes to reach equilibrium between the aqueous and the stationary phase. The absorption time profile was studied by monitoring the area counts as a function of exposure time, so the fiber was exposed to standard solutions of the analytes in a concentration of 3 μg l^{-1} for increasing time intervals in the range from 5 to 90 min. All the extractions were carried out at a temperature of 25°C and with continuous stirring in order to ensure that the aqueous sample is perfectly agitated and to reduce the equilibration times [34]. The pH of the sample was not adjusted and salt was not added. After the absorption process the analytes were thermally desorped into the injection port of a gas chromatograph at 250°C for 2 min.

From the results obtained it can be seen that the equilibrium is compound dependent and can vary significantly among the different compounds. A desorption time of 45 min was selected although for some of the analytes the equilibrium was not reached even after 90 min. An exposure time of 45 min is a reasonable compromise for an acceptable time and good response of the analytes. For the triazine

herbicides and molinate it can be seen that the peak area at first rises significantly as the absorption time increases but after 30 min it approaches a plateau. The relative peak response of the triazine compounds is seen to decrease after extraction in comparison to a standard chromatogram; this has previously been observed by other authors [27,28] and may be explained by differences in the hydrophobicity, expressed by the octanol–water partitioning coefficient, P_{ow}. In general, for the organochlorine pesticides which are cyclodienes, except for β-endosulfan, the equilibrium times are greater than those for hexachlorocyclohexanes as has previously reported by other authors although they use a PDMS fiber [30].

As an illustrative example, Fig. 1 shows the equilibrium time profiles of the triazine and cyclodiene pesticides between the aqueous and the polyacrylate phase.

The next step was to optimize the absorption temperature. This parameter was determined by maintaining the exposure time of the fiber to the aqueous sample at 45 min and the other experimental parameters were the same as for the optimization of the absorption time. The study was carried out by varying the temperature in the range from 25 to 65°C. It was observed that at higher temperature some air bubbles appeared which can significantly affect the precision if they are adsorped at the stationary phase so they should be avoided and removed before the fiber is exposed to the sample.

From the results obtained from studying the

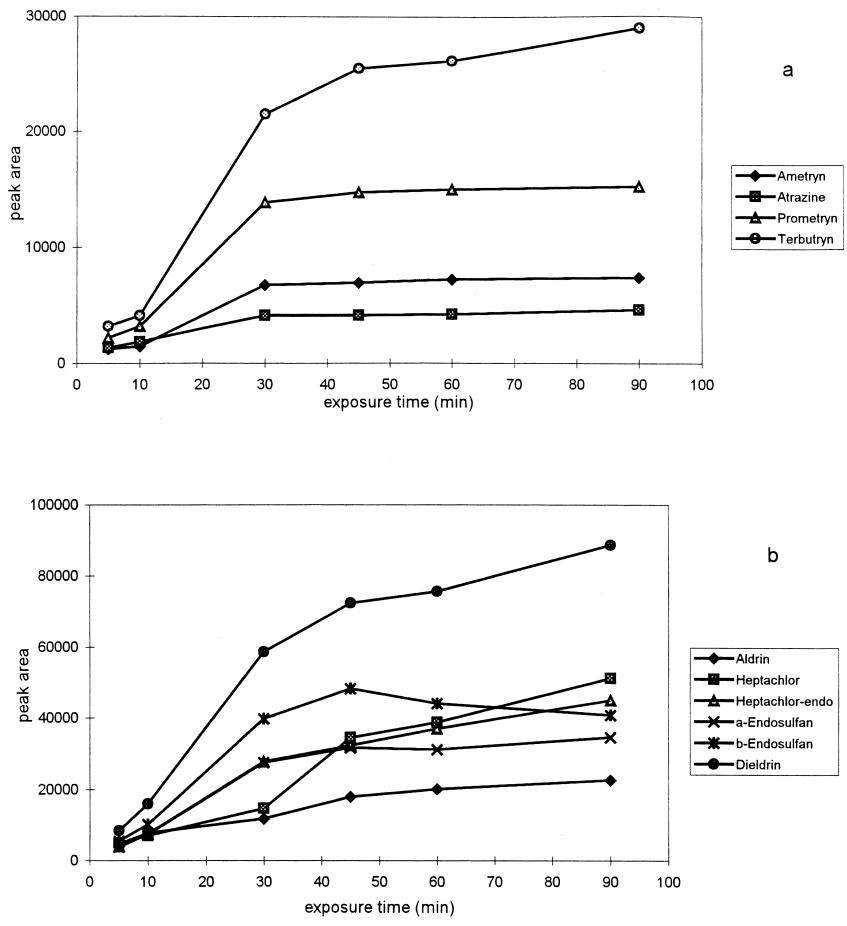

Fig. 1. Time dependence for the equilibration of the triazine (a) and the cyclodiene (b) pesticides between the aqueous and the polyacrylate phase. For experimental conditions, see Section 2.

optimum temperature of the extraction process it can be seen that the effect of this parameter varies substantially for the different pesticides. The temperature chosen in this study was 55°C since under these conditions the peak area for most of the pesticides had a maximum value. There are some compounds, such as α-HCH and β-HCH for which the temperature of the extraction step does not have a significant effect but for other compounds, such as aldrin, dieldrin, heptachlor, prometryn and terbutryn, the variation in this parameter causes a pronounced change in their response.

After the absorption conditions had been determined, the desorption conditions, the temperature and the time required to completely desorb all the analytes from the fiber coating, were optimized. Firstly, the desorption temperature was determined by testing different values between 225 and 275°C while maintaining a constant desorption time of 2 min and for the extraction process the time of fiber exposure was maintained at 45 min at 55°C. A temperature of 250°C was chosen since this provides the best results for most of the analytes although for aldrin, heptachlor and heptachlor epoxide the maximum peak area values were obtained at high desorption temperatures. On the other hand, the response for other compounds such as lindane, prometryn and terbutryn was seen to decrease at desorption temperature above 250°C. This may be because the desorption of an analyte from an SPME fiber depends on its boiling point and also on the temperature of the injection port; those compounds with higher boiling points are successfully desorbed at higher temperatures. Fig. 2 shows the effect of

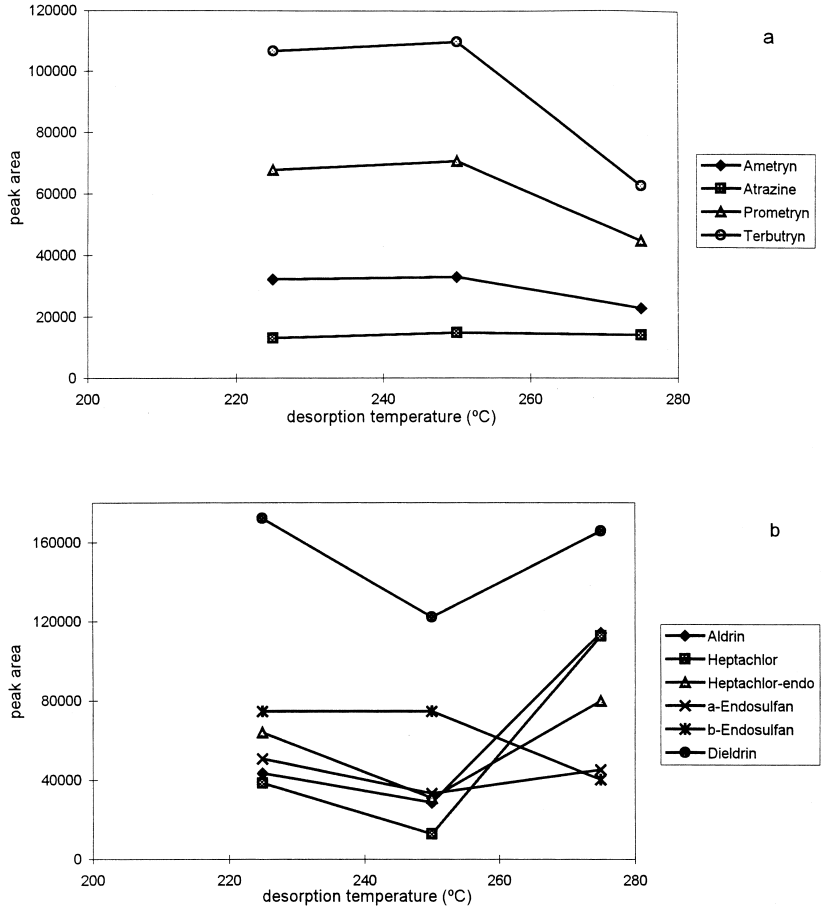

Fig. 2. Effect of varying the desorption temperature for the triazine (a) and cyclodiene (b) pesticides included in this study.

varying the desorption temperature for the triazine and cyclodiene pesticides included in this study.

Another step was to ensure that the exposure time of the fiber in the GC injector was long enough to completely desorb the compounds from the stationary phase. This parameter was studied by leaving the polyacrylate fiber in the injector for lengths of time ranging from 1 to 5 min. The experiments were carried out at 250°C. A desorption time of 2 min was chosen because after this period of time all the pesticides are completely desorbed and by increasing the value of this parameter the response is kept constant. Another important consideration of the desorption process is the presence of carryover. That is to say, if the analytes are not completely desorbed they are left in the coated phase and may give false signals in subsequent analyses; after 2 min of desorption no carryover effect was observed.

The pH and the ionic strength of the sample, which may affect SPME, were also optimized. Firstly, the effect of the pH was analyzed using different samples in the range from 2 to 8 by adding hydrochloric acid or sodium hydroxide, respectively. When the pH was lowered to 2, the response obtained for some of the analytes such as aldrin and heptachlor epoxide increased, but for other compounds such as lindane, heptachlor, α-endosulfan, β-endosulfan or molinate, the acidic conditions lead to a considerable decrease in the response obtained. At pH 8 significant differences were obtained for all the pesticides under study, as happens at pH 2. For some pesticides such as prometryn and terbutryn there is a considerable increase in their corresponding response, but for another pesticides such as dieldrin, lindane, α-endosulfan and β-endosulfan a basic pH value decreases the corresponding peak area. Further analyses were carried out without adjusting the pH. It was maintained at 6, since most analytes have an acceptable response at this value, although some compounds respond better under acidic or basic conditions. Fig. 3 shows the effect of the pH value on the extraction efficiency for the cyclodiene and hexachlorocyclohexane pesticides.

Finally, the addition of sodium chloride was studied, because previous studies have been shown that for some compounds higher ionic strength

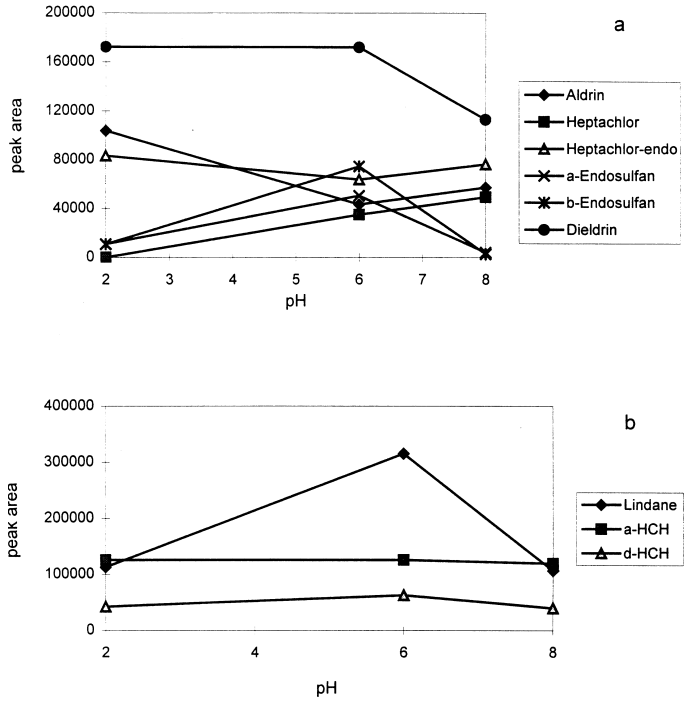

Fig. 3. Effect of varying the pH of the sample for the cyclodiene and hexachlorocycloxenane pesticides included in this study.

increases retention [8,24,27,31,32]. The effect of the ionic strength on the extraction efficiency was determined by analyzing samples which contained different amounts of NaCl in the range from 0 to 20 g l^{-1}. The results obtained showed that the addition of sodium chloride improves extraction, in particular for those compounds with a lower hydrophobicity, because the higher their ionic strength, the lower their solubility in the aqueous phase and this improves the retention of the analytes into the fiber coating. It was decided to add 5 g l^{-1} because this quantity provides acceptable results for all the pesticides under study and, for some compounds recoveries were greater than when no NaCl was added, especially for the organochlorines which are cyclodienes, the hexachlorocyclohexanes α-HCH and β-HCH and the triazines prometryn and terbutryn. The addition of higher concentrations of salt to the sample provided similar results to the ones obtained for lower concentrations and for some compounds, such as dieldrin, heptachlor and terbutryn, it even caused a decrease in the peak area.

The linearity of the response in Milli-Q water for MS in both modes of acquisition, SIM and full-scan, was studied under optimum conditions. Using SPME and quantifying the base peak of each compound in the scan acquisition mode, the linearity of response for most of the compounds was in the range from 0.07 to 30 μg l^{-1} and the correlation coefficients, r^2, were higher than 0.994. The limits of detection, calculated using a statistical criterion [33] and differed considerably for all the compounds studied, ranging between 0.01 to 0.1 μg l^{-1}. When the SIM acquisition mode was applied the linearity was found to be between 0.005 and 10 μg l^{-1} for most compounds and correlation coefficients, r^2, from 0.995 to 0.999; the limits of detection calculated were between 0.001 to 0.01 μg l^{-1}.

3.3. Analysis of real samples

The performance of the method for real samples was tested in tap and Ebro river water samples. First, a blank of tap water was analysed in order to verify the presence of different peaks in the corresponding chromatogram at the same retention times as the pesticides being studied, but the peaks that appear could not be assigned to any of them, although a peak at the same retention time as heptachlor appeared and this meant that this pesticide could not be quantified. Some of the non-identified peaks were assigned to unknown matrix components which compete with the pesticides to be absorbed into the fiber and there are also some peaks due to fiber interferences. When real samples are analyzed, the analytes in the hot injector of the gas chromatograph were desorbed for a period of 5 min to avoid possible memory effects. The recoveries for tap water obtained under the previously optimized SPME conditions and for GC–MS-SIM and referred to Milli-Q water were between 72 and 99%; from these results it can be seen that the process is not influenced by the matrix. When tap water spiked with different levels of pesticides was analyzed under full-scan acquisition, good linearity was obtained for most compounds between 0.07 and 30 μg l^{-1}, and r^2 values were between 0.991 and 0.999; the limits of detection were calculated to be between 0.01 to 0.2 μg l^{-1}. The results obtained for tap water under full-scan are shown in Table 1. Fig. 4 shows the chromatograms obtained when tap water spiked at 0.5 μg l^{-1} and unspiked was analyzed by SPME–GC–MS under full-scan acquisition.

When SIM acquisition mode was used the linearity of the response was checked in the range from 0.005 to 10 μg l^{-1} and the responses for most of the pesticides were linear in the range studied with r^2 values between 0.995 to 0.999. The limits of detection were between 0.002 to 0.01 μg l^{-1}. Table 1 shows the results obtained for tap water using SIM acquisition mode. Fig. 5 shows the chromatogram obtained for the analysis of an unspiked tap water sample and tap water spiked at 0.1 μg l^{-1} level in the SIM acquisition mode. The methods developed enable levels of 0.1 μg l^{-1} to be determined in tap water as required by EU rules.

The repeatability of the method was determined by performing five extractions for tap water with a concentration of 0.5 μg l^{-1} of pesticides and relative standard deviation (R.S.D.) values were between 6 and 21% for MS under full-scan acquisition and between 10 and 24% for SIM. The reproducibility between days was also checked and R.S.D. values ($n=5$) were from 9 to 36 and 12 to 34% for MS under full-scan and SIM acquisition modes, respectively. It should be pointed out that the US EPA

Table 1
Linearity range, correlation coefficients and limits of detection obtained for tap water by MS using full-scan and SIM acquisition modes

Compound	Full-scan			SIM		
	r^2	Linearity range ($\mu g\ l^{-1}$)	LOD ($\mu g\ l^{-1}$)	r^2	Linearity range ($\mu g\ l^{-1}$)	LOD ($\mu g\ l^{-1}$)
Molinate	0.997	0.20–30	0.08	0.999	0.005–10	0.002
α-HCH	0.998	0.07–30	0.02	0.999	0.005–10	0.001
Atrazine	0.999	0.50–30	0.10	0.995	0.05–10	0.01
Lindane	0.995	0.07–30	0.02	0.998	0.02–10	0.005
δ-HCH	0.997	0.07–30	0.02	0.997	0.005–10	0.002
Heptachlor	0.997	0.07–30	0.01	n.q.[a]		
Ametryn	0.991	0.50–30	0.20	0.99	0.05–10	0.01
Prometryn	0.994	0.07–30	0.02	0.998	0.05–10	0.02
Terbutryn	0.995	0.07–30	0.02	0.998	0.05–10	0.01
Aldrin	0.992	0.07–30	0.01	0.996	0.005–10	0.001
Heptachlor-endo	0.993	0.07–30	0.02	0.999	0.05–10	0.01
α-Endosulfan	0.998	0.07–30	0.01	0.998	0.05–10	0.01
Dieldrin	0.999	0.05–30	0.02	0.995	0.0005–10	0.002
β-Endosulfan	0.993	0.05–30	0.02	0.997	0.05–10	0.01

[a] n.q.: Not quantified.

requires a method to have an R.S.D. of under 30% [31] so the precision of SPME method was deemed acceptable for all the compounds under study.

The performance of the method was also validated for the analysis of Ebro river water samples. None of the target analytes were detected in a blank of this sample, although a peak at the same retention time as heptachlor appeared and this meant that this pesticide could not be quantified; this peak was assigned to a matrix interference. The linearity of the response was checked for an Ebro river sample under full-scan acquisition in the same range as for tap water with correlation coefficients between 0.990 to 0.999 and detection limits were between 0.07 to 0.2 $\mu g\ l^{-1}$. For SIM acquisition, the results obtained were also similar to the corresponding values for tap water; the linearity range was between 0.005 and 10 $\mu g\ l^{-1}$ with correlation coefficients higher than 0.991. The limits of detection were calculated to be between 0.002 to 0.2 $\mu g\ l^{-1}$. The precision of the method, expressed in terms of repeatability and reproducibility was determined for river water in the same way as for tap water and the corresponding values were similar to the ones obtained with tap water.

Different Ebro river and Ebro delta waters were also analyzed, first by GC–MS under full-scan conditions and then under SIM conditions, and molinate was detected in some of them. For instance, Fig. 6 shows the total ion chromatogram (TIC) obtained under full-scan acquisition mode for a river Ebro water sample. A peak at the same retention time as molinate appear in the chromatogram and the assignation could be possible through the comparison between the experimental spectra and that of the standard. The insert of Fig. 6 also shows the spectrum corresponding to the peak of molinate. However, it could not be quantified because molinate was found in a concentration between the detection limit and the quantification limit of the method. Quantification was possible when SIM detection was used and the concentration of molinate resulting from an average value of four different measurements was found to be 0.13 $\mu g\ l^{-1}$ and the R.S.D. value was calculated as 13%.

4. Conclusions

In this study, SPME has been used to determine different classes of pesticides in aqueous samples. A 85-μm polyacrylate coated silica fiber was used. The

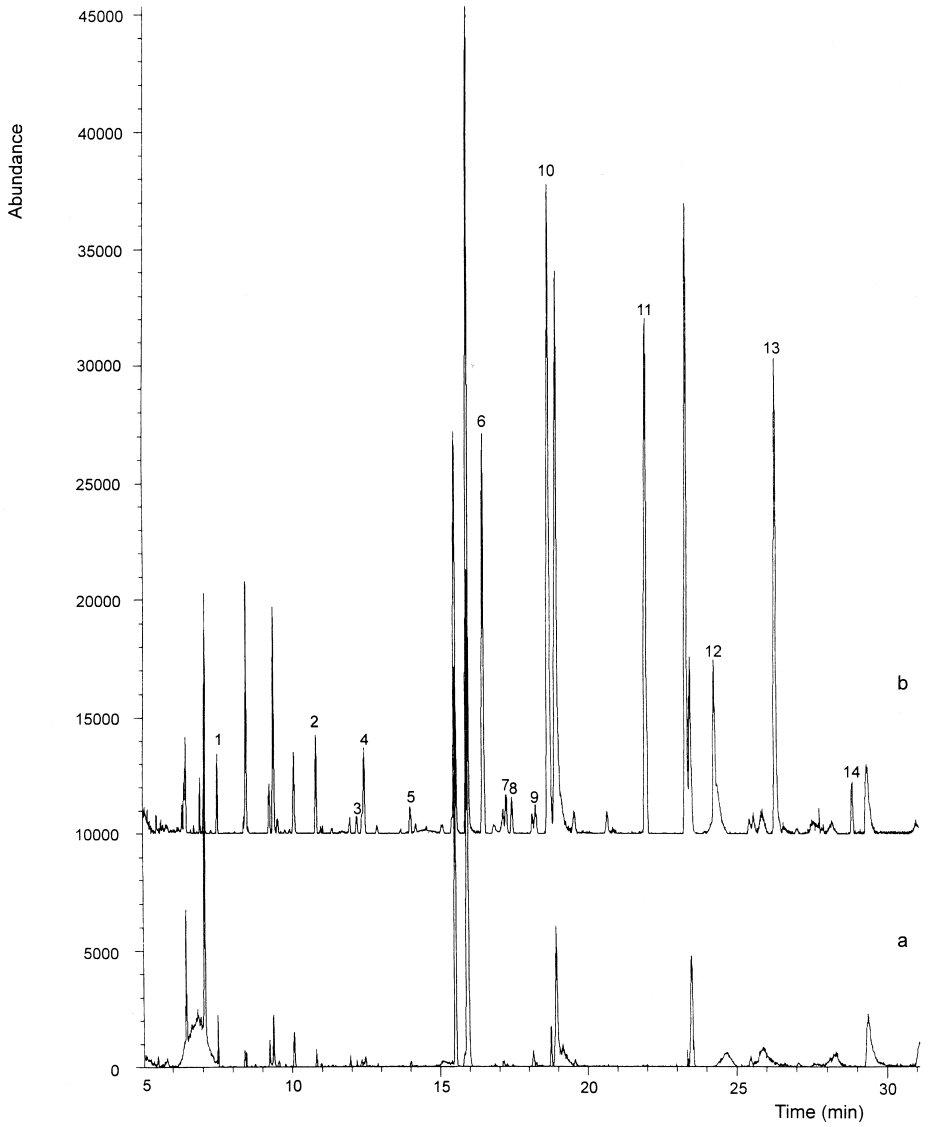

Fig. 4. Chromatograms obtained by SPME–GC–MS under full-scan acquisition of (a) tap water and (b) tap water spiked with a standard solution of pesticides at 0.5 μg l^{-1} level. Peak assignment: (1) molinate, (2) α-HCH, (3) atrazine, (4) lindane, (5) δ-HCH, (6) heptachlor, (7) ametryn, (8) prometryn, (9) terbutryn, (10) aldrin, (11) heptachlor-endo, (12) α-endosulfan, (13) dieldrin, (14) β-endosulfan.

effect of several parameters on SPME has been investigated. The optimum conditions for SPME were found to be a temperature of 55°C and the time of 45 min for the absorption process and 250°C for 2 min for the desorption process. The pH value of the sample need not to be adjusted before the extraction and the addition of 5 g l^{-1} of NaCl increases the amount extracted of most pesticides.

The combination of SPME with GC–MS either in the full-scan and SIM acquisition modes enables very low limits of detection to be achieved. Detection limits of pesticides in real samples of 0.01 μg

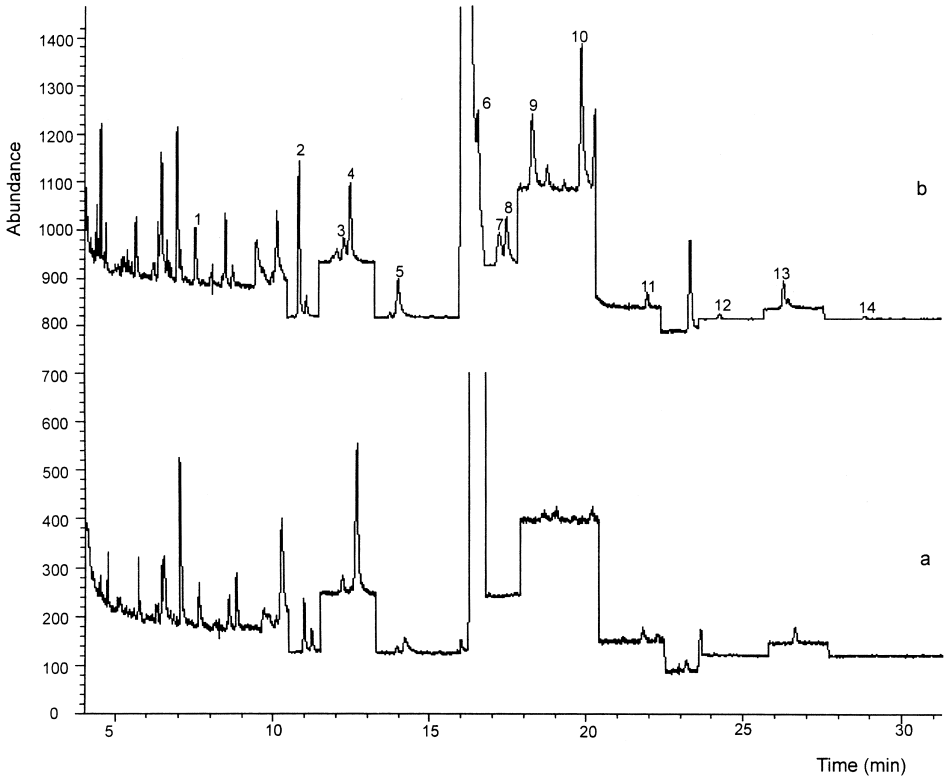

Fig. 5. Chromatograms obtained by SPME–GC–MS under SIM acquisition of (a) tap water and (b) tap water spiked with a standard solution of pesticides at 0.1 μg l^{-1} level. For peak designation, see Fig. 4.

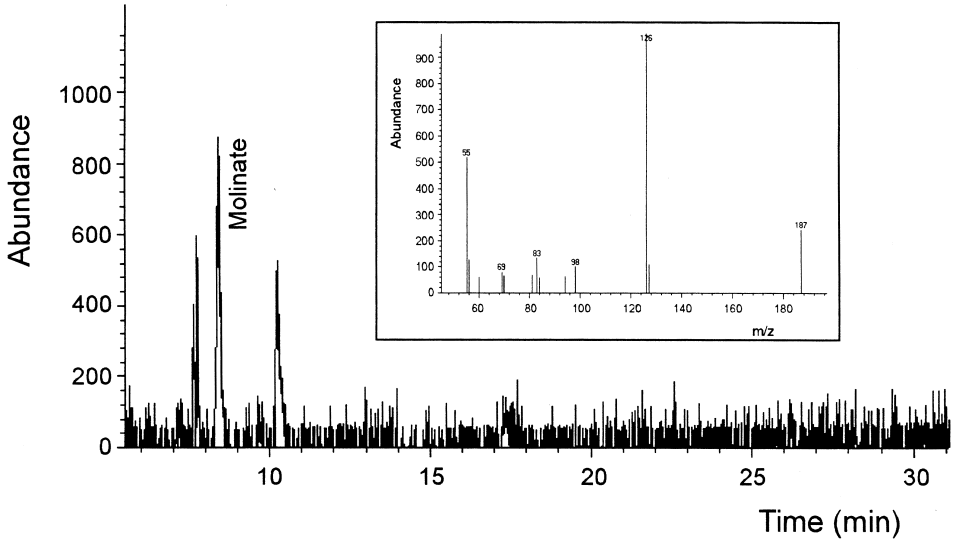

Fig. 6. TIC obtained by SPME–GC–MS under full-scan acquisition of a river Ebro water sample. The insert shows the spectrum of the peak molinate.

l^{-1} for GC–MS under full-scan acquisition and 0.002 μg l^{-1} under SIM may be reached for most compounds.

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