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Optimisation of a solid-phase microextraction procedure for the determination of triazines in water with gas chromatography–mass spectrometry detection☆

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Abstract

A procedure based on solid-phase microextraction (SPME) and gas chromatography–mass spectrometry, operating in the chemical ionisation mode, was developed and optimised in order to determine 10 triazines in water samples. Five different SPME fibers available for analysis [polydimethylsiloxane (PDMS) 100 μm, polyacrylate (PA) 80 μm, PDMS–divinylbenzene (DVB) 65 μm, Carbowax (CW)–DVB 65 μm, and Carboxen (CAR)–PDMS 75 μm] were tested, and PDMS–DVB was selected. To enhance the sensitivity of the SPME, variables affecting adsorption and desorption steps such as temperature, time, pH and ionic strength of the solution were optimised. Detection limits obtained were ranged between 2 and 17 ng l^{-1}, and precision values were below 8% for the selected PDMS–DVB fiber. The optimised method was applied to real water samples and no triazines were detected.

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

1. Introduction

Pollution of surface and ground water is a problem causing increasing environmental concern. Thus, the determination of pesticides is receiving increasing attention nowadays because of their toxicity. Herbicides such as triazines are applied as pre and post emergent weed control agents to improve crop yields, and this group of herbicides is one of the most widely used soil-applied herbicides in Europe. The pollution of water by pesticides is governed by the characteristics of the compounds, properties of the medium, and external factors such as rain, wind or topology of the zone. The most important physicochemical properties of the pesticides are their solubility in water, capacity to be retained by the organic matter of the soil, and degradation rate. Herbicides have half-lives of weeks to several months, and under environmental conditions are degraded to more water-soluble compounds [1,2].

Normally, the determination of pesticides is carried out by gas chromatography (GC) using mainly mass spectrometric (MS) detection [3], electron-cap-

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ture detection (ECD) [4] and nitrogen–phosphorus detection (NPD) [5]. Permissible levels in the European Union (EU) countries are 0.1 μg l^{-1} for each pesticide taken individually, and 0.5 μg l^{-1} for the total pesticides present [6], and a sensitive analytical technique is therefore necessary for their quantification in water samples. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have been the most frequently used extraction methods as has been described in many papers and in several US Environmental Protection Agency (EPA) methods [7–11]. However, these methods have important disadvantages: LLE requires large amounts of solvents, which are frequently toxic, and it is time-consuming and laborious. SPE also has the disadvantage of having to use an organic solvent for the elution step, and it can be expensive since the cartridges are discarded after one extraction. In addition, SPE offers high blank results and the entire analysis can be lengthy with intermediate washing and drying stages slowing the process. Thus, solid-phase microextraction (SPME), introduced by Pawliszyn and co-workers [12,13], appears to be an effective alternative to these classical extraction methods. SPME is not a solvent sample preparation technique, it is easy and fast, automated, and it does not require large amounts of samples for the analysis. This technique has been successfully applied in the environmental field [14–16], and especially to the determination of pesticides in water samples [4,17–23], and herbicides such as oxadiazion [24], phenylurea [25], chlorinated phenoxy acid herbicides [26], alachlor [27], dinitroaniline herbicides [28], and triazines [3,14,29–35].

From the bibliographic data it can be observed that Eisert and Levsen [33] determined four triazine herbicides using the polyacrylate (PA) fiber and GC with flame ionisaton detection (FID). Ferrari et al. [34] have realised an inter-laboratory validation of the SPME procedure for the determination of nine triazines, testing three different fiber coatings [PA, PDMS–DVB and CW–DVB]. In the inter-laboratory study the CW–DVB fiber was selected. Aguilar et al. [3] determined a mixture of pesticides (four of them were triazines) by means of SPME with a PA fiber and GC–MS. Hernández et al. [30] analysed seven herbicides (five of them were triazines), comparing four fibers [PA, PDMS, CW–DVB and CAR–PDMS]. These authors selected the CW–DVB fiber because it proved to be more efficient in the extraction of several herbicides than other fibers. Barnabas et al. [32] analysed four triazines by means of SPME comparing two fibers with the same coating but a different film thickness (PDMS 100 and 7 μm), obtaining better extraction efficiencies with PDMS 100 μm. Dugay et al. [14] analysed a mixture of pesticides, of which three were triazines, using SPME and testing six fibers (PA, PDMS of 100, 30 and 7 μm, CW–DVB and PDMS–DVB) obtaining in general greater extracted amounts with the PDMS–DVB fiber. In a recent work, Gonçalves and Alpendurada [35] determined four groups of pesticides (including seven triazines), testing six different SPME fibers: PA, PDMS of 100, 30 and 7 μm, CW–DVB and PDMS–DVB. The authors concluded that triazines were better extracted with PDMS–DVB.

The aim of this work was the optimisation of a SPME procedure for the determination of triazines since all the methods developed do not include a wide group of these compounds. The studied compounds were selected on the basis of the frequency of use by the farmers, and the legal importance of these herbicides. The optimisation of the SPME procedure included: fiber selection (testing five different fibers), desorption temperature and time, adsorption time, pH and ionic strength of the sample. Finally, the application of the SPME–GC–MS method for the determination of these compounds in waters at the real concentration level was developed.

2. Experimental

2.1. Chemicals

All herbicides were obtained from Riedel-de Haën (Seelze-Hannover, Germany) with a purity higher than 98%. The triazines studied were the following: (1) prometon, (2) trietazine, (3) propazine, (4) terbutylazine, (5) atrazine, (6) prometryn, (7) terbutryn, (8) simazine, (9) ametryn, and (10) simetryn. A stock solution of each herbicide was prepared in methanol at 100 mg l^{-1}. A working standard solution of all triazine compounds (500 μg l^{-1}) was

prepared by volume dilution with methanol. All solutions prepared were stored in darkness at 4 °C.

HPLC-grade methanol was from Merck (Darmstadt, Germany). Ultrapure Milli-Q water (Millipore, France) was used to prepare the working aqueous solutions.

2.2. Equipment

An automatic SPME device used in all extractions was purchased from Supelco (Bellefonte, PA, USA). Five different SPME fibers from Supelco were studied: PDMS 100 μm, PA 80 μm, PDMS–DVB 65 μm, CW–DVB 65 μm, and CAR–PDMS 75 μm. The fibers were conditioned prior to use as the manufacturer recommends in the gas chromatograph injection port, heating them at temperatures between 250 and 300 °C for 30 to 60 min.

Chromatographic analysis was performed using a Varian CP-3800 gas chromatograph equipped with a Varian 1079 split–splitless injector, and a Varian Saturn 2000 mass spectrometric detector. A gas chromatography capillary column 60 m×0.25 mm I.D., 0.5 μm film thickness (DB-WAX) from Agilent Technologies (Folsom, CA, USA) was used. The column oven temperature program was as follows: 40 °C for 3 min, ramped at 20 °C min^{-1} to 120 °C and held for 3 min, and ramped at 5 °C min^{-1} to 240 °C and held for 31 min.

Helium was used as carrier gas with an optimised flow of 2 ml min^{-1}. The mass detector was used in the chemical ionisation (CI) mode, using methanol as reagent gas, and the conditions were the following: transfer line temperature 240 °C, electron multiplier voltage 100 V, and mass range for full-scan experiments 180–300 m/z. For each compound, the most abundant ion produced by chemical ionisation was monitored: 226 for prometon, 230 for trietazine, propazine, and terbutylazine, 216 for atrazine, 242 for prometryn, and terbutryn, 202 for simazine, 228 for ametryn, and 214 for simetryn. The detector was delay the first 35 min. All experiments were developed using 2-ml amber glass vials.

To determine the elution order, a standard solution of 20 μg l^{-1} of each triazine was injected using the mass detector in the electron impact ionisation (EI) mode and full-scan acquisition. Then, triazine peaks were compared with those obtained by means of CI using methanol as chemical reagent, observing that better results were obtained with CI.

2.3. SPME procedure

To test the different fibers used, variables that affect the SPME procedure were modified. Thus, desorption of the herbicides retained in the fiber was optimised as a function of the temperature (ranged according to manufacturer) and time (ranged between 1 and 45 min). The effect of the pH on the extraction efficiency was investigated by varying the pH between 3 and 8.9. The effect of the ionic strength was studied adding NaCl at three levels: 0, 5.6 and 10.4%. When NaCl was used for the salting out effect, after each injection the SPME fiber was washed with Milli-Q water to prevent salt accumulation on the fiber surface and to increase the fiber lifetime. The adsorption time profiles were obtained by ranging the extraction time from 1 to 120 min. Once optimised the SPME procedure, precision, reproducibility, linear range, and detection limit values were obtained for the fiber selected.

Spiked water samples at 20 μg l^{-1} of each triazine used in the optimisation procedure were prepared by adding an appropriate volume of the methanol working standard solution of triazines.

2.4. Real water samples

Surface water samples collected from different areas were analysed in triplicate using the recommended SPME procedure. Prior to analysis, water samples were filtered through a 0.45-μm membrane filter from Millipore (Bedford, MA, USA).

3. Results and discussion

3.1. SPME optimisation

In order to select the optimal conditions for the determination of a group of 10 herbicides an optimisation procedure was realised. Thus, the different parameters that affect the extraction efficiency in both the extraction and desorption steps were optimised: adsorption time, desorption temperature and

time, and the effect of pH and ionic strength, were optimised step-by-step for the fiber selected.

Selection of an appropriate fiber is essential for the establishment of a SPME method, and depends on the chemical nature of the target analytes. Five fiber coatings: PA, PDMS, CW–DVB, PDMS–DVB and CAR–PDMS were evaluated to select the most suitable for the method, by analysing a spiked water sample at a level of 20 μg l^{-1} with each triazine. The extraction time was 45 min at room temperature, and the desorption temperature was 240 °C for 5 min for all fibers. The mean peak areas of three replicate and the confidence interval for the mean at 95% confidence level, for each analyte with the different fibers are shown in Table 1. As can be seen, the best overall results were obtained with the bipolar PDMS–DVB fiber, which gave higher peak areas for all the analytes than the remaining fibers. Another fiber with high extraction efficiency was CAR–PDMS, while the worst results shown were those obtained with the PDMS and CW–DVB fibers. The use of the PDMS–DVB fiber for the SPME increases the signal up to 560 times (prometryn) with respect to the signal obtained using the CW–DVB fiber. The lowest increase was obtained for simazine (14.8 times higher signal). The benefits of this fiber for the analysis of triazines have been demonstrated in a recent paper [35]. The PDMS–DVB fiber was therefore selected for further studies.

The next step was the optimisation of the desorption conditions for the PDMS–DVB fiber. During the desorption process, the temperature of the GC injector must be sufficiently high and the desorption time long enough to completely desorb all extracted analytes. Nevertheless, a maximum temperature is recommended by the suppliers to avoid the degradation of the polymeric fiber. To determine the optimal desorption temperature, after extraction the fiber was desorbed ranging the temperature of the injector from 200 to 250 °C. Temperatures higher than 250 °C were not tested because this is the maximum working temperature of the capillary column. The temperature selected was 240 °C as compromising value to avoid thermal degradation of the fiber and to increase the lifetime. Different desorption times (1–45 min) were tested, the best results being obtained for 5 min since after this time no significant increase was observed in the response. To ensure that the exposure conditions were sufficient to achieve complete desorption of the compounds from the fiber, an empty vial was injected after each sample injection. Under the optimal desorption conditions no carryover effect was observed.

Previous studies have shown that for some compounds a higher ionic strength improves the retention of the analytes in the fiber coating, especially for the most hydrophobic compounds [3,30,31,34,36]. In a

Table 1
Extraction efficiencies expressed as mean peak area counts and confidence interval of the mean (at 95% of confidence level) of five different SPME fiber coatings for sampling triazines (each triazine at 20 μg l^{-1})

Compound	Fiber coating				
	PDMS	CAR–PDMS	PDMS–DVB	CW–DVB	PA
Prometon	26.3[a]±0.5[b]	209.5±3.1	1990.8±35.8	33.2±0.6	30.3±0.6
Trietazine	113.2±2.0	3196.3±58.2	8050.4±141.1	40.0±0.7	359.1±6.2
Propazine	10.8±0.5	438.6±21.8	1185.5±53.2	8.8±0.3	127.0±6.5
Terbutylazine	54.3±1.2	1040.7±32.3	2655.7±82.3	19.3±0.7	270.2±8.9
Atrazine	4.5±0.3	117.7±7.1	140.4±11.0	3.1±0.2	43.1±3.3
Prometryn	102.8±2.5	1489.3±36.1	7082.3±165.4	12.3±0.3	325.7±7.1
Terbutryn	166.7±6.4	2278.3±101.4	9441.0±422.7	54.4±2.7	481.9±20.7
Simazine	3.1±0.2	49.1±3.9	50.2±3.7	3.4±0.3	19.0±1.3
Ametryn	35.7±0.7	712.7±12.7	3305.9±65.4	17.8±0.4	153.4±2.7
Simetryn	13.0±0.6	255.3±9.8	978.2±32.7	9.6±0.4	47.9±2.4

Experimental conditions for all fibers were as follow: 1.2 ml of sample extracted for 45 min at room temperature with agitation, neither salt addition nor pH adjustment, and desorption for 5 min at 240 °C

[a] Peak area counts $\cdot 10^3$ (three replicates).

[b] Confidence interval of the mean (at 95% of confidence level).

recent paper, Hernández et al. [30] using an optical microscope observed that when using a higher salt content a very fast degradation of the fiber occurred. A complete removal of the fiber coating was produced after 15 extractions using a sodium chloride content of 30%. For this reason, we studied the effect of the addition of sodium chloride varying the percentage of this salt at three levels: 0, 5.6 and 10.4%. The effect of salt concentration on the extraction for the PDMS–DVB fiber coating can be seen in Table 2, that shows the mean peak area of three replicate of each triazine and the confidence interval for the mean at 95% confidence level. Better response was obtained by increasing the amount of salt. From Table 2 we selected 10% sodium chloride.

Table 2
Influence of the salt content on the SPME response expressed as peak area count for the PDMS–DVB fiber

Compound	NaCl content (%)		
	0	5	10
Prometon	29.0[a]±0.8[b]	58.8±1.3	105.1±2.4
Trietazine	115.1±2.2	246.0±4.6	313.2±5.2
Propazine	22.8±1.4	32.9±1.8	80.8±3.7
Terbutylazine	45.2±1.3	91.3±2.7	132.9±3.5
Atrazine	17.7±1.5	25.4±1.4	33.5±2.1
Prometryn	112.3±2.4	234.8±5.3	336.6±7.6
Terbutryn	232.3±10.4	305.3±12.4	376.2±17.8
Simazine	7.9±0.8	13.7±1.4	23.5±2.2
Ametryn	66.2±1.3	119.0±2.9	178.9±3.3
Simetryn	19.8±0.9	30.1±1.1	63.0±2.2

Response is expressed as mean area peak counts ($\cdot 10^6$)±the confidence level at 95% confidence level of the mean (three replicates were injected). Experimental conditions were: 1.2 ml of sample extracted for 45 min at room temperature, and 5 min of desorption at 240 °C.

[a] Mean peak area counts of three replicates ($\cdot 10^5$).

[b] Confidence interval of the mean (at 95% of confidence level).

According to some authors, pH is a controlling variable for ionisable compounds such as herbicides [3,37,38]. Triazines are basic herbicides, and it is therefore assumed that at basic pH values better extractions are obtained. The effect of the pH was analysed using samples with pH values ranging between 3 and 8.9 by addition of nitric acid or sodium hydroxide solutions. Table 3 shows the effect of the pH value on the extraction efficiency for the PDMS–DVB fiber. The pH was maintained at 6 since most analytes have an acceptable response at this value, and increasing the pH did not lead to higher extraction efficiencies.

Once the SPME parameters were in the most favourable conditions, the extraction time necessary to reach the equilibrium between the aqueous and the stationary phase for the analytes was optimised. The adsorption time profile was obtained by plotting on a graph the peak area counts for each herbicide when varying the exposure time. Time profiles are dependent on the nature and the thickness of the fiber, as well as on the analyte. Therefore, PDMS–DVB fiber was exposed to a standard solution of the analytes at a concentration of 20 μg l^{-1}, the exposition time ranging from 1 to 120 min, without pH adjustment and with 10% of NaCl. After adsorption, analytes were desorbed at 240 °C for 5 min.

Fig. 1 shows the adsorption time profiles for each analyte (1 μg l^{-1}) using the higher-efficiency PDMS–DVB fiber. It can be seen from the curves that most compounds are no longer under equilibrium conditions even after 120 min. The extraction increases notably with time up to 60 min, and slightly thereafter between 60 and 120 min. However, a compromise extraction time of 60 min was selected in order to use an acceptable analysis time with good extraction efficiencies of the analytes. Therefore, it was possible to develop one run while the extraction of another sample was carried out. The application of SPME under non-equilibrium con-

Table 3
Effect of pH on the SPME the extraction efficiency, expressed as area peak counts, with the PDMS–DVB fiber

Compound	pH		
	3.0	5.8	8.9
Prometon	10.8[a]±0.2[b]	18.6±0.4	16.9±0.3
Trietazine	20.3±0.5	34.0±0.8	31.4±0.6
Propazine	10.4±0.7	16.1±0.9	15.4±1.0
Terbutylazine	17.7±0.6	27.9±1.2	25.3±0.9
Atrazine	6.2±0.3	9.5±0.5	9.2±0.7
Prometryn	24.4±0.6	37.7±0.9	35.8±1.0
Terbutryn	21.4±1.2	42.3±2.2	35.5±1.8
Simazine	8.8±0.8	10.6±1.0	10.5±0.9
Ametryn	15.2±0.6	22.1±0.7	20.1±0.6
Simetryn	9.8±0.3	14.7±0.6	13.6±0.7

Experimental conditions: 1.2 ml of sample extracted for 45 min at room temperature under agitation, 10% NaCl, and desorption for 5 min at 240 °C.

[a] Mean peak area counts of three replicates ($\cdot 10^6$).

[b] Confidence interval of the mean (at 95% of confidence level).

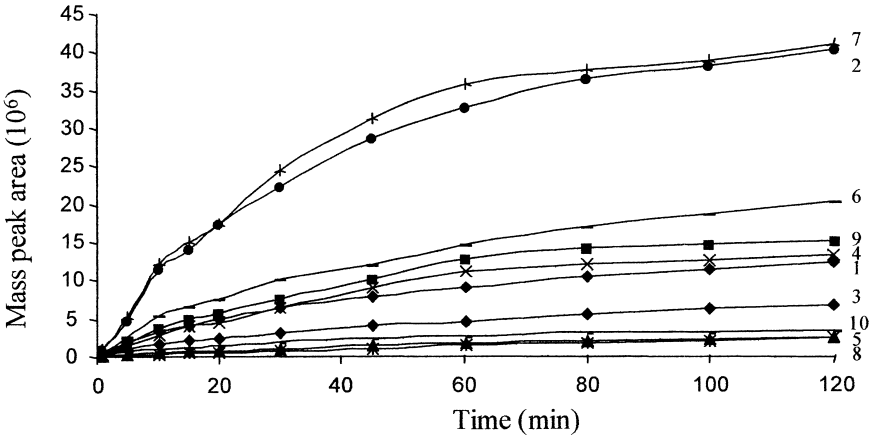

Fig. 1. Extraction efficiency–time profiles of the triazines studied. Experimental condition as follow: extraction of 1.2 ml of sample at room temperature with agitation, 10% NaCl, pH 6, and desorption for 5 min at 240 °C.

ditions has been largely used for the quantitation of several organic compounds and pesticides in aqueous matrices with satisfactory results [5,14,30,38]. The sole requisite to obtain high accurate results under these conditions is to control the extraction time.

3.2. Analytical characteristics

After the SPME procedure was optimised, several experiments were carried out in order to determine analytical characteristics such as linear range, precision, reproducibility and detection limits for the PDMS–DVB fiber.

The linear range was tested over a range between 0.01 and 1.0 μg l^{-1} using six concentration levels (injections in triplicate) and applying a statistical regression model to obtain the calibration curves. All calibration curves were linear in the range studied. As can be seen in Table 4, regression coefficients (r) were higher than 0.9943 (trietazine).

The precision of the method was determined by analysing six spiked surface water samples at 1 μg ml^{-1} of each triazine. The results obtained are shown in Table 4, and it can be observed that the relative standard deviation (RSD) values were below 8.0% in all cases. These values are lower than those reported in the literature for SPME determination of triazines [3,30,36]. Reproducibility was also determined by analysing five replicates of water spiked at 1 μg l^{-1} on 3 different days (n=15). RSD values obtained are also shown in Table 4, and ranged between 5.0% (prometon) and 9.7% (terbutryn),

Table 4
Regression coefficients (r), detection limit, linear range, precision, and reproducibility of each analyte for the PDMS–DVB fiber after optimisation

Compound	r	LOD (μg l^{-1})	Linear range (μg l^{-1})	Precision (RSD, %)	Reproducibility (RSD, %)
Prometon	0.9980	0.002	0.002–50	1.9	5.0
Trietazine	0.9943	0.004	0.004–80	1.8	8.1
Propazine	0.9964	0.007	0.007–40	4.9	6.9
Terbutylazine	0.9970	0.011	0.011–40	3.1	6.1
Atrazine	0.9951	0.006	0.006–40	7.1	8.1
Prometryn	0.9986	0.010	0.010–50	2.4	6.3
Terbutryn	0.9979	0.014	0.014–50	4.5	9.7
Simazine	0.9961	0.013	0.013–50	7.9	7.9
Ametryn	0.9974	0.010	0.010–50	2.1	7.0
Simetryn	0.9981	0.017	0.017–40	4.0	6.0

which is in accordance with EPA requirements [39]. Thus, the SPME procedure using the PDMS–DVB fiber seems suitable for all triazines under study.

Limits of detection (LODs), calculated as the peaks having a signal-to-noise ratio of 3, are presented in Table 4. As can be seen, the detection limits values varied between 0.002 μg l^{-1} (prometon) and 0.017 μg l^{-1} (simetryn). The method described showed very good sensitivity with detection limits in the low ng l^{-1} range for all triazines. These LOD values were below to those required by the EU for the determination of this group of compounds [6], which establish a maximum concentration of 0.1 μg l^{-1} for each pesticide. The values obtained are comparable although slightly lower than those found in the literature, that ranged

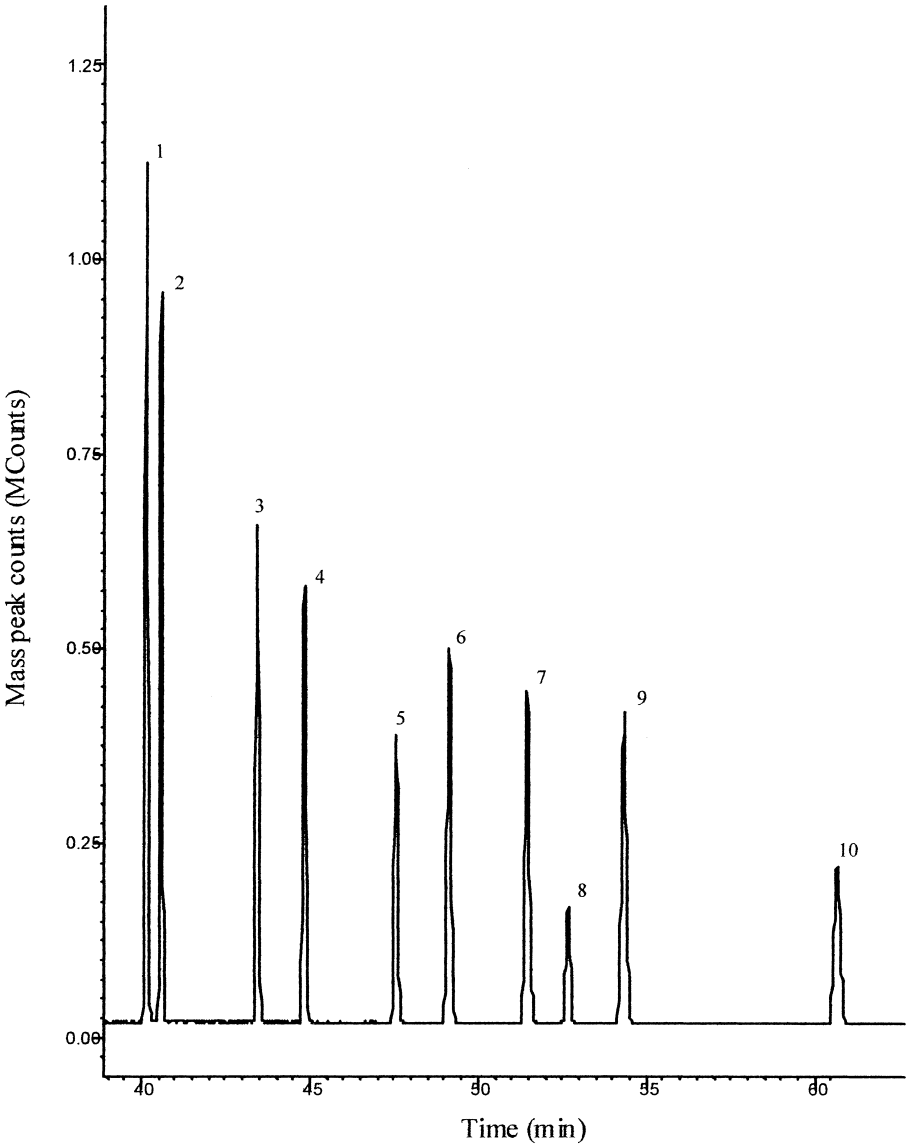

Fig. 2. Chromatogram of a spiked sample at 1 μg l^{-1} of each triazine extracted with PDMS–DVB fiber in the optimal conditions (for identification see Section 2.1).

between 0.010 μg l^{-1} (atrazine) and 0.080 μg l^{-1} (simazine) [3,30,36,38].

Fig. 2 shows a chromatogram of a spiked sample at 1 μg l^{-1} of each pesticide extracted with PDMS–DVB fiber under the optimal conditions. As can be seen, a high efficiency and good extraction for all peaks are obtained.

3.3. Analysis of real water samples

The optimal SPME procedure with the PDMS–DVB fiber was applied to real water samples collected from different areas of Tenerife Island (Spain). This area is of great agricultural importance, being especially devoted to banana cultivation. The samples were injected in triplicate and analysed using the SPME optimised procedure and MS. No triazine compounds appeared in the analysed samples, which allowed us to assert that water from Tenerife is free of these toxic compounds. Fig. 3 shows a chromatogram of a water matrix contaminated with herbicide residues. Only prometon and terbutryn were detected at the low-ng l^{-1} level.

4. Conclusions

The use of a PDMS–DVB fiber for the SPME procedure in the determination of triazine compounds was shown as the best fiber tested for the extraction of triazines from water samples. The results were compared with those given in the literature, better LODs being observed in general. The combination of the SPME device with the selective MS detector allowed this group of compounds to be quantified at a lower level than EPA requirements. The optimised procedure revealed satisfactory precision with RSD values lower than

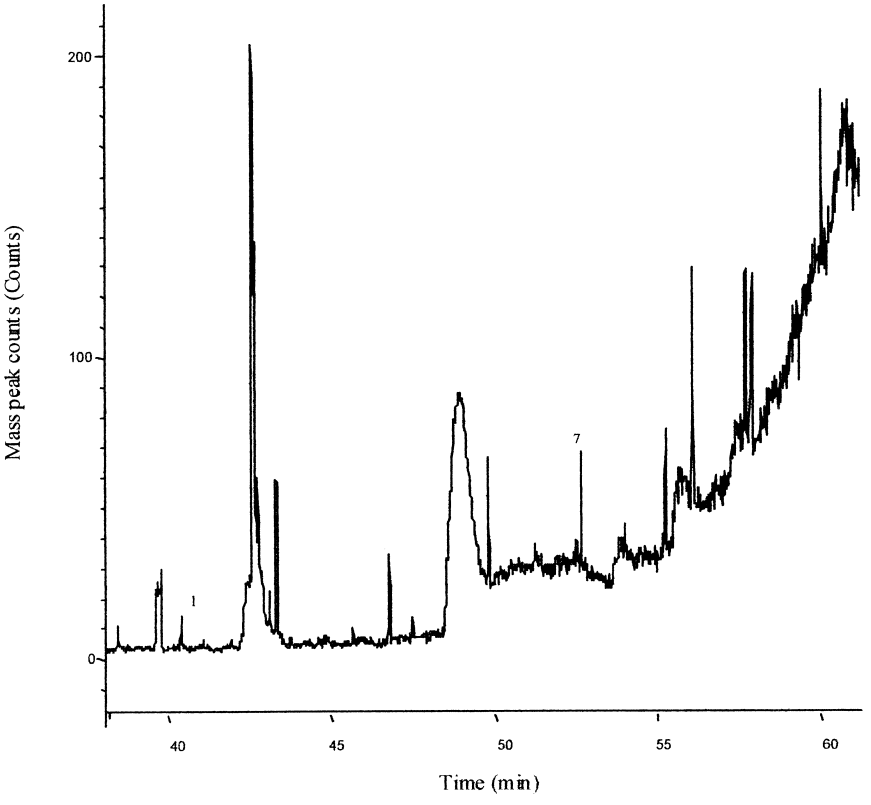

Fig. 3. Chromatogram obtained after SPME of a ground water sample contaminated with triazine residues using the optimised conditions. For identification see Section 2.1.

8.0% and LODs lower than 0.017 μg l^{-1}. The method was applied to real water samples, but no triazine compounds were detected in surface waters from Tenerife Island.

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