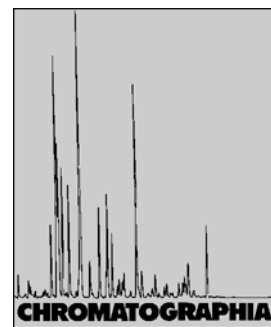


Development and Validation of a Solid-Phase Microextraction Method for the Analysis of Volatile Organic Compounds in Groundwater Samples



2003, 57, 369–378

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Key Words

Gas chromatography
Solid-phase microextraction
Volatile organic compounds
Environmental analysis
Groundwater

Summary

Solid-phase microextraction is a relatively recent extraction technique for sample preparation. It has been used successfully to analyse environmental pollutants in a variety of matrices such as soils, water and air. In this work, a simple and rapid method for the analysis of volatile organic and polar compounds from polluted groundwater samples by SPME coupled with gas chromatography (GC) is described. Different types of fibres were studied and the extraction process was optimised. The fibre that proved to be the best to analyse this kind of samples was CAR-PDMS. The method was validated by analysis of synthetic samples and comparison with headspace – GC. The optimised method was successfully applied to the analysis of groundwater samples.

Introduction

Groundwater pollution by volatile organic chemicals is widespread in the developed countries. Improper disposal of used solvents, leaks from storage tanks and an inadequate design of landfills are the main potential sources of liquid chemicals that can pollute soils and groundwater. To monitor such pollution and determine the success of the remediation measures it is necessary to apply simple and inexpensive analytical methods due to the large number of samples collected.

Nowadays, volatile compounds are analysed using either static headspace (HS) [1] or purge-and-trap (dynamic HS) [2–4] techniques, while for semi-volatile and non-volatile compounds, liquid-liquid extraction (LLE) [5] and solid-phase extraction (SPE) [6–8] are commonly used. All these techniques are effective but have limitations [2, 3, 9]. Headspace sampling is an excellent method to analyse complex or environmental samples, although the analysis is restricted to the volatile compounds with relatively high concentration. Purge-and-trap sampling is recommended by the United State Environ-

mental Protection Agency (USEPA) coupled with full-scan mass spectrometry. The purge-and-trap method applied to volatile compounds can be affected by a contaminated trap and requires large amounts of liquid nitrogen. In LLE, the main problems are the difficulties to automate the methods and the large volume of expensive solvents necessary, which must also be of high purity. Many of these solvents are toxic and even carcinogenic, and their disposal is difficult. LLE has been largely replaced in the last few years by SPE using different sorbents [10]. SPE can be automated and uses very little solvent, however, it is still a multi-step process prone to losing analytes if it is not fully automated and still needs toxic organic solvents for the elution step. Moreover, a large volume of sample is required for trace analysis, and it is susceptible to high baseline blanks, channelling and, if the sample contains particles, plugging of the sorbent beds. Furthermore, SPE is restricted to semi-volatile compounds since the boiling point of the analytes must be substantially above that of the solvent.

In the recent years, there has been a generalized trend to substitute these conventional sample preparation techniques, by more environmentally friendly and less laborious methods.

Solid-phase microextraction is a relatively new extraction technique. The initial concepts of the SPME application were published in 1989 by Belardi and Pawliszyn [11] and were subsequently developed by Pawliszyn and co-workers [12–16]. SPME is a valuable advance in sample preparation and has a number of advan-

tages compared to the conventional techniques for the extraction of organic compound from environmental samples. It does not require organic solvents, which are frequently expensive and harmful to health and the environment. The technique is simple and fast, the whole extraction and analyte transfer process usually takes only a few minutes [12] and it is easily automated, portable and inexpensive [13]. Besides, only a small volume of sample is needed. SPME can be coupled easily with gas chromatography (GC), and with some modifications, with high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) [17–21].

SPME is based on the partition equilibrium of the target analytes between a polymeric stationary phase, which is coated onto a fused silica fibre, and the sample or the headspace of the sample in a closed vial. Once equilibrium is reached, the fibre is transferred into the liner of a standard split/splitless injector, where the organic compounds are thermally desorbed from the polymeric phase. The theory and application of SPME have been recently summarized in several books [22–24].

SPME has been successfully used to analyse gaseous, liquid and solid samples. A wide range of analytes ranging from volatile to non-volatile compounds has been determined by SPME. Although this technique was introduced to determine the volatile compounds in environmental samples [17, 25, 26], nowadays its use has extended to a wide variety of matrices and analytes. They include environmental pollutants such as pesticides [18, 27], phenols [28, 29], polychlorinated biphenyls (PCBs) [36–38], polycyclic aromatic compound (PAHs) [18, 31–33], and to a lesser extent, inorganic compounds [34] and drugs [35].

This work focuses on the development of an analytical method for the routine analysis of groundwater samples from the Najerilla aquifer. Previous studies [36] of groundwater samples carried out by GC/MS showed the presence of the following compounds in this aquifer: acetone, ethyl acetate, methyl isobutyl ketone (MIBK), methyl-tert-butyl-ether (MTBE), benzene, toluene, ethylbenzene, ortho-, meta- and para-xylene (BTEX), 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene.

The behaviour of five fibres supplied by Supelco, Bellefonte, PA, USA, coated with different stationary phases and

mixed phases, i.e., poly(dimethylsiloxane) (PDMS), poly(acrylate) (PA), poly(dimethylsiloxane)/poly(divinylbenzene) (PDMS/DVB), poly(divinylbenzene)/Carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS) and Carboxen/poly(dimethylsiloxane) (CAR/PDMS), for the determination of the abovementioned compounds has been studied, both by direct extraction and by headspace-SPME (HS-SPME). The best results were obtained with a CAR/PDMS fibre. The validation of the optimised method was carried out by analysing synthetic samples and by comparison with HS analysis. Finally, the optimised method was applied to the analysis of real groundwater samples from the network of control wells of the Najerilla aquifer.

Experimental

Instrumentation

All the SPME extractions were carried out using an automatic Varian 8200 injector and a Varian 3800 gas chromatograph (Sunnyvale, CA, USA) equipped with a split/splitless injector, a capillary column HP-624 (30 m × 0.25 mm i.d. × 1.4 μm film thickness), and a flame ionisation detector (FID). The column flow rate of the helium carrier gas was 1.3 mL · min⁻¹, and the detector (FID) temperature was set at 300 °C. The GC oven was kept at 35 °C for 5.0 min after the injection, the temperature was then increased at a rate of 10 °C · min⁻¹ up to 225 °C, and this temperature was held for 1.0 min. During the desorption, the fibre was desorbed in the splitless mode for 0.5 min, and then the injector switched to the split mode (1:50) for the rest of the run. A narrow liner (0.8 mm i.d.) was used to achieve a high linear flow around the fibre during the desorption, thus reducing the desorption time. The automatic injector was programmed to keep the fibre in the injector for a further 15 min to avoid carry-over effects caused by impurities, and then was removed. The injector temperature varied according to the coating fibre and was set following the manufacturer's recommendations.

The HS-GC experiments were performed using an automatic Combipal (CTC Analytics) injector and a Varian 3800 gas chromatograph equipped with an FID. A CP-Select 624 (30 m × 0.32 mm i.d. × 1.8 μm) column was used. The chromatographic conditions were as follows:

carrier gas: helium; column flow: 1.7 mL · min⁻¹; injector temperature: 250 °C; detector temperature: 300 °C; oven temperature program: 45 °C for 5 min, 10 °C · min⁻¹ up to 225 °C for 1 min; split/splitless program: initial on 1:20, ratio 1:50 at 5 min. The headspace conditions were as follows: syringe temperature 100 °C; agitator speed 500 r.p.m.; injection volume 500 μL.

SPME Coating

The following automatic solid phase microextraction coated fibres supplied by Supelco were used:

- 50/30 μm divinylbenzene/carboxen over poly(dimethylsiloxane) (DVB/CAR/PDMS)
- 75 μm carboxen/poly(dimethylsiloxane) (CAR/PDMS)
- 85 μm polyacrylate (PA)
- 100 μm poly(dimethylsiloxane) (PDMS)
- 65 μm poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB)

Polydimethylsiloxane (PDMS) and polyacrylate (PA) were the first coated fibres to be used for SPME. PDMS is a very rugged liquid coating which is able to withstand high temperatures. It is non-polar and has a high affinity for non-polar compounds such as BTEX, VOCs and pesticides (molecular weight range: 60–275). PA is a low density solid polymer at room temperature, which allows analytes to diffuse into the coating, but the diffusion coefficient are lower compared to PDMS. PA is a more polar coating and extracts more polar compounds, such as phenols and derivatives (molecular weight range: 80–300). Some new coatings with more porous and adsorbent materials, i.e., divinylbenzene (DVB) and carboxen (CAR) blended in PDMS, are more polar than PA and suitable for extracting more polar compounds such as alcohols and ethers. CAR/PDMS is a coating suitable for extracting gases with a low molecular weight (molecular weight range: 30–225), however PDMS/DVB is recommended for volatile compounds, amines and nitroaromatic compounds (molecular weight range: 50–300). DVB/CAR/PDMS is a highly cross-linked phase equivalent to a partially cross-linked phase, except for some bonding with the core. This coating is recommended for flavours (volatiles and semi-volatiles, C3-C20) and odours (molecular weight range: 40–275).

All the fibres were conditioned following the manufacturer's recommendations.

Reagents and Standards

Stock standard solutions were prepared from the standard solutions supplied by Supelco:

- PVOC/GRO 2000 mg · L⁻¹ of benzene, ethylbenzene, toluene, 1,2,4-trimethylbenzene (1,2,4 TMB), 1,3,5-trimethylbenzene (1,3,5-TMB), methyl-*tert*-butyl-ether (MTBE), *m*-xylene, *p*-xylene, *o*-xylene and naphthalene in 1 mL methanol.
- Solution 2000 mg · L⁻¹ of ethyl acetate in 1 mL methanol,
- Solution 5000 mg · L⁻¹ of methyl isobutyl ketone (MIBK) in 1 mL methanol.
- Solution 2000 mg · L⁻¹ of acetone in 1 mL methanol: water (90:10).

Each solution was prepared with ultra-pure MilliQ water (Millipore, Bedford, MA, USA) and plunger-operated Transferpette pipettors (20–200 µL or 100–1000 µL) were used.

Using the commercial standard solutions, a solution with 13 analytes (acetone, ethyl acetate, methyl isobutyl ketone (MIBK), methyl-*tert*-butyl-ether (MTBE), benzene, toluene, ethylbenzene, *ortho*-, *meta*- and *para*-xylene (BTEX), 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene) was prepared with intermediate concentrations of 80 mg · L⁻¹ (200 mg · L⁻¹ for MIBK) by volumetric dilution with methanol (HPLC grade, Carlo Erba). This solution was kept in sealed vials minimizing the headspace, which were refrigerated at -20 °C. From this solution, MilliQ calibration solutions of 10–1000 µg · L⁻¹ were prepared by dilution with water (the final methanol content was less than 1%).

Sample Preparation

For the SPME-GC, the solutions were transferred directly using a micropipette into a 2 mL vial (1.2 mL of solution for direct SPME immersion and 0.6 mL for HS-SPME). For static HS sampling, 10 mL of solution were directly used in a 20 mL vial.

In general, the amount extracted increases with increasing salt concentration in the aqueous phase when increasing the polarity of the compound [23]. To avoid

the matrix effect that can be caused by different saline concentrations in real samples and the calibration solutions, both were saturated with sodium chloride NaCl RPE (for analysis) (Carlo Erba) before the extraction.

The samples exceeding the upper calibration limit were diluted with MiliQ water. All the samples were analysed in triplicate.

Real samples from the control wells of the Najerilla aquifer were obtained using a Grundfoss 6 cm diameter pumping equipment with an electric generator. The pump was submerged below the piezometric level and the pumping started at 0,5 L · s⁻¹, monitoring the temperature, pH and the conductivity of the water. Once these parameters were stable, the samples were collected in hermetically sealed glass bottles preventing the formation of bubbles and free headspace. Finally, they were kept at 4 °C until the analytic determination.

Results and Discussion

SPME Optimisation

In order to establish the optimum conditions for the SPME procedure, the influence of a number parameters was investigated. The amount of analyte extracted by the fibre in the SPME can be affected by several parameters, i.e., the characteristics of the coating, the time and temperature of the extraction process, the addition of salt or an organic solvent to the sample, the agitation of the sample, and the sample volume.

The first parameter studied was the kind of stationary phase coating. Although the general principle of "like dissolves like" can be applied, in this work the behaviour of five different SPME fibres, i.e., DVB/CAR/PDMS, CAR/PDMS, PA, PDMS, and PDMS/DVB, was studied for the extraction of the 13 analytes. Using the temperature conditions recommended by the manufacturer, the behaviour of each fibre for each analyte was studied in a standard solution of 1 mg · L⁻¹ with different equilibration times. The extraction was performed, both by direct immersion of the fibre into the sample and by immersion into the headspace. Figures 1, 2 and 3 show the signal obtained against the extraction time for each fibre and each analyte in two ways: immersion and headspace. Each

point represents the mean of three determinations.

Figures 1 and 2 show that the coated CAR/PDMS fibre provided the best results, very different from the other stationary phases, in the extraction of acetone, MIBK, ethyl acetate, MTBE, benzene and toluene. The CAR/PDMS fibre also had a good behaviour for the rest of the compounds under study (Figures 2 and 3), particularly when the extraction was performed by immersion of the fibre into the sample (direct SPME). The naphthalene and the TMB determinations gave the worst results with this fibre.

On the other hand, for ethylbenzene, xylenes, TMBs and naphthalene, the best results were obtained with the DVB/CAR/PDMS fibre and the PDMS fibre, by immersion in both cases. However, the results of these fibres for the more polar compounds were very low.

Given the variety of the target analytes in terms of polarity and volatility, it was necessary to reach a compromise solution to obtain, using only one fibre, the best possible results for all the compounds. Thus, the CAR/PDMS fibre was selected as the best to determine the mixture of 13 compounds.

Although the same kind of fibre was used, in general, the graphs show that the signal was higher in the determinations carried out by immersion than in the determinations performed in the headspace (HS). Nevertheless, another factor to be taken into account is the lifetime of the fibre, and this is longer in the HS mode than in the immersion mode, since the fibre is not in direct contact with the samples, which have a high NaCl content. A higher reproducibility was also obtained by HS-SPME than by direct SPME. Taking into account all these factors, it was decided to use the CAR/PDMS fibre with the headspace method (HS-SPME). Although the injector temperature is usually set at the maximum temperature at which the fibre coating remains stable, a lower temperature of 280 °C was selected to extend the lifetime of the fibre.

Note that although the desorption was completed in less than 0.5 min, the fibre was left inside the injector at 280 °C for a longer period (15 min) with the split valve open to ensure that no compounds remained in the fibre coating and appear in subsequent analyses (carry-over effect).

The time needed to reach the partition equilibrium depends on the type and the properties of the analyte, the sample and

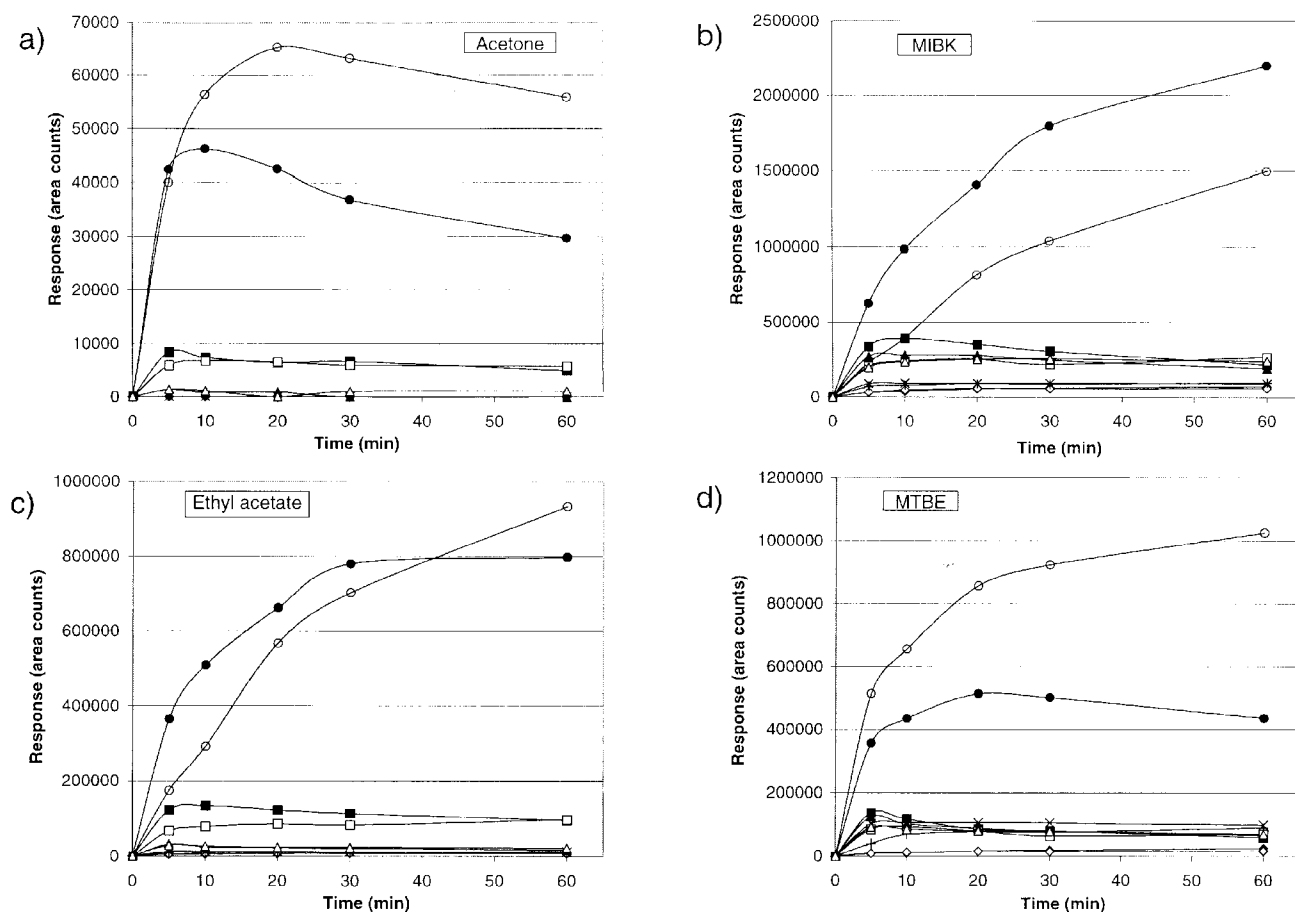


Figure 1. Extraction time profiles of **a)** acetone, **b)** MIBK, **c)** ethyl acetate and **d)** MTBE using the coating fibers by direct SPME: DVB/CAR/PDMS (■), CAR/PDMS (●), PA (◆), PDMS (×), PDMS/DVB (▲); and by HS-SPME: DVB/CAR/PDMS (□), CAR/PDMS (○), PA (◇), PDMS (+), PDMS/DVB (△).

the coating. In SPME, the equilibrium time is generally defined as the time necessary to reach $\geq 95\%$ of the maximum achievable extraction yield. In general, the time required using fibre directly immersed in the sample is higher than time needed by HS-SPME [13] for volatile analytes. This behaviour was observed with most of the aromatic compounds, whereas for the most polar ones such as acetone, ethyl acetate and MTBE (Figure 1), a lower equilibrium time was observed by immersion than by HS.

Compared with the exposure time profiles of other fibres, the equilibrium times with CAR/PDMS were longer. It was possible to use a non-equilibrium condition and take times shorter than the equilibrium time, but in this case lower extraction yields are obtained, so a compromise is needed between the extraction time and the yield.

The acetone extraction profile did not behave in the same way as the other compounds (Figure 1). For the CAR/PDMS fibre, a peak maximum was observed at 20 min by HS-SPME and at 10 min by di-

rect SPME, and in both cases the response area decreased beyond this time. A possible explanation for this behaviour might be the so-called "displacement effect" mentioned by Górecki et al. [37] for other compounds. This phenomenon occurs only for fibres extracting the analytes by adsorption rather than by absorption, due to the limited number of adsorption sites on the surface of the coating and the displacement of the compounds with low distribution ratios (acetone) by compounds with high distribution ratios (mainly MIBK). Also the use of a Varian autosampler, where the fibre vibration is used to agitate the samples during the headspace sampling, and so the process of transferring a large amount of molecules through the headspace to the fibre coating takes a long time when the compounds have a large overall distribution ratio. Therefore, the compound with the lowest distribution ratio (acetone) will reach equilibrium before the compounds with high distribution ratios.

The higher distribution ratio of MIBK is shown in Figure 1, where the long equi-

librium time needed is due to the large number of molecules that have to be transported from the bulk of the sample to the fibre.

Taking into account all these factors, a shorter extraction time is recommended, and 15 min was finally chosen as optimal for further experiments.

The effect of the agitation was considered. The agitation of the SPME fibre was performed automatically by the injector (Varian 8.200 model), which produced a high-frequency vibration of the fibre during the extraction/equilibration step inside the vial. The behaviour of the different analytes with and without agitation was studied. It was verified that agitation in HS-SPME, did not have a substantial impact. The fibre vibration enhances the diffusion of the analyte towards the fibres coating but it does not facilitate the mass transfer between the aqueous phase and the headspace. In this work, it was observed that the signals are more difficult to reproduce with agitation, perhaps because some drops of liquid might be deposited on the surface of the fibre and al-

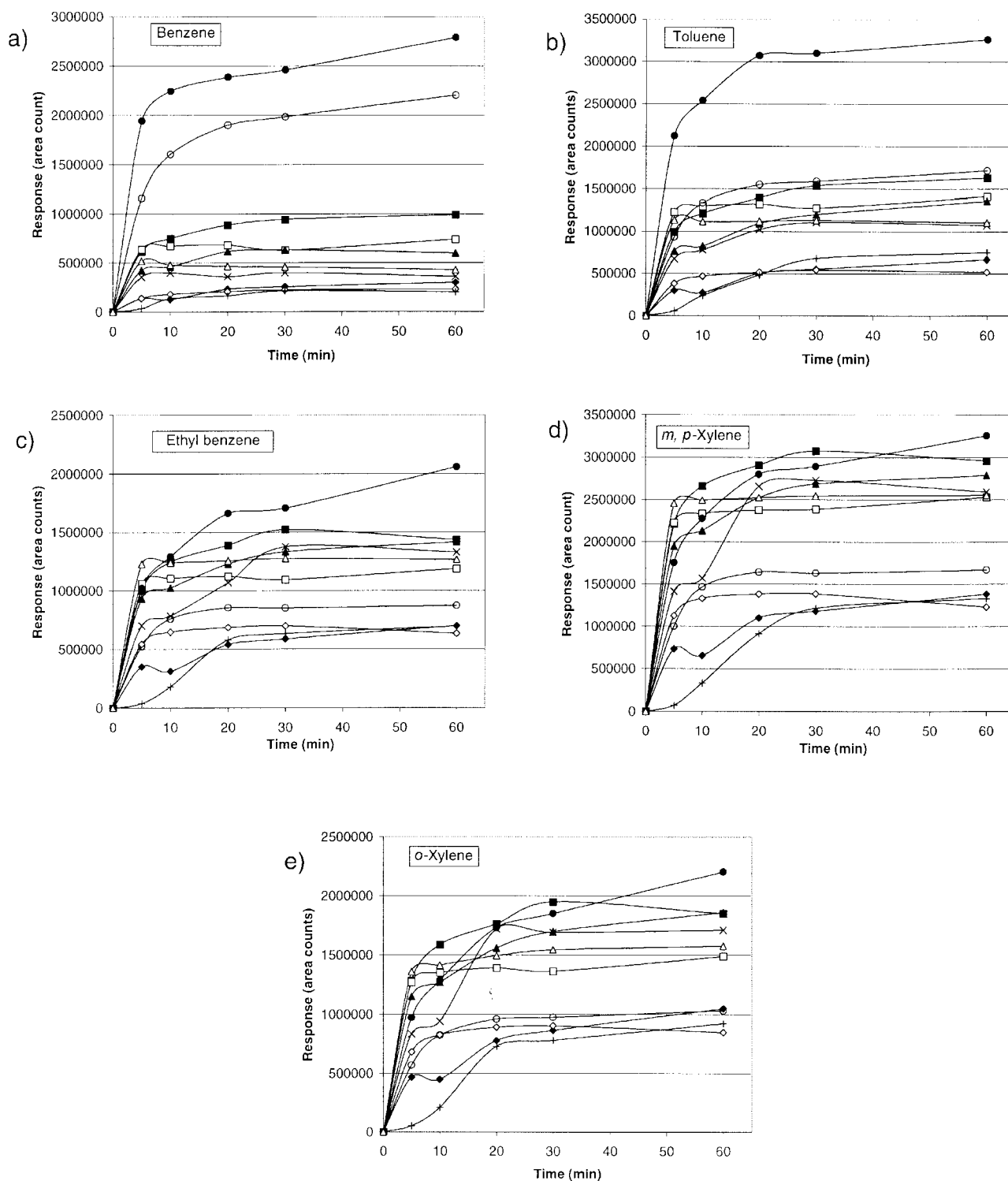


Figure 2. Extraction time profiles of **a)** benzene, **b)** toluene, **c)** ethyl benzene **d)** *m,p*-xylene and **e)** *o*-xylene using the coating fibers by direct SPME: DVB/CAR/PDMS (■), CAR/PDMS (●), PA (◆), PDMS (×), PDMS/DVB (▲); and by HS-SPME: DVB/CAR/PDMS (□), CAR/PDMS (○), PA (◇), PDMS (+), PDMS/DVB (△).

ter its behaviour. Therefore, it was decided to perform HS-SPME without agitation, putting the reproducibility of the results before the speed of analysis.

The extraction was carried out under saturated salt conditions. It is well known [37] that the addition of salt may increase by 3–5 times the peak area in headspace

sampling. This addition of salt usually increases the ionic strength of the sample, which reduces the solubility of more easily retained analytes. Direct SPME is not practicable when salt is used as a matrix modifier as it causes faster degradation of the coating.

In the HS-SPME of aqueous samples and volatile analytes, the volume of headspace usually must be small in order to concentrate the analytes before they diffuse towards the fibre coating. If the headspace volume is too large, the sensitivity is considerably reduced [22]. So 2 mL vials were selected, using a 0.6-mL sample vo-

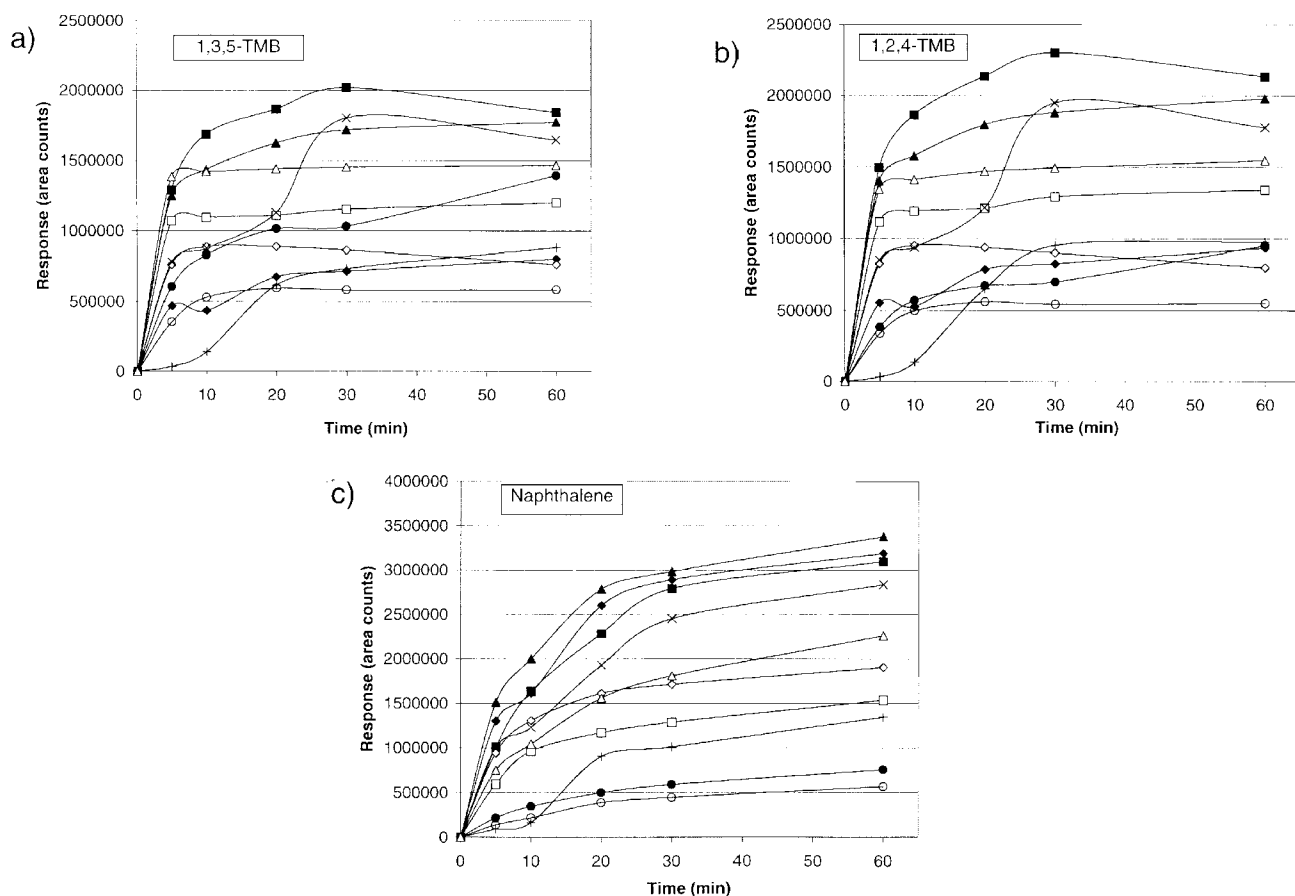


Figure 3. Extraction time profiles of **a)** 1,3,5-TMB, **b)** 1,2,4-TMB and **c)** naphthalene using the coating fibers by direct SPME: DVB/CAR/PDMS (■), CAR/PDMS (●), PA (◆), PDMS (×), PDMS/DVB (▲); and by HS-SPME: DVB/CAR/PDMS (□), CAR/PDMS (○), PA (◇), PDMS (+), PDMS/DVB (△).

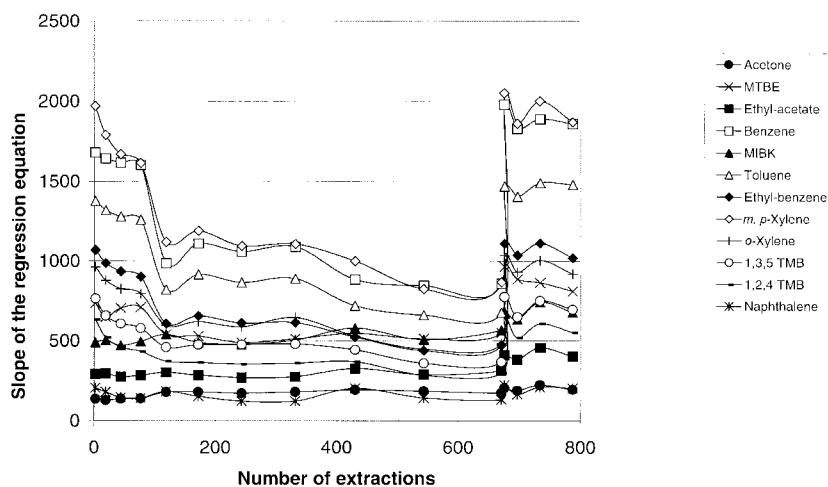


Figure 4. Evolution of the slope of the regression equation versus the number of extraction developed by the same fiber of CAR/PDMS.

lume (larger volumes would not provide space for the needle and the SPME fibre).

The lifetime of the fibre selected was evaluated studying the variation in the slope of the regression equation versus the number of extractions carried out with the same fibre. Figure 4 shows the behaviour of the slope of the linear calibration using

a CAR/PDMS fibre after 680 extractions. For most of the compounds, the slope decreased slightly until the 100 first extractions, after which a marked decrease was observed in the extraction of BTEX. However, in the case of acetone, ethyl acetate and MIBK, a minimum variation in the slope was observed. From extrac-

tion 680 onwards, the fibre was replaced, and the slopes reached the initial values again.

Features of the HS-SPME Method

The linearity of the method was assessed by processing water samples spiked with the volatile compound mixture at different concentration ranging from 10 to 1000 $\mu\text{g} \cdot \text{L}^{-1}$ (25–2500 $\mu\text{g} \cdot \text{L}^{-1}$ in the case of MIBK). The correlation coefficients for the calibration lines were ≥ 0.996 . The detection limits, defined as the concentration of the mean peak area three times the standard deviation of a blank, were within the range of 0.1 $\mu\text{g} \cdot \text{L}^{-1}$ for MTBE, benzene and 1,3,5 TMB, and 6 $\mu\text{g} \cdot \text{L}^{-1}$ for acetone. The results are shown in Table I.

The reproducibility ($n = 15$) was evaluated by the peak area obtained in the analysis of water samples spiked with all the analytes at a concentration of 100 $\mu\text{g} \cdot \text{L}^{-1}$ (250 $\mu\text{g} \cdot \text{L}^{-1}$ in the case of MIBK). Although poor reproducibility of the

Table I. Features of the HS-SPME method: regression equations, correlation coefficients, limits of detection (LOD) and relative standard deviation (RSD) obtained by the HS-SPME method using a CAR/PDMS coated fiber, for the compounds studied.

Compound	Equation*	r	Linear Range ($\mu\text{g} \cdot \text{L}^{-1}$)	L.O.D ($\mu\text{g} \cdot \text{L}^{-1}$)	% R.S.D. ($n = 15$)
acetone	$y = 109 (\pm 2)c + 6743 (\pm 843)$	0.996	10–750	6	9
methyl- <i>tert</i> -butyl-ether	$y = 633 (\pm 6) c$	0.999	10–750	0.1	5
ethyl acetate	$y = 287 (\pm 3)c + 1155 (\pm 904)$	0.999	10–750	1	9
benzene	$y = 1438 (\pm 23)c$	0.998	10–750	0.1	6
methyl isobutyl ketone	$y = 383 (\pm 5)c$	0.998	25–1875	0.2	10
toluene	$y = 988 (\pm 17)c$	0.997	10–750	4	4
ethylbenzene	$y = 747 (\pm 15)c$	0.996	10–750	0.4	5
<i>m,p</i> -xylene	$y = 1362 (\pm 25)c$	0.997	10–750	1	6
<i>o</i> -xylene	$y = 659 (\pm 11)c$	0.997	10–750	1	5
1,3,5-trimethylbenzene	$y = 504 (\pm 10)c$	0.996	10–750	0.1	7
1,2,4-trimethylbenzene	$y = 393 (\pm 7)c$	0.998	10–750	0.5	9
naphthalene	$y = 122 (\pm 2)c - 2135 (\pm 692)$	0.998	10–750	1	7

* y and c denote peak area and concentration in $\mu\text{g} \cdot \text{L}^{-1}$, respectively. Values in brackets are slope and intercept standard errors.

CAR/PDMS fibre had been reported by Chai and Pawliszyn [38], the values obtained in this work, expressed as relative standard deviations (RSDs), were between 4 and 10%. Hence, the method is precise enough to analyse volatile mixtures in water.

Optimisation of the Static HS Method

Three incubation temperatures (40 °C, 60 °C and 80 °C) were studied with an incubation time of 10 min. The other variables have already been described. The results show that the signal obtained increased with increase in temperature since it favours the displacement of the compounds from the liquid to the vapour phase. It was verified that this effect is more significant in the compounds with the highest and the lowest molecular weights (acetone, MTBE, ethyl acetate, MIBK and naphthalene), and is less significant in the compounds with a medium molecular weight (BTEX and TMBs). Taking this into account, the working temperature was set at 80 °C.

Then, using a temperature of 80 °C, the incubation time was optimised. Four times were examined: 2 min, 5 min, 10 min and 15 min. The results in Figure 5 show that after 10 min, the amount of compound did not improve. Therefore, the optimal incubation time was taken as 10 min.

Similarly to the HS-SPME method, the linearity of the method was assessed by processing water samples spiked with the volatile compound mixture at different concentration levels ranging from 10 to 1000 $\mu\text{g} \cdot \text{L}^{-1}$ (25–2500 $\mu\text{g} \cdot \text{L}^{-1}$ in the case of MIBK). The correlation coefficients

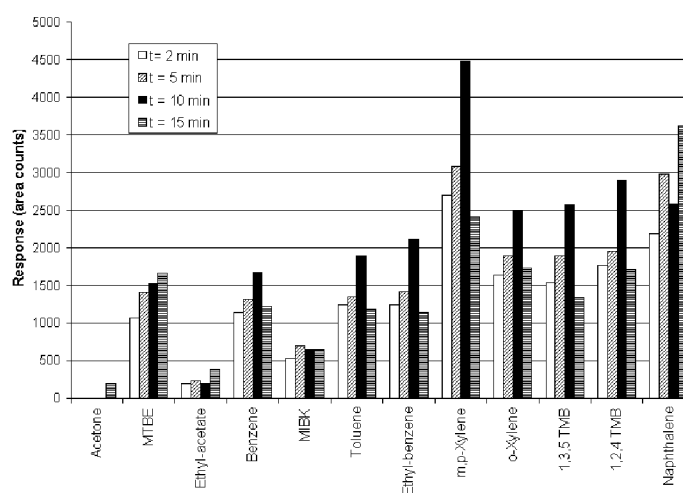


Figure 5. Optimization of the incubation time in HS method. Four different times of 2, 5, 10 and 15 minutes were studied.

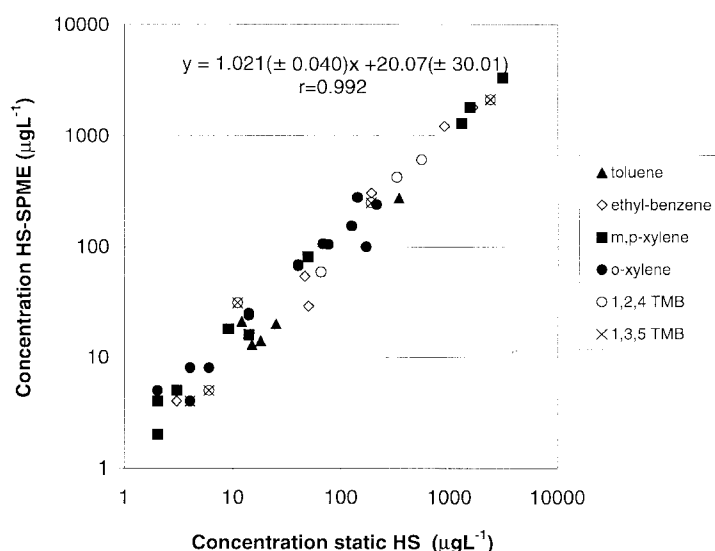


Figure 6. Comparison of the results obtained by HS-SPME method versus HS static method in the analysis of ten real groundwater samples.

for the calibration lines were ≥ 0.995 . The detection limits for acetone, ethyl acetate and MIBK were poorer by

HS than by HS-SPME. The detection limits were within the range of 0.1 $\mu\text{g} \cdot \text{L}^{-1}$ to 4.0 $\mu\text{g} \cdot \text{L}^{-1}$ except for acetone with a

Table II. Features of the HS method: regression equations, correlation coefficients, limits of detection (LOD) and relative standard deviation (RSD) obtained by the HS static method.

Compound	Equation*	r	Linear Range ($\mu\text{g} \cdot \text{L}^{-1}$)	L.O.D ($\mu\text{g} \cdot \text{L}^{-1}$)	% R.S.D. ($n = 10$)
acetone	$y = 1.70 (\pm 0.05)c$	0.996	45–750	45	10
methyl- <i>tert</i> -butyl-ether	$y = 33.9 (\pm 0.6)c$	0.997	10–750	0.1	6
ethyl acetate	$y = 7.2 (\pm 0.2)c$	0.997	10–750	2	8
benzene	$y = 45 (\pm 1)c$	0.996	10–1000	0.1	6
methyl isobutyl ketone	$y = 18.9 (\pm 0.3)c$	0.998	25–1875	0.9	5
toluene	$y = 46.2 (\pm 0.9)c$	0.997	10–1000	0.1	5
ethylbenzene	$y = 43 (\pm 1)c$	0.996	10–1000	0.4	4
<i>m,p</i> -xylene	$y = 87 (\pm 2)c$	0.996	10–1000	0.5	5
<i>o</i> -xylene	$y = 52 (\pm 1)c$	0.995	10–1000	0.7	5
1,3,5-trimethylbenzene	$y = 47 (\pm 1)c$	0.996	10–1000	0.1	5
1,2,4-trimethylbenzene	$y = 49 (\pm 1)c$	0.996	10–1000	0.1	5
naphthalene	$y = 66 (\pm 1)c$	0.996	10–750	4	5

* y and c denote peak area and concentration in $\mu\text{g} \cdot \text{L}^{-1}$, respectively. Values in brackets are slope and intercept standard errors.

LOD of $45 \mu\text{g} \cdot \text{L}^{-1}$. The results are shown in Table II. The repeatability ($n = 10$), expressed as relative standard deviations, was between 4 and 10%.

Validation of the Method

The HS-SPME method developed using CAR/PDMS fibres was validated by analysis of synthetic samples at four concentration levels: 50, 250, 500 and $750 \mu\text{g} \cdot \text{L}^{-1}$ (125, 625, 1250 and $1875 \mu\text{g} \cdot \text{L}^{-1}$ for MTBE). The results obtained are shown in Table III. The means of the relative errors were 7.3% at $50 \mu\text{g} \cdot \text{L}^{-1}$ ($125 \mu\text{g} \cdot \text{L}^{-1}$ for MTBE), 8.4% at $250 \mu\text{g} \cdot \text{L}^{-1}$ ($625 \mu\text{g} \cdot \text{L}^{-1}$ for MTBE), 3.6% at $500 \mu\text{g} \cdot \text{L}^{-1}$ ($1250 \mu\text{g} \cdot \text{L}^{-1}$ for MTBE) and 4.6% at $750 \mu\text{g} \cdot \text{L}^{-1}$ ($1875 \mu\text{g} \cdot \text{L}^{-1}$ for MTBE).

A comparison between the VOC concentrations of groundwater samples found by the HS-SPME method and those obtained by HS sampling were carried out. A set of ten samples were analysed by both methods and good agreement was found between them. The concentrations of the VOCs obtained by both methods are represented in Figure 6 in a log-log scale to display better the data close to the origin. The t -paired test applied to both set of results showed that the calculated t -value ($t = 1.92$) was lower than the critical t -value ($t_{n-1} = 1.96$, $n = 40$, $P = 0.05$). Thus the method may be considered to give comparable results. In addition, the regression equation between the results shows a correlation coefficient of 0.992 ($n = 42$). The intercept was 20.070, with upper and lower confidence limits of ± 30.017 ($t_{n-2} = 1.96$, $P = 0.05$); this range includes the ideal value of zero. The slope of the graph was 1.021 with a 95% confidence interval of 0.982–1.061, indicating a good agreement between both methods.

Analysis of Real Groundwater Samples Using the Optimised HS-SPME Method

The HS-SPME method developed was applied to the analysis of real samples extracted from the network of control wells of the Najerilla aquifer. Since January 2001 the network of control wells has been monitored monthly, providing a large amount of data. The monitoring gives information on the evolution and recovery of the aquifer. This work shows, by way of example, the results of monitoring the 12 different control wells for two consecutive months (January and February 2001). The results obtained are shown in Table IV. The table shows that pollution by TMBs and ethylbenzene was identified in most of the control wells. The main pollutants seem to be the aromatic organic compounds. Fewer wells showed pollution by acetone, ethyl acetate and MIBK. Although some compounds showed a small variability during two consecutive months, the more important fact was that the concentration of these compounds could even represent a health hazard.

Conclusions

In this work, an SPME method for the analysis of specific volatile organic pollutants in groundwater samples is presented. The compounds studied were: acetone, ethyl acetate, benzene, methyl isobutyl ketone (MIBK), methyl-*tert*-butyl-ether (MTBE), toluene, ethylbenzene, *ortho*-, *meta*- and *para*-xylene (BTEX), 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene.

The SPME parameters were optimised. The carboxen-PDMS coating showed the

best behaviour to extract the target mixture of organic compounds. The headspace method proved to be more reproducible than the immersion one. The detection limits for most of the compounds studied were around $1 \mu\text{g} \cdot \text{L}^{-1}$ (1 ppb) using FID detection. The validation of the method by analysis of synthetic samples was satisfactory. The comparison of the optimised method with static headspace sampling was carried out with a good regression.

The methods were finally applied to the analysis of real groundwater samples, which showed high levels of VOCs. This fact supported the urgency to apply a remediation process for groundwater contamination in the area.

Acknowledgements

This study was supported by a Research Project of the Plan Nacional de I+D co-financed by the European Fund FEDER: 2FD97-1708 and by the Research Project ANGI-2000/32 within the I Plan Riojano de I + D. The authors thank the Dirección General de Calidad Ambiental del Gobierno de La Rioja for its help.

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Table III. Analysis of synthetic samples.

Compound	Sample 1			Sample 2			Sample 3			Sample 4		
	Conc (µg L ⁻¹)	Found conc (µg L ⁻¹)*	relative error	Conc (µg L ⁻¹)	Found conc (µg L ⁻¹)*	relative error	Conc (µg L ⁻¹)	Found conc (µg L ⁻¹)*	relative error	Conc (µg L ⁻¹)	Found conc (µg L ⁻¹)*	relative error
acetone	50	56 (±4)	+12%	250	268 (±6)	+7%	500	484 (±17)	-3%	750	701 (±45)	-7%
methyl- <i>tert</i> -butyl-ether	50	53 (±2)	+7%	250	281 (±3)	+12%	500	501 (±27)	0%	750	775 (±26)	+3%
ethyl acetate	50	53 (±2)	+5%	250	251 (±8)	0%	500	444 (±11)	-11%	750	774 (±53)	+3%
benzene	50	54 (±4)	+9%	250	288 (±10)	+15%	500	525 (±44)	+5%	750	768 (±4)	+2%
methyl isobutyl ketone	125	137 (±2)	+9%	625	702 (±20)	+12%	1250	1268 (±39)	+1%	1875	2231 (±125)	+8%
toluene	50	49 (±1)	-2%	250	277 (±9)	+11%	500	496 (±45)	-1%	750	724 (±6)	-3%
ethylbenzene	50	43 (±1)	-14%	250	275 (±25)	+10%	500	491 (±54)	-2%	750	725 (±4)	-3%
<i>m,p</i> -xylene	50	54 (±1)	+9%	250	268 (±15)	+7%	500	501 (±59)	0%	750	757 (±9)	+1%
<i>o</i> -xylene	50	44.4 (±0.1)	-11%	250	270 (±2)	+8%	500	518 (±56)	+3%	750	794 (±6)	+6%
1,3,5, trimethylbenzene	50	47 (±2)	-6%	250	278 (±7)	+11%	500	533 (±66)	+7%	750	815 (±13)	+9%
1,2,4 trimethylbenzene	50	52 (±9)	+4%	250	268 (±15)	+7%	500	514 (±71)	+3%	750	819 (±15)	+9%
naphthalene	50	54 (±5)	0%	250	254 (±38)	+1%	500	463 (±20)	-7%	750	815 (±15)	+9%

(* mean concentrations (± s.d), n = 3.

Table IV. Analysis of real groundwater samples from control wells of Najerilla aquifer. Concentration (mean ± s.d.) in µg L⁻¹ or * mg L⁻¹.

Compound	Control well number (month)	acetone	ethyl acetate	benzene	MIBK	toluene	ethylbenzene	<i>m,p</i> -xylene	<i>o</i> -xylene	1,3,5-TMB	1,2,4-TMB	naphthalene
Control well 1 (Jan.)		<ql	n.d.	n.d.	n.d.	18 ± 3	20 ± 3	42 ± 7	<ql	10 ± 2	22 ± 6	n.d.
Control well 1 (Feb.)		<ql	n.d.	n.d.	n.d.	10 ± 2	22 ± 2	63 ± 5	<ql	16 ± 1	35 ± 2	n.d.
Control well 2 (Jan.)		10 ± 3*	76 ± 3	22 ± 0	<ql	647 ± 5	3.96 ± 0.06*	5.54 ± 0.09*	199 ± 5	60 ± 1	190 ± 7	11 ± 1
Control well 3 (Feb.)		<ql	n.d.	<ql	n.d.	141 ± 3	24 ± 1	23 ± 1	<ql	51 ± 2	151 ± 4	<ql
Control well 4 (Jan.)		380 ± 11	<ql	n.d.	<ql	815 ± 94	2.39 ± 0.09*	3.5 ± 0.1*	1.47 ± 0.05*	45 ± 2*	143 ± 6*	405 ± 22
Control well 5 (Feb.)		<ql	n.d.	<ql	n.d.	197 ± 3	478 ± 15	5.70 ± 0.07*	14 ± 0	391 ± 21	1.17 ± 0.09*	<ql
Control well 6 (Jan.)		<ql	n.d.	<ql	n.d.	192 ± 27	315 ± 28	3.8 ± 0.3*	18 ± 1	389 ± 26	1.11 ± 0.08*	<ql
Control well 6 (Feb.)		<ql	n.d.	<ql	n.d.	<ql	<ql	<ql	<ql	<ql	13 ± 6	n.d.
Control well 7 (Jan.)		<ql	n.d.	10 ± 1	<ql	341 ± 42	16.6 ± 0.7*	13 ± 0	<ql	18 ± 1	30 ± 2	<ql
Control well 7 (Feb.)		<ql	<ql	19 ± 0	n.d.	94 ± 1	12.9 ± 0.3*	25 ± 1*	69 ± 5	130 ± 30	486 ± 154	12 ± 2
Control well 8 (Jan.)		<ql	n.d.	<ql	n.d.	59 ± 4	1.82 ± 0.05*	10.2 ± 0.4*	15 ± 1	126 ± 1	703 ± 40	29 ± 5
Control well 9 (Jan.)		2.6 ± 0.4*	95 ± 16	11 ± 1	39 ± 4	26.2 ± 0.2*	2.89 ± 0.03*	2.80 ± 0.03*	655 ± 41	1.32 ± 0.03*	4.03 ± 0.05*	18 ± 1
Control well 9 (Feb.)		466 ± 6	28 ± 1	10 ± 1	27 ± 1	25 ± 2*	3.3 ± 0.2*	3.1 ± 0.2*	652 ± 28	1.9 ± 0.1*	5.4 ± 0.3*	24 ± 1
Control well 10 (Jan.)		<ql	n.d.	<ql	12 ± 0	55 ± 5	126 ± 9	309 ± 22	241 ± 14	4.8 ± 0.3*	12.5 ± 0.9*	75 ± 7
Control well 10 (Feb)		<ql	n.d.	<ql	<ql	26 ± 4	127 ± 21	336 ± 56	244 ± 43	5.6 ± 0.7*	14 ± 1*	85 ± 11
Control well 11 (Jan)		n.d.	n.d.	n.d.	n.d.	<ql	<ql	<ql	<ql	28.3 ± 0.8	337 ± 6	<ql
Control well 11 (Feb)		<ql	n.d.	n.d.	n.d.	<ql	<ql	<ql	<ql	<ql	82 ± 19	<ql
Control well 12 (Jan)		<ql	n.d.	n.d.	n.d.	24 ± 5	21 ± 1	50 ± 7	<ql	27 ± 7	65 ± 18	n.d.
Control well 12 (Feb)		<ql	n.d.	n.d.	n.d.	<ql	20 ± 3	49 ± 7	<ql	32 ± 4	75 ± 11	n.d.

n.d.: non detected; <ql: below the quantification limit.

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Received: Jun 24, 2002
 Revised manuscript
 received: Sep 24, 2002
 Accepted: Oct 17, 2002